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Environmental Assessment of the Alaskan Continental Shelf

Annual Reports of Principal Investigators for the year ending March 1977

Volume XIII. 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

March 1977

U.S. DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
Environmental Research Laboratory

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Bureau of Land Management

DISCLAIMER

VOLUME XIII

CONTAMINANT BASELINES

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* indicates final report

Annual Report

Contract #01-6-022-11469
Research Unit #43

Reporting Period
March 16, 1976 - March 15, 1977

Stephen N. Chesler
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April 1, 1977

I SUMMARY OF OBJECTIVES, CONCLUSIONS, AND IMPLICATIONS WITH RESPECT TO OCS OIL AND GAS DEVELOPMENT.

The objective of the task undertaken by NBS is to assess the quality of the chemical data obtained by NOAA laboratories and contractors. This objective will be met by: (1) conducting an interlaboratory comparison of hydrocarbon analyses on intertidal sediments homogenized and distributed by NBS; (2) conducting a second interlaboratory exercise with a marine tissue sample homogenized and distributed by NBS; (3) acting as a sample-split coordinating laboratory (10% of all samples collected by NOAA principal investigators are supposed to be sent for NBS analysis and/or redistribution); (4) acting as a consultant laboratory to other NOAA principal investigators involved in hydrocarbon analysis.

The sediment intercalibration exercise was completed during the 4th quarter, and the results demonstrate the problems associated with interpreting complex, organic chemical, environmental data; analyses for the low hydrocarbon burden (Katalla) sediment differed by as much as a factor of 50. A detailed discussion is presented in the draft of a paper appended to the summary of 4th quarter operations. The tissue intercalibration exercise is scheduled to begin during June 1977. No sample-split activities were undertaken this year, since no samples were sent to NBS by NOAA principal investigators in spite of the requirements outlined in (3) above.

II INTRODUCTION

A. General Nature and Scope of Study.

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

B. Specific Objectives.

The objectives of this study are to: (1) serve as the quality assurance laboratory for hydrocarbon analyses done under the NOAA-BLM Alaska program; (2) act as a consultant to NOAA-sponsored laboratories engaged in hydrocarbon analyses.

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 the different laboratories. Until such a time as certified Standard Reference Materials are available, a quality monitoring (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.

A. Gulf of Alaska

B. Bering Sea.

V. SOURCE METHODS AND RATIONALE OF DATA COLLECTION.

N/A

VI - VII. RESULTS AND CONCLUSIONS.

Results and discussion of experimental work during the period from March 16, 1976, to September 15, 1976, has been presented in a semi-annual report. These data, while concerned with FY 76 tasks, are presented below in an abbreviated form.

A. Liquid Chromatograph (LC) - Fluorescence Analysis for Polynuclear Aromatic Hydrocarbons (PAH's).

The Annual Report (April 1, 1976) gave the results of the method development for LC-fluorescence analysis.

Several sediment and tissue samples have been analyzed by this procedure. Sediment samples are analyzed by Soxhlet or ultrasonic extraction and injection of the concentrated extract directly into the LC system. Katalla River sediment extract gives four major peaks each of which is fluorescent at 400 nm. These peaks have been identified as phenanthrene, chrysene, and their alkylated homologs. Extracts of sediments taken from Siwash Bay, Wells Bay, and Hinchinbrook Island show no measurable PAH content.

B. Hydrocarbon Analysis in Tissue Matrix.

An analytical method has been developed for the determination of petroleum hydrocarbons in various marine tissue samples. The method involves dynamic headspace sampling of the tissue homogenate followed by liquid chromatographic removal of the biogenic polar components. High resolution gas chromatography is then used for quantitation of the petroleum hydrocarbons present after LC clean-up. Recovery data for aliphatic and aromatic internal standards are given in Table I. It was assumed that the aliphatic hydrocarbons were being retained in the lipid fraction in the tissue homogenate and the partition coefficient for these hydrocarbons between the headspace sampling gas and the organophilic lipid fraction was quite unfavorable. It was found that the addition of 2 M KOH to digest the tissue matrix improved the aliphatic recoveries slightly.

By extending the headspace sampling period from 4 hours (2 hours at room temperature and 2 hours at 70 °C) to ∿16 hours at 70 °C, recoveries for the higher aromatics (e.g., phenanthrene) and most aliphatics from water were increased to nearly 100 percent. Recoveries from the mussel tissue homogenate for the extended headspace sampling period were also approximately 100 percent for the aromatics, but only ∿30 percent for the aliphatic components.

A comparison of hydrocarbon levels obtained with and without LC clean-up is given in Table II for various tissue samples and a sediment sample. The data indicate that the LC removal of the polar biogenic components is necessary in order to measure accurately baseline hydrocarbon levels in tissue.

The results of initial analyses of Mytilus from various sites in the Prince William Sound/Northeastern Gulf of Alaska are listed in Table III. Work is continuing on the analyses from these sites and additional sites in order to determine the baseline hydrocarbon levels.

C. Laboratory Intercalibration Exercises.

Results of the sediment intercalibration exercises are presented with the summary of the 4th quarter activities (*vide infra*).

VIII. CONCLUSIONS.

Of the Alaskan sediment samples analyzed by the LC method, only Katalla River sediment showed the presence of PAH's. Since there is a low level, natural oil seep on the Katalla River, the presence of PAH's in the river sediment is to be expected. The other sediment collection stations must be considered to be free from any detectable PAH contamination.

The methodology for the analysis of hydrocarbon content in biological tissue samples has been completed and verified. The method will be used to determine the hydrocarbon baseline in Mytilus samples backlogged at NBS.

The sediment intercalibration exercise results indicated that wide (factor of 50) variations can occur when different laboratories analyze the same low-level hydrocarbon samples. Detailed evaluation of the results indicates that the numbers are not in the same population, and therefore no statistical evaluation of the data (other than reporting ranges) can be made. These observations confirm the need for a strong program in quality assurance.

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.

The sediment intercalibration exercise has been completed. A list of laboratories which were provided samples for the exercise, and those which did not respond are indicated below:

Dwight G. Ballinger,	EPA, Cincinnati	- Did not respond.
John A. Calder,	Florida State Univ.	
Ronald A. Hites,	MIT	
Isaac (Ian) R. Kaplan,	UCLA (NOAA P.I.)	- Did not respond.
C. Bruce Koons,	Exxon, Houston	- Did not respond.
John L. Laseter,	Univ. of New Orleans	
William MacLeod,	NOAA, Seattle (NOAA P.I.)	
John McGuire,	EPA, Athens	- Did not respond.
Steven J. Martin,	Geochem Laboratories	
Patrick L. Parker,	Univ. of Texas	
David Shaw,	Univ. of Alaska (NOAA P.I.)	
J. Scott Warner,	Battelle-Columbus (NOAA P.I.)	- Did not respond.

As can be seen, 7 out of the 12 laboratories have responded. The laboratories are identified in the attached report only by numbers, and these numbers bear no relation to the order in which the laboratories are listed above.

A sediment sample collected, spiked with Southern Louisiana crude oil, and mixed by Ian Kaplan has been distributed and NBS has sent out a letter stating the parameters to be reported and the deadline date for return of results to NBS. A copy of the letter is attached to this report. The following laboratories received the letter:

Rudolf Bieri,	VIMS
John A. Calder,	Florida State Univ.
John Farrington,	Woods Hole
Isaac R. Kaplan,	UCLA
John L. Laseter,	Univ. of New Orleans
William MacLeod,	NOAA-Seattle
Patrick L. Parker,	Univ. of Texas
David Schultz,	USGS-Reston
David Shaw,	Univ. of Alaska
Warren Steele,	Energy Resources Co., Inc.
J. Scott Warner,	Battelle-Columbus

REVISED MILESTONE CHART

Milestones	Date
1) Collect intertidal sediment samples at Katalla River and Hinchinbrook Island for intercalibration exercises. (Mussels also collected.) Sufficient material collected to allow periodic analyses over the course of two years.	5/76
2) Return of first intercalibration exercise results (sediment) to NBS and completion of detailed lab analysis of sediment by NBS.	1/77
3) NBS report to NOAA on results of FY-76 quality assurance program.	3/77
4) Coal Oil Point mussel collection for intercalibration.	12/76
5) Send out samples for second sediment intercalibration exercise. These samples were collected and homogenized by Dr. I. Kaplan, UCLA.	3/77[1]
6) Completion of mussel homogeneity studies.	5/77[1]
7) Dissemination of mussel samples to participating laboratories (contingent upon satisfactory results in homogeneity study).	6/77
8) Return of second sediment intercalibration exercise results to NBS and completion of detailed lab analysis by NBS.	5/77[1]
9) Return of mussel intercalibration exercise results to NBS and completion of detailed lab analysis by NBS.	9/77[1]
10) Split of P.I. field samples for quality assurance purposes.	when received
11) NBS report to NOAA on results of FY-77 quality assurance program.	10/77

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[1] Revised milestones to reflect change in sequence of FY77 intercalibration exercises (sediment preceding Mytilus).

March 14, 1977

Dr. Rudolf Bieri
VIMS
Gloucester Point, VA 23062

Dear Rudi:

By now you should have received a Southern California benthic sediment from Dr. Ian Kaplan of UCLA. If the sample has not been received, please contact Dr. Kaplan directly (213-825-1805). This sediment has been spiked with Southern Louisiana crude oil. NBS will be performing a homogeneity check on the sample during the course of this round robin. The results of this intercomparison study should be mailed to the National Bureau of Standards·by May 1, 1977. Mr. James Cimato of BLM has requested that all BLM contract labs mail him a copy of their results.

For the purposes of intercalibration we are interested in obtaining the following data:

1) total hydrocarbons in the GC elution range (roughly C_{10}-C_{30}); please specify the exact range you are reporting.

2) total extractable hydrocarbons.

3) pristane/phytane ratio and the amount of these present.

4) % water.

5) identities and amounts of the three most abundant aliphatic and the three most abundant aromatic hydrocarbons.

6) total polynuclear aromatic hydrocarbon (PAH) concentration (4 rings and larger).

7) identity and amount of the most abundant PAH (4 rings or larger).

8) the level of your analytical blank; the frequency of obtaining and precision of the blank value.

Please respond to as many of the categories as you can and give results on a dry weight basis. Please report precision data when replicate analyses are performed. Also, please enclose as much of your raw data as possible. Finally, intercomparison of results is facilitated if you include a description of the methodology used in doing the analyses.

As mentioned at the beginning of this letter the deadline for submitting results is May 1, 1977. We look forward to hearing from you.

Sincerely yours,

Harry S. Hertz, Ph.D.
Research Chemist
Bioorganic Standards Section
Analytical Chemistry Division

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Table I - Internal Standard Recovery (%)

Sample	Mesitylene	Naphthalene	Trimethyl-naphthalene	Phenanthrene	MeC$_{11}$	MeC$_{14}$	MeC$_{16}$	MeC$_{18}$
Water (4 hour headspace sampled)	8±6 (6)*	29±10 (6)		12±10 (6)	17±12(6)	62±8(6)	74±8 (6)	57±18(6)
Water (18 hour headspace sampled)	6±1 (3)	52±16 (3)	95±9 (3)	92±7 (3)	31±14(3)	84±6(3)	97±6 (3)	94±5 (3)
Mussels (4 hours)	18±16(2)	76±31 (3)	47±19 (3)	12±7 (3)	12±6 (3)	11±4(4)	4±0.5(4)	2±1 (4)
Mussels, 2M KOH (4 hours)	--- **	83±25 (2)	88± 9 (2)	40± 8 (2)	4±1 (2)	7±4(2)	2±2 (2)	2±1 (2)
Mussels, 3M KCl (4 hours)	5± 1 (2)	40± 7 (2)	20± 4 (2)	7± 1 (2)	8±4 (2)	11±1(2)	6±0 (2)	3±1 (2)
Mussels, 2.5M NaOH (18 hours) No LC clean-up	---	66± 8 (4)	102± 28(4)	101±13 (4)				
Mussels, 2.5M NaOH (18 hours) LC clean-up	---	26± 6 (8)	80± 20(8)	80±14 (8)				

---

*( ) denotes number of samples analyzed.
**--- denotes no recovery of internal standard.

Table II

Comparison of Volatile Hydrocarbon Levels Obtained with and without LC cleanup (μg/kg)

	No LC	LC
Mytilus (site unknown)	1406 ± 139 (2)[1]	540 ± 79 (3)
Oysters (Middle Marsh, SC)	1834 (1)	652 (1)
Clams A (control)	509 ± 16 (2)	377 ± 124 (2)
Clams B (1 ppm oil)[2]	1421 ± 161 (2)	491 ± 153 (3)
Clams C (10 ppm oil)[3]	1704 (1)	1413 ± 560 (2)
Katalla River sediment	566 ± 52 (2)	574 (1)

---

[1] ( ) denotes number of samples analyzed.

[2] exposed to 1 ppm crude oil in the water.

[3] exposed to 10 ppm crude oil in the water.

Table III

Mytilus Tissue Analysis

Site	Hydrocarbon Level (µg/kg)
Simpson Bay	411 ± 51 (2)*
Bligh Island	364 ± 85 (3)
Hinchinbrook Island	250 ± 68 (3)
Wells Bay	179 ± 111 (4)

---

*( ) denotes number of samples analyzed.

Appended to RU 43

Interlaboratory Comparison of Analyses for Trace Level Petroleum Hydrocarbons in Marine Sediments

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S. N. Chesler, and H. S. Hertz

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Abstract

Results of analyses for petroleum hydrocarbons at the μg/kg (ppb) level in marine sediments have been compared among eight laboratories. Values for concentrations of total extractable hydrocarbons scattered between 9 to 500 μg/kg and 49 to 6625 μg/kg for the two sites examined. Scatter of results for hydrocarbons in the gas chromatographic elution range, the most abundant aliphatic and aromatic hydrocarbons, and total polynuclear aromatic hydrocarbons (four rings and larger) were similar. Results for percent water and pristane/phytane ratio were somewhat more consistent. Sample inhomogeneity and analysis uncertainty contributed to an observed intralaboratory precision (1σ) of ±25 percent for nine replicate analyses of one sediment sample. The data are discussed with regard to the reliability and comparability of current methods for environmental baseline measurements.

Keywords:
Gas chromatography; gas chromatography-mass spectrometry; hydrocarbons; intercalibration; liquid chromatography; marine sediment; polynuclear aromatic hydrocarbons.

Brief

Results of the analysis for trace level petroleum hydrocarbons in two marine sediments are compared among eight laboratories.

Introduction

Analytical methodology for the determination of petroleum hydrocarbons in sediments is evolving at a rapid rate. Studies on the fate of hydrocarbons that enter the marine environment from natural sources such as seeps or that are introduced through man's activity in the form of pollution with fossil fuels have recently been reviewed (1,2). Uptake by intertidal and benthic sediments is one such fate. Since the oil may then persist for years, resulting in continuous exposure of the marine ecosystem, measurement of petroleum hydrocarbon content in sediments must be an integral part of oil pollution studies. Intensified research efforts arising from environmental and public health questions have resulted in numerous methods for the measurement of hydrocarbons in sediments (3-8). The toxicity of petroleum is well documented for a number of different compound classes and specific compounds such as naphthalene, benzo(a)pyrene, and toluidine (9). Polynuclear aromatic hydrocarbons (PAH) have been studied extensively in recent years due to reported mutagenic and carcinogenic properties (10). Environmental PAH concentrations must be monitored in order to assess potential human exposure.

Analyses of environmentally significant molecules present at trace levels are currently being performed in many laboratories, and the environmental analytical chemist is being called upon to report narrower confidence limits at lower levels of petroleum pollution. Ultimately, he must seek to extend the range of analysis to the sub-ppb level for accurate measurement and assessment of the hydrocarbon burden.

For many of the environmental analyses there is little or no knowledge of comparability of data from different laboratories and, in most cases, probably little knowledge of intralaboratory precision. In order that the data from diverse methods be meaningful and reliable, there must be a basis for intercomparability. Furthermore, unless the data can be put on an equivalent basis, environmental standards can be neither set nor enforced.

Farrington _et_ _al_. have intercalibrated gas chromatographic analyses for hydrocarbons in spiked cod liver lipid extracts and tuna meal samples and found good agreement among three laboratories (11). Results of an initial feasibility study consisting of an intercalibration of sediment analysis between two laboratories have recently been published (12). The results of an eight laboratory intercomparison exercise for the determination of hydrocarbons in two intertidal sediment samples from the Northeastern Gulf of Alaska are described below. It was decided to intercalibrate on 'real world' samples (i.e., samples containing hydrocarbons from natural sources and not "spiked"), recognizing that the mixture of chemicals in petroleum is highly complex and that the products of weathering and microbial degradation compound this complexity. It is also true that sample inhomogeneity may complicate intercalibration studies of a natural sample. If these problems can be controlled effectively, these data could be uniquely valuable in assessing the variability and reliability of current sediment hydrocarbon analyses from sample work-up through measurement and interpretation.

Experimental

The intercalibration material consisted of two intertidal sediment samples from the Prince William Sound and Northeastern Gulf of Alaska. Two sites were selected for sampling:

Hinchinbrook Island: 146° 41' W, 60° 21' N; this site is at the ocean entrance to the Prince William Sound and is constantly being washed with water from the Gulf of Alaska.

Katalla River: 144° 35' W, 60° 11' N; this site is downstream from a known oil seep and provides samples with hydrocarbons known to be of petroleum origin.

All samples were collected during low tide and stored in precleaned 1-gallon tin-plated steel cans. Samples were frozen immediately with dry ice and maintained in that state except for a brief period when the sediments were homogenized. The bulk sediment from each site was homogenized by mixing for three hours in a specially modified cement mixer which had been cleaned with pentane prior to use. Subsamples ($\sim$350g) of each sediment were removed from the rotating mixer with a stainless steel trowel and placed in 16-oz, acid-washed, glass bottles. The bottles were sealed with plastic screw caps containing aluminum foil cap liners. These samples were refrozen immediately after packaging.

Two bottles each of the Katalla and Hinchinbrook sediment samples were shipped frozen to each participating laboratory. The following data were to be obtained for each sample:

1. Total hydrocarbons in GC elution range (approximately C_{10}-C_{30}),
2. Total extractable hydrocarbons,
3. Pristane/Phytane ratio and the amount of each of these present,
4. Percent water,
5. Identities and amounts of the three most abundant aliphatic and three most abundant aromatic hydrocarbons,
6. Total polynuclear aromatic hydrocarbon (PAH) concentration (4 rings and larger),
7. Identity and amount of the most abundant PAH (4 rings or larger).

The analytical methods employed by each of the participating laboratories are summarized briefly in Table I.

Results and Discussion

The importance of establishing environmental baselines for hydrocarbon levels in sediments is well accepted; however, these baselines are only meaningful if one can assess the accuracy and precision of the data. This intercalibration exercise was conducted to determine the adequacy of analytical procedures for hydrocarbon determinations in sediments and to indicate the uncertainty with which results from different laboratories may be compared. The current, most commonly used analytical approach for determining hydrocarbons in sediments involves an organic solvent extraction, saponification, and column or thin layer chromatography to isolate the hydrocarbons (1,13). Within this general scheme, however, there exists a variety of analytical methods. Since the 'true' or 'actual' values cannot be verified with current state-of-the-art methodology, one cannot conclude which is the 'best' method or result. It is imperative, however, that one be cognizant of the limitations of each method; knowledge of how a procedure compares with others is extremely important when environmental decisions with far reaching economic and social consequences are to be made.

Examination of the Hinchinbrook and Katalla sediments showed both to be predominantly fine to medium grain sand. Homogeneity studies on the two sediments were conducted by the National Bureau of Standards utilizing the dynamic headspace sampling technique previously described (8). The results of these studies are summarized in Table II. The relative standard deviation for the Katalla sediment (910 μg/kg ± 25%, n=9) is slightly better than that for the Hinchinbrook sediment (420 μg/kg ± 30%, n=12). An internal standard of phenanthrene was added to both sediments at the 20 μg/kg concentration level; an average of 83 percent was recovered from the Katalla sediment, while only 41 percent was recovered from the Hinchinbrook sediment. Mesitylene, naphthalene, and trimethylnaphthalene also exhibited similar recovery behavior from the two sediments. The Hinchinbrook sediment thus appears to have greater affinity for hydrocarbons than the Katalla sediment.

Intercomparison Results

Table III contains the results of percent water analyses for the two sediments. The agreement is generally good with the exception of high results from lab No. 7, which accounts for the large standard deviations (Hinchinbrook = 6.7 ± 4.3% H_2O, Katalla = 25.3 ± 5.2% H_2O). However this uncertainty or even larger uncertainties have no significant effect on the remaining data, which are reported on a dry weight basis.

The amount of extractable hydrocarbons obtained for the sediments is reported in Table III. Laboratories 5, 6, and 8 dried the samples (freeze dried or otherwise) prior to extraction. The drying process results in some loss of hydrocarbons (up to C_{20}, depending on the procedure, temperature, etc.) from the mixture of hydrocarbons to be measured. Farrington (14) has suggested an alternative method to circumvent this loss which employs a headspace analysis of the sediment, followed by freeze drying and solvent extraction. Losses of volatile hydrocarbons would be minimized with such a procedure and a broader molecular weight range of compounds could be analyzed.

Data obtained for the Hinchinbrook sediment, including hydrocarbons in the GC range, pristane/phytane ratio, and the most abundant aliphatic and aromatic hydrocarbons are presented in Table IV; analogous data for the Katalla sediment are shown in Table V. The results of measurement of hydrocarbons in the GC range vary widely among the eight laboratories; the agreement is better for the Katalla sediment than for the Hinchinbrook sediment. This variability, which exists even for laboratories employing similar extraction and/or work-up procedures, may be partially a result of the different manner in which the gas chromatographic quantification was carried out. GC analysis of the saturated or aliphatic fraction of the sediment extract usually produces a chromatogram with an unresolved complex mixture of alkanes and cycloalkanes with a wide range of molecular weights. Quantitative data based solely on resolved chromatographic peaks differs from that in which a contribution from the unresolved "envelope" is considered. Studies were conducted at NBS in which a sediment sample was headspace extracted and analyzed by capillary column gas chromatography. The resulting chromatogram was quantified both on the basis of resolved peaks only, and resolved peaks plus a contribution from the unresolved envelope. Values for the hydrocarbon concentration showed a variability as high as 300 percent.

In cases where quantitation was based on an external standard, the percent recovery for each component of the standard must be known. Warner (15) has shown that diethyl ether extraction recoveries for napthalene, dimethylnaphthalene, and biphenyl from spiked marine organisms may be as low as 40 percent for concentrations below 0.1 μg/g. The addition of an internal standard prior to any analysis step would seem logical in order to correct for such losses. The internal standard should contain both aliphatic and aromatic components characteristic of the molecular weight range and concentration of compounds to be analyzed in the samples. Losses during sample work-up are compensated for by a similar loss of the internal standard. The sample must be analyzed with and without the internal standard, however, to insure that components in the standard are not also present in the sample; or if they are present, their contribution can be taken into account. The underlying assumption in methods involving an internal standard is that the standard is incorporated into, and equilibrated with, the sample matrix. This may or may not be the case, however, and errors may result. Values for the most abundant aliphatic hydrocarbons in the Katalla sediment (Table V) show that the headspace extraction recovered the volatile, lower molecular weight components, C_9-C_{11}, which may be lost during the sample drying step or the solvent concentration step required in methods employing an organic extraction.

Sample extracts were saponified to reduce the problem of separating hydrocarbons from lipids coextracted from the sediments by laboratories 3, 6, 7, and 8. These compounds may co-elute or overlap with peaks of interest on certain chromatographic systems (14). Methods which do not remove these polar compounds may be expected to give results for hydrocarbon content which are high. Even when saponification is carried out, there is a potential problem of transesterification with the potassium hydroxide-methanol extraction usually used. Methyl esters of fatty acids may be produced at concentrations which are significant when analyzing for hydrocarbons at the ppm level (16). Farrington has noted that saponification in the presence of 25 percent water will reduce transesterification considerably (3). Laboratory 1 (NBS) employed high-performance liquid chromatography (HPLC) to remove the polar biogenic compounds in the extraction procedure, but not in the headspace procedure (see Table I). It was found that an HPLC clean-up of headspace sampled sediment resulted in no change in the results of the GC analysis. This result indicates that these interfering compounds were removed from the sample matrix during solvent extraction only and not during headspace sampling.

Values for relative amounts of pristane and phytane are used to differentiate natural sources of hydrocarbons such as biogenic hydrocarbons from petroleum-based pollutants (5). Experimental values for the pristane/phytane ratio (Tables IV and V) are in sufficient agreement to answer this question.

Results for the polynuclear aromatic hydrocarbon (PAH) content of the samples are presented in Table VI. Only three of the eight laboratories involved in the intercomparison submitted results for PAH concentrations. It seems clear from this limited response that this higher molecular weight fraction, which may be the most critical in terms of toxicity, carcinogenicity, and persistence, cannot be easily determined by gas chromatography alone. Labs 2 and 4 both found the methylpyrenes to be the most abundant PAH (4 rings and larger) in the Katalla sediment. Lab 4 identified methyl-substituted pyrenes and fluoranthenes, and chrysene in the Katalla sediment by comparison of their mass spectra with known standards. NBS used HPLC and fluorescence emission spectroscopy to identify methylchrysene as the most abundant PAH in the Katalla sediment.

Conclusions

The results of this study indicate the high variability of state-of-the-art hydrocarbon analyses on 'real world' sediment samples. Unlike intercalibration on spiked samples where a substrate is added to a matrix at a suitable concentration and assumed to be incorporated into and equilibrated with the matrix, intercalibration on real samples requires no such assumption. In setting environmental baselines, use of inaccurate and imprecise consensus values is always a danger; we feel the intercomparison data for a common (homogeneous) sediment sample are a necessary addition to such baseline data. We hope other laboratories will be encouraged to undertake such interlaboratory comparisons with sediment samples in the future, especially as new methods are developed and applied to environmental analyses. Such studies are needed to determine when different numbers generated by different laboratories using different methods are environmentally significant.

If nothing else, the results of this intercomparison study should serve as a warning against overinterpretation of currently generated trace-level hydrocarbon determinations. The results should not be used as an argument against further intercomparison exercises, but should be used as encouragement for the continued development of the state-of-the-art of trace organic analysis. Ultimately, the goal of the

National Bureau of Standards is to produce a Standard Reference Material with certified trace-level concentrations of environmentally significant organic compounds in a "real" matrix. Unfortunately, methods for preparing and certifying such a material have not yet been developed. Problems associated with sample homogeneity, stability, matrix effects, etc. must also be resolved before any such standard can become available. The low concentration of hydrocarbons anticipated in many pollution baseline studies necessitates the development of sensitive analytical techniques. Finally, some form of information exchange or intercomparison must exist among laboratories in order to assess the uncertainty of the data from these new analytical techniques.

In order to specify procedures adequately, it has been necessary to identify commercial materials in this report. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material identified is necesarily the best available for the purpose.

Acknowledgments

The authors wish to thank P. D. LaFleur for his critical reading of this manuscript. The following laboratories and scientists participated with NBS in the intercomparison study: John A. Calder, Florida State University; Ronald A. Hites, M.I.T.; John L. Laseter, University of New Orleans; William MacLeod, NOAA-Seattle; Steven J. Martin, Geochem Laboratories;

Patrick L. Parker, University of Texas; David Shaw, University of Alaska.

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Table I - Methods of Sediment Analysis

Lab	Extraction	Separation	Gas Chromatography	
			Column	Standard
NBS	a) Dynamic headspace extraction of 100g sediment in 500 ml pure H_2O. Volatiles trapped on Tenax GC adsorbent.		100m SE-30 SCOT 80 °C for 4 min→275° at 4°/min.	Aliphatic and aromatic internal standard added prior to sample work-up at start of analysis.
	b) Diethyl ether and methylene chloride Soxhlet extraction of 100g wet sediment.	Liquid chromatography on µBondapak NH_2 to remove polar biogenic compounds.	Same as above.	Squalene internal standard added at start of analysis.
2	Diethyl ether extraction of 100g wet, acidified sediment on ball-mill tumbler for 18 h.	Column chromatography on activated silica gel. Aliphatics eluted with petroleum ether. Aromatics eluted with methylene chloride in petroleum ether.	20-30m SE-30 WCOT 60 °C for 10 min→250° at either 2 or 4°/min.	Hexamethylbenzene standard added prior to GC analysis.
3	300g wet sediment dried by washing with methanol. Reflux extraction with benzene-methanol (3:2) for 14 h. Saponification with 0.5N KOH in methanol; extraction into benzene and taken to dryness. Residue taken up in hexane.	Column chromatography on alumina:silica gel (1:3). Aliphatics eluted with hexane. Aromatics eluted with benzene. Polar fraction eluted with methanol.	6' 4% FFAP on Gas Chrom Z. 80 °C→225° at 4°/min. or 6' 3% SP 2100 on Supelcoport 100 °C→325° at 4°/min.	External standard containing several aliphatic, aromatic, and olefinic hydrocarbons.
4	250g wet sediment extracted with methanol and benzene: methanol azeotrope. Reduced volume and extractd with hexane and methylene chloride. Reduced volume.	Organic extract partitioned in Nitromethane: Cyclohexane to give polycyclic fraction. Column chromatography on silica gel; eluted with hexane.	3% OV-17. 70 °C→300° at 8°/min.	External standard containing polynuclear aromatic hydrocarbon.

Table I - Methods of Sediment Analysis (cont'd)

			Gas Chromatography	
Lab	Extraction	Separation	Column	Standard
5	150g dried sediment extracted with heptane on ball-mill tumbler for 4 h.	Column chromatography on alumina:silica gel (1:1) aliphatics eluted with heptane; aromatics eluted with benzene.	20' 5% eutechic ($LiNO_3$, $NaNO_3$, KNO_3) on Chromosorb G 150 °C→280 °C at 20°/min.	Spiked blanks: C_{18}, C_{20}, phytane, anthracene, pyrene.
6	Freeze-dried sediment reflux extracted with toluene:methanol (3:7) for 14 h; Sediment reextracted with hexane. Combined extracts saponified with KOH in methanol and toluene. Extracted nonsaponifiables into hexane.	Column chromatography on alumina:silica gel (1:2) Aliphatics eluted with hexane; aromatics eluted with benzene.	5% FFAP on Gas Chrom Q 70 °→270 °C at 6°/min.	External standard n-C_{16}, C_{18}, C_{21}, C_{24}, C_{28}, C_{32}, pristane, phytane.
7	80g wet sediment saponified in KOH: methanol under reflux for 24 h. Extracted into hexane.	Column chromatography on alumina:silica gel (1:1) aliphatics eluted with hexane; aromatics eluted with benzene.	OV-101 80 °C for 2 min→280° at 8°/min.	Spiked blank and n-alkane external standard.
8	100g freeze-dried sediment reflux extracted with toluene:methanol (3:7). Extract saponified in 6N KOH:methanol:water; extraction into hexane.	Column chromatography on alumina:silica gel aliphatics eluted with heptane; aromatics eluted with benzene.	152m stainless steel capillary coated with 10% Apiezon L. 155° for 8 min→280° at 2°/min.	External standard

Table II - Homogeneity Studies on Intercalibration Materials, Results of Replicate Analyses

Hinchinbrook Sediment		Katalla Sediment	
Bottle	Hydrocarbons in GC range (μg/kg)	Bottle	Hydrocarbons in GC range (μg/kg)
H-4	437 318 290	K-21	709 816 767
H-23	564 470	K-36	1071 728
H-39	399 352	K-1	1226 1093 1175
H-30 + H-31 homogenized	282 723 394 386 408	K-15	602
Average[a]	418 ± 124 (30%) (n=12)[b]	Average	910 ± 231 (25%) (n=9)[b]

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[a] Precision expressed as the standard deviation (1σ).

[b] n indicates number of analyses.

Table III - Analyses of Hinchinbrook and Katalla Sediments[a]

	Percent Water		Total extractable hydrocarbons (μg/g)	
Laboratory	Hinchinbrook	Katalla	Hinchinbrook	Katalla
NBS	4.4 ± 0.1	22.5 ± 0.2	0.22	2.5
2	4.7	23.5	4.4	12.8
	4.4	22.6	6.2	11.0
3	5.0	23.5	24.3[b]	65.8
	5.8	22.8	7.9	57.6
4	-	-	-	-
5	4.3	22.4	-	-
	4.3	22.2	-	-
6	4.79	26.3	3.12	109
	-	21.3	7.92	10.7
7	15.4 ± 5.7	36.5 ± 6	2.9	5.4
	14.3 ± 2.1	34.3 ± 2.1	0.64	3.9
8	-	-	-	-
Range	4.3 - 15.4	21.3 - 36.5	0.22 - 7.92	2.5 - 109

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[a] Some laboratories supplied results of duplicate analyses. In such cases both results are presented in the Table. Where presented, precision is expressed as the standard deviation (1σ).

[b] Laboratory 3 reported that this result is probably in error.

Table IV - Hinchinbrook Sediment[a,b]

	Hydrocarbons in GC range (μg/kg)			Pristane/Phytane Ratio	Most abundant hydrocarbons (μg/kg)			
Laboratory	Aliphatic	Unsat/Aromatic	Total		Aliphatic		Aromatic	
NBS (headspace)			420 ± 120	0.9 ± 0.2	C_{19} 16 ± 12 C_{18} 15 ± 8 C_{17} 12 ± 1		Me-Naph 2 ± 1 C_2-Naph 1 C_2-Naph 1	
NBS (extraction)			250	0.8	C_{25} 7 C_{24} 7 C_{23} 6		- - -	
2	140 93	4 10	144 103	2.59 -	C_{25} 40 C_{26} 20 C_{24} 19	C_{25} 30 C_{24} 12 C_{26} 12	C_3-Naph 1.3 Phen 0.7 C_2-Fluor 0.2	C_3-Naph 2.7 Phen 0.7 2-Me-Naph 0.3
3	54 57	21 23	75 80	2.05 2.78	Prist 4 C_{18} 4 C_{19} 4 C_{27} 4	C_{17} 5 C_{18} 5 C_{19} 5	unk 7 unk 3 unk 3	unk 3 unk 3 unk 3
4	-	-	-	-	-		-	
5	9 26	35 12	44 38	- -	- - -		unk 6 - -	unk 3 unk 2 unk 1
6			15.9 34.1	- 1.67	C_{18} 1.4 C_{20} 1.3 C_{19} 1.1	C_{21} 4.7 C_{22} 4.5 C_{20} 3.3	unk 1.8 unk 1.5 unk 1.2	unk 0.6 unk 0.5 unk 0.4
7	100 ± 50 500 ± 600	40 ± 30 400 ± 100	140 900	- -	- -		- -	
8	-	-	-	2.71 3.6	C_{17} 0.39 Prist 0.38 C_{18} 0.32	C_{17} 2.9 C_{18} 1.9 C_{19} 1.8 Prist 1.6	-	
Range	9 - 500	4 - 400	15.9 - 900	0.8 - 3.6				

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[a] Some laboratories supplied results of duplicate analyses. In such cases both results are presented in the Table. Laboratory 7 submitted a summary of multiple analyses on each bottle of sediment. All precision data is expressed as the standard deviation (1σ).

[b] In the Table, unk is used as an abbreviation for unknown; C_x represents n-alkane containing x carbons; Prist is pristane; Me is methyl; Naph, Phen, and Fluor are naphthalene, phenanthrene, and fluoranthene, respectively. A dash (-) is used when results were not supplied by a participating laboratory.

Table V - Katalla Sediment[a,b]

Laboratory	Hydrocarbons in GC range (µg/kg) Aliphatic	Unsat/Aromatic	Total	Pristane/Phytane Ratio	Most abundant hydrocarbons (µg/kg) Aliphatic		Aromatic	
NBS (headspace)			910 ± 230	1.9 ± 0.02	C_{10} 32 ± 11		Me-Naph 16 ± 5	
					C_{11} 25 ± 7		C_2-Naph 15 ± 3	
					C_9 23 ± 13		C_2-Naph 14 ± 4	
NBS (extraction)			2700	1.7	C_{11} 66		C_2-Naph 54	
					C_{14} 66		C_2-Naph 27	
					Prist 58		Me-Naph 24	
2	610	120	730	3.27	C_{25} 42	C_{25} 98	Phen 9.7	Phen 9.1
	880	130	1010	3.27	C_{19} 24	C_{24} 60	C_2-Naph 7.1	C_2-Naph 7.4
					Prist 23	C_{26} 57	2-Me-Naph 5.3	2-Me-Naph 5.7
3	1940	530	2470	3.55	C_{17} 180	Prist 110	unk 50	unk 72
	1420	710	2130	6.32	C_{15} 180	C_{19} 100	unk 50	unk 58
					Prist 140	unk 90	unk 40	unk 29
4	-	-	-	-	-		-	
5	3454	401	3855	2.81	C_{24} 75	C_{23} 194	unk 19	unk 14
	6625	417	7042	2.69	C_{23} 57	C_{24} 179	unk 14	unk 13
					C_{25} 53	C_{25} 138	unk 8	unk 5
6	196	14	210	3.71	C_{21} 19.9	C_{22} 4.3	unk 2.9	unk 0.8
	49.4	4.2	53.6	2.38	C_{22} 18.7	C_{21} 4.1	unk 2.5	unk 0.7
					C_{20} 13.7	C_{20} 3.9	unk 2.1	unk 0.7
7	200 ± 200	300 ± 300	500	-	C_{17}+Prist 47		-	
	400 ± 200	80 ± 10	480	-	C_{16} 36		-	
					C_{18}+Phyt 21		-	
8	-	-	-	3.25	Prist 28.8	Prist 19.9	-	
				3.10	C_{19} 22.7	C_{27} 16.2	-	
					C_{20} 22.7	C_{17} 15.5	-	
Range	49.4 - 6625	4.2 - 710	53.6 - 7042	1.7 - 6.32				

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[a] Some laboratories supplied results of duplicate analyses. In such cases both results are presented in the Table. Laboratory 7 submitted a summary of multiple analyses on each bottle of sediment. All precision data is expressed as the standard deviation (1σ).

[b] Abbreviations are the same as in Table IV, in addition Phyt is phytane. A dash (-) is used when results were not supplied by a participating laboratory.

Table VI - Polynuclear Aromatic Hydrocarbons in Sediments[a,b]

	Hinchinbrook Sediment		Katalla Sediment	
Laboratory	Total PAH (μg/kg) 4 rings and larger	Most abundant PAH (μg/kg)	Total PAH (μg/kg) 4 rings and larger	Most abundant PAH (μg/kg)
NBS	5 ± 0.5	chrysene 0.3	40 ± 2	Me-chrysene 3
2	-	pyrene 0.08	10	Me-pyrene 3.9
		pyrene 0.1	8.6	Me-pyrene 3.2
4	3.8	chrysene 1 Me-pyrenes and Me-fluoranthenes 1	74	Me-pyrenes and Me-fluoranthenes 28
Average	4.4 ± 0.85 (n=2)[c]		33.2 ± 31 (n=4)	

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[a] Results of duplicate analyses are presented for Laboratory 2. All precision data is expressed as the standard deviation (1σ).

[b] A dash (-) indicates no results were supplied.

[c] n indicates the number of values averaged.

Research and Evaluation of Trace Element
Methodology for the Analysis of Sea Water

Final Report Submitted to
National Oceanic and Atmospheric Administration
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Research Unit 47

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Introduction

The literature of marine water analysis reflects the considerable difficulty in establishing an accurate and precise method of analysis for trace metals. Conflicting reports of the average concentrations of metals show that the complex matrix defies a simplified approach. For example, specific sampling techniques, container contamination, differences in salinity, suspended particulate matter, and analytical technique have to be considered. In the past decade analytical instrumentation and techniques have been developed to vastly improve the precision of the analytical measurement. However, little attention has been paid to the problem of sampling and storage of the sample prior to chemical analysis. The solving of the analytical analysis problem is of little use until a representative sample can be taken, free of contamination, and properly stored until analysis.

It is important to remember that trace elements in sea water have three very closely related interfaces with its environment: the atmosphere, the lithosphere, and the biosphere [1]. Each of these areas are actively involved and each has special properties which can drastically effect the metal content of the sea. Therefore, it is no wonder that much of the early analytical data is unreliable [2].

Components of sea water can be conveniently divided into two groups: major components (present in quantities greater than 1 mg/1) and minor components (present in quantities less than 1 mg/1). Major components are present in the same proportions throughout the oceans of the world, whereas minor components vary with locality, depth, etc. The average composition of sea water has been tabulated by Goldberg [3] and more recently by Segar and Cantillo [4]. As can be seen from reviewing these and other data in the literature of individual elements, considerable variations have been reported. This is due in part to variations in different parts of the ocean and at different times; although some of the variation is due to the differences in analytical methods used to analyze the samples. In general, it is agreed by most workers that contamination plays a major role.

This report does not attempt to answer questions regarding the accuracy of sampling or even of subsequent contamination of the samples during storage. By the method of sample splits and exchange of samples between laboratories it should be possible to demonstrate whether or not the actual analytical methods being used are reliable. For this purpose, the choice of samples to be analyzed is not too important. While attempts have been made to minimize sampling or contamination errors, it is recognized that these samples are far from ideal and probably will give only a fair estimate of the true trace element content in Alaskan waters.

Separation

Most of the trace metals listed as minor components cannot be determined by conventional analytical methods (flame atomic absorption spectrometry (AAS), polarography, or colorimetry) without a separation and/or preconcentration step. The most common concentration techniques are co-precipitation, electrolysis, solvent extraction and ion-exchange resins. Co-precipitation has the disadvantages of being a lengthy process and of requiring the removal of the precipitation ion. Burrell [5] and Chau et al. [6] co-precipitated trace elements in sea water with ferric hydroxide, followed by chelation and solvent extraction to remove the iron. The procedure was tedious and it was necessary to apply large blank corrections. Sato and Saitoh [7] co-precipitated chromium from a liter of sea water with zirconium hydroxide. The zirconium hydroxide was removed by filtration and then dissolved in 2N hydrochloric acid. The analysis was by AAS using a carbon furnace. Feldman and Rains [8] used sodium tetraphenylboron to separate cesium and rubidium from five liters of sea water and then completed the analysis by flame emission spectrometry.

For the analysis of cadmium, lead, and zinc in sea water the elements were electrolyzed on a hanging mercury drop electrode [9]. The mercury was washed and then transferred to a graphite boat. The mercury was vaporized at 440 °C, the metals atomized at 1700 °C and determined by AAS. Some problems encountered were loses of analyte during electrolysis in which the electrolysis cell had to be coated with silicon. A disadvantage of the technique is that only certain elements can be separated and only a fraction of the analyte is electrolyzed which reduces the sensitivity of the method. In a variation Lund and Larsen [10] electrodeposited cadmium on a tungsten filament which was then heated electrically and the cadmium determined by AAS.

The chelation of metals with organic ligands and subsequent extraction into various solvents has long been used as an analytical technique. Table 1 lists several organic ligands used to preconcentrate trace elements in sea water. Is is well known that ammonium pyrrolidine dithiocarbamate (APDC) is a useful chelating agent for a number of transition metals [11-15]. Gilbert and Clay [16] extracted Cr (VI) from 800 ml of sea water with APDC-MIBK (methyl isobutyl ketone) and then determined the chromium by AAS. The chromium is oxidized with permanganate in a 50 °C hot water bath, the sample is acidified to pH 2, cooled, and then the chromium APDC complex extracted into MIBK. A major difficulty of preconcentration with APDC-MIBK is the effect of the aqueous (V_a)/organic (V_o) phase ratio [13]. The degree of extraction

Kingston [22] found quantitative recovery of Cu, Fe, Mn, Ni, and Zn from four liters of sea water at a flow rate of 33 ml per minute. The collection of ions was done between pH 5.0 and 5.5 uniformly for all the elements of interest with hydrochloric acid used as the elutant. The final analysis was completed by flame AAS.

Davey and Soper [23,24] have constructed a Chelex 100 *in situ* column sampler and have found, of the ions tested, ^{65}Zn, ^{115m}Cd, ^{54}Mn, ^{64}Cu were retained at $\geq$99 percent, while ^{210}Pb, ^{63}Ni, and ^{59}Fe were retained at 92-95 percent. These results were obtained however using the natural pH of sea water ($\sim$8.1) which is higher than suggested by other researchers for this separation.

Experimental

Sampling, Storage, and Contamination Control

There are nearly as many methods of sampling as there are investigators and virtually all methods contain some deficiencies. However, it is not the purpose of this project to resolve sampling problems, but rather to investigate analytical differences between sample splits of an arbitrary group of samples. Although the method and type of sample taken for this experiment are immaterial, a few comments are made about the NBS sampler.

The sampler used was that developed by Harrison et al. [25] and is unique in its design and method of construction. While there are, unavoidably, a few metal parts, these are made entirely of aluminum and have been double coated with a very tough, thick coating of Teflon FEP fluorocarbon resin. The rest of the sampler is constructed from a block of virgin Teflon TFE. The only remaining parts are nylon (nuts, bolts, and washers) and nylon rope to raise, lower, open and close the sampler. An integral attachment machined from Teflon TFE is designed to permit on site filtering of the sample through a 47 mm Nuclepore 0.4 micron membrane filter. For reference, further details are reproduced in Appendix I.

A common deficiency of many samplers is the inappropriate selection of materials used in the sampler which unavoidably cause contamination of the sample. The NBS sampler was designed specifically for very low contamination levels. Before transporting to Alaska for taking samples, the NBS samplers were completely disassembled and cleaned in acid. These parts were stored in clean polyethylene bags to be reassembled on the sampling site in Alaska. Metal parts whose Teflon coating was scratched or damaged were replaced with parts having new or intact coatings.

Another common cause of contamination is in the selection and cleaning of bottles for sample storage. Maienthal and Becker [26] have reviewed the literature on the handling and storage of liquid and solid samples. Moody and Lindstrom [27] have investigated the applicability of commercially available bottles to the storage of liquid samples. The least contaminating bottles were found to be bottles constructed of Teflon and polyethylene, respectively. Methods were also developed to assure adequate cleaning of these bottles.

For the NBS sampling trip to Alaska, 40 one-liter Teflon FEP bottles were subjected to very rigorous cleaning [28]. Half of these bottles were then filled with the highest purity distilled water. To the remaining 20 clean Teflon bottles 44 g of ultra high purity HNO_3 was added for the purposes of acidifying a one-liter sea water sample to 0.5N with HNO_3. The acid and water used at these stages represent one of the few remaining chances for contamination of the sample. Even though the acid is of the highest attainable purity, a glance at the impurity levels will still reveal the need to make a correction for some elements for contamination due to the acid blank. Further details about reagents used are reproduced in Appendix II.

The NOAA ship *Surveyor* was used to transport men and equipment from Juneau to the selected sample site, Glacier Bay, Alaska. The original NBS plans were to sample four different ways. Half of the samples were to have been filtered through 0.4 micron Nuclepore filters and the rest were to have been unfiltered. Half of each of these samples were to have been acidified and half were to have been unacidified. Thus the sample classification would have been filtered (acidified and non-acidified) and unfiltered (acidified and non-acidified).

Unfortunately, once on board, it was learned that the sampling time allocated to NBS was far less than was needed to complete the project. Using the 0.4 µ filter and two samplers, it was possible to filter about 500 ml every 15-20 minutes. The total time allocation for inorganic sampling was less than one hour, much of which was lost trying to set up and clean the sampler and filter apparatus. If filtered samples had been taken, the entire trip would have yielded exactly 1.5 liters of sea water, a quantity which was insufficient. Therefore, the decision was made to abandon the filtering and to get as many other samples as possible. In a period of 1/2 hour, just under 40 liters of sea water was collected. The following procedures were used.

Prior to the actual sampling, the ship *Surveyor* was directed toward and allowed to drift into a current of water. A platform was lowered off the forward bow from which the samplings were made. Under these circumstances, the sampler was always between the ship's hull and the current of water.

Under the prevailing conditions, contamination from the ship's hull would have been swept away from the sampler. While these were not ideal conditions they were the best possible under the circumstances.

After assembly, the sampler was rinsed off with distilled water from the Teflon bottles. The sampler was immersed in the sea water to a depth of about two meters, opened to collect the sample, closed, and then hauled up to the platform. The contents of the sampler were then transferred to a Teflon bottle. Several samplings were required to fill each bottle. Polyethylene gloves and bags were used to handle the equipment during these transfer steps. Additional bags were used to enshroud the bottle and sampler to help prevent particulate contamination from the atmosphere.

As soon as each bottle (unfiltered, either acidified or unacidified) was filled, it was placed in a cooler chest and surrounded by blocks of dry ice. Twenty liters of unfiltered, unacidified water were collected and frozen and approximately 16 liters of unfiltered and acidified (to 0.5N with ultra-pure HNO_3) were collected and frozen. Some bottles containing HNO_3 had leaked so these bottles were not used due to the loss of acid and the likelihood of contamination.

All bottles were stored in protective polyethylene bags with twist-tie closures at all times. The bottles were packed together with large amounts of dry ice in insulated boxes. On the return trip to Washington, DC, commercial deep freeze lockers were used during layovers to extend the lifetime of the dry ice. Upon arrival at NBS in Gaithersburg, Md., all samples were solidly frozen with large amounts of dry ice remaining. The samples were transferred to a large freezer maintained at -40 °C and kept there until needed for analysis. Sample duplicates were provided to Dr. Burrell, University of Alaska, directly from this freezer.

Sample splits were received from the University of Alaska in a variety of ways. Most had been frozen at one time but were received at NBS (both water and sediment) in a thawed condition. Thawed samples were not re-frozen. Samples which were received frozen were stored at -40 °C. Certain samples were never frozen and were received and kept at room temperature. Most bottles had some degree of dirt on the outside since they were not sealed in polyethylene bags. This required that the outside of the bottle be cleaned prior to opening and sampling the contents. Sample splits received from the University of Alaska were both acidified and unacidified, filtered and unfiltered and were sampled from a variety of sites.

Preconcentration

The frozen sea water samples were thawed at room temperatures for approximately 12 hours. After the samples were completely thawed but were still below room temperature, they were inverted 40-50 times to assure homogeneity. Several samples exhibited inhomogeneity due to a residue of undissolved white crystals. The nature of these crystalline residues has been investigated and is included in this report. A 100 ml pycnometer was used to determine the density of a sea water sample which was found to be 1.018 g/ml.

Triplicate samples were obtained by weighing out 101.8±0.2 g (100.0±0.2 ml) from the sample bottle into clean tared Teflon beakers. These beakers had been previously cleaned in hot (1+1) HCl for one day, hot (1+1) HNO_3 for one day and then were thoroughly rinsed in ultra-pure distilled water [28]. Known amounts of analytes were spiked to one sample from each triplicate set of sea water samples for the purpose of determining the recovery and to permit a check of the results.

The pH of the samples was determined using a Beckman Model SS-2 expanded scale pH meter equipped with Beckman glass and reference electrodes. A drop of pH 5 buffer was added to each sample and the sample pH was adjusted to pH 5.1-5.5 [29] using ultra-pure HNO_3 or NH_4OH manufactured from NH_3 cylinder gas and ultra-pure water. The electrodes were washed with large volumes of ultra-pure water.

A column of 200-400 mesh Chelex 100 fitted with a 25 ml reservoir was cleaned using ultra-pure 2.5N HNO_3 [28]. The pH adjusted sample was loaded on the column by adding small portions of sample directly from the sample beaker to the column The effluent flow rate under these conditions was 50 ml per hour. The column was washed with pH 5 buffer and ultra-pure water after all of the sea water sample had been passed through the column. After washing, the column was stripped of sample ions using ultra-pure 2.5N HNO_3 and the sample was collected in clean, tared 7 ml polyethylene bottles. The bottles were capped and re-weighed to determine the volume of their contents. Analytical blanks were carried through the same procedure [29].

AAS Apparatus. The instrumental system used in this study consists of a Perkin-Elmer Model 603 atomic absorption spectrometer with an HGA-2100 graphite furnace. The samples were introduced into the furnace with an AS-1 auto sampler. The instrumental parameters are given in Table 3.

Reagents. All standard stock solutions were prepared from high purity metals or salts in ultra high purity acids [28]. Working solutions were prepared as needed.

AAS Sample Preparation

Standard working solutions are prepared in ultra pure 1.25M HNO_3 from the standard stock solution. Aliquots of these solutions are then transferred to clean and dry sample cups on the AS-1 auto sampler. Duplicate aliquots of the unknowns are transferred to sample cups. To one cup an equal volume of ultra-pure water is added while to the second cup an equal volume of the analyte is added. The cups are then placed on the AS-1 turn-table and the AAS measurements are made automatically.

Measurement

The AAS instrument is turned on and the hollow cathode lamp for the analyte is inserted in the instrument and adjusted to the proper lamp current. The wavelength and slit widths are adjusted as listed in Table 3. The D_2 arc lamp is turned on and the two lamps are allowed to warm up for 15 minutes. Then the two beams are balanced. The AAS instrument is set on peak height and an integration time of five seconds. The other instrumental parameters are set as given in Table 3.

A calibration curve is established using three to five standard solutions with the AS-1 auto sampler. The calibration curve is repeated until the absorbances are within ±2 percent. Then the absorbances of the unknown solutions are measured using the bracketing technique. For example, the absorbance of a lower standard, the unknown, and then a higher standard is measured. This operation is repeated until the desired precision is attained. The net absorbances are obtained and a calibration curve is prepared using a least square fit on a hand calculator. The concentrations of the unknown are obtained from this calibration curve. If the recovery of the standard addition is not 100 percent, the concentration is corrected by the following equation:

$$c = x \cdot \frac{s}{y-x}$$

where x = ng/ml of analyte in the unknown as determined from the calibration curve.

s = amount of standard added, ng/ml in final volume.

y = ng/ml of analyte found in unknown with standard added as determined from the calibration curve.

c = concentration, ng/ml.

Results and Discussion

Interferences

Interferences encountered with the graphite furnace can be classified as physical, chemical, and interelement in nature. Physical interferences are more pronounced with the graphite furnace than in most flame systems. Light scatter due to incomplete volatilization of inorganic compounds is of major importance. To minimize this type of interference, the time of charring is carefully controlled. However, if it persists, background measurements should be made with a continuum light source or at a nearby nonabsorbing line and then substracted from the absorbance value obtained for the analyte.

Three possible mechanisms account for chemical interferences. The analyte may be lost by the formation of a volatile compound, by occlusion in a nonvolatile matrix, and by the formation of carbides. As an example, lead chloride which boils at 950 °C has a considerable vapor pressure at lower temperatures and can be lost in the charring step. Therefore, the nitrate ion is preferred for graphite furnace AAS. The standards must be prepared in the same concentration of anion as the analyte. As an example, when the absorbance of 1 ng of Pb in 0.5 and 10 percent HNO_3 were compared, the 10 percent HNO_3 suppressed the lead absorbance by 40 percent. Another major interference is from the reaction of the furnace material to form nonvolatile metal carbides. Although carbide formation does occur, it can be controlled with the use of a pyrolytic coating on the inner surface of the graphite rod.

The interelement effect is more pronounced in the flameless technique than in flame systems. It occurs when the analyte reacts with another element which may produce a suppression at certain atomic ratios and an enhancement under certain other conditions. This type of interference can sometimes be corrected by the standard addition method; however, the best technique is to prepare the standards in a similar matrix as the unknowns.

Matrix Modification

In sea water the high salt content makes it difficult to volatilize effectively the matrix without loss of the analyte. The major component, sodium chloride, has both a relatively high volatilization temperature (B.P. 1415 °C) and heat of formation (ΔH, 98 kcal/mole). In order to char such a matrix, the components have to be volatilized and then either decomposed or diffused out of the graphite cell in a manner which precludes loss of the analyte. Also, trace metals in sea water are present mainly as the chlorides which have a lower volatilization temperature than sodium chloride.

To overcome this difficulty Ediger et al. [30] proposed the technique of matrix modification for the determination of a series of elements in sea water. They added an aliquot of a 50 percent solution of ammonium nitrate to the sample in the graphite furnace which assists in the removal of the sodium chloride during the charring cycle. The ammonium nitrate converts the sodium chloride to a more volatile compound. However, in most preconcentration steps the calcium and magnesium are also concentrated and the ammonium nitrate had little or no effect on these elements.

The cadmium values for all the NBS collected samples were less than 0.01 ng/ml which represents our detection limit by graphite furnace AAS when the trace metals are preconcentrated by a factor of 20. Since the reagent blanks for cadmium was not a limiting factor, a positive value could be obtained if a larger sample was pretreated and concentrated.

For lead the reagent blank was 0.1 ng which determined the detection limit. If larger samples were preconcentrated without the use of additional reagents, the detection limits for lead could be lowered. The major difficulty for lead is contamination as exemplified in sample EGA 11. It is very likely the 0.08 ng/ml of lead is due to contamination.

The effect of acidification before and after filtration is clearly shown when comparing manganese values in NBS 500 and 502 with NBS 509 and 518. These results show that acidification caused the Mn concentration to increase by at least a factor of two. The reagent blank for manganese is less than 0.02 ng which would certainly not be a contributing factor. In one sample, NBS 509, the lead value was several orders of magnitude higher than the unacidified samples. The addition of 44 g of HNO_3 to a liter of sea water as in NBS samples 509 and 518 was calculated to be insignificant for Cd, Mn, Ni and Pb [28].

The nickel reagent blank (0.2 ng) was the highest of the analytes tested. Since the nickel values in sea water were considerably higher, this high reagent blank was not considered a serious problem.

Sample Inhomogeneity Caused by Crystalization. Inhomogeneity was found in four samples; two samples from the University of Alaska and two of the NBS samples. These two NBS samples were not analyzed; other, homogeneous samples were substituted from the same site. The samples upon thawing had noticable white and clear crystals at the bottom of the sample bottle. In each case the samples were unfiltered and not strongly acidic (see Table 5). EGA 24 was the only sample in which the crystals redissolved at room temperature. In the remaining samples with crystalline precipitates the precipitate was stable at room temperature and did not dissolve.

The crystals were extracted from NBS Bottle Number 3 and dried in a Teflon beaker. Upon addition of nitric acid, a violent evolution of gas was noted accompanied by instantaneous solubility. The solution was evaporated to a single drop in Teflon and subjected to spark source mass spectrometry. The dominent cation was found to be Ca. Small amounts of Na, K, and Mg were found, probably resulting from absorption to the surfaces of the crystals. No amounts of heavy metal or trace ions were found. This coupled with the evolution of gas upon acid addition would indicate that the dominent species would be a hydrated calcium carbonate ($CaCO_3 \cdot xH_2O$).

The crystals were too numerous and of sufficient mass not to be noticed in the original sampling. It is much more likely then that they were formed in the sample during storage and handling. No crystals were noticed in strongly acid samples which would be expected since the low pH would preclude their formation.

Why the crystals were found in some samples and not others of similar character is unclear. No other perceptible difference between the homogeneous and inhomogeneous samples was obvious except for the crystals. There were samples from the University of Alaska and NBS of equal or higher pH which did not contain crystals. The fact that only unfiltered samples were subject to this phenomenon could indicate nucleation or some other aspect of solid particle influence aiding the formation of the crystals.

Samples EGA 24 and EGA 15 were analyzed and there is no evidence to indicate that the inhomogeneity caused by the crystals caused any significant alteration in the results in relation to samples of the same general area. Any effect would, however, have to be one to two orders of magnitude larger before obvious alterations could be detected with these unknown samples.

Summary

As a result of work reported here and elsewhere it has been determined that a number of plastic materials may be suitable for the collection and storage of samples of sea water [27]. It has been demonstrated, for example, that conventional polyethylene containers if properly cleaned do not materially contribute to inorganic trace metal contamination and if protected from vapor losses are probably suitable for at least several years storage. Problems of contamination which might appear upon long term storage have not been resolved. It would appear that immediate freezing of water samples and storage of these in the frozen state until analysis is to be recommended.

It is shown here that analysis for a variety of elements may be done accurately on as little as 100 ml of water even in the extremely clean waters of Alaska using graphite furnace atomic absorption spectrometry, if extreme care is taken to prevent contamination during the preconcentration procedure. A new preconcentration procedure has been developed here which should substantially help in these analyses in that only minimal handling of the sample is required, only regents for which ultra purification procedures are available are required and the procedure appears adaptable to field or shipboard use. In addition, the procedure removes elements (i.e., Na, K, Ca, and Mg) that are interferences in many analytical methods and thus makes possible the use of a variety of techniques such as atomic absorption (flame or flameless), neutron activation and x-ray fluorescence.

Suggestions for Future Work

Because of the very low level of trace elements in sea water the accurate analyes of these is a difficult job under even ideal conditions. The problems in preventing contamination during the analysis are severe. Those encountered during the collection and storage are even more formidable. It is believed that progress has been made in the area of storage and may be minimized by the proper cleaning of containers and by freezing the samples as soon as possible.

Preventing contamination during collection, however, requires much attention. If only total elemental concentrations are required, that is, no distinction between suspended and dissolved elements is to be made, then acidification simultaneously with collection, followed by freezing, may be used as shown here. If, however, filtration is to be done to distinguish between suspended and dissolved elements then it is apparent from this work that the filtration must be done as the sample is collected. Sampler-filters such as that of Harrison et al. [25] accomplish this for shallow water collection effectively but are not applicable (in the present state) for duplicate water collection and are difficult to use in a harsh environment. We believe that an effective technique may be to filter and preconcentrate the samples in one step as collection proceedures using an adaptation of the Chelex 100 procedure reported here and are proceeding with this work.

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Table 1. Organic Ligands used to Separate Trace Elements in Sea Water.

Organic Ligand	Solvent	Element
APDC [11-16]	MIBK	Bi, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn
NaTϕB [8]	MIBK-Cyclohexane	Cs, Rb
Oxine [11]	MIBK	Mg, Mn, Ni

APDC - Ammonium pyrrolidene dithiocarbamate

NaTϕB - Sodium tetraphenylboron

Oxine - 8-hydroxyquinoline

Table 2. Solubility of Solvents in Water [17].

Solvent	Solubility, ml/l at 25 °C
Ethyl Acetate	9
MIBK	20
Cyclohexane	<<1
2-Butyl Alcohol	155
Methyl Isobutyl Carbinol	22

pling problems are exceedingly more difficult than for most synthetic materials, which may be homogeneous. In the environment, the system sampled is generally *not* homogeneous over the area of interest. The fluid systems, water and air, are in a state of continuous chemical and physical change, even during their sampling and storage. Therefore, obtaining and storing representative samples are not considered trivial problems.

In this work, an attempt was made to develop and evaluate a preanalysis scheme for trace elements in water. This includes the sampling protocol, as well as storage and handling techniques. If such a research technique can be evaluated thoroughly and quantitatively, it should be useful in studying less expensive and faster protocols which may be necessary for environmental surveillance work.

The preanalysis design presently used in this laboratory consists of an all Teflon, Teflon-coated metal, and nylon sampler to minimize contamination from construction materials. After sampling, immediate filtration is carried out in the field followed by fast freezing of the aqueous portion of the sample in liquid nitrogen. Upon return to the laboratory, samples are stored frozen and, prior to analysis by neutron activation, are preconcentrated by freeze drying.

When designing this scheme of sampling and sample handling it was felt that the total number of liquid sample transfers must be kept to a minimum to avoid unnecessary random sources of contamination. This goal was achieved by keeping the total number of sample transfers to one.

II. Procedure

The NBS water sampler is illustrated in figure 1. The sampler consists of a horizontal Teflon cylinder mounted on an "ice clamp action" type of frame, with flat Teflon end caps in place of what would be ice hooks. The frame, though made of metal (aluminum and stainless steel), has a baked-on Teflon coating. The Teflon cylinder has an interior thread on one end (fig. 2) to provide for attachment of a filtering mechanism, to be described below. A Teflon-coated rudder may be attached to the bottom of the cylinder to allow its proper orientation with the current flow. All parts of the sampler are assembled with nylon screws, bushings, washers, *etc.*

One of the unique features of the sampler is that it provides an option for sample filtration during the transfer to the storage container. A Teflon adaptor is threaded to mate the sampling cylinder with a polycarbonate filter holder. The components of this filtering mechanism are pictured in figure 3.

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Methyl Isobutyl Carbinol	22

Table 3. Instrumental Parameters.

		- - P&E 603 - -		- - - - - - - HGA-2100 - - - - - - -		
Element	Wavelength nm	SBW nm	Scale Expansion	Drying Temp./Time	Charring Temp./Time	Atomization Temp./Time
Cd	228.8	0.7	1	100/30	200/20	2100/7[a]
Mn	279.5	0.7	2.0	100/30	300/30	2700/7[a]
Ni	232.0	0.7	7.0	100/40	1000/30	2700/6[a]
Pb	283.3	0.7	3.0	100/40	400/30	2200/7[b]

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[a] Inert gas in the Interrupt mode.

[b] Inert gas in the Normal mode.

Note: Temperatures are in °C; Time in seconds.

Table 4. Analysis of Cadmium, Lead, Manganese, and Nickel in Sea Water.

Sample/Location	Sample Treatment[a]	Original pH	- - - - - ng/ml - - - - -			
			Cd	Mn	Ni	Pb
WGA, Station 1:2	F,A,b	1.7	0.14 0.05	0.72 0.68	0.65 0.78	17 11
EGA 24 (410 m)	F,A	3.5	0.11 0.10	0.05 0.06	0.24 0.32	0.02 0.05
WGA 110 (173 m)	F,A	5.1	0.07 0.13	0.22 0.28	0.36 0.34	0.20 0.32
EGA 11 (135 m)	F,A	5.2	0.05 0.06	0.03 0.03	0.27 0.29	0.08 <0.02
WGA 110 (173 m)	UF,A	5.4	0.09 0.08	0.18 0.18	0.41 0.45	<0.02 <0.02
EGA 15 (1500 m)	F,A	6.6	0.10 0.14	<0.02 <0.02	1.7 0.8	<0.02 <0.02
EGA 24 (410 m)	UF,A	3.6	0.12 0.13	0.02 0.02	0.49 0.40	<0.02 <0.02
EGA 11 (1350 m)	UF,A	6.5	0.11 0.12	<0.02 <0.02	0.36 0.38	<0.02 <0.02
EGA 15 (1500 m)	UF,A	5.4	0.13 0.12	<0.02 <0.02	0.90 0.78	<0.02 <0.02
NBS 500	Fc,UA	7.3	<0.01 <0.01	0.45 0.37	1.2 1.7	0.18 0.17
NBS 500	UF,UA	7.2	<0.01 <0.01	0.59 0.67	0.90 0.70	<0.02 <0.02
NBS 502	Fc,UA	8.3	<0.01 <0.01	0.40 0.46	0.49 0.53	<0.02 <0.02
NBS 502	UF,UA	8.2	<0.01 <0.01	0.71 0.64	0.66 0.71	<0.02 <0.02
NBS 509	UF,A	0.4	<0.01 <0.01	1.3 1.4	0.45 0.59	4.5 5.8
NBS 518	UF,A	1.3	<0.01 <0.01	1.4 1.3	0.41 0.45	<0.02 <0.02

[a] All samples stored frozen except b which was stored at ambient temperature. F-filtered, Fc-filtered after thawing, A-acidified, UF-unfiltered, UA-unacidified. Less than values are AAS detection limits based on 100 ml test portion.

Table 5. Samples Having Crystaline Precipitates.

Sample	Sample Preparation	pH of Samples after Thawing
University of Alaska		
EGA 24	unfiltered, acidified, frozen	3.6
EGA 15	unfiltered, acidified, frozen	6.7
NBS Samples		
Bottle No. 3	unfiltered, unacidified, frozen	8.2
Bottle No. 507	unfiltered, unacidified, frozen	8.2

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SAMPLING AND SAMPLE HANDLING FOR ACTIVATION ANALYSIS OF RIVER WATER

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A complete preanalysis scheme for determining trace elements in river and estuarine water by instrumental neutron activation analysis is described. The design, operation and evaluation of a new Teflon water sampler is included in the presentation of the preanalysis scheme. The evaluation of this water sampler consists of replicate sampling experiments and a comparison with a commercial sampling bottle (Van Dorn). The water sampler described allows for filtration of the sample as it is transferred from the sampler to a storage container. Lyophilization (freeze drying) is used as the preconcentration technique for the dissolved species, *i.e.*, liquid portion of the sample. Normalization of suspended particulate data to the element scandium is presented as a useful technique for locating man-made heavy metal input sources.

Keywords: Filtering water; river water; sampling water for trace elements; suspended particulates in water; Teflon water sampler; trace elements; trace elements in water; water.

I. Introduction

The current interest in sampling and sample handling for trace constituents is evidenced by the large attendance at this symposium. Previous speakers have discussed general problems associated with trace element sampling and sample handling so this point will not be belabored.

Sampling for trace elements is difficult in any matrix. However, if some component of the geochemical environment is to be investigated, the sampling problems are exceedingly more difficult than for most synthetic materials, which may be homogeneous. In the environment, the system sampled is generally *not* homogeneous over the area of interest. The fluid systems, water and air, are in a state of continuous chemical and physical change, even during their sampling and storage. Therefore, obtaining and storing representative samples are not considered trivial problems.

In this work, an attempt was made to develop and evaluate a preanalysis scheme for trace elements in water. This includes the sampling protocol, as well as storage and handling techniques. If such a research technique can be evaluated thoroughly and quantitatively, it should be useful in studying less expensive and faster protocols which may be necessary for environmental surveillance work.

The preanalysis design presently used in this laboratory consists of an all Teflon, Teflon-coated metal, and nylon sampler to minimize contamination from construction materials. After sampling, immediate filtration is carried out in the field followed by fast freezing of the aqueous portion of the sample in liquid nitrogen. Upon return to the laboratory, samples are stored frozen and, prior to analysis by neutron activation, are preconcentrated by freeze drying.

When designing this scheme of sampling and sample handling it was felt that the total number of liquid sample transfers must be kept to a minimum to avoid unnecessary random sources of contamination. This goal was achieved by keeping the total number of sample transfers to one.

II. Procedure

The NBS water sampler is illustrated in figure 1. The sampler consists of a horizontal Teflon cylinder mounted on an "ice clamp action" type of frame, with flat Teflon end caps in place of what would be ice hooks. The frame, though made of metal (aluminum and stainless steel), has a baked-on Teflon coating. The Teflon cylinder has an interior thread on one end (fig. 2) to provide for attachment of a filtering mechanism, to be described below. A Teflon-coated rudder may be attached to the bottom of the cylinder to allow its proper orientation with the current flow. All parts of the sampler are assembled with nylon screws, bushings, washers, *etc.*

One of the unique features of the sampler is that it provides an option for sample filtration during the transfer to the storage container. A Teflon adaptor is threaded to mate the sampling cylinder with a polycarbonate filter holder. The components of this filtering mechanism are pictured in figure 3.

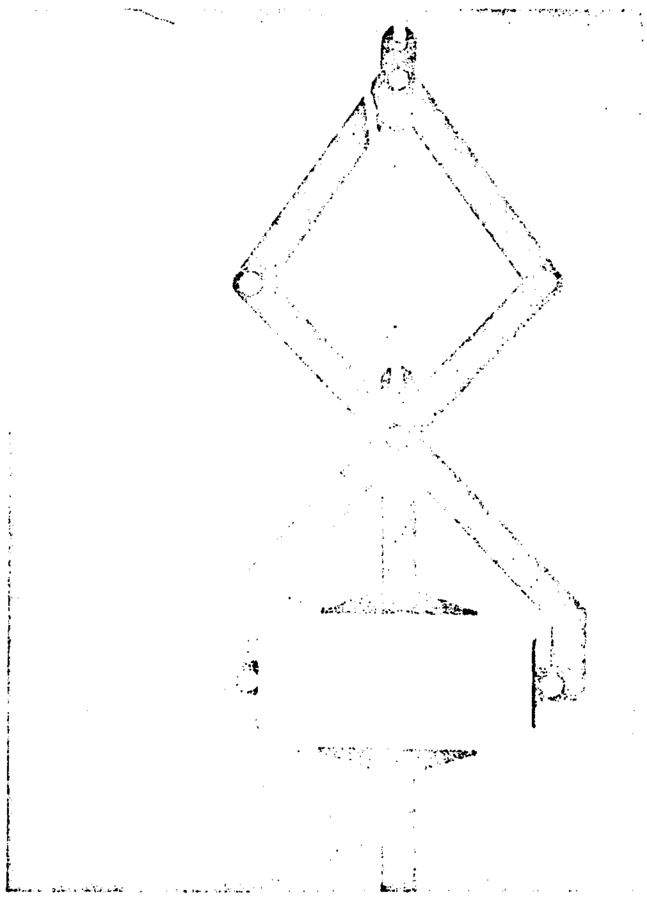

Figure 1. Teflon water sampler in vertical, closed position.

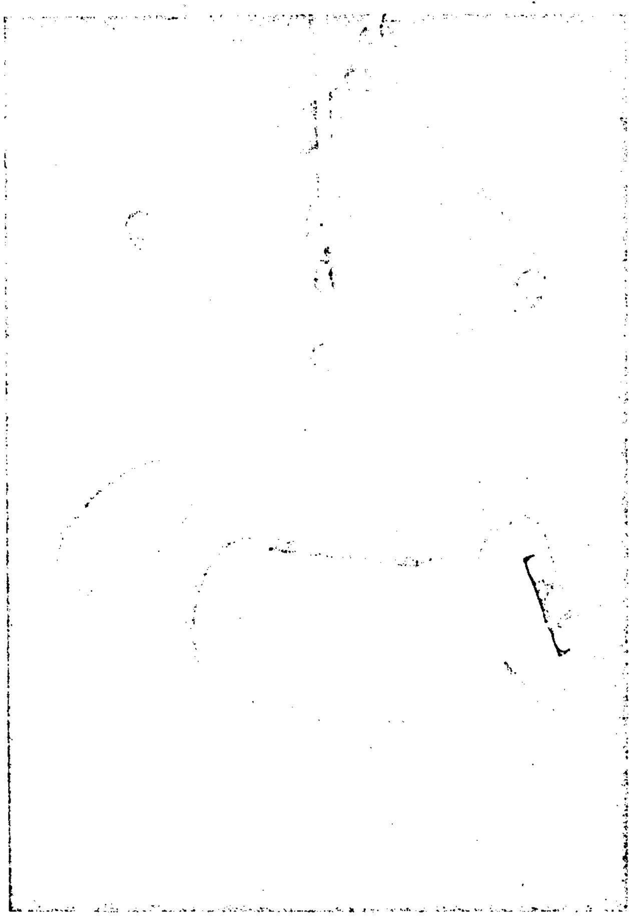

Figure 2. Teflon water sampler in vertical, partially open position, showing interior threads for attachment of filtering unit.

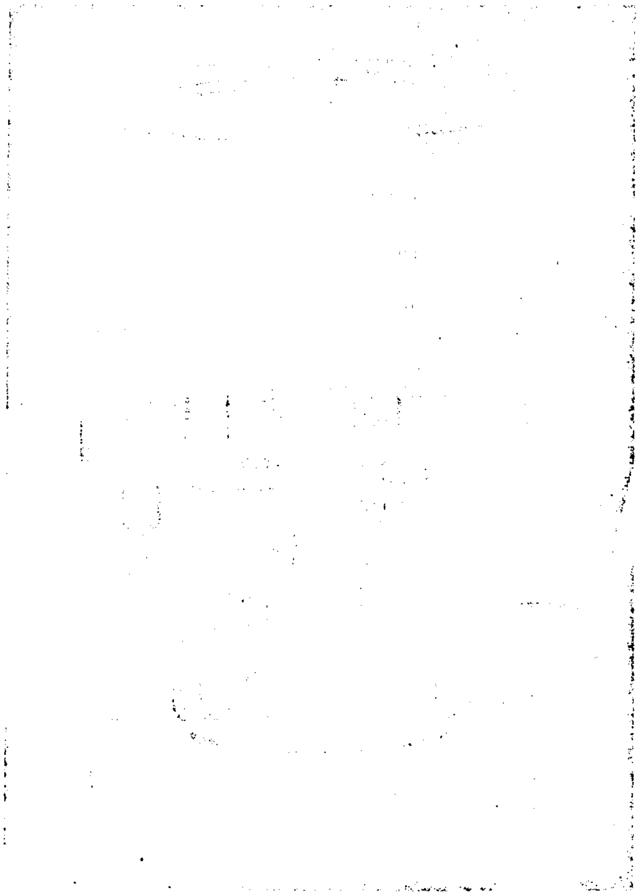

Figure 3. Attachment of polycarbonate filtering unit to filled water sampler through use of Teflon adaptor.

Generally, the filters used are a 47 mm diameter, 0.4 μm pore Nuclepore filter covered with a 47 mm diameter, 8 μm pore Nuclepore filter as a roughing filter. The filters are sealed between the Teflon adaptor and the filter support with a silicone O-ring. The receiver flask attached below the filter holds a polyethylene film bag. This bag serves as the sample container throughout the storage, freeze drying and analysis procedure. A hand pump is used to provide the vacuum for filtration in the field, *e.g.*, from a 14-ft rowboat. The complete sampling system assembled and ready for filtration is shown in figure 4.

One of the main advantages of the NBS water sampler is its capability of being lowered below the water surface in a closed configuration, avoiding contamination of the inner surface of the sampler with possible surface slicks or microlayers. After lowering the sampler to a depth of about 0.3 meters it may be opened by pulling a second rope.[1] The sampler is then lowered to the desired depth and allowed to equilibrate. The first rope is pulled to close the end caps and the water sample is brought back to the surface.

After attaching the filtering unit the sample may be filtered directly from the Teflon cylinder into the polyethylene storage bag. This is the only sample transfer in the entire procedure. The liquid sample contained in the polyethylene bag is frozen in the field in liquid nitrogen and stored in a cleaned plastic bag. The filters containing the suspended particulates are transferred to a cleaned plastic petri dish. Both the frozen liquid and filter portions of the sample are stored in dry ice until returning to the laboratory where they are transferred to a freezer.

The frozen liquid samples are prepared for analysis by preconcentrating using lyophilization (freeze drying). The technique for freeze drying has been described in detail elsewhere [1,2], however, a brief description may be appropriate here. The basic freeze drying unit, shown in figure 5, consists of a sample chamber, cold trap and source of vacuum. The frozen sample, still in the polyethylene film bag, is placed in the chamber which is then opened to the vacuum line. During the freeze drying process, water sublimes and a residue of solids accumulates at the bottom of the bag. After the process is finished the bag is folded up with the residue sealed inside, to make a small package for neutron irradiation.

Considerable work has been completed to evaluate the retention yields of trace elements during freeze drying. The results appear satisfactory for all elements investigated except for mercury and iodine (fig. 6). Recently, Filby, Shah and Funk [3] reported quantitative retention of mercury in a tracer study of the lyophilization of water.

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[1] The NBS water sampler must be operated by two ropes, one supports the weight of the sampler while holding the end caps against the cylinder, the other supports this weight using it to pull the end caps up and away from the cylinder allowing for an uninterfered flow-through system.

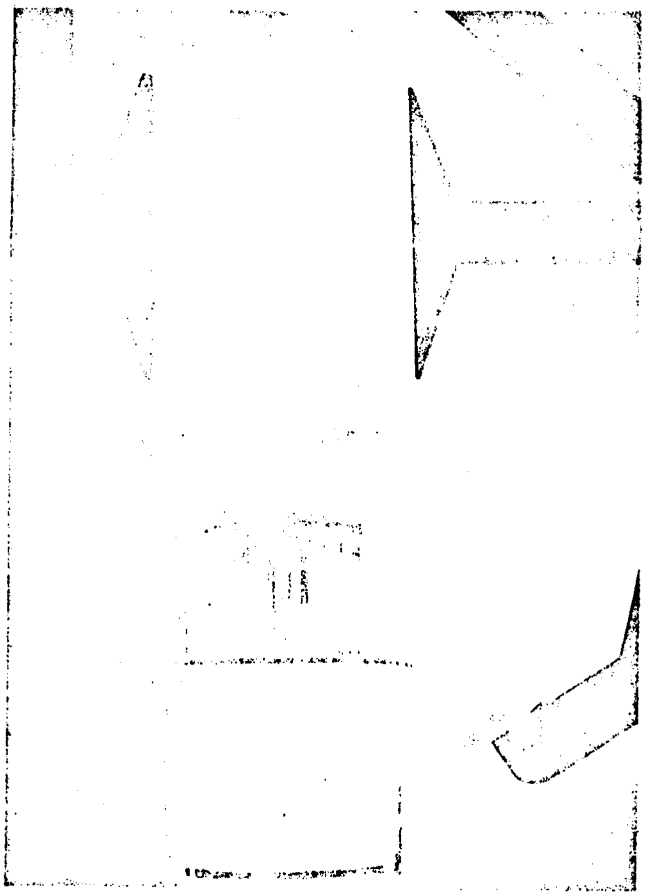

Figure 4. Teflon water sampler with filtering apparatus attached, ready for vacuum filtration into a clean polyethylene storage bag inside the filtering unit.

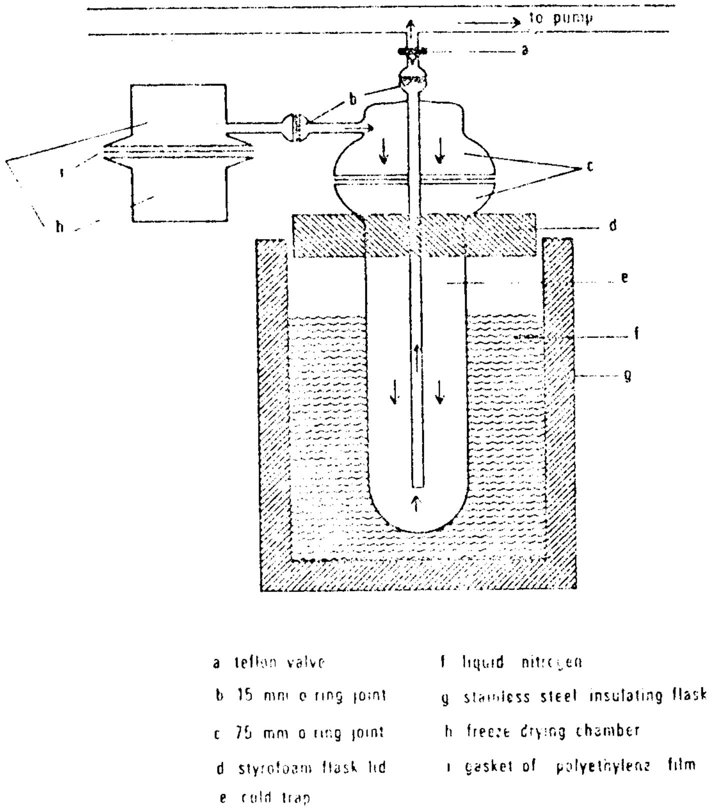

Figure 5. Schematic diagram showing one unit of the freeze drying system.

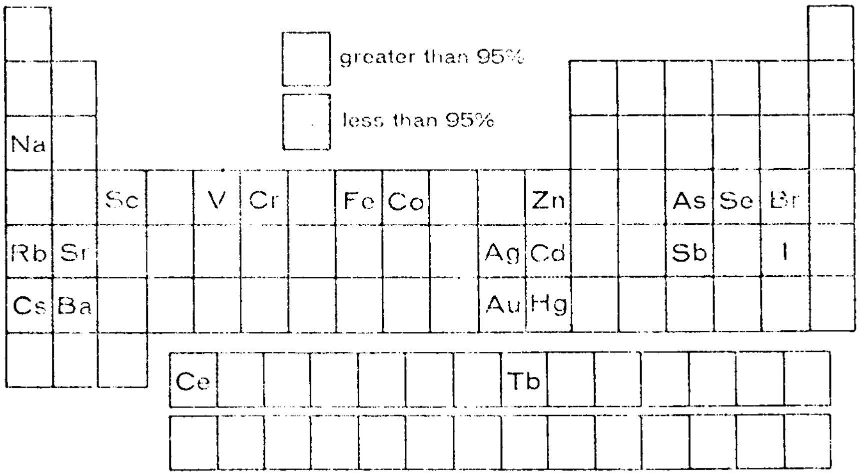

Figure 6. Retention yields of trace elements during freeze drying using radioactive tracers.

III. Results and Discussions

One of the main objectives of this work was to determine variability of data due to sampling. The approach used was to take replicate samples from a given location over as short a period of time as possible, usually 2 to 4 hours. It should be pointed out that in a field experiment it is difficult to distinguish between concentration variations due to time or position. In an estuarine or river system it is almost impossible to sample the same water mass over a 2- to 4-hour time interval.

The first station chosen for this kind of work was the Patuxent River at Laurel, Maryland. At this point the river is just a fresh water stream and it was necessary to wade to midcurrent to obtain the samples. Of course, bottom sediment is stirred up when wading but due to a rather swift current that day the disturbance created by wading subsided in several minutes and a sample could be taken upstream to minimize these effects.

At this location eight samples were taken. That is, eight separate wadings to midstream were made with processing of each sample on shore before the next one was initiated. Obviously, these replicate samples could not be considered to be taken from exactly the same body of water.

The results of instrumental neutron activation analysis (INAA) of the Laurel samples appear in tables 1 and 2. For the dissolved species, the coefficients of variation for the 13 elements determined in these "replicate samples" vary from a surprisingly low 3.0 percent for manganese to 80 percent for cobalt. A few outliers are obvious, cobalt in sample L-13 and chlorine in sample L-9. The high cobalt value in L-13 does not correlate with high values for scandium, iron, or thorium, elements which would be present in crustal particulate contamination. The low value for chlorine in sample L-9 is equally unexplainable. A low value of a halide in water might be explained by oxidation to the elemental form and volatilization during freeze drying. This idea is untenable since the bromide ion is more readily oxidized than chloride ion, and the value obtained for bromine in L-9 is just below one standard deviation from the average. Of these eight samples, originally weighing from 60 to 90 grams each, nine of the 13 elements determined exhibited coefficients of variation of 20 percent or less.

The results of INAA of the Laurel suspended particulates are shown in table 2. These samples were collected, freeze dried, irradiated and counted on polycarbonate film filters. Only the first six of the suspended particulate samples were analyzed for some of the elements which have long radioactive half-lives on irradiation. Technical difficulties prevented the analysis of the others. The elements measured in the suspended particulates have been normalized to scandium which is an element which

TABLE 1. *Concentration of dissolved species in Laurel samples*

Number	Elements												
	Ca (μg/g)	Na (μg/g)	Cl (μg/g)	Mn (μg/g)	Br (μg/g)	Mg (μg/g)	V (μg/g)	Sc (μg/g)	Fe (μg/g)	Co (μg/g)	La (μg/g)	Th (μg/g)	Sb (μg/g)
L-8	8.38	3.91	6.65	0.124	0.447	3.60	0.263	0.0251	174	0.907	0.214		0.0950
L-9	8.94	3.88	0.101	.119	.375	3.60	.358	.0326	239	1.03	.350		.0711
L-10	7.85	4.21	7.59	.115	.485	3.06	.507	.0415	215	.545	.303		.130
L-11	8.08	3.84	7.21	.113	.399	3.99	.274	.0272	173	.316	.260	0.0311	.0495
L-12	8.58	4.12	7.05	.116	.468	3.85	.215	.0293	171	.393	.305	.0421	.0703
L-13	8.46	4.31	6.82	.121	.465	4.28	.529	.0405	212	2.38	.348	.0408	.110
L-14	9.45	5.10	7.51	.117	.369	3.85	.615	.0676	232	.588	.224	.0370	.0879
L-15	8.61	4.28	7.69	.120	.560	4.03	.372	.0689	257	.514	.378	.0851	.0754
Average	8.54	4.21	6.33	.118	.450	3.78	.392	.0416	209	.834	.298	.0472	.0861
			7.21	(Minus L-9)									
Coefficient of Variation, %	5.7	9.7	40	3.9	14	10	37	42	16	80	20	20	30
			5.5	(Minus L-9)									

TABLE 2. *Concentration of suspended particulates in Laurel samples*

Number	Elements									
	Al (μg/g)	Mn (μg/g)	V (μg/g)	Cl (μg/g)	Na (μg/g)	Sc (μg/g)	Fe (μg/g)	Co (μg/g)	Th (μg/g)	Sb (μg/g)
L-8P	2.34	23.8	3.79	15.9	4.57	0.366	1.36	0.542	0.367	0.014
L-9P	2.20	20.9	2.80	18.3	6.17	.345	1.25	.552	.306	
L-10P	2.50	27.0	3.67	21.3	6.69	.405	1.38	.605	.354	.032
L-11P	2.55	23.9	2.76	14.7	10.8	.370	1.36	.534	.357	.016
L-12P	2.24	21.3	3.20	11.3	5.38	.359	1.27	.510	.409	.0093
L-13P		25.3		13.9	6.57	.360	1.25	.507	.392	.012
L-14P	2.30	24.6	3.53	14.7	7.95					
L-15P	2.66	25.0	3.64	30.2	8.61					
Average	2.40	24.0	3.34	17.5	7.09	.368	1.31	.542	.364	.017
CV[a], %	7.2	8.5	13	34	28	5.5	4.7	6.6	9.8	52
CV/[Sc][b], %	4.4	6.2	13	19	32		3.4	4.8	11	47

[a] Coefficient of variation.

[b] Coefficient of variation when the average elemental concentration is ratioed to the scandium concentration.

may be indicative of contributions due to clay particles and crustal weathering from natural sources. This is a procedure which has been used in transport studies of heavy metals in sediment [4]. The coefficient of variation is improved for nearly all elements when values are normalized to scandium, with only slight increases for the exceptions, thorium and sodium.

The fast moving fresh water stream at Laurel appears to be a well-mixed system and a single 50 to 100 gram sample under these conditions generally gives a relative standard deviation of 20 percent or less at concentrations down to the subnanogram/gram level for the elements analyzed.

A set of samples similar to those taken at Laurel were taken from the side of a boat anchored at the mouth of the Susquehanna River in the Chesapeake Bay (Turkey Point). In figure 7 are illustrated the results of the suspended particulates taken from this estuarine location. Again, for suspended particulates, the coefficient of variation for each element is significantly diminished (with the exception of manganese) when the data is normalized to scandium.

The importance of normalizing data obtained from suspended particulates using an element indicative of purely crustal weathering or natural sources is illustrated in figures 8, 9, and 10. In figure 8 is presented results for chromium in the suspended particulates of the Back River, just east of Baltimore, Maryland. A very large sewage treatment plant is located on the Back River. Station 1 is at the mouth of the river, which flows into the Chesapeake Bay. Station 6 is directly in the plume of the midstream effluent outfall of the sewage treatment plant. When the chromium concentration is plotted with respect to distance (as approximated by station number) from the effluent outfall a slight rise is observed as station 6 is approached. (Plotting the chromium data with respect to salinity instead of distance from effluent outfall gives an almost identical curve.) However, if the data is normalized to scandium a much more striking increase is seen as one approaches the plant effluent outfall. This indicated that there is an anthropogenic source of chromium in the particulate material coming from the sewage treatment plant or another upstream location.

Iron in the Back River exhibits a similar behavior and is shown in figure 9. However, in the case of iron no concentration gradient is observed in proceeding upstream from the mouth of the river. On the other hand, normalization against scandium shows a pronounced upstream gradient which apparently indicates a source of noncrustal iron upstream.

When the concentration of thorium and of thorium relative to scandium are plotted for the Back River suspended particulates (fig. 10), only a smoothing out of the data is obtained by normalizing to scandium, indicat-

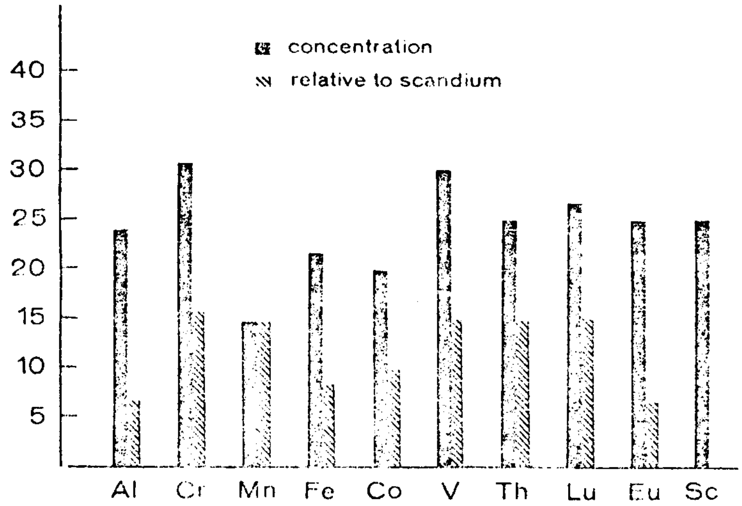

Figure 7. Coefficients of variation for trace elements from replicate samples of estuarine water, suspended particulates only.

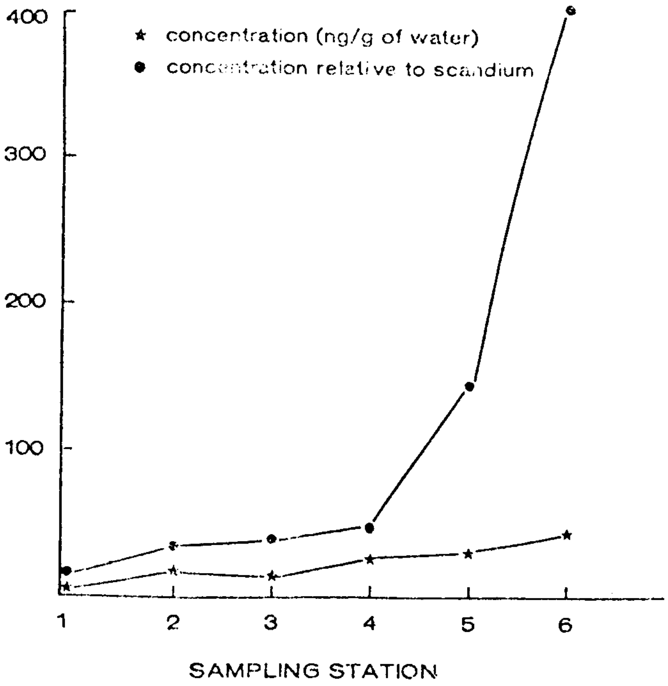

Figure 8. Chromium in back river suspended particulates.

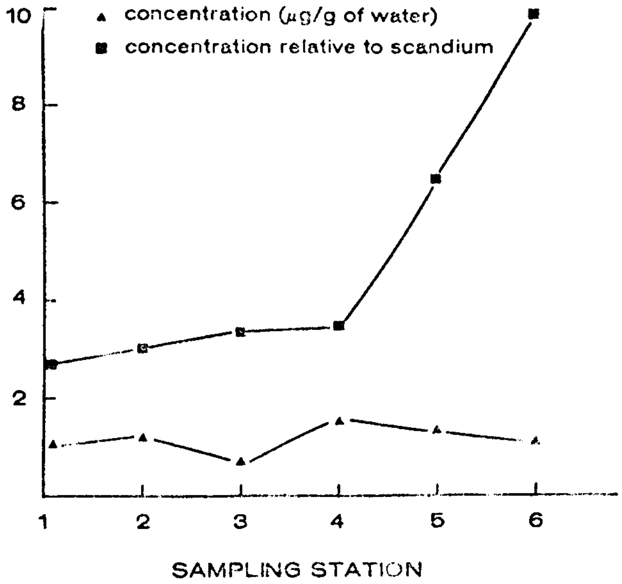

Figure 9. Iron in back river suspended particulates.

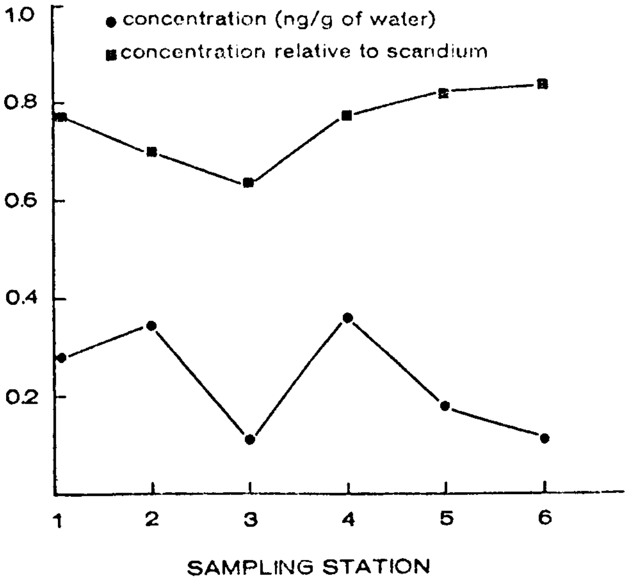

Figure 10. Thorium in back river suspended particulates.

ing no significant input of thorium from an anthropogenic source. It is felt that the added information obtained by this normalization technique should be useful in detecting sources of man-made heavy metal input.

In the Susquehanna River experiment, replicate samples taken with the NBS sampler were compared to samples taken with a Van Dorn commercial sampler. This particular Van Dorn sampler was part of the routine equipment on the research vessel used for this experiment and it is likely that the sampler has been used at least 3 days a week and up to 10 times a day for the past several years. The sampler was therefore expected to contaminate the samples. The results are found in table 3 in the chronological order in which they were taken. It has already been mentioned that it is very difficult to get a body of water to stay still during a replicate sampling experiment. This difficulty is demonstrated by noting the values for sodium in table 3. The sampling had begun at low tide, but the tide soon started coming in, leading to increasing salinity during the sampling period and possibly stirring up some of the bottom sediments.

The comparison of data for Van Dorn samples (VD1, VD2, VD3) to those for our Teflon sampler (NBS1, NBS2, NBS3, NBS4, NBS5) seems to indicate that the commercial sampler is contributing little if any contamination to the sample at the concentration levels found here. This may be explained in two ways: The sample from the Van Dorn was transferred immediately (< 3 min) to the Teflon cylinder for filtration, leaving very little time for container-sample interactions. Alternatively, this particular Van Dorn sampler, which is made of PVC, rubber and surgical tubing, could have been used so often that all or most of the leachable contaminates had since been removed and it had reached an equilibrium with Chesapeake Bay water.

Other interesting features of the data in table 3 are the inconsistently high values for cobalt, iron and scandium in samples VD3 and NBS4. This could be suspended particulate contamination due to improper filtration or external contamination. These high values could also be real and caused by the disturbance of the sediments with the changing tide. In addition, the variability in samples from fresh water streams seems less than for samples from estuarine water, over a short timespan.

It is felt that the evaluation of the sampling of natural water using this system has just begun. Further work in evaluating the sampling of river and estuarine water is planned as well as initiating sampling studies in coastal ocean water.

TABLE 3. *Trace element concentrations in replicate samples of estuarine water*
(Dissolved Species Only)

Sample	Zn (μg/g)	Sr (μg/g)	Co (μg/g)	Fe (μg/g)	Se (μg/g)	Ag (μg/g)	Sc (μg/g)	Na (μg/g)
NBS[a]1	2.6	94	0.22	28	0.18	0.07	0.011	4.5
VD[b]1	8.9	108	.20	35	.14	.86	.008	6.6
NBS2	4.0	117	.27	44	.15	.39	.017	34
VD2	6.3	101	.24	38	.13	.27	.009	43
NBS3	3.9	121	.27	46	.22	.12	.024	44
VD3	7.1	121	.44	122	.14	.42	.034	45
NBS4	12	115	.67	266		.15	.28	48
NBS5	11	92	.26	44		.90	.024	36

[a] NBS = National Bureau of Standards samples.
[b] VD = Van Dorn samples.

IV. Acknowledgements

We are especially grateful to James Suddueth of the Analytical Chemistry Division at NBS for the design for this water sampler.

V. References

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APPENDIX II

Production and Analysis of Special High-Purity Acids Purified by Sub-Boiling Distillation

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Sub-boiling distillation from pure quartz or Teflon (Du Pont) stills has been investigated for the production of high-purity inorganic acids and water. Nitric, hydrochloric, hydrofluoric, perchloric, and sulfuric acids produced by this method contained significantly lower cationic impurities than high-purity acids from commercial sources. A complete system, including the Class 100 environment, production, and storage of these high-purity reagents is described. A method based on spark source mass spectrographic isotope dilution analysis has been developed for the simultaneous determination of 17 elements in these materials. Results of the analyses of both the acids purified by sub-boiling distillation and the ACS reagent grade acids used as starting materials are reported. The sum of the common impurity elements determined in the purified acids ranged from 2.3 ppb in nitric acid to 27 ppb in sulfuric acid. No element in any of the purified acids exceeded 10 ppb and most were well below the 1-ppb level.

THE ANALYTICAL CHEMISTRY DIVISION at the National Bureau of Standards has become increasingly involved with the analysis of samples and Standard Reference Materials (SRM's) requiring the determination of elements at the low parts per million (ppm, 10^{-6} g/g) to the parts per billion (ppb, 10^{-9} g/g) concentration range. This is illustrated by recent analyses which include lead at 3.31 ppm in lunar samples (*1*), uranium at 72.1 ppb in Trace Elements in Glass (SRM 616) (*2*), nickel at 1.3 ppm in Orchard Leaves (SRM 1571) (*2*), and strontium at 0.14 ppm in Bovine Liver (SRM 1577) (*2*). The low level of these elements puts stringent requirements on the purity of reagents used in the analytical procedure.

Inorganic acid purity is of particular importance because of the relatively large amount of these acids required for sample dissolution and other chemical operations. These procedures can require quantities of acids in excess of ten times the sample weight. To take full advantage of the sensitivity and accuracy of an analytical technique, the reagent blank should be held to no more than a few per cent of the amount being determined. Therefore, the accurate determination of an element near the 1-ppm level will depend on the availability of acids containing no more than 1 ppb of the element.

High-purity inorganic acids have been available for some time from commercial sources. Although these acids are satisfactory for many trace element determinations, they are not always adequate for low level trace work either through a lack of purity or high upper limit specifications. [Emission spectrography (*3*), the technique usually applied to the analyses of high-purity acids, lacks sensitivity causing upper limits to be set at 1 ppb or higher.] The determination of the isotopic composition and concentration of lead in lunar samples can be cited as a recent example. A reagent blank of 340 ng Pb was calculated from the producer's values for lead in commercial high-purity acids and the volume of these acids required to dissolve one gram of lunar rock and separate the lead from other constituents. Since the expected Pb concentration was only a few ppm, the introduction of this quantity of external lead (of a different isotopic composition) would have precluded a reliable determination of the Pb present either as to amount or isotopic composition. Using acids purified by sub-boiling distillation, the total blank was determined to be 5 ng for the actual analysis. Consequently, because of this experience and other problems associated with the determinations of trace metals in a variety of materials, the Analytical Chemistry Division at NBS recently set up facilities for the "in-house" purification, analyses, and distribution of inorganic acids.

Sub-boiling distillation was selected as the method of purification for the inorganic acids. No single purification procedure is capable of removing all classes of impurities from these acids. Since the trace element program at NBS is mainly concerned with trace metals, the technique which appeared to be most efficient in removing metallic or cationic impurities, sub-boiling distillation, was studied. In sub-boiling distillation, infrared radiators vaporize the surface without boiling the liquid in the vaporizer compartment. The vapor is condensed on a tapered cold finger and the distillate is collected in a suitable container. Sub-boiling distillation was selected over conventional or boiling distillation since studies have shown that in the latter method significant contamination of the distillate occurs from creeping of the unrectified liquid and entrainment of particulates in the vapor stream formed during bubble rupture (*4*). Sub-boiling distillation completely eliminates the entrainment problem since no bubbles are formed. Creeping of unrectified liquid from the vaporizer is minimized by the position of the cold finger type condenser. It should be pointed out that while this is an extremely efficient still for the separation of impurities of low vapor pressure such as metal ions, it offers little purification from impurities of high vapor pressure such as organic matter or many of the anions.

Commercial quartz sub-boiling stills which were designed for the production of high-purity water have been used for the production of high-purity mineral acids of low-level lead content at the Carnegie Institution of Washington (*5*). Similar sub-boiling quartz stills (Quartz Products Corp., Plainfield, N.J.) were installed at NBS for the production of

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hydrochloric, nitric, perchloric, and sulfuric acids as well as water. An all Teflon (Du Pont) sub-boiling still was designed and constructed at NBS for the production of high-purity hydrofluoric acid.

Efficient purification by the still only partially solves the problem of producing and distributing pure acids. Airborne particulate contamination and container contamination must also be minimized to ensure a high quality product. Airborne particulate contamination can be virtually eliminated by enclosing the still and distillate containers in a Class 100 clean air chamber. Teflon FEP bottles which have been vigorously cleaned with nitric and hydrochloric acids are used as containers for the purified acids and high-purity quartz is used for water.

To evaluate the purity of the acids and water produced by this process, an analytical method based on isotope dilution spark source mass spectrometry (SSMS) was developed. This method has limits of detection as low as 0.01 ppb for common impurity elements. Seventeen elements were determined simultaneously in each of the high-purity acids and water produced by sub-boiling distillation and the ACS grade acids used as starting materials.

APPARATUS FOR THE SUB-BOILING DISTILLATION OF HIGH-PURITY ACIDS AND WATER

Quartz Sub-Boiling Still. The commercially available sub-boiling still shown in Figure 1 is made of quartz. This type still is used for the production of HCl, HNO_3, $HClO_4$, H_2SO_4, and H_2O. Heating of the liquid being distilled is done by a pair of infrared radiators positioned on both sides of the condenser. These elements, inside quartz tubes, heat the surface of the liquid and evaporate it without causing it to boil. This positioning also serves to heat the walls above the liquid tending to keep them dry which minimizes creep of liquid along the walls between the liquid reservoir and the condensing cold finger. The condenser is tilted downward toward the distillate outlet to allow the condensed liquid to flow to the tip above the outlet. The still is fed by a 6 8 pound bottle of ACS reagent grade acid through a liquid level control which maintains the liquid to just below the overflow height. Approximately 400 to 500 ml of liquid are thus maintained inside the still at all times. A three-way stopcock on the liquid level control is used to drain the still after the consumption of each bottle of ACS reagent grade feed acid. All parts of the liquid feed system are made of Teflon.

Teflon Sub-Boiling Still. An all-Teflon (Du Pont) sub-boiling still having all the essential features of the quartz still was designed and constructed for the production of hydrofluoric acid. This still, shown in Figure 2, was fabricated starting with a commercial 2-liter Teflon bottle. The heaters, condenser, acid inlet, and the overflow were inserted into what was originally the bottom of the bottle and the distillate outlet was inserted at the bottle cap. For the heaters, Teflon rods are machined to form 19-mm o.d. closed end tubes. Heating coils inside glass tubes are then inserted into the heater tubes. The maximum operating temperature of the still is limited by the softening point of the Teflon around the heater. The glass tubing serves to support the heating tube. The cold finger condenser is similarily machined into a 25-mm o.d. tube from solid rod. Both the condenser and heater tubes are threaded at the open ends to fit into conversion fittings which are in turn threaded into tapped holes in the bottom of the bottle. The tapped hole in the condenser fitting is machined at an angle such that the condenser is tilted downward toward the distillate outlet. Because HF and other liquids do not adhere readily to Teflon, the distillate drips off instead of flowing down along the condenser. Therefore, a trough is secured under the condenser to catch the HF and direct it to the distillate outlet. A piece of tubing inserted through the bottle cap using commercial Teflon fittings serves as a collector for the distillate. The tube is provided with an umbrella at the end to protect the collection bottle from possible fall-out contamination. The acid feed and overflow tubes are attached with Teflon fittings threaded into the bottle bottom. Teflon tape is used when necessary on the threads of the fittings to ensure a liquid tight seal.

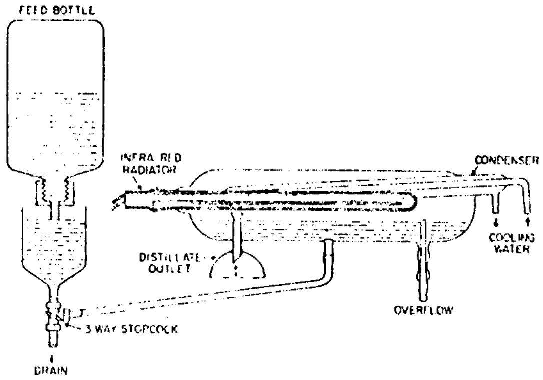

Figure 1. Pure quartz sub-boiling still

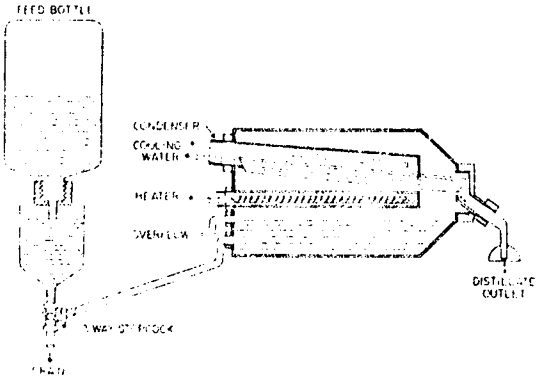

Figure 2. All-Teflon sub-boiling still

Clean Air Chamber. Each sub-boiling still is housed in a clean air chamber (Environmental Air Control, Inc., Annandale, Va.) to protect the distillation process from external particulate contamination. All parts on the clean air side of the chamber including the HEPA filter frame and diffuser are constructed of aluminum or plastic. The chambers meet Class 100 specifications that is, they remove 99.97% of all particulate matter larger than 0.3 μm. The air flow through the chamber is adjusted to match the exhaust rate through a plenum assembly at the back-bottom of the unit. By this means, the acid purification operation is protected from room contaminates and at the same time, acid fumes are minimized in the room.

Containers for Reagent Storage. Acid distillates are collected and stored in Teflon-FEP bottles. These bottles are cleaned by soaking for 24 hours first in hot 8*M* HNO_3 and then in hot 6*M* HCl for 24 hours. They are then rinsed with sub-boiling distilled water and finally with the acid being stored. The containers are reused for the same acid after first being rinsed with distilled water and then rinsed with the acid. Water from the sub-boiling still is stored in quartz containers which are cleaned in the same manner as the Teflon bottles.

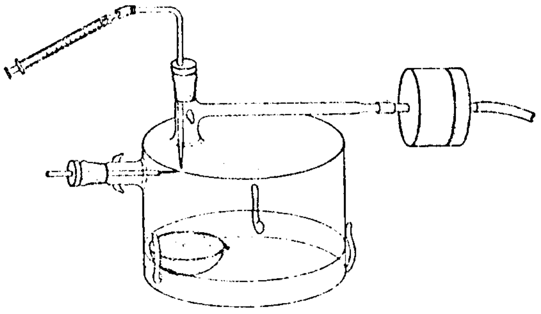

Figure 3. Clean environment evaporator and transfer system

APPARATUS AND REAGENTS FOR ANALYSIS OF ACIDS AND WATER

Enriched Isotope Spike Solutions. The individual isotopic spikes for the elements being determined were on hand as 1 mg/ml solutions. Compatible spiking elements were combined to give 50 μg/ml concentrations of each element in a pair of master spiking solutions. One solution contained the HCl soluble elements, the other solution the HNO_3 soluble elements.

Clean Air Exhaust Hood. In the analysis of the acids, evaporations were performed on a hot plate in a Class 100 exhausted fume hood. The basic unit is similar to the clean chamber except that the air is exhausted down through a grill of Teflon that serves as a "floor" for the hood and then out through a standard acid fume exhaust system. Teflon is used extensively throughout those parts of the hood exposed to acid fumes.

Evaporator and Liquid Transfer System. The apparatus, shown in Figure 3, provides a clean environment for evaporating a spiked sample and transferring the residual volume onto high-purity gold wires. Nitrogen flowing through a 0.1-μm cellulose filter provides a clean atmosphere, sweeps out evaporating acid, and prevents entry of particulate contamination. A pure quartz pipet inserted off center in a Teflon stopper at the top is used to transfer the last few drops of evaporating acid onto pure gold wires positioned from the side joint.

PROCEDURE FOR ANALYSIS OF ACIDS AND WATER BY ISOTOPE DILUTION SSMS

The isotope dilution analyses were performed on the acids and water produced by sub-boiling distillation and on the ACS reagent grade acids used as starting materials. In addition, we have also included results obtained in previous analyses of commercial high-purity acids. This variety in the type and source of acids analyzed has resulted in some changes of the procedures used.

Hydrofluoric Acid. Due to its reactivity with quartz and glassware, HF was handled exclusively in Teflon-FEP containers, otherwise it was treated the same as the other acids from a similar source.

Water from the Sub-Boiling Still. Because the purity of the sub-boiling distilled water was higher than that of the acids, the water was preconcentrated before spiking. Two liters of water were evaporated to approximately 100 ml in the original storage container before being removed and spiked. The water was not spiked in the storage container because of our reluctance to contaminate the container with the enriched spike isotopes. The spiked 100-ml water sample was then handled in the same manner as the acids purified by sub-boiling distillation.

Sample Spiking. All samples were spiked using 1 μg/ml solutions freshly diluted from the 50 μg/ml master spike solutions. Acids purified by sub-boiling distillation were all spiked for a nominal concentration of 1 ppb; nitric and hydrochloric acids were also spiked for 0.1 ppb. The nominal 1-ppb spike contained 100 ng of each spike element in 100 grams of acid (1 ng/g); the 0.1 ppb spike had 30 ng/300 grams of acid. The 1 ng/g spike gives an altered isotopic ratio of approximately one at a concentration of 1 ppb for most of the impurity elements. Concentrations up to ten times higher and more than ten times lower than the spiked for value can be determined from the measured ratios, but with greater uncertainty.

The ACS reagent grade acids used as starting materials for the sub-boiling distillation were spiked at 1 ppb, 10 ppb, and 100 ppb in order to cover the expected concentration range for the different impurity elements. An element was only measured for the sample where the spike came closest to the actual concentration. One half of the spiked sample was used for each analysis.

The commercial high-purity acids analyzed previously were spiked for many but not all of the elements surveyed in the ACS reagent grade and sub-boiling still acids. One hundred-gram samples were spiked for concentrations in the 1- to 100-ppb range. Because of the higher level of impurities only 20 grams of the 100-gram sample were required for the analyses.

Sample Evaporation and Transfer to Pure Gold Wires. The clean environment evaporator shown in Figure 3 was used to vaporize commercial high-purity acids in a standard laboratory fume hood prior to our obtaining a Class 100 clean air fume hood. A single sample at a time was evaporated to a few tenths of a milliliter and then transferred with the pure quartz pipet to the tip of "six nines grade" gold wires and dried.

The ACS reagent grade acids and the acids purified by sub-boiling distillation were evaporated in the Class 100 fume hood in open quartz and/or Teflon beakers on a hot plate. The clean environment evaporation dish was used however to transfer the last few drops of the spiked sample to the gold wires for drying. The gold wires were then heated to 425 °C for 15 minutes to drive off hydrocarbons and occluded acid. At this point partial loss due to incomplete transfer or loss on heating can be ignored inasmuch as the quantitative analytical data are a function of the altered isotopic ratio and the only requirement is that enough of each element be retained for an adequate measurement.

Spark Source Mass Spectrographic Determination of Altered Isotopic Ratios. The pair of gold wires was mounted in the spark source such that several millimeters of the wire ends, which were coated with the spiked sample residue, would be overlapping and parallel to each other. When a source vacuum of 1×10^{-7} Torr was reached, a graded series of exposures was made. The electrodes were moved relative to each other during sparking in order to spark new spiked sample residue on each exposure. One half of the surface of each electrode was sampled during this first graded series of exposures. A second identical series of graded exposures was then made on the remainder of the sample. A single photographic plate was used for each sample.

The photographic plates were processed using the bleach and internal image developer for reducing plate fog developed by Cavard (*6*).

The photoplates were examined visually to select exposures which would give optimum sensitivity for each element determined and for evidence of interferences at the same nominal mass such as unresolved doublets, abnormally wide lines, or isotopic ratios which varied from one exposure to the next. If an interference was indicated for the +1 lines of an element, the less sensitive +2 or +3 lines were considered for measurement. The selected exposures for each element were then densitometered measuring both the spike and natural isotopes on each exposure. From four to six exposures were measured for each element if available.

(6) A. Cavard in "Advances in Mass Spectrometry," E. Kendrick, Ed., The Institute of Petroleum, London, 1968, pp 419-29.

Calculation of Impurity Concentrations. The amounts of impurities present in each acid were computed from the sample weight, the weight of each spike added, and the measured altered isotopic ratios using the usual formula for isotopic dilution analysis as described in earlier papers (*7, 8*). Impurity concentrations were calculated for each isotopic ratio measured for an element. These values were then averaged. This system gives a more realistic evaluation of the uncertainty in the results than using an averaged ratio to calculate one concentration value. This is especially critical when the measured (altered) isotopic ratio is close to that of either the spike or natural element.

When only the spike isotope for an element was detected, an upper limit of concentration was computed by substituting twice the noise level of the photographic plate at the position of the natural isotope for the intensity of the natural isotope. The concentration of mononuclidic sodium was estimated by assuming it has the same sensitivity as potassium and measuring intensity-areas of the ^{23}Na compared to that of either the ^{39}K or the ^{41}K isotope of the same exposure.

The results of these analyses of the acids and water are presented in a later section describing the operating procedure used for the production of each of the acids by sub-boiling distillation.

DISCUSSION OF ANALYSIS PROCEDURE

The acids purified in the sub-boiling still and the ACS reagent grade starting materials were analyzed for 17 elements simultaneously by the spark source. The elements measured represent elements found as impurities in reagents, elements commonly determined in many types of analytical samples, and elements from different groups of the periodic table. It was felt that this selection of elements would give a representative view of the overall reagent purity.

The analysis technique itself is subject to blank problems which cannot be properly evaluated. Care was taken during the analysis to prevent contamination of the samples from containers and the external environment. Based upon the lowest values found in repeated analysis of the acids produced by sub-boiling distillation, estimates can be made of the probable blank contributions. In general any element reported near the 0.1-ppb level or below may have a considerable blank contribution and the value should therefore be considered as an upper limit. Concentrations significantly above this level represent actual reagent impurities with uncertainties ranging from ± 10 to 30% depending on the value of the altered ratio.

Interfering lines having the same nominal mass as either the spike or natural abundance isotope of an element being determined were sometimes encountered during these analyses. These interferences are normally most prevalent for the lower mass elements and for the more impure acids. The three major sources of these lines are hydrocarbons, anions, and anion fragments, and various molecular combinations of the major impurities with themselves and the acid anion. Heating of the sample to 425 °C before sparking and the heating that occurs during sparking greatly reduced interference from the hydrocarbon and anion lines.

Examples of anion fragment interferences are $^{37}Cl^{16}O^+$ with the $^{53}Cr^+$ spike and $^{35}Cl^{16}O_2^+$ with the $^{67}Zn^+$ spike in perchloric acid analysis, and $^{32}S^{16}O_2$ with natural $^{64}Zn^+$ in sulfuric acid. The perchloric acid interferences can be evaluated by monitoring the line from the other chlorine isotope.

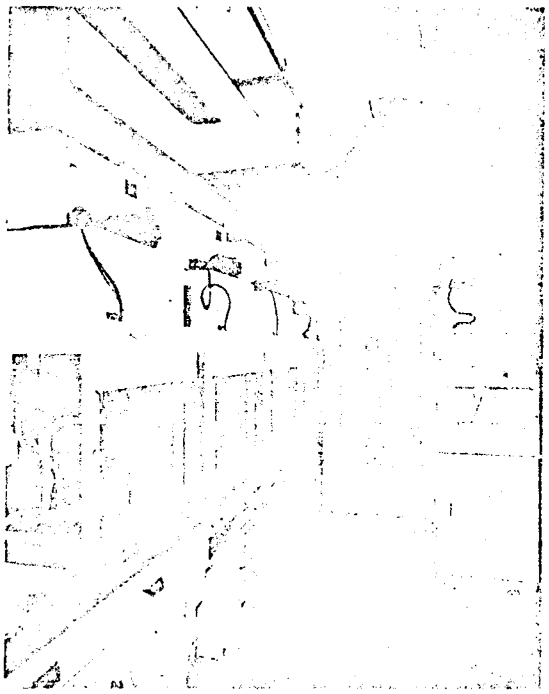

Figure 4. Laboratory for production of high-purity acids

ACS reagent grade $HClO_4$ with high levels of Na and K showed lines for: NaO^+, NaK^+, Na_2^+, K_2^+, Na_2Cl^+, K_2Cl^+, Na_2ClO^+, K_2ClO^+, $Na_2ClO_2^+$, etc. Some of these lines represented potential interferences; however, this type of interference was not significant for the acids purified by sub-boiling distillation since their cationic impurities were always at a very low level.

Measurement of the isotopic ratio of an element at the +2 or +3 charge state will eliminate all three types of interfering lines since these molecular species fragment rather than form a multiply-charged ion. When such interferences existed, Ag, Cu, and K isotope ratios were measured on +2 ions and Zn, Ni, Cr, and Ca isotope ratios were measured on +3 ions.

PRODUCTION AND ANALYSIS OF HIGH-PURITY ACIDS AND WATER

Figure 4 shows the laboratory setup for the production of high-purity acids. Each quartz sub-boiling still and distillate container is housed in a separate Class 100 clean air unit to prevent particulate contamination during distillation. Any extraneous acid vapor produced is exhausted through the balanced plenum assembly which serves four clean air units. The Teflon sub-boiling still is housed in a separate clean air chamber and extraneous acid vapors are exhausted by a standard laboratory hood. The ACS reagent grade acid to be purified is fed to each still from a container just outside the clean air chamber through a liquid level control which maintains the pre-set liquid level. In this manner, acid is constantly fed to the still as distillate is removed. Since impurities are concentrated in the pot liquid, the still is drained after the consumption of each 6- to 8-pound feed bottle.

After distillation, each acid was allowed to stand in its Teflon-FEP container for at least two weeks before analysis to allow for any impurities in or on the container walls to react with the acid.

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(7) R. Alvarez, P. J. Paulsen, and D. E. Kelleher, ANAL. CHEM., **41**, 955 (1969).

(8) P. J. Paulsen, R. Alvarez, and D. E. Kelleher, *Spectrochim. Acta*, **24B**, 535 (1969).

Table I. Hydrochloric Acid

Impurity concentrations ppb by wt (ng/g)

	Acid from sub-boiling still	ACS reagent grade	Commercial high purity
Pb	0.07	0.5	<1
Tl	0.01	0.1	...
Ba	0.04	2	...
Te	0.01	0.1	...
Sn	0.05	0.07	<6
In	0.01	...	...
Cd	0.02	0.03	0.5
Ag	0.03	0.05	0.2
Sr	0.01	0.05	...
Zn	0.2	2	4
Cu	0.1	4	1
Ni	0.2	6	3
Fe	3	20	7
Cr	0.3	2	0.3
Ca	0.06	70	24
K	0.5	200	10
Mg	0.6	10	20
Na	1	500	...
	Σ 6.2 ppb	Σ 820 ppb	Σ 70 ppb

Table II. Nitric Acid

Impurity concentrations ppb by wt (ng/g)

	Acid from sub-boiling still	ACS reagent grade acid	Commercial high purity
Pb	0.02	0.2	0.3
Tl	...	0.2	...
Ba	0.01	8	...
Te	0.01	0.1	...
Sn	0.01	0.1	1
In	0.01	...	...
Cd	0.01	0.1	0.2
Ag	0.1	0.03	0.1
Sr	0.01	2	...
Se	0.09	0.2	...
Zn	0.04	4	8
Cu	0.04	20	4
Ni	0.05	20	3
Fe	0.3	24	55
Cr	0.05	6	130
Ca	0.2	30	30
K	0.2	10	11
Mg	0.1	13	...
Na	1	80	...
	Σ 2.3 ppb	Σ 220 ppb	Σ 240 ppb

Table III. Perchloric Acid

Impurity concentrations ppb by wt (ng/g)

	Acid from sub-boiling still	ACS reagent grade acid	Commercial pure acid
Pb	0.2	2	16
Tl	0.1	0.1	...
Ba	0.1	>1000	10
Te	0.05	0.05	...
Sn	0.3	0.3	<1
Cd	0.05	0.1	4
Ag	0.1	0.1	0.5
Sr	0.02	14	...
Zn	0.1	7	17
Cu	0.1	11	3
Ni	0.5	8	0.5
Fe	2	330	10
Cr	9	10	18
Ca	0.2	760	7
K	0.6	200	9
Mg	0.2	500	4
Na	2	600	...
	Σ 16 ppb	Σ >3400 ppb	Σ 100 ppb

The purified acids were then analyzed by the isotope dilution mass spectrometric method described previously. These analyses characterize the acid as delivered to the user rather than as produced, since this is what is of interest to the analyst.

The Teflon-FEP bottles will be used repeatedly over again to contain the same high-purity acid. It is reasoned that the container should become cleaner with use and cause less contamination to future lots of acids. Any acid not used within a few months will be replaced with freshly distilled reagent.

Hydrochloric Acid. Hydrochloric acid and water form a constant boiling mixture at 6*N* hydrochloric acid. Initial experiments were with starting acid of this concentration. Further experiments showed that the starting concentration could be increased to 10*N* HCl without causing bubble formation and that the distilled product was also 10*N*. However, concentrated 12*N* acid could not be used because of bubble formation on heating. Apparently, acid of higher concentration than constant boiling 6*N* can be produced because the azeotropic mixture that condenses on the cold finger absorbs HCl from the HCl-rich vapor to reach the concentration of the acid in the pot.

ACS reagent grade hydrochloric acid diluted to 10*N* or 31 weight per cent with high-purity water was used as the feed acid. The still heaters were adjusted to 225 W of power. About 2 liters of 10*N* high-purity hydrochloric acid were produced per day under these conditions.

Table I shows the analysis of the high purity acid produced by sub-boiling distillation, the starting ACS reagent grade acid, and a lot of commercial high-purity acid. A summation of these impurity elements shows that the sub-boiling distilled acid contained 6.2 ppb, the ACS reagent grade contained 820 ppb, and commercial high-purity 70 ppb. The only element found in the sub-boiling distilled acid at levels higher than 1 ppb was iron at 3 ppb. The other elements were at the sub-ppb level, generally lower than 0.1 ppb.

Nitric Acid. The sub-boiling distillation of concentrated 70% ACS reagent grade nitric acid required a low heater temperature to prevent the HNO_3 vapor in the proximity of the heater from disproportionating to form nitrogen dioxide with resulting discoloration of the distillate. Experiments showed that at a heater power setting of 107 W, little or no discoloration of the distillate took place. As a result, only about 500 ml per day of nitric acid was produced. Titration showed the distillate to be 70% HNO_3, the same concentration as the starting acid.

Table II shows the results of the analysis of the sub-boiling distilled acid, ACS grade starting acid, and a lot of commercial high-purity acid. The totals of the impurity elements determined were 2.3 ppb for the sub-boiling distilled acid, 220 ppb for the ACS starting acid, and 240 ppb for the commercial high-purity acid. The sub-boiling distilled nitric acid was the purest of the acids produced. No element was found at a concentration greater than 1 ppb and only sodium was detected at that level, and this accounts for almost half of the total impurities found. Most elements were in the 0.05- to 0.01-ppb range.

Perchloric Acid. Initial experiments on the sub-boiling distillation of concentrated 70% perchloric ($HClO_4 \cdot 2H_2O$) showed that high heater temperatures caused the perchloric

Table IV. Sulfuric Acid

Impurity concentrations ppb by wt (ng/g)

	Acid from sub-boiling still	ACS reagent grade acid
Pb	0.6	0.5
Tl	0.1	0.1
Ba	0.3	0.2
Te	0.1	0.1
Sn	0.2	0.6
Cd	0.3	0.2
Ag	0.3	0.6
Sr	0.3	0.4
Zn	0.5	2
Cu	0.2	6
Ni	0.2	0.5
Fe	7	6
Cr	0.2	0.2
Ca	2	123
K	4	9
Mg	2	4
Na	9	50
	Σ 27 ppb	Σ 200 ppb

Table V. Hydrofluoric Acid

Impurity concentration ppb by wt (ng/g)

	Acid from sub-boiling still	ACS reagent grade acid
Pb	0.05	0.8
Tl	0.1	0.2
Ba	0.1	0.5
Te	0.05	0.1
Sn	0.05	11
Cd	0.03	2
Ag	0.05	0.1
Sr	0.1	0.5
Zn	0.2	4
Cu	0.2	3
Ni	0.3	12
Fe	0.6	110
Cr	5	20
Ca	5	14
K	1	28
Mg	2	10
Na	2	100
	Σ 17 ppb	Σ 320 ppb

Table VI. Water

Impurity concentrations ppb by wt (ng/g)

	Water from sub-boiling still
Pb	0.008
Tl	0.01
Ba	0.01
Te	0.004
Sn	0.02
Cd	0.005
Ag	0.002
Sr	0.002
Zn	0.04
Cu	0.01
Ni	0.02
Fe	0.05
Cr	0.02
Ca	0.08
K	0.09
Mg	0.09
Na	0.06
	Σ 0.5 ppb

acid in the still to turn bright yellow, probably because of the formation of chlorine dioxide. At lower power settings, little or no color was noted and the distillate was colorless. Another problem with this distillation was that in the earlier work, crystals would occasionally build up on the cold finger condenser. This material was probably perchloric acid monohydrate ($HClO_4 \cdot H_2O$) which has a melting point of 50 °C. Crystal formation could be controlled by changing either the flow rate of the condenser water or the heater temperature. However, this problem was noted only in the earlier work. For the last six months, no crystal formation on the cold finger has been noted even when the still is operated continuously for weeks. The power setting used for the production of purified perchloric acid was 240 W, and the production rate was about 600 ml of perchloric acid per day. Titration has shown that the distillate is 70 wt % of $HClO_4$, the same as the starting ACS grade acid.

Table III shows the results of the analyses of the sub-boiling distilled acid, the starting ACS grade acid, and a lot of commercial high-purity acid. The total of the impurity elements found was 16 ppb for the sub-boiling distilled acid, 3400 ppb for the starting acid, and 100 ppb for the commercial high-purity acid. These analyses demonstrate the efficiency of sub-boiling distillation when the concentration of impurity elements in the purified product is compared to the starting acid. The concentration of barium which was greater than 1000 ppb was reduced to 0.1 ppb, a purification factor of greater than 10,000. Another example is calcium which was reduced to 0.2 ppb in the purified acid from 760 ppb in the starting acid, a factor of 3,800. It should also be noted that chromium which was present at 10 ppb in the starting acid was not significantly changed in the purified acid. This is probably due to the fact that chromium can be volatilized from hot perchloric acid solutions as chromyl chloride, CrO_2Cl_2, so little, if any, purification can be expected by sub-boiling distillation. Chromium accounts for over half of the total impurities found in the purified acid.

Sulfuric Acid. Initial experiments with the sub-boiling distillation of sulfuric acid showed that, because of the density of H_2SO_4, the acid that condensed on the cold finger tended to drop off before reaching the collection tube. Another problem was that even at the highest power setting, the distillation rate was extremely slow. Modification of the still by increasing the angle of incline of the cold finger condenser solved the condensate problem, and the rate of distillation was increased by using a platinum foil reflector around the still. At the maximum power setting of 427 W, the rate of distillation is now about 300 ml per day. Titration has shown that the purified acid is 96 wt % H_2SO_4, the same as the starting ACS grade acid.

Table IV shows the results of the analyses of the sub-boiling distilled acid and the starting sulfuric acid. The total of the impurities found in the starting acid was 200 ppb, the lowest of any of the ACS grade acids, and the purified acid contained 27 ppb, the highest of the purified acids. Sodium was the principal contaminant in the high-purity acid at 9 ppb with iron right behind it at 7 ppb. These two elements account for over half the total impurities found in the purified sulfuric acid.

Hydrofluoric Acid. Hydrofluoric acid was purified in the all-Teflon sub-boiling still shown in Figure 2 which was designed and built at NBS. Hydrofluoric acid and water form a constant boiling mixture at 36% HF. . Because of the previous experience with hydrochloric acid, the sub-boiling distillation of concentrated 48% HF was attempted. Titration showed that the distilled product was also 48% HF. Ap-

Table VII. Summary of Experimental Conditions for Producing High-Purity Acids and Water by Sub-Boiling Distillation

Reagent	Concentration of still feed acid, % by wt	Still heater power, W	Concentration of distillate, % by wt	Production rate, ml/24 hr
HCl	31	225	31	2,000
HNO_3	70	107	70	500
$HClO_4$	70	240	70	600
H_2SO_4	96	427	96	300
HF	48	164	48	300
H_2O	...	200	...	4,000

parently, as in the case of hydrochloric acid, the azeotropic mixture that condenses on the cold finger absorbs HF from the HF rich vapor to reach the same concentration as the acid in the still.

Since the heaters of the Teflon still for the purification of hydrofluoric acid are enclosed in Teflon tubes, the temperature of the heater had to be kept below the softening point of Teflon. As a result the maximum power setting for this still was 164 W which produced a distillation rate of 300 ml per 24 hour day.

Table V shows the results of the analyses of the starting ACS grade HF and the purified product. The total of the impurities in the purified acid is 17 ppb compared to 320 ppb in the starting ACS grade acid. The two principal impurities in the purified acid are Ca and Cr, both at 5 ppb, and they account for over half the total impurity found. The only other elements found at a concentration of greater than 1 ppb are K at 1 ppb, Mg at 2 ppb, and Na at 2 ppb.

Water. Water has been included in this study because it is the most commonly used chemical reagent and because sub-boiling distillation has been used to produce high-purity water both here at NBS and elsewhere. Initially, water of higher purity than the distilled water from the laboratory distribution system was obtained by re-distillation in a commercial, continuous-feed still. This still had a tin-coated evaporator and baffle and was equipped with a quartz condenser. This unit was designed to disengage CO_2 and other gases from the distillate and vent them off. Water produced by this still was used as the feed water to the sub-boiling still. The entire assembly of feed apparatus, quartz sub-boiling still, and quartz collector was contained in a Class 100 clean air chamber. The distillation rate at a power setting of 200 W was 4 liters per day.

The analysis of the sub-boiling purified water is given in Table VI. This water contained a maximum of 0.5 ppb total of the 17 elements determined. No element was detected at a concentration of greater than 0.1 ppb. Since no correction for an analysis blank could be made, the values must be regarded as upper limits for the purity of the water. The water may in fact be more pure than the analysis indicates.

The optimum conditions for the production of each high-purity acid and water by sub-boiling distillation described above are summarized in Table VII.

The impurity elements determined in the acids and water (Tables I VI) are tabulated in order of decreasing mass. This reveals that the major impurities for the acids purified by sub-boiling distillation are all low mass elements. None of the NBS purified acids have an impurity level as high as 1 ppb for elements above iron in mass. Elements from iron on down sometimes exceed 1 ppb but none exceeded 10 ppb.

A number of the major impurities found in the ACS reagent grade and commercial high purity acids are elements common to their glass storage containers. It would appear that the means of storing the acids are as responsible for the acid purity as the purification method. It should be noted that of all the acids analyzed, only the ACS grade perchloric acid showed an element (Ba) that exceeded the 1-ppm level.

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The Distribution, Composition and Transport of Suspended Particulate Matter in the Northeastern Gulf of Alaska, Southeastern Bering Shelf and Lower Cook Inlet

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A. The Southeastern Bering Shelf

The distribution of suspended matter at the surface in the southeastern Bering Shelf is controlled by the discharge of sedimentary material from the coastal rivers and the semipermanent counterclockwise currents which dominate the water circulation in Bristol Bay. A large plume of suspended matter extends to the southwest from Cape Newenham. Suspended matter originating from the Kvichak and Nushagak Rivers is carried to the west until it reaches Cape Newenham where it combines with a portion of the material discharged from the Kuskikwim River and is deflected to the southwest. Chemical analysis of suspended matter from the plume indicates that it is essentially of terrestrial origin.

A second plume extends to the southwest from Kuskokwim Bay. High concentrations of suspended matter extend as far west as Nunivak Island. This material is derived from the Kuskokwim River.

Along the Alaska Peninsula surface suspended matter concentrations decrease rapidly away from the coast. As the Pacific Ocean water passes through Unimak Pass and is deflected to the northeast along the coast of the Alaska Peninsula, suspended matter of marine origin is carried into Bristol Bay. When this water mixes with the highly turbid Shelf water, it is rapidly diluted producing the sharp gradients in the suspended matter distributions near the coast.

In the region north of Unimak Pass, large suspended matter plumes appear to be the result of increased productivity during the summer months.

Below the surface, the particulate matter distributions follow the same distribution pattern as at the surface. However, suspended matter concentrations increase sharply near the bottom indicating that resuspension of bottom sediments is occurring.

Studies of the major and trace element composition of the suspended matter show significant spatial variations which are directly related to the supply of terrestrially derived suspended matter from coastal rivers and local variations in primary productivity.

B. Gulf of Alaska

The distribution of suspended matter in the northeastern Gulf of Alaska is affected by a number of parameters which combine to form a unique distribution pattern. East of Kayak Island the surface particulate matter distributions are dominated by the discharge of sedimentary material from the coastal streams which drain the Bering, Guyot and Malaspina Glaciers. As this material is discharged into the Gulf, the westward flowing currents quickly deflect it to the west along the coast until it reaches Kayak Island where it is deflected to the southwest and is trapped by a clockwise gyre.

The major source of sedimentary material to the Gulf of Alaska is the Copper River. Once discharged into the Gulf, the suspended material from the Copper River is carried to the northwest along the coast until it reaches Hinchinbook Island where a portion of the material passes into Prince William Sound and the remaining material is carried to the southwest along the coast of Montague Island.

In general, concentrations of suspended matter in the Gulf are high at the surface with an average concentration of approximately 1.0 mg/ℓ. Beneath the surface, concentrations generally decrease with depth until the sea floor is approached. Close to the sea floor suspended matter concentrations increase sharply and the highest concentrations are found within 5 meters of the seawater-sediment interface. Studies of the temporal variability of suspended matter near the bottom show evidence for resuspension and redistribution of bottom sediments. These processes have occurred as a result of interactions between tidal and storm-induced bottom currents and the surficial sediments.

Studies of the chemical composition of the suspended matter show significant spatial and seasonal variations which have been correlated with seasonal variations in primary productivity, variations in the supply and transport of terrestrially derived suspended matter from the coastal rivers, and resuspension of bottom sediments.

II. Introduction

Suspended particles in marine coastal waters play an important role in regulating the chemical form, distribution, and ultimate deposition of many pollutants. Some toxic elements in particulate form are transported to the oceans, via river runoff, where they are desorbed at the freshwater-seawater interface (Turekian, 1971; and Martin et al., 1971). Other contaminants, such as certain trace elements and petroleum hydrocarbons, are adsorbed onto the surfaces of suspended particles and are subsequently removed to the sediments as the particles settle (Kharkar et al., 1968; Kolpack, 1971; and Sholkovitz, 1966).

In areas where the bottom environment is especially dynamic, near bottom processes such as resuspension and redistribution of bottom sediments might affect the ultimate deposition of pollutants. An understanding of the processes controlling the distribution, composition, and transport of suspended particulate matter is essential to the assessment of the fate of toxic pollutants in the coastal waters of Alaska.

The major objective of the particulate matter program in the Gulf of Alaska, Lower Cook Inlet and Shelikof Strait, and the southeastern Bering Shelf is to determine the seasonal variations in the distribution, composition, and transport of suspended matter. Other objectives include: (1) the high frequency (hourly) variability in the distribution of suspended matter; (2) an investigation of the processes controlling resuspension and redistribution of bottom sediments; and (3) an investigation of the adsorptive characteristics of suspended matter from Cook Inlet for crude oil.

III. Current State of Knowledge

A. Southeastern Bering Shelf

There is very little published information about the distribution and composition of suspended particulate matter in the southeastern Bering Shelf.

Sharma et al. (1974) compared some particulate matter distributions taken during June-July 1973 in the southern Bering Sea and Bristol Bay region with ERTS multispectral scanner images of the same area which were obtained on October 2, 1972. The surface contours of suspended load distributions indicate several regions of relatively turbid water which originate from a variety of sources. These turbid regions include:

(1) A region of turbid water which is north of the Aleutian Islands. This is probably due to the high level of primary productivity that is the result of the mixing of nutrient-rich deep water with the Alaskan Stream which flows into the Bering Sea from the south.

(2) A region of turbid water which extends south from Kuskokwim Bay and west from northern Bristol Bay. This plume probably represents suspended sediments derived from the Kuskokwim River from the north and the Kvichak and Nushagak Rivers from the east.

(3) A region of slightly turbid water extending to the southwest from Bristol Bay which may represent suspended matter derived from the Kvichak and Nushagak Rivers.

The ERTS imagery indicates that the Nushagak River is a major source for particulate matter in the Bristol Bay area. The suspended particles from the Kvichak and Nushagak Rivers are carried to the west by the prevailing counterclockwise current. Sharma et al. (op. cit) state that although the river plumes remain close to shore, offshore transport of material in suspension is probably brought about by tidal currents.

There is only a small amount of information about the chemical composition of the suspended matter in the southeastern Bering Shelf. Loder (1971) studied the distribution of particulate organic carbon (POC) north of Unimak Pass and found high POC concentrations (221-811 μgC/ℓ) in the thermally stabilized upwelled water north of Unalaska Island. Lower POC concentrations were found north of Unimak Island and west Akutan Pass which presumably were due to current mixing.

Tsunogai et al. (1974) studied the distribution and composition of particulate matter from six stations in the south central and southeastern Bering Sea and northern North Pacific Ocean. They found the highest concentrations of particulate matter occurred at a depth of 20 meters which appeared to be due to the high productivity and the slow decomposition of organic matter just below the surface. The organic portion of the suspended matter was about 67 percent for the samples from the Bering Sea and 80 percent for the samples south of the Aleutian Islands in the northern North Pacific.

B. Northeastern Gulf of Alaska

Reimnitz (1966) studied the sedimentation history and lithology of sediments from the Copper River Delta. He estimated the particulate matter supply of the Copper River to be 107 x 10^6 tons/yr which mostly consists of fine grain sands and silts.

Sharma et al. (1974) compared some surface particulate matter distributions taken during February 24-28, 1973 between Kenai Peninsula and Kayak Island with ERTS multispectral scanner images of the same region which were obtained on October 12, 1972 and August 14, 1973. The ERTS images show that the Copper River and Bering Glacier provide most of the sediment load to this region. The westward flowing current deflects a portion of the Copper River plume to the west. The suspended matter moves along the coast, with some material entering Prince William Sound through the passages on either side of Hinchinbrook Island and the remaining material is carried along the southeast shore of Montague Island.

Carlson et al. (1975) used ERTS imagery to study the transport of suspended material in nearshore surface waters of the Gulf of Alaska. During the late summer and early fall months large quantities of fine-grain silt and clay-sized material from the Bering, Guyot and Malaspina Glaciers are discharged into the Gulf between Kayak Island and Yakutat Bay. This material is carried to the west by the Alaska Current until it reaches Kayak Island where it is deflected to the south.

El Wardani (1960) studied the distribution of organic phosphorus in the Bering Sea, Aleutian trench and the Gulf of Alaska. He demonstrated that particulate organic phosphorus in the upper 200 meters of the water column bears an inverse relationship to inorganic phosphorus. Below 200 meters no detectable particulate organic phosphorus was found.

C. Lower Cook Inlet

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

A. Southeastern Bering Shelf

The southeastern Bering Shelf (Fig. 1) is a relatively shallow embayment which is bounded by the Kilbuk Mountains to the north and east, and the Alaska Peninsula to the south. Except for some small depressions near the Alaska Peninsula, the shelf floor is extremely smooth with an average slope of about 0.0003 (Sharma, 1974).

The region receives sedimentary material from the Kuskokwim, Kvichak, and Nushagak Rivers. The largest river, the Kuskokwim, discharges approximately 4.0 x 10^6 tons of sediments annually (Nelson, 1974). Figure 2 shows the range and mean values of the monthly mean discharge of the Kuskokwim for the period of record (Water Supply Papers, U.S. Geological Survey). The maximum discharge occurs during the months of May through September.

A counterclockwise movement generally dominates the water motion in the Bristol Bay region. Pacific Ocean water enters the Bering Sea through the Aleutian Island passes and flows to the northeast along the coast of the Alaska Peninsula. The water moves along the northern coastline by tidal and wind-driven currents until it reaches Nunivak Island where it is turned to the north.

The permanent currents in the southeastern Bering Shelf appear to be somewhat sluggish. Current velocities ranging from 2.0 to 5.0 cm/sec have been observed north of the Alaska Peninsula (Hebard, 1959). However, tidal currents are dominant in northeastern Bristol Bay where tidal velocities of up to 125 cm/sec have been observed in Nushagak Bay (U.S. National Ocean Survey, 1973).

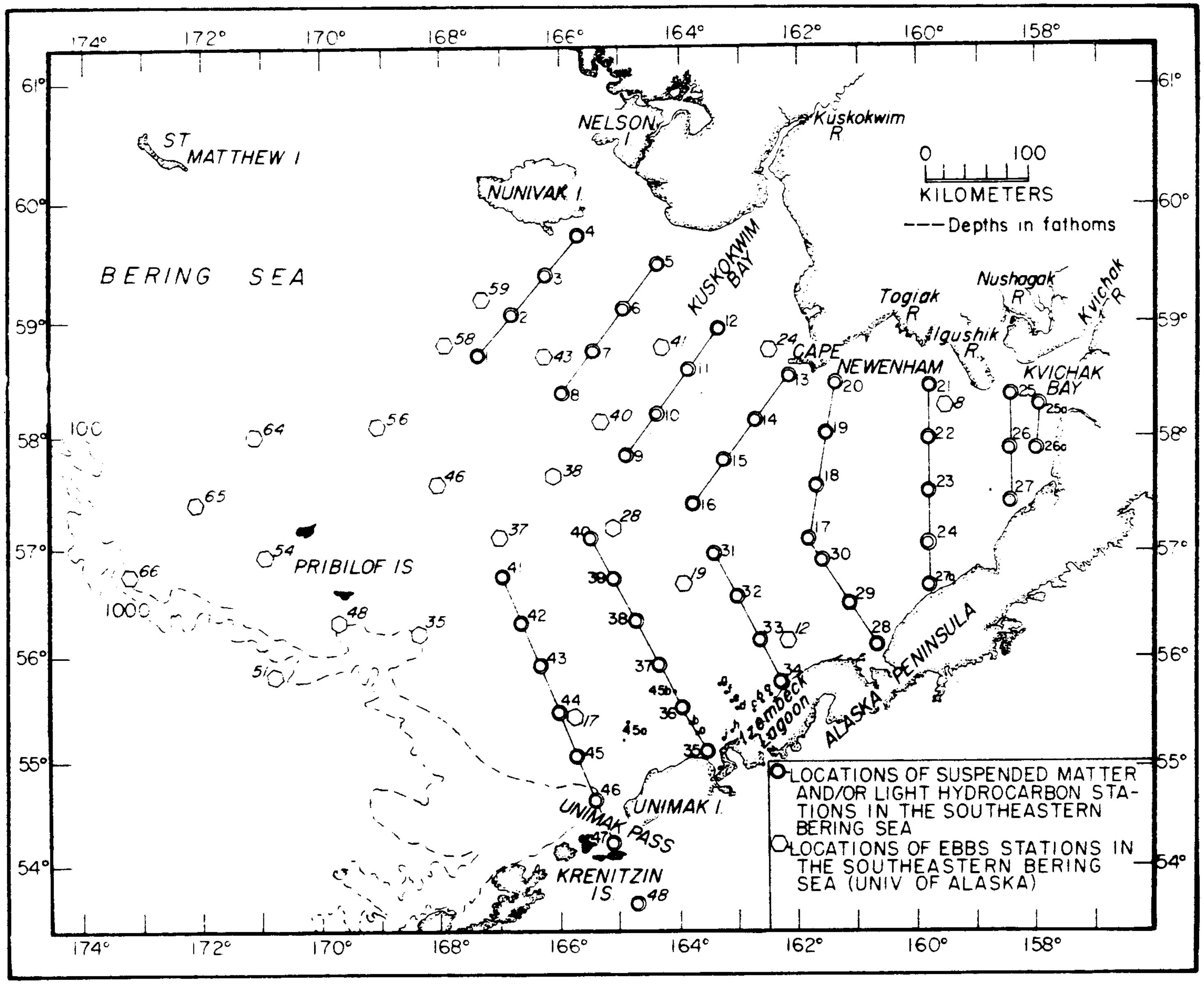

Figure 1. Locations of suspended matter stations in the southeastern Bering Shelf (Cruises RP-4-Di-75B-III, 12 Sept. - 5 Oct. 1975 and RP-4-MW-76B-VIII, 24 June-9 July 1976).

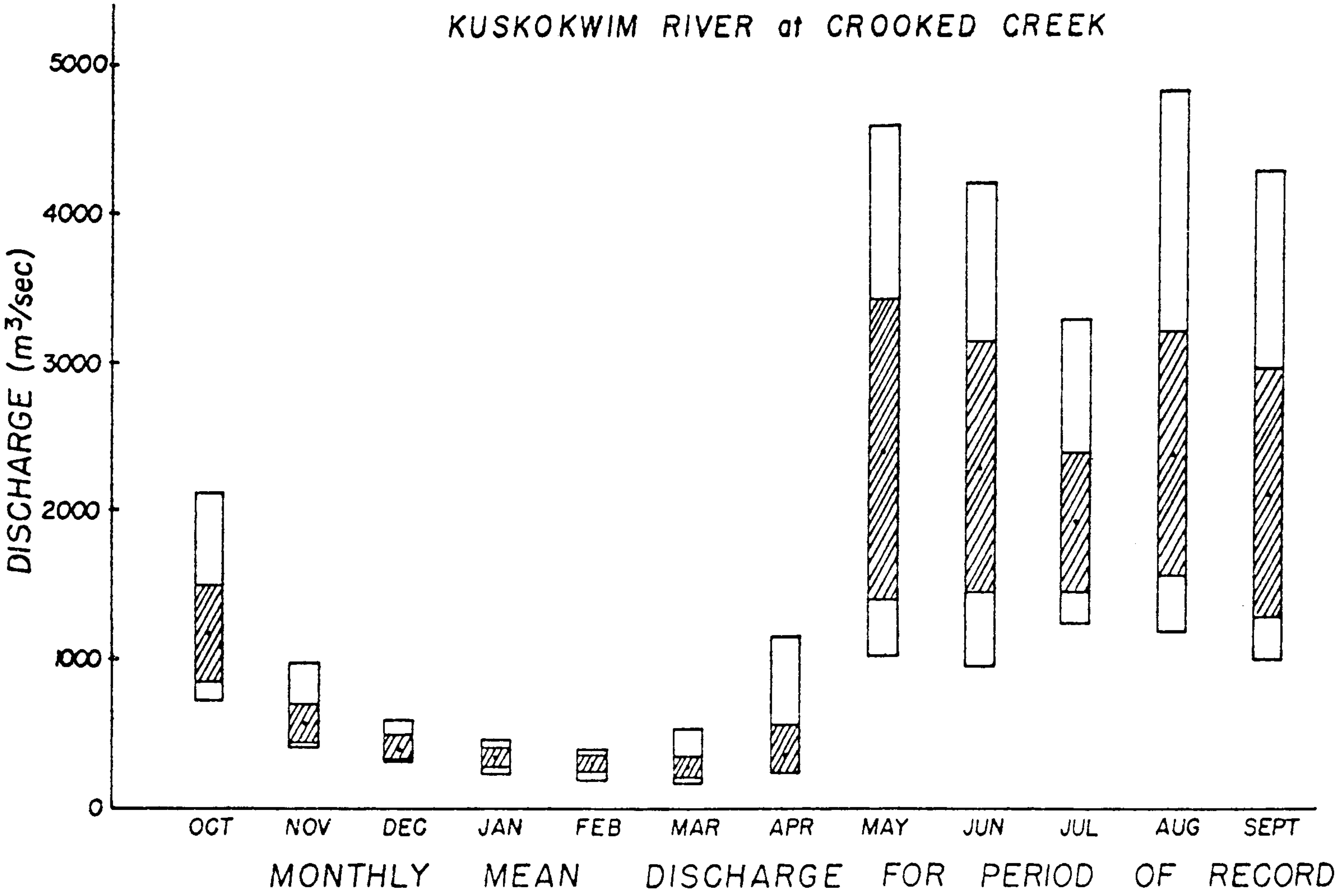

Figure 2. Range, mean and standard deviation of the monthly mean discharge of the Kuskokwim River at Crooked Creek for the period of record through 1974 (Water Supply Papers, U.S. Geological Survey).

B. The Northeastern Gulf of Alaska

The northeastern Gulf of Alaska (Fig. 3) is bordered by a mountainous coastline containing numerous glaciers which deliver large quantities of suspended material to the Gulf during the summer months when maximum discharge occurs. The major sediment discharge is from the Copper River. Reimnitz (1966) estimates that approximately 107 x 10^6 tons of fine-grain material are delivered annually to the Gulf by way of the Copper River system. Figure 5 shows the range and mean values of the monthly mean discharge of the Copper River for the period of record (Water Supply Papers, U.S. Geological Survey). The maximum discharge of the Copper River occurs during the months of June through September.

Additional inputs into the Gulf occur along the coastline east of Kayak Island where coastal streams containing high sediment concentrations drain the Bering, Guyot and Malaspina Glaciers. Since there are no permanent gauging stations on these streams, there is no information about the quantities of materials that are discharged into the Gulf from these sources.

The current systems in the Gulf are dominated by the large counterclockwise gyre of the Alaskan Stream. It is usually characterized by a core of relatively warm (5.5°-6.2°C) water at about 130 meters (Galt and Royer, 1976). The Alaskan Stream comes in contact with the shelf just east of Icy Bay where it is turned to the west and appears to follow the 150 meter isobath.

West of Cape St. Elias the Alaskan Stream is deflected to the southwest, leaving the large shelf area between Middleton Island and the Copper River Delta relatively free of its influence. In this region the circulation is affected by seasonal wind patterns. In the summer, the winds are predominantly from the southwest. This produces an Ekman drift of surface waters offshore. During the winter, the winds are from the southeast which results in an Ekman drift onshore and downwelling in subsurface waters.

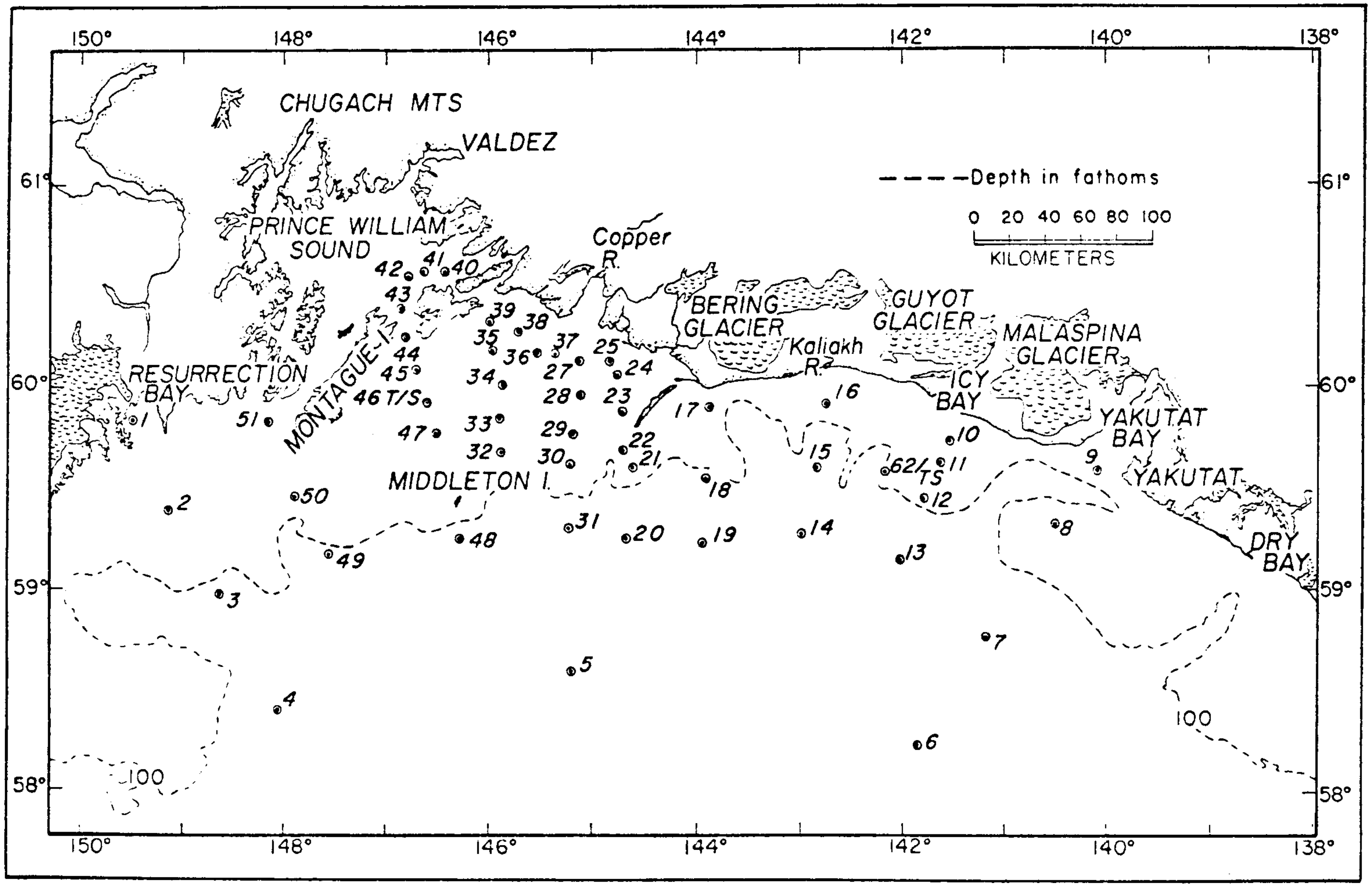

Figure 3. Locations of suspended matter stations in the northeastern Gulf of Alaska (Cruise RP-4-Di-75C-I, 21 Oct. - 10 Nov. 1975).

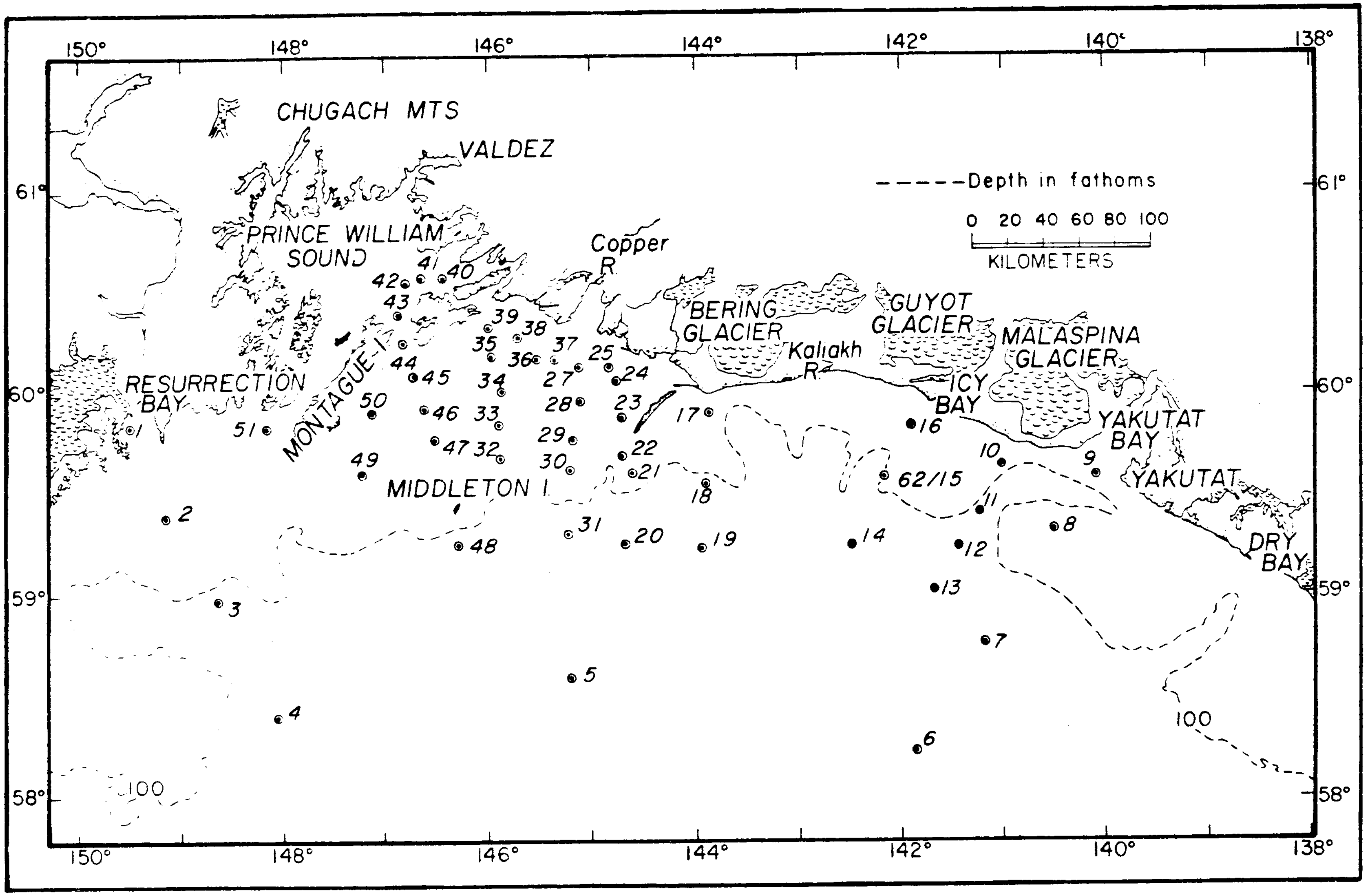

Figure 4. Locations of suspended matter stations in the northeastern Gulf of Alaska (Cruises RP-4-Di-76A-III, 13 - 30 April 1976 and RP-4-Di-76B-I, 19 - 31 July 1976).

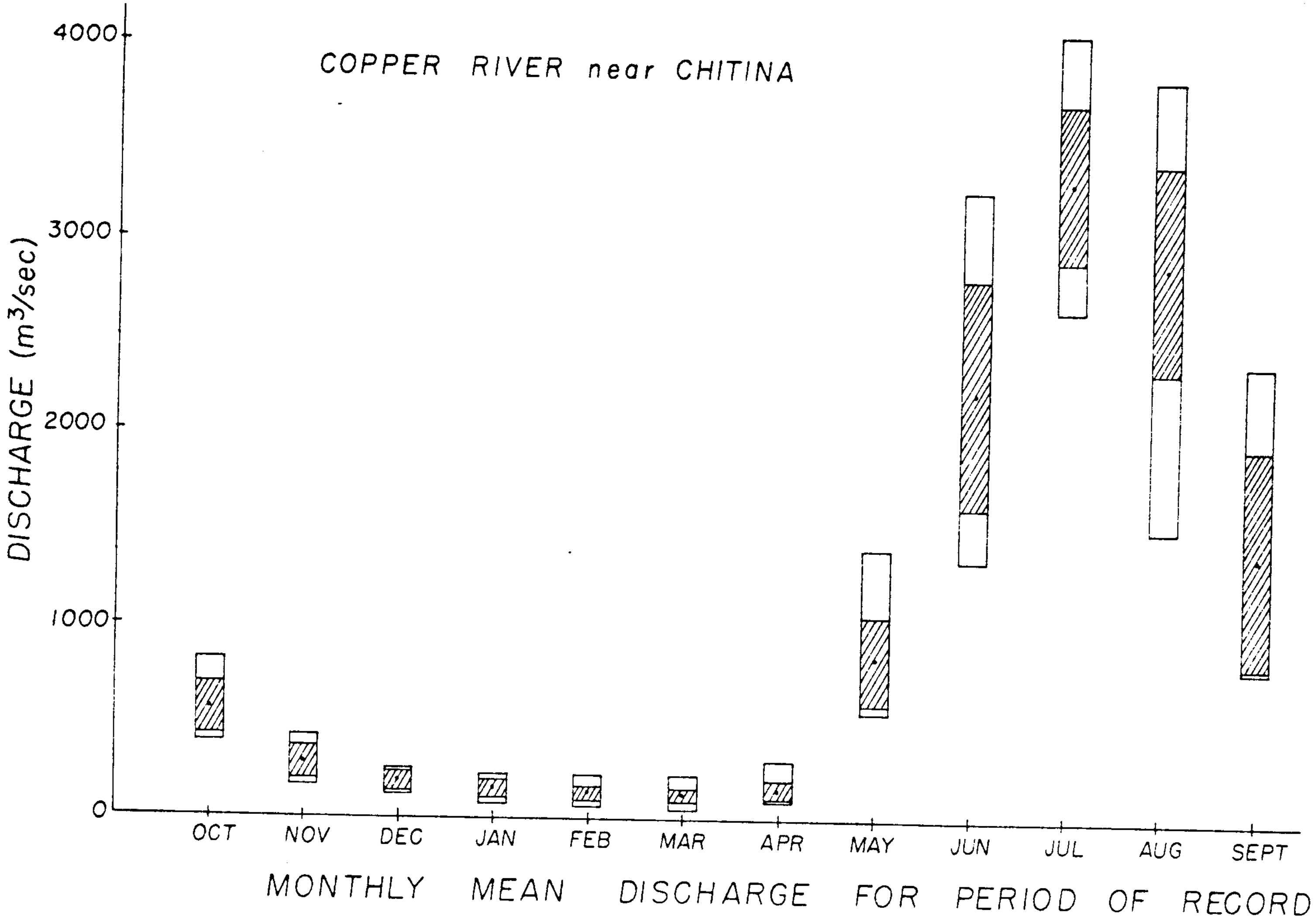

Figure 5. Range, mean and standard deviation of the monthly mean discharge of the Copper River near Chitina for the peroid of record through 1974 (Water Supply Papers, U.S. Geological Survey).

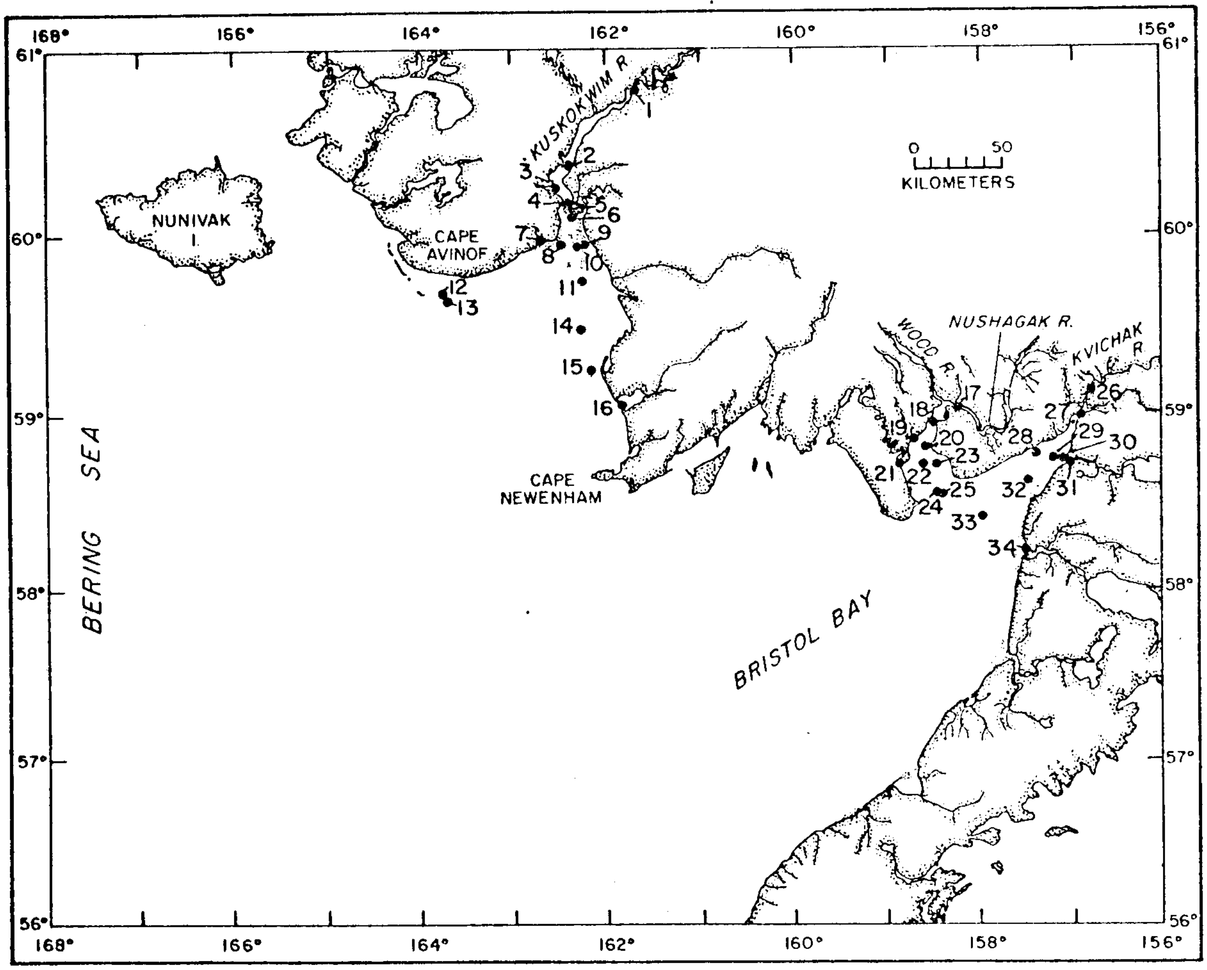

Figure 6. Locations of suspended matter stations in the major rivers draining into the southeastern Bering Shelf (12 - 21 Sept. 1976).

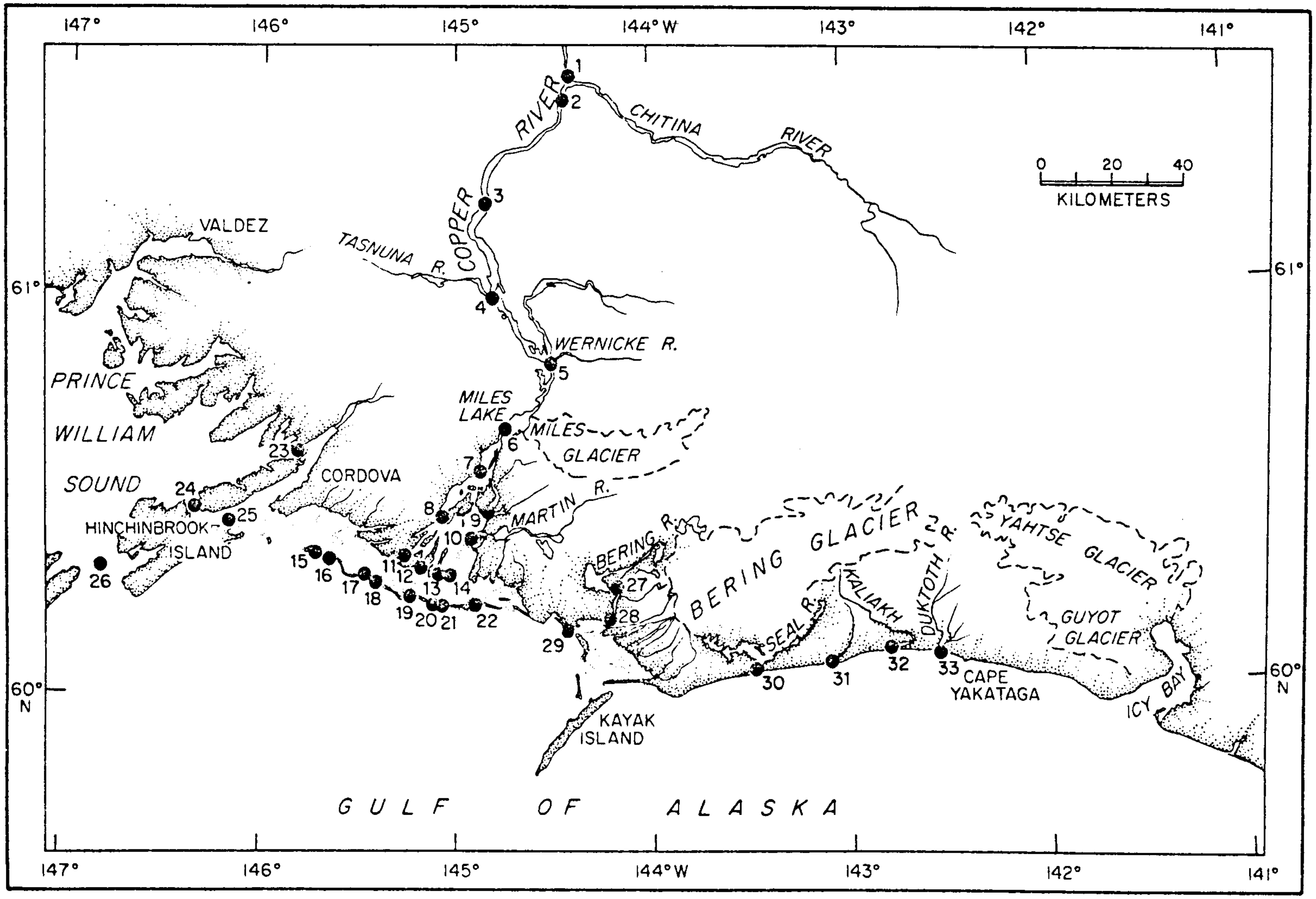

Figure 7. Locations of suspended matter stations in the major rivers draining into the northeastern Gulf of Alaska (22 - 27 June 1976).

C. Lower Cook Inlet

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 three major rivers: the Matanuska River at the head of Knik Arm and the Susitna and Beluga Rivers to the northwest. 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 eastside 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, occasional silt and clay-sized sediments have been observed.

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 three cruises in the Gulf of Alaska and two cruises in the Bering Sea during the present fiscal year. The field program has been integrated with the physical, geological, and biological programs so that concomitant information about water mass transport, primary productivity, and recent sedimentation has been obtained.

In addition to the seasonal distributions, we have conducted a number of high frequency (hourly) time series studies at selected locations. This has provided valuable information about the variability in the distribution of suspended matter that may be due to waves, 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 has been concerned with the processes of sediment resuspension and redeposition. Observations of light scattering profiles from the Gulf of Alaska have indicated evidence of near bottom turbidity layers which may be due to resuspension of bottom sediments. The erosion and transport of bottom sediments are expected to be related to the action of near bottom currents. These currents are presumably influenced mainly by the actions of waves, tides, and storms.

To determine how these processes affect the near bottom distribution of particulate matter a small mooring was deployed in the eastern Gulf at approximately 200 meters (Station 62, Figure 3). The mooring contained an Aanderaa current meter and a nephelometer located within 3 meters of the bottom. The mooring was maintained for approximately two months.

A. Sampling Methods

Sample collection has occurred concurrently with STD-nephelometer hydrocasts so that the particulate matter distributions can be related to the hydrography. Water samples were collected in 10-liter PVC Model 1070 Drop-top Niskin® bottles and filtered through preweighed 0.40 μm Nuclepore® filters. The filters were washed with three 10-ml aliquots of deionized filtered water, dried in a desiccator, stored in plastic petri dishes, and returned to the laboratory. At the laboratory, the filters were reweighed on a seven-place Cahn® Model 4700 Electrobalance. Additional water samples were filtered through appropriate filters for the determination of organic carbon and nitrogen.

B. Analytical Methods

The major (Mg, Al, Si, K, Ca, Ti, and Fe) and trace (Cr, Mn, Ni, Cu, Zn, and Pb) element chemistry of the particulate matter is being 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; and Massoth et al., in preparation). The inherent broad band of radiation from a Ag x-ray tube is used to obtain a series of characteristic emission lines from a single element secondary target which then more efficiently excites the thin film sample. Se and Zr secondary targets are used to analyze the samples for both major and trace elements. Standards are 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 ten replicate analyses of a largely inorganic sample of approximately mean mass was less than 3 percent for the major constituents and as high as 5 percent for the trace elements. However, when sampling precision is considered, the coefficients of variation increase, averaging 12 and 24 percent for major and trace elements, respectively.

Analysis of total particulate carbon and nitrogen is carried out 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 percent for carbon and 7 to 14 percent for nitrogen.

C. Nephelometry

The vertical distribution of suspended particulate matter was determined using a continuously recording integrating nephelometer (Sternberg et al., 1974). The nephelometer consists of a flashing light source, a scattered light detection system, a data transmission system, and Ni-Cd batteries mounted in a self-contained, easily portable, deep sea housing.

The instrument has been interfaced into the Plessey CTD system using the sound velocity channel (14-16 kHz) such that real time measurements of forward light scattering can be obtained. Since the light scattering measurements are relative, the instrument must be calibrated against discrete samples for a given area. Figure 8 shows the relationship between total suspended matter and light scattering (reported as a frequency) for 55 near bottom samples from the Gulf of Alaska[1] using the PMEL nephelometer under uniform operating conditions. The figure indicates that the relationship between light scattering and total suspended matter is linear to some degree. This suggests that the light scattering profiles may be used to estimate suspended matter concentrations near the bottom.

VI. Results and Discussion

To date we have completed all five cruises in the Gulf of Alaska and southeastern Bering Shelf scheduled for FY 76. The first cruise was conducted in the southeastern Bering Shelf during the fall of 1975 (12 September-5 October). The second cruise was conducted in the northeastern Gulf of Alaska during late fall

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[1] Since the nephelometer is adversely affected by ambient light in the near surface waters, the light scattering data will only be used to provide information about near bottom processes where ambient light levels are well below the 1 percent level.

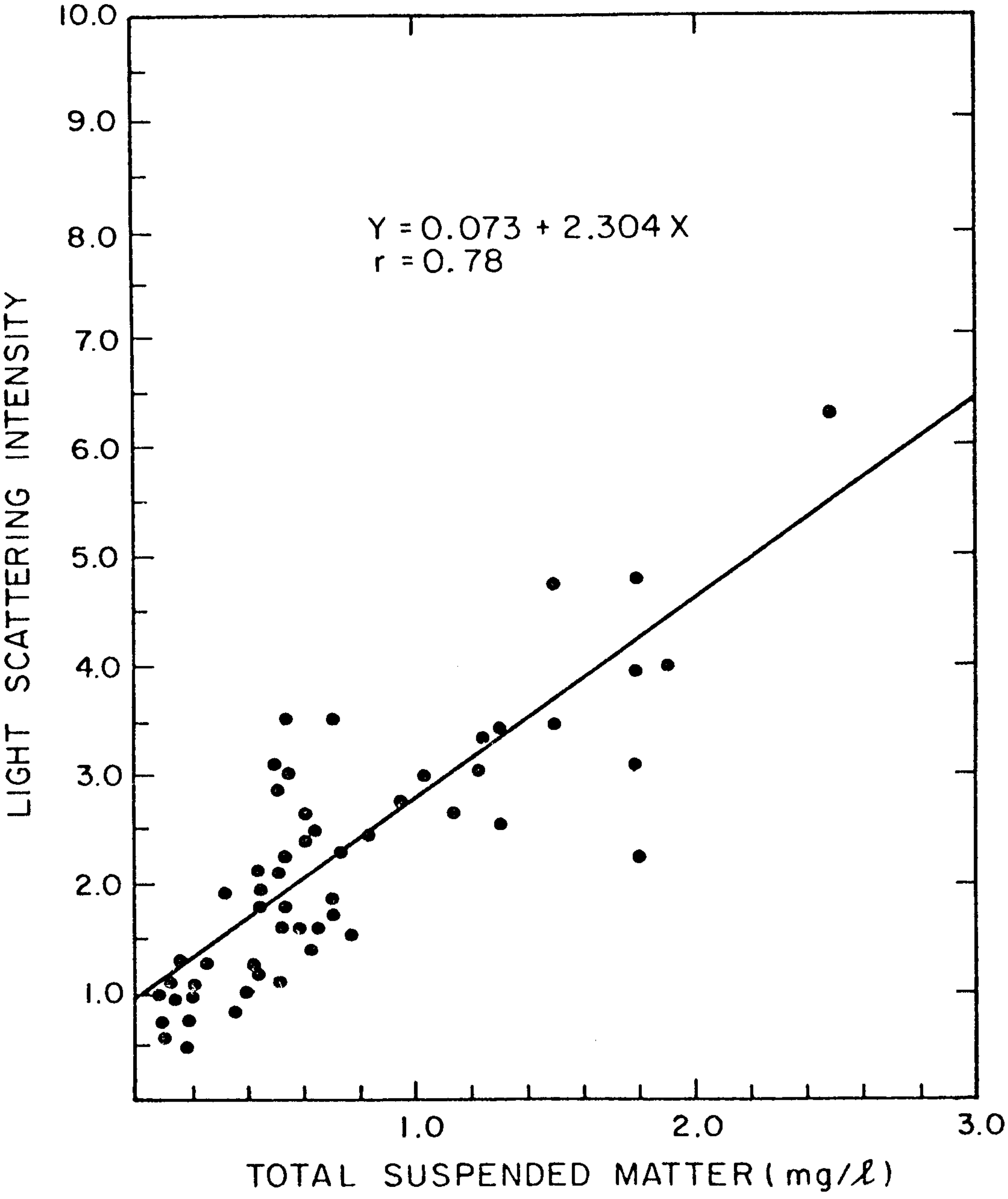

Figure 8. Scatter plot of the output of the nephelometer versus total suspended matter for 55 near bottom samples from the northeastern Gulf of Alaska.

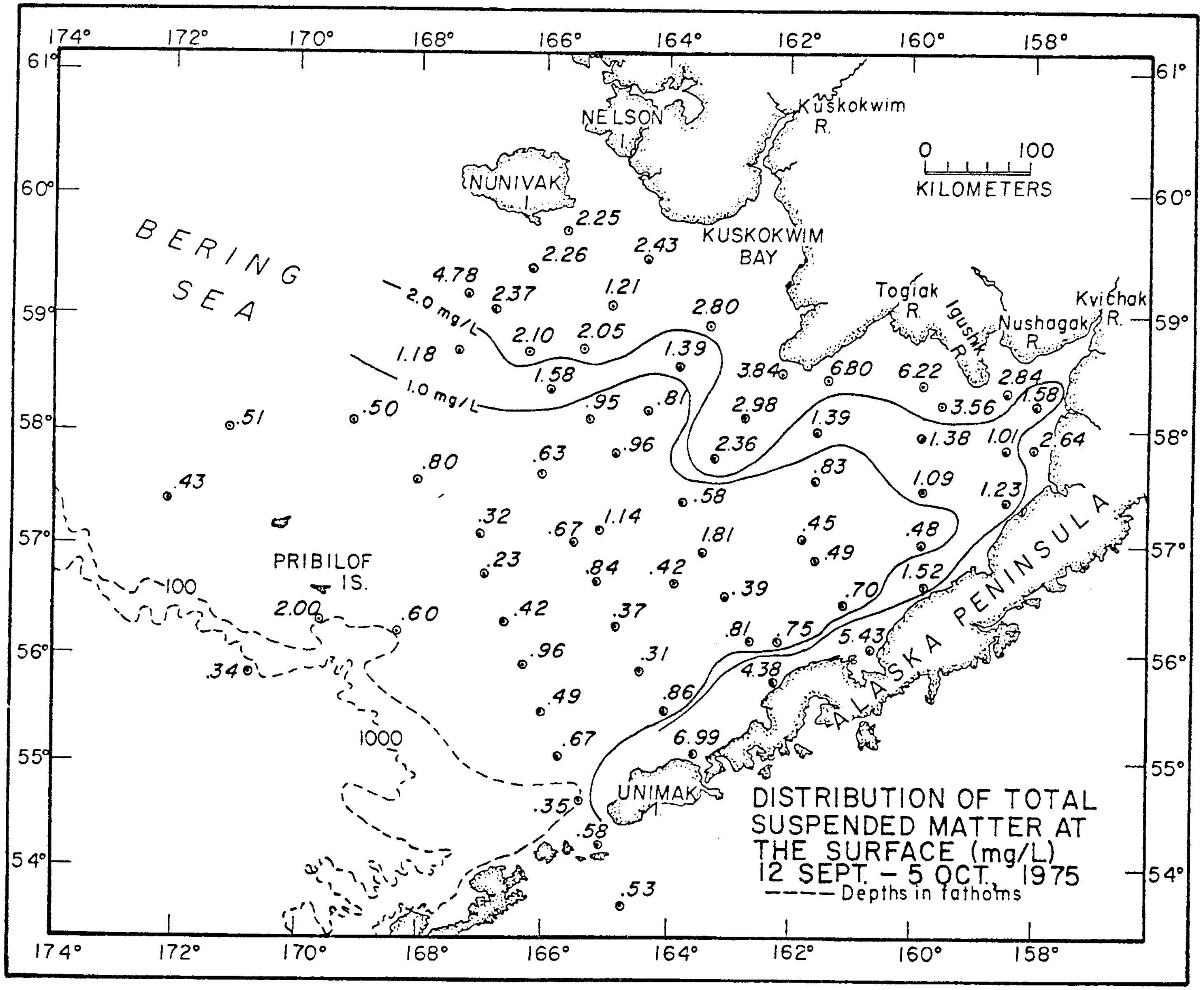

Figure 9. Distribution of total suspended matter at the surface in the southeastern Bering Shelf (Cruise RP-4-Di-75B-III, 12 Sept. - 5 Oct. 1975).

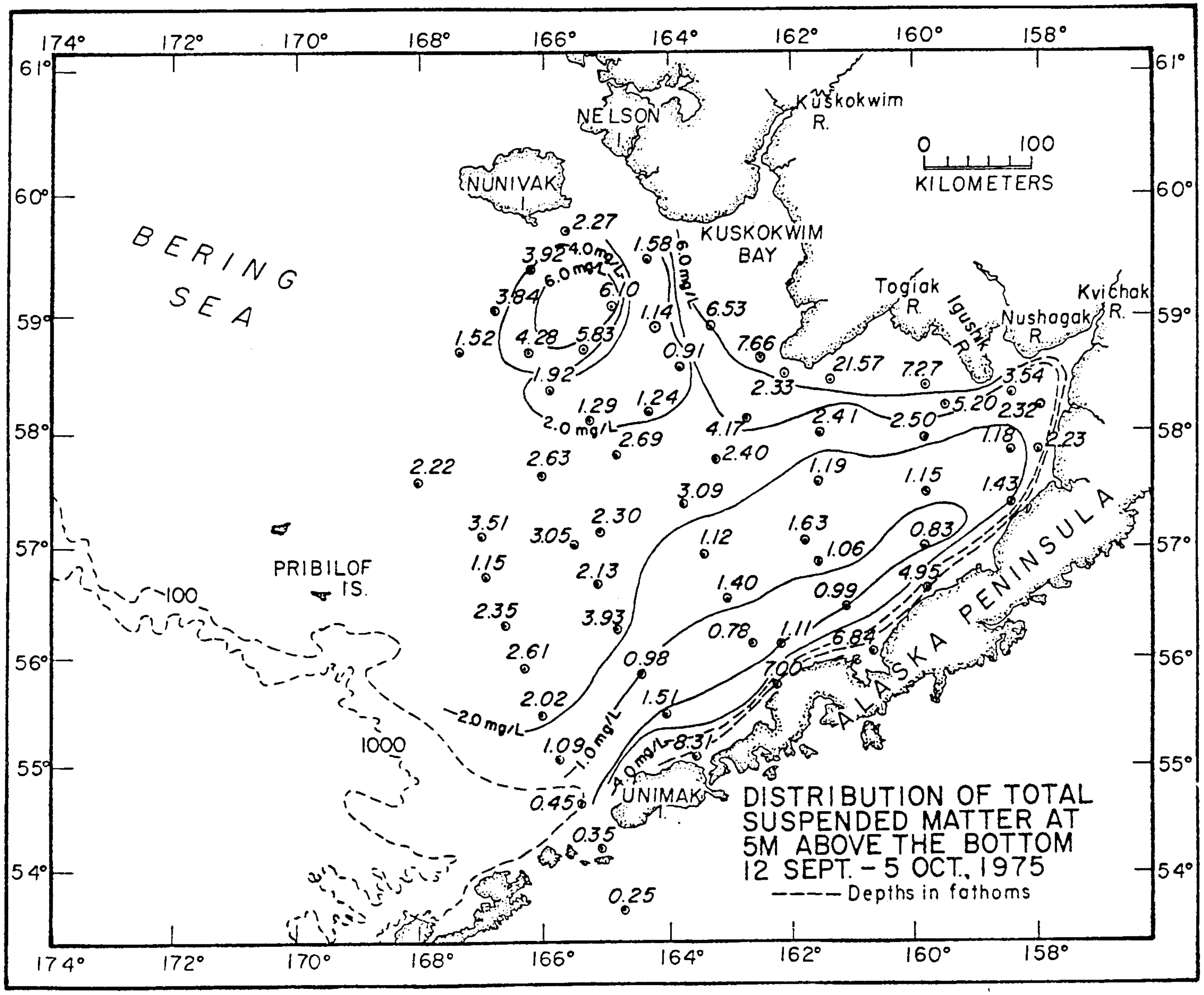

Figure 10. Distribution of total suspended matter 5 meters above the bottom in the southeastern Bering Shelf (Cruise RP-4-Di-75B-III, 12 Sept. - 5 Oct. 1975).

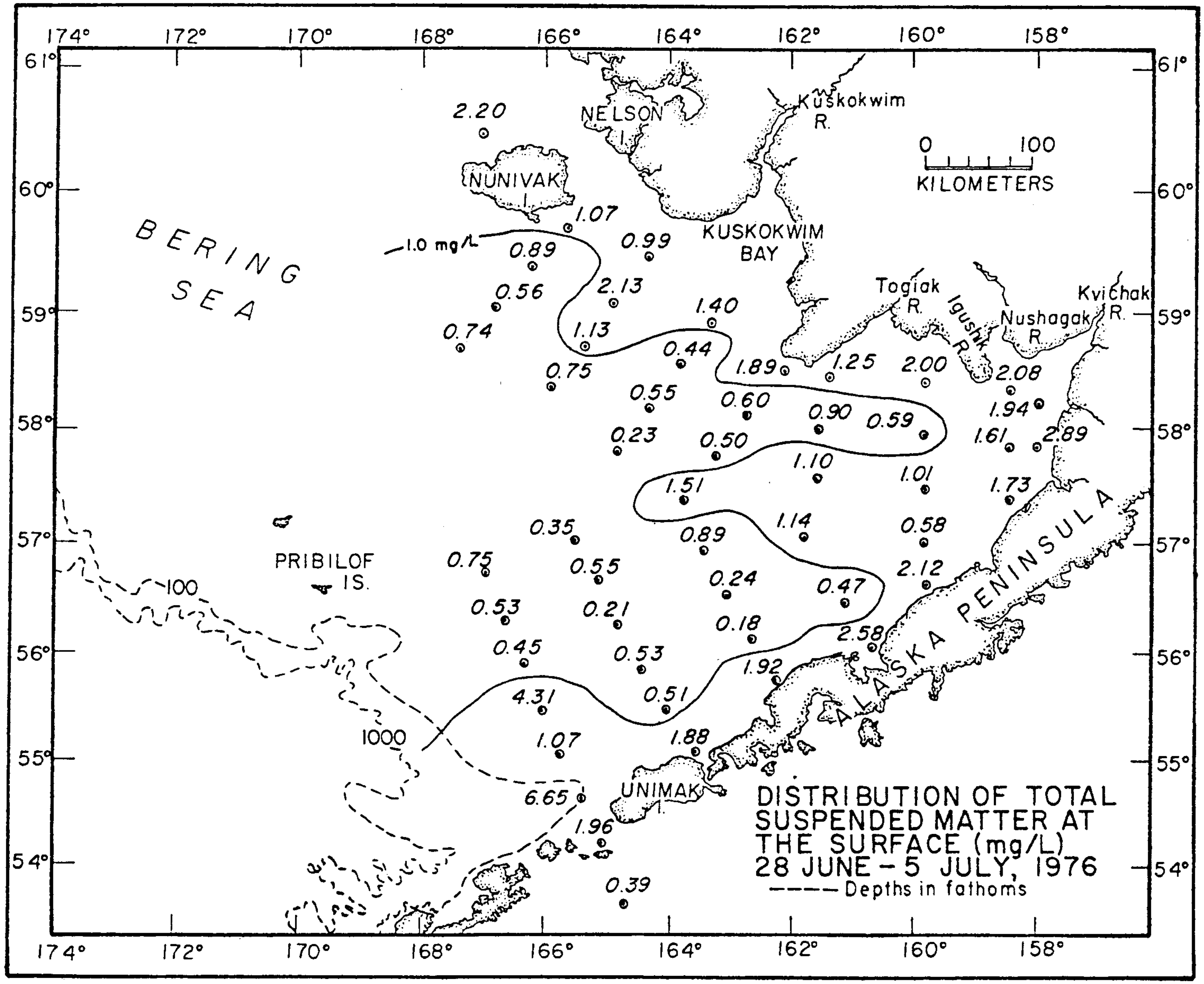

Figure 11. Distribution of total suspended matter at the surface in the southeastern Bering Shelf (Cruise RP-4-MW-76B-VII, 24 June - 9 July 1976).

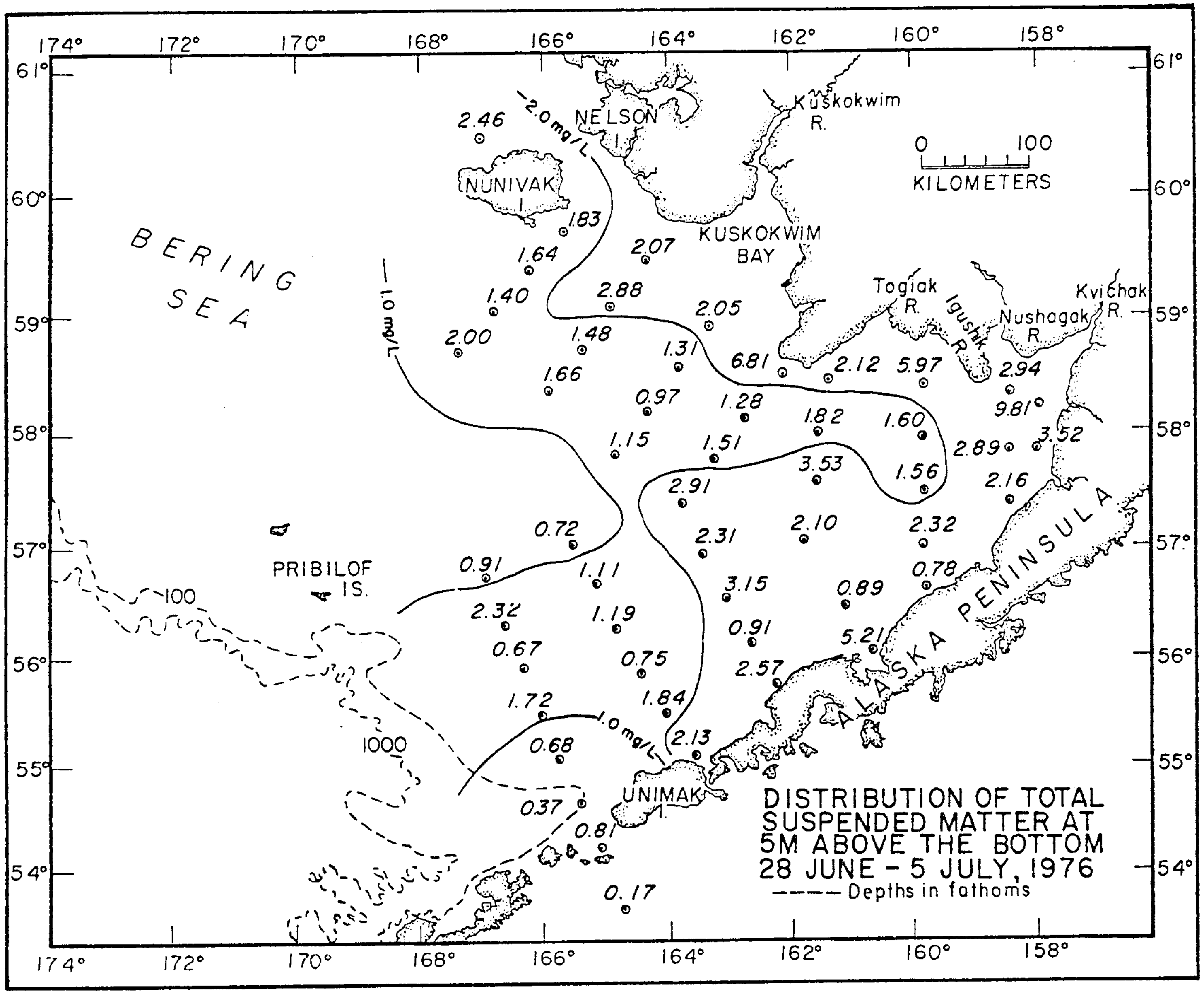

Figure 12. Distribution of total suspended matter 5 meters above the bottom in the southeastern Bering Shelf (Cruise RP-4-MW-76B-VII, 24 June - 9 July 1976).

of the same year (21 October-10 November). The third cruise, also in the northeastern Gulf, was conducted in early spring of 1976 (13-30 April). The fourth cruise was conducted in the southeastern Bering Shelf in early summer of 1976 (24 June-9 July). The last cruise was conducted in the northeastern Gulf of Alaska during the summer of 1976 (19-31 July). The station locations for the two cruises in the Bering Sea are shown in Figure 1. Figures 3 and 4 show the locations of the suspended matter stations in the northeastern Gulf.

In addition to the five cruises, two field expeditions, designed to collect suspended matter samples from the major rivers discharging into the southeastern Bering Shelf and the northeastern Gulf of Alaska, have been completed. Figures 6 and 7, respectively, show the locations of the suspended matter stations for the river sampling expeditions in the southeastern Bering Shelf and northeastern Gulf of Alaska.

At this point, approximately 1500 samples have been collected and weighed for suspended load determinations. Also, approximately 600 samples have been collected for elemental analysis of the particulate material.

Southeastern Bering Shelf

A. Particulate Matter Distributions

Figures 9 through 12 show the distribution of suspended matter at the surface and 5 meters above the bottom for the fall and summer cruises in the southeastern Bering Shelf (RP-4-Di-76B-III, 12 September-5 October 1975 and RP-4-MW-76B-VIII, 24 June-9 July 1976). As shown in Figures 9 and 11, the surface particulate matter distributions are dominated by the discharge of suspended material from the northern rivers. Large plumes of suspended matter extend to the southwest from Kuskokwim Bay and the region east of Cape Newenham. Similar suspended matter distributions were found by Sharma et al. (1974)

from samples collected during June-July 1973. The authors suggested that suspended material originating from the Kvichak and Nushagak Rivers moves generally to the west until it reaches Cape Newenham where it combines with a portion of the material discharged from the Kuskokwim River and is deflected to the southwest. Chemical analysis of the particulate matter suggests that the material is essentially of terrestrial origin (> 76% inorganic[2]).

Along the Alaska Peninsula surface suspended matter concentrations decrease rapidly away from the coast. This is due to rapid mixing of the highly turbid Shelf water with the relatively clear Pacific Ocean water which originates from the passes west of the Alaska Peninsula and is deflected to the northeast along the coast of the Alaska Peninsula.

At the time of the summer cruise, plumes of turbid water were observed north of Unimak Island and in the region west of the northern end of the Alaska Peninsula which were not observed during the fall cruise (Figure 9). These plumes might be attributed to the large seasonal variations in primary productivity which are characteristic of this region. Sharma et al. (1974) observed turbid plumes in the region northwest of Unimak Pass which they attributed to similar processes.

Near the bottom, suspended matter concentrations are high (> 1.0 mg/ℓ) throughout most of the study region, indicating possible resuspension of bottom sediments. Figures 13 and 14 show vertical cross-sections of the distribution of particulate matter from Kuskokwim Bay to Unimak Island for both cruises. The figures show increasing suspended matter gradients near the bottom which

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[2] For the purpose of this report, the inorganic particulate matter is defined as the percentage of the total particulate matter that is due to terrigeneous and skeletal debris. This value is determined by calculating the sum (in mg/ℓ) of the major inorganic elements expressed as oxides and presenting the data as a percentage of total suspended matter.

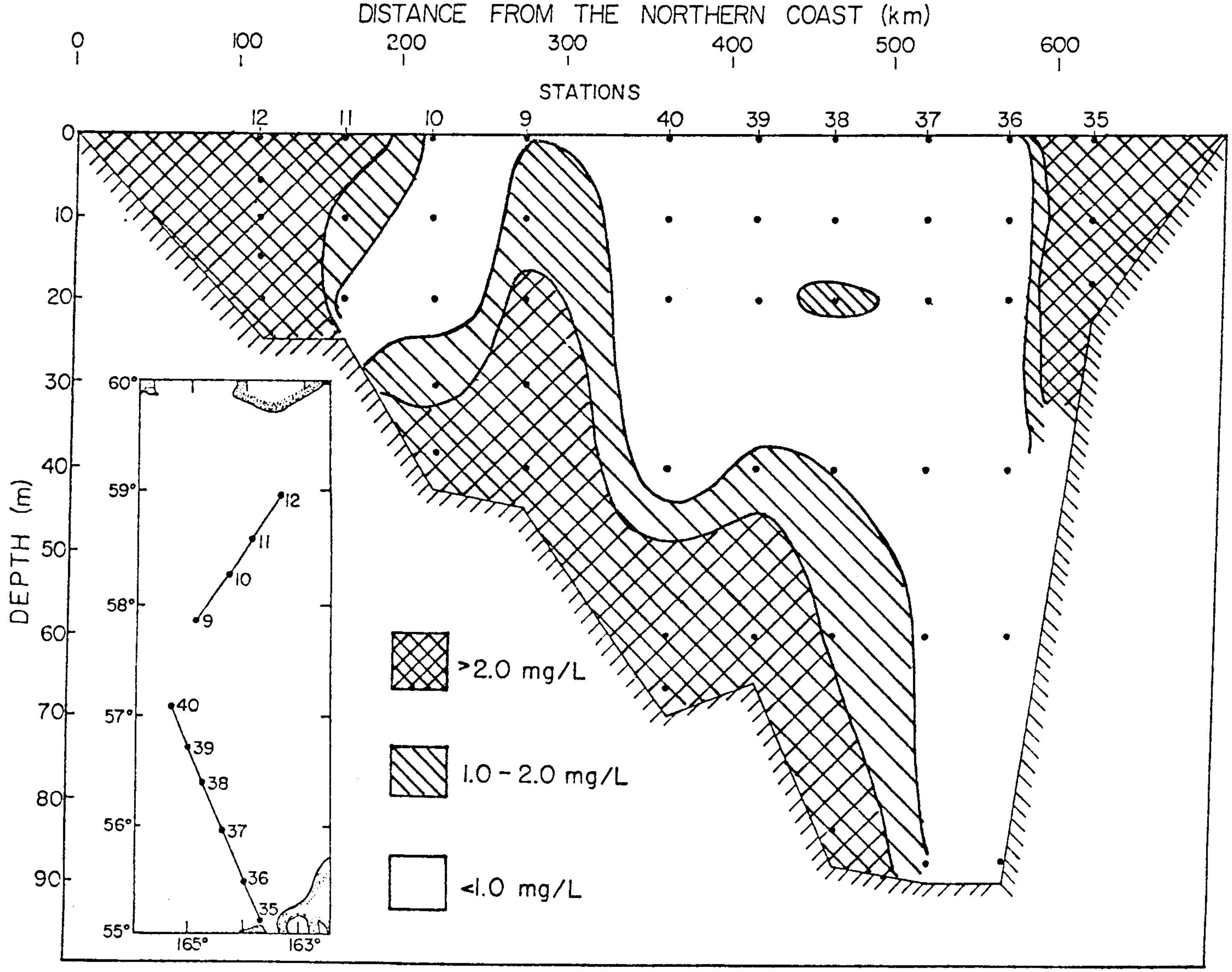

Figure 13. Vertical cross section of the distribution of total suspended matter for stations 9 thru 12 and 35 thru 40 in the southeastern Bering Shelf (Cruise RP-4-Di-75B-III, 12 Sept. - 5 Oct. 1975).

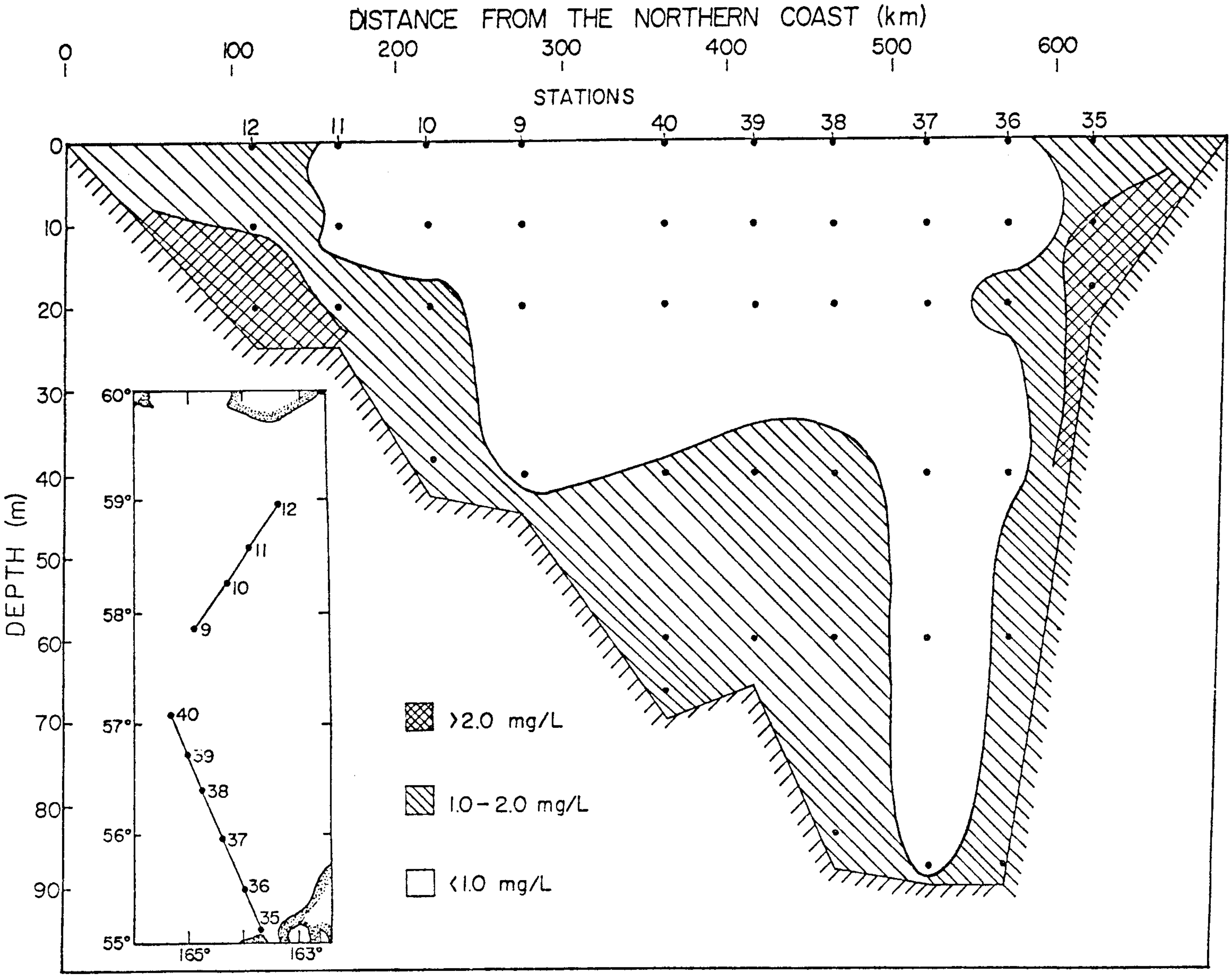

Figure 14. Vertical cross section of the distribution of total suspended matter for stations 9 thru 12 and 35 thru 40 in the southeastern Bering Shelf (Cruise RP-4-MW-76B-VII, 24 June - 9 July 1976).

are attributed to resuspension and redistribution of bottom sediments. Since Bristol Bay is a relatively shallow embayment, it is entirely possible that waves and tides play a major role in the redistribution of sediments. The suspended matter concentrations near the bottom were 2-3 times higher in the fall. This may be due to the increased effect of storms which occur more regularly during the fall months.

B. Elemental Chemistry of the Particulate Matter

Tables I and II, respectively, summarize the data on the elemental composition of the particulate matter from the major rivers discharging into Bristol Bay and from 42 stations on the Shelf. For convenience, the surface data in Table II have been arranged into three groups. Group I contains all the northern stations in which the sum of the major inorganic element concentrations (expressed as oxides) is greater than 60 percent of the total weight of material on the filter. Group II contains all the southern stations in which the sum of the major inorganic element concentrations is also greater than 60 percent of the total weight. Group III contains all the stations in between in which the sum is less than 60 percent of the total suspended load. Figure 15 shows the percentage of the total suspended matter that is due to the sum of the major inorganic elements for each station.

As shown in Table II, Groups I and II are very similar and appear to be dominated by the supply of terrigeneous material from the Kuskokwim, Nushagak, and Kvichak Rivers to the north (for Group I) and the coastal streams and lagoons to the south (for Group II). Several authors have suggested that since Mg, Al, K, and Ti are almost exclusively associated with aluminosilicate minerals, the presence of these elements in particulate matter is indicative of terrestrial input (Spencer and Sachs, 1970; Price and Calvert, 1973; and Feely, 1975). The

TABLE I

Summary of the elemental composition of particulate matter from the major rivers that discharge into the southeastern Bering Shelf. (Surface samples were obtained with a precleaned 4-ℓ polyethylene bottle extended from a helicopter, 12-21 Sept. 1976.)

Sample Location	No. of Samples	C wt. %	N wt. %	Mg wt. %	Al wt. %	Si wt. %	K wt. %	Ca wt. %	Ti wt. %	Cr ppm	Mn ppm	Fe wt. %	Ni ppm	Cu ppm	Zn ppm	Pb ppm
Kuskokwim River	9	2.96 ±2.63	0.38 ±0.42	2.13 ±0.39	7.77 ±0.98	32.13 ±2.86	1.68 ±0.16	1.59 ±0.07	0.56 ±0.04	105.3 ±14.9	1498 ±105	6.57 ±0.45	69.8 ±4.8	77.6 ±7.3	281.4 ±34.2	73.6 ±4.9
Kvichak River	6	2.66 ±0.15	0.23 ±0.15	1.24 ±0.44	4.26 ±1.07	26.78 ±10.30	0.81 ±0.16	0.48 ±0.13	0.41 ±0.11	62.2 ±18.3	941 ±53	4.36 ±1.32	36.3 ±10.9	63.3 ±8.7	232.1 ±108.8	54.5 ±15.6

TABLE II

Summary of the elemental composition of the particulate matter samples from the southeastern Bering Shelf (Cruise RP-4-Di-75B-III, 12 Sept.-6 Oct. 1975)

Sample Description	No. of Samples	C wt. %	N wt. %	Mg wt. %	Al wt. %	Si wt. %	K wt. %	Ca wt. %	Ti wt. %	Cr ppm	Mn ppm	Fe wt. %	Ni ppm	Cu ppm	Zn ppm	Pb ppm
Surface (Group I)	24	17.7 ±10.3	2.1 ±1.3	0.86 ±0.14	3.52 ±2.22	25.85 ±5.28	0.51 ±0.17	1.32 ±0.28	0.24 ±0.06	41.2 ±19.3	893 ±285	2.68 ±0.63	24.1	41.9 ±13.9	210.7 ±88.0	43.5 ±22.6
Surface (Group II)	4	22.9		1.75 ±0.08	6.11 ±1.32	31.74 ±6.40	0.37 ±0.14	2.66 ±0.89	0.28 ±0.07		1377 ±519	3.15 ±0.35		42.4 ±21.8	353.0 ±127.0	42.0 ±16.0
Surface (Group III)	11	35.3 ±19.3	4.8 ±2.7			10.89 ±6.73	0.26 ±0.20	1.14 ±0.50	0.18 ±0.07	60.4 ±32.2	355 ±233	1.92 ±0.66	56.5 ±11.7	64.0 ±31.4	256.0 ±215.0	
5 m above the bottom	42	12.2 ±7.6	1.8 ±1.1	1.45 ±0.66	3.92 ±1.27	29.45 ±6.12	0.53 ±0.17	1.64 ±0.65	0.28 ±0.07	50.0 ±20.9	581 ±304	3.16 ±0.82	30.7 ±17.9	54.2 ±47.7	219.6 ±107.6	59.9 ±22.0

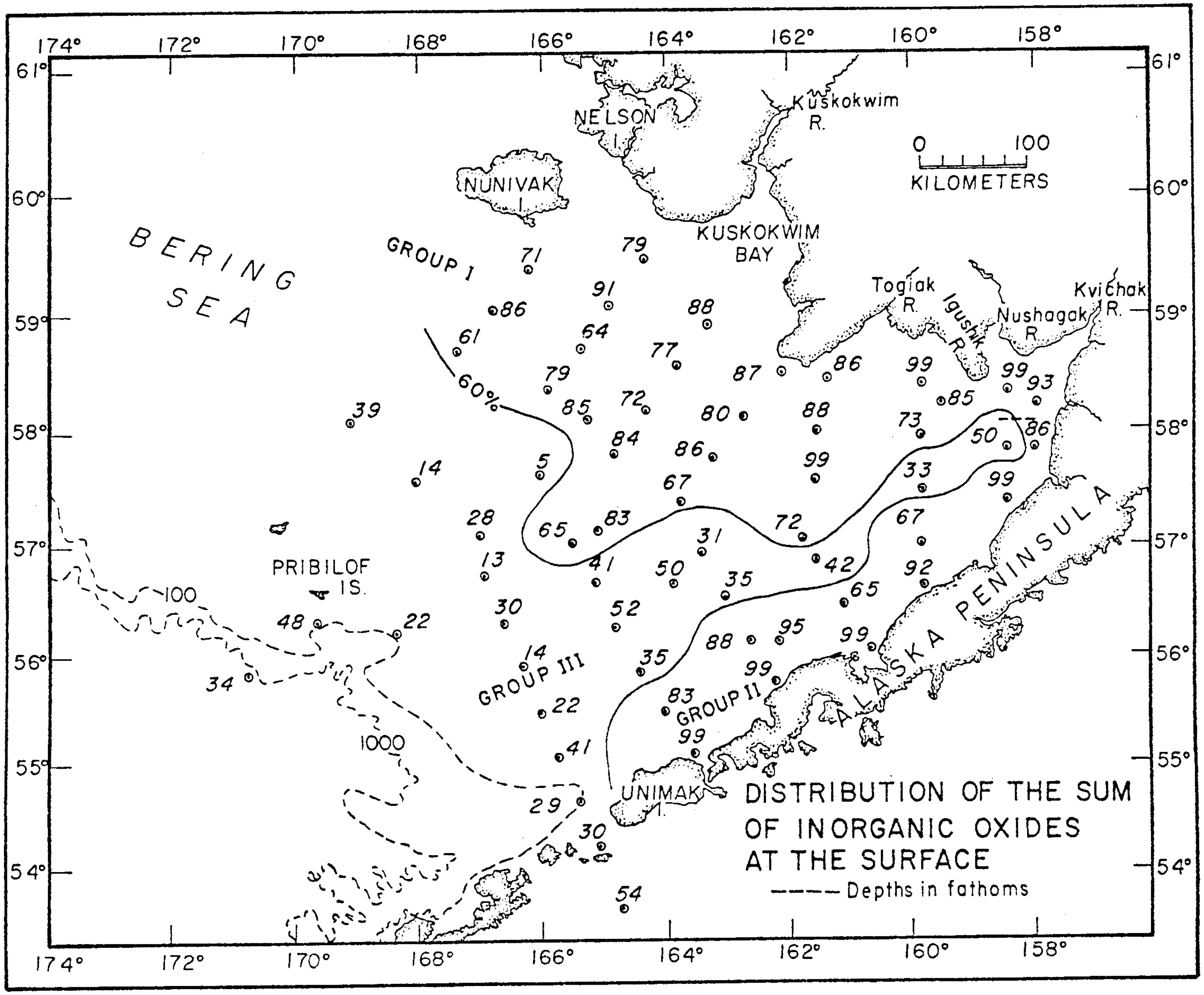

Figure 15. Map of the surface distribution of the percentage of total suspended matter that is due to the sum of the major inorganic elements expressed as oxides (Cruise RP-4-Di-75B-III, 12 Sept. - 5 Oct. 1975).

high concentrations of these elements in the samples from Groups I and II indicate that aluminosilicate minerals are the most dominant solid phase in the particulate matter. The data from Table I show that for Groups I and II approximately 35-60 percent of the particulate matter is aluminosilicate material of terrestrial origin. In contrast, the particulate matter samples from Group III only contain about 20 percent aluminosilicate material.

The Group III samples are significantly depleted in particulate Mg, Al, Si, K, Ca, Ti, Mn, and Fe and are enriched in Ni, Cu, and Zn. The trace element enrichments are 134, 53, and 21 percent, respectively, for Ni, Cu, and Zn. However, considering the large sample variability associated with the low sample loadings, these enrichments may not be significant.

Since the early work of Menzel and Vaccaro (1964), many investigators have used particulate carbon as a tracer of particulate organic matter in the oceans. 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 the 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 has C:N ratios which range between 15-22. In contrast, ratios for marine organic matter range between 5-15.

The distribution of particulate carbon and nitrogen at the surface in the southeastern Bering Shelf are presented in Figures 16 and 17. Generally speaking, the surface distributions follow the same pattern as total suspended matter. High concentrations of particulate carbon and nitrogen are found along the coast with concentration gradients decreasing slowly in a seaward direction from the northern coast and rapidly from the coast of the Alaska Peninsula. A plume of turbid water containing high concentrations of particulate carbon and nitrogen extends

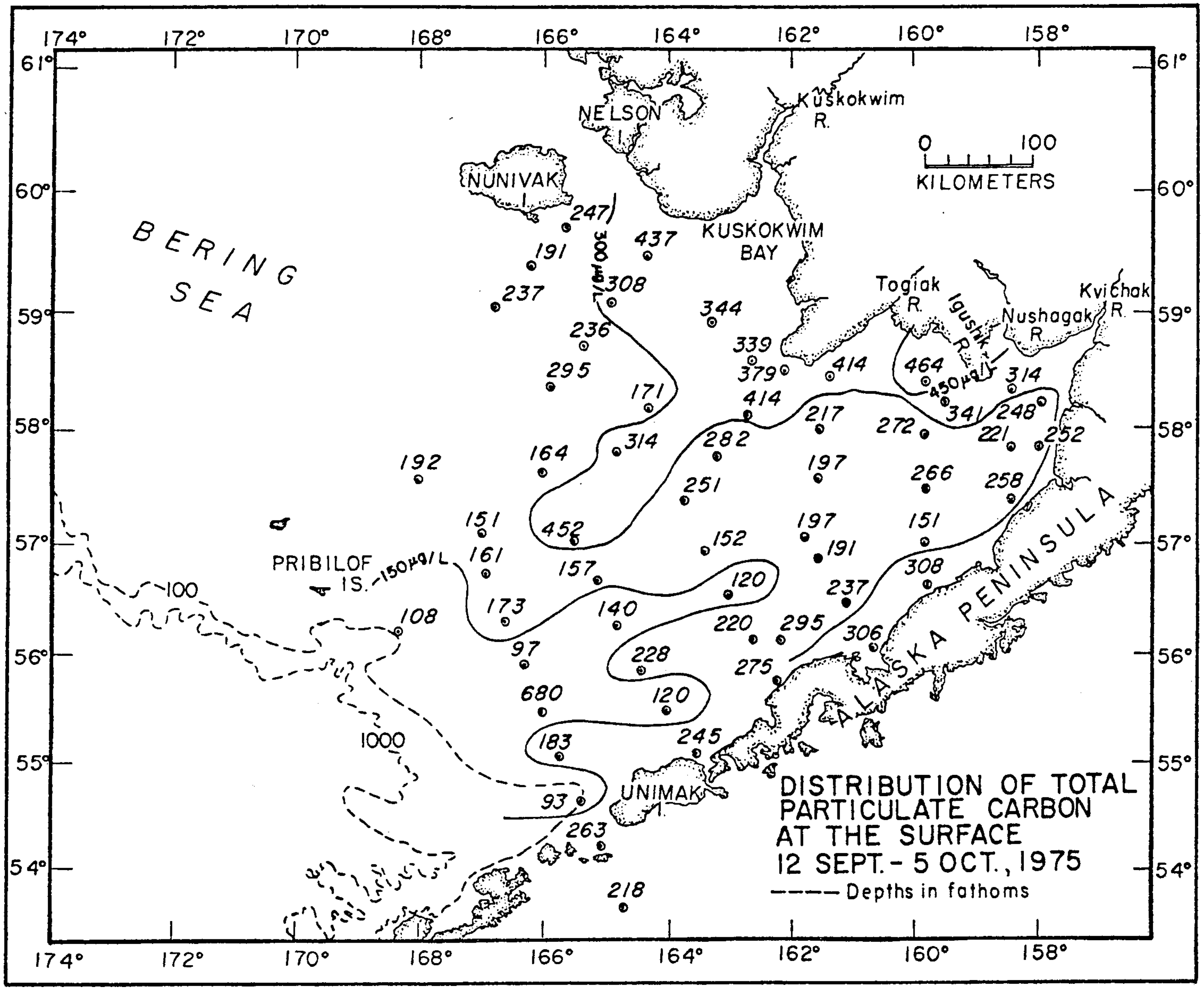

Figure 16. Distribution of total particulate carbon at the surface in the southeastern Bering Shelf (Cruise RP-4-Di-75B-III, 12 Sept. - 5 Oct. 1975).

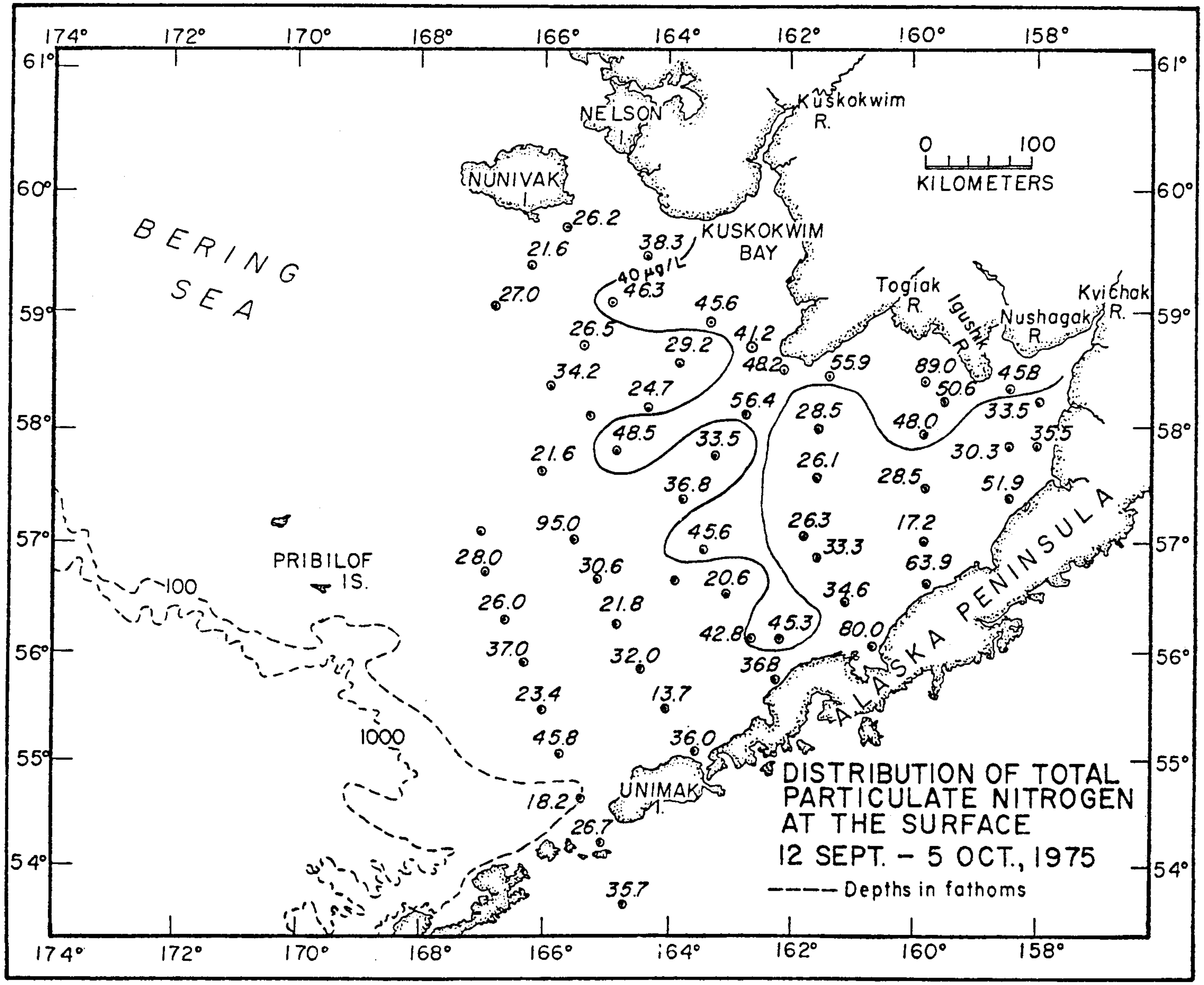

Figure 17. Distribution of total particulate nitrogen at the surface in the southeastern Bering Shelf (Cruise RP-4-Di-75B-III, 12 Sept. - 5 Oct. 1975).

to the southwest from Kuskokwim Bay. Apparently, the semipermanent counterclockwise currents which appear to be controlling the distributions of total particulate matter at the surface also control the distribution of particulate carbon and nitrogen.

The carbon to nitrogen ratios in the particulate matter at the surface indicate that the organic matter is of marine origin. Ratios range from 0.7 to 29.4 with a mean 7.2. Although the ratios increase slightly from south to north, studies of the variability of C:N ratios in marine phytoplankton indicate that these small differences are probably not significant (Banse, 1974).

Near the bottom, particulate carbon and nitrogen distributions tend to be more localized and appear to follow the bathymetry. Figure 18 shows a vertical profile of total suspended matter and total particulate carbon for station 40 in central Bristol Bay. Concentrations of total particulate carbon are high at the surface (450 μgC/ℓ). Beneath the surface, concentrations of particulate carbon decrease rapidly until a constant level of about 150 μgC/ℓ is reached below 40 meters. In contrast, total suspended matter concentrations are relatively low and constant in the top 40 meters. Below 40 meters, concentrations of total particulate matter increase sharply near the bottom indicating possible resuspension of bottom sediments. Apparently, resuspension of bottom sediments has little effect on the distribution of particulate organic matter near the bottom.

Northeastern Gulf of Alaska

A. Sedimentary Discharge from Coastal Rivers and Streams

Since there are no gauging stations near the mouths of the major rivers discharging into the northeast Gulf of Alaska, there is very little information about the quantities of sedimentary materials that are discharged into the Gulf

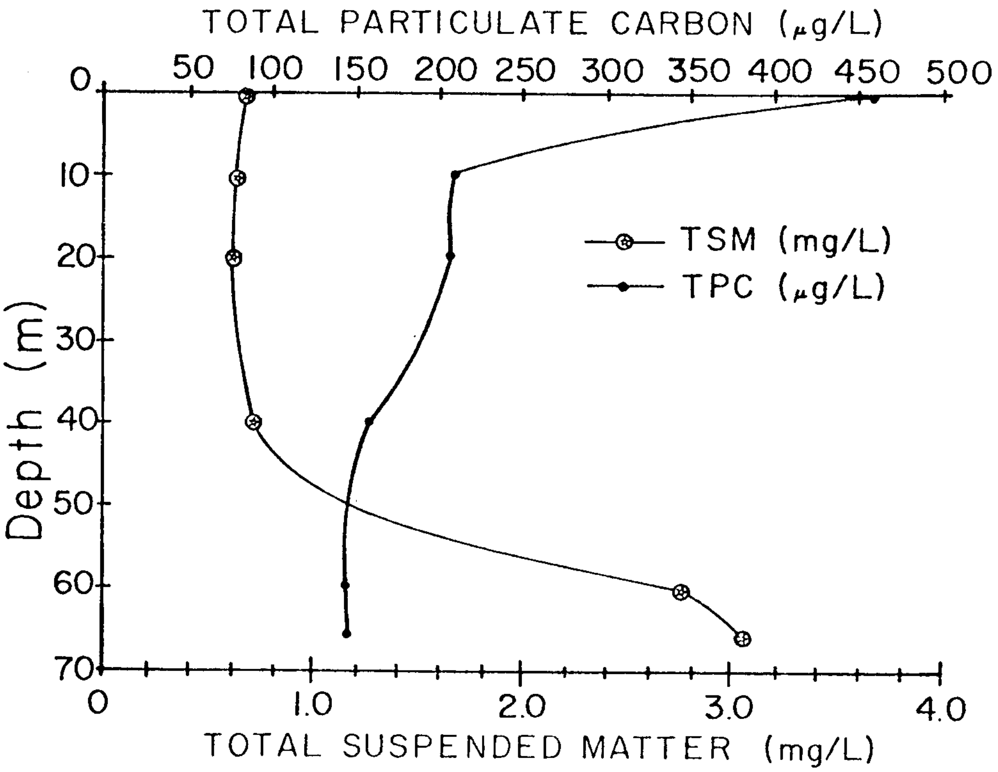

Figure 18. Vertical distribution of total suspended matter and particulate carbon at station 40 in the southeastern Bering Shelf (Cruise RP-4-Di-75B-III, 12 Sept. - 5 Oct. 1975).

of Alaska from these important sources. From careful analysis of discharge data for the Copper River near Chitina, Reimnitz (1966) estimated that approximately 1.07 x 10^{14} g yr^{-1} of fine grain material are delivered annually to the Gulf by way of the Copper River system.

In order to obtain an order of magnitude verification of the estimates made by Reimnitz, river samples were collected near the mouths of the major rivers discharging into the northeast Gulf (see Figure 7). River samples were obtained with a precleaned 4-liter polyethylene bottle lowered from a Bell 206B helicopter hovering within 2 meters of the water surface, 22-27 June 1976. Figure 19 shows the results of those measurements. Near the mouth of the Copper River, suspended matter concentrations average 0.525 ± .09 g/ℓ. Using this value and the approximation of the annual water discharge at the mouth of the Copper River (estimated by Reimnitz to be approximately 8.0 x 10^{13} ℓ yr^{-1}), the estimated annual mean discharge of approximately 0.42 x 10^{14} g yr^{-1} is calculated. This estimate is approximately 2.5 times lower than the estimate of Reimnitz. However, considering the large variations that may result from annual and seasonal fluctuations in discharge rates and sediment concentrations, the small difference between these estimates may not be significant. More accurate determinations of annual sediment fluxes are not possible without permanent gauging stations.

East of Kayak Island the coastal rivers which drain the Bering, Guyot and Malaspina Glaciers have widely varying suspended matter concentrations. Surface concentrations at the river mouths range from 11 mg/ℓ for the Tsivat River to 1496 mg/ℓ for the Ducktoth River. These variations are probably related to the water and suspended matter discharge patterns of the nearby glaciers. At this time no estimates of water discharge from these rivers are available, and consequently, no estimates of sediment fluxes can be made.

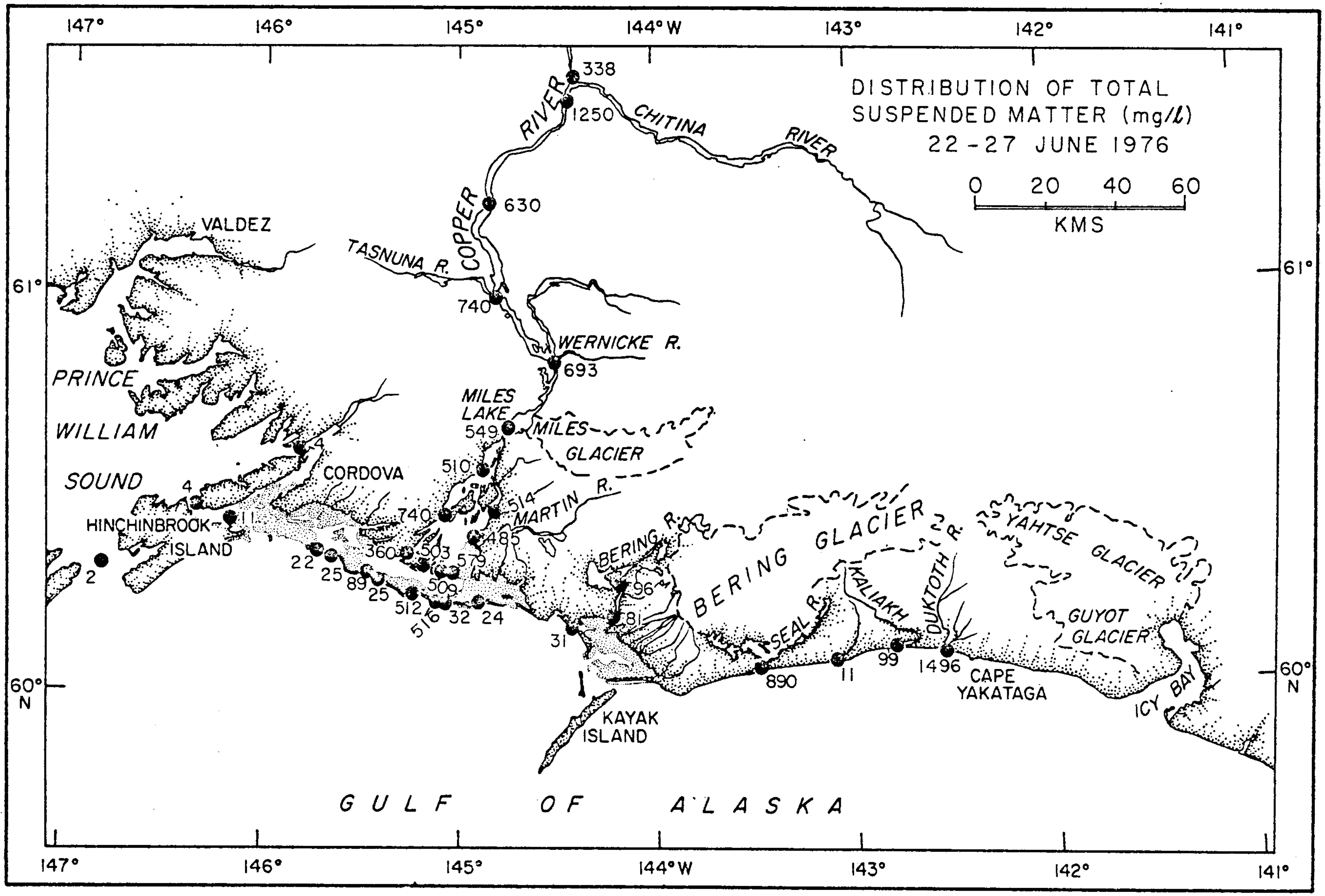

Figure 19. Distribution of total suspended matter at the surface in the major rivers draining into the northeastern Gulf of Alaska (22 - 27 June 1976).

B. Particulate Matter Distributions

Figures 20 through 25 show the distribution of suspended matter at the surface and 5 meters above the bottom for the fall, spring, and summer cruises. The surface distributions show significant variations which can be related to variations in sediment flux from the coastal rivers, formation of wind-generated eddies, and local variations in current patterns and transport processes.

East of Kayak Island the surface particulate matter distributions are dominated by the discharge of sedimentary material from the coastal streams which drain the Bering, Guyot and Malaspina Glaciers. As this material is discharged into the Gulf, the westward flowing currents quickly deflect it to the west along the coast. Comprehensive analyses of ERTS imagery for this region (Sharma et al., 1974; Burbank, 1974; and Carlson et al., 1975) have indicated that most of the material that is discharged from the rivers east of Kayak Island remains relatively close to the coast (within 40 km) until it reaches Kayak Island where it is deflected to the southwest. The surface suspended matter distributions for the October-November cruise and the April cruise follow this same general pattern. Along the transects southeast of Icy Bay (Stations 10-13), particulate matter concentrations decreased from > 1.0 mg/ℓ near the coast to < 0.5 mg/ℓ approximately 40 km off the coast for both cruises. During the summer cruise, on the other hand, a plume of turbid water was observed extending outward from the coast. This plume was not observed during either of the previous two cruises and may be the result of increased sediment flux from the coastal rivers during the summer. However, from careful analysis of ERTS imagery for this region Burbank (1974) observed that occasionally wind-generated counterclockwise eddies were formed which transported significant quantities of terrestrial material seaward. It is probable that both factors, high sediment flux and the

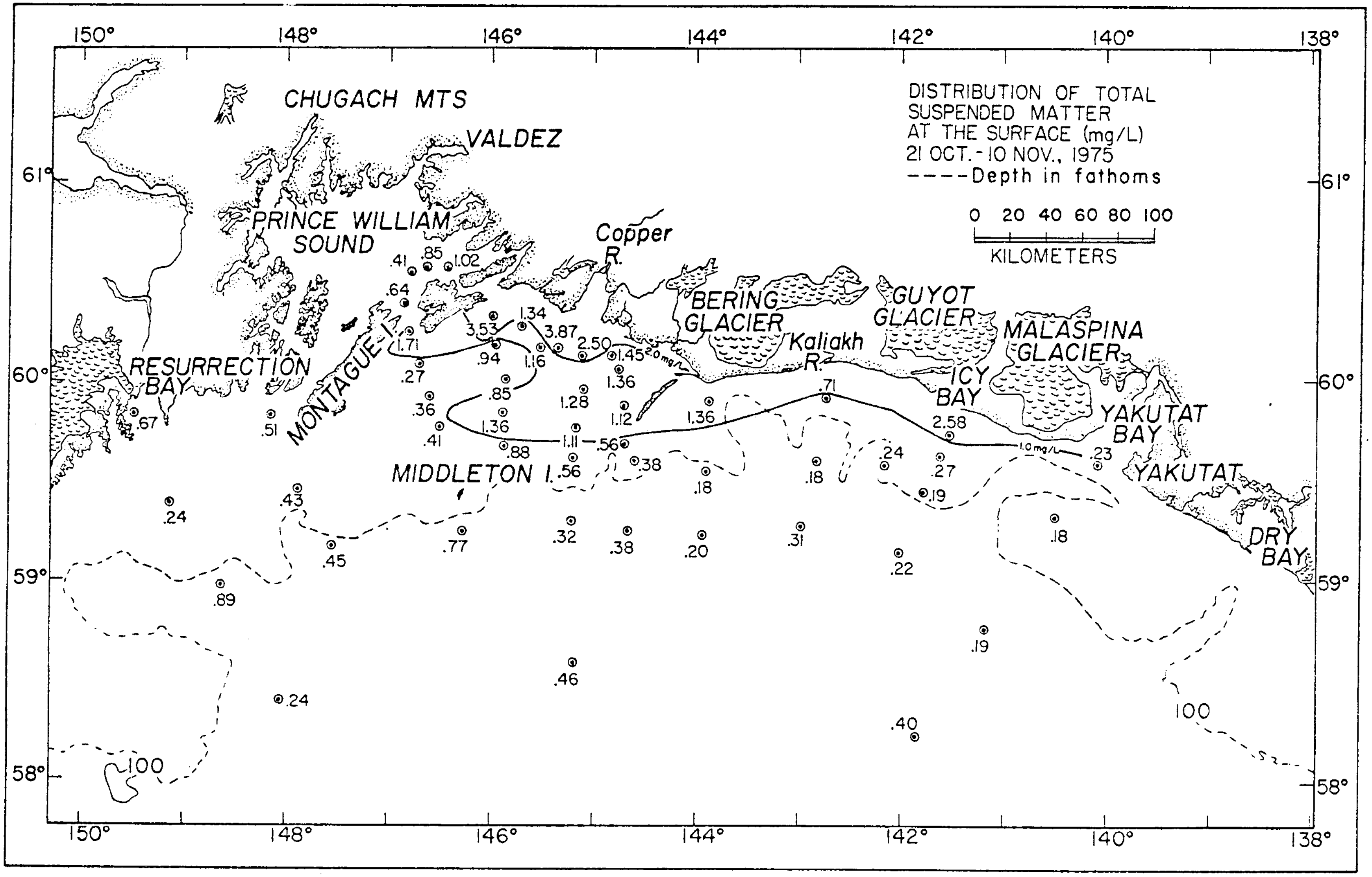

Figure 20. Distribution of total suspended matter at the surface in the northeastern Gulf of Alaska (Cruise RP-4-Di-75C-I, 21 Oct. - 10 Nov. 1975).

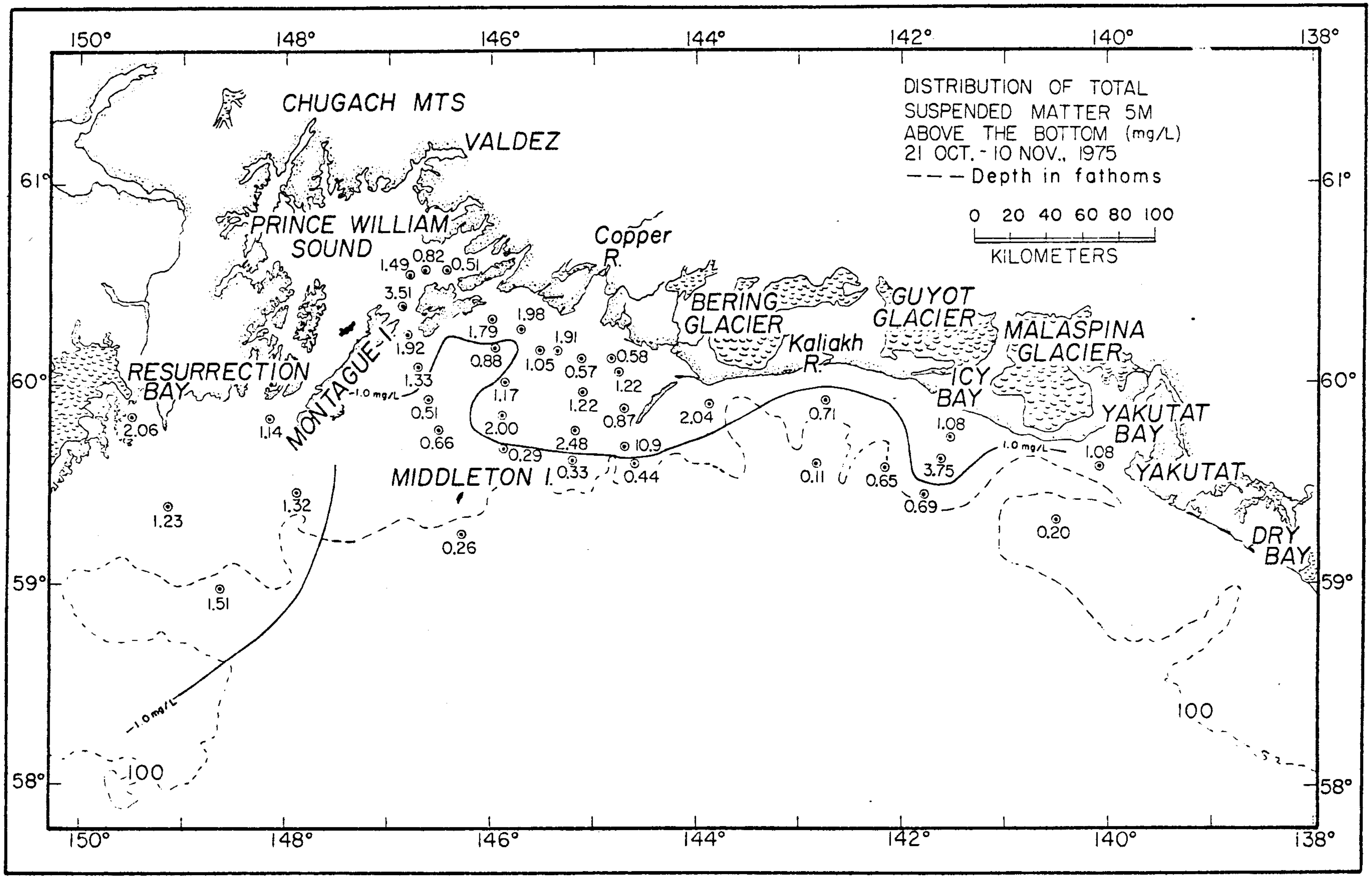

Figure 21. Distribution of total suspended matter at 5 meters above the bottom in the northeastern Gulf of Alaska (Cruise RP-4-Di-76B-I, 21 Oct. - 10 Nov. 1975).

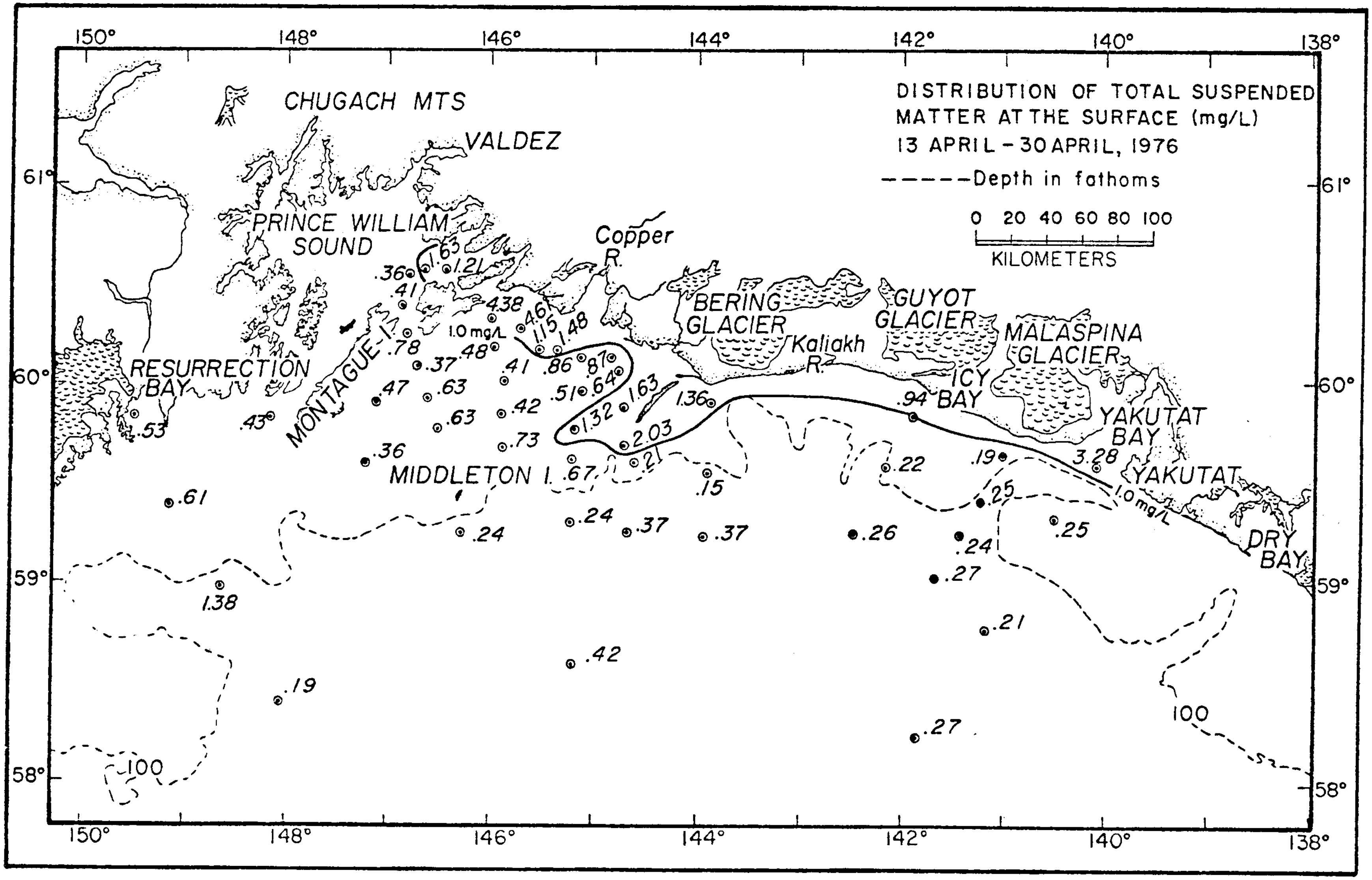

Figure 22. Distribution of total suspended matter at the surface in the northeastern Gulf of Alaska (Cruise RP-4-Di-76A-III, 13 - 30 April 1976).

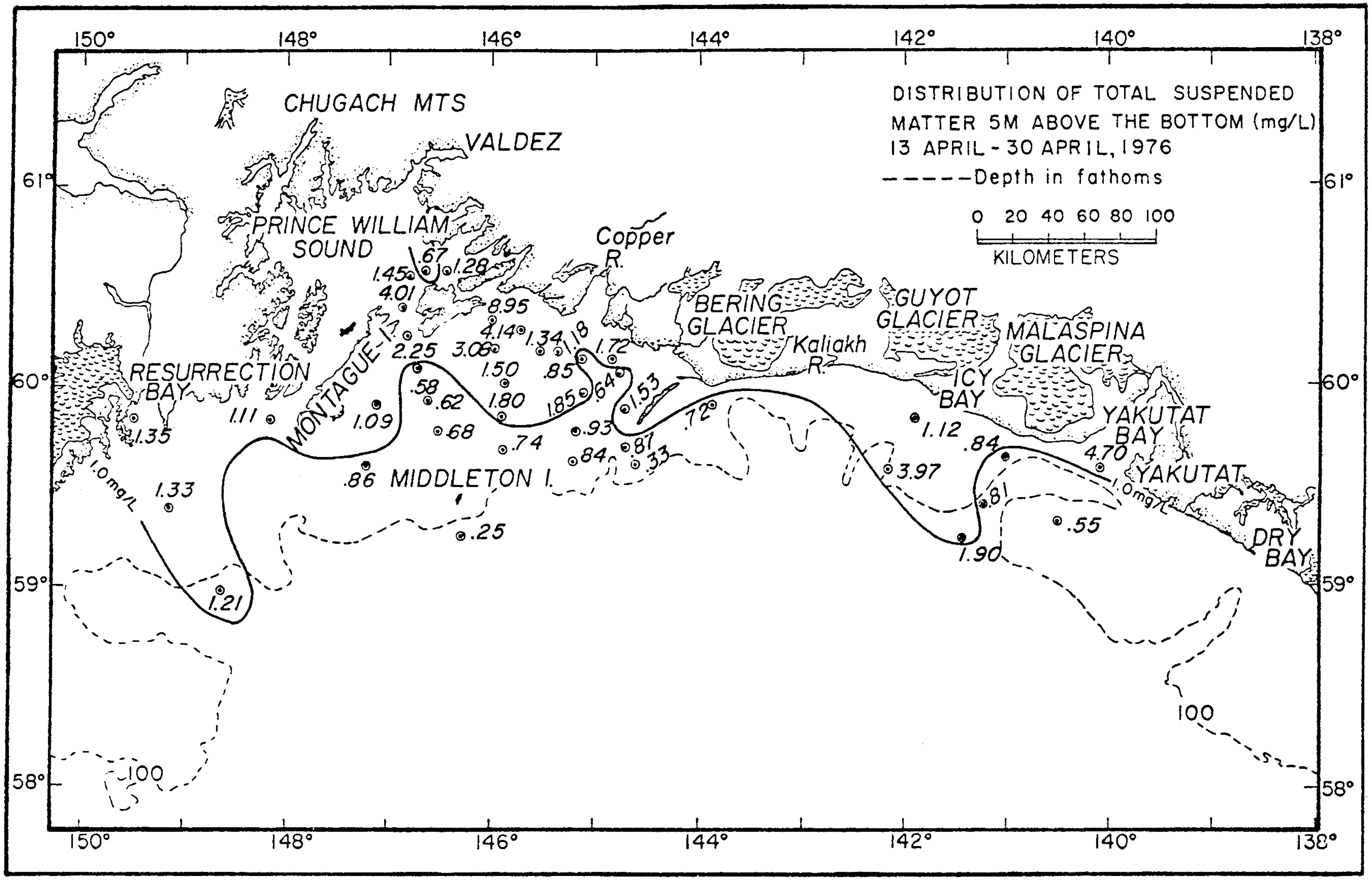

Figure 23. Distribution of total suspended matter at 5 meters above the bottom in the northeastern Gulf of Alaska (Cruise RP-4-Di-76A-III, 13 - 30 April 1976).

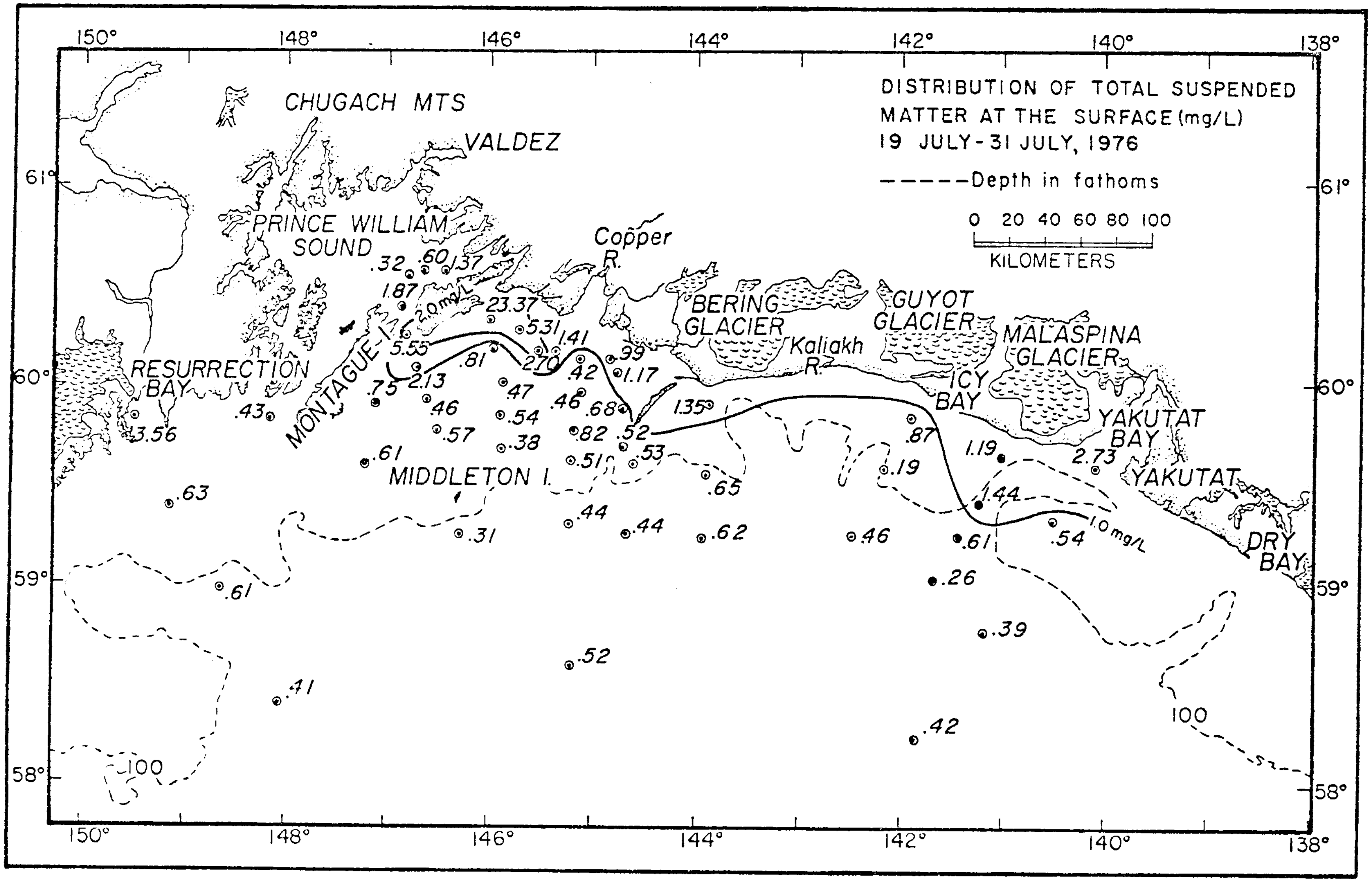

Figure 24. Distribution of total suspended matter at the surface in the northeastern Gulf of Alaska (Cruise RP-4-Di-76B-I, 19 - 31 July 1976).

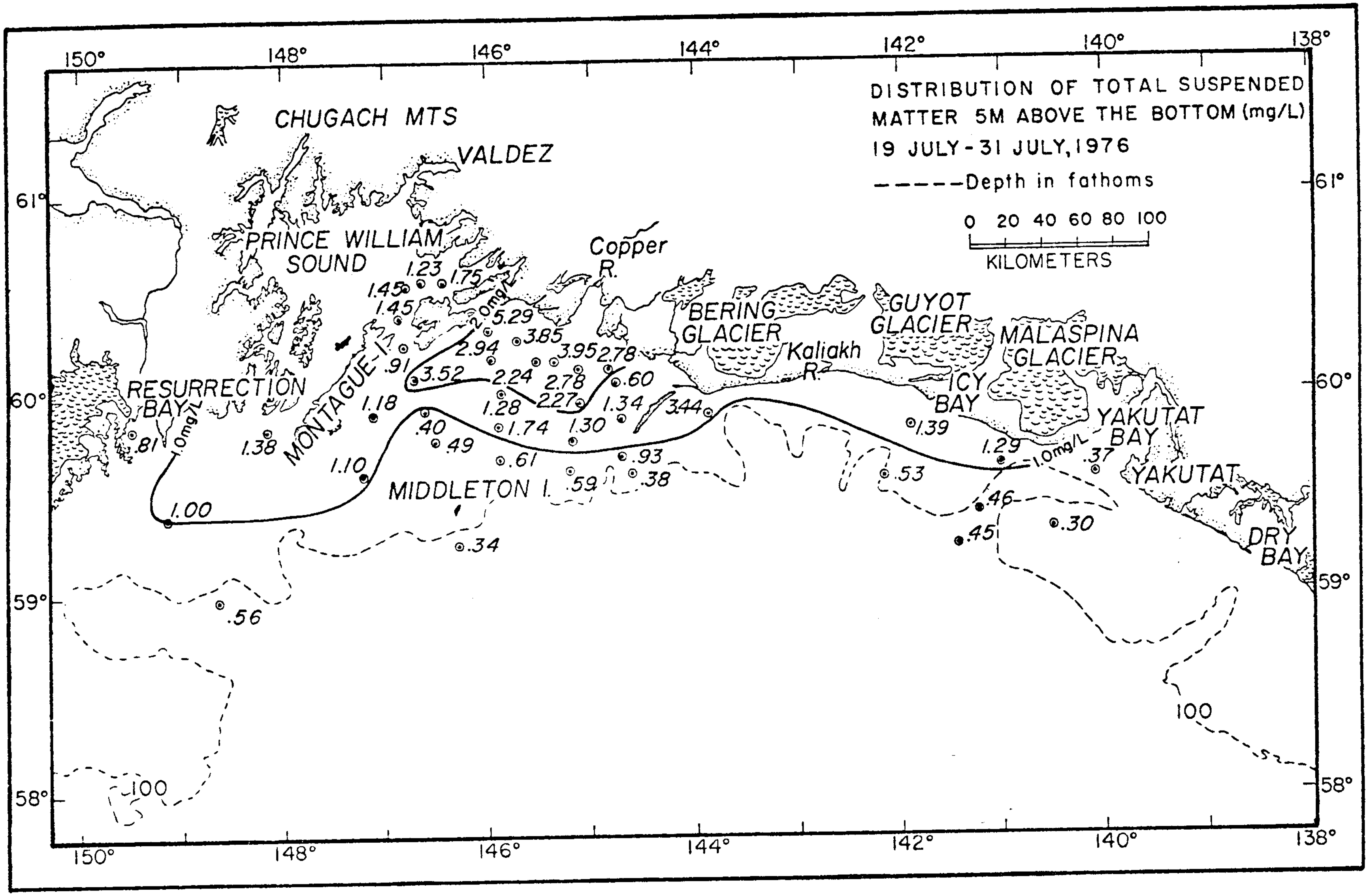

Figure 25. Distribution of total suspended matter at 5 meters above the bottom in the northeastern Gulf of Alaska (Cruise RP-4-Di-76B-I, 19 - 31 July 1976).

formation of wind-generated eddies, contribute to offshore transport of suspended matter in this region. Although such ephemeral processes are difficult to document without extensive supportive physical oceanographic data, there is a strong possibility that these eddies play a major role in the offshore transport of suspended matter.

During the fall and spring cruises significant quantities of terrestrial suspended matter were transported to the southwest from Kayak Island by a large clockwise eddy. During the summer cruise terrestrially derived suspended matter remained relatively close to the coastline on either side of Kayak Island (Figure 24). Observations of ERTS imagery taken on 14 June 1976 (Figure 26) show very similar suspended matter distribution patterns. Apparently, the large clockwise eddy which is characteristic of this region moved offshore far enough to allow terrestrial suspended matter to be transported around the southern tip of Kayak Island.

In the vicinity of the Copper River, a plume of highly turbid water extends offshore as far as 40 km. Suspended matter concentrations within the plume are high, averaging 6.7 mg/ℓ, which reflects the increased sediment discharge during the month of July. As with the previous two cruises, the sedimentary material from the Copper River is carried to the west along the coast until it reaches Hinchinbrook Island, where a portion of the material passes to the southwest along the southeastern coast of Montague Island.

Although the surface suspended matter distribution patterns are somewhat similar for the three seasonal cruises in the northeastern Gulf, the vertical distribution patterns are not. Figures 27, 28, and 29 show vertical cross sections of the distribution of total suspended matter for Stations 27 through 31 and Station 5 for the fall, spring, and summer cruises, respectively. The vertical cross sections were determined from discrete samples (the locations of the

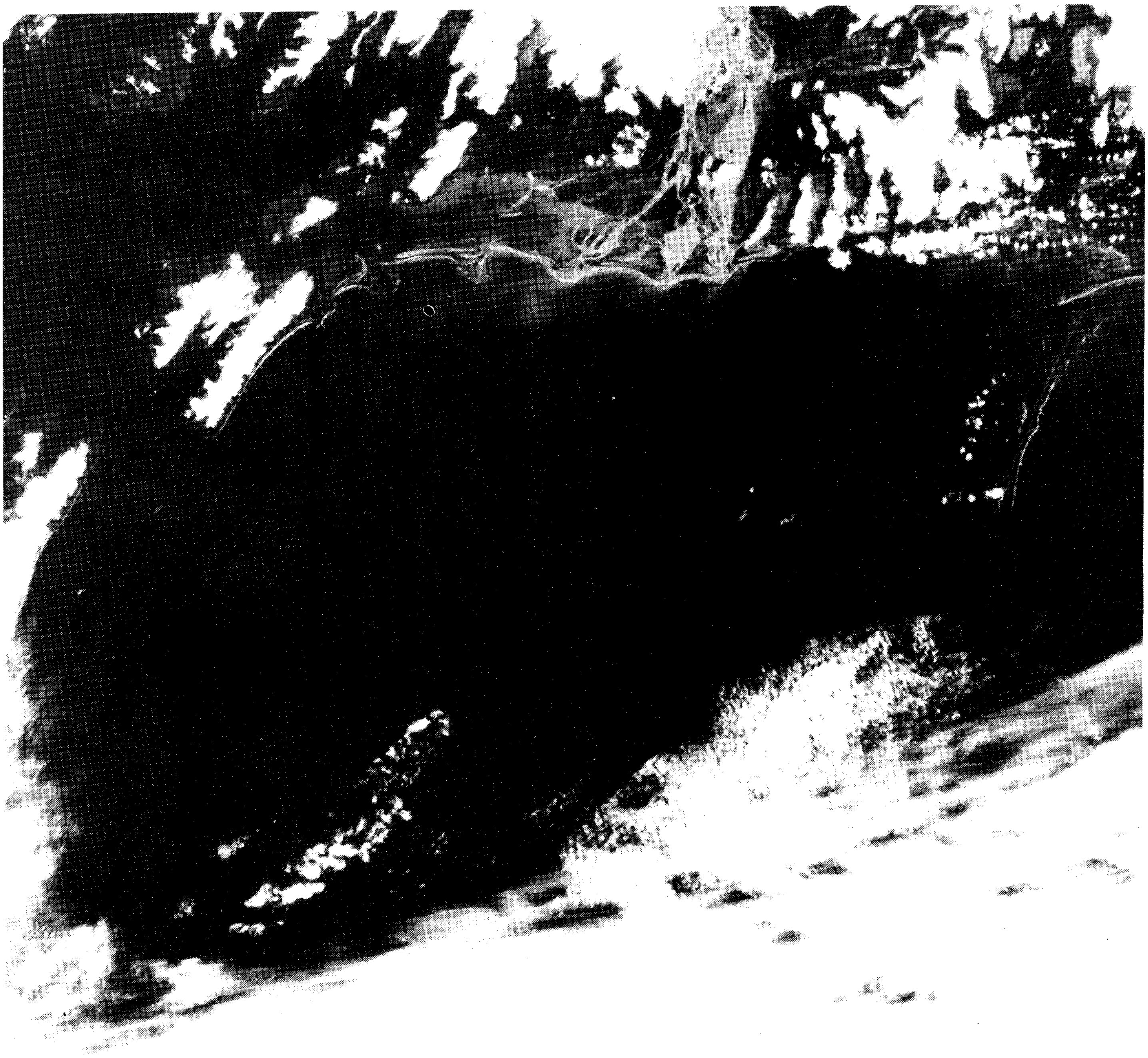

Figure 26. ERTS-I image of the region between Montague Island and Kayak Island showing evidence for suspended matter transport along the coast. The image was obtained on 14 June 1976.

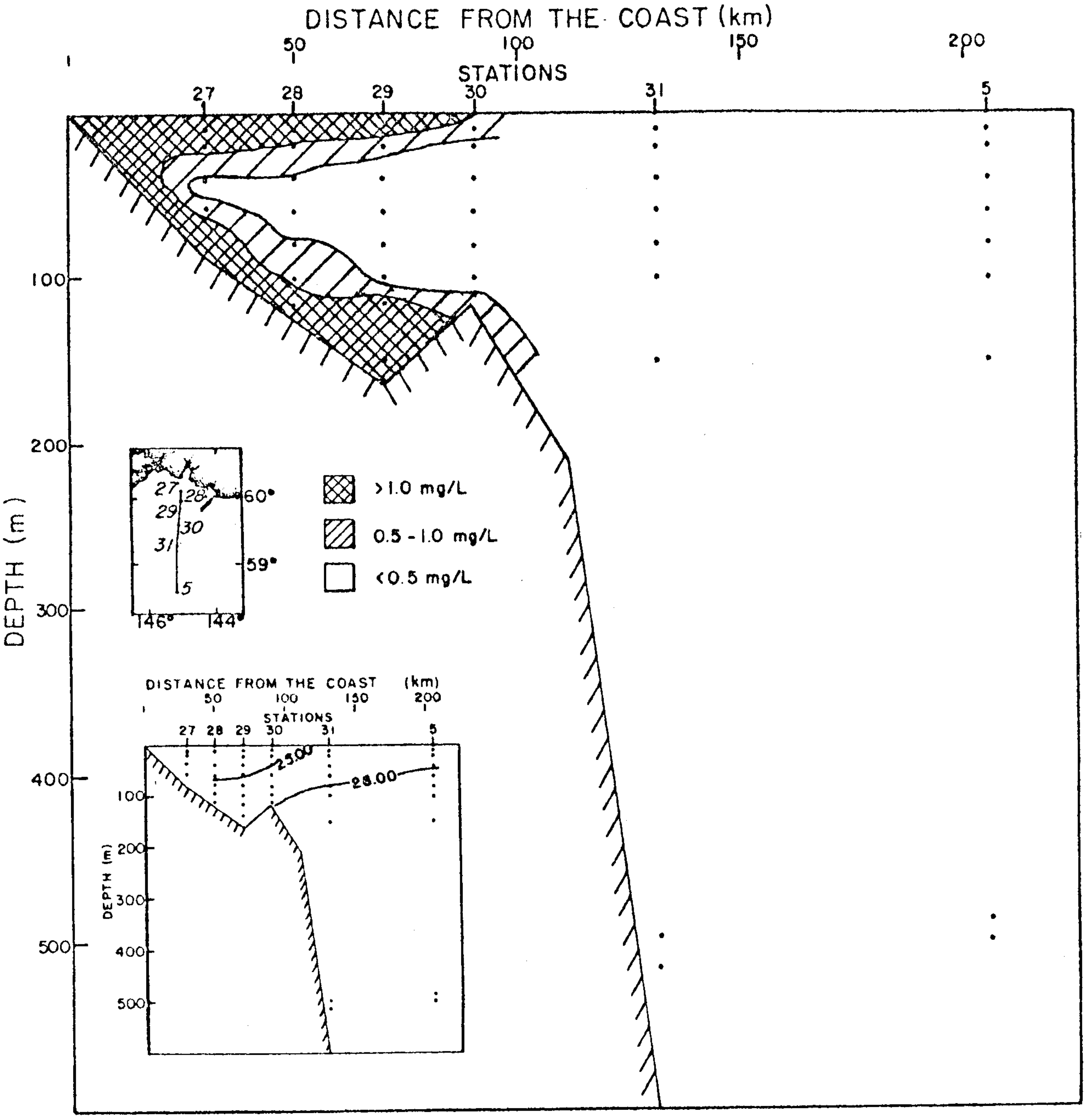

Figure 27. Vertical cross section of the distribution of total suspended matter for stations 27 thru 31 and station 5 in the northeastern Gulf of Alaska (Cruise RP-4-Di-75C-I, 21 Oct. - 10 Nov. 1975). The insert shows the σ_T surfaces.

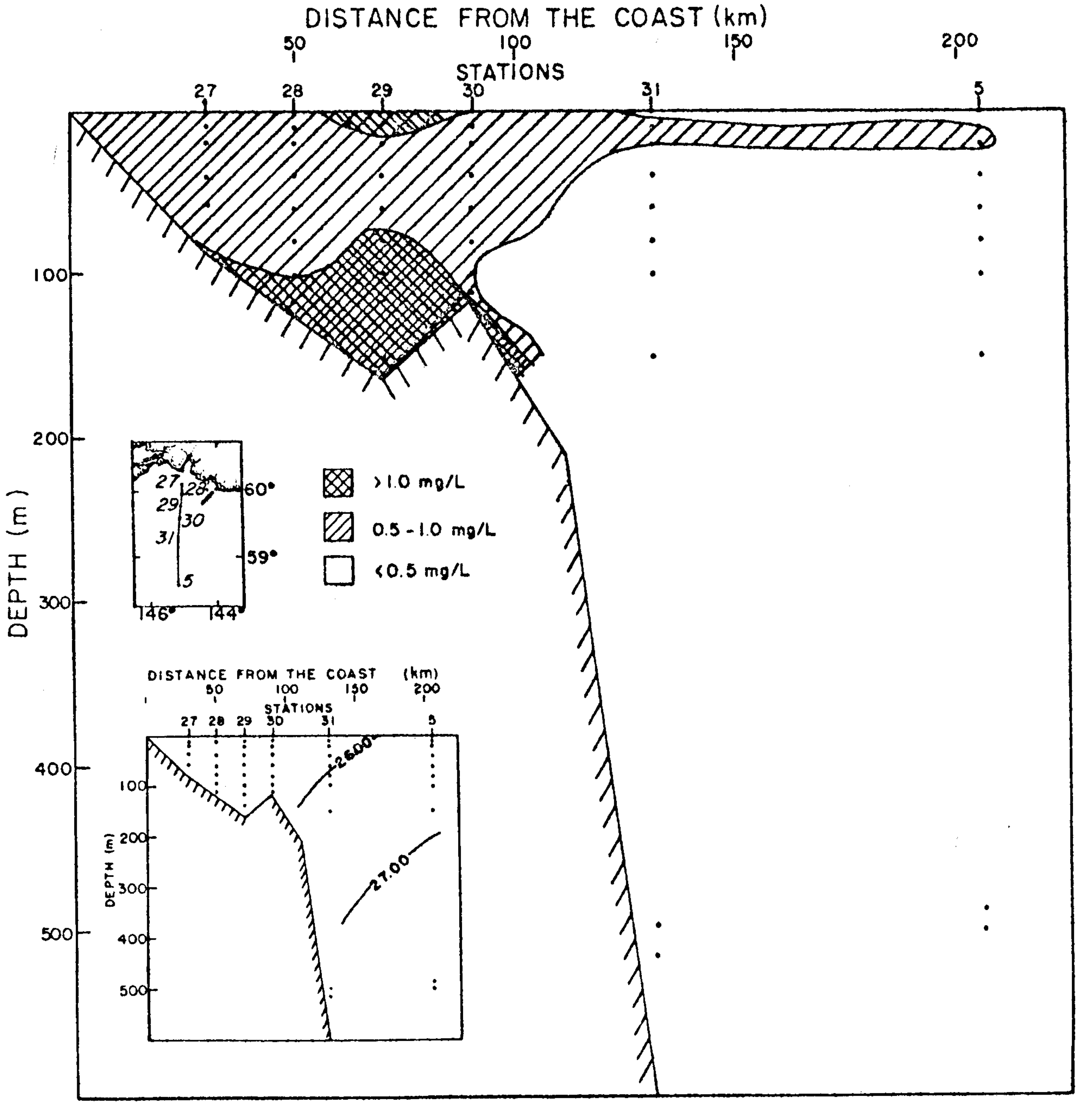

Figure 28. Vertical cross section of the distribution of total suspended matter for stations 27 thru 31 and station 5 in the northeastern Gulf of Alaska (Cruise RP-4-Di-76A-III, 13 - 30 April 1976). The insert shows the σ_T surfaces.

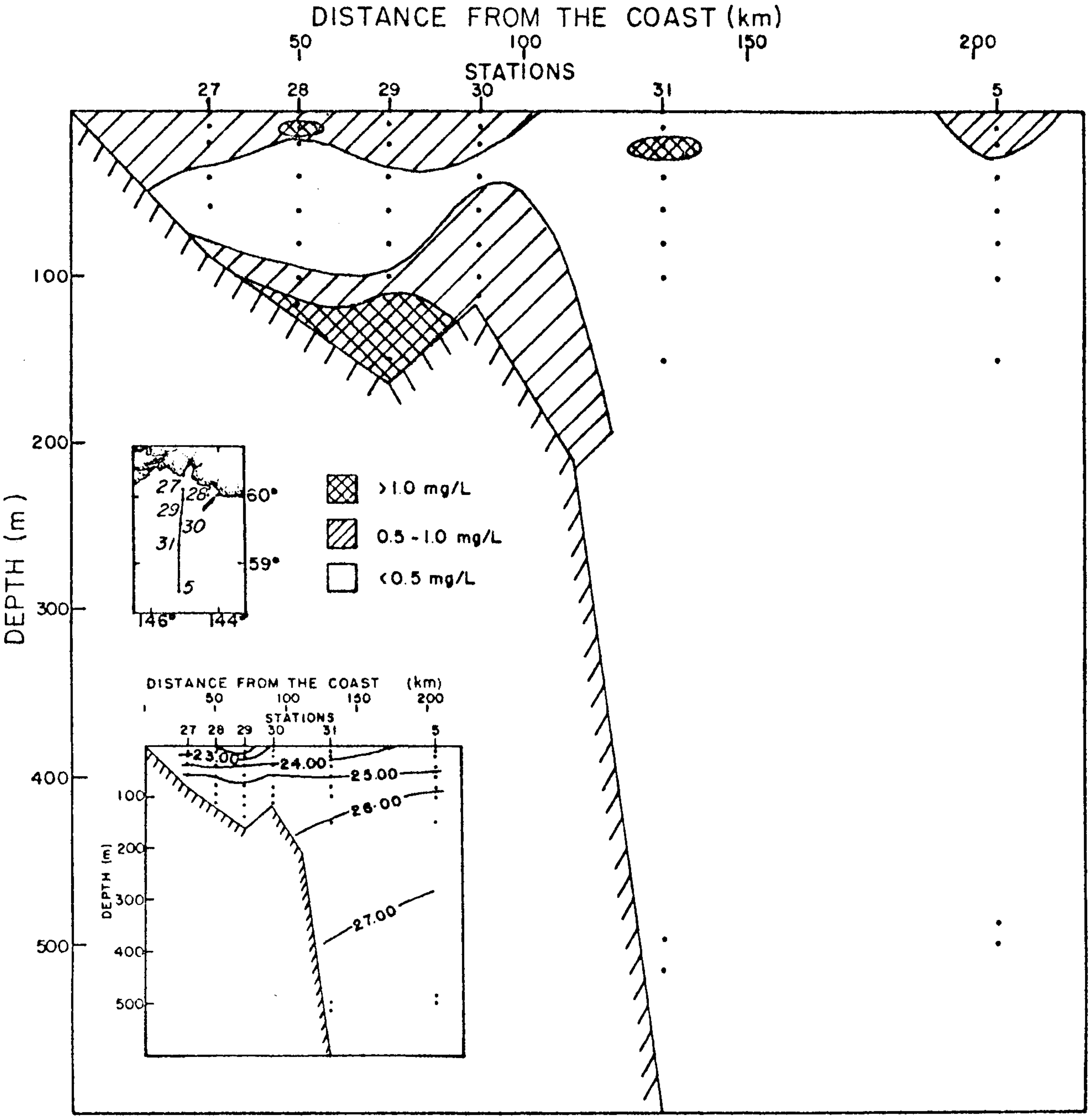

Figure 29. Vertical cross section of the distribution of total suspended matter for stations 27 thru 31 and station 5 in the northeastern Gulf of Alaska (Cruise RP-4-Di-76B-I, 19 - 31 July 1976). The insert shows the σ_T surfaces.

samples are represented in the figures as dots) and light scattering measurements. During the summer and fall cruises the water column was vertically stratfied, as shown in the figures by the insert of the vertical distribution of the σ_T surfaces. These cruises are characterized by large vertical suspended matter gradients. In contrast, the spring cruise, which shows very little stratification of the water column, is characterized by weak vertical gradients of suspended matter. Drake (1971) demonstrated that in Santa Barbara Channel vertical gradients in suspended matter distributions were strongly influenced by temperature-induced density gradients. Our data appear to support these findings. For example, at the time of the fall cruise the water column was thermally stratified. The temperature gradient at Station 28 was approximately $-0.05^{\circ}C/M$ from 50 to 100 meters. In contrast, the temperature gradient at the same station during the spring cruise was only about $-0.003^{\circ}C/M$. Thus, it is apparent that the water column stability, which on the continental shelf of the northeast Gulf is primarily controlled by temperature-induced density gradients, strongly influences the vertical transport and subsequent residence times of particles in suspension

C. Replicate Studies

In order to evaluate the reproducibility of the measurements for total suspended matter, a number of replicate experiments were conducted during the fall cruise in the Gulf. Surface samples were collected in 10-liter Top Drop Niskin® bottles and simultaneously filtered through 47 mm diameter 0.4 μm Nuclepore® filters. The results are presented in Table III. The average relative standard deviation for the replicate studies is 7.8 percent. Since the precision of our weighing techniques (based on replicate studies of standard reference filters) is less than 1 percent, most of the variability in the data appears to be due to the inhomogeneity of particulate matter in the water sample. This suggests that one must be extremely careful when comparing small differences in the suspended matter distributions. For the Gulf of Alaska, only differences greater than ±0.13 mg/ℓ are considered to be significant at the 95 percent confidence level.

In order to obtain some information about the high frequency (hourly) time variations in the distribution of suspended matter, two 36-hour time series experiments were conducted at Stations 46 and 62. Water samples were collected every 4 hours from the surface and 5 meters above the bottom. The results of these experiments are also given in Table III. The relative standard deviations of the data from the two time-series stations are significantly higher than the relative standard deviations from the replicate studies. This suggests that high frequency time variations, which may be due to the action of waves, tides, and local variations in productivity, are highly significant and must be carefully considered if seasonal particulate matter distribution maps are to have any significance. Using a mean value of 1.02 mg/ℓ for total suspended matter at the surface and the maximum relative standard deviation of 47.6 percent from the time series at Station 62 a value of ±0.77 mg/ℓ is significant at the 95 percent confidence level for seasonal variations. For these reasons, the contour intervals on the suspended matter distribution maps have been limited to ±1.0 mg/ℓ.

D. Temporal Variability of Suspended Matter Near the Seabed

In order to obtain some information about the processes that control resuspension and redistribution of bottom sediments along the shelf, a digital recording nephelometer was placed onto a current meter array at approximately 1.5 meters above the bottom (Station 62, 59°34'N and 142°10'W), which is located southeast of Icy Bay and has been used as the site for extensive measurements of bottom currents by the physical oceanographers at PMEL. It is situated near the shelf

TABLE III

Comparison of replicate samples collected in 10-liter Top-Drop Niskin® bottles and filtered through 47 mm diameter, 0.4 μm Nuclepore® filters with samples collected every 4 hours during a 36-hour time series experiment

Station	Depth	Number of Replicates	TSM Mean (mg/ℓ)	Std. Dev.	Rel. Std. Dev.
PMEL 1	sfc	4	0.510	0.029	0.057
PMEL 5	sfc	4	0.495	0.089	0.179
PMEL 9	sfc	3	1.241	0.099	0.079
PMEL 10	sfc	4	2.728	0.162	0.059
PMEL 16	sfc	3	0.635	0.023	0.036
PMEL 17	sfc	4	2.211	0.044	0.020
PMEL 39	sfc	4	3.482	0.123	0.035
PMEL 51	sfc	4	0.465	0.075	0.161
<u>Time-Series Stations</u>					
PMEL 46	sfc	9	0.333	0.066	0.199
PMEL 62	sfc	9	0.238	0.113	0.476
PMEL 46	60 m	9	0.512	0.119	0.232
PMEL 62	184 m	9	0.504	0.181	0.359

break at a depth of 184 meters. The nephelometer was deployed on 4 March 1976 and recovered on 16 May 1976. Figure 30 shows the record of the light scattering measurements for the period from 6 March through 31 March 1976 for which useful data were recovered. Figure 30 also shows the unfiltered (resolved with respect to the net drift axis and represented by dots) and the 35-hour low pass filtered (represented by vectors) current meter records from the current meter at 100 meters for the same time period. This current meter was chosen for this comparison as an alternative choice because the current meter that was deployed 1 meter above the nephelometer failed and no usable data were recovered. Considering the distance between the nephelometer and the current meter (≃ 80 meters), a comparison of this nature would seem to be marginal at best. However, we have examined current meter records from 1975 using linear regression and rotary coherence techniques and have found that a positive correlation ($r = 0.62$) exists between the currents measured at 100 meters and the currents measured near the bottom for the winter months between September and March (J. D. Schumacher, personal communication, 1976).

The light scattering record has two salient features. First, associated with almost every maxima in the unfiltered current meter record above a threshold velocity of approximately 17 cm/sec are corresponding peaks in the light scattering record. Spectral diagrams for both the current meter and nephelometer records, which are presented in Figures 31 and 32, respectively, show that the major peaks have frequencies of 0.3, 1.0, 1.7, and 1.9 cycles per day. These peaks are attributed to storm, diurnal, inertial, and semidiurnal events (Charnell et al., 1976) respectively, and appear to have a significant effect on the concentration of suspended matter near the bottom. The diurnal and semidiurnal events can be attributed to tidal activity which causes suspended matter fluctuations on the order of ± 0.4 mg/ℓ (previous calibration of

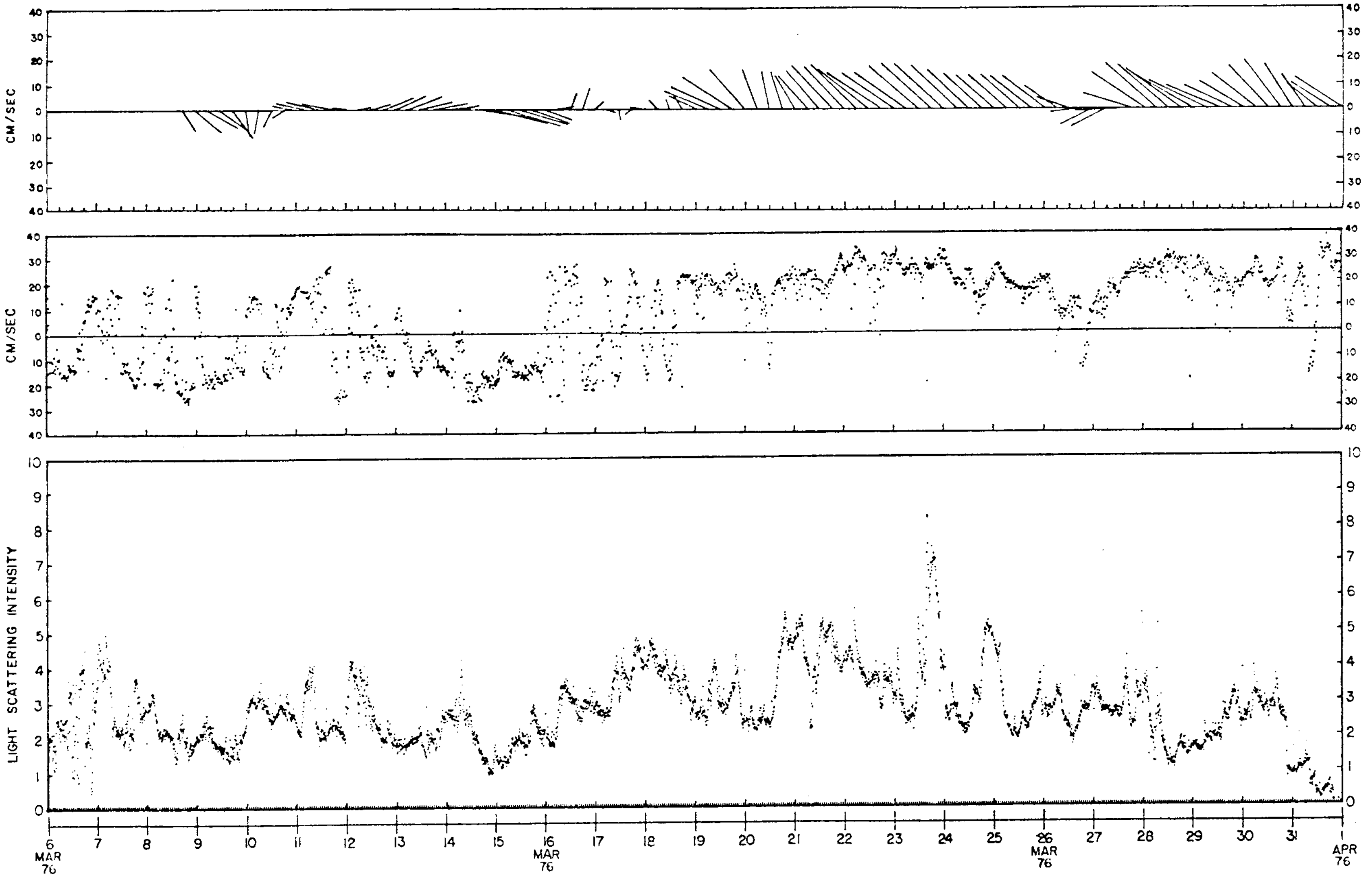

Figure 30. Comparison of the 26-day nephelometer record (bottom) from station 62 with the unfiltered (middle) and the 35-hour filtered (upper) current meter record at 100m. The current meter data were supplied by R. L. Charnell and J. D. Schumacher.

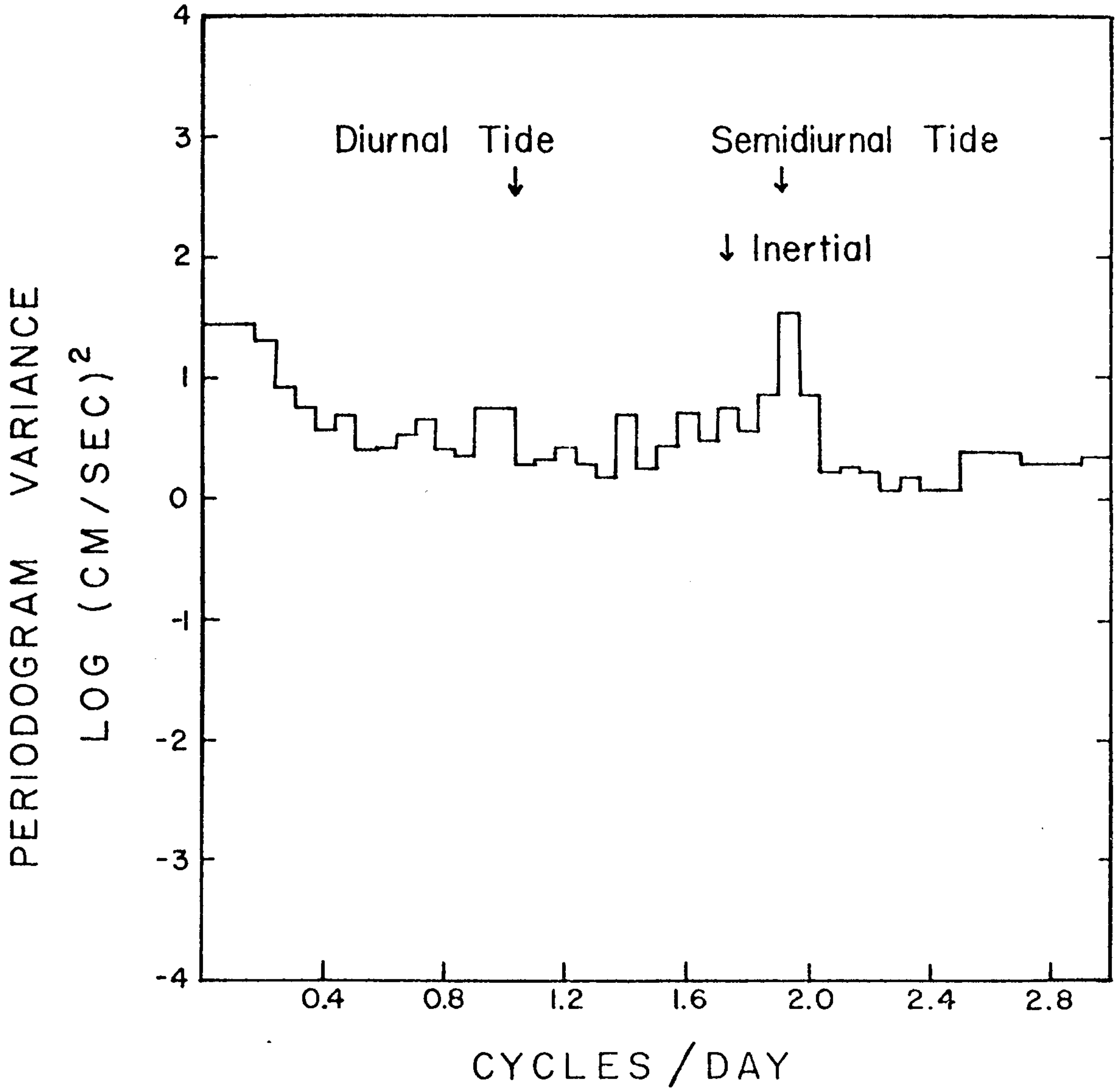

Figure 31. Energy spectra histogram of the 100m current meter at station 62. Energy is given by logarithm of periodogram variance.

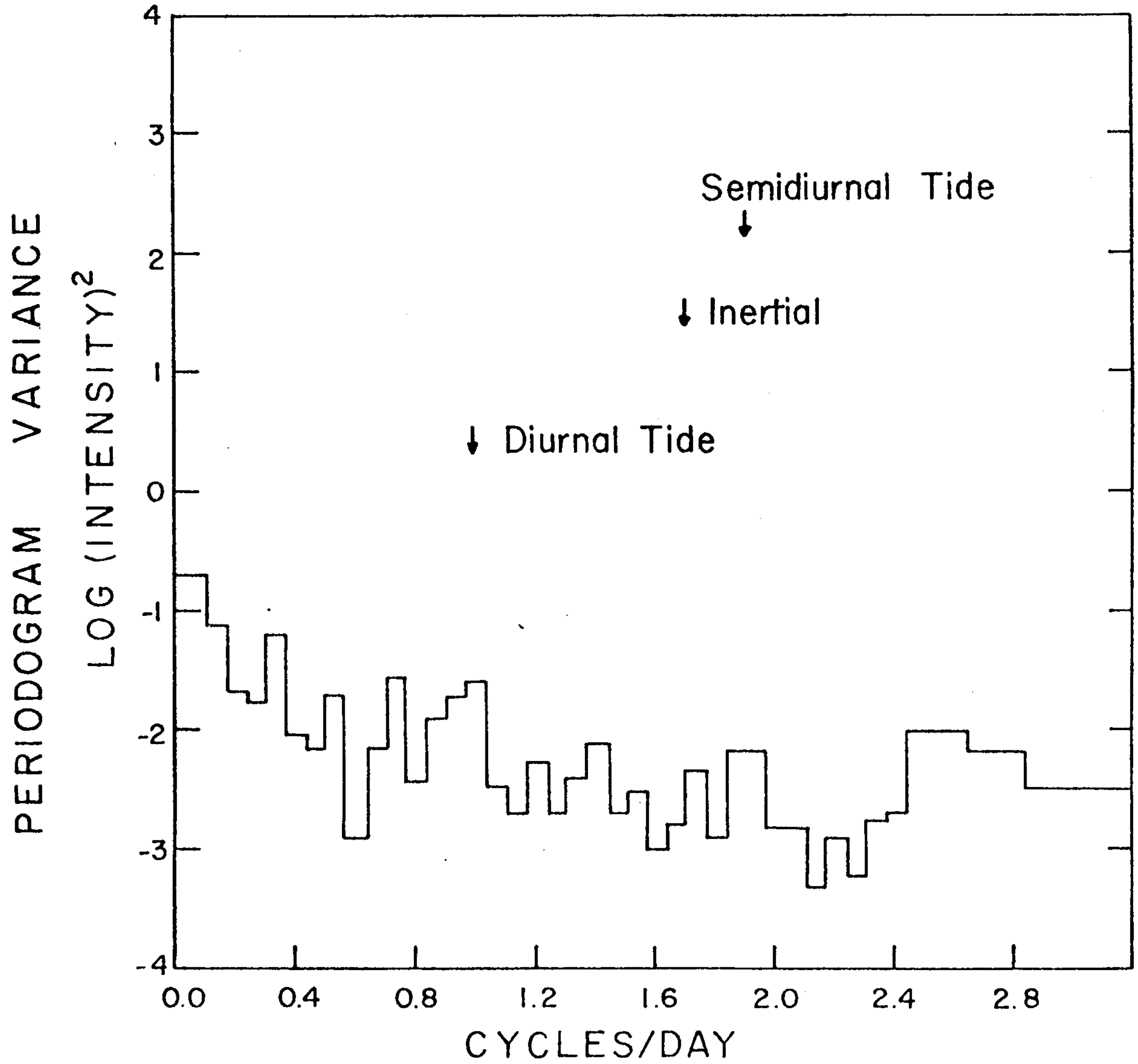

Figure 32. Energy spectra histogram of the nephelometer record at station 62. Energy is given by logarithm of periodogram variance.

the nephelometer indicates that a light scattering intensity of 2.0 corresponds to a suspended matter concentration of approximately 0.5 mg/ℓ and a light scattering intensity of 4.0 corresponds to a suspended matter concentration of 2.0 mg/ℓ). These findings suggest that tidal currents near the bottom are of sufficient velocity to resuspend bottom sediments at Station 62.

The second feature of the nephelometer record is the presence of a large gradual increase in light scattering which begins on 16 March 1976 and continues through 26 March. There is a significant correlation between this feature and a similar event in the 35-hour filtered current meter record which shows the development of a strong onshore current having a net velocity of approximately 25 cm/sec at 310°TN. This event is characteristic of storm-induced bottom currents (Hayes and Schumacher, 1976) and represents a net water transport of approximately 230 km. The light scattering record indicates a corresponding increase in the near bottom suspended matter concentrations from about 0.5 mg/ℓ to about 3.0 mg/ℓ. Thus, the near bottom nephelometer and current meter records at Station 62 clearly show that significant amounts of bottom sediments are being resuspended and transported by storm-induced bottom currents.

E. Elemental Chemistry of the Particulate Material

Tables IV and V compare summaries of the data on the elemental composition of suspended matter from the Copper and Bering Rivers with summaries of the surface and near-bottom data from the Gulf of Alaska (Cruise RP-4-Di-75C-I, 21 Oct.-10 Nov. 1975). The data for the Gulf surface samples have been arranged into two groups. Group I contains all the samples in which the sum of the major inorganic element concentrations (expressed as oxides) is greater than 60 percent of the total suspended load; all samples of lesser inorganic sum comprise Group II. Group I samples are primarily composed of clay-sized terrestrial particles from the coastal rivers. The samples in Group II consist primarily of organic detritus and biogenic tests. Figure 33 shows the percentage of the total suspended matter that is due to the inorganic elemental sum for each surface station. The 60 percent isopleth divides the stations into their respective groups.

As shown in Table V, the elemental composition of the suspended matter is remarkably different for Groups I and II. Within the statistical limits of the measurements the samples from Group I have very nearly the same major element composition as the samples from the Copper and Bering Rivers. This is especially true for Al, K, and Ti which have been shown to be almost exclusively associated with aluminosilicate minerals of terrestrial origin (Sackett and Arrhenius, 1962; Spencer and Sachs, 1970; Price and Calvert, 1973; and Feely, 1975).

The Group I data indicate that aluminosilicate minerals are the most abundant solid phases in the particulate matter. As much as 90 percent of the particulate matter from Group I is aluminosilicate material of terrestrial origin. In contrast, the particulate matter samples from Group II only contain about 20 percent aluminosilicate material.

In contrast to the Group I data, the Group II samples are significantly depleted in particulate Mg, Al, Si, K, Ti, Cr, Mn, and Fe, and are enriched in particulate Ni, Cu, and Zn (77, 58, and 11 percent, respectively). However, considering the large variability associated with the low sample loadings and the somewhat arbitrary method by which the data groups are selected, only the enrichments for Ni and Cu are significant at the 95 percent confidence level.

Table V also summarizes the elemental composition of 37 samples taken 5 meters above the bottom. In general, the major element concentrations of the near-bottom samples are similar to the Group I and river samples. However, the trace elements Ni and Cu are depleted in the samples from this region.

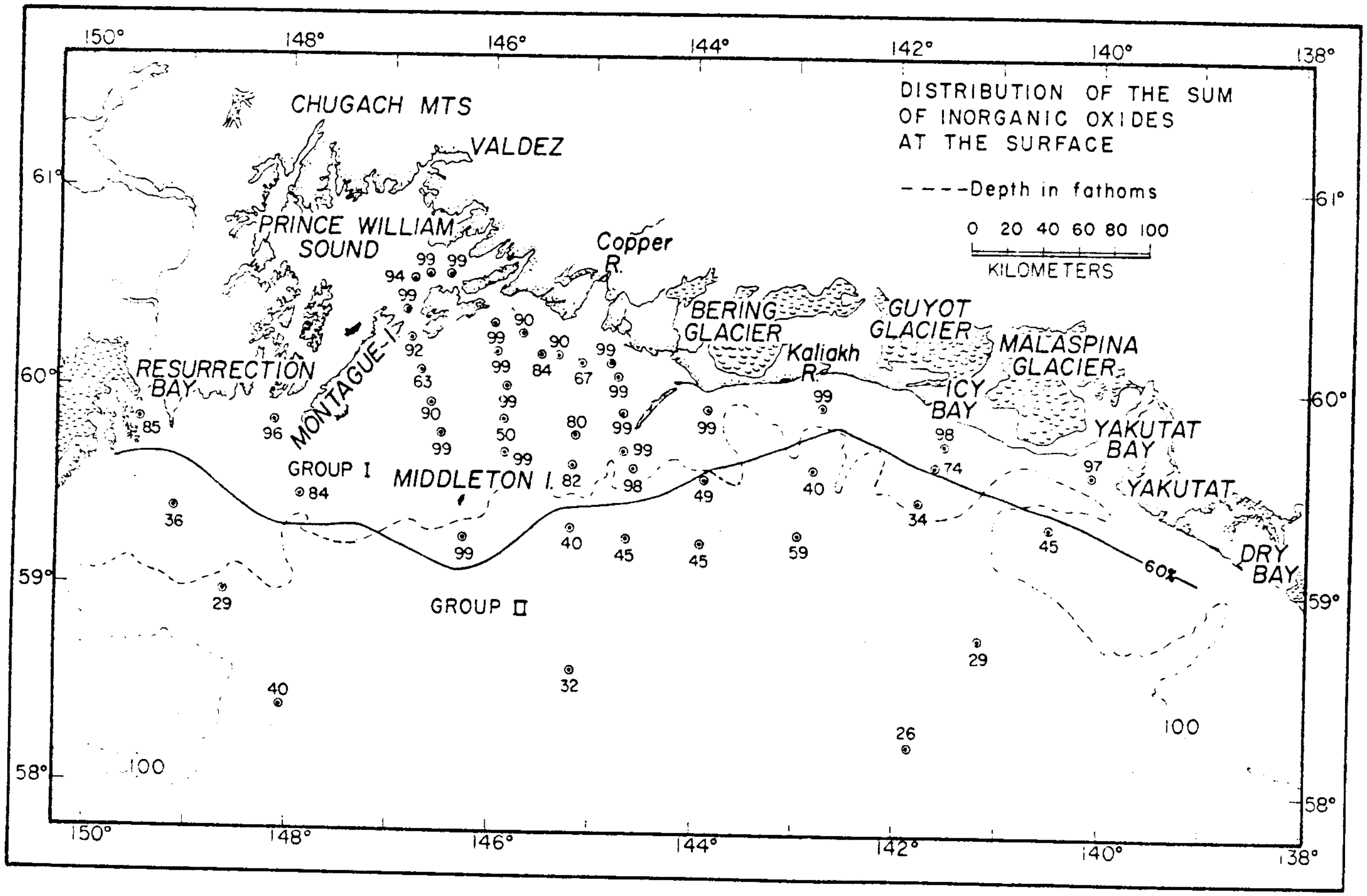

Figure 33. Map of the surface distribution of the percentage of total suspended matter that is due to the sum of the major inorganic elements expressed as oxides (Cruise RP-4-Di-75C-I, 21 Oct. - 10 Nov. 1975).

TABLE IV

Summary of the elemental composition of suspended matter from the major rivers that discharge into the northeastern Gulf of Alaska. (Surface samples were obtained with a precleaned 4-ℓ polyethylene bottle extended from a Bell 206B helicopter, 22-27 June 1976.)

Sample Description	No. of Samples	C wt. %	N wt. %	Mg wt. %	Al wt. %	Si wt. %	K wt. %	Ca wt. %	Ti wt. %	Cr ppm	Mn ppm	Fe wt. %	Ni ppm	Cu ppm	Zn ppm	Pb ppm
Copper River	15	1.04 ±0.51	0.09 ±0.06	6.10 ±1.26	10.31 ±1.10	27.31 ±2.85	1.62 ±0.19	3.93 ±0.99	0.55 ±0.05	103.9 ±19.8	1085 ±99	6.16 ±0.71	88.1 ±12.5	105.8 ±20.8	209.6 ±37.3	48.7 ±9.9
Bering River	1	1.56	0.62	6.65	13.16	25.87	1.88	5.02	0.50	129.8	1012	6.02	87.9	99.7	246.5	67.2

TABLE V

Summary of the elemental composition of the particulate matter samples from the northeastern Gulf of Alaska (Cruise RP-4-Di-75C-I, 21 Oct.-10 Nov. 1975)

Sample Description	No. of Samples	C wt. %	N wt. %	Mg wt. %	Al wt. %	Si wt. %	K wt. %	Ca wt. %	Ti wt. %	Cr ppm	Mn ppm	Fe wt. %	Ni ppm	Cu ppm	Zn ppm	Pb* ppm
Surface (Group I)	35	18.69 ±11.81	2.69 ±1.78	4.81 ±1.22	9.10 ±2.21	26.51 ±5.45	1.26 ±0.45	2.69 ±0.90	0.55 ±0.13	87.1 ±18.6	1007 ±281	3.76 ±1.30	82.9 ±38.0	103.9 ±37.0	187.2 ±38.0	53.1 ± 10.3
Surface (Group II)	13	40.20 ±17.59	6.56 ±2.06	1.75 ±1.17	1.92 ±1.66	12.29 ±3.67	0.43 ±0.17	2.49 ±0.56	0.27 ±0.09	61.8 ±28.0	579 ±262	1.66 ±0.90	147.0 ±137.0	165.0 ±90.0	209.0 ±63.0	47.0 ± 15.6
5 m above the bottom	37	11.56 ±9.12	1.52 ±1.18	5.16 ±1.62	8.78 ±2.74	26.68 ±5.93	1.35 ±0.36	2.22 ±1.24	0.48 ±0.14	93.7 ±19.8	1104 ±324	5.36 ±1.60	46.6 ±14.3	69.2 ±27.3	176.0 ±58.8	55.0 ± 14.3

*Only 14 surface samples had sufficient loadings for the analysis of lead.

Table VI shows the average elemental concentration ratios to aluminum for the samples from the various groups. The Si/Al and Ca/Al ratios from Group II are considerably elevated over the ratios for the river samples. This is due to the presence of diatom frustules and coccolith tests in the suspended matter. Price and Calvert (1973) and Feely (1975) demonstrated that the amount of biogenic silica and carbonates can be estimated by assuming a constant Si/Al and Ca/Al ratio due to suspended aluminosilicates. Any excess Si and Ca is assumed to be of biogenic origin. Using the Si/Al and Ca/Al ratios of the aluminosilicate material from the Copper River, values of approximately 16 and 4 percent by weight of the Group II samples are estimated to be composed of biogenic silica and carbonate, respectively. In contrast, it is estimated that on the average the Group I samples only contain about 5 percent by weight of biogenic silica and no biogenic carbonate.

The surface distributions of particulate Al, Cr, Fe, and Cu are presented in Figures 34a and 34b. As shown in Figures 34a and 34b, the distributions of particulate Al, Cr, and Fe show significant decreases in concentration in a seaward direction. The data from Table V corroborate these findings. The concentrations of these elements are significantly lower in the Group II samples (offshore stations) relative to the samples from Group I (nearshore stations). Apparently, the concentrations of Al, Cr, and Fe are highest in the fine-grain terrestrial material that is discharged from the coastal rivers. Particles of marine origin (diatoms, coccoliths, etc.) tend to dilute the samples relative to the above elements. Similar distribution patterns are observed for particulate Mg, K, Ti, and Mn.

The particulate Cu distributions, on the other hand, show significant concentration increases for the offshore stations (Figure 34d). Similar increases also exist for particulate Ni, Zn, and Pb (Table V). These elements

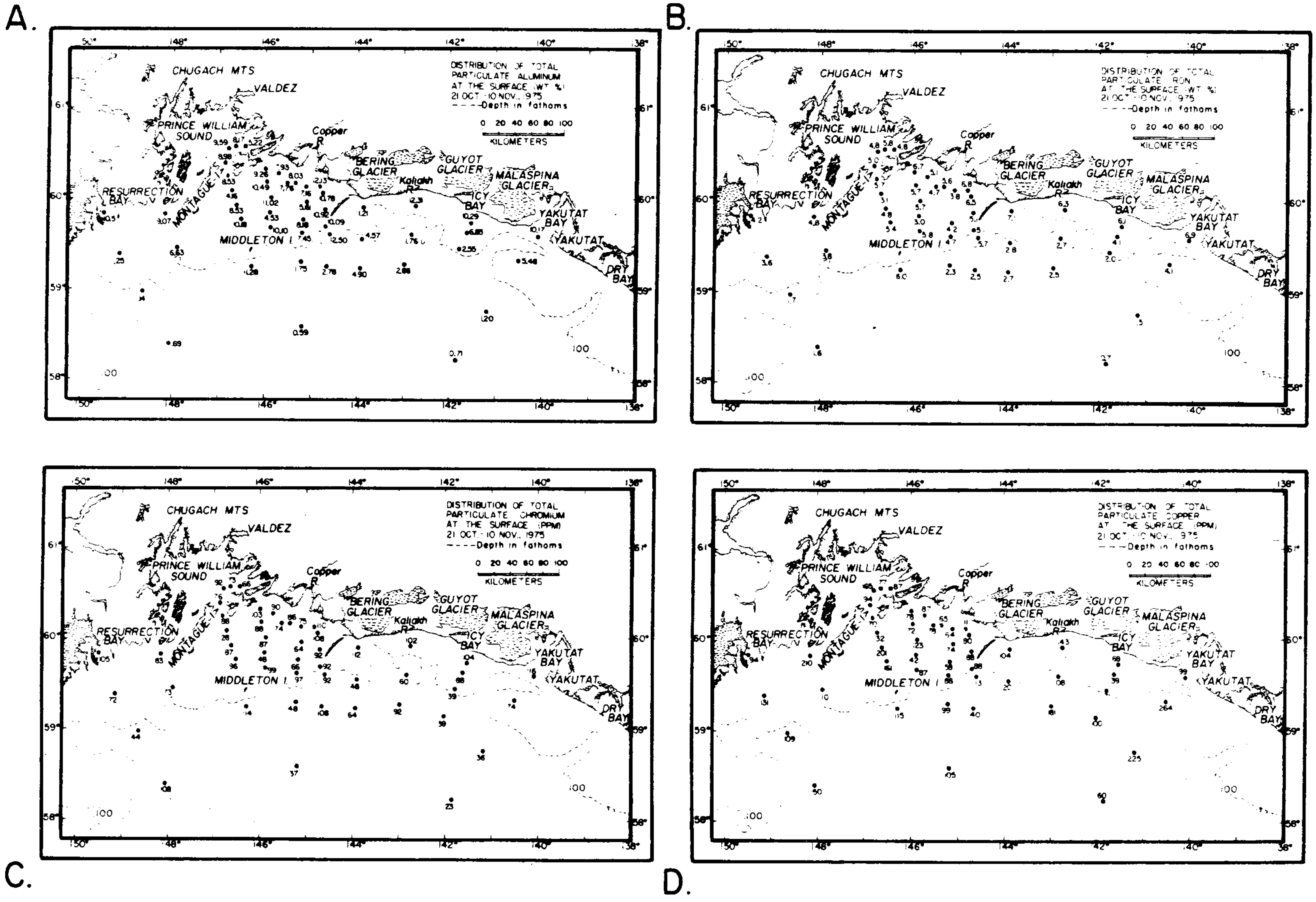

Figure 34. Distribution of: a. particulate aluminum (wt. percent); b. particulate iron (wt. percent); c. particulate chromium (parts per million); and d. particulate copper (parts per million) in the total particulate matter at the surface (Cruise RP-4-Di-75C-I, 21 Oct. - 10 Nov. 1975).

TABLE VI

Elemental ratios to aluminum for the particulate matter samples from the northeastern Gulf of Alaska (Cruise RP-4-75C-I, 21 Oct. - 10 Nov., 1975) and the Copper and Bering Rivers

Sample Description	No. of Samples	Mg/Al	Si/Al	K/Al	Ca/Al	Ti/Al	Cr/Al	Mn/Al	Fe/Al	Ni/Al	Cu/Al	Zn/Al	Pb/Al
Surface (Group I)	35	0.53	2.91	0.14	0.30	0.06	0.0009	0.011	0.41	0.0009	0.0011	0.0021	0.0008
Surface (Group II)	13	0.91	6.40	0.23	1.92	0.14	0.0032	0.030	0.86	0.0076	0.0086	0.0109	0.0068
5 m above the bottom	37	0.59	3.03	0.15	0.25	0.05	0.0011	0.012	0.61	0.0005	0.0008	0.0020	0.0007
Copper River	15	0.59	2.65	0.16	0.38	0.05	0.0010	0.011	0.60	0.0008	0.0010	0.0020	0.0005
Bering River	1	0.51	1.96	0.14	0.38	0.04	0.0011	0.008	0.46	0.0007	0.0008	0.0019	0.0005

have been shown to be highly correlated to biological activity and significant uptake during primary production may be occurring (Knauer and Martin, 1973).

In order to develop an understanding of the processes controlling the variability of trace elements in marine particulate matter and sediments many authors have examined interelement scatter plots (Spencer and Sachs, 1970; Price and Calvert, 1973). Usually one of the elements is a structural component of one or more solid phases in the particulate matter. In this way, the concentration variability of a particular element can be directly related to the variability of a particular solid phase.

Figures 35a and 35b show iron and chromium concentrations plotted as a function of the aluminum concentration for all samples. The strong correlation of iron and chromium with aluminum suggests that these elements are associated with the structural components of the terrestrial rock debris that is discharged from the coastal rivers and/or the resuspended sediments. Scatter plots for Mg, K, Ti, and Mn show similar results.

If it is accepted that a linear correlation between a particular element and aluminum is a direct result of the element:aluminum ratio in the weathered rock debris, then it follows that a nonlinear or poorly correlated relationship is indicative of a distinctly different source for the element in question. Figure 35c shows a scatter plot between copper and aluminum for all the samples. The plot shows that for the surface samples little, if any, correlation between copper and aluminum exists. However, when copper is plotted against particulate carbon, a fairly good correlation results (Figure 35d). This suggests that the distribution of copper in the surface samples is primarily controlled by the amount of particulate organic matter that is present.

The distributions and scatter plots for nickel and zinc are similar to copper although not quite as well-defined. It is possible that two distinct

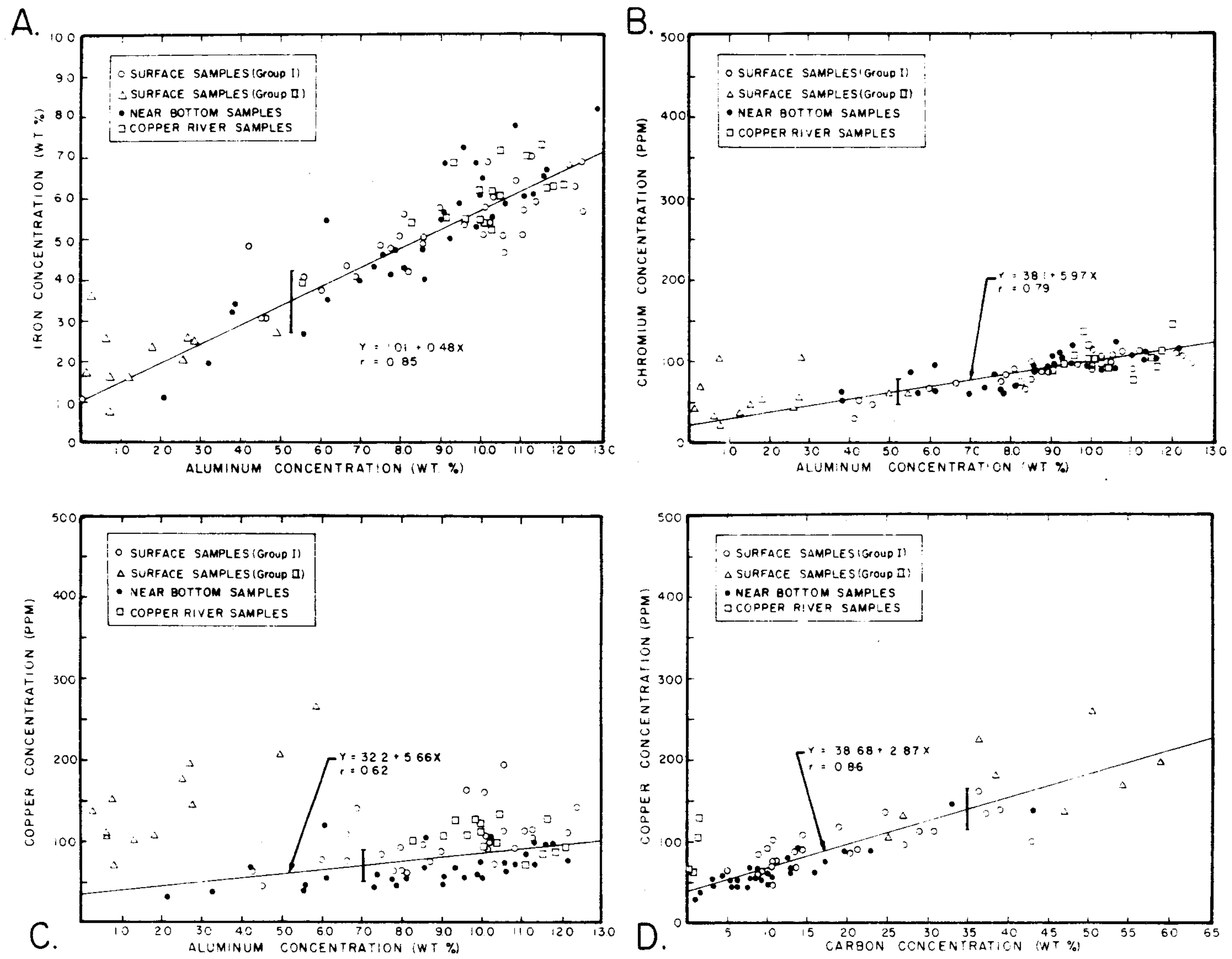

Figure 35. Scatter diagrams of: a. iron versus aluminum; b. chromium versus aluminum; c. copper versus aluminum; and d. copper versus carbon (Cruise RP-4-Di-75C-I, 21 Oct. - 10 Nov. 1975. The error bar represents the standard error for the least square fit of the data.

phases, terrigenous material and particulate organic matter, may both be important in controlling the overall concentrations of Ni and Zn in the particulate matter.

Tables VII and VIII show data summaries of the elemental composition of the surface and near-bottom suspended matter for the spring and summer cruises in the northeastern Gulf (Cruises RP-4-Di-76A-III, 13-30 April and RP-4-Di-76B-I, 19-31 July 1976). The data for these cruises have been arranged into data groupings in exactly the same manner as the data for the fall cruise (Table V). Except for Ca, there does not appear to be any significant difference in the major inorganic element concentrations of the suspended matter for the three cruises. However, the Group II surface samples from the spring and summer cruises show significant particulate Ca depletions relative to corresponding samples from the fall cruise. This difference might be related to seasonal variations in the production of Ca-bearing Coccoliths which are common to this region.

The particulate carbon and nitrogen data show significant seasonal variations (Tables V, VII and VIII). The lowest surface concentrations of particulate carbon and nitrogen (averaging 60 μg/ℓ and 11 μg/ℓ, respectively) were observed at the time of the spring cruise when primary productivity was near minimum values (Larrance and Tennant, 1977). During the summer cruise, surface concentrations of particulate carbon and nitrogen increased by factors of 2.3 and 2.6, respectively. Observations of primary productivity rates at Station 4 of the study region show corresponding increases (17 mg C/M^2/hr for April vs 100 mg C/M^2/hr for July). Gordon (1977) observed similar increases in particulate carbon concentrations for a line of stations between Halifax and Bermuda which the author attributed to seasonal variations of primary productivity.

TABLE VII

Summary of the elemental composition of the particulate matter samples from the northeastern Gulf of Alaska (Cruise RP-4-Di-76A-IV, 12-30 April 1976)

Sample Description	No. of Samples	C wt. %	N wt. %	Mg wt. %	Al wt. %	Si wt. %	K wt. %	Ca wt. %	Ti wt. %	Cr ppm	Mn ppm	Fe wt. %	Ni ppm	Cu ppm	Zn ppm	Pb ppm
Surface (Group I)	29	9.62 ±7.71	1.93 ±1.81	5.19 ±1.57	8.85 ±2.25	28.06 ±6.14	1.25 ±0.31	2.24 ±1.34	0.47 ±0.14	98.5 ±24.7	1022 ±228	5.40 ±1.40	73.4 ±20.9	50.6 ±19.8	212.5 ±55.6	59.4 ±22.4
Surface (Group II)	9	24.30 ±3.50	4.57 ±1.16	1.51 ±0.87	1.85 ±1.34	12.43 ±4.16	0.26 ±0.20	0.73 ±0.25	0.12 ±0.07	49.8 ±27.7	490 ±317	1.92 ±1.03	49.4 ±20.0	26.1 ±5.6	203.9 ±83.0	50.8 ±16.5
5 m above the bottom	38	4.86 ±2.39	0.78 ±0.45	5.12 ±1.89	9.26 ±2.91	27.39 ±7.25	1.40 ±0.34	2.81 ±0.98	0.54 ±0.11	104.5 ±22.1	1123 ±260	6.22 ±1.57	76.2 ±14.1	55.0 ±11.6	223.6 ±48.2	61.6 ±19.7

TABLE VIII

Summary of the elemental composition of the particulate matter samples from the northeastern Gulf of Alaska (Cruise RP-4-Di-76B-I, 19-31 July 1976)

Sample Description	No. of Samples	C wt. %	N wt. %	Mg wt. %	Al wt. %	Si wt. %	K wt. %	Ca wt. %	Ti wt. %	Cr ppm	Mn ppm	Fe wt. %	Ni ppm	Cu ppm	Zn ppm	Pb ppm
Surface (Group I)	17	14.85 ±8.13	3.19 ±1.92	4.25 ±1.54	7.41 ±2.01	25.29 ±6.03	1.05 ±0.45	2.05 ±1.15	0.37 ±0.14	82.2 ±24.1	942 ±271	4.40 ±1.70	62.3 ±16.0	98.1 ±15.8	205.2 ±24.3	47.8 ±8.3
Surface (Group II)	16	28.20 ±12.01	5.02 ±2.17	1.55 ±1.19	1.47 ±1.11	11.57 ±4.22	0.45 ±0.61	0.50 ±0.26	0.08 ±0.05	47.6 ±21.4	294 ±201	1.33 ±0.82	40.3 ±12.5	114.5 ±21.5	204.5 ±39.3	32.5 ±3.8
5 m above the bottom	38	6.85 ±6.55	0.92 ±0.85	5.32 ±1.34	8.99 ±2.06	27.63 ±4.58	1.38 ±0.34	2.46 ±0.64	0.50 ±0.10	97.6 ±20.2	1203 ±283	5.91 ±1.22	69.6 ±14.7	84.1 ±10.6	217.8 ±38.8	48.5 ±13.9

The seasonal variations of primary productivity and the resulting changes in the carbon content of the suspended material directly affect the ratio of organic matter to inorganic matter in the total particulate matter. This ratio is also affected by the supply of inorganic material that is discharged from the coastal rivers and streams. Thus, the organic to inorganic ratio of the particulate matter represents the result of a number of independent processes acting concurrently. It would be expected, therefore, that any element that is primarily associated with particulate organic matter or particulate inorganic matter would show concentration variations that vary directly with the organic/inorganic ratio of the particulate material. This appears to be the case for all of the trace elements. Particulate Cr, Mn, and Fe, which are primarily associated with the inorganic matter, are significantly depleted in samples with high organic to inorganic ratios (Tables V, VII and VIII). Particulate Cu, which is primarily associated with particulate organic matter, shows the greatest amount of enrichment when the organic to inorganic ratio is highest, i.e., the fall cruise (Table V). Particulate Zn, on the other hand, which is nearly equally distributed between organic and inorganic phases shows little, if any, variability in space or time.

It should be pointed out here that the above discussion is limited to open shelf surface waters where near-shore processes and/or near-bottom processes are insignificant. The data from Tables V, VI, and VII indicate no significant seasonal variations in the chemical composition of suspended matter near the bottom. If it is assumed that the near-bottom suspended matter is primarily resuspended sediments, then season variations in the chemical composition of suspended matter would not be expected unless the bottom currents were of sufficient energy to cause differential erosion of bottom sediments.

F. Sampling and Analytical Precision

In order to compare the reproducibility of the analytical techniques for determining the chemical composition of the suspended matter with the variability of the samples, a number of replicate experiments were conducted during the fall cruise in the Gulf. A surface sample from Station 9 was collected in a 10-liter Niskin® bottle and simultaneously filtered through ten 0.4 μm pore size Nuclepore® filters. All ten filters were analyzed for major and trace inorganic elements and the results are shown in Table IX. In addition, a single rock standard was prepared in exactly the same manner as the samples and analyzed once a day during 53 sequential days of analysis and the results are shown in Table X. Table IX shows the variability of the samples and Table X shows the precision of the x-ray fluorescence technique. As shown in Table X, the analytical precision ranges from 1.2 to 3.1 percent for the major elements and 2.2 to 8.9 percent for the trace elements. In contrast, the sampling precision ranges from 9.6 to 17.9 percent for the major elements and 9.4 to 52.3 percent for trace elements. These results clearly illustrate that with respect to the quantities of material analyzed the sample-to-sample variability is significantly greater than the analytical variability for all the elements that were studied.

Lower Cook Inlet

The suspended matter studies in Lower Cook Inlet will be conducted on two cruises. The first cruise will be conducted in April of this year on the NOAA ship DISCOVERER (Cruise RP-4-Di-77A-IV). The second cruise will be conducted in June-July 1977 aboard the R/V ACONA. Suspended matter samples will be collected from 59 stations for determination of particulate matter distributions and elemental compositions. In addition, at selected locations large volume water samples will be collected and the indigenous suspended matter will be

TABLE IX

Replicate study of ten individually filtered water samples from a single Niskin® bottle taken from the surface at Station 9 in the northeastern Gulf of Alaska (RP-4-75C-I, 21 Oct.-10 Nov. 1975).

Replicate#	Mg(wt.%)	Al(wt.%)	Si(wt.%)	K(wt.%)	Ca(wt.%)	Ti(wt.%)	Cr(ppm)	Mn(ppm)	Fe(wt.%)	Ni(ppm)	Cu(ppm)	Zn(ppm)	Pb(ppm)
1	6.94	9.04	23.95	1.37	4.48	0.42	84.2	956	5.70	42.1	52.2	159.8	71.5
2	7.82	11.77	31.02	1.74	5.50	0.55	150.6	1227	7.45	61.0	74.9	212.5	84.4
3	7.72	11.17	30.11	1.65	5.91	0.53	117.8	1212	7.21	147.7	64.6	191.9	77.7
4	6.88	10.71	29.67	1.68	5.94	0.54	117.3	1188	7.30	49.6	60.5	175.7	74.5
5	7.41	11.20	31.02	1.71	5.86	0.56	119.5	1241	7.51	53.5	63.0	201.8	72.6
6	6.54	10.04	27.44	1.53	5.08	0.49	101.9	1098	6.61	49.6	71.3	198.0	103.2
7	7.69	11.47	30.15	1.64	5.78	0.53	114.3	1189	7.16	52.8	77.1	232.1	99.1
8	7.52	11.42	32.87	1.80	6.28	0.59	131.1	1348	8.14	57.2	79.1	225.9	97.0
9	5.92	9.01	25.86	1.42	5.17	0.48	96.0	1053	6.37	40.7	54.6	203.9	73.0
10	6.22	11.83	32.25	1.94	3.05	0.54	138.2	1220	6.55	46.2	50.6	179.7	84.8
Mean	7.40	10.76	29.44	1.65	5.30	0.52	117.0	1173	6.99	60.1	64.8	198.1	83.8
STD. DEV.	1.22	1.06	2.84	0.17	0.94	0.05	19.8	110	0.69	31.4	10.5	22.4	12.0
Coeff. of variation (%)	16.4	9.8	9.6	10.3	17.9	9.3	16.9	9.4	9.9	52.3	16.1	11.3	14.3

TABLE X

Ten replicate analyses of a single USGS W-1 standard. The rock standard was prepared by passing a suspension of the rock material through a 37 μm polyethylene mesh followed by collection of the suspensate on a Nuclepore® filter (0.4 μm nominal pore size, 2.5 cm^2 active collection area). Replicates were randomly chosen from 53 sequential days of analysis.

Replicate #	Seq. #	Mg (wt. %)	Al (wt. %)	Si (wt. %)	K (wt. %)	Ca (wt. %)	Ti (wt. %)	Cr (ppm)	Mn (ppm)	Fe (wt. %)	Ni (ppm)	Cu (ppm)	Zn (ppm)
1	2	3.99	7.57	24.72	0.53	7.82	0.62	105	1,266	7.70	86	104	90
2	16	4.23	8.27	25.42	0.57	7.95	0.65	106	1,308	7.83	86	125	94
3	17	4.19	8.30	25.75	0.57	8.08	0.66	115	1,315	7.93	90	123	88
4	23	4.18	8.08	25.70	0.57	7.99	0.67	116	1,338	7.89	87	130	93
5	26	4.00	8.18	25.24	0.57	7.95	0.65	112	1,299	7.85	91	126	93
6	31	4.17	8.27	25.42	0.56	7.93	0.65	108	1,287	7.80	87	130	93
7	34	4.20	8.34	25.87	0.57	8.05	0.66	111	1,314	7.87	86	136	93
8	38	4.05	7.80	24.67	0.55	7.80	0.64	107	1,264	7.67	85	132	91
9	39	3.96	8.27	25.34	0.56	7.85	0.65	107	1,303	7.72	90	136	89
10	49	4.03	7.95	25.13	0.56	7.84	0.64	106	1,291	7.72	89	149	93
Mean		4.10	8.10	25.33	0.56	7.93	0.65	109	1,299	7.80	88	129	92
Std. Dev.		0.10	0.25	0.41	0.02	0.10	0.01	4	23	0.09	2	12	2
Coef. of Variation (%)		2.5	3.1	1.6	2.3	1.2	2.1	3.6	1.7	1.2	2.4	8.9	2.2

extracted by centrifugation. The extracted particulate samples will be used for subsequent hydrocarbon adsorption experiments. The results of these studies will be presented in a future report.

VIII. Conclusions

A. Southeastern Bering Shelf

The most significant conclusions of the suspended matter program in the southeastern Bering Shelf are listed below.

1. The surface suspended matter distributions appear to follow the general pattern of circulation in Bristol Bay. Terrestrial suspended matter from the northern rivers is generally carried to the west and southwest by the counterclockwise currents.
2. Large plumes of suspended matter can be seen extending to the southwest from Cape Newenham and to the west from Kuskokwim Bay. Apparently these plumes represent sedimentary material derived from the Kvichak, Nushagak, and Kuskokwim Rivers.
3. Suspended material of marine origin is carried into Bristol Bay along the northern coast of the Alaska Peninsula. In the region north of Unimak Pass large suspended matter plumes have been observed in the early summer. These plumes appear to be the result of increased productivity during the summer months.
4. Sharp increases in suspended matter concentrations near the bottom indicate that resuspension of bottom sediments is occurring.

B. Gulf of Alaska

The most significant conclusions of the particulate matter studies in the northeastern Gulf of Alaska are listed below.

1. The distribution of suspended matter at the surface appear to follow the general pattern of water circulation in the Gulf. East of Kayak Island sedimentary material, which is discharged along the coast, is quickly deflected to the west by the westward flowing currents. This material is carried to the west along the coast until it reaches Kayak Island where it is deflected to the southwest and is trapped by a clockwise gyre.
2. Sedimentary material from the Copper River is carried to the northwest along the coast until it reaches Hinchinbrook Island where a portion of the material passes into Prince William Sound and the remaining material is carried to the southwest along the southeastern coast of Montague Island.
3. Comparisons of surface suspended matter distribution maps for the three cruises in the Gulf show significant variations which can be related to seasonal variations in the discharge of terrestrially derived suspended matter, seasonal variations in primary productivity, and occasional offshore transport of suspended matter by wind-generated eddies.
4. A bottom nepheloid layer is present throughout most of the Gulf. The height of the nepheloid layer appears to be dependent upon the bottom topography and the currents. Studies of the temporal variability of suspended matter near the bottom show evidence for resuspension and redistribution of bottom sediments. These processes have occurred as a result of interactions between tidal and storm-induced bottom currents and the surficial sediments.
5. Studies of the chemical composition of the suspended matter show significant spatial and seasonal variations. These variations

have been correlated with: (1) seasonal variations in primary production; (2) seasonal variations in the supply and transport of terrestrially derived suspended matter from coastal rivers; and (3) resuspension of bottom sediments.

IX. Needs for Further Study

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

1. There is very little information about the adsorptive capacity of suspended matter for petroleum hydrocarbons. Some preliminary studies have shown that mechanically weathered riverborne suspended matter has very little capacity to adsorb certain dissolved aliphatic and aromatic hydrocarbons. However, not all terrestrially derived suspended matter from Alaskan rivers can be described as mechanically weathered rock debris; and therefore, we need to study the adsorptive characteristics of suspended matter from several other lease areas. We are presently initiating hydrocarbon and adsorption experiments on suspended matter from Lower Cook Inlet. Future studies should include studies on chemically weathered rock debris and studies on suspended particles having varying amounts of organic coatings.
2. The region west of Kayak Island is especially interesting for several reasons. This area is highly active biologically, including large concentrations of commercial fishes, crabs, seabirds, and marine mammals. Physical oceanographic studies of the area have indicated evidence for two gyres which rotate in opposite directions. Drogue studies have indicated that the waters within

the gyres may have residence times which are considerably longer than water from areas outside the gyres. It is highly possible that anthropogenic contaminants originating east of Kayak Island will probably be contained within the gyres for some time.

Future suspended matter studies in this region should include the use of sediment traps to determine particle fluxes and residence times. These measurements will provide valuable information about the mechanisms and time scales of contaminant transport through the water column.

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 and summer cruises and to deploy the WIST array.

B. Field Activities from 1 January-1 April 1977

1. Ship Schedule
   a. DISCOVERER Cruise (RP-4-Di-77A-III, 13-22 March 1977)
2. Participants from PMEL
   a. Dr. Richard A. Feely, Oceanographer
   b. Ms. Jane S. Fisher, Oceanographer
3. Methods
   a. Particulate Matter - Water samples were collected in 10-liter Niskin® bottles and filtered under vacuum through preweighed 0.4 μm Nuclepore® and Selas® silver filters. The filters were removed from the filtration apparatus, placed into individually marked petri dishes, dried in a desiccator for 24 hours and stored for shipment to the laboratory.

b. Nephelometry - The vertical distribution of suspended matter was determined with a continuously recording integrating nephelometer. The instrument was interfaced into the Plessey CTD system using the sound velocity channel (14-16 KHz) such that real time measurements of forward light scattering were obtained at each station.

C. Laboratory Activities from 1 January-1 April 1977

During the second quarter most of our laboratory work has been concerned with the analysis of the samples from the summer cruises. We have completed all of the weight determinations and analytical work. Data reduction is presently underway and the completed data will be 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 format 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 reported in a future report.

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Distribution of Light Hydrocarbons, C_1-C_4, in the Northeast Gulf of Alaska, Lower Cook Inlet, Southeastern Bering Shelf, Norton Sound and Southeastern Chukchi Sea

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April 1, 1977

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1. GENERAL SUMMARY

1.1 Objectives

The low molecular weight hydrocarbon program was initiated in 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, ethylene, propane, propylene, 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 monitored, they also provide a practical procedure by which the accumulation of petroleum hydrocarbons may be studied.

In support of the basic objectives, attention is being given to natural hydrocarbon sources, namely gas and oil seeps, production of hydrocarbons from near-surface sediments, and biogenic sources within the euphotic zone.

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 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 present findings indicates that the LMWH will be excellent tracers of petroleum input in the Bering Sea because of their naturally low ambient concentrations. Surface methane concentrations in the northeast Gulf of Alaska are higher and more variable than those observed in the Bering Sea, which will reduce its effectiveness as a tracer of petroleum. On the other hand, the concentrations of the C_2-C_4 fractions are extremely low, providing a monitoring team with excellent tag of petroleum or natural gas containing these components. Our studies have also shown that normal production of methane from shelf sediments can be traced for distances greater than 100 km from known sources. Based on these preliminary observations, it is concluded that surface exchange and *in situ* consumption of low molecular weight hydrocarbons may be sufficiently slow so as to allow them to be used as tracers of the soluble fractions of crude oil. 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.

The distribution of methane may also serve as a qualitative or semiquantitative measure of local circulation. If benthic fluxes can be estimated, together with *in situ* consumption rates of methane, subtle near-bottom circulation processes may be characterized that are not resolved readily by routine velocity field observations. A case in point is the near-bottom methane plume observed near Tarr Bank and the Copper River Delta.

2. INTRODUCTION

2.1 General Nature of Study

The development of petroleum resources in the Gulf of Alaska 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.

Petroleum contains three broad classes of compounds: alkanes, cycloalkanes, and aromatics, but not 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 (Wilson, 1975). By way of analogy, the analysis of the reservoir fluid of the Sadlerochit oil pool, Prudhoe Bay, shows a C_1-C_4 mole fraction of 54 percent (Anonymous, 1971). 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 cruide 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., 1973b).

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., 1973b).

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 and the southeastern Bering Sea. The objectives of the program are to determine the distributions and natural sources of methane, ethane, ethylene, propane, propylene, 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 successful implementation of this subprogram 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 dissolved hydrocarbon fractions because of the sensitivity of the method (i.e., parts per trillion), ease of the analysis, and real time data access. Utilizing a pumping system, sample processing, extraction and analysis can be readily accomplished in less than 30 minutes, or nearly in real time. This provides the monitoring team with the capability of ascertaining the time and space scales of the subsurface dispersion plume and to outline probable lateral boundaries for more detailed hydrocarbon sampling.

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. 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. CURRENT KNOWLEDGE

Prior to these investigations, no observations had been made on the ambient concentrations of LMWH in the Gulf of Alaska or the Bering Sea (Rosenberg, 1972). In contrast, a few analyses are available from Cook Inlet (Kinney et al., 1970). In this particular investigation, elevated concentrations of methane were observed in the vicinity of the Forelands, north of Kalgin Island, but no definitive conclusions could be drawn as to the probable source. Gas seeps were cited as a possible source, but biological methane production could not be ruled out. Unfortunately, the analysis of the C_2-C_4 fraction was not reliable; hence, confirming data on the possible source of the methane were not available.

Recent studies carried out by us in the northeast Gulf of Alaska and the southeastern Bering Sea have determined characteristic LMWH distributions for the spring, summer, and fall seasons. Local hydrocarbon sources have been identified and some measure of the diurnal variability documented. Both vertical and horizontal distributions are available from our observations. Details of our findings to date will be presented in sections 6 and 7 of this report.

4. STUDY AREAS

4.1 Bering Sea

Observations for LMWH were conducted according to the station grid shown in Figure 4-1. The PMEL survey grid was developed primarily for the suspended particulate matter program, but because of its uniform coverage it was adopted as an operational grid for hydrocarbons as well. The PMEL grid was supplemented by observations from the Institute of Marine Science (IMS) cruise track, which increased the areal coverage toward the west. During the fall of 1975, a total of 80 stations were occupied, 69 of which (51 PMEL and 18 EBBS stations) were sampled in vertical profile. Because of the shallow depths encountered in Bristol Bay, 3-4 nominal depths were selected at each station. The remaining 18 PMEL stations were invoked to investigate the surface transport of LMWH from Izembeck Lagoon. Only surface samples were acquired at these stations. The survey grid shown in Figure 4-1 was also occupied in June-July of 1976, during which time early summer conditions were established. A total of 55 stations were occupied at that time. Cruise logistics and sampling protocol are shown in Table 4-1 for all observation periods in southeastern Bristol Bay.

4.2 Northeast Gulf of Alaska

Observations for LMWH were conducted at the stations shown in Figure 4-2. The grid shown in Figure 4-2 was developed primarily to investigate the distributions of suspended particulate matter, but because of its uniform coverage it was adopted as an operational sampling grid for hydrocarbons as well. The northeast Gulf of Alaska, including a preliminary effort in lower Cook Inlet, was sampled during late fall in 1975, then again in spring and summer of 1976. Approximately 50 stations were occupied in vertical profile during each visit, with 5-6 discrete depths being sampled at each station. Surface and near-bottom

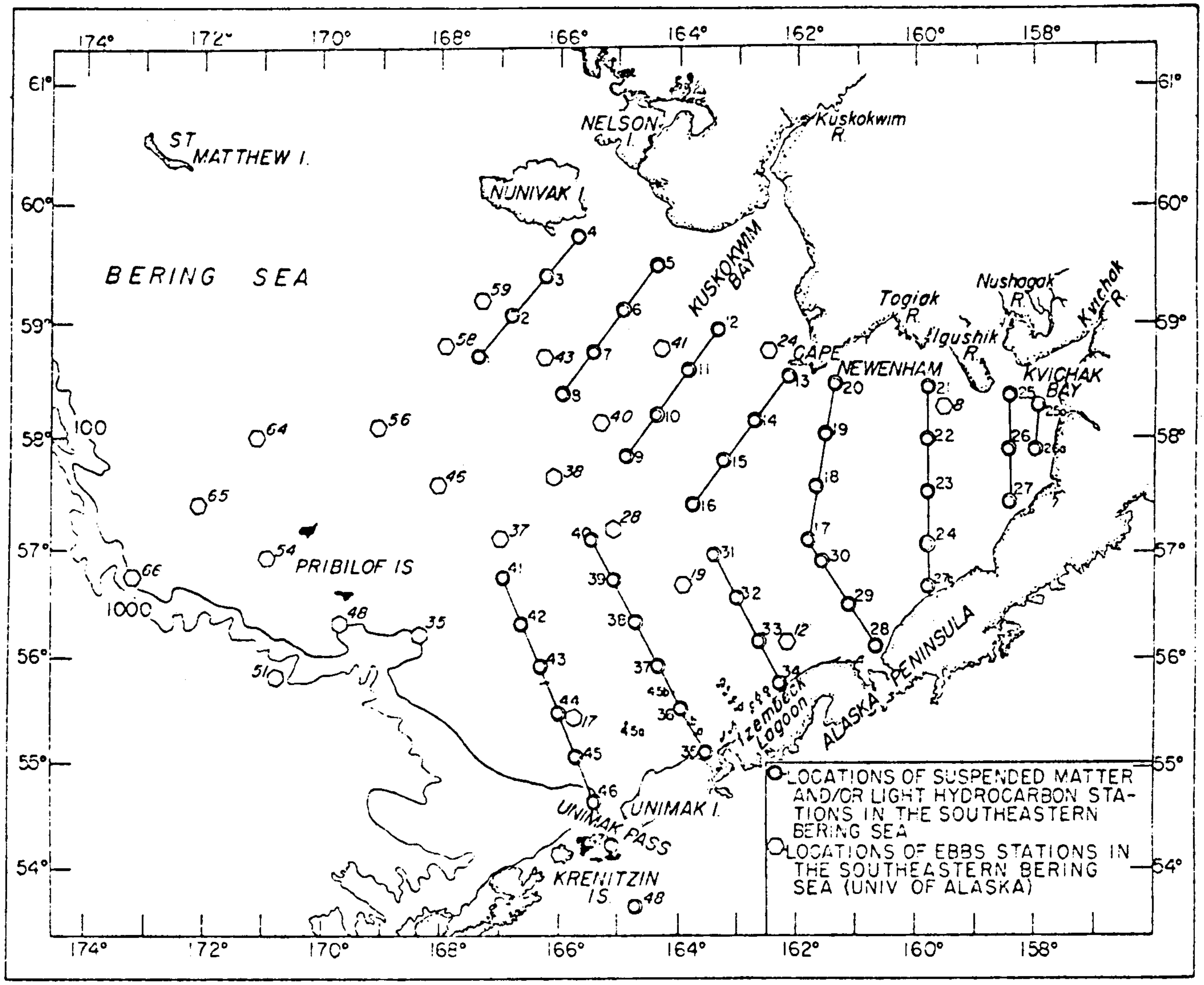


Figure 4-1 Station locations in the southeastern Bering Sea. The PMEL grid is denoted by 0; the IMS grid by ⬡. Surface stations near Izembeck Lagoon are shown in lowercase letters (i.e., a,b,c, etc.)

Table 4-1 Summary of the sampling protocol and cruise logistics for all field expeditions except Lower Cook Inlet

	Southeastern Bering Shelf		Northeast Gulf of Alaska			Norton Sound Chukchi Sea
Activities	RP-4-DI-75B-3 9/14/75-10/1/75	RP-4-MW-76B-8 6/25/76-7/8/76	RP-4-DI-75C-1 10/21/75-11/9/75	RP-4-DI-76A-4 4/13/76-4/30/76	RP-4-DI-76B-1 7/19/76-7/31/76	RP-4-DI-76B-4 9/8/76-9/24/76
Stations Occupied	72[c]	55	51	47	47	79
Miles of Trackline	1740	2827[a]	1075	3100	1354	2440
Samples Analyzed	316	319[b]	274	355	276	339
Standards Analyzed	64	68	80	94	55	125
Reproducibility Studies	3	4	3	2	3	8
Number of Analyses	9	11	9	9	12	32
Time Series	2	0	2	1	0	2
Obs. Freq./Duration	4 hr/36 hr	-	4 hr/36 hr	2 hr/64 hr	-	2 hr/24 hr
Number of Analyses	73	-	84	107	-	78

[a] This figure includes approximately 600 miles of surface profiling in the western Gulf between Kodiak and Unimak Pass.

[b] This total includes 86 analyses performed during surface transects in the western Gulf and western Bristol Bay near the Pribilof Islands.

[c] Of this total, 29 surface stations were occupied near Izembeck Lagoon.

samples (bottom -5 m) were taken uniformly at each station. Cruise logistics and sampling protocol are shown for all NEGOA cruises in Table 4-1.

An attempt was made to identify gas seeps or gas-charged sediments along the southeast site of Kayak Island. However, the probable locations were in shallow, uncharted depths and it was not possible to sample the proposed sites without endangering the vessel (RP-4-DI-75C-1, October 21, 1975 thru November 9, 1975).

4.3 Lower Cook Inlet

Observations by LMWH were conducted at the stations shown in Figure 4-3. This field exercise was hastily assembled and piggybacked on a PMEL biological cruise (RP-4-DI-76A-3, April 5-12, 1976). Only 9 stations were occupied in vertical profile at that time with 38 samples analyzed. Intensive areal coverage is contemplated for spring and summer of 1977.

4.4 Norton Sound and Southeastern Chukchi Sea

Observations for LMWH were conducted in Norton Sound and the southeastern Chukchi Sea in September of 1976. The station locations are shown in Figures 4-4 and 4-5 and represent a standard 30 nm sampling grid. During the survey of Norton Sound, a detailed grid (i.e., 5 nm grid) was implemented in the region directly south of Nome to delineate the extent and source of LMWH observed there. This sampling grid is shown in Figure 4-6.

Because of the shallow water depths over most of the survey region, vertical sampling was conducted at 3 to 4 discrete depths.

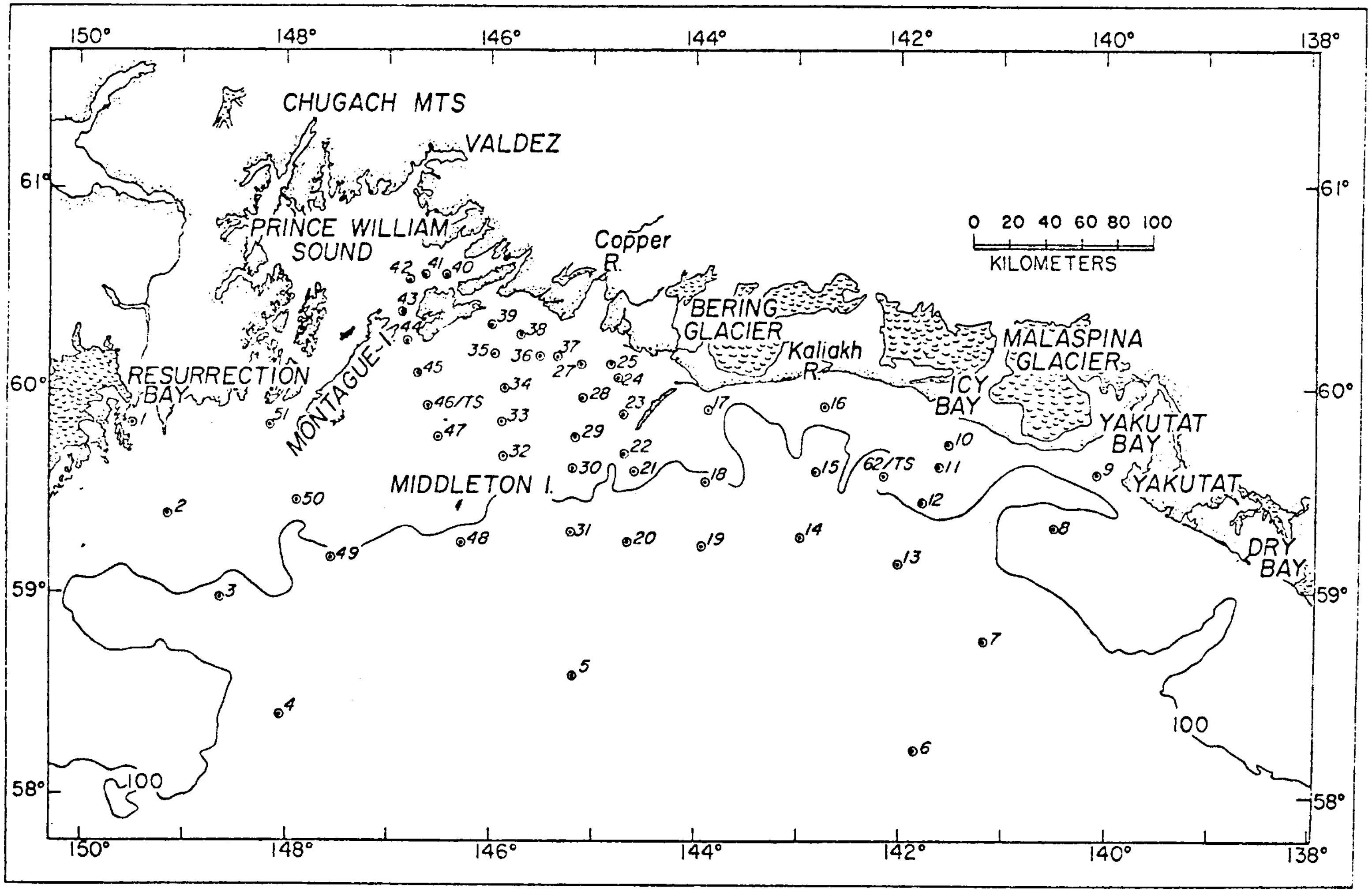


Figure 4-2 Station locations in the northeastern Gulf of Alaska. Investigations of gas-charged sediments near Kayak Island were conducted near station 22.

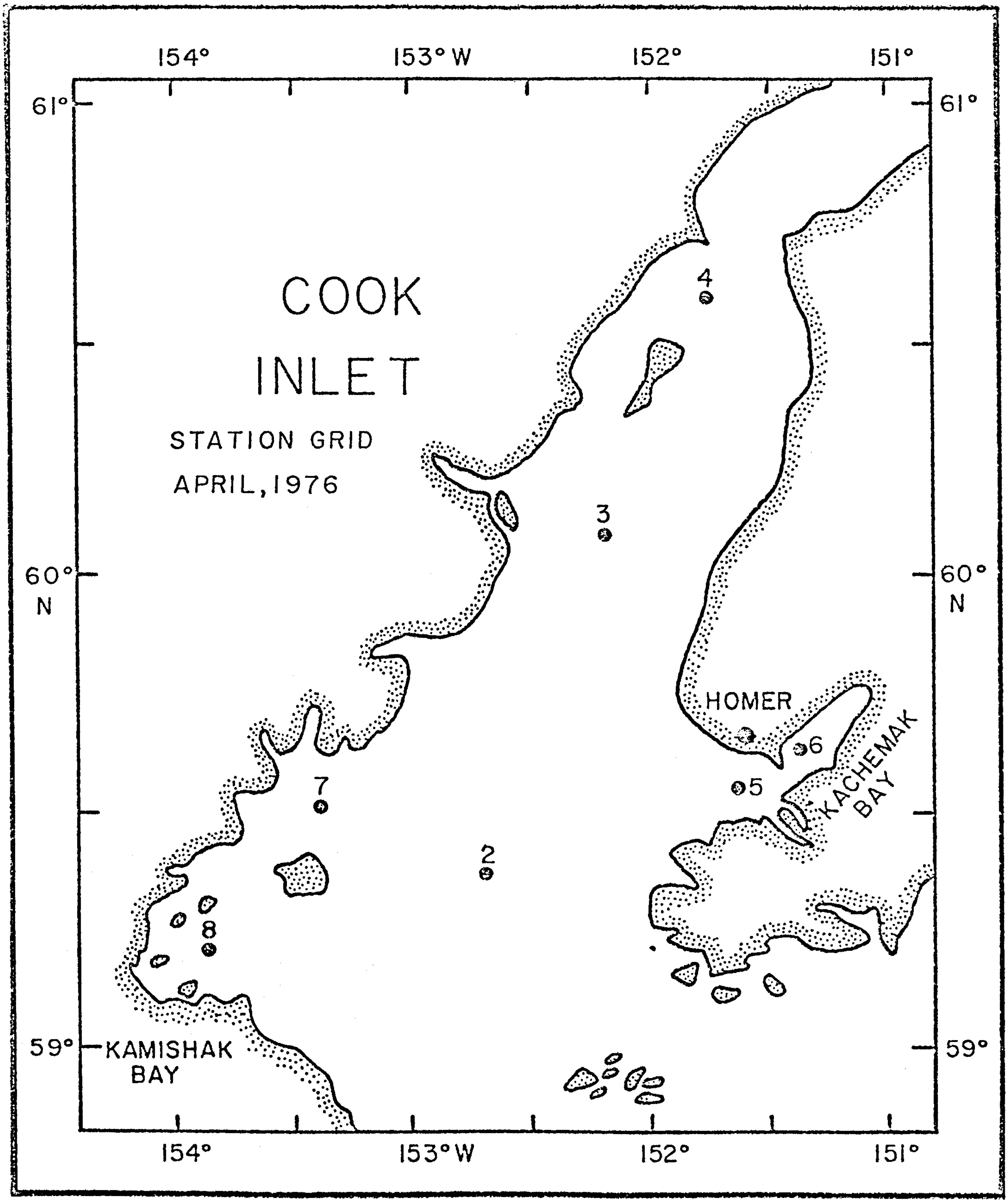


Figure 4-3 Sample locations in Lower Cook Inlet during April 1976.

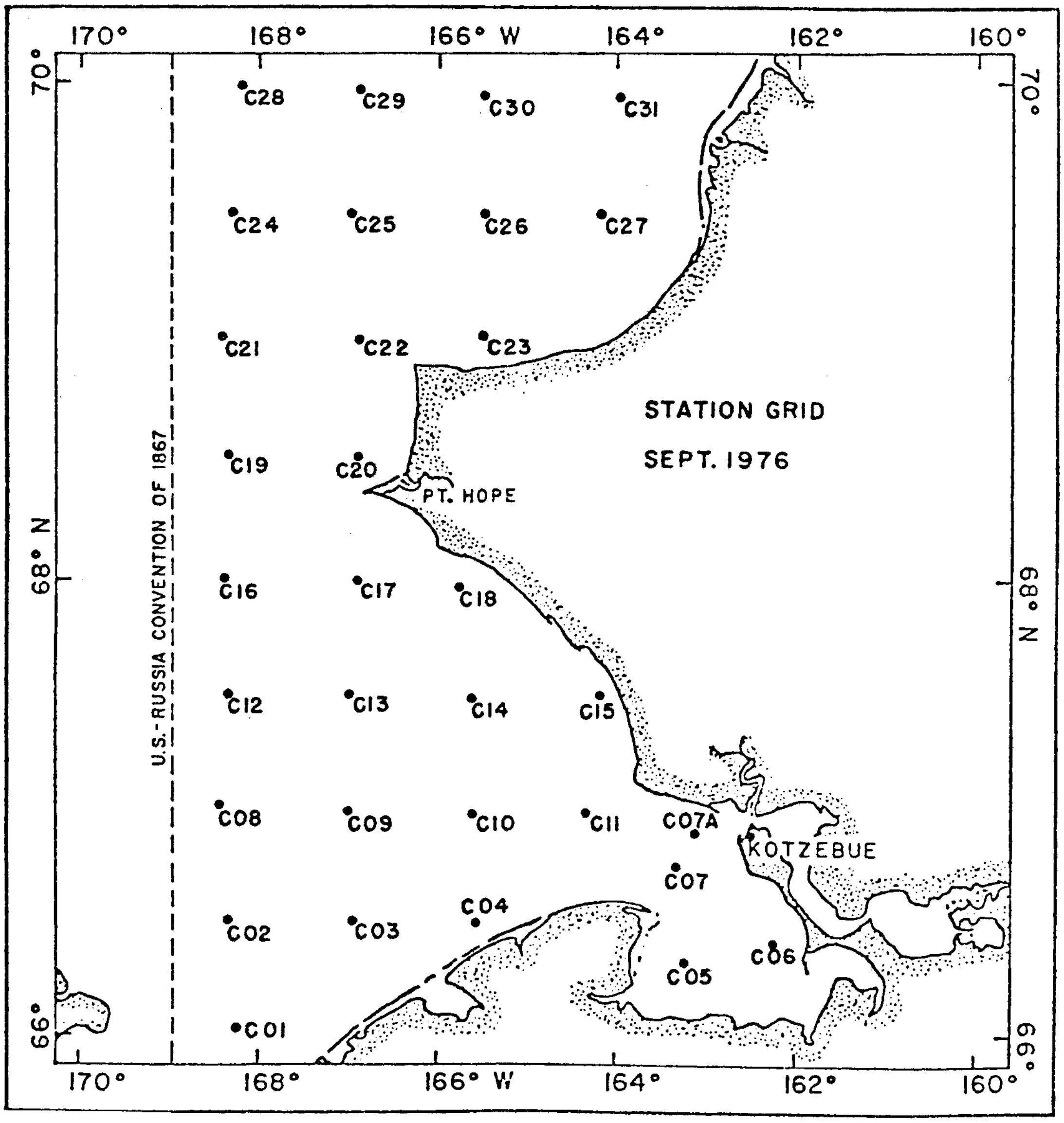


Figure 4-4 Station locations in southeastern Chukchi Sea and Lotzebue Sound.

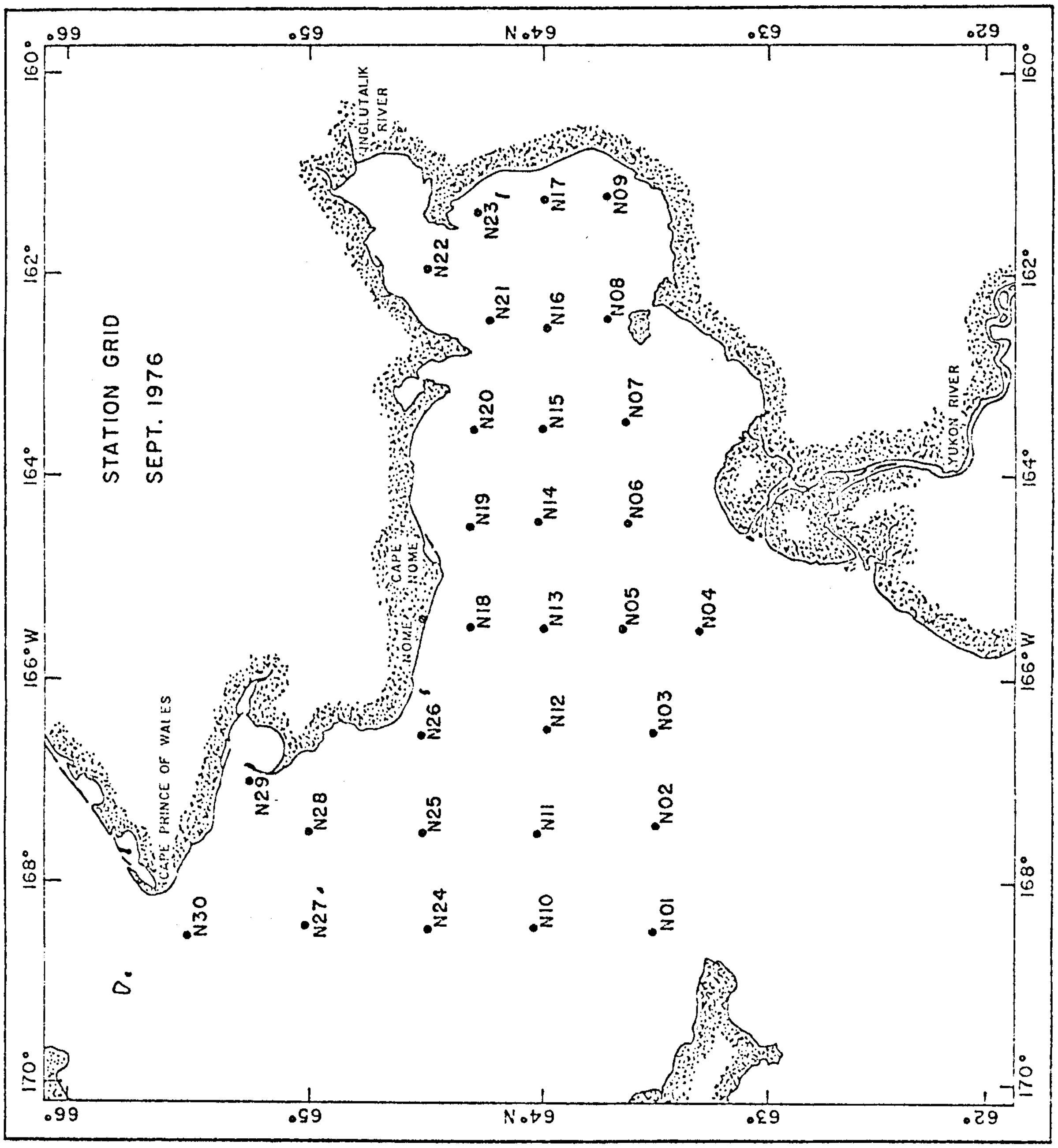


Figure 4-5 Station locations in Norton Sound and northern Bering Sea.

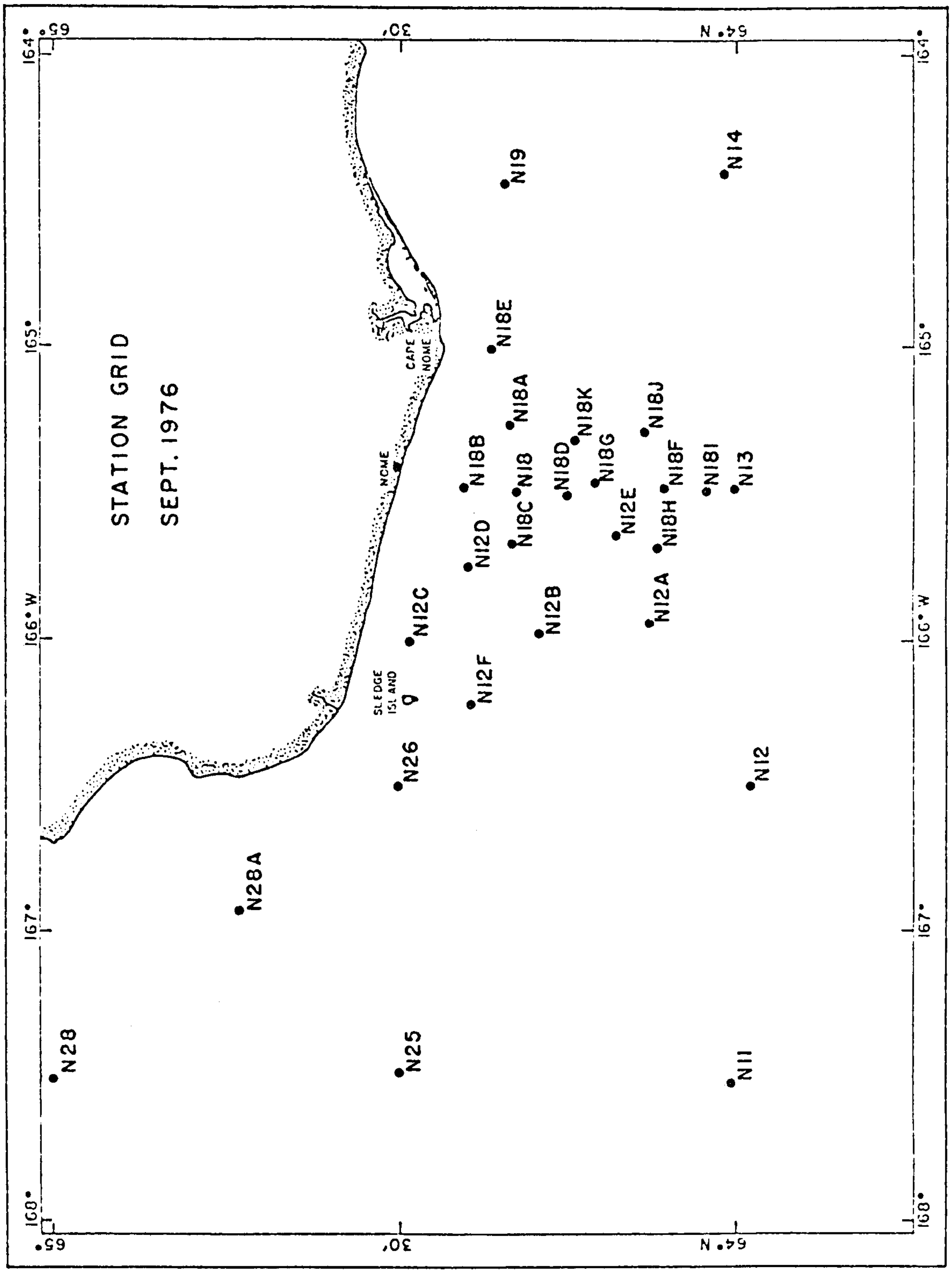


Figure 4-6 Station locations in the vicinity of the gas seep.

5. METHODOLOGY

5.1 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 5-1. Although the system actually used in these studies is somewhat simpler in detail than that shown in Figure 5-1, the principle remains the same.

Hydrocarbons are removed in a stream of ultra-pure He (120-140 ml/min) and condensed 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 allowed to pass into the gas chromatograph (GC).

5.2 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 60 ml/min and detected sequentially as they emerge from the columns. In order to obtain optimum peak resolution between the alkanes and alkenes, 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 110-150°C, has resulted in sharper peaks, better separation and reduced retention times for all components (Figure 5-2). The GC utilized was a Hewlett Packard® model 5711, equipped with dual FID's.

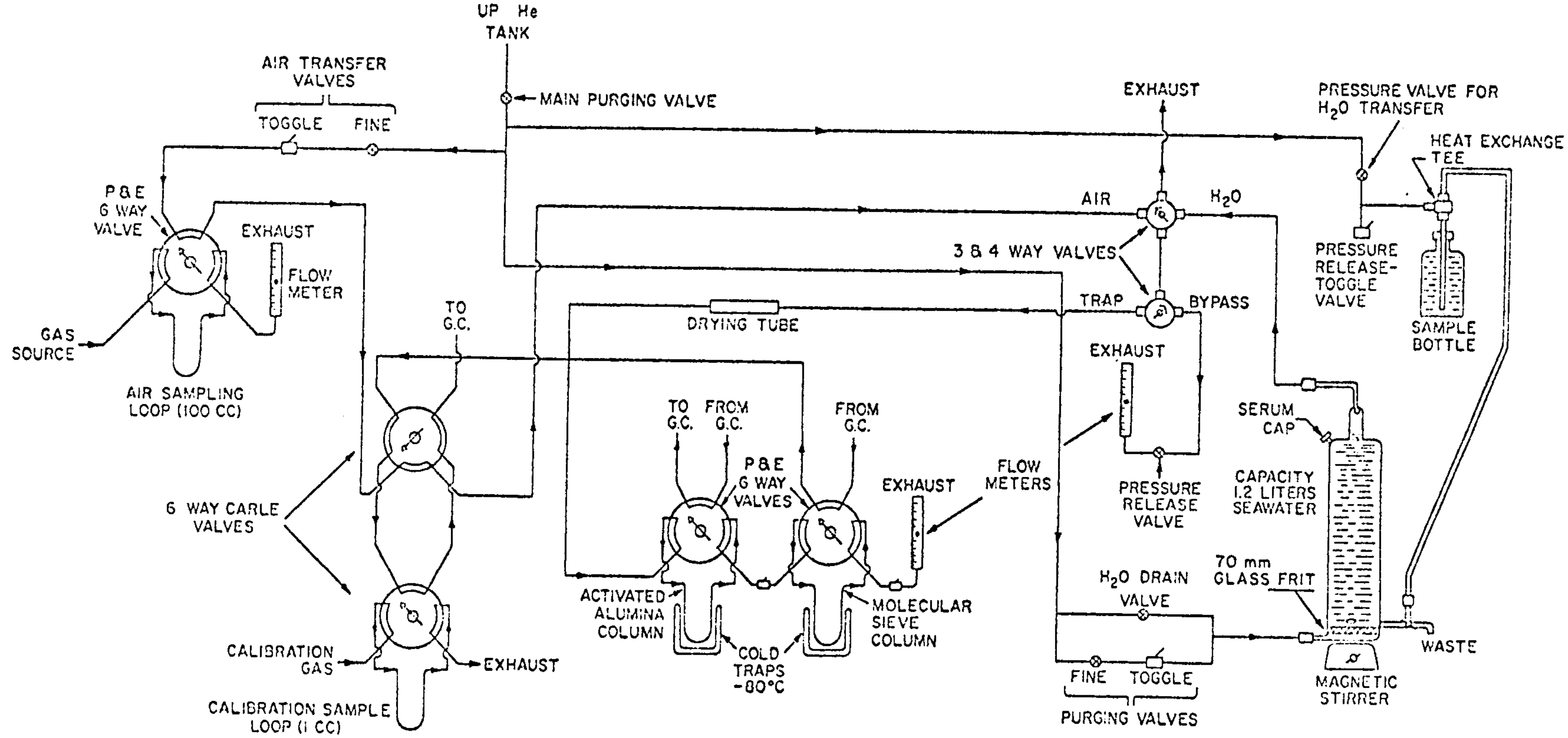
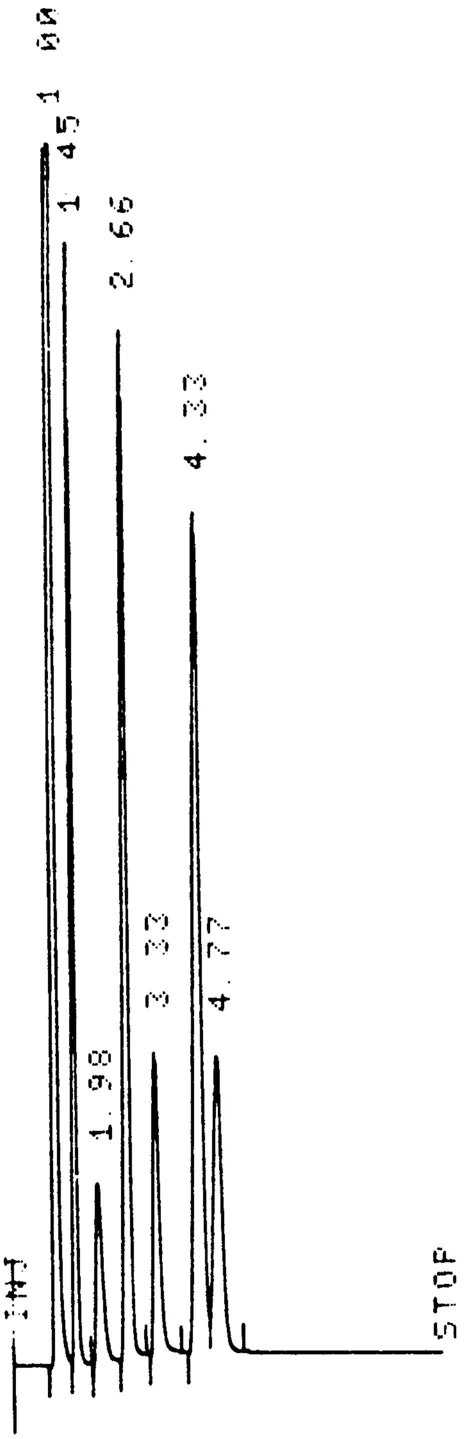


Figure 5-1 Low molecular weight hydrocarbon extraction system (Swinnerton and Linnenbom, 1967; Swinnerton et al., 1968). The extraction system shown is a recent modification given to us by Mr. R. Lamontagne of the Naval Research Laboratories, Washington, D.C.



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RT     TYPE     AREA

1.00            173637
1.45    M        15983
1.98              5919
2.56    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 5-2 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.

5.3 Data Quality Control

5.31 Accuracy

The LMWH analysis was referenced to specially prepared hydrocarbon mixtures supplied and certified by Matheson Gas Products. The concentrations of the 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 5-1. 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 5-1 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

5.32 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 5-2, 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 5-3 in terms of the mean concentration ($\overline{X}$) and the relative error. Ignoring the results obtained for the butanes, since their concentration was everywhere at or below the detection limit (~ 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. Precise measurement of low concentrations of iso- and n-butanes presented a problem, primarily because of inherent difficulties in obtaining quantitative stripping of the C_4 fraction.

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 5-4, methane - 0.12 nℓ/ℓ, ethane - 0.06 nℓ/ℓ, ethylene - 0.07 nℓ/ℓ, propane - 0.04 nℓ/ℓ, propylene - 0.04 nℓ/ℓ, isobutane - 0.03 nℓ/ℓ, and n-butane - 0.03 nℓ/ℓ.

Table 5-2 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 5-3 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	-	-

Table 5-4 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

5.4 Data Collection Rationale

The original scope of the baseline study was to determine horizontal, vertical, and seasonal variations of LMWH in the study areas as a precursor to petroleum development. Stress was placed on the distributions of ethane, propane, and butanes as their presence in elevated amounts is much stronger evidence for petroleum hydrocarbon input. The investigation of seeps was only tangentially approached as our sampling grid was not "tight" enough to unequivocally locate seeps. We did, however, attempt to locate seeps along the 10-fathom fault line southeast of Kayak Island with a dedicated 12-hour study (Carlson et al., 1975).

In addition to the baseline survey, two 36-hour time series stations were planned in each area, although time restriction prohibited us, in some instances, from effecting this aspect of the program. The purpose of these investigations was to ascertain the short-term temporal changes in hydrocarbons, and thereby establish normal ambient variability against which future observations might be compared.

Ethylene and propylene, while not characteristic components of natural gas or petroleum, were determined routinely in conjunction with the normal aliphatic components. Chromatographic separation of the olefins from the parent aliphatics results in a more accurate assessment of the concentrations of the latter, since the alkenes are usually found in greater amounts. It will be shown later in the discussion that the $C_{2:0}/C_{2:1}$ and $C_{3:0}/C_{3:1}$ ratios are reliable indicators of petroleum hydrocarbons because of the absence of the unsaturates in petroleum.

In addition to the investigations carried out on the distribution of LMWH, considerable effort was mounted to elucidate natural hydrocarbon sources. To accomplish this, surface- and near-bottom samples were taken. In the Gulf of Alaska, sampling of the surface layers was carried out in conjunction with the productivity observations to ascertain possible hydrocarbon input due to photosynthetic or related biological processes. Near-bottom samples were taken to characterize hydrocarbon sources in sediments. The origin of natural hydrocarbons, together with their variability, must be understood before effective monitoring measures can be effectively mounted.

6. RESULTS

6.1 NEGOA, Southeastern Bering Sea, Lower Cook Inlet, Norton Sound, and Chukchi Sea

The last general field survey was completed in Norton Sound and the Chukchi Sea in September 1976. The results of these field activities have been reported sequentially in previous quarterly and annual reports and will not be repeated here. In lieu of that procedure, the discussion section which follows will dwell on the important features of the LWMH distributions observed seasonally in some of these areas and will attempt to present a summary of our findings relevant to environmental problems associated with petroleum development. In the development of the discussion section, to be treated geographically by area, we will rely largely on the previously presented illustrations.

7. DISCUSSION

7.1 Southeastern Bering Sea (Bristol Bay)

Observations for LMWH were conducted in September-October 1975 and again in June-July of 1976. These measurements represent conditions as they existed during the fall and summer seasons. Sampling protocol and sample analysis were similar on both occasions.

7.11 Methane

The areal distribution of methane at the surface and near the bottom is shown in Figures 7-1 thru 7-4. Surface methane concentrations in the fall of 1975 were generally low, near saturation values with respect to the atmosphere, and generally reflected the quiescent biological condition existing at that time (Figure 7-1). Surface equilibrium values should fall in the range of 50-70 nℓ/ℓ (Lamontagne et al., 1973a). Only near Herendeen Bay were the concentrations considerably above saturation values, presumably from biogenic sources within the embayment.

In contrast, methane concentrations in the surface layers during the following summer were considerably above saturation, particularly near Herendeen Bay (Figure 7-2). 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, 1976a).

Near-bottom conditions for the two seasons are shown in Figures 7-3 and 7-4. The strong source of methane that was observed in the area of the Golden Triangle in the fall of 1975 was not observed in the summer of 1976. This would imply that circulation was less vigorous in the fall compared to conditions

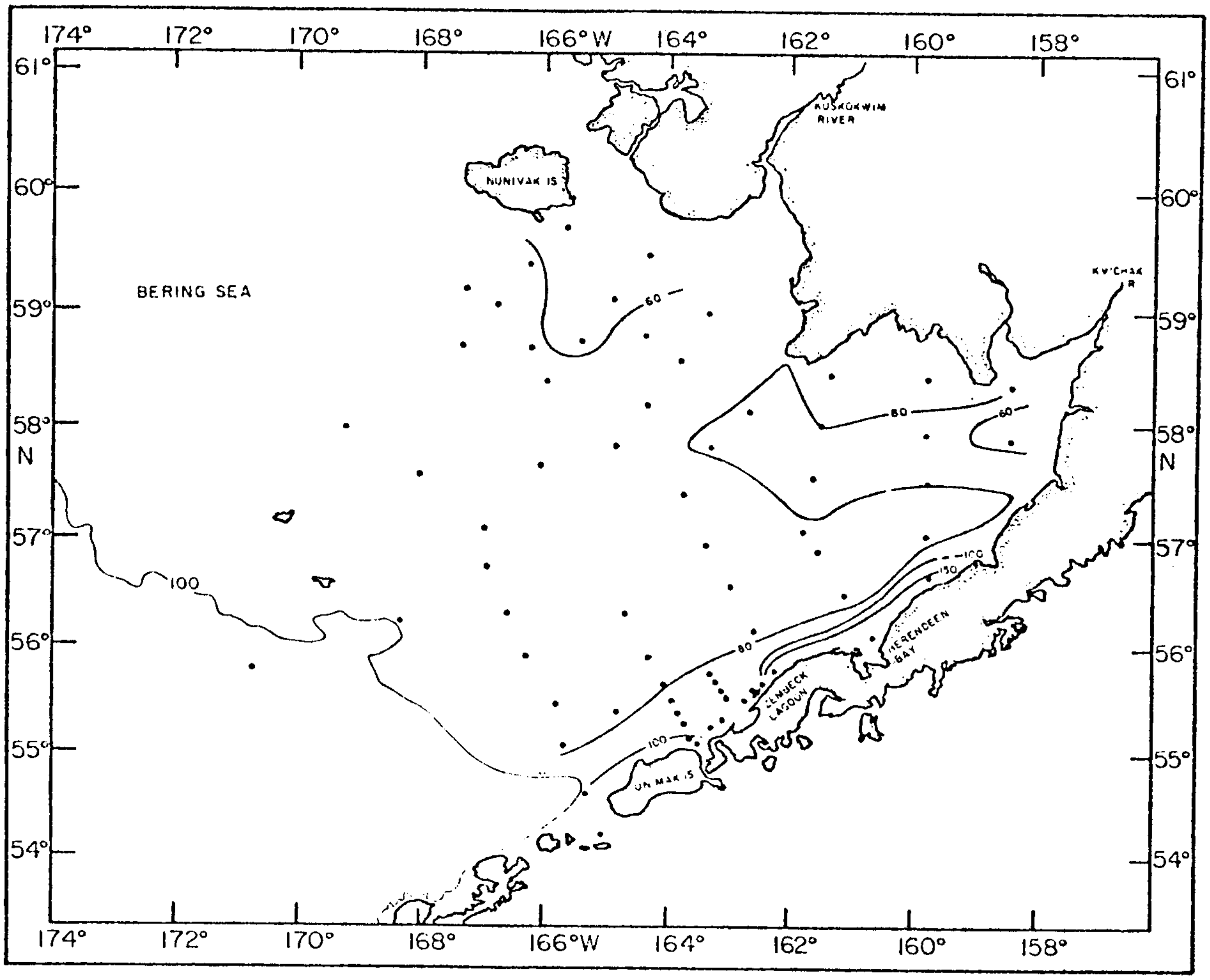

Figure 7-1 Areal distribution of methane in surface waters during Sept.-Oct. 1975. Concentrations are expressed in $n\ell/\ell$ (STP).

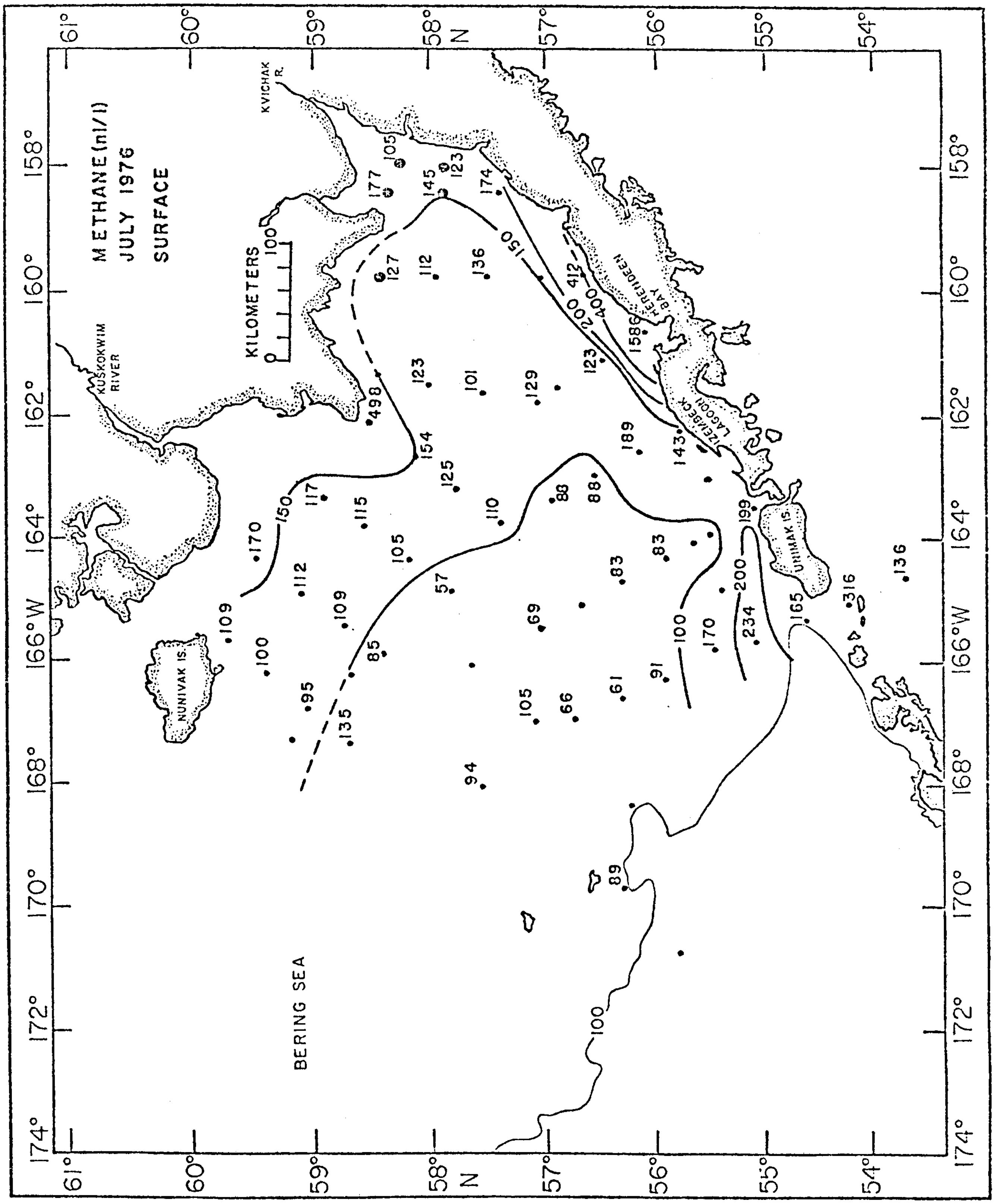

Figure 7-2 Areal distribution of methane within 5 m of the bottom in June-July 1976. Concentrations are expressed in nℓ/ℓ (STP).

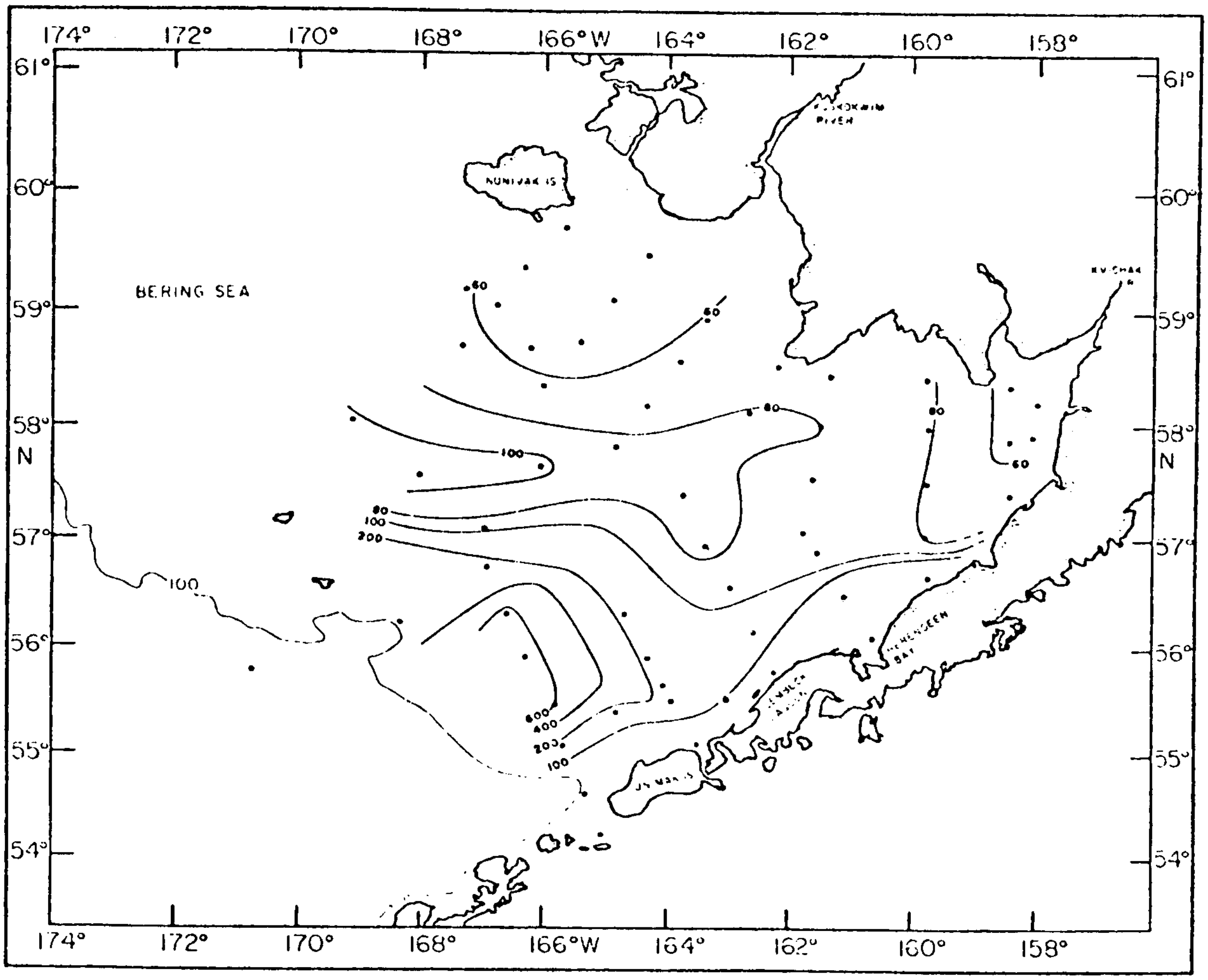

Figure 7-3 Areal distribution of methane 5 m from the bottom during Sept.-Oct. 1975. Concentrations are expressed in nℓ/ℓ (STP).

existing in summer of the following year. It might also be the result of a diminished bottom source during summer, although this is difficult to envision. With the aforementioned exception, the concentrations of methane near the bottom were systematically higher than those observed in the fall of 1975 (Figure 7-4), 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 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 originating from the surface layers.

7.12 Ethane

Seasonal distributions of ethane in both the surface layers and near the bottom are shown in Figures 7-5 thru 7-8. Surface concentrations of ethane showed little spatial variability for the two seasons, although significant increases were observed during the summer season (Figures 7-5 and 7-6). Concentrations averaged about 0.5 nℓ/ℓ during the fall of 1975, and between 0.3 and 2.9 nℓ/ℓ during the summer. The large increase observed in the eastern portion of Bristol Bay is related to high levels of primary productivity (Cline and Feely, 1976; Figure 7-6). It appears that ethene, arising from biochemical

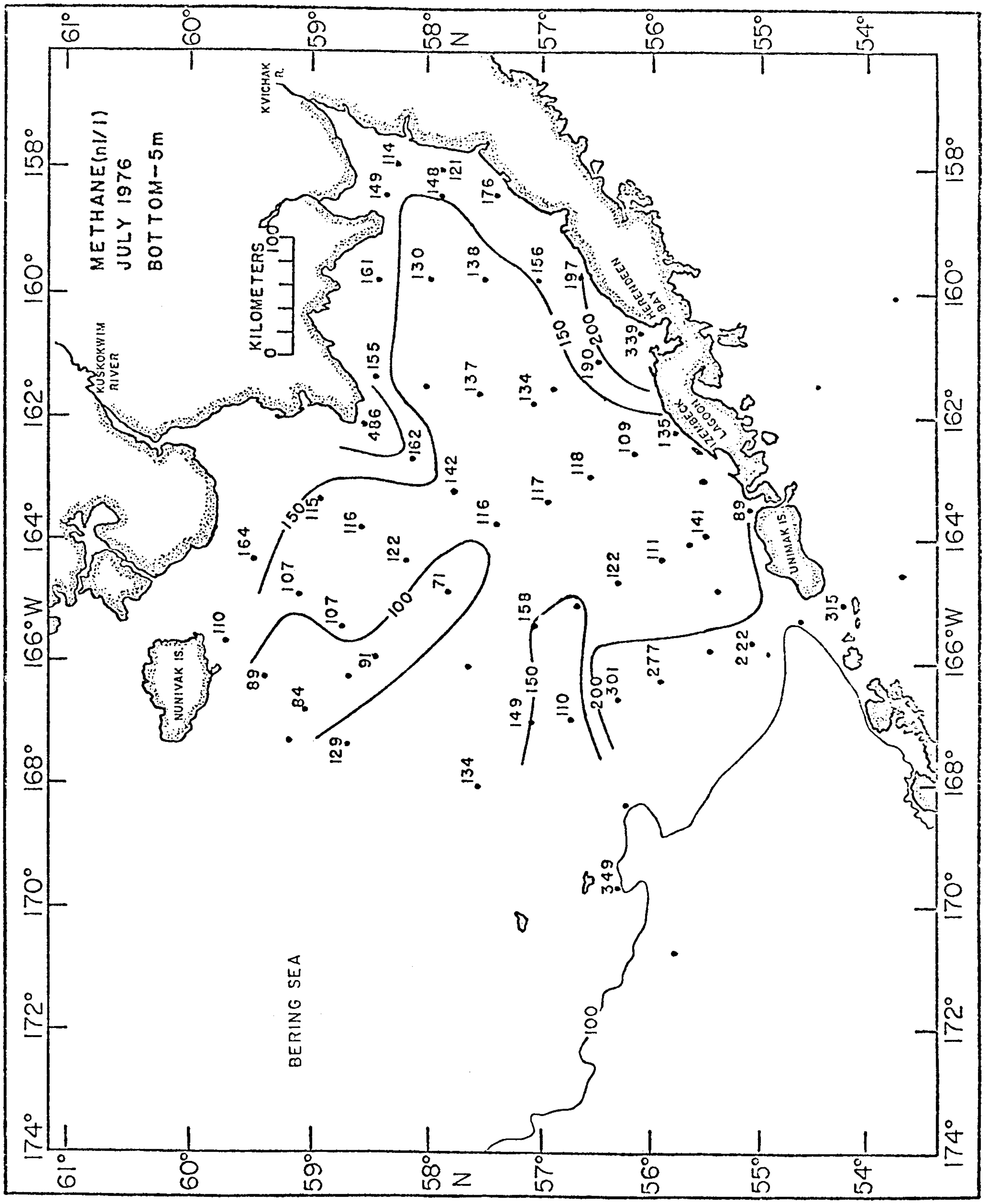

Figure 7-4 Areal distribution of methane within 5 m of the bottom in June-July 1976. Concentrations are expressed in nℓ/ℓ (STP).

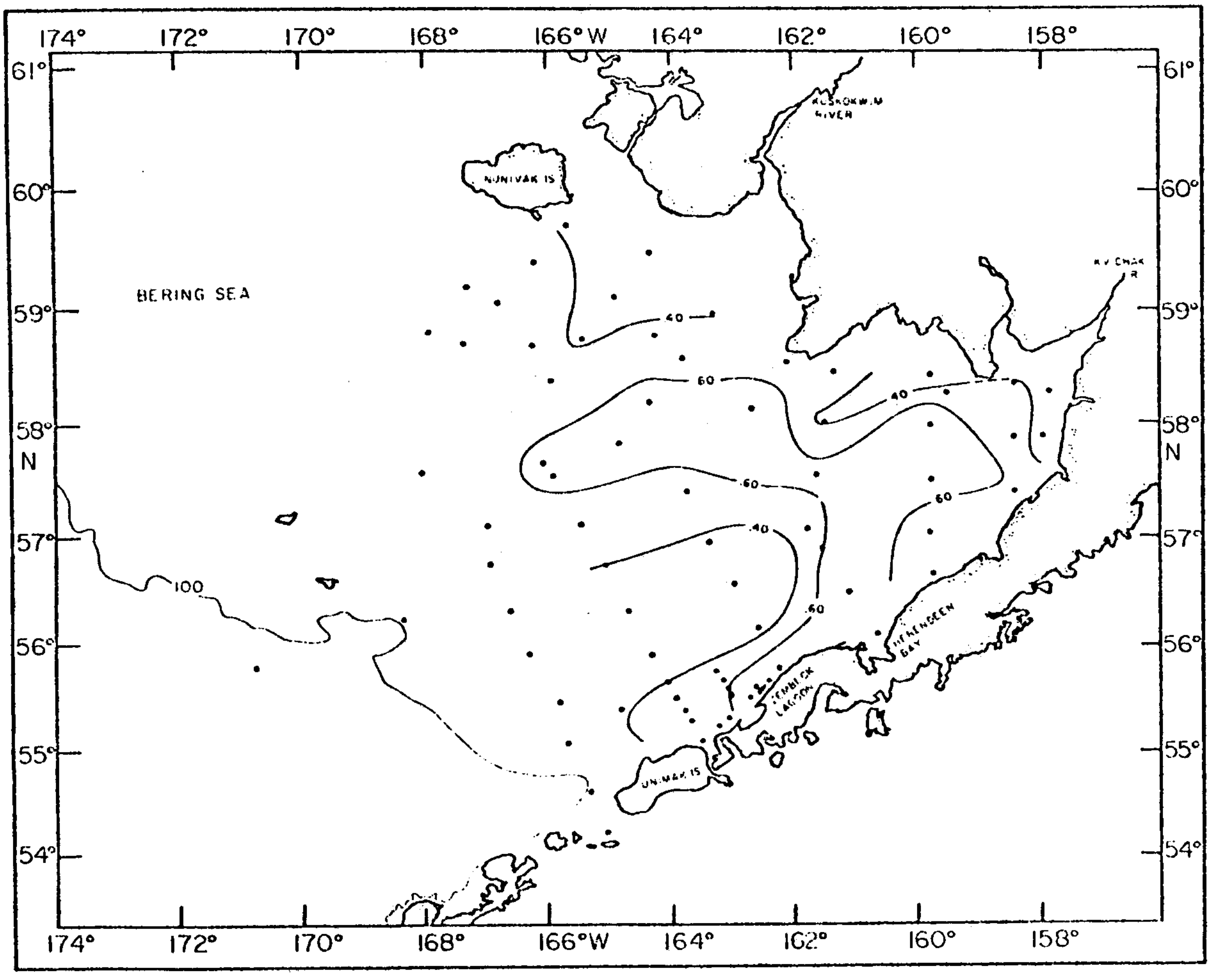

Figure 7-5 Areal distribution of ethane in surface waters during Sept.-Oct. 1975. Concentrations are expressed in nℓ/ℓ (STP).

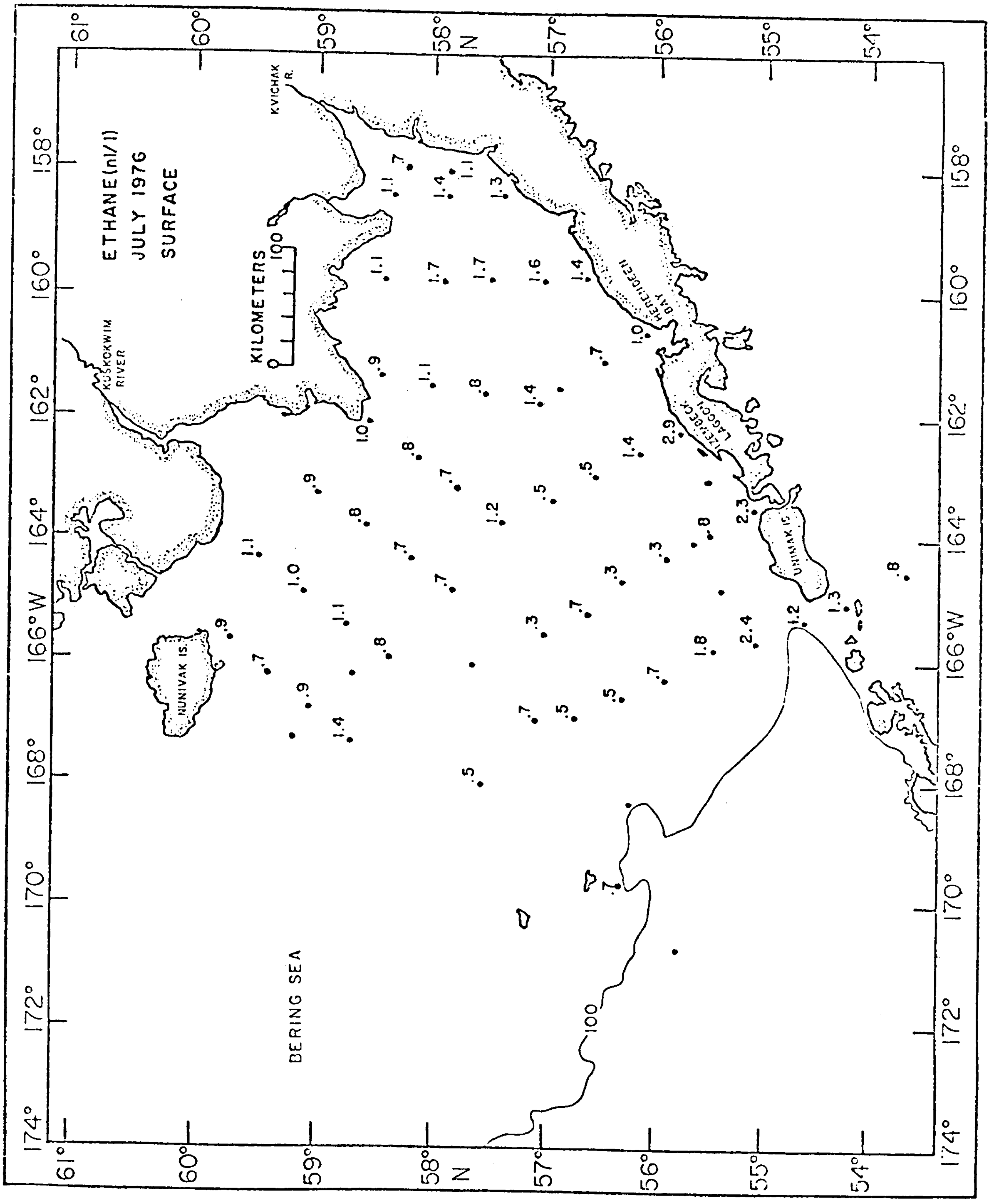

Figure 7-6 Areal distribution of ethane in surface waters during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

processes associated with primary production, is reduced to ethane in the surface layers (Figure 7-9; J. Brooks, Texas A&M, personal communication). Thus, we feel that the high surface signature of ethane does not imply a petroleum source, when accompanied by similarly elevated concentrations of ethene.

Based on these limited observations, we would expect surface concentrations of ethane to vary seasonally from approximately 0.3 to 3 nℓ/ℓ. As we shall see later, the crucial factor is the $C_{2:0}/C_{2:1}$ ratio, not the absolute concentration of ethane.

In the fall of 1975, the near-bottom concentration of ethane varied from 0.5 nℓ/ℓ to approximately 1 nℓ/ℓ (Figure 7-7). A similar pattern was observed during the following summer, except the near-shore areas of the Alaskan Peninsula showed marked increases, which correlate reasonably well with near-bottom methane concentrations. The region near Izenbeck Lagoon was particularly unusual, because methane concentrations in this region did not appear to be excessively high. However, the near-bottom concentration of ethene was high and the $C_{2:0}/C_{2:1}$ was less than 1. In fact, the elevated concentration of ethene near the bottom was strikingly high all along the perimeter of Bristol Bay (Figure 7-10). We assume that not unlike that observed in the surface layers, the ethane has arisen from the biochemical reduction of ethene to ethane.

Our observations would suggest that the ethane concentration would range seasonally from 0.5 nℓ/ℓ to a high of nearly 3 nℓ/ℓ; the higher values being indicative of general increased levels of primary production and the attendant production of organic carbon.

7.13 Propane and Propene

The seasonal distributions of propane in both the surface and near-bottom layers are shown in Figures 7-11 thru 7-14. Surface concentrations were exceedingly low during both seasons, although slightly higher in the summer months

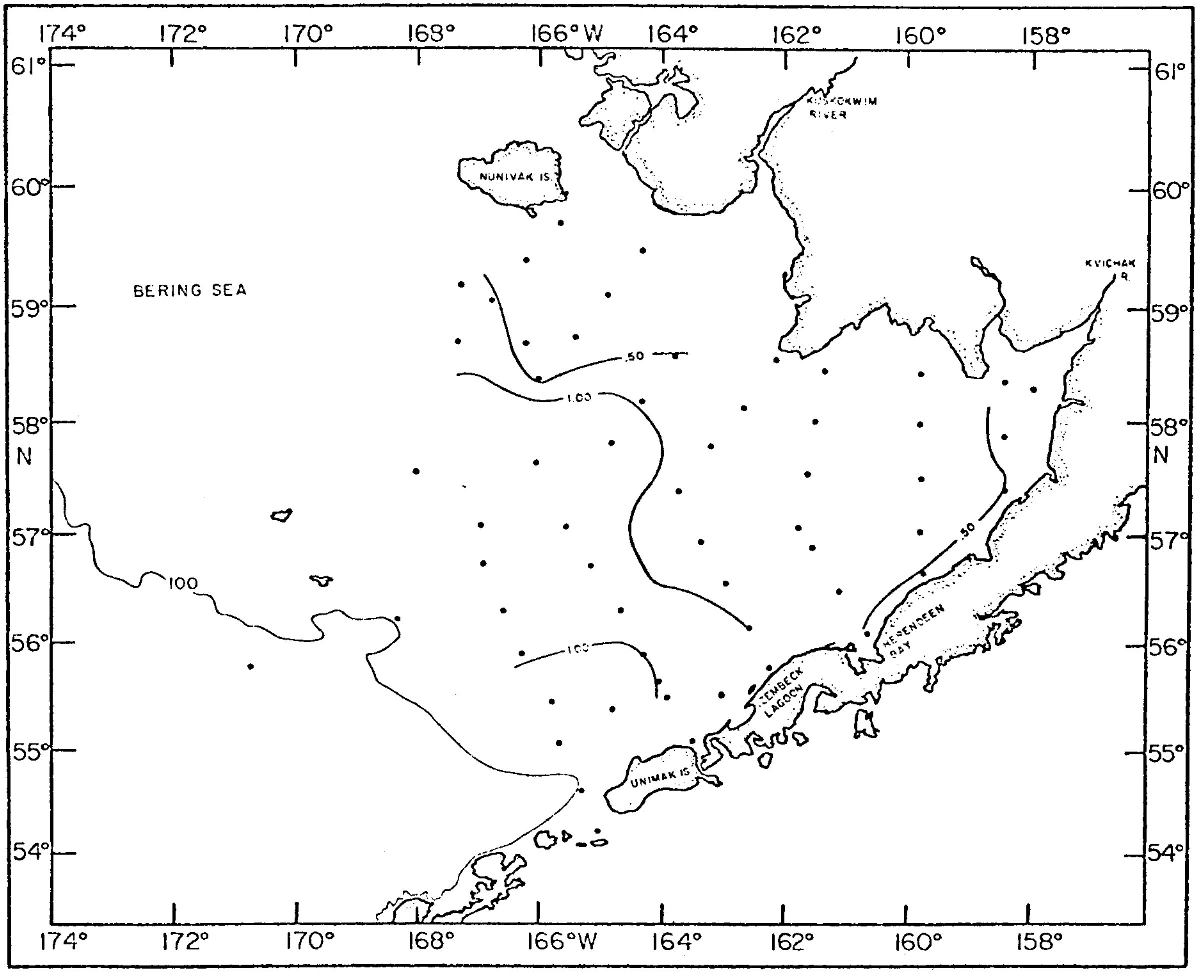

Figure 7-7 Areal distribution of ethane 5 m from the bottom during Sept.-Oct. 1975. Concentrations are expressed in nℓ/ℓ (STP).

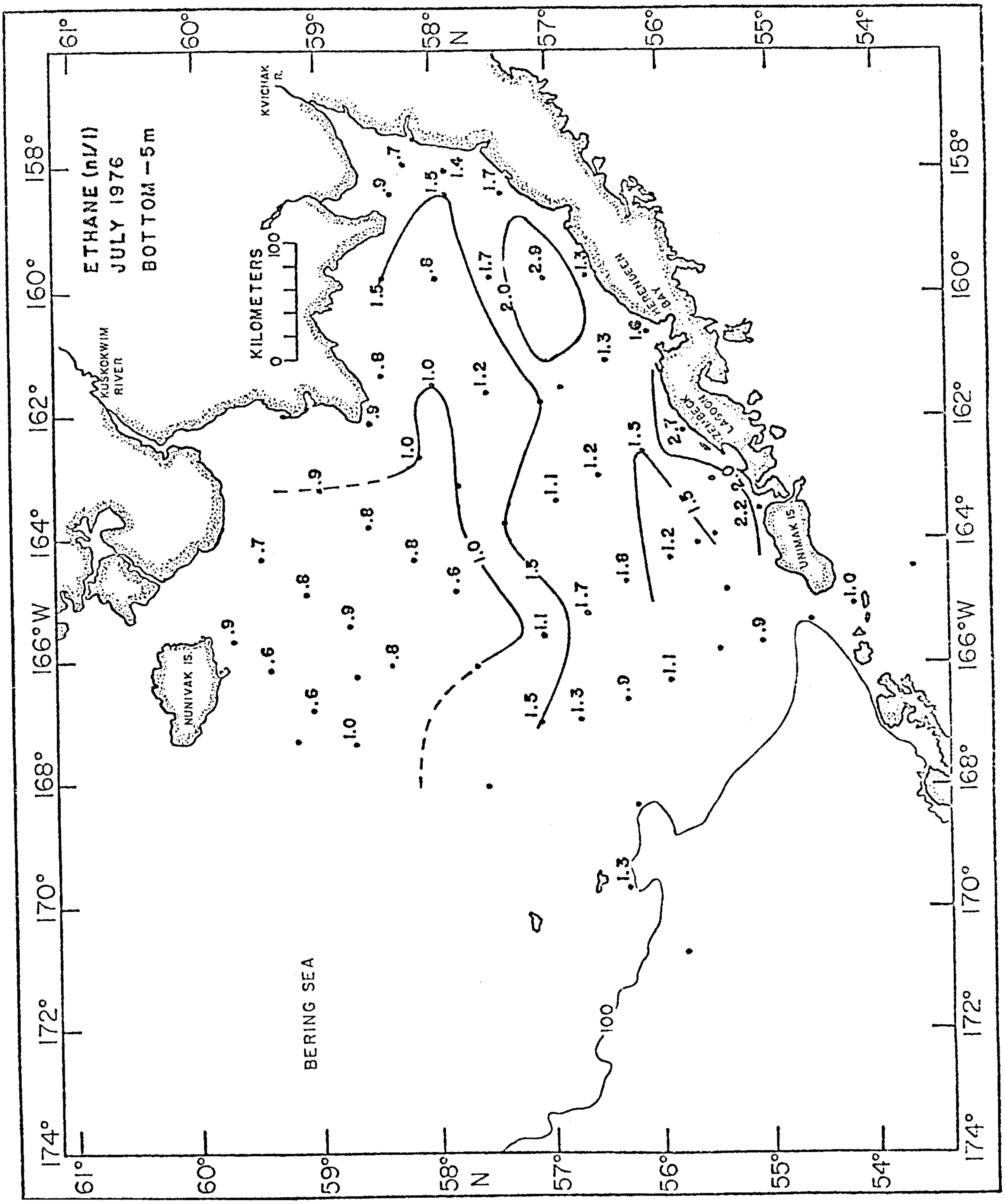

Figure 7-8 Areal distribution of ethane within 5 m of the bottom in July 1976. Concentrations are expressed in nℓ/ℓ (STP).

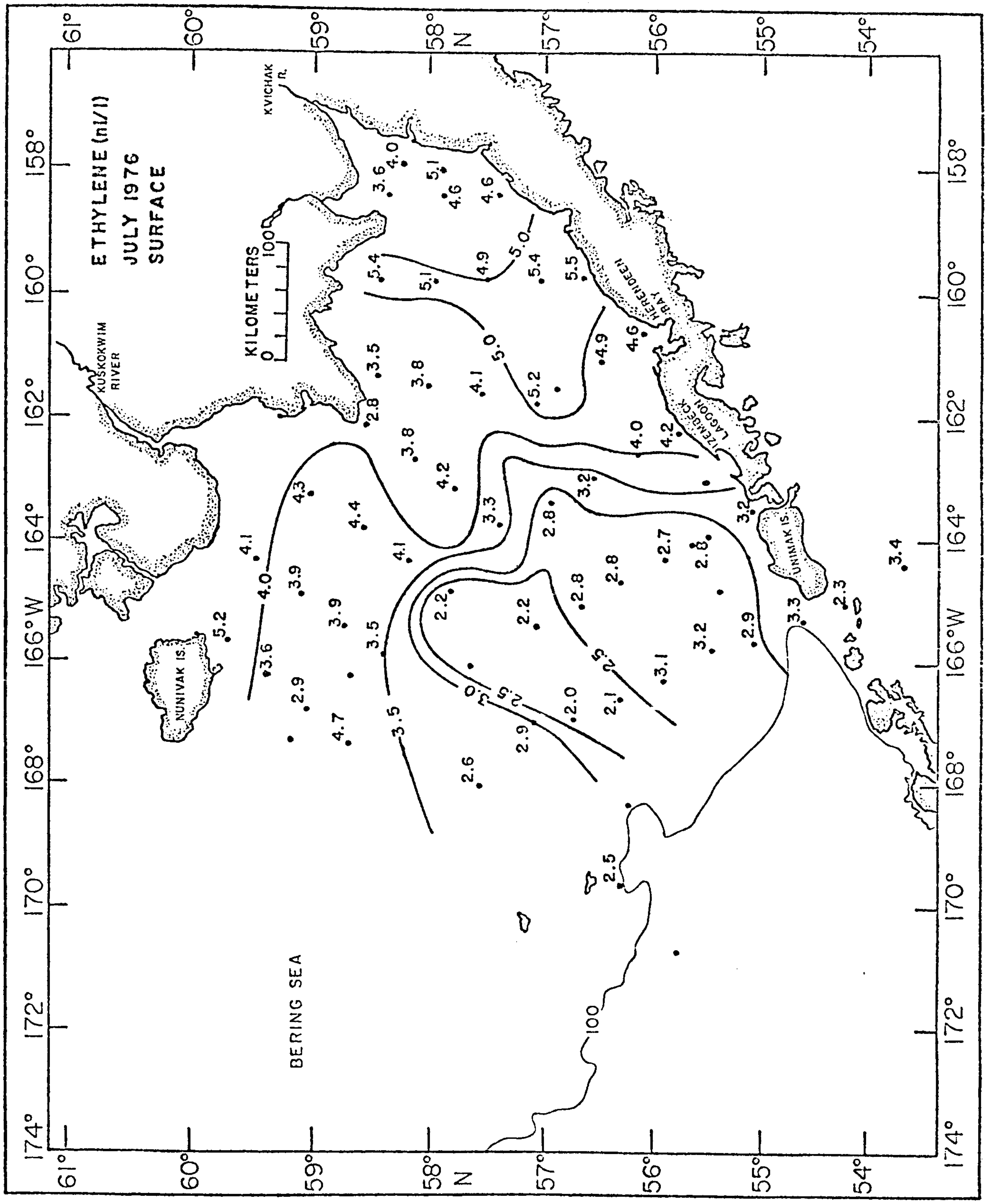

Figure 7-9 Areal distribution of ethene in surface waters during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

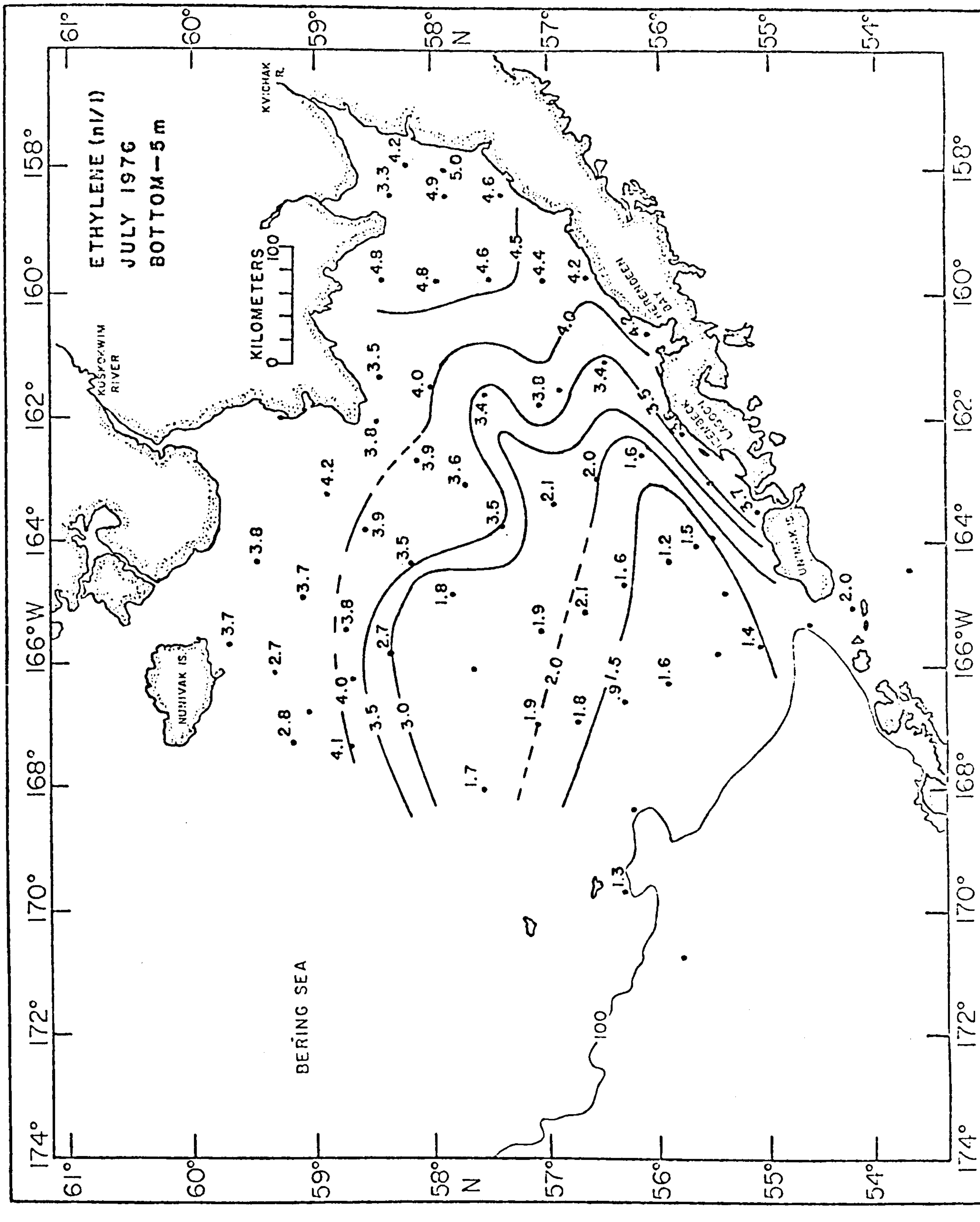

Figure 7-10 Areal distribution of ethene within 5 m of the bottom during July 1976. Concnetrations are expressed in nℓ/ℓ (STP).

(Figures 7-11 and 7-12). No significant spatial variation was observed on either occasion, although the concentration of propane was significantly higher near the shore in July of 1976 (Figure 7-12). The highest value observed was 1.8 nℓ/ℓ near the Kuskokwim River with average values for both seasons between 0.2 and 0.8 nℓ/ℓ. No evidence was found of petroleum introduction based on the propane abundance or distribution.

Surface propene concentration in July 1976 was significantly higher than that observed in the preceding fall (Cline and Feely, 1976a, Figure 17). 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 regions. As was the case for ethene, propene appears to be produced in conjunction with elevated levels of primary production.

Near-bottom levels of propane were only slightly higher in July compared to October with no significant spatial variation (Figures 7-13 and 7-14). The average value is near 0.5 nℓ/ℓ with a range from 0.2 to 0.9 nℓ/ℓ. These values would presumably hold for other seasons as well.

7.14 Isobutane 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 0.03 nℓ/ℓ. These concentration levels are extremely low and presumably reflect normal background production or equilibration levels with respect to the overlying atmosphere. In contrast with these studies, analogous measurements taken over the Texas shelf indicate concentrations of iso- and n-butane approximately 100 times the levels reported here (Brooks and Sackett, 1973).

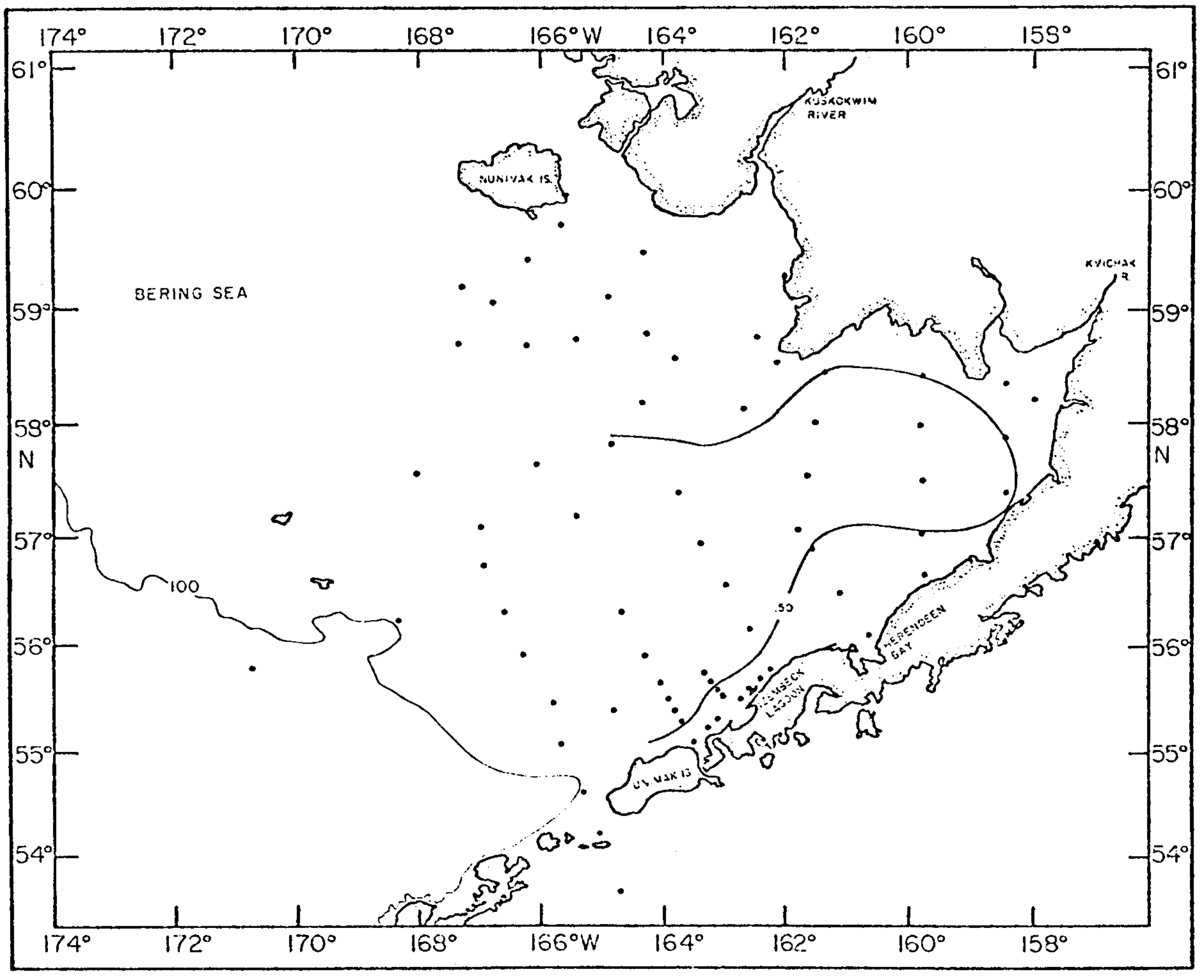

Figure 7-11 Areal distribution of propane plus propene in surface waters during Sept.-Oct. 1975. Approximately 2/3 of the total is propene based on complete chromatographic analysis at selected stations.

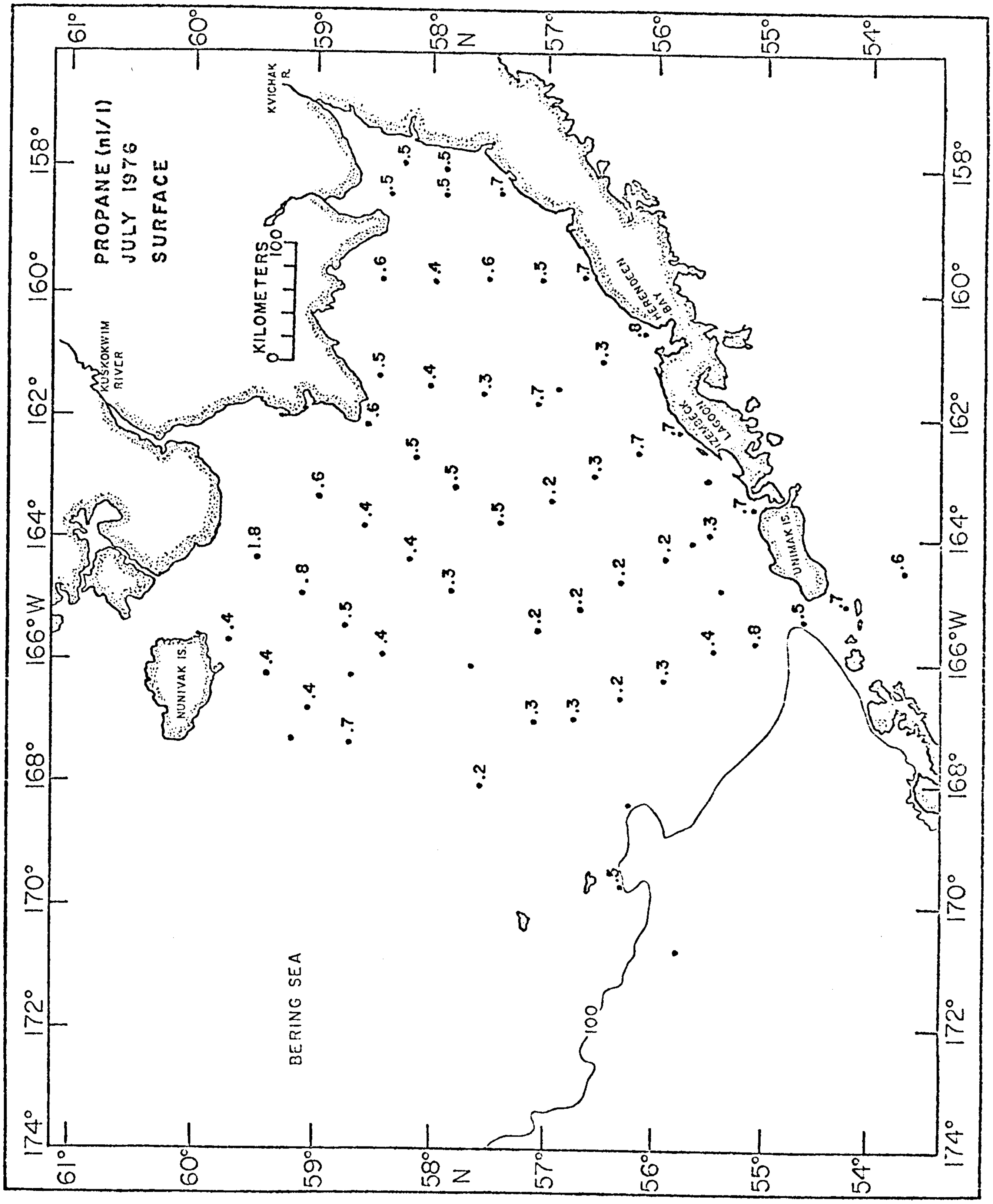

Figure 7-12 Areal distribution of propane in surface waters during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

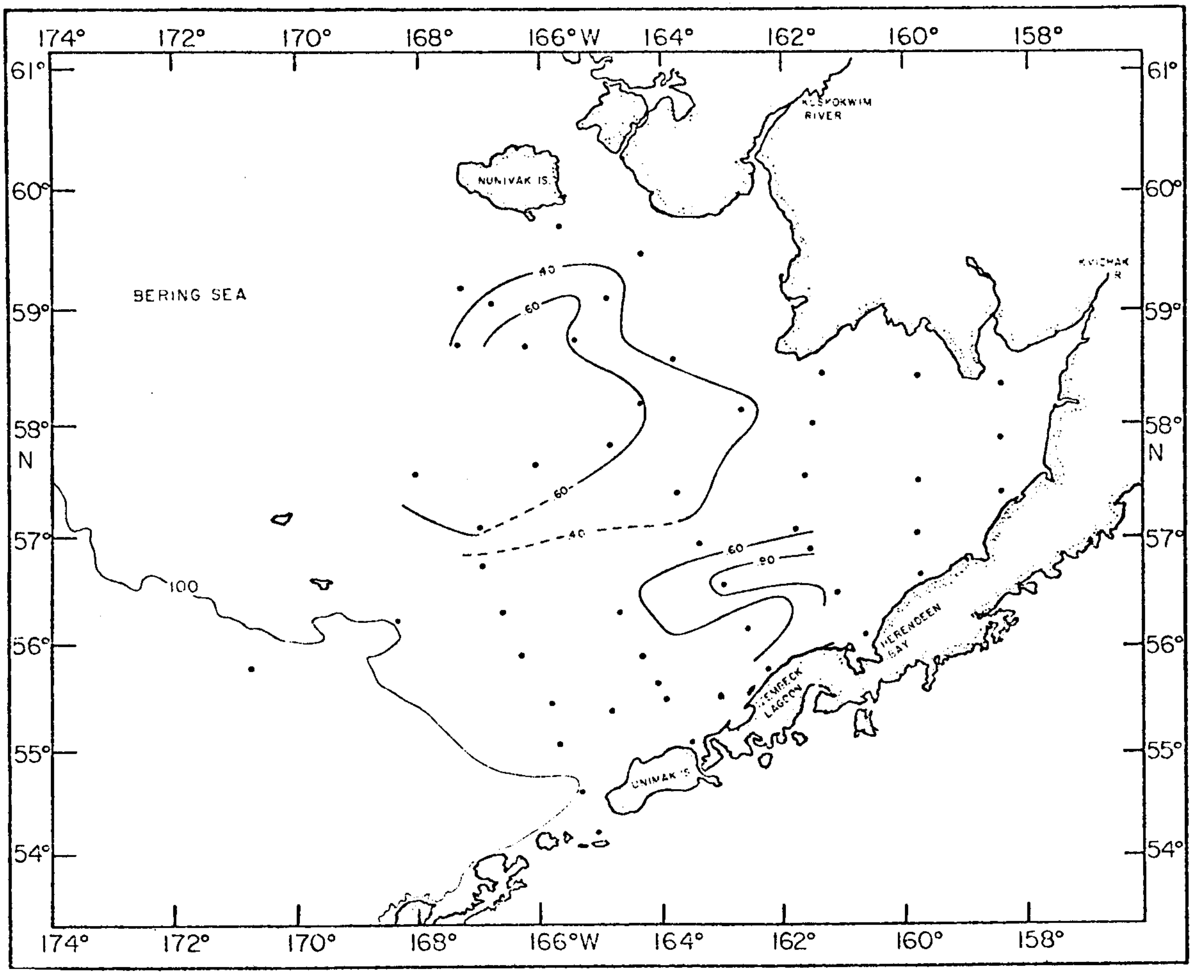

Figure 7-13 Areal distribution of propane plus propene 5 m from the bottom during Sept.-Oct. 1975. Approximately 2/3 of the total is propene, based on complete chromatographic analysis at selected stations.

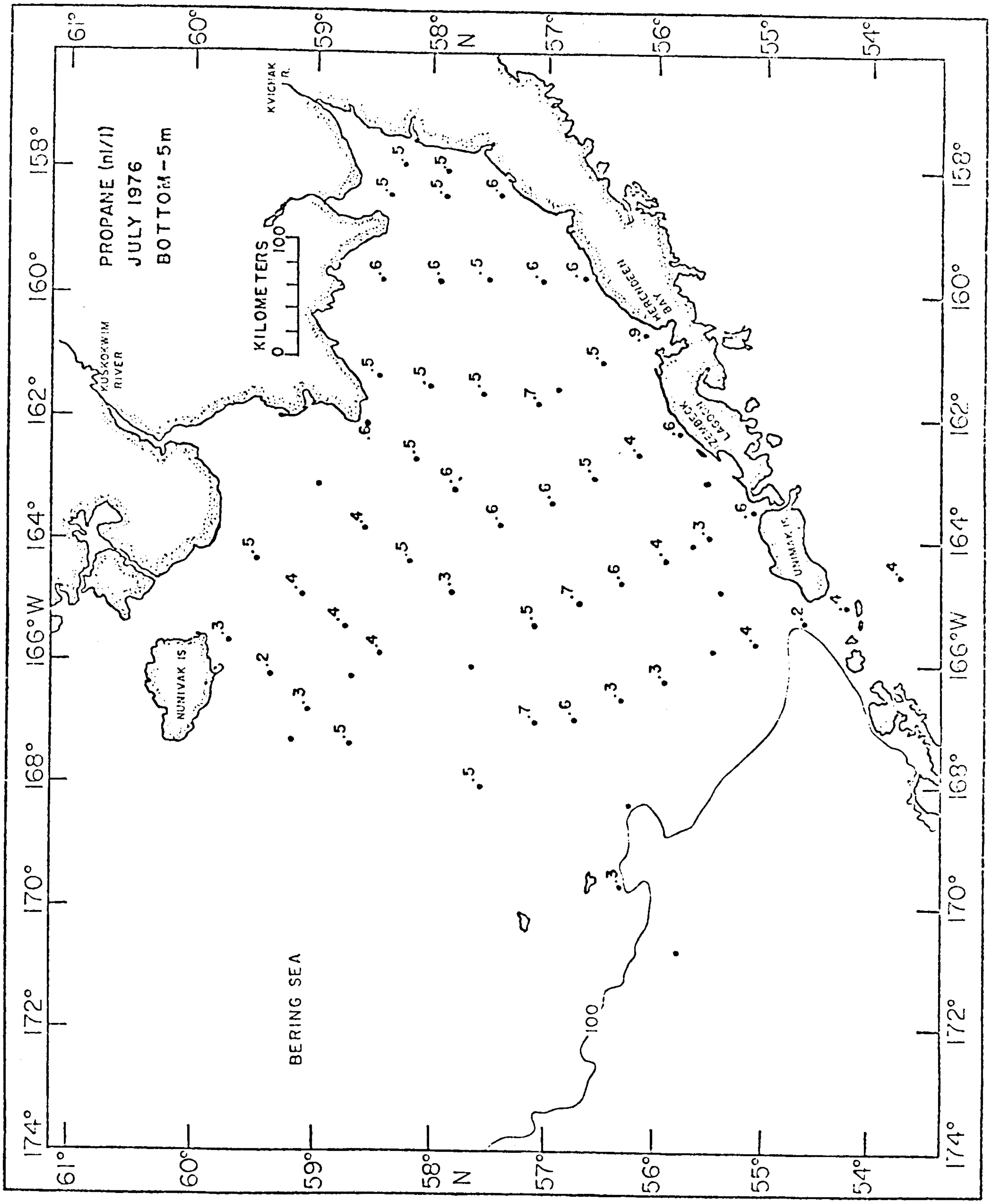

Figure 7-14 Areal distribution of propane within 5 m of the bottom during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

7.2 Norton Sound, Chukchi Sea, and Lower Cook Inlet

In each of these survey regions, only single season observations are available. Hydrocarbon abundances and distributions are discussed in the Quarterly Report covering the period 1 October-31 December 1976 (Cline, 1976), and additional elaboration is not possible at this time. However, the discovery of a gas seep in Norton Sound has been amplified in a report to be submitted to *Science* and will be presented as an appendix to this report.

A survey of LMWH in Lower Cook Inlet was made in April 1976 and is covered completely in the appropriate quarterly report (Cline and Feely, 1976b). Only nine stations were occupied at that time, but two intensive surveys are planned for this spring and summer.

7.3 Northeast Gulf of Alaska

Observations of LMWH were taken in October-November 1975, April 1976, and again in late July 1976. These measurements represent early winter, spring, and summer conditions as they existed at the time of sampling. Sampling protocol and analyses were uniform for all three cruises. NEGOA is the only OCS area in which one-year seasonal studies are available.

7.31 Methane

The surface distribution of methane is shown for the three seasons in Figures 7-15 thru 7-17. The surface shelf waters uniformly contain more than 100 nℓ/ℓ of methane during all seasons, representing a minimum supersaturation level of approximately 150 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, 1977) observed in that region (Figures 7-15, 7-16, and 7-17). In July of 1976, high concentrations of methane (600 nℓ/ℓ) were observed in the Icy Bay vicinity and may have related to sustained high

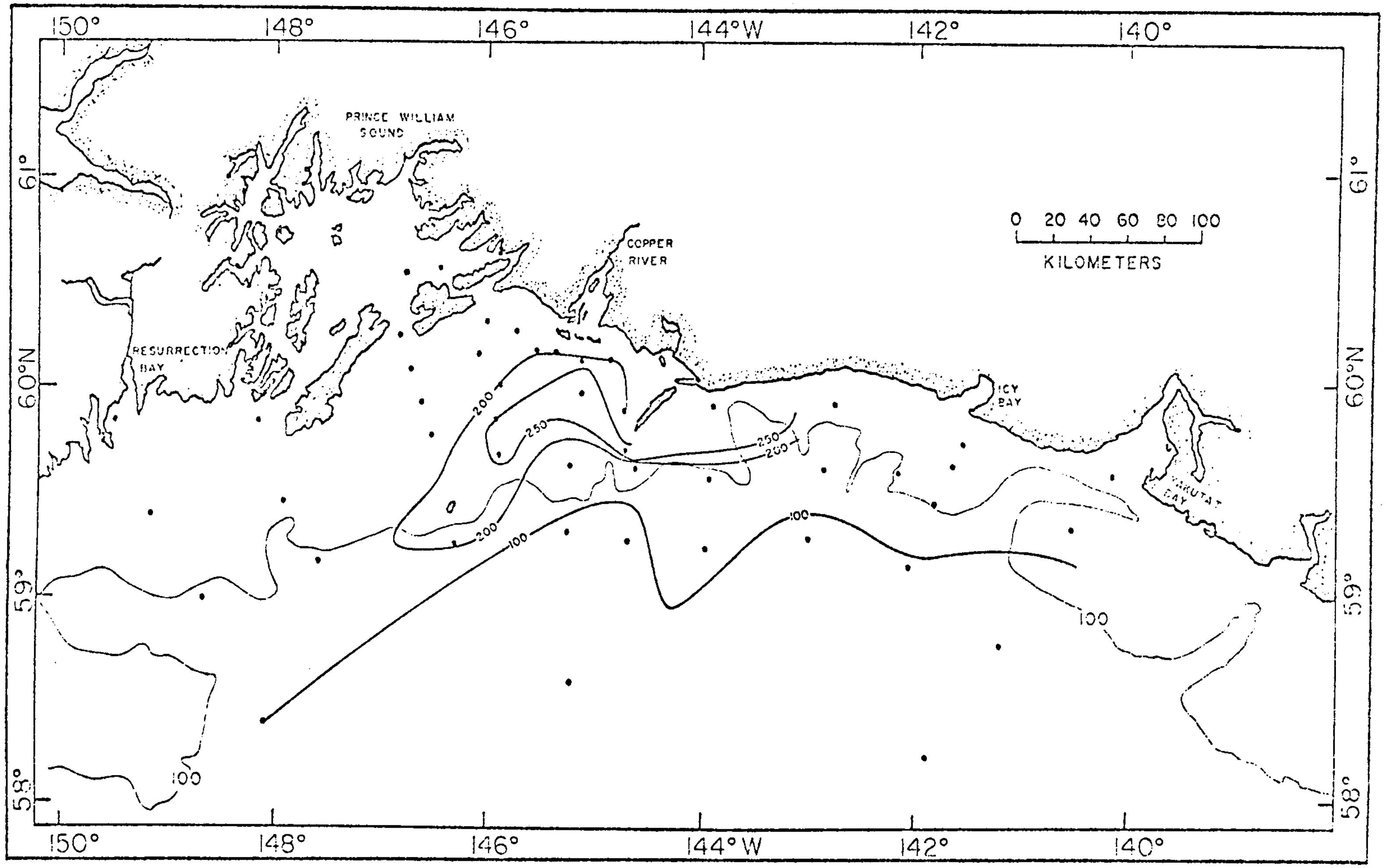

Figure 7-15 Areal distribution of methane in the surface waters during Oct.-Nov. 1975. Concentrations are expressed in nℓ/ℓ (STP).

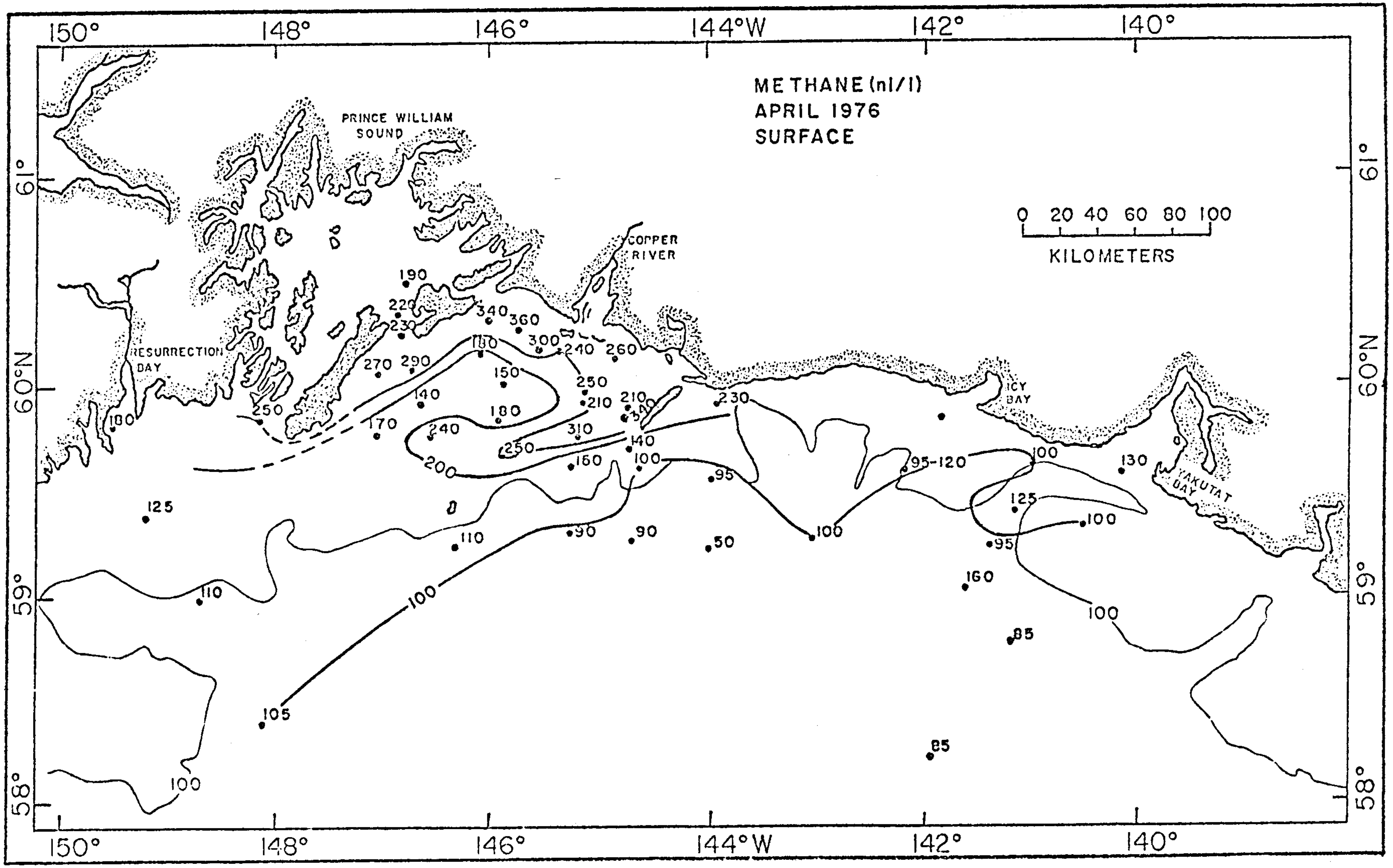

Figure 7-16 Areal distribution of methane in the surface waters during April 1976. Concentrations are expressed in nℓ/ℓ (STP).

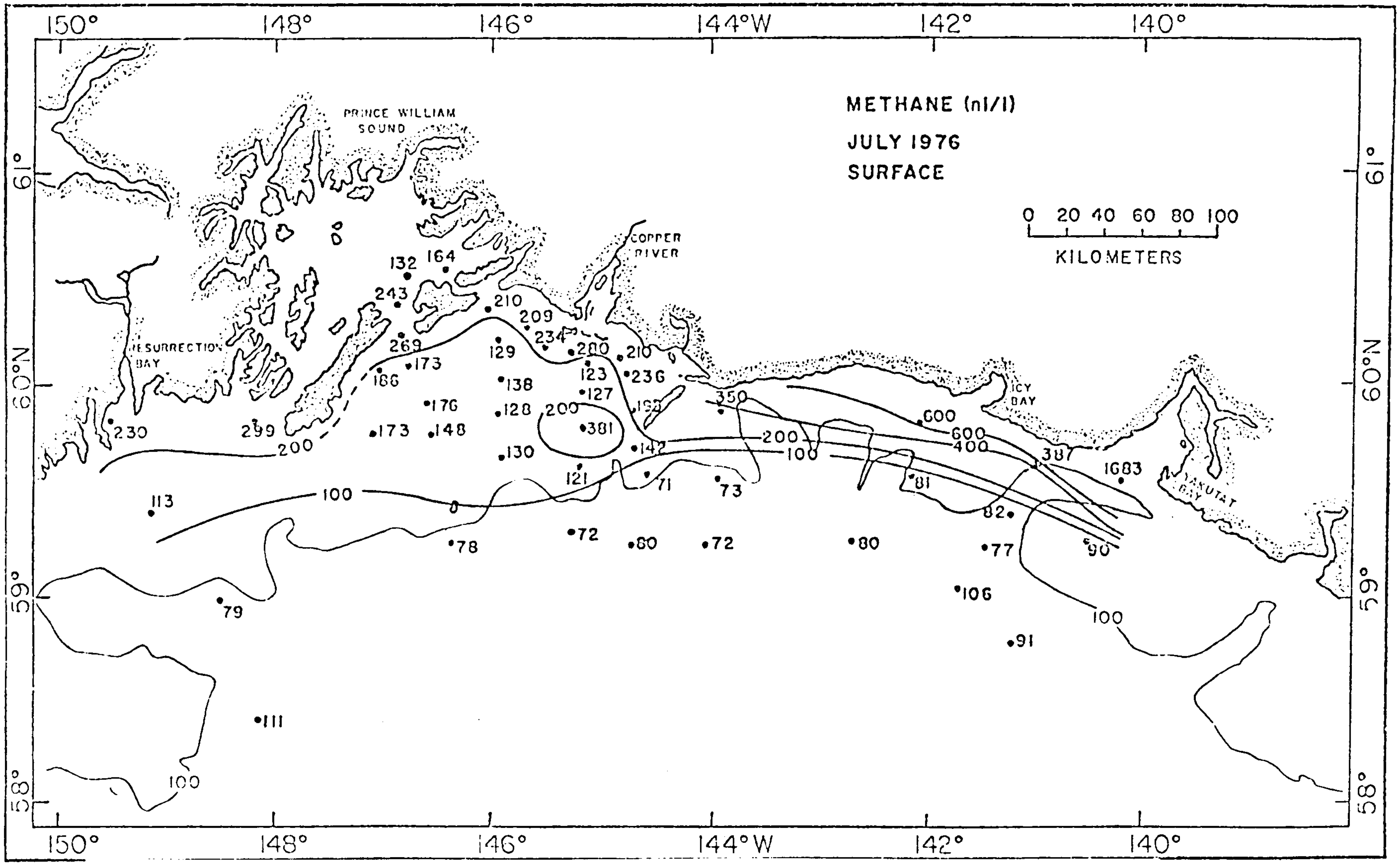

Figure 7-17 Areal distribution of methane in surface waters during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

productivity levels that were observed at the same time. In this instance, the surface concentrations of methane exceeded the concentrations near the bottom (Figure 7-20), implying that high levels of productivity had resulted in *in situ* methane production in the water column. The highest concentration of methane was 1683 nℓ/ℓ observed at the entrance to Yakutat. This value represents a supersaturation concentration with respect to the overlying atmosphere of 25. 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 petroleum-related hydrocarbons arising from the interior Yakutat Bay, it cannot be ascertained with certainty at this time.

With the exception of localized accumulations of methane in the surface layers, the concentration of methane over the shelf varies from 100-300 nℓ/ℓ, with offshore values less than 100 nℓ/ℓ. Offshore concentrations presumably reflect near saturation with the overlying atmosphere. Elevated surface concentrations found over the shelf are largely the result of microbial production in organic-rich sediments.

The near-bottom distributions of methane are shown in Figures 7-18 thru 7-20. In general, the concentrations 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. In July 1976 (Figure 7-20), 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

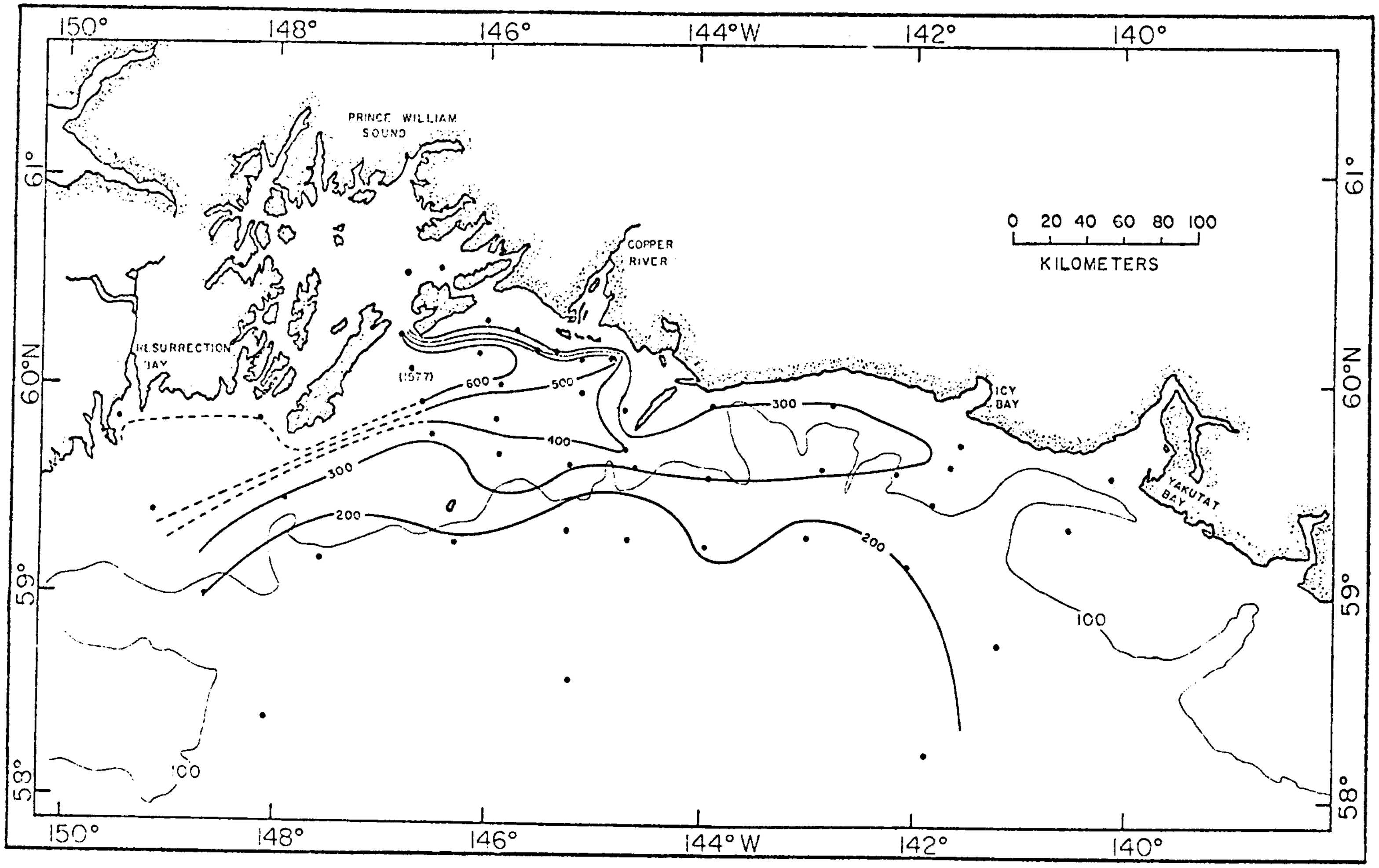

Figure 7-18 Areal distribution of methane 5 m from the bottom during Oct.-Nov. 1975. Concentrations are expressed in nℓ/ℓ (STP).

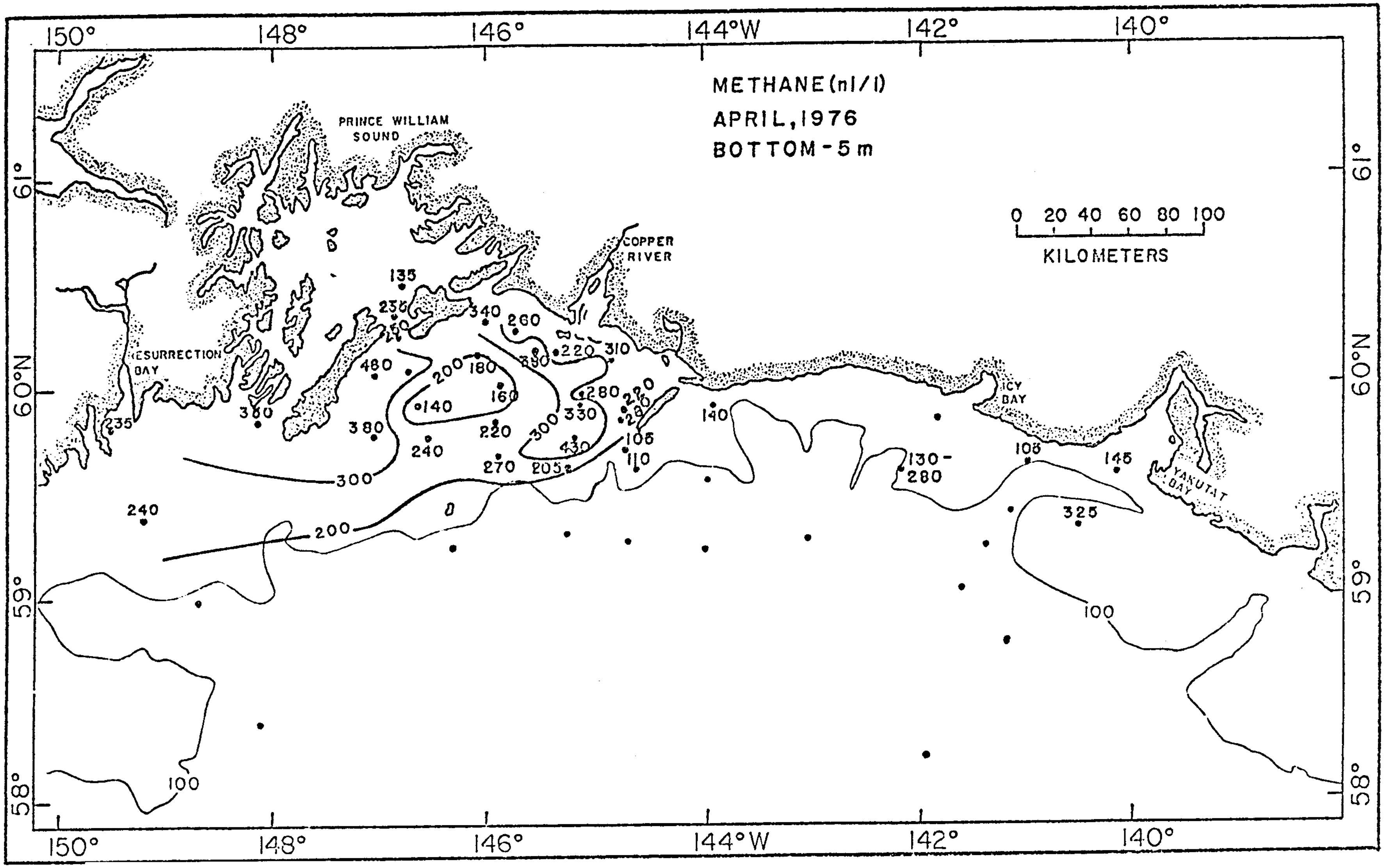

Figure 7-19 Areal distribution of methane 5 m from the bottom during April 1976. Concentrations are expressed in nl/l (STP).

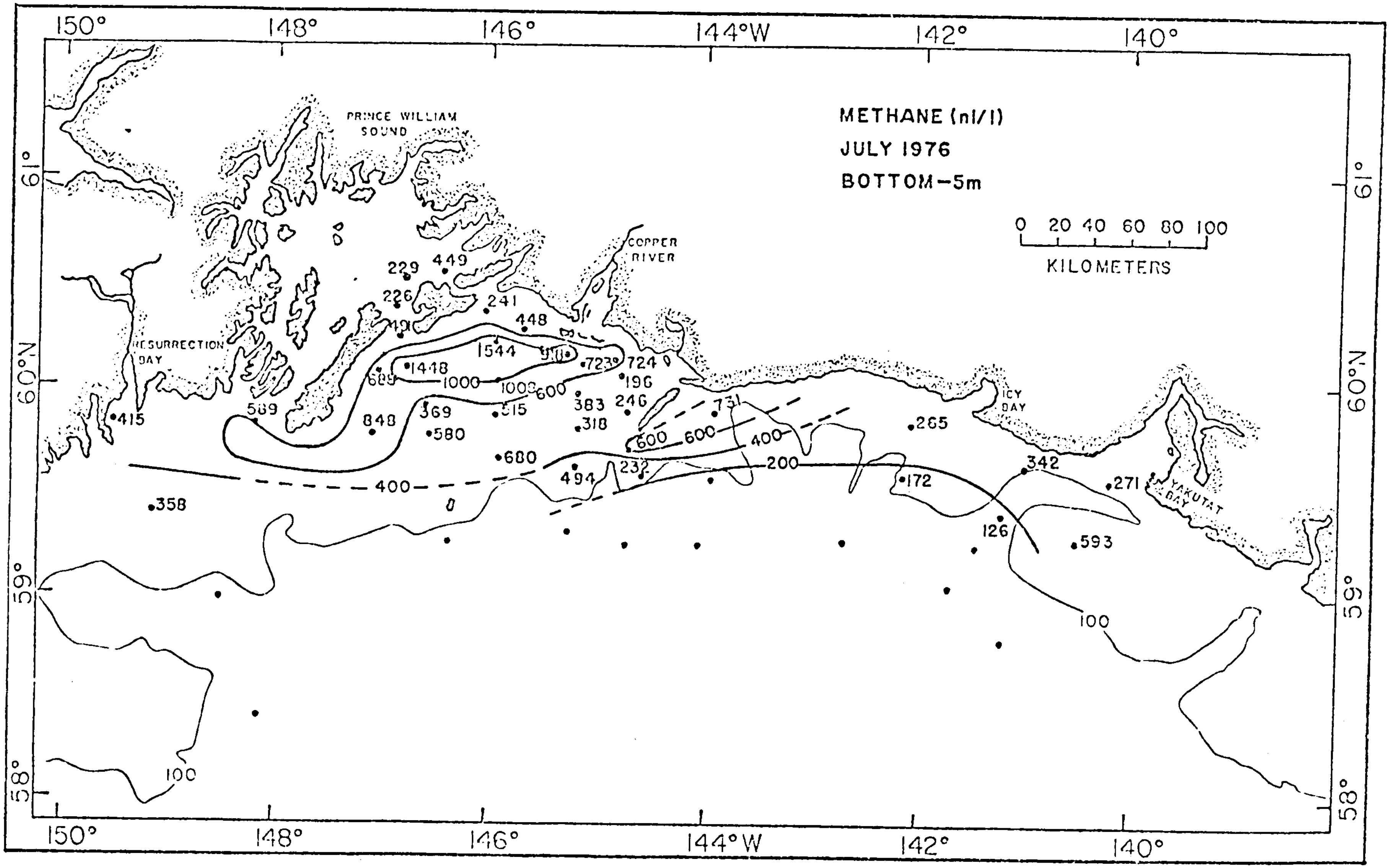

Figure 7-20 Areal distribution of methane 5 m from the bottom during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

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. Note the pool of relatively low methane water over Tarr Bank (Figure 7-19).

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 characterized 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.

7.32 Ethane and Ethene

The concentration of ethane in the surface layers was rather uniform throughout the seasonal studies just concluded. From observations conducted in 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, 1976a; Cline and Feely, 1976b). There were no apparent localized sources for ethane and we conclude that these minimal concentrations probably reflect ambient 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 7-21). 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

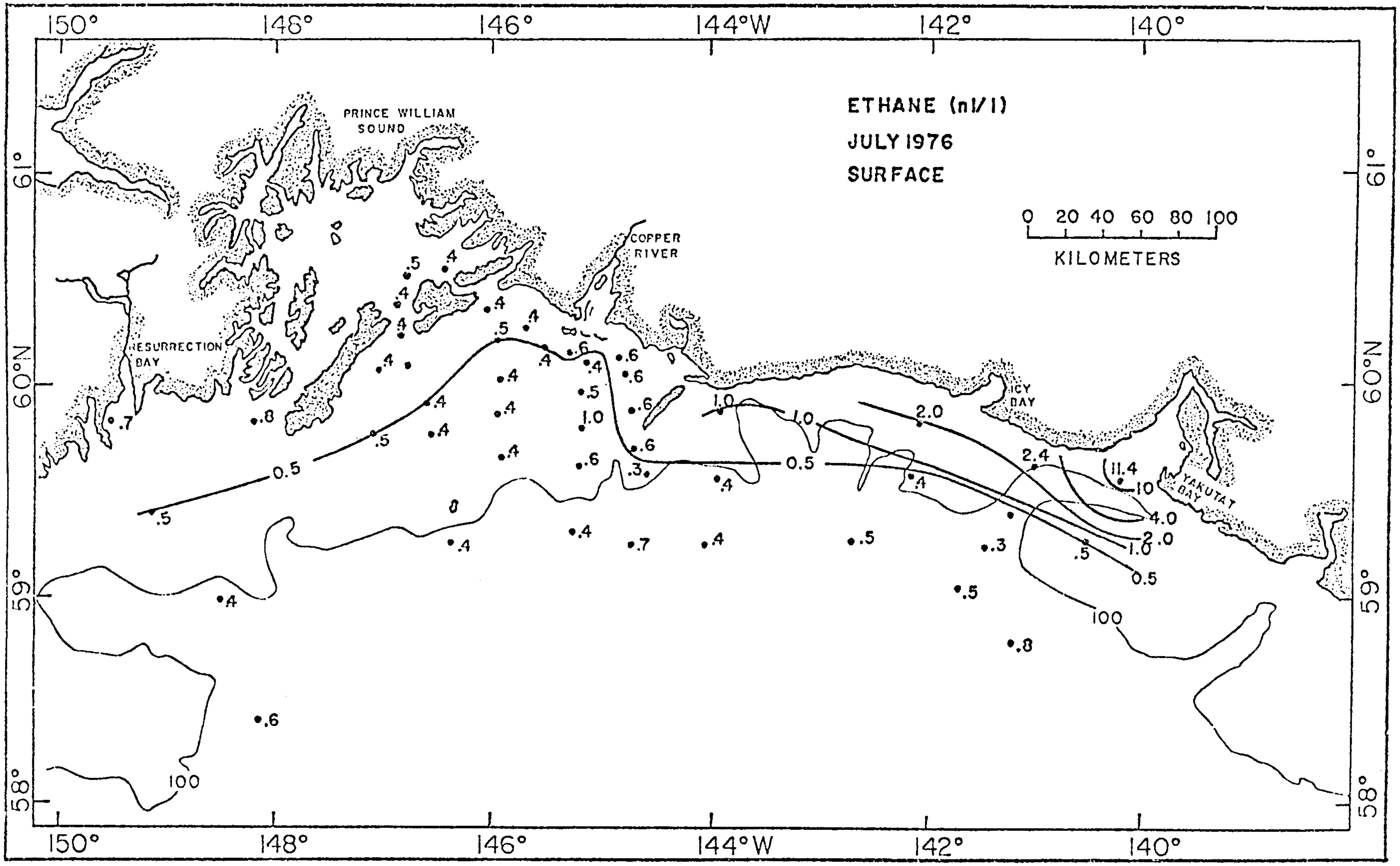

Figure 7-21 Areal distribution of ethane in the surface waters during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

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 7-22), suggesting that the source may have been a gas and/or oil seep. 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. Unfortunately, ship time was not available to investigate the source of the hydrocarbons.

Seasonal variations of ethane concentrations within 5 m of the bottom were uniform, ranging from 0.2 to 1.3 nℓ/ℓ (Cline and Feely, 1976a,b). 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.

7.33 Propane and Propene

Surface concentrations of propane, not unlike ethane, showed little areal or seasonal variations (Cline and Feely, 1976a,b). In the region south of Prince William 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 7-23), but was not accompanied by similar increases in propene (Figure 7-24). The source of the propene is not known, but may be related to gas seepage in Yakutat Bay or possibly, a biological phenomenon (see section 7.32).

Near-bottom concentrations of propane are spatially and temporally invariant (Cline and Feely, 1976a,b). 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.

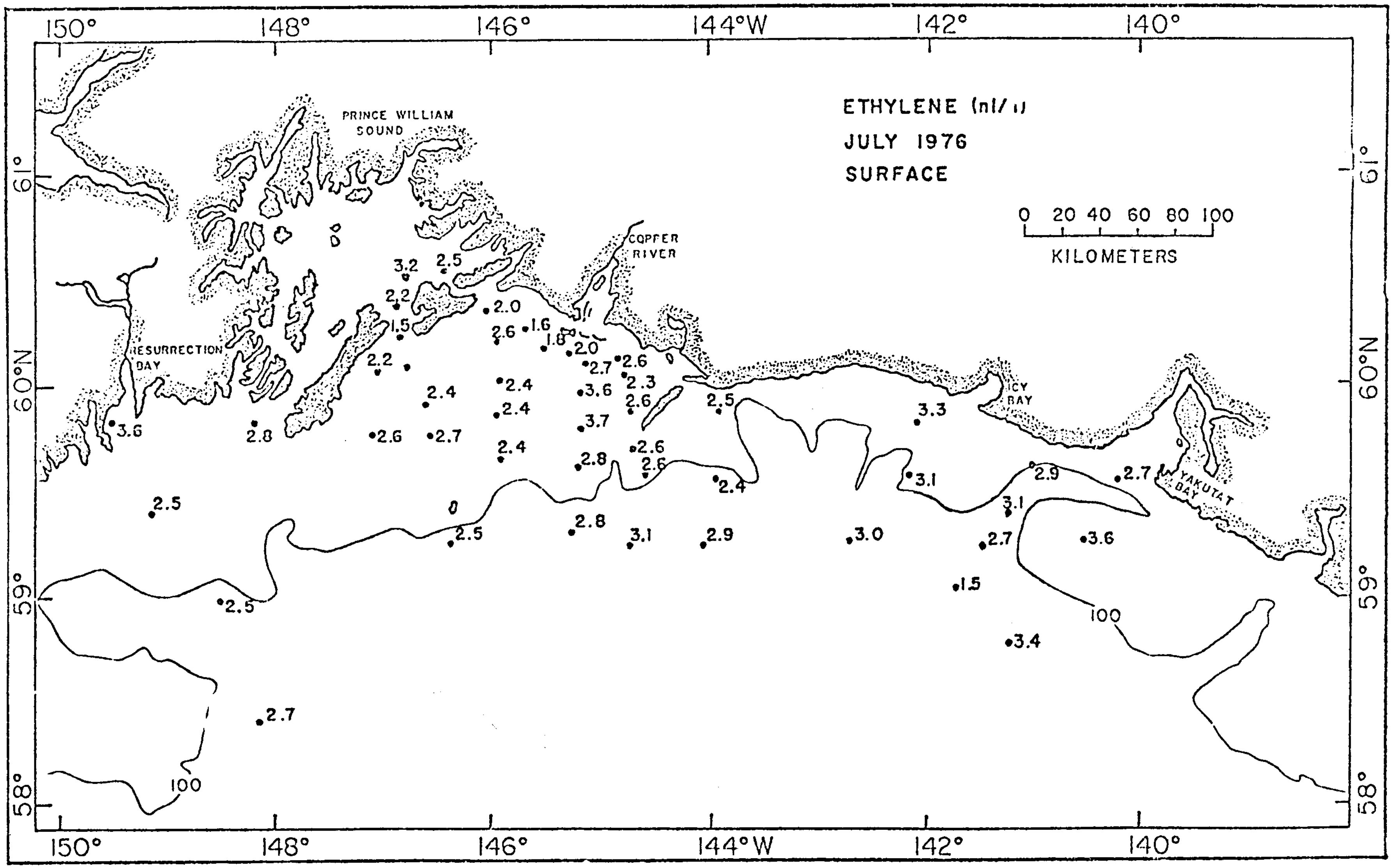

Figure 7-22 Areal distribution of ethene in the surface waters during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

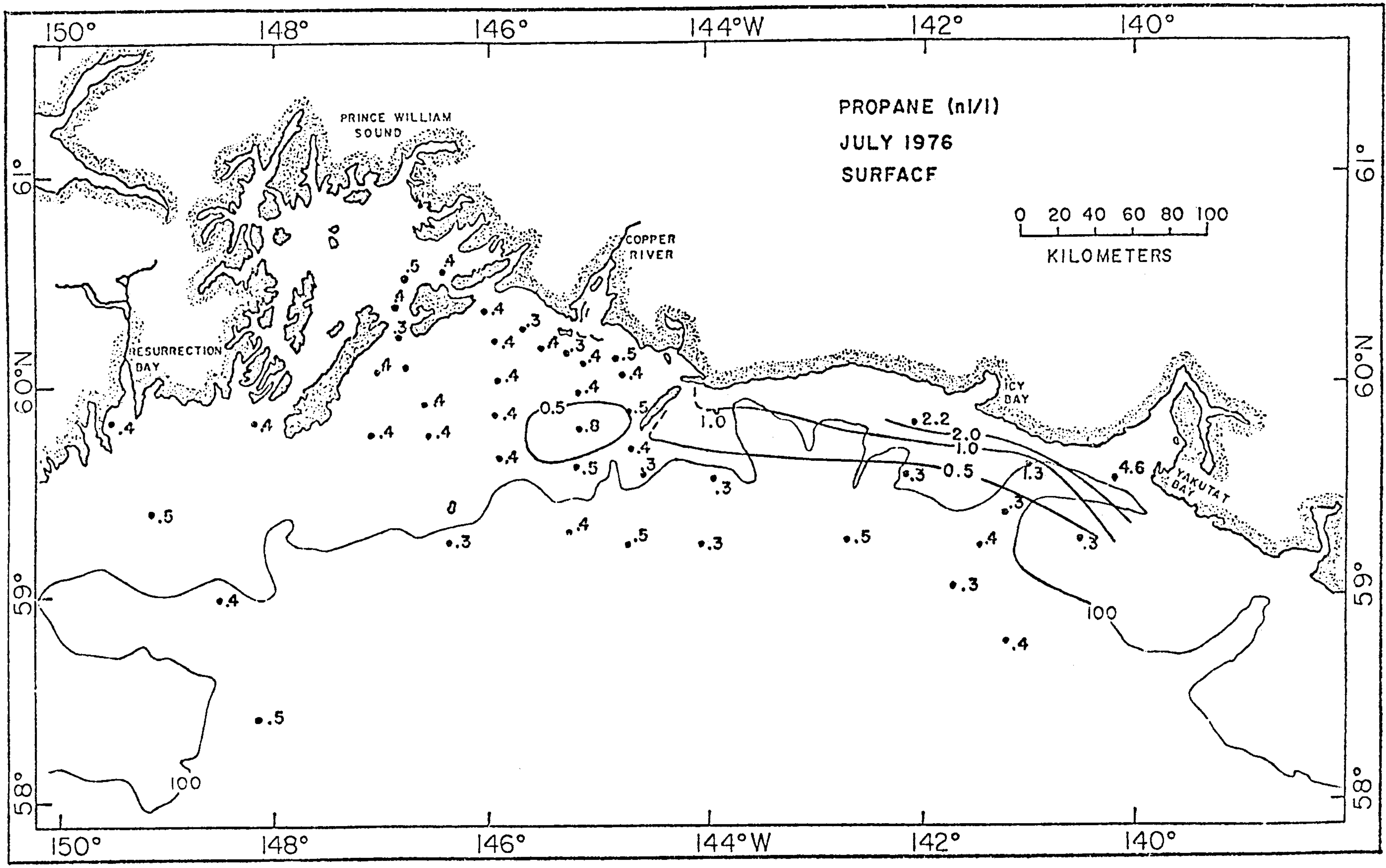

Figure 7-23 Areal distribution of propane in the surface waters during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

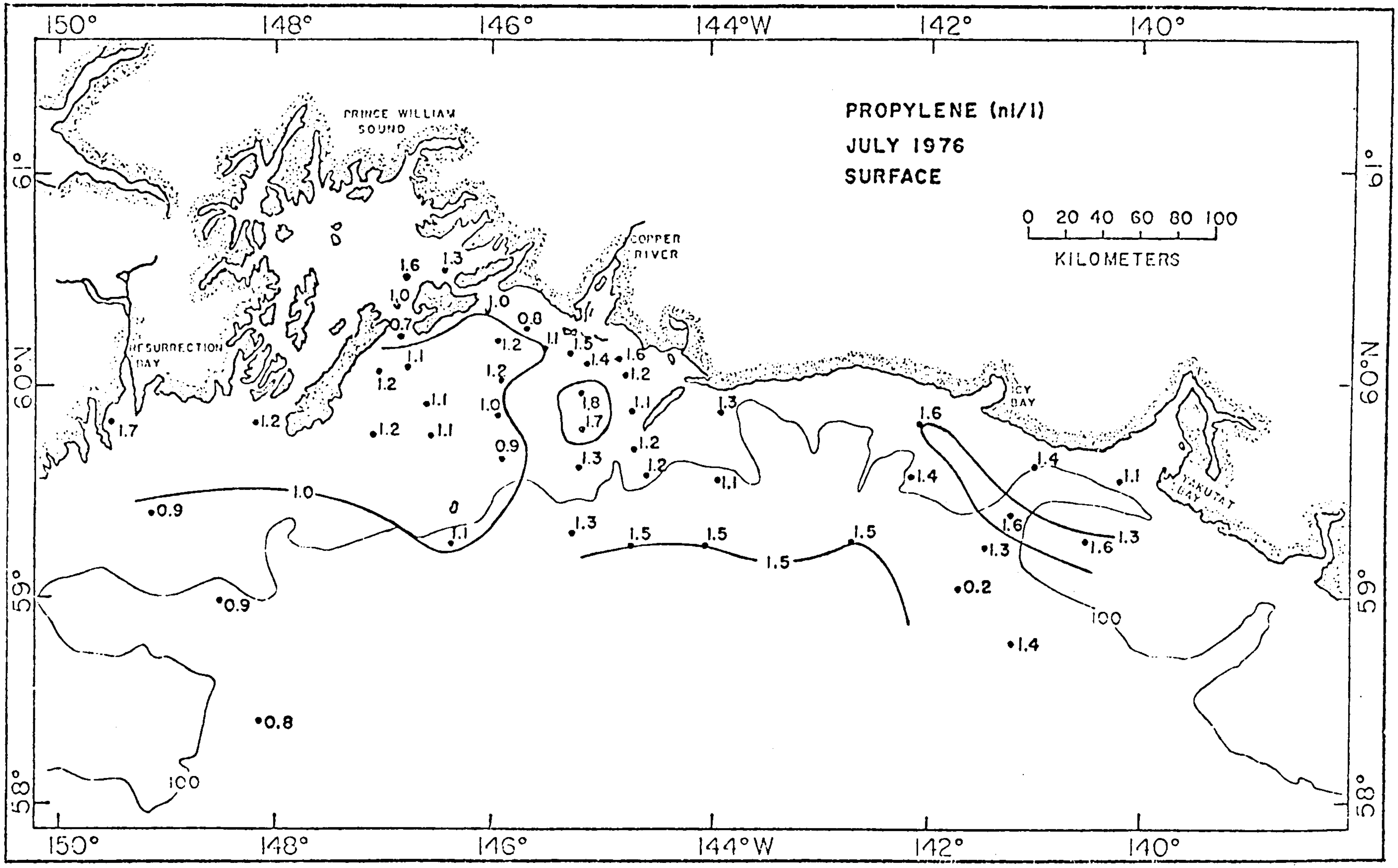

Figure 7-24 Areal distribution of propene in the surface waters during July 1976. Concentrations are expressed in nℓ/ℓ (STP).

7.34 Isobutane and n-Butane

Similar to the situation observed in Bristol Bay, the seasonal concentrations of the butanes were everywhere at or below the detection limit of 0.03 nℓ/ℓ. This was true in both the surface waters as well as at depth.

7.4 Diagnostic Indicators of Petroleum Introduction

Observations conducted to date in the OCS shelf waters of Alaska suggest that little or no petroleum is entering the marine environment, with the possible exception of the gas seep noted in Norton Sound. The Alaskan shelf waters appear to be pristine with respect to petroleum hydrocarbons, at least in the areas we have investigated. However, the gas seep in Norton Sound affords a unique opportunity to test various diagnostic parameters for the characterization of gas or liquid petroleum.

In exhaustive LMWH studies conducted in the shelf and offshore waters of the Gulf of Mexico, Brooks and coworkers at Texas A&M have utilized alkane ratio, C_1/C_2+C_3 and δC^{13} compositions for the distinction of biogenic hydrocarbons from those produced by thermal processes (Frank et al., 1970; Bernard et al., 1976). Relying on the fact that little or no olefinic compounds are found in crude oil or natural gas, we have explored the test ratio $C_{2:0}/C_{2:1}$ as a reliable indicator of petroleum introduction. Before evaluating this parameter, it became necessary to establish background ratios of ethane to ethene. Some examples are shown in Figures 7-25 thru 7-29 for near-bottom samples only, as seeping gas or oil will leave the strongest signature at the point of entry.

Figures 7-25 and 7-26 show a plot of ethane versus ethene in late fall of 1975 and again for early summer in Bristol Bay. Although the statistics are poor, the late fall season is characterized by low, variable levels of both ethane and ethene. The equation of the line is $C_{2:0} = 0.54\ C_{2:1} + 0.38$; the

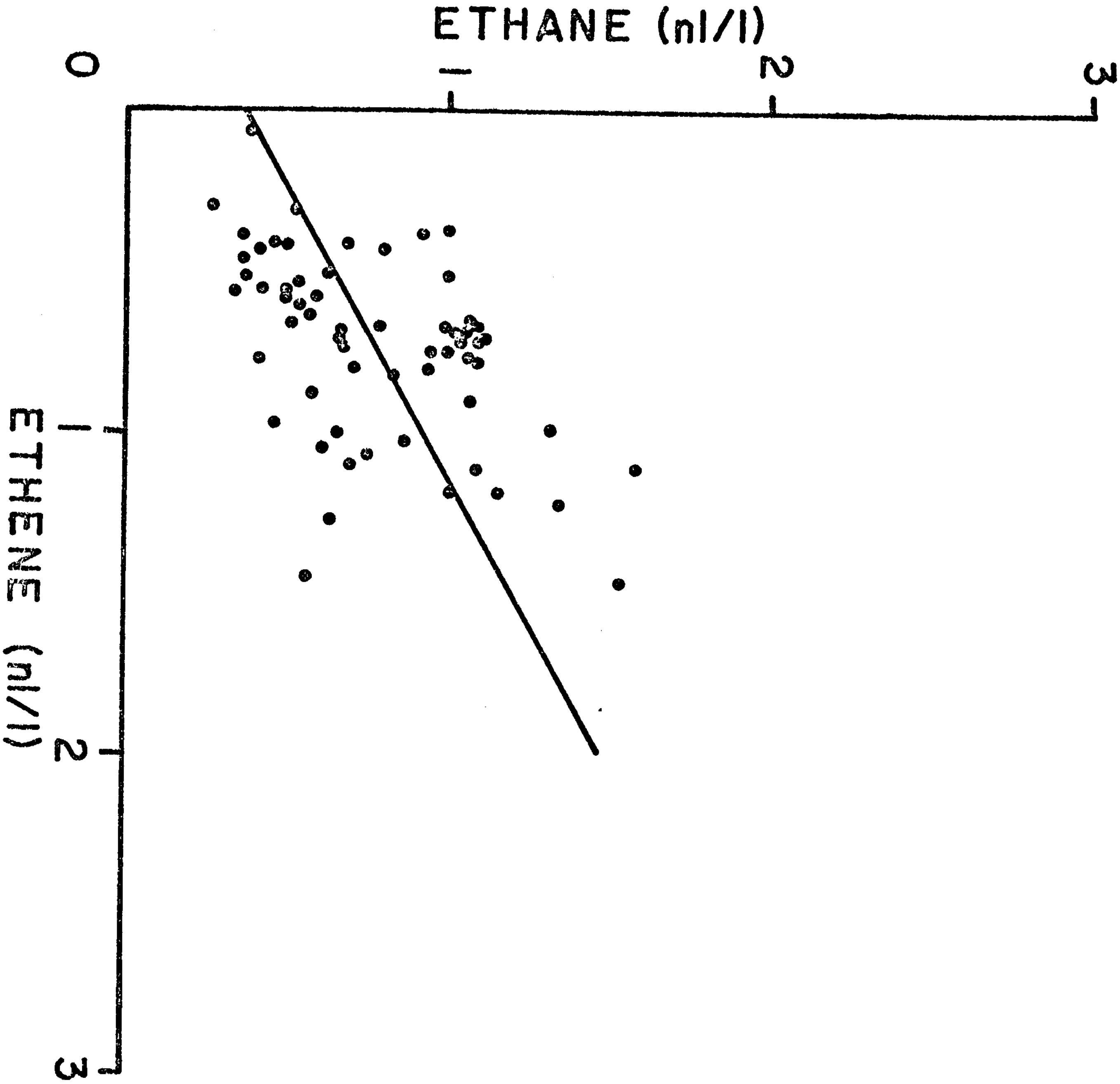

Figure 7-25 Relationship between ethane and ethene concentrations found in the lower 5 m of the water column during Sept.-Oct. 1975. Observations were made in southeastern Bering Sea.

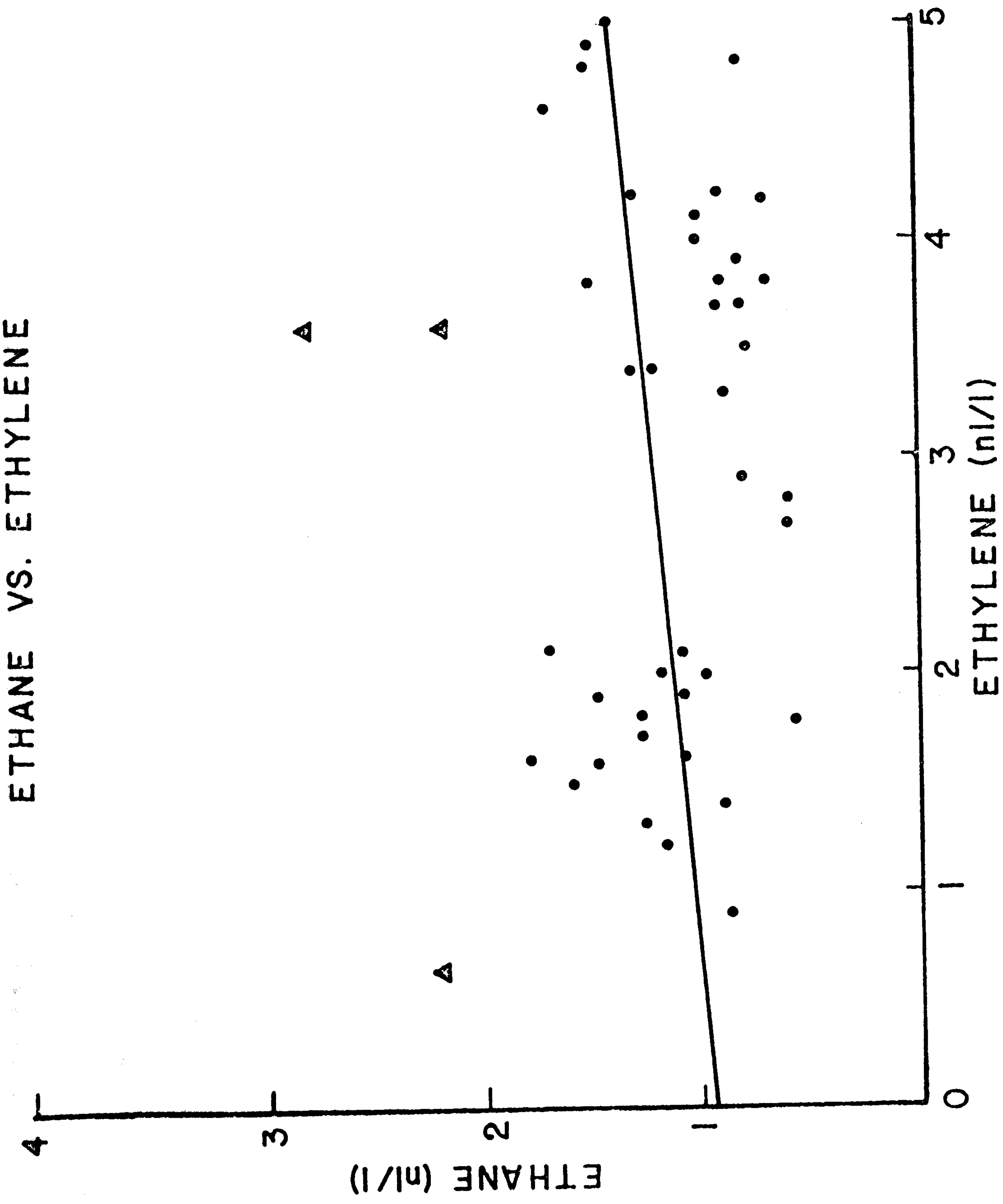

Figure 7-26 Relationship between ethane and ethene concentrations found in the lower 5 m of the water column in July 1976. Observations were made in southeastern Bering Sea.

standard error in the slope is 0.12. In early summer, higher levels of primary production obtained increasing dramatically the levels of ethene in the upper water column. Some of this was vertically mixed down gradient to increase the bottom water concentration as well as being supplemented by what appears to be near-bottom production of the C_2 alkene. Because of the shallow depths, it is difficult to distinguish between the two sources. The relationship between ethane and ethene for July 1976 is shown in Figure 7-26 and reveals a shallower slope. The equation of this line is $C_{2:0} = 0.08\ C_{2:1} + 0.97$ with an uncertainty in the slope of 0.05. The ethane concentration has remained nearly constant with substantial increases in the concentration of ethene, presumably due to biological activity.

The points indicated by the triangles were taken off the mouths of lagoons and do not represent samples typical of open shelf waters.

A similar relationship between ethane and ethene was observed in the northeast Gulf of Alaska, although less scatter was apparent. In Figures 7-27 and 7-28 are shown the $C_{2:0}$ and $C_{2:1}$ ratios for late fall 1975 and summer 1976. In the first instance, the slope of the line (includes all observations) is 0.45; in the latter it is near 0.3. Thus, in both areas studied we conclude that the normal $C_{2:0}/C_{2:1}$ ratio is less than 0.5 statistically. Moreover, the ratio was never greater than 1 except as noted in the bottom waters of Norton Sound and in the surface waters off Yakutat Bay.

For comparison, we show the $C_{2:0}/C_{2:1}$ ratio for near-bottom observations in Norton Sound taken in September of 1976 (Figure 7-29). The slope of this line is near 0.3, not unlike that found in the northeast Gulf of Alaska. The dashed line indicates the $C_{2:0}/C_{2:1}$ ratio equals 1. The waters near the seep (see Appendix I) show a preponderance of alkanes relative to the alkenes and would plot on Figure 7-29 well above the dashed line. We conclude from all

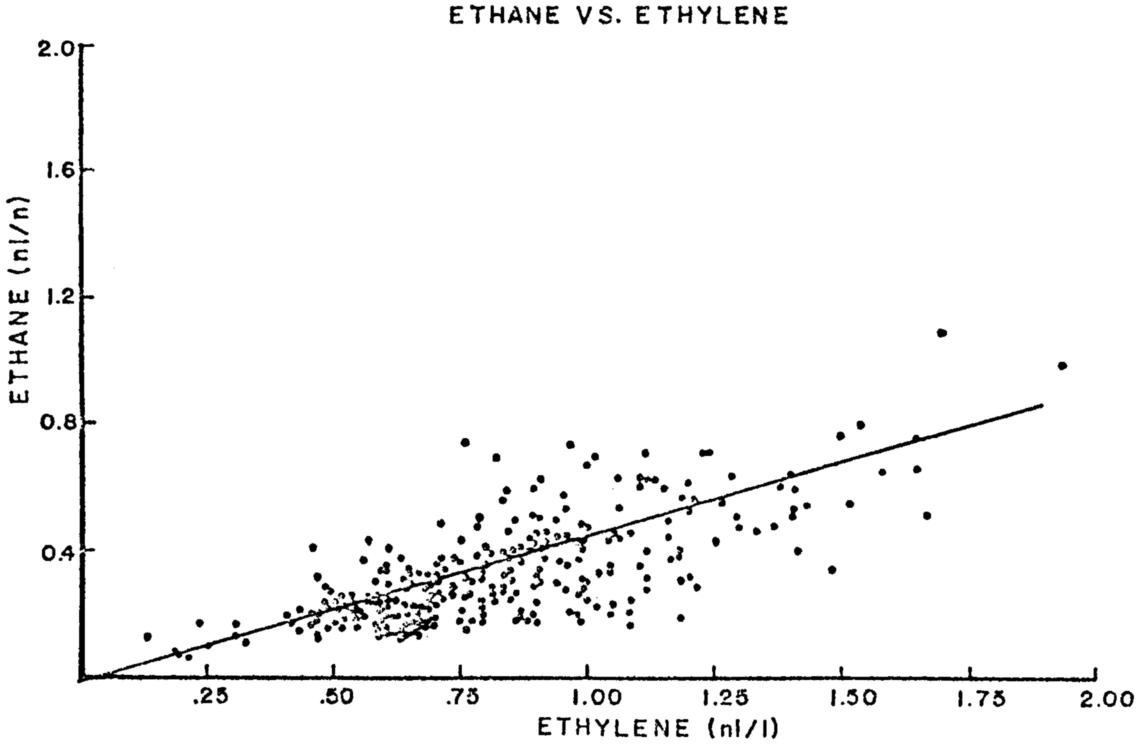

Figure 7-27 The relationship between ethane and ethene concentrations for all observations in the northeast Gulf of Alaska. The slope of the line is 0.45 ± 0.03 (r = 0.66).

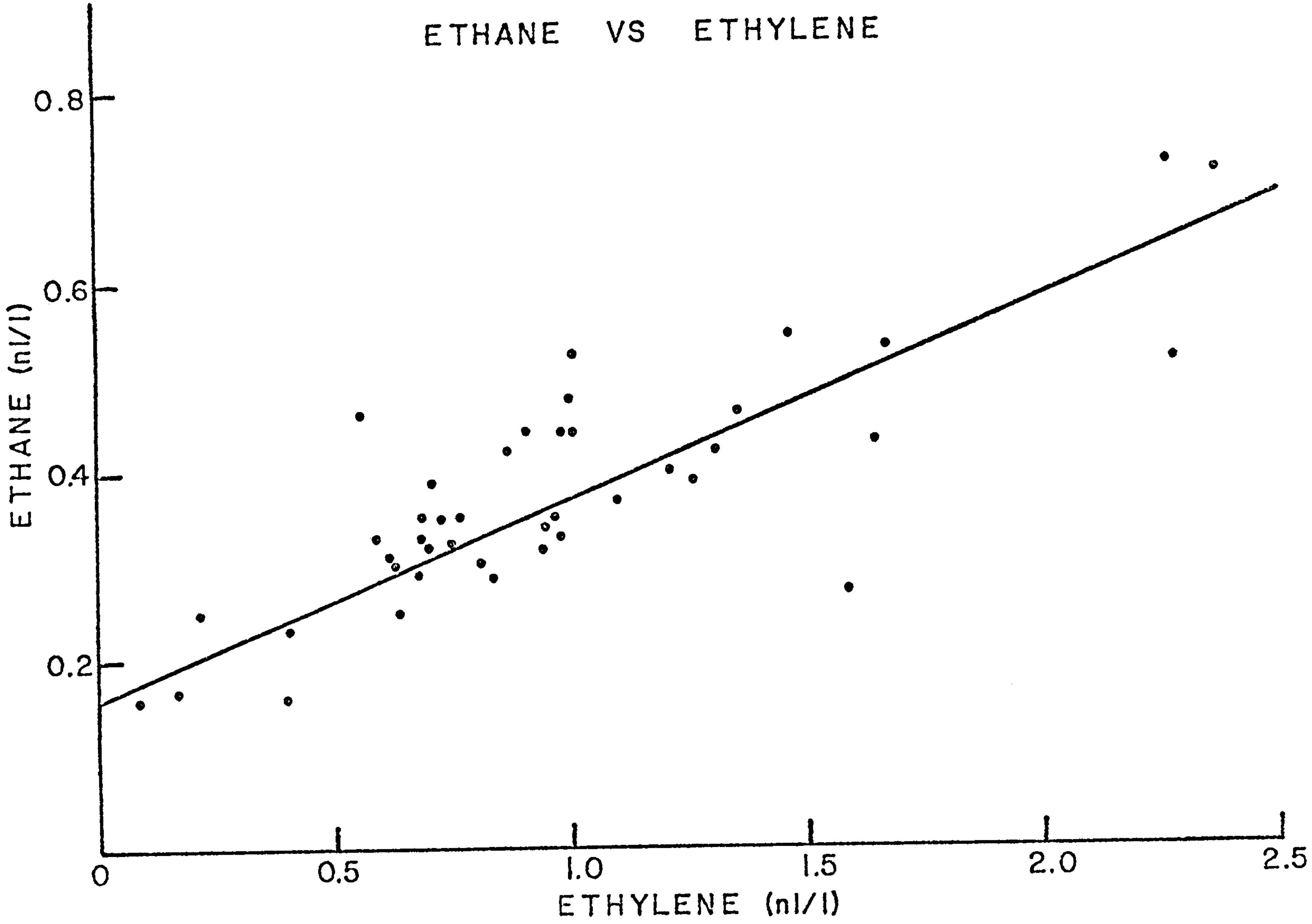

Figure 7-28 The relationship between ethane and ethene for near-bottom samples taken in the northeast Gulf of Alaska during July 1976. The slope of the line is 0.3.

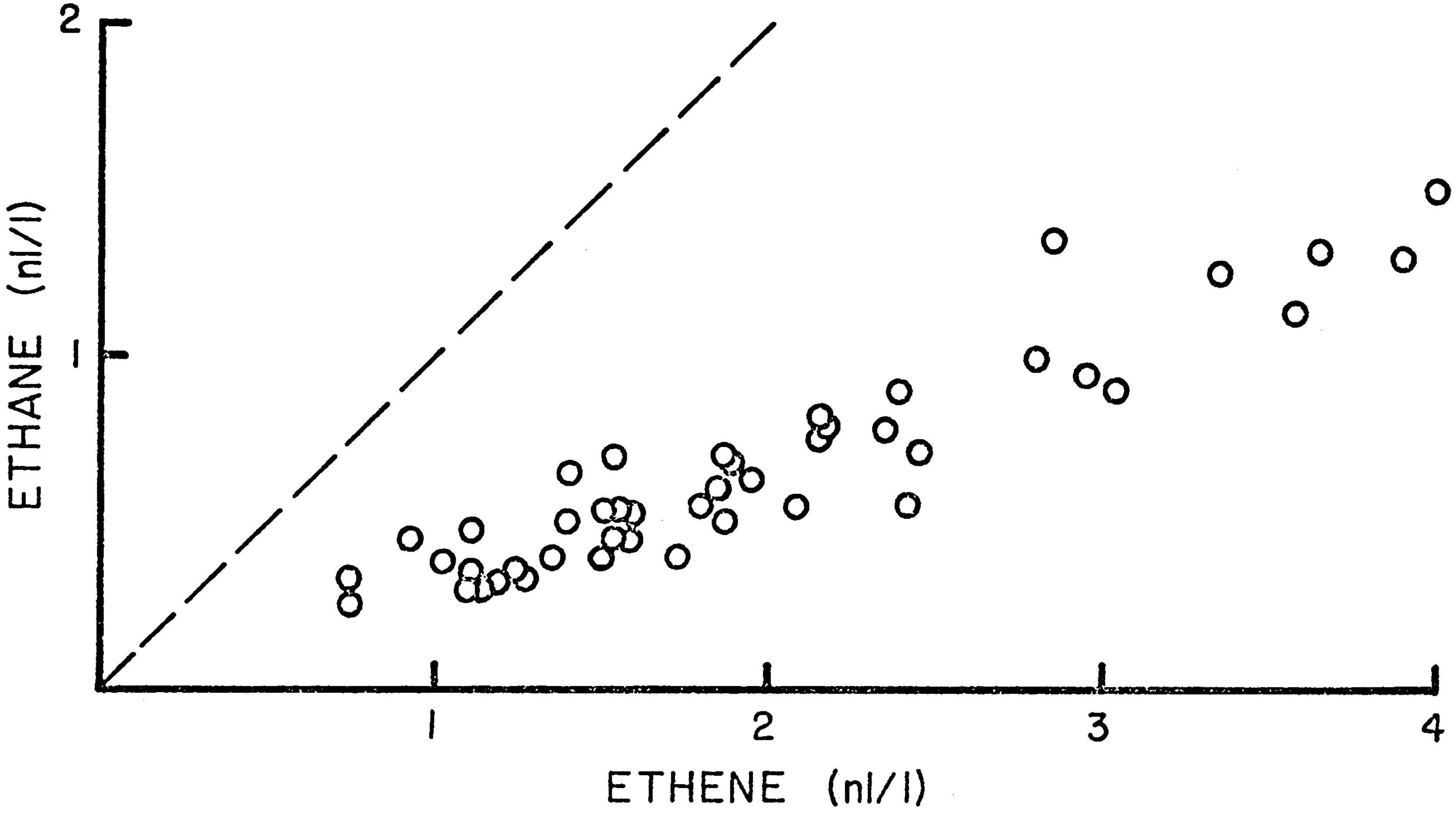

Figure 7-29 The relationship between the concentration of ethane and ethene in the near-bottom waters of Norton Sound during Sept. 1976. The dashed line represents an ethane/ethene ratio of 1.

our measurements taken to date in OCS waters of Alaska that rarely does the $C_{2:0}/C_{2:1}$ ratio exceed 0.5, except when natural gas or petroleum is present.

Other parametric ratios have been used to trace petroleum hydrocarbon introduction into the marine environment. One such parameter is the alkane ratio $C_1/C_2 + C_3$ popularized by Frank et al. (1970), and has been used extensively in delineating hydrocarbon seeps in the Gulf Coast area. Because bacterial methane production in surficial marine sediments is usually accompanied by only trace quantities of the higher homologs, the aforementioned ratio has been useful in documenting natural gas and oil seeps.

In Figures 7-30 and 7-31 are shown the $C_1/C_2 + C_3$ ratio for southeastern Bering Sea and Norton Sound. The range of values in Bristol Bay was from a low of 13 near Nunivak Island (probably spurious) to a high of 357 northeast of Unimak Island. Frank et al. (1970) suggest that a value of 50 is the transition point between compositions arising from biogenic and petrogenic processes. Hydrocarbons arising by petrogenic processes tend to be rich in the higher homologs of methane. In contrast, the minimum value observed in Norton Sound was 50 in an area characterized by a known gas seep (Figure 7-31). We suspect from our measurements that the absolute value of the $C_1/C_2 + C_3$ alkane ratio is not as important as its relative value. Moreover, because methane, ethane, and propane are known to be produced biologically and to be important components of both natural gas and petroleum, it seems that a more definitive parameter is required. Our measurements would suggest the $C_{2:0}/C_{2:1}$ and $C_{3:0}/C_{3:1}$ ratios are more appropriate in Alaskan Shelf waters, and possibly elsewhere, primarily because of the absence of the olefinic compounds in petroleum. A more in-depth treatise of this problem will be made in the final report.

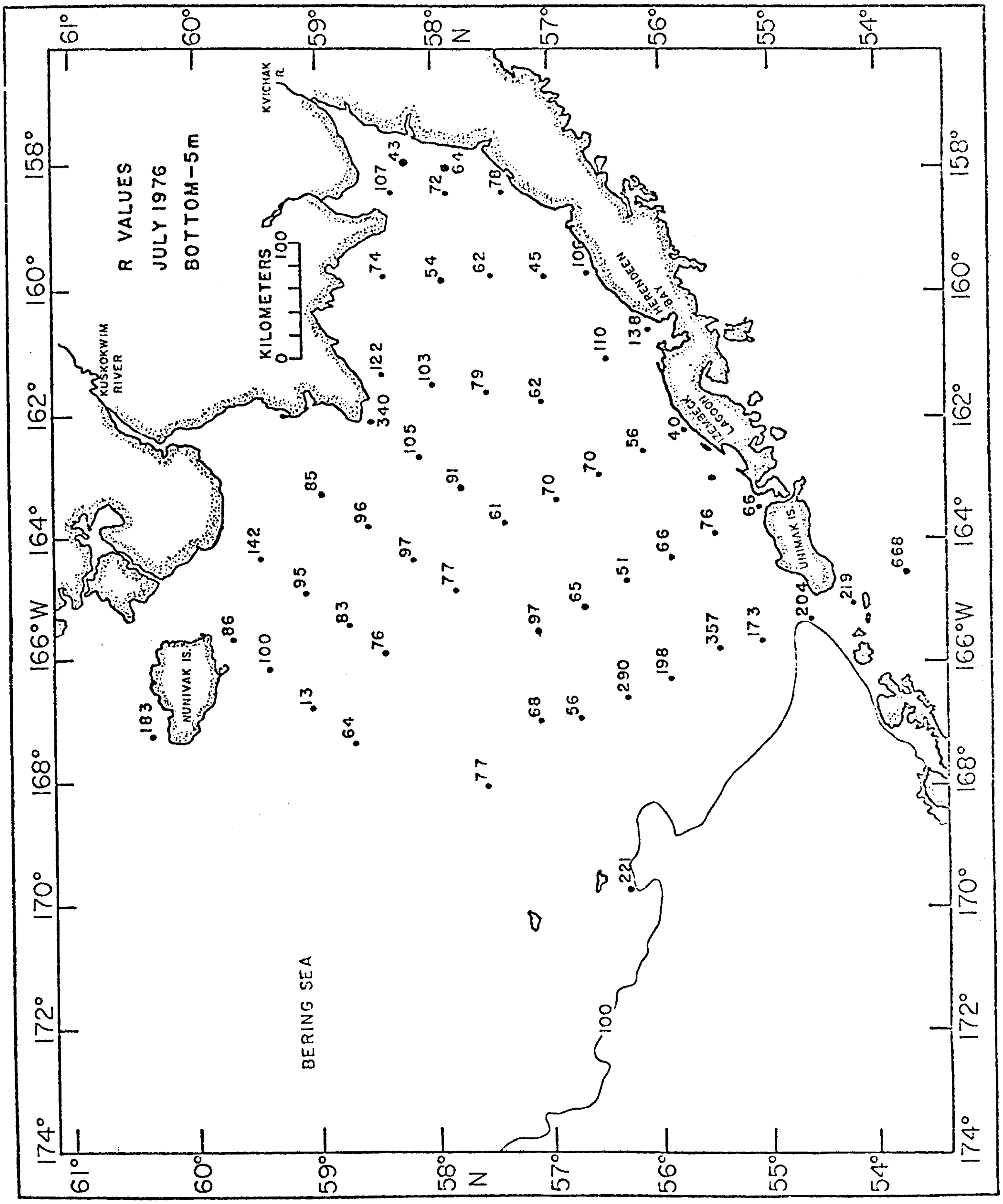

Figure 7-30 The ratio of the concentrations of methane to ethane plus propane ($C_1/C_2 + C_3$) observed 5 m from the bottom in Bristol Bay in July 1976.

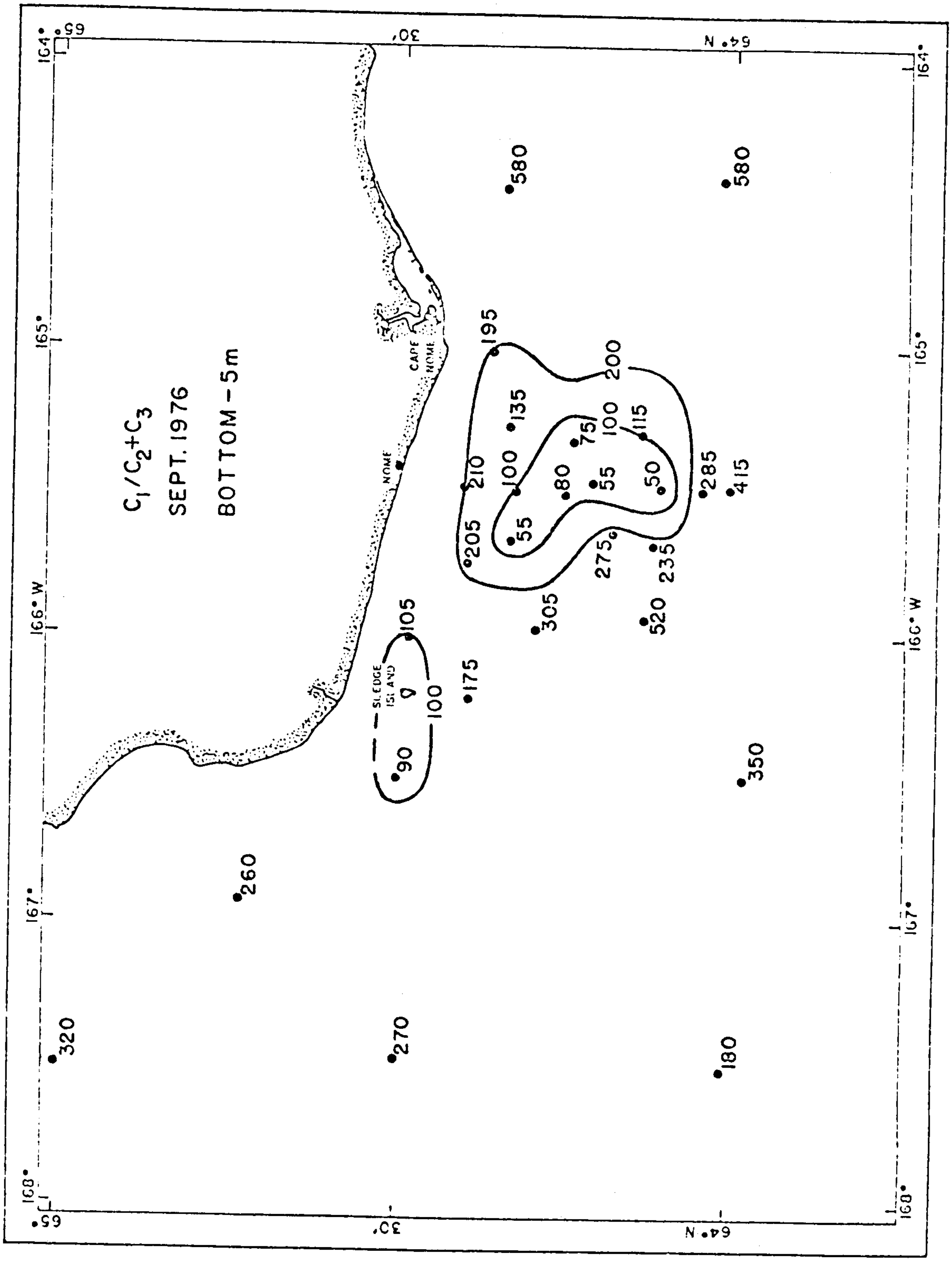

Figure 7-31 The ratio of the concentrations of methane to ethane plus propane ($C_1/C_2 + C_3$) observed 5 m from the bottom in Norton Sound during Sept. 1976.

8. CONCLUSIONS

Baseline surveys have been completed in the northeast Gulf of Alaska, southeastern Bering Sea, Norton Sound, and southeastern Chukchi Sea. Some measurements have been made in Lower Cook Inlet and in the western Gulf, but these are too sparse to be of any value in establishing baseline or benchmark conditions in these areas. Field expeditions planned for April and July of this year should provide much additional information relevant to hydrocarbon distributions and sources in these regions.

Not all the areas were visited seasonally, but the data obtained to date is probably sufficient to delineate the background levels of the low molecular weight aliphatic hydrocarbons to be expected in a future monitoring activity.

8.1 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 8-1 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

Table 8-1 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 observational periods in each survey area is given in parentheses.

Region	NEGOA (3)	LCI[1] (1)	Bristol Bay (2)	Norton Sound[1,2] (1)	Chukchi Sea[1] (1)
Component	nℓ/ℓ (STP)				
Methane	100-1500	100-1400	60-600	200-2000[3]	200-3000[3]
Ethane	0.2-1	0.3-0.9	0.5-2	0.3-1.3	0.3-3
Ethene	0.5-3	0.0-1	0.5-5	0.3-4	1-4
Propane	0.2-0.6	0.1-0.3	0.2-0.7	0.2-0.5	0.2-1.3
Propene	0.2-0.6	0.0-0.6	0.2-2	0.2-0.9	0.3-0.8
isobutane	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05
n-butane	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05	≤ 0.05
$C_{2:0}/C_{2:1}$	< 0.5	-	< 1	< 0.5	< 1

[1] Given ranges represent a single observational period.

[2] Values do not include observations from region of gas seep.

[3] These unusually high concentrations of methane are the result of strong thermal stratification that existed at the time of the measurements.

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 interior eel gross communities. The concentrations of ethane and propane were everywhere near or below 1 nℓ/ℓ, 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.

8.2 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 8-1.

The waters of the northeast 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 producers 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. Studies to be conducted this spring on benthic sources of LMWH should provide additional insight into the sources of the LMWH and their primary origin.

The single anomalous feature in the northeast Gulf 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 are the highest concentrations 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.

8.3 Lower Cook Inlet

During April of 1976, a minimal observational program was initiated in Lower Cook Inlet in cooperation with biological productivity studies. The few data that were collected have been discussed in the fifth quarterly report (1 April-30 June 1976, Cline and Feely, 1976c) and are not of sufficient density to represent baseline conditions. Ranges of hydrocarbon concentrations observed in April are included in Table 8-1 for completeness. Intensive studies clarify localized sources of hydrocarbons, including those likely to be present in the area north of Kalgin Island where active production is currently taking place.

The anomalous hydrocarbon distributions were observed near Kalgin Island, where high concentrations of methane (~1500 nℓ/ℓ) were accompanied by significant amounts of ethane and propane (1 and 0.5 nℓ/ℓ, respectively), but no ethene or propene. Little vertical water column structure was evident at the time of the observations, thus the source of the hydrocarbons could not be unequivocally identified. Because the region just north of Kalgin Island is actively producing both gas and petroleum, it would not be unexpected to observe trace quantities of petroleum-derived hydrocarbons or components of natural gas in the water column.

8.4 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 attached report (Appendix I), 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 $n\ell/\ell$ 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 $n\ell/\ell$ over all of Norton Sound, except the seep area. The olefinic C_2 and C_3 components are generally greater than 1 $n\ell/\ell$ 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.

8.5 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 8-1). Maximum concentrations of methane were in excess of 3000 nℓ/ℓ near the town of Katzebue, 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 ethene 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 Washington, 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 8-1).

9. FUTURE RESEARCH ENDEAVORS

The present research activity centers largely on the seasonal and spatial variations in low molecular weight hydrocarbons with some attention being given to significant source regions. Our present field scheduling in the Bering Sea, Norton Sound, Chukchi Sea and the northeast Gulf of Alaska will, for the most part, satisfy our commitment to the establishment of baseline levels of LMWH in these areas. Since some of the geographical areas will be visited three times, others only once, 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.

Detailed measurements of anomalous hydrocarbon sources, such as those revealed near Hinchinbrook Entrance and Norton Sound, should be undertaken. Emphasis should be placed on near-bottom gradients and trajectories of the hydrocarbon plume. These efforts should be supported with detailed examination of the hydrocarbon content of the underlying sediments, particularly on surficial gradients from which flux calculations can be carried out. Attention should be given to the composition of the gases with particular regard for the C_2-C_7 fraction, including aromatics. If the concentration of methane is sufficiently high, it should be extracted and analyzed isotopically for $\delta^{13}C$ composition. The isotopic composition of the methane should reveal its primary source, whether it be principally biogenic in origin or the result of the percolation of natural gas from underlying reservoir rocks.

As the result of our observations made last September 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 1978.

Similar detailed studies of natural gas and petroleum seep elsewhere would also be indicated. Here, the Geological Survey should be consulted as to the seep location, input activity, and possible hydrocarbon composition. We are continuing our dialogue with the Conservation Division and the Gas and Oil Branch of the USGS as to the location of promising seep areas in the OCS.

Lastly, we feel that the current production of petroleum in Upper Cook Inlet should be examined in terms of LMWH. The results of Kinney et al. (1970) indicated elevated levels near the Forelands, which they ascribed to possible gas seeps. Observations will be conducted this spring and summer in Lower Cook

Inlet and special attention will be given to the Forelands area. Based on these results, as well as geological data on the occurrence of seeps and sub-bottom geological structures, a study should be conducted into the sources of the hydrocarbons (i.e., platforms or natural seeps).

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 sediment 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 mechanisms and environmental control parameters.

10. FOURTH QUARTER FIELD ACTIVITIES

10.1 Summary

No field operations were conducted during the fourth quarter, although staging and equipment development is going forward for the major cruise to LCI in April of this year. Equipment design and development includes the sediment gas harpoon and associated gas extraction apparatus.

Data synthesis has continued with all the LMWH data taken to date with emphasis placed on the Norton Sound gas seep. Attached to this report is a preprint of the manuscript being submitted to *Science*.

10.2 Estimate of Funds Expended through 1 April 1976

	Allocated	Expended to Date	Balance
Salaries and overhead	$41,238	$19,916	$21,322
Major equipment	8,400	4,600	3,800
Expendable supplies	4,500	2,084	2,416
Travel and per diem	4,740	2,100	2,640
Shipping	1,000	250	750
Publications	1,000	300	700
	$60,878*	$29,250	$31,628

*Not shown in this figure is approximately 4K in FY 76 funds, which were not carried forward.

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Additional Report with RU 153

SUBMARINE SEEPAGE OF NATURAL GAS IN NORTON SOUND, ALASKA

by

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Abstract. During a 1976 survey of petroleum hydrocarbon distributions in the waters of Norton Sound, relatively large concentrations of dissolved C_2-C_4 alkanes were observed in a localized area approximately 40 km south of Nome, Alaska. The hydrocarbons, apparently originating from a point source in the sea floor, could be identified in the near-bottom waters down-current for more than 100 km. Concentrations of ethane, propane, iso- and n-butanes near the locus of the seep were above ambient levels by a factor of 10 or more. Preliminary estimates of the composition of the initial gas phase composition predict methane:ethane and ethane:propane ratios of 24 and 1.7, respectively, assuming the hydrocarbons were introduced via bubbles. Taken at face value, the low C_2:C_3 ratio is indicative of gas from a liquid petroleum source rather than from nonassociated or biogenic natural gas.

Preliminary data on the structural geology of Norton Basin support this interpretation based on the observed chemical and physical characteristics of the plume. Strata truncated by an unconformity dip basinward from the seep locus; velocity pulldowns, and numerous steeply dipping faults in the immediate vicinity of the seep provide corroborating evidence for gas or petroleum-charged sediments and strata with favorable avenues for migration of mobile hydrocarbons to the sea floor. These factors, taken in concert with the sedimentalogical regime, recent revision (increase) of basin depth estimates, and the highly localized origin of the hydrocarbons, strongly suggest a thermogenic rather than a recent biogenic origin for these gases.

Introduction

Environmental studies currently being conducted in the waters of the outer continental shelf (OCS) of Alaska include measurements of the distribution and abundance of the low molecular weight aliphatic hydrocarbons (1) to evaluate their efficacy as potential indicators of petroleum hydrocarbons arising from both human activities and natural sources. Because the saturated LMWH (C_1-C_4) are present in significant amounts in most natural gases and crude oils (2) and because they are relatively soluble in natural waters (3), these components have been used extensively to monitor and document the introduction of petroleum-related hydrocarbons entering the marine environment from production, shipping, and transfer operations (4-7). In addition, the ease with which these particular hydrocarbons can be surveyed has led to their use as an adjunct exploration tool for the detection of submarine gas and/or oil seeps (8).

Although many submarine petroleum seeps have been reported (9) few have been well documented, partially because of observational problems associated with the marine environment and partially because offshore exploration has thus far yielded few data that have entered the public domain (9). Of the relatively few marine seep regions that have been identified and reported, very few have been studied in detail, the major exception being the large volume seep swarm observed near Coal Oil Point in the Santa Barbara Channel of the southern California Bight area (10). Numerous gas seeps have been identified in the northern Gulf of Mexico and some have been studied chemically. A review of these studies can be found in the work by Bernard et al. (7) and the references contained therein.

In this report, we discuss the occurrence of relatively high concentrations of C_2-C_4 alkanes in Norton Sound, a large shallow bay south of Seward Peninsula.

Based on both chemical and geological evidence, we believe that these hydrocarbons may originate as petroleum-associated gases and may therefore indicate the occurrence of petroleum in the rocks beneath Norton Sound.

The hydrocarbons were analyzed by He extraction and gas chromatography according to a suitably modified procedure originally developed by Swinnerton and Linnenbom (11). Briefly the procedure is as follows: Individual water samples were taken from predetermined depths in 10 ℓ Niskin samplers attached to a rosette sampler. The volatile hydrocarbons were removed from 1 ℓ aliquots of seawater in a stream of ultra pure helium and concentrated on a column of activated alumina maintained at -196°C. After warming the cold trap to 100°C, the volatilized components were chromatographed on a polymer bead (Poropak® Q) and detected sequentially with a flame ionization detector as they emerged from the column. Samples were collected aboard the NOAA research vessel DISCOVERER in September 1976.

Historic Petroleum Seeps and Shows

Onshore oil shows and marine seeps have been reported at several places along the shores of Norton Sound (Fig. 1). Prospecting for oil was carried out at Hastings Creek near Cape Nome in 1906 (12). Two wells were drilled; one showed a trace of oil and the other encountered flammable gas at 37 m in nonmarine coal-bearing rocks (12, 13). The gas was at sufficient pressure to blow a 550 kg stem 23 m up the hole. Cathcart et al. (12) also mention oil-like films on the lagoons near Nome and Cape Nome, and a beach foam resembling paraffin which was brought in by the onshore (southerly) winds.

Other oil seeps have been reported at the mouth of the Inglutalik River on Norton Bay (13, 14), and 32 km northwest of Nome in the Sinuk Valley which may be underlain by infolded, unmetamorphosed Cretaceous or Tertiary sediments (13).

An outcrop of middle Cretaceous oil shale has also been reported on Besboro Island in Norton Sound 40 km northwest of Unalakleet (13).

Geologic Setting

The geology of Norton Basin, the sedimentary prism beneath Norton Sound, has been discussed by Scholl and Hopkins (15), Grim and McManus (16), Nelson et al. (17), Walton et al. (18), Tagg and Greene (19), Moore (10), and others. Reconnaissance seismic reflection survey data suggest that the basin area is about 130,000 km^2 (15). Maximum basin depth has recently been estimated as approximately 5.5 km (21); the 100,000-km^3 volume calculated by Scholl and Hopkins (15) may therefore need to be increased by as much as 50-80 percent.

Seismic reflection profiles show the basin fill to consist of two major stratified units comprising the Main Layered Sequence (15) covered by a thin mantle of Quaternary deposits (17, 19). The major units are separated by an unconformity which lies at a depth of approximately 500-700 m near the basin axis. Greene and Perry (22) suggest that this unconformity represents a change in the rate of subsidence during middle or late Pliocene time, and Hopkins (23) notes that the Bering Land Bridge had been reestablished through most of the Pliocene. Norton Basin is underlain by an acoustic basement formed by strata which are probably analogous to the diverse older Paleozoic and Mesozoic rocks that occur on land around the basin margins (24, 25, 26).

Although Quaternary deposits everywhere cover the older Cenozoic and Mesozoic basin fill, some onshore outcrops and drill-hole data give clues to the nature of these deposits. Nonmarine coal-bearing strata of late Oligocene age are exposed on northwestern St. Lawrence Island (22), and several offshore holes drilled by the U.S. Bureau of Mines near Nome encountered marine sands and clayey silts of early Pliocene age at a subbottom depth of approximately

18 m (15, 17). Late Miocene or early Pliocene marine limestone was recovered from a dredge haul 30 km south of St. Lawrence Island, just outside the basin. Considering these facts and regional stratigraphic patterns, the basin fill probably consists of late Cretaceous and lower to middle Tertiary sedimentary rock in the lower major unit and upper Tertiary and Plio-Pleistocene sedimentary rocks and sediments in the upper major unit. All direct evidence suggests that the lower unit is nonmarine, but the size of the basin is such that unseen transitions to marine facies could occur within this unit.

Strata of the lower major unit form a broad synclinorium whose principal axis trends generally east-west. The beds of the upper unit are more nearly flat-lying above the angular unconformity. Normal faults occur in many places around the basin periphery (15, 16, 22). Some faults form scarps on the sea floor (16), and some offsets at the acoustic basement surface can be correlated with fault traces (15).

Single channel reflection profiling operations were carried out in Norton Sound on a joint USGS-University of Washington cruise in 1967 (16) and by the University of Washington and NOAA (then ESSA) during the summer of 1969 (18). Three tracklines passed near the seep location and are shown in Figure 1. The reflection records are reproduced in Figure 2 and show: 1) the southward dip toward the basin axis of the lower unit of the Main Layered Sequence (15), and 2) the angular unconformity separating the major basin units. The southward dipping unconformity rises to within 60-70 m of the sea floor in the vicinity of the seep; 10 km north of the seep it is covered by only 10-15 m of Quaternary sediment where it passes over an anticlinal crest and dips to the north. The basin fill is more than 1.2 km thick beneath the seep site, although the acoustic basement signature is difficult to discern.

Several steeply dipping normal faults are shown by the reflection records in the vicinity of the seep. Some of these faults displace only the strata of the lower unit and may be growth faults associated with basin subsidence. More recent USGS geophysical work also indicates the existence of a northwest trending near-surface fault near the seep (Hans Nelson, personal communication). The record along line TT18-C20 (Fig. 2) shows some sea floor depressions in the vicinity of the seep, with reliefs ranging from 2 to 8 m. Tagg and Greene (19) noted many discontinuous surface and buried channels trending generally west and southwest off Nome, and the well-developed depression at 0630 appears to be a channel created by fluvial processes. The poor quality of the record does not permit definite conclusions regarding the origin of the other irregularities; some may be expressions of near-surface faulting in the basin sediments.

Acoustic responses which may be velocity "pull-downs" appear on two of the records. These suggest the presence of low velocity gas-charged sediment within 100-200 m of the sea floor. The many faults, the basinward dipping strata truncated by an unconformity, and the velocity "pull-downs" all indicate that the geology in the area of the seep is compatible with a model for hydrocarbon fluids seeping toward the surface from deep sources.

Results

Relatively high concentrations of C_2-C_4 alkanes were observed approximately 40 km south of Nome in water 20 m deep. Shown in Figure 1 is the near-bottom distribution of ethane ($n\ell/\ell$ STP); the plume structure being rather similar to those observed for propane, iso- and n-butanes. Concentrations of ethane reached 9.6 $n\ell/\ell$ near the locus of the seep, or a factor of about 20 above the background levels observed just south and east of the seep location. Similar enrichments in the concentrations of propane, iso- and n-butanes also were observed. Maximum concentration of propane was 3.3 nℓ/ℓ, whereas the levels of iso- and n-butanes reached 0.5 nℓ/ℓ. These concentrations also are at least a factor of 10 above ambient levels (Table 1).

The plume of ethane-rich waters appears to emanate from a point source in the sea floor and drift (advect) north toward the coast. Several weeks after these observations were made, current measurements near the locus of the seep showed a weak north-setting current of less than 10 cm sec^{-1} (27). In accord with the general cyclonic circulation that was observed in outer Norton Sound during this season (27), the ethane-bearing waters were advected to the west past Sledge Island to at least 168°W longitude, the western terminus of our survey grid.

This is a distance of nearly 140 km from the suspected seep source. The "puff" structure of the plume shown in Figure 1 may be due to several factors. Suggested causes include multiple sources, episodic seep activity, and possible meso-scale fluctuations of the mean circulation. The second of these seems most probable (9), but we can't rule out short-term meteorologically induced fluctuation in the mean circulation.

No gas bubbles or surface slicks were noted by visual observations from the deck of the ship. However, much of the sampling was conducted during hours of darkness. Similarly, no evidence of gas bubbles was detected on the ship's precision depth recorder.

Discussion

A summary of the observed dissolved hydrocarbon composition near the locus of the seep (sta. N18F) is compared to similar data from a typical station 15 km to the south in Table 1. The relatively high concentrations of ethane, propane, and butanes are unusual features of this gas seep, along with the preponderance of alkanes versus alkenes, and the apparent relative deficiency in methane.

Natural gases originate in a variety of ways and show a wide range of chemical compositions. Methane of microbial origin (marsh gas) is widespread, of shallow origin, isotopically light, and is initially accompanied by no more than trace quantities of the heavier homologs of methane. Methane from "dry gas" accumulations not associated with liquid petroleum may be of deeper origin, a product of thermochemical coalification of deeply buried sedimentary organic matter containing less than 6 weight percent hydrogen (28-30). Methane from thermogenic "dry gas" accumulations tends to be isotopically heavier than bacterial methane and can be accompanied by variable amounts of the higher molecular weight alkanes, ranging from trace amounts upward to about 1-2 percent. With increasing contents of higher homologs and other more complex hydrocarbon compounds, natural gases from "dry gas" deposits grade into "wet gases," gas-condensate systems, and the gases associated with crude oil accumulations, either in gas phase "gas caps" or in natural solution with the oil.

The relatively deficient methane content of the gases exsolved from Norton Sound waters is of special interest because it affords a diagnostic approach toward understanding the genesis of these gases. The conspicuous deficiency of methane may be the result of several factors operating separately or in concert: (1) seep gases are naturally deficient in methane relative to the more complex hydrocarbons; (2) the composition has been fractionated during migration from the deep source beds; (3) selective microbial oxidation, either in the sediments or in the water column, has resulted in the observed ratios, or (4) the components of the seep gases have been physically fractionated during the solution process. In the first case, nitrogen or carbon dioxide would presumably make up the bulk of the seep gas, although such compositions are relatively uncommon (31). Selective fractionation of the hydrocarbons during migration through the sediment column is possible, but we're not able to assess the significance of this process at this time.

Similarly, preferred microbial oxidation of methane is possible, either in the surficial layers of the sediments or in the overlying water; however, if the flux of the seep gases is sufficiently high, this fractionation mechanism would be minimized. The last process affords a possible explanation for the hydrocarbon ratios observed. If the hydrocarbons are injected into the water via bubbles, Schink et al. (32) have shown, using a simple stagnant film boundary layer model, that gaseous hydrocarbons would be fractionated between the gas and the aqueous phases according to their partial pressures, solubilities, and molecular diffusivities. Other factors such as hydrostatic pressure, bubble surface area, and buoyancy velocity affect the absolute transfer rate of gas, but presumably would not selectively fractionate the gases. Although we have no information at present on the hydrocarbon flux, bubble size frequencies, or even the appropriateness of the stagnant film model in this instance, a few qualitative statements are possible. If the depth of water is shallow and the bubbles consequently large, only a small amount of gas actually dissolves before the bubble escapes to the atmosphere. For example, the model profiles presented by Schink et al. (32) show that for large bubbles ($r_0 >$ 0.14 cm; mass > 30 μg) and shallow depths ($Z < 30$ m), less than 0.5 percent of the mass is lost for each meter of water column traversed. If we confine our arguments to the lower 10 m of the water column, less than 5 percent of each component would be transferred to the dissolved state, and probably much less, depending on the actual dimension of the bubbles. The time required to achieve equilibrium between the water and the gas bubbles also depends on the current field strength over the seep. Current measurements taken in early October in the vicinity of seep would suggest near-bottom velocities of 0-20 cm sec^{-1} (27), although they could be locally higher during periods of storms or freshwater runoff.

By way of analogy, the waters of Norton Sound are grossly undersaturated in the C_1-C_4 hydrocarbons with respect to the pure component at hydrostatic pressures encountered (33). If gas bubbles being released were pure methane, the equilibrium concentration would be approximately 1×10^8 nℓ/ℓ, or a factor of 2×10^5 above the observed levels. From this we conclude that either the partial pressure of methane in the gas phase was exceedingly low or that only modicum quantities of methane and other hydrocarbons have actually dissolved in the water column as the result of seep activity. High microbial oxidation rates also may be operative, but our extensive measurements in the OCS areas of Alaska shows dissolved methane to be quasi-conservative, at least over meso-space scales.

Although we have little information on the physical and chemical characteristics of the seep, some tentative assignment can be made as to the probable methane:ethane:propane ratios in the seep gas. Using the equations presented by Schink et al. (32), the incremental increase in the concentration ratio for methane and ethane may be estimated (34).

$$\Delta C_1/\Delta C_2 = (\alpha_1/\alpha_2)(D_1/D_2)(p_1/p_2). \qquad (1)$$

To solve for the hydrocarbon partial pressure ratio in the gas phase, we adopted the solubility coefficients presented by McAuliffe (3) and the molecular diffusivities of methane, ethane, and propane at 4°C given by Witherspoon and Bonoli (35). Measurements made by these authors showed that the ratios of the molecular diffusivities (i.e., D_1/D_2 and D_2/D_3) did not differ significantly from 1.24 in the temperature range 4°C to 20°C. In both instances, no corrections were made for the ionic strength of the water. We assumed that specific interactions due to the ionic nature of seawater would nearly cancel in the calculation of respective ratios, at least to the level of significance desired here.

The incremental increase of methane, ethane, and propane concentrations (ΔCi) was estimated by comparing concentration levels at the locus of the seep with stations to the south and east. The incremental increases in concentrations of methane, ethane, and propane were approximately 200 $n\ell/\ell$, 9 $n\ell/\ell$, and 3 $n\ell/\ell$, respectively. Estimation of incremental increases in methane concentrations was hampered because of high temporal and spatial variability. However, 200 $n\ell/\ell$ would represent an upper limit for ΔC_{CH_4}, although Table 1 suggests a value closer to 300 $n\ell/\ell$. Substitution of these values into equation (1) yielded the following partial pressure ratios in the source gas: $P_{CH_4}/P_{C_2H_6} = 24$, and $P_{C_2H_6}/P_{C_3H_8} = 1.7$. The dissolved ethane:propane ratio in the near and far field of the dispersion plume was calculated by means of two-way linear regression analysis. The relationship between ethane and propane was found to be $C_{C_2H_6}$ ($n\ell/\ell$) = $2.9\ C_{C_3H_8} + .07$ ($n = 14$, $r = 0.983$). Accepting this ratio as indicative of the seep gas, the partial pressure ratio of ethane to propane would be 1.7, the same as calculated above. Interestingly, the analysis of the reservoir fluid from the Sadlerochit oil pool, Prudhoe Bay, also yields a mol percent ethane:propane ratio of 1.7 (36).

Nikonov (37), in a detailed study of the compositions of over 3500 gas and oil deposits in the U.S.S.R. and the U.S., has characterized various petroleum and gas provinces on the basis of their C_2/C_3 ratio. Briefly, Nikonov observed that the C_2/C_3 ratio decreased systematically from 5 for natural "dry" gas to approximately 2 for gases of oil deposits. Ignoring any compositional fractionation that may have occurred during migration from the original source strata to the sea floor, Nikonov's interpretation suggests that the low C_2/C_3 ratio calculated here (1.7) is indicative of gases associated with oil deposits (C_2/C_3 = 2) rather than a natural gas (C_2/C_3 = 5).

Although the concentrations of the C_1-C_4 fraction in the vicinity of the seep are relatively high compared to levels observed immediately upstream, the concentrations remain well below expected saturation values. We believe this to be the result of kinetic rather than compositional factors. We suggest that solution equilibrium between a gas phase and the bottom waters of Norton Sound is not even closely approached. Low abundances of the low molecular weight hydrocarbons are probably due to small or episodic seep activity, persistent horizontal currents over the seep, and the injection of relatively large bubbles as the result of shallow water depths ($P_{total} \leq 3$ atm).

Other diagnostic chemical characteristics of the seep hydrocarbons (sta. N18F) are compared with those from a nearby station (sta. N13) in Table 1. The most striking feature is the ethane:ethene ratio and the methane to ethane plus propane ratio. Because of the low biogenic production of higher homologs of methane and the near absence of olefins in petroleum, both these ratios are useful indicators of petroleum-derived hydrocarbons. The C_1/C_2+C_3 ratio has been used by Bernard and co-workers (7) and others in the Gulf of Mexico to distinguish biogenic and thermogenic hydrocarbon sources or mixtures of same. In general, ratios less than 50 are considered to be indicative of thermogenic sources; higher ratios imply significant biogenic input (7). As can be seen in Table 1, the minimum ratio observed in Norton Sound as approximately 40 near the locus of the seep, compared to background levels of 400 or greater outside the seep. Thus regional variations may be more diagnostic than the absolute value of the C_1/C_2+C_3 ratio.

Similarly, the high ethane:ethene ratios in the area of the seep are indicative of the near-zero input of the C_2 unsaturated hydrocarbon. Comparison of the concentrations of ethene and propene at stations N13 and N18F reveals a difference of only 0.3 nℓ and 0.0 nℓ/ℓ, respectively; these not being significantly different when sampling and analytical uncertainties are considered. Analyses of many samples from the near-bottom shelf waters of Alaska, including Norton Sound, have shown that the normal ethane:ethene ratio rarely exceeds 0.5.

In summary, the observed distributions of ethane, propane, and butanes, taken together with geological inferences on sediment accumulations, source material, and probable migration pathways for petroleum-derived hydrocarbons, suggest a possible thermochemical origin for the seep gas. Estimations of the probable C_2/C_3 mol ratio in the seep gas suggests that the hydrocarbon deposit from which the gas is leaking contains liquid petroleum in addition to natural gas, although the evidence at this point is circumstantial and equivocal. Future studies are planned in which a broader range of hydrocarbon classes (heavy aliphatics, aromatics) will be investigated in both the water column and the bottom sediments. It is hoped that these investigations will lead to a clearer understanding of the compositional complexity of the seep hydrocarbons, their probable source, their impact on the local marine biological community, and their possible implications regarding the prospectiveness of Norton Basin as a source for commercially exploitable petroleum.

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34. The fractional mass loss (Δm) out of a bubble per unit time (Δt) is given by the expression

$$\Delta m = \frac{A \cdot P_t \cdot \alpha \cdot M \cdot D}{R \cdot T \cdot \Delta h} \cdot \Delta t,$$

where A is the bubble surface area, P_t is the total gas pressure in the bubble (hydrostatic + surface tension), α is the bunsen coefficient, M is the molecular weight of the component, D is the molecular diffusivities of the component in water, R is the gas constant, T is the absolute temperature, and Δh is the boundary film thickness. Since $\Delta m/M$ is equal to the concentration increase (ΔC_i) per unit time, the concentration ratio of two components is simply proportional to the respective partial pressures, solubilities (bunsen coefficients), and molecular diffusivities.

$$\Delta C_1/\Delta C_2 = (\alpha_1/\alpha_2)(D_1/D_2)(p_1/p_2).$$

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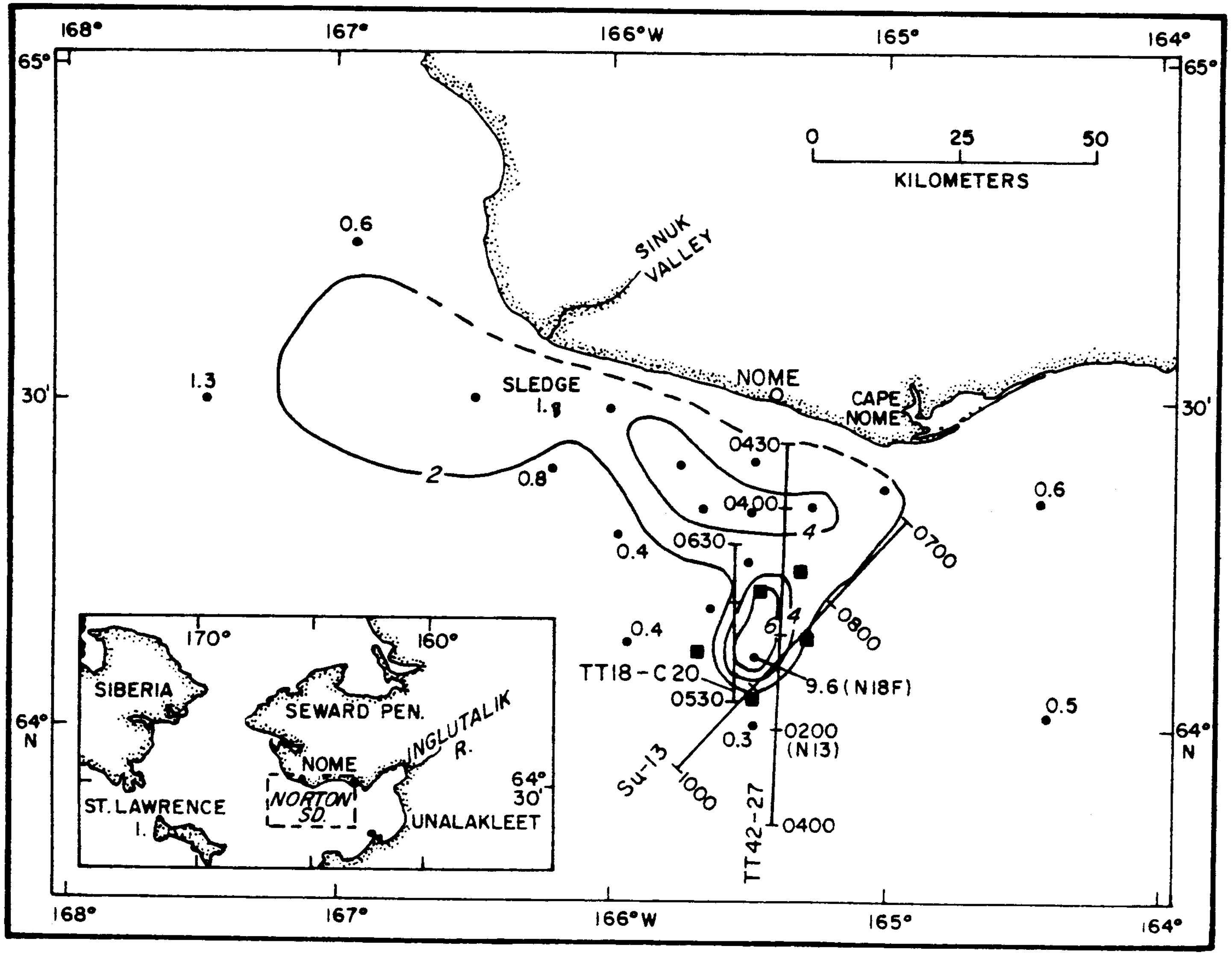
Figure Captions

Figure 1. Distribution of ethane (nℓ/ℓ, STP) is shown within 5 m of the bottom in September 1976. Station N18F is the nearest approach to the locus of the seep; station N13 is the control station. The grid was occupied on two separate occasions: the first (●) on 13 Sept., the second (■) on 23 Sept. Station N18F was visited on both occasions, although due to imprecise navigation, the 23 Sept. occupation was approximately 4 km to the northwest. Concentration of ethane at this time was 4.8 nℓ/ℓ, or approximately 50% of that observed on 13 Sept. Also represented are the seismic reflection tracks with reference time ticks, and locations of onshore petroleum seeps and shows (▲).

Figure 2. Seismic reflection records obtained near the seep along tracklines shown in Fig. 1. Lines TT18-C20 and TT42-27 from University of Washington 1967 and 1969 cruises. Line SU-13 from NOAA 1969 cruise (22). Arrows indicate following: CPA - closest point of approach to seep site (sta. N18F); F - fault; VP - velocity "pull down" or other acoustic anomaly indicating possible gas charged sediments.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SLEDGE I.
0.6
1.3
1.9
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0.4
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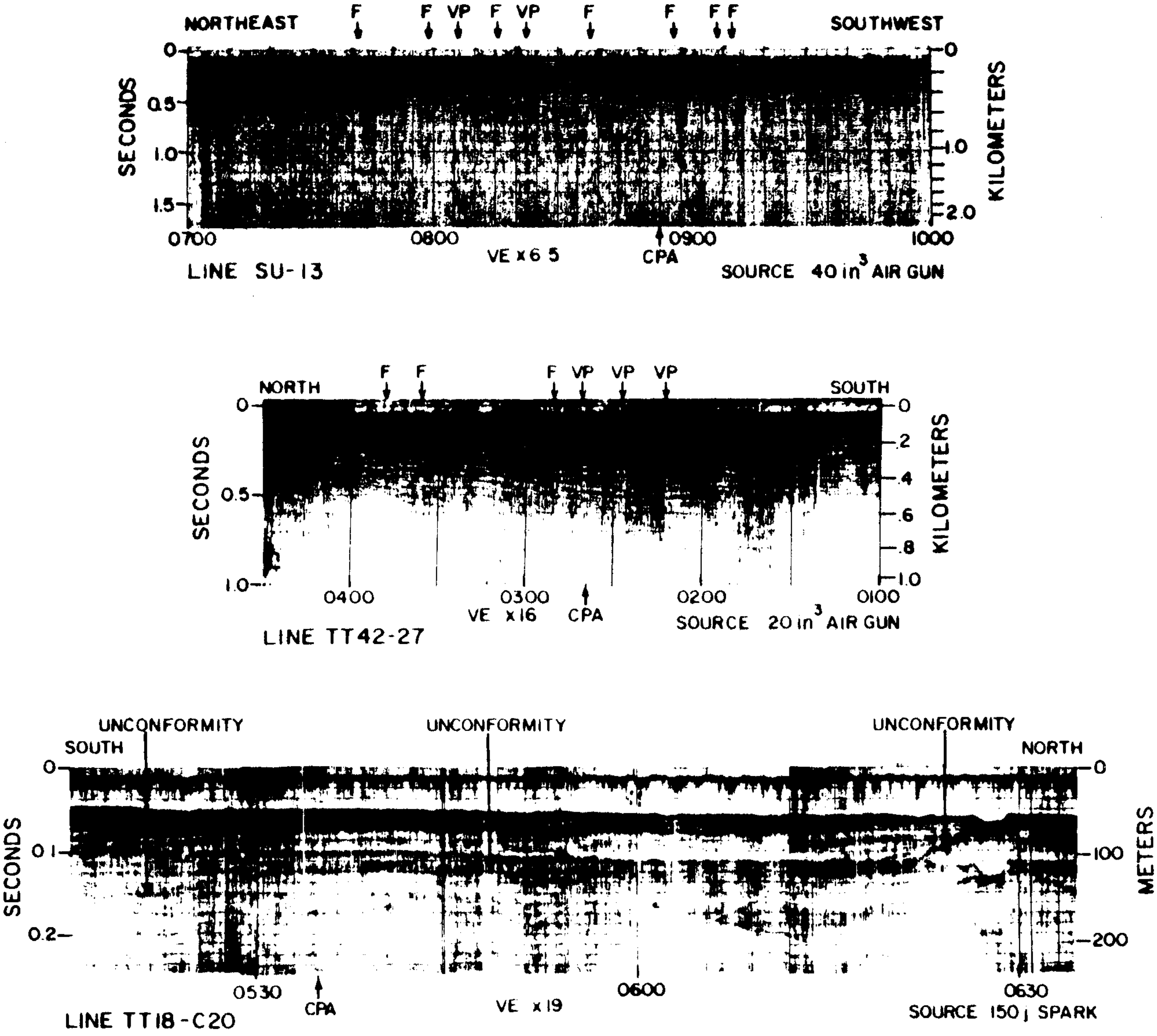
2
4
6
0430
0400
0630
0700
0800
0530
TT18-C20
9.6 (N18F)
0200 (N13)
0400
Su-13
1000
TT42-27
SIBERIA
170°
160°
SEWARD PEN.
NOME
INGLUTALIK R.
ST. LAWRENCE I.
NORTON SD.
64° 30'
UNALAKLEET

Figure 1.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KILOMETERS
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0800
0900
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SOURCE 40 in³ AIR GUN
NORTH
F F
F VP VP VP
SOUTH
SECONDS
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0
.2
.4
.6
.8
1.0
0400
0300
0200
0100
VE x16
CPA
SOURCE 20 in³ AIR GUN
LINE TT42-27
UNCONFORMITY
UNCONFORMITY
UNCONFORMITY
SOUTH
NORTH
SECONDS
0
0.1
0.2
METERS
0
100
200
0530
CPA
0600
VE x19
0630
SOURCE 150 j SPARK
LINE TT18-C20

Figure 2.

Tables

Table 1. Dissolved hydrocarbon concentrations within 5 m of the bottom near the locus of the seep (sta. N18F; 64°07.3'N, 65°29.5'W) are compared to similar measurements at station N13 (63°59.7'N, 165°29.7'W).

Station No.	Depth (m)	Methane	Ethane	Ethene	Propane	Propene	iso-Butane	n-Butane	$C_{2:0}/C_{2:1}$	C_1/C_2+C_3
		nℓ/ℓ (STP)								
N18F	17	525	9.6	1.5	3.3	0.4	0.5	0.6	6.4	50
N13	17	219	0.3	1.2	0.2	0.4	<0.03	<0.03	0.2	413

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NATURAL DISTRIBUTION OF TRACE HEAVY METALS AND ENVIRONMENTAL BACKGROUND IN ALASKAN SHELF AND ESTUARINE AREAS

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I. SUMMARY

During the current contract period, the scope of this project was extended to include lower Cook Inlet, Norton Sound and the southern part of the Chukchi Sea in addition to the three shelf areas previously included (Gulf of alaska, S. Bering and Beaufort Seas). Baseline collection and analysis of water column samples is now considered to be complete although some areas, notably the Beaufort Sea, have been very poorly covered. For the soluble contents analysed to date, *viz* Cd, Cu, Pb, Ni, Hg and V, concentrations in filtered seawater from all shelf regions of Alaska are generally lower than commonly accepted oceanic means. As expected for such open ocean areas, distributions are quite uniform.

Surficial sediment samples have been collected in a uniform, contamination-free fashion in all these areas and a number of heavy metals have been determined both as concentrations in extractable (i.e., "available") fractions from the sediment surface and as "whole rock" totals. In all cases the heavy metal contents are a function of the sediment grain size fractionation and the lithology i.e., finer grain sediments are enriched in metals and specific suites of trace elements are associated with, for example, calcareous sediments. As a by product of the water analysis, a number of particulate sediment samples have also been determined. The concentrations of particulate heavy metals in the water are related to the particulate sediment load with enhanced concentrations adjacent to the sediment interface and in coastal waters. The clay mineralogy of all the fine grained fractions have also been determined and are discussed here.

Our collection of biota "index species" is still very sparse and we have been unable to interpret possible seasonal or life-cycle effects.

A fairly representative spread of two intertidal benthic species - *Mytilus* and *Fucus* - have been analysed. Our data show heavy metal contents as low or lower than in other regions. The latter are frequently based in favor of industrial or otherwise impacted regions. As noted also last year, the Alaskan shelf regions could well serve as a type example of pristine coastal environments.

It is concluded that future efforts in this program should be directed towards a better understanding of processes and reactions controlling the distribution and migration of heavy metals in type localities around the Alaskan shelves. Particular emphasis should be paid to food web transfer studies and to estuarine and near-shore environments where natural chemical gradients are best developed and where future oil spills would be physically confined to effect maximum impact on the water, sediment, and coexisting (predominately benthic) biota.

II. INTRODUCTION

Relationship Between Oil Development and Heavy Metal Distributions

A general discussion of the principles of heavy metal distributions in the marine environment has been given in both previous Annual Reports and will not be reiterated here. Similarly we have previously discussed the possible ways in which the natural geochemical distributions of the metals may be affected by industrial development and potential impingement of massive doses of hydrocarbons in the shelf and coastal regions. Three types of impacts were considered in detail in the 1975-1976 Report (Burrell, 1976):

i. Heavy metals indigenous to crude oil

ii. Heavy metals in the associated formation waters, drilling muds and engineering structures

iii. Perturbation of the geochemical environment by massive oil spills leading to mobilization or removal of "available" forms of the metal.

We have always maintained that the only possible quantitatively important effect must be of type (iii), although sampling programs have been designed to yield the necessary background data to assess (i) and (ii) also. Largely because of the overwhelming importance of the deposited sediments as the marine heavy metal sink, we have previously emphasized potential reactions at the sediment-water interface and have stressed the use of benthic fauna as "index species". Metals chosen for study have therefore not necessarily been those particularly concentrated in crude oil since the sediments carry all heavy metals at enhanced concentrations over those in the coexisting marine waters. Instead we have been concerned with metals which either:

i. are highly toxic to man and hence of major importance in any impact study

ii. are suitable geochemical process indicators.

Further comments on these basic premises follow.

Heavy metal toxicity

There is surprisingly little known concerning the toxicology of specific metals in the marine environment. There is a wealth of data for bioassay tests on various marine organisms of the LD_{50} variety but these are mostly for large doses of single elements under non-natural conditions. A very few sub-lethal, chronic effects have also been documented. In a program of this type it seems best to take as a point of departure the toxicity limits for water and food established for human consumption, even though such have been frequently designated based on minimal scientific rationale. Clearly, many marine organisms can naturally accumulate certain metals to levels which, if present in similar concentration in man, would be very harmful. There seems to be no meaningful way of constructing "pollution indices" for the oceans given our present poor understanding of concentrations and processes. Such attempts have been made, however. For example, Figure 1 illustrates, in a general way, the physiological "character" of the major heavy metals. Column A of Table I lists "toxicities" (NAS, 1973), and column B gives the pollution ratio (suggested concentration in seawater - here values *circa* 1970 - over toxicity) of Ketchum (1975). It may be seen that several metals - notably nickel, zinc, copper and cadmium - are, according to this compilation, either at or very close to being present in toxic concentrations in the present oceans. This is an interesting concept, since clearly the present influx of anthropogenic pollutant metals into the oceans has not caused any overall changes to the natural steady state concentrations as far as can be determined. The suggestion, made elsewhere on other evidence, that copper, for example, may be present in certain open ocean areas in concentrations which inhibit plankton growth has been discussed by Burrell (1977). The suggestion of imminent widespread toxicity in the oceans may be most obviously alleviated by feeding in the more recently obtained values for soluble concentrations (column C of Fig. 1). However, this type of exercise is futile since it ignores the processes of toxicity; for example the roles of the various chemical forms of each element in seawater. The highly toxic effects of mercury and arsenic, for example are, in part, related to ready physological interconversions between polar and non-polar species with transport in the former form and affinity with lipid material in the latter. Wood (1973) has discussed available natural mechanisms for accomplishing such chemical

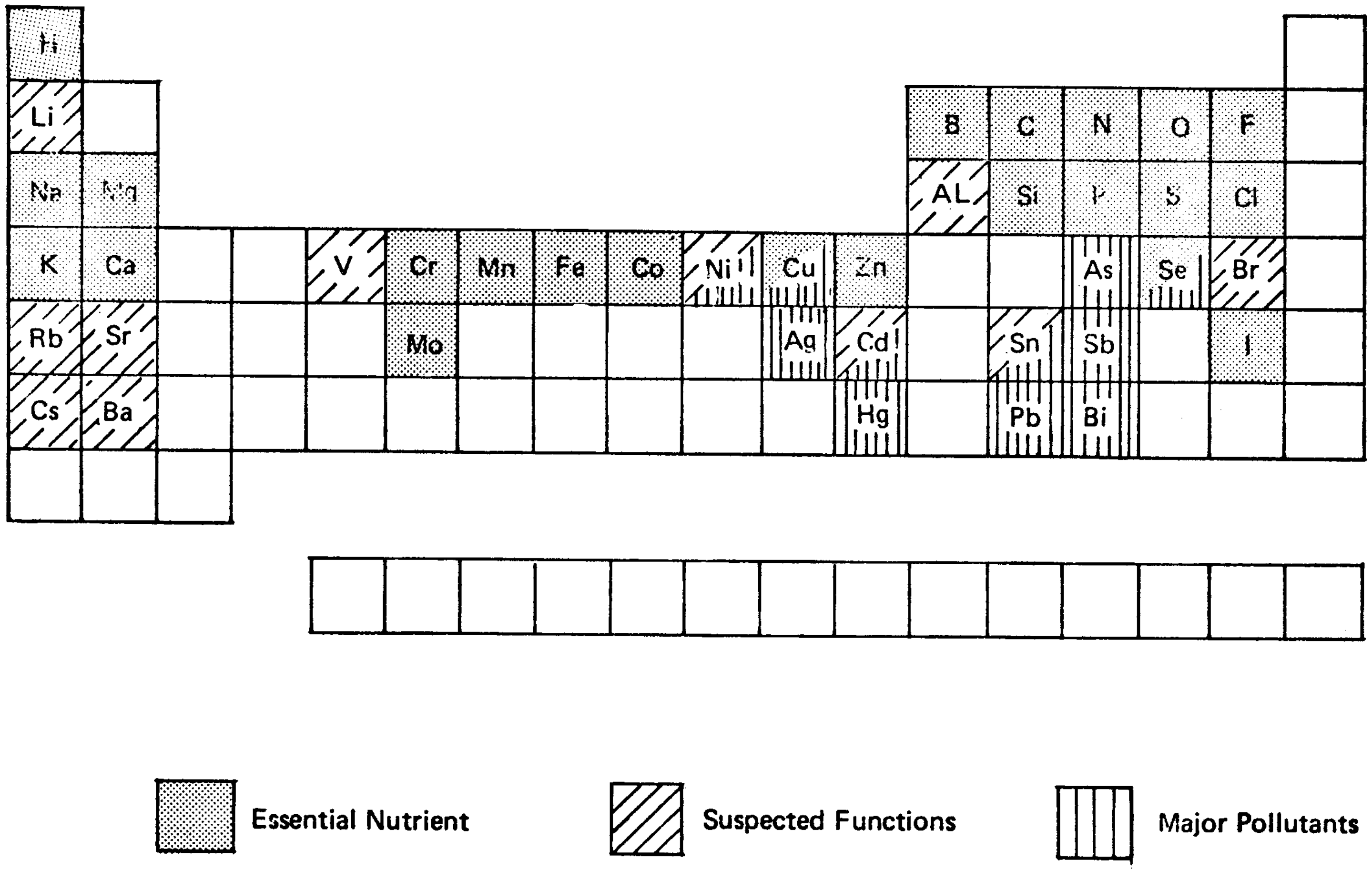


Figure 1. Physiological "character" of heavy metals

TABLE I

TOXICITY INDICES USED IN THE LITERATURE

	A	B	C
Hg	0.1	0.5	0.07
Cd	0.2	0.25	0.15
Ag	1	0.1	0.01
Ni	2	1	0.5
Se	5	0.1	0.02
Pb	10	0.003	0.003
Cu	10	0.3	0.02
As	10	0.25	0.25
Zn	20	0.25	0.25
Mn	20	0.1	0.01

[A] Toxicity, μg/ℓ, NAS (1973)

[B] Ratios of A/soluble concentrations given by Ketchum (1975)

[C] Ratio of A/currently accepted soluble concentrations; see text conversions and has concluded that, whereas Hg may be metabolically methylated in the environment, metals such as lead and cadmium cannot.

The long term thrust of an impact program such as this must be towards a better understanding of the chemical form of the metals in the environment, their natural pathways and fluxes, and hence the predicted changes likely to be wrought by various types of pollutional impact.

Importance of the sediment interface

The benthic boundary layer is of paramount importance with regard to interconversions of the chemical forms of heavy metals and corresponding remobilization and removal mechanisms. We have, for example, documented the partial remobilization of copper, carried to the ocean floor in the particulate phase, with reflux back into the bottom water column (Heggie and Burrell, 1977). Anthropogenic impact at this interface is likely to modify the natural gradients by, for example, disturbing the natural microbial populations which are considered to effect many chemical species transformations such as microbial mediation of methylation reactions noted above. Oil might, *a priori* be considered a nutrient to heterotrophic microorganisms but considerably more research is needed in this area.

Sorption of oil on particulates

An important current controversy regards the role of suspended sediment in transporting surface spilled oil. In temperate climatic regions, open ocean particulates consist of organic detritus, and silicate material found near-shore is generally organically coated. These solid phases are well suited to sorb hydrocarbon contaminants in the water column and to permit transportation to the sediment surface. Conversely the suspended sediment fraction found in the coastal waters of the Gulf of Alaska contains varying proportions of mechanically ground, highly polar, silicate flour. Preliminary experiments using sediment collected off the mouth of the Copper River, which is predominantly composed of this latter material, show very poor sorption characteristics for oil. It would be suspected, therefore, that oil spilled on the surface in these regions would be denied this transport route to the benthic boundary. In other regions at certain seasons, however, plankton material and detritus will predominate; little is known of these reactions in Alaskan waters.

Selection of index species

There is no need here to reiterate the problems associated with the selection of or even the concept of "indicator species". For reasons expounded in the previous annual report we have concentrated on benthic organisms, and intertidal species in particular (see below). The advantages of using sessile molluscs are well known (Goldberg, 1975). However, variables such as variations in size and weight of internal organs and feeding habits with season, and the presence of non-assimilated matter in the digestive tracts, are well known (see for example, the discussion by Phillips, 1976).

We have not been able to collect our own samples to date and much of the trace metal data generated is subject to these uncertainties. Improvement of this important program, following the completion of the baseline survey, is discussed in Section IX.

Importance of physically confined marine environments

The little evidence available at this time suggests that, in the subarctic regions of Alaska at least, oil spilled on the sea surface will be both physically dispersed and chemically degraded in the order of days. It is believed that the toxicological impact will, in general, be confined to the sea surface and to those coastal regions which will be impacted prior to weathering of the oil. This immediately suggests that intertidal and immediately sub-tidal regions should be studied in preference to the deep benthos. More importantly, however, we believe that major ecological disturbance and damage is likely to result where spills occur such that the oil is physically confined and where the sediment impact area is large, i.e., predominantly the coastal estuaries.

General Nature and Scope of Study

For the first part of the current contract period the baseline survey aspects of this program, as outlined in the 1975-1976 Annual Report, were continued. Several important field areas had not yet been visited and the site-specific program had not been finalized. As for the previous year the baseline survey included analysis of water, biota and sediment.

1. Water: This is the reservoir which would be initially impacted. Natural concentrations of trace metals are not known for these (or most other) areas, and available analytical techniques are largely insufficiently sensitive to detect small perturbations. There has been a need, however, to determine general baseline conditions and to check for natural anomaly areas such as might be associated with the major rivers.

Sea water is the transportation conduit for metals passing to or between the major solid phase reservoirs. Studies of transfer rates and routes necessitate quite detailed knowledge of the concentrations, local gradients and chemical forms of the metals in solution.

2. Sediment: We have flagged the bottom sediments as the major trace metal reservoir and hence a major concern in this study. It is believed that oil deposited on the sediment could potentially mobilize or increase the rate of mobilization, of a range of metals. Many such elements have known toxic properties and others would be expected to behave similarly. In addition, the metals may be solubilized in more stable (and potentially more toxic) forms, and as complexes which may be incorporated more readily, and to higher levels, in organisms.

As explained in the work statement, we have been primarily concerned with determining, not the total heavy metal contents of the sediments, but those fractions most likely to be solubilized. This latter might be variously considered the sorbed, loosely bound, or "available" fraction. None of these terms has much scientific exactitude but the intent is to isolate the labile from the structural content. In general it would be expected that the structural fraction would be quite small compared with the "extractable" so that, in practice, probably little error is introduced by performing a "whole-rock" analysis.

3. Biota: Environmental assessment programs are ultimately concerned with deleterious effects on man. The end product of this investigation, therefore, is an evaluation of the actual or potential effects of heavy metals on food species; both in terms of immediate or chronic effects on food species *per se*, but also the impact of pollutant metals on the overall food web.

In keeping with the primary emphasis of this program on the sediment-water interface region, we have proposed benthic organisms as primary "index species". One continuing objective, therefore, has been to determine baseline contents of heavy metals in a range of marine organisms, but emphasizing sub- and inter-tidal benthos.

4. Sedimentological program: Uptake and release of trace metals on and from sediments is a surface phenomenon and hence a function of the nature and, more importantly, the surface area of the sediment particles. As a simplification it may be supposed that greater quantities of metals will be exchanged from finer grained sediments than from equal quantities of coarser grained material. During the early stages of this program we hoped to coordinate this chemical program with the complementary geological programs, but to no avail. We have therefore continued a support function within the trace metal chemistry program which provides mineralogical and sedimentological data on splits of the samples analysed for the heavy metals.

5. Long term objectives: The long term objectives of this program are to recognize pollutional impact on the ecosystems, and to predict the effects of such pollution in terms of transport and changes in reservoir contents. Since this can only realistically be studied in certain judiciously selected sub-areas, we have started to coordinate our efforts during the current contract period in specific-study sites.

Specific Objectives During the Current Contract Period

1. To continue, and wherever possible, complete, the required baseline survey of the present concentrations of a suite of heavy metals in the water column, surface sediments and selected biota within the study area.

During the period covered by this report, the initial three field areas (NE and NW Gulf of Alaska, S. Bering Sea and Beaufort Sea) were expanded to include lower Cook Inlet, Norton Sound and S. Chukchi Sea.

2. The necessary (see above) sedimentological analysis program was continued during the initial stages but was deleted from the program because of imposed financial restraints in October 1976.

3. In conjunction with other disciplines involved in this program, to carefully select, and commence work in, geographically restricted regions within the major lease areas. These field sites, generally termed "specific study sites" are included to serve as type areas, in one or more major respect, for each overall lease area.

4. To continue collection and compilation of available literature pertinent to these various problem areas.

5. To develop sampling, sample treatment and analysis procedures as needed to carry out objective (1) and to relate and compare our methods to other OCS programs.

III. CURRENT STATE OF KNOWLEDGE

Background Work on Heavy Metals

An extensive literature search concerning heavy metal distributions in the marine environment of all the Alaskan shelf areas has been compiled by Dr. T. Gosink. This 97 page report has been submitted to NOAA/OCS as a special data report under the title: "A literature search on selected elements: Data and comments on their distribution and significance in the marine system and a summary of available data for the Alaskan shelf areas".

Background Work on Sedimentology of the Alaskan Shelves

Dr. A. S. Naidu has compiled all currently available literature in a report entitled "A bibliography of the available literature on recent sediments of the continental shelves of Alaska" (Appendix II). These literature references have been collected in separate sections for each major oceanographic region: Gulf of Alaska, and the Bering, Chukchi and Beaufort Seas.

IV. STUDY AREAS

N.E. Gulf of Alaska

Although no further sampling was possible during this contract period, much of the data considered in this report derives from the standard hydrographic grid discussed in previous reports. This station network is shown in Figure 2. Much of the biological data reported for the NEGOA-OCS area - and particularly the benthic - has been obtained on this grid also. Unfortunately, as previously explained the GS geology samples have been obtained at other localities and the sedimentological data produced by this latter group are not immediately applicable to our work. We have been able to obtain a few size fractionations on spilts of our samples within this program.

Biological samples from NEGOA have been collected for us by various biological co-investigators. Our most complete collection relates to intertidal benthic material obtained for us by Dr. Zimmerman's group. Localities of the Gulf stations are given in Figure 3 and Table II.

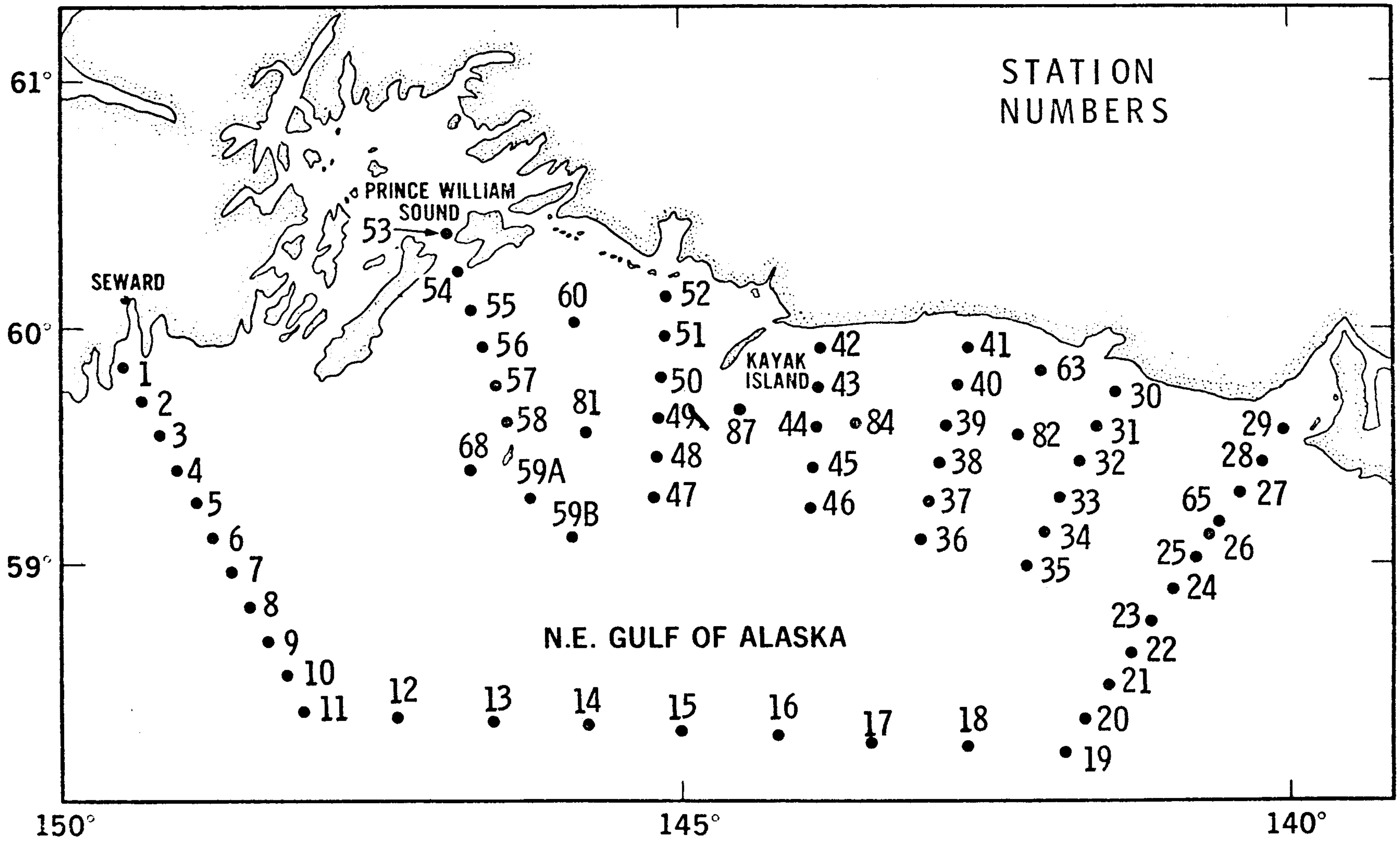


Figure 2. Standard trace metal station localities (hydrographic grid) in N.E. Gulf of Alaska.

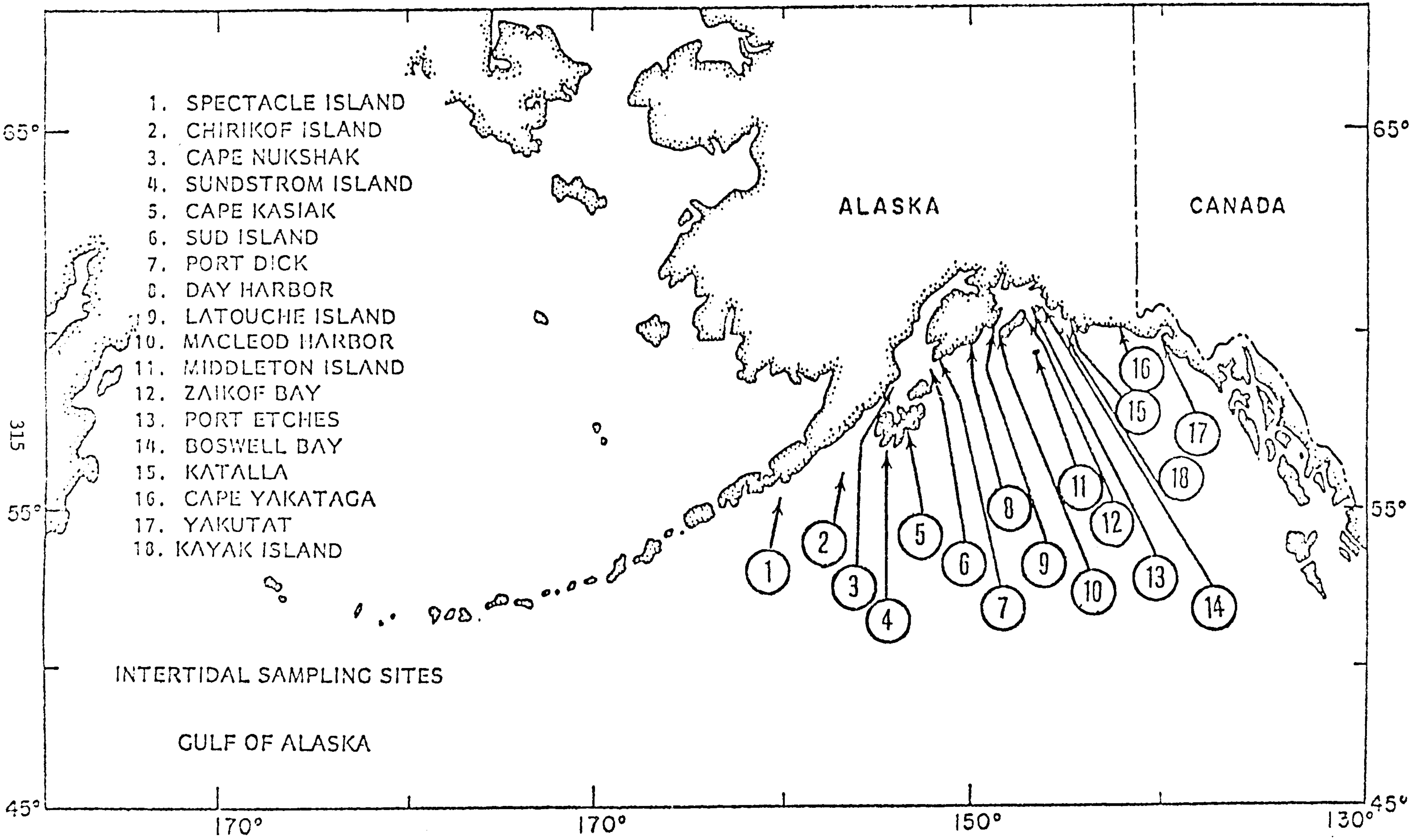


Figure 3. Intertidal sampling sites in the Gulf of Alaska.

TABLE II

NE 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

As described in the following section of this report, from October 1976 the program direction changed to emphasis restricted study sites in place of the broad-brush approach employed previously. Our choice (see Appendix 1) for the initial specific study locality in the NE Gulf of Alaska was one of the coastal fjord estuaries sited adjacent to the primary lease area. Two such were visited on the initial cruise: Icy Bay and Yakutat Bay. These environments are shown in Figures 5 and 6.

Lower Cook Inlet

No systematic trace metal sampling grid was determined for this region since a crash program only was mounted. Our sediment biota grid devised by Dr. Feder's group.

Specific sampling localities on either side of lower Cook Inlet have now been designated for seasonal collection of *Mytilus, Fucus* and *Macoma.*

N.W. Gulf of Alaska

Water and sediment samples collected for the trace metal analyses reported here have been taken on the standard hydrographic grid illustrated in Figure 7. This station network consists of a series of traverses normal to the peninsula and Aleutian Islands as shown. The chemistry (and benthic biology) programs have been concerned only with those stations located on the narrow shelf.

Localities of intertidal benthic samples collected from this region, and from Kodiak Island are listed in Tables III and IV and shown in Figure 3.

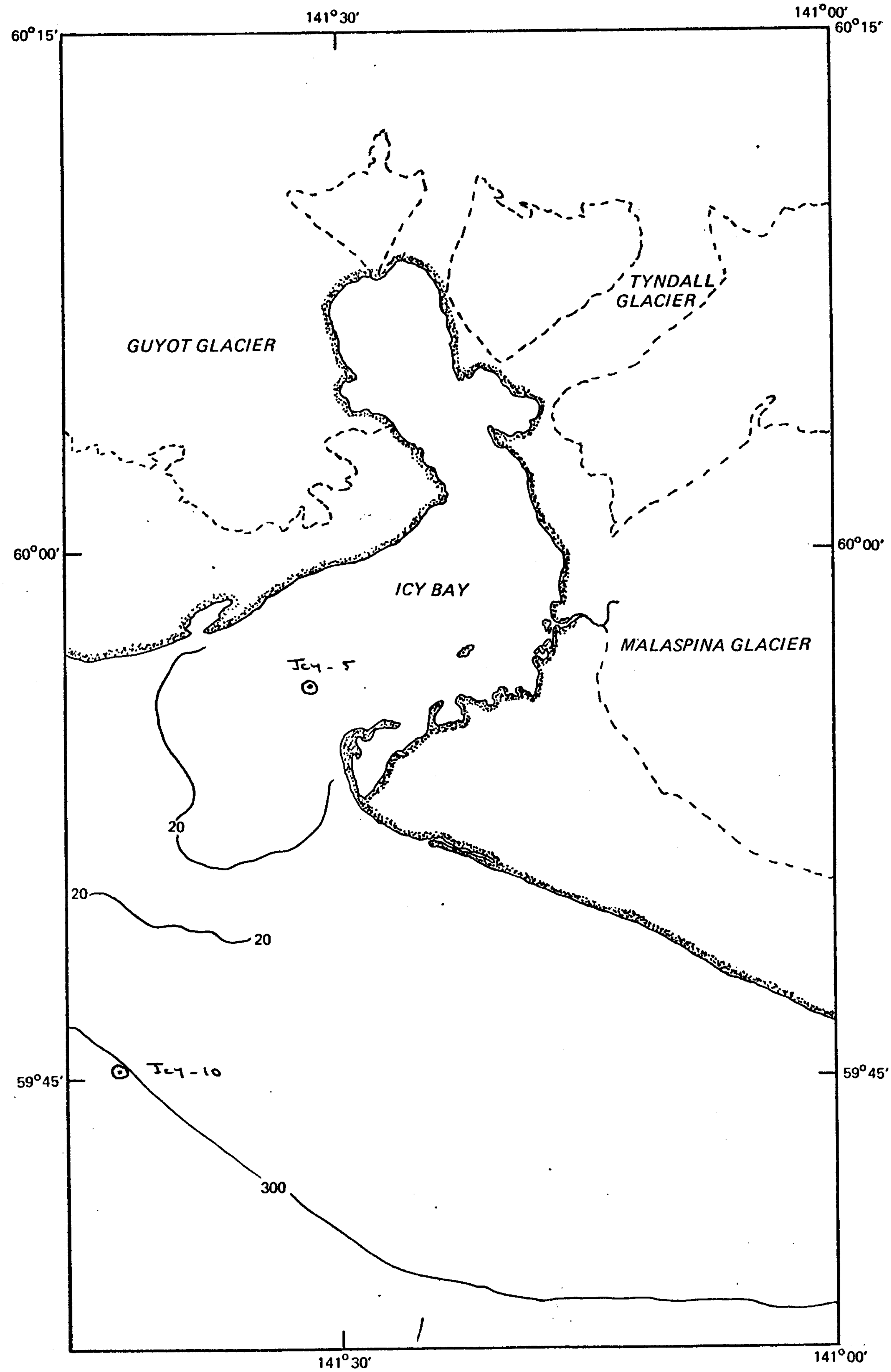


Figure 5. Initial sampling stations and environment of Icy Bay, N.E. Gulf of Alaska.

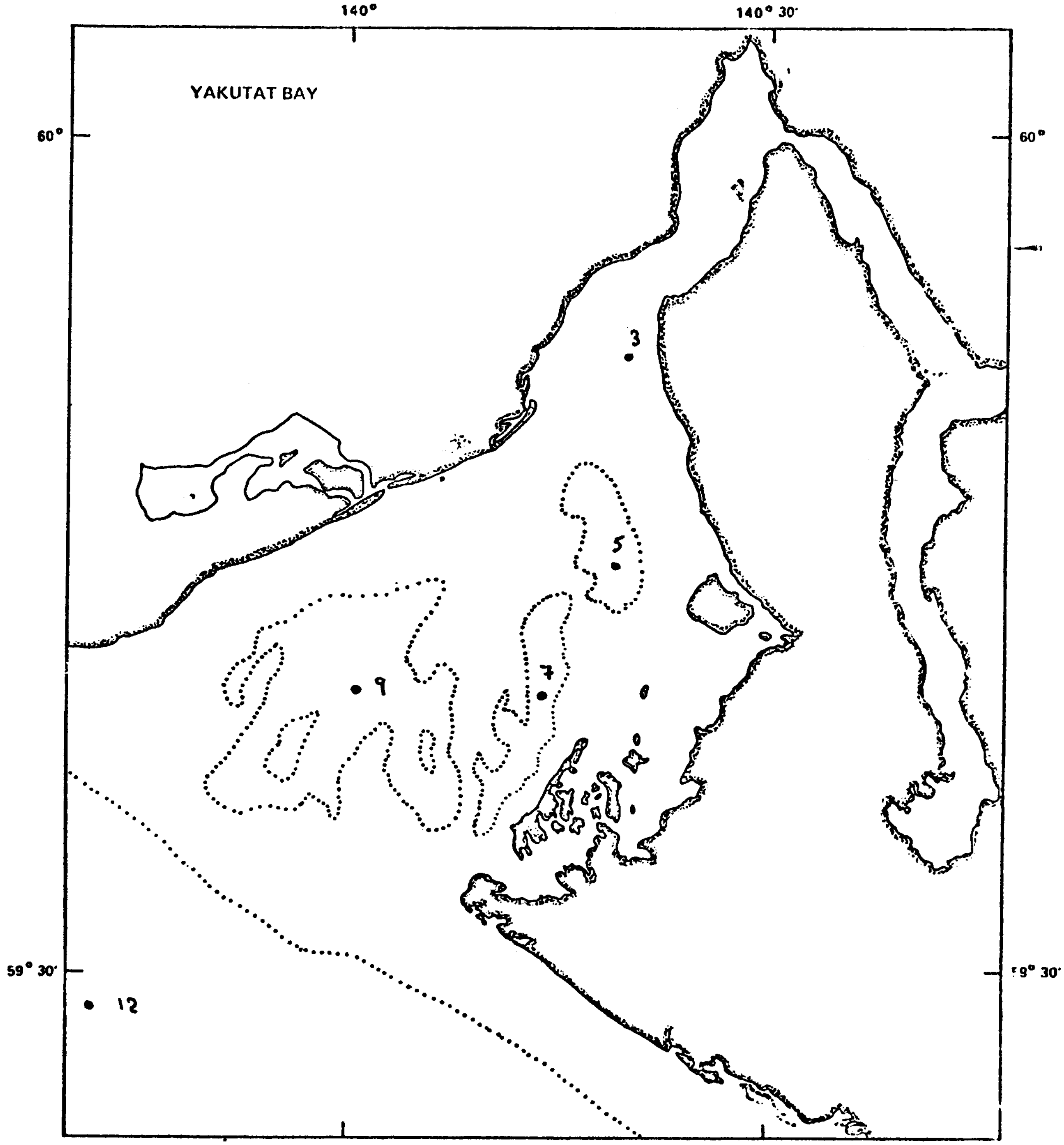


Figure 6. Initial sampling stations and environment of Yakutat Bay, N.E. Gulf of Alaska.

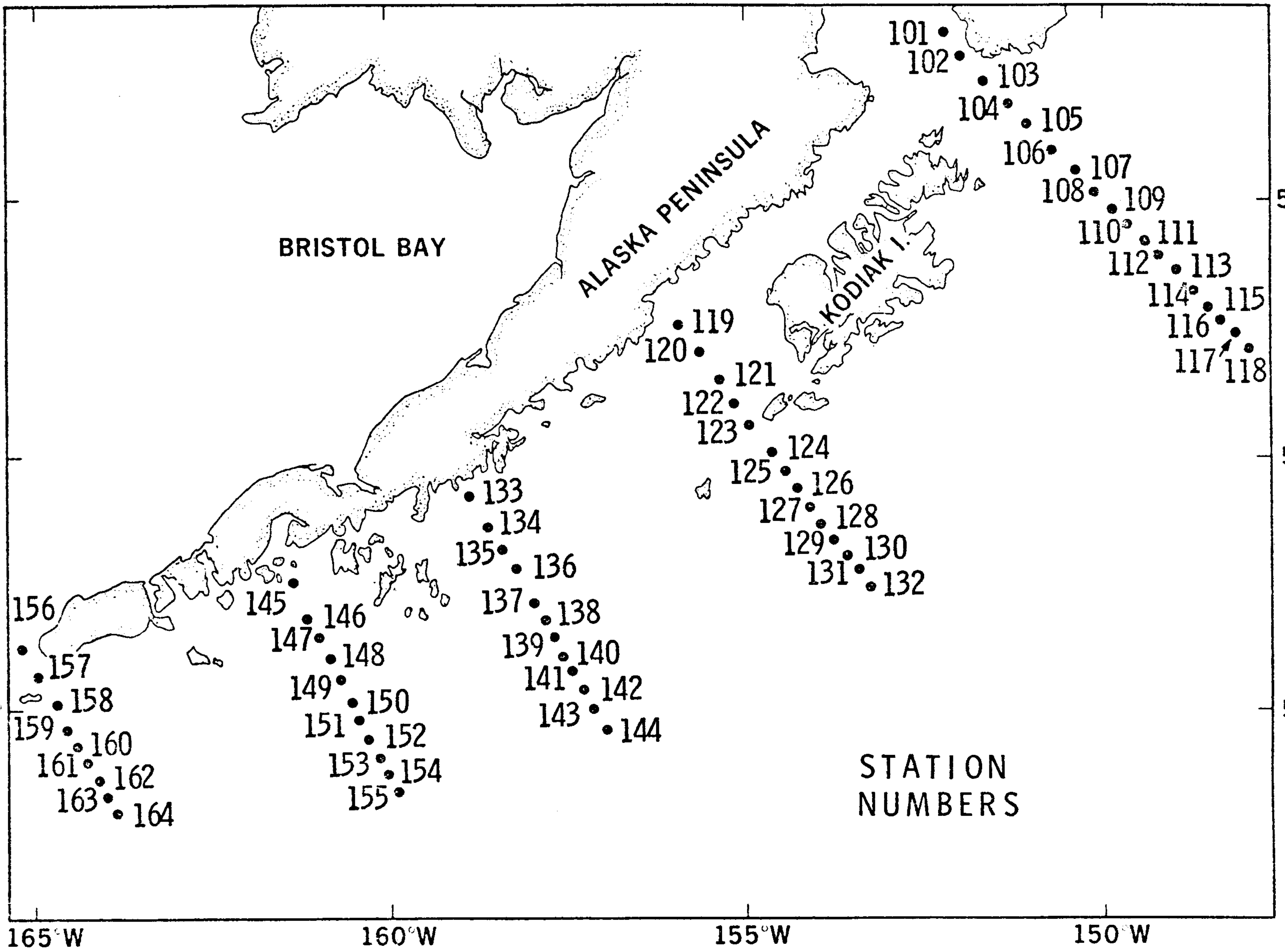


Figure 7. Standard hydrographic grid in N.W. Gulf of Alaska.

TABLE III

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 Nukshak	58	23.4	153	59.4

TABLE IV

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

S. Bering Sea

The survey grid occupied during the first part of this program is shown as Figure 8. Future studies will most probably be directed towards open-ocean food-web relationships. We have, for example, already started to analyse a series of marine mammal samples collected from the St. Georges Basin.

Intertidal benthic biota sampling localities for the S. Bering Sea are given in Table V.

Norton Sound and S. Chukchi Sea

Sediment and water samples have been taken on the Norton Sound and Chukchi Sea grids shown on Figures 9 and 10 and listed in Tables VI and VII.

A major expedition to Norton Sound is planned for the summer of 1978. At that time a more detailed station grid will be occupied within Norton Sound and efforts will be made to sample within the plume area and outer delta reaches of the Yukon River.

Beaufort Sea

Because of our need to deploy large, contamination-free water and sediment samples, it has been possible to cover the field area occupied by the *Glacier* cruises only. This coverage is shown in Figure 11. No extension of this limited coverage is planned, but analyses of samples obtained from various previous icebreaker cruises have been included in this program.

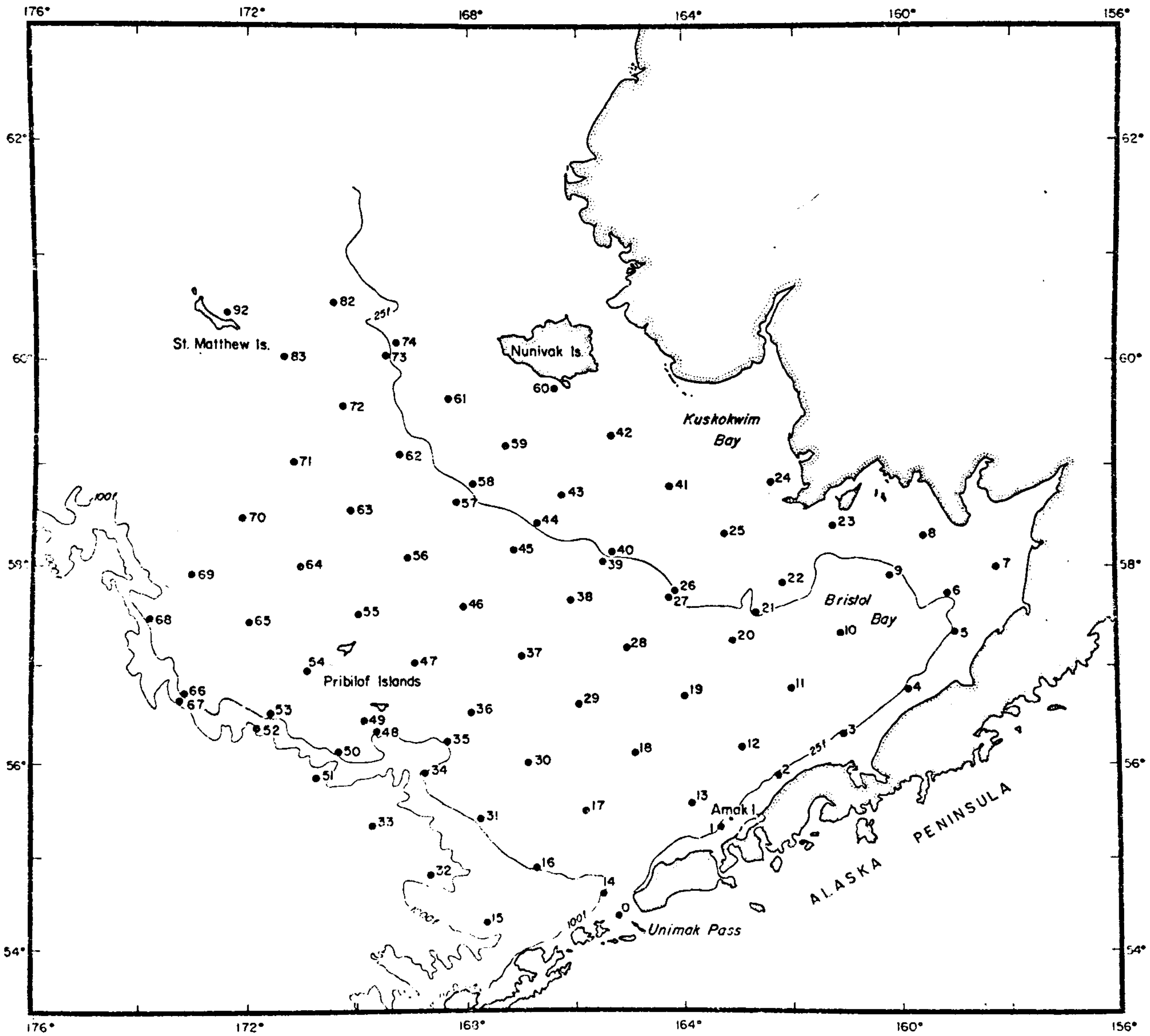


Figure 8. Standard heavy metal and benthic biology stations in the S. Bering Sea.

TABLE V

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	169	39.8
Otter Island	57	03.0	170	23.8

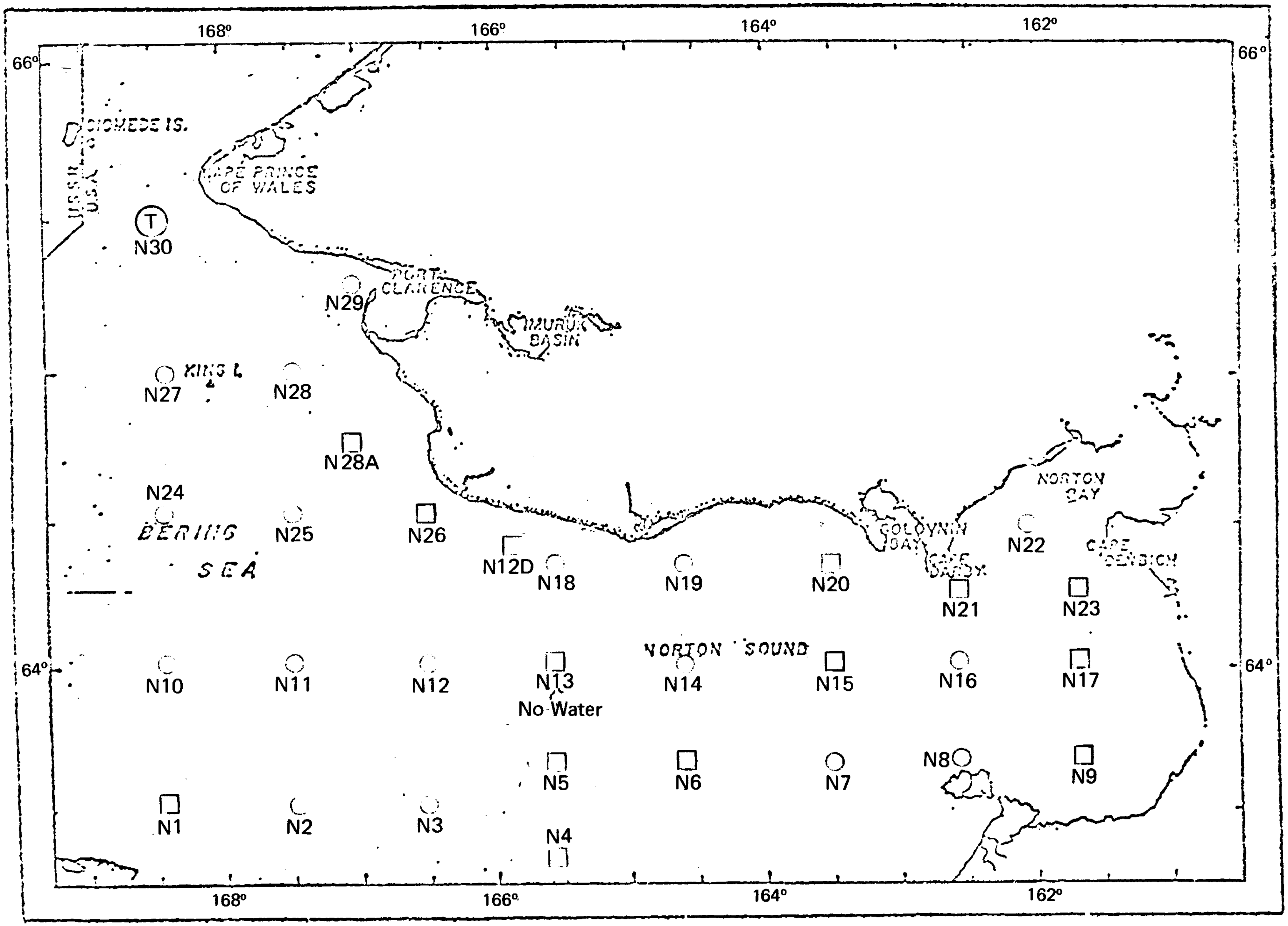


Figure 9. N. Bering Sea (Norton Sound) *Discoverer* Leg IV September 8-24, 1976. Station locations: Open circle = water column samples, open squares = Haps cores.

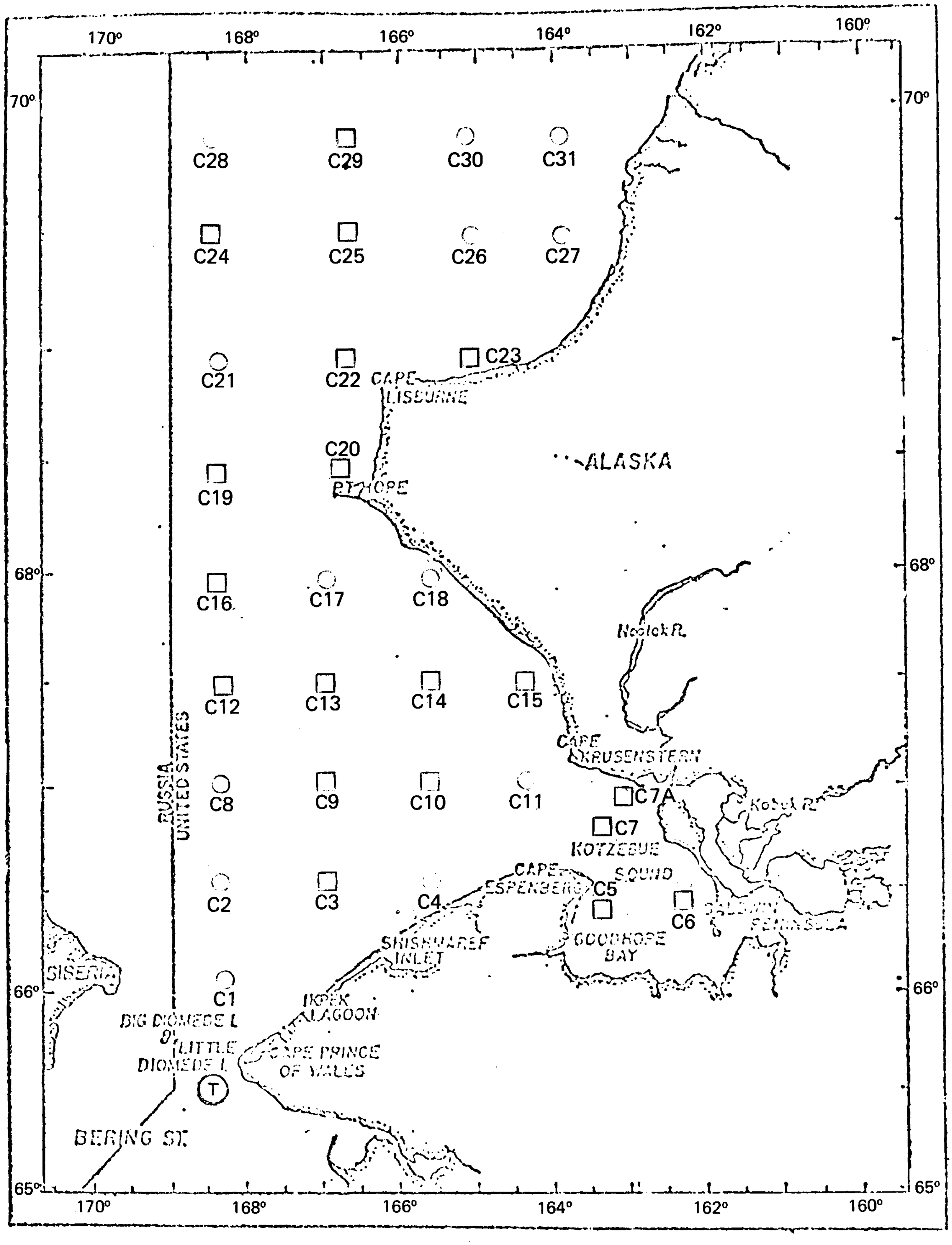


Figure 10. Chukchi Sea *Discoverer* Leg IV September 8-24, 1976. Station locations: Open circles = water column samples, open squares = Haps cores.

TABLE VI

NORTON SOUND (N. BERING SEA)

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

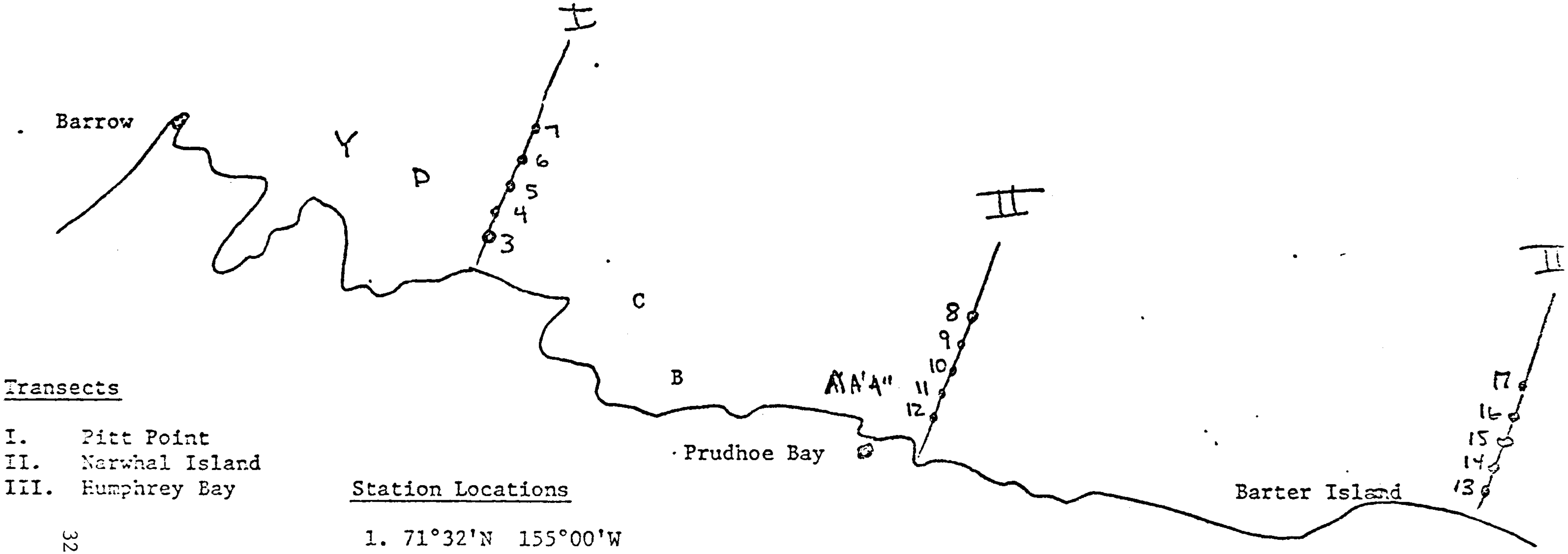
Station No.	Depth	Latitude	Longitude	Sampling Operations
N 1	29 m	63°31.8	168°32.2	van Veen Grab, HAPS, water
N 2	29	63°30.6	167°29.0	van Veen Grab, water
N 3	26.5	63°29.9	166°29.7	van Veen Grab, water
N 4	21	63°19.7	165°29.9	van Veen Grab, HAPS water
N 5	22	63°39.5	165°32.1	van Veen Grab, HAPS water
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 VII

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



Transects

I. Pitt Point
II. Narwhal Island
III. Humphrey Bay

Station Locations

1.	71°32'N	155°00'W
2.	71°21'N	153°50'W
3.	71°08'N	152°55'W
4.	71°19'N	152°33'W
5.	71°26'N	152°22'W
6.	71°36'N	152°12'W
7.	71°46'N	151°52'W
8.	71°08'N	146°30'W
9.	70°57'N	146°50'W
10.	70°47'N	147°00'W
11.	70°25'N	147°15'W
12.	70°31'N	147°24'W
13.	70°06'N	142°43'W
14.	70°18'N	142°08'W
15.	70°29'N	141°53'W
16.	70°40'N	141°37'W
17.	70°51'N	141°22'W

Precise locations to be supplied by the chief scientist, Dr. Rita Horner, along with salinity and temperature time data and station depth data. Eleven stations - 3, 4, 5, 7, 11, 12, A, B, C, D, and Y were occupied.

Figure 11. Station localities occupied in Beaufort Sea on *Glacier* Leg II, 23 August-3 September 1976.

V. PROCEDURES

Operations conducted during this reporting period have been transitional between the base-line survey phase of the program and more comprehensive process-study programs directed to specific problems and localities.

Base-line Surveys: Sampling; Types of Samples

During the period April-September 1976 the primary objective was to complete the field sampling program in the original lease areas (Gulf, S. Bering, Beaufort) and to sample in the two additionally specified areas: Lower Cook Inlet and Norton Sound, S. Chukchi Sea.

1. Types of samples collected: The same three types of samples discussed in the previous Annual Report (filtered water, surface sediments and selected biota) were obtained for trace metal analysis to fulfill the objectives discussed above. In addition some data have also been obtained for depth profiles from the cores and for the suspended sediment resulting from the water filtering procedure (below). We have collected all our own water and sediment samples and the severe restraints imposed by the need to obtain contamination-free samples have limited these operations. Only certain sampling platforms appear to be suitable for our needs: among the available vessels for deep-sea work, notably only the *Discoverer*. We managed to collect a few surficial sediment samples from the Beaufort Sea from the *Glacier* but water samples could not be obtained cleanly and those few collected were subsequently discarded.

Biota samples during this phase of the program were to be collected by the biology OCS investigators, but only intertidal samples were collected for us systematically and in a form suitable for trace metal analysis although we report here on a few non-systematic samplings of a few open-ocean benthic species obtained from various trawl cruises.

Water samples were collected at each station only adjacent to the sea surface and close to the sediment-water interface. While not to be expected on physical chemistry grounds, some real differences in the soluble concentration of some metals with depth are now beginning to be observed under open-ocean conditions, presumbaly attributable to biological mediation. For example, a consistent increase of Cd with depth at one estuarine locality is noted below. For the purposes of this present program, however, it was not considered to be possible to obtain detailed profiles over such large areas. "Mean concentrations" of all the metals present in trace amounts in seawater are still the subject of much debate. One major goal of this work was therefore to determine precise data in these uncontaminated waters. These endeavors are discussed below. In the event, it appeared that many of the "surface" water samples showed evidence of contamination and, although all these values are reported in the various quarterly reports our discussions here are mainly confined to means of bottom water samples.

2. Sampling procedures: Sampling procedures for the OCS water and sediment samples were standardized during this contract period.

Water samples have been obtained in 10 ℓ drop-top bottles attached to a rosette sampler. Water from these container was pressure filtered through an in-line 0.4 μm Nuclepore filter into standard 1 ℓ storage bottles. These latter containers were purchased in a single batch and were prepared (leached, washed) by Battelle Northwest Laboratories. Each sample bottle was opened in a glove bag and acidified with ultrex acid before being frozen and stored until required for analysis.

All sediment samples have been obtained in a stainless-steel HAPS corer. This instrument obtains shallow surficial samples only but the sediment surface is retrieved undamaged. Each core is trimmed after being extruded from the core barrel and the trimming are retained for sedimentological analysis. The remaining portion of the core is split longitudinally and retained in wide-mouthed bottles for heavy metal analysis.

The instructions issued for the collection of biota samples were to handle as little as possible, to place whole samples in polyethylene bags and to freeze immediately. Because these samples were not directly collected by our personnel it was unfortunately not possible to purge organisms of stomach contents or to remove epiphytic material.

3. Sampling trips: Samples for the baseline survey program have been collected on the following cruises and collection trips (in chronological order):

a. S. Bering Sea, April 1976. A second batch of sub-tidal trawl samples was collected by Dr. Feder's group on the *Miller Freeman* in the Bering Sea in April. These samples were to replace the previously collected batch which thawed and was lost during storage due to a local power failure (see January-March 1976 quarterly report). The new samples were received in Fairbanks at the beginning of June. It should be noted that the station grid occupied by the NMFS personnel, who were the primary operators of this cruise, bears no relationship to the grids previously established by the benthic and chemistry programs.

b. Lower Cook Inlet, March-April 1976. *Moana Wave* cruise, March 31-April 15, 1976. We attempted to respond to a last minute request to obtain samples from this area for the heavy metal program. G. Landreth was dispatched on the above referenced benthic biology cruise and collected sediment samples as shown in Table VIII. Sediment suitable for trace metal analysis could not be collected on most stations because of the nature of the bottom. Water could not be obtained on this cruise and there was no request for biota.

TABLE VIII

MOANA WAVE MARCH 31-APRIL 15
OPERATIONS - LOWER COOK INLET

Station No.	Bottom depth (m)	Sediment sample
04	26	Haps
10	25	Haps
11	29	Haps
12	38	Haps
18	133	van Veen
19	100	van Veen
25	55	van Veen
26	64	Haps
30	71	Haps

c. N.E. and N.W. Gulf and S. Bering Sea. Intertidal biota samples - *Fucus* and *Mytilus* - were collected for us by Dr. Zimmermann's group. Sample batches were received by us in Fairbanks on March 25 and June 24th.

Sample localities are given elsewhere in this report (Tables II through V).

d. Lower Cook Inlet. R/V *Acona* cruise 25 June through 2 June 1976. A single *Fucus* sample was collected for us by the organic chemistry group.

e. Beaufort Sea. C.G.C. *Glacier* Leg I - first half of August Chemical technician for Dr. Weiss's laboratory (Naval Under-Sea Center, San Diego) participated. Sediment samples collected for mercury analysis. Sampler for water column did not function correctly.

f. Beaufort Sea, August-September 1976. C.G.C. *Glacier* Leg II - 23 August to 3 September. Personnel: T. Gosink and G. Landreth. Station localities are shown on the accompanying figure. Number and types of samples taken: 11 sediment samples taken with the HAPS corer for sediment extract and activation analysis work; 22 water samples taken for shipboard Se and Cr analysis. Additional water samples were collected also for the soluble heavy metal analysis program. Unfortunately, the trace-metal free water sampler required for this work were apparently damaged in transit to Long Beach so that it was necessary to utilize ship-provided sampler. These water samples were unsuitable for heavy metal analysis.

g. N.E. Gulf of Alaska, September 1976. NEGOA Specific Study Site - Icy Bay and Yakutat Bay. R/V *Acona* cruise 11-16 September, 1976. Personnel: D. C. Burrell. A reconnaissance survey of Icy Bay, the initial agreed choice for the specific study site in the N.E. Gulf of Alaska. Approximately 10 miles of bathymetric track were run and two hydrographic stations in Icy Bay and five in Yakutat Bay were occupied (see Figs. 5 and 6).

h. Norton Sound and S. Chukchi Sea, September 1976. OSS *Discoverer* Leg IV, 8-24 September 1976. Personnel: T. Manson. Sixty water column samples were taken at 39 stations. In addition, 31 uncontaminated HAPS core samples for heavy metal analysis, and 62 van Veen grab samples for sediment size analysis were collected. Sample localities are given in Figure 9 (Norton Sound) and Figure 10 (Chukchi Sea). Operations are listed in Tables VI and VII.

Trace Metal Analysis: Metals Analysed; Analytical Techniques; Accuracy and Precision

Metals analysed

The elements studies in this program have been selected based on the following criteria:

a. Metals recognized as major pollutants affecting man: Ag, As, Cd, Cu, Hg, Pb, Sb, Se, Zn,

b. Natural petroleum "index" metals: Cr, Ni, V, also Ba, and

c. Indicators of environmental changes to the sediments: Fe, Mn, Co.

Determination of these elements in the various phases has required a fairly large number of diverse analytical techniques. These are listed below and in Tables IX, X and XI (the senior investigator responsible for each procedure is listed in parentheses):

a. Cadmium, copper, lead and zinc (the latter determined in the "free" form at ambient pH) in 0.4 μm filtered seawater by thin-film, differential pulse, anodic stripping voltammetry (Dr. D. C. Burrell).

b. Silver, arsenic, abrium, cobalt, chromium, iron, manganese, antimony and selenium in total sediment samples by thermal neutron activation analysis (Dr. D. Robertson).

c. Selenium and chromium in seawater, biota and sediment extracts and some particulate sediment phases by gas chromatography (Dr. T. Gosink).

d. Vanadium in filtered seawater samples by thermal neutron activation (Dr. D. Robertson).

e. Additional cadmium and silver analyses of filtered seawater samples by carbon filament atomic spectroscopy (Dr. D. C. Burrell).

f. Manganese (and aluminum) of total suspended sediment samples by neutron activation analysis (Dr. D. Robertson).

g. Mercury contents of whole rock sediment samples by neutron activation analysis (Dr. H. V. Weiss).

h. Nickel in unfiltered seawater samples following extraction by conventional flame atomic absorption (Dr. D. C. Burrell).

i. Iron, manganese, nickel, cadmium copper and zinc contents of sediment extracts by carbon furnace atomic spectroscopy (Dr. D. C. Burrell).

TABLE IX

TECHNIQUES USED FOR ANALYSIS OF SOLUBLE HEAVY METALS IN SEA WATER

	NAA	ASV	GC	FAA	SE/AA	AAA
Ag	-	-	-	(X)	-	-
As	-	-	-	-	-	-
Cd	-	X	-	(X)	-	-
Co	-	-	-	-	-	-
Cr	-	-	X	-	-	-
Cu	-	X	-	-	-	-
Fe	-	-	-	-	-	-
Hg	-	-	-	-	-	X
Mn	-	-	-	-	-	-
Ni	-	-	-	-	X	-
Pb	-	X	-	-	-	-
Sb	-	-	-	-	-	-
Se	-	-	X	-	-	-
V	X	-	-	-	-	-
Zn	-	(X)	-	-	-	-

NAA - Neutron activation
ASV - Anodic stripping voltammetry
GC - Gas liquid chromatography
FAA - Filament atomic absorption
SE/AA - Solvent extraction/flame atomic absorption
AAA - Ambient temperature atomic absorption

TABLE X

TECHNIQUES USED FOR ANALYSIS OF TOTAL HEAVY METALS IN BIOTA

	AA	GC
Ag	–	–
As	–	–
Cd	X	–
Co	–	–
Cr	–	X
Cu	X	–
Fe	–	–
Hg	–	–
Mn	–	–
Ni	X	–
Pb	–	–
Sb	–	–
Se	–	X
V	–	–
Zn	X	–

AA - Flame/Furnace atomic absorption

GC - Gas-liquid chromatography

TABLE XI

TECHNIQUES USED FOR ANALYSIS OF SEDIMENT EXTRACTS (X) AND WHOLE-ROCK SAMPLES (t)

	NAA	GC	FAA
Ag	t	-	-
As	t	-	-
Cd	-	-	X
Co	t	-	-
Cr	-	X	-
Cu	-	-	X
Fe	t	-	X
Hg	t	-	-
Mn	t	-	X
Ni	-	-	X
Pb	-	-	-
Sb	t	-	-
Se	t	X	-
V	t	-	-
Zn	-	-	X

NAA - Neutron activation analysis

GC - Gas-liquid chromatography

FAA - Furnace atomic absorption

j. Soluble mercury species in filtered seawater by ambient temperature, long path length atomic absorption (Dr. H. V. Weiss).

k. Copper, zinc, cadmium and nickel contents of biota samples by atomic absorption spectroscopy (Dr. D. C. Burrell).

Analysis techniques

Water

1. Cadmium, copper, lead and zinc by DPASV (D. C. Burrell) - These metals have been determined in filtered seawater samples by differential pulse, anodic stripping voltammetry (DPASV) using a thin mercury film, glassy carbon electrode (GCE). Zinc has been determined at ambient pH and copper, cadmium and lead at pH2.5.

2. Nickel by AA (D. C. Burrell) - Nickel has been determined in acidified seawater samples (pH 4) by APDC/MIBK extraction and atomic absorption analysis (Brooks *et al.*, 1967). This is a self-compensating method in which incomplete extraction of the nickel complex is corrected for by extracting the standards from previously extracted seawater. This is not an ideal procedure but has the advantage of having been used in a large number of investigations so that the data should be consistent.

3. Selenium by GLC (T. A. Gosink) - Two liters of seawater were drawn into polypropylene bottles (from the Niskin bottles described above) which had been rinsed three times with *ca.* 50 ml portions of the seawater. One liter portions were then filtered through an all-plastic filtration system using Gelman filter holders with teflon sealed magnetic clamps. A 0.45 μ Millepore filter was used in this step and this was subsequently stored in *ca.* 2 ml of 1-3 M HNO_3 in teflon lined screw-cap culture tubes for subsequent acid digestion and analysis (Nuclepore filters are too resistant to acid and char towards the completion of the digestion procedure).

The filtrate was transferred to a teflon separatory funnel and pre-extracted for 1 minute with *ca.* 25 ml of nanograde benzene.

A solution of 4-nitro-o-phenylenediamine (4-NO_2) was prepared fresh every 48 hours (or sooner as required) by dissolving 0.25 g of the reagent in *ca.* 1 M HCl and extracting the solution x 3 with *ca.* 25 ml portions of nanograde benzene. This solution was stored refrigerated in a plastic atuomatic dispenser. A 0.1 M solution of the disodium EDTA salt was prepared in deionized water and stored in a similar fashion. 5 ml each of the EDTA and 4-NO_2 solutions were added to the cleaned, filtered seawater samples. The funnels were shaken and allowed to stand for at least 2 hours after which 2 ml of nanograde benzene were added and the piazselenol derivative was quantitatively extracted by vigorous shaking of the separatory funnel for 5 minutes. A 2 μl portion of the benzene layer was subjected to GLC analysis immediately. See Gosink and Reynolds (1975) and Gosink (1975); the latter specifically for details of the instrumental analysis procedures.

4. Chromium by GLC (T. A. Gosink) - Samples from the drop-top Niskin bottles were filtered as described for Se. The filtrate (225-230ml) was added to a pre-cleaned bottle containing 20 ml of Htfa and 5 ml of buffer solution. A stock solution of Hfta (trifluoroacetylacetone) was prepared by diluting 1 ml of reagent in 100 ml benzene and stored refrigerated. The buffer solution was prepared in a teflon separatory funnel by adding 28 g reagent grade sodium acetate and 4 ml glacial acetic acid to 300 ml of deionized water. This solution was purified by adding 100 ml of the Hfta stock solution, shaking the solution and allowing it to stand overnight. The aqueous phase was washed twice with 100 ml of fresh nanograde benzene.

The samples prepared as described above were shaken periodically over a 24 hour perioa (the reaction is quantitative in approximately 2 hours at ambient laboratory temperatures or in 10 minutes at 55-60°C). A 1-2 ml portion of the benzene solution was then washed twice with 2-4 ml portions of 0.1 M NaOH in a clean teflon-lined screw-cap culture tube with a 2 µl portion used for analysis (Gosink, 1975).

5. Mercury by AA (H. V. Weiss) - This is a procedure which has not been previously utilized in this program so that full details are included below. Water samples were collected at the standard northeast and northwest Gulf of Alaska stations and filtered (0.4 mµ) in the fraction described previously. Aliquots of each sample have been U.V. irradiated to oxidize any metal found in organic complexes so that the data are for the dissolved inorganic and total soluble fractions respectively. Details of the analysis procedure used follow:

Reagents

Compressed nitrogen gas, ultrapure.

Stannous chloride solution: 200 g of reagent grade $SnCl_2.2H_2O$ was added to 60 ml of conc. HCl. This mixture was heated until complete dissolution. The volume was raised to 1-liter with 3 N H_2SO_4.

Mercury Standard

A 10 part per billion mercury standard was prepared by dilution of a 1000 part per million commercial standard (F&J Scientific) with 1.6 N HNO_3.

Instrument

Measurements were made with the Mercury Monitor (Laboratory Data Control, Riviera Beach, Fla.). This instrument was coupled to a Perkin Elmer recorder for quantification of the response.

Apparatus

A blubbler flask (250-ml) served as the sample container in which the mercury reduction occurred. One arm of the flask was attached to the source of pure nitrogen while the other to a drying tube charged with silica gel (6-16 mesh). The drying tube was connected to the entrance port of the Mercury Monitor.

A constant temperature bath (50°C) was used to warm the sample prior to reduction and during the time of nitrogen sweep.

Ultraviolet Irradiation

For the aliquots of the samples to be irradiated with ultraviolet rays, a 100 ml aliquot was placed in a quartz tube fitted with a ground quartz cap. Two drops of H_2O_2 were added and the sample was irradiated for 1-hour. The intensity of the ultraviolet source was such that mercury in the compound, methyl mercuric chloride, was quantitatively released for reduction with stannous chloride after a 1-minute irradiation.

Procedure

Samples were usually thawed at room temperature overnight and analyzed during the course of the following day. A 100-ml aliquot of the untreated or irradiated sample was transferred to the bubbler flask and the flask was immersed in the water bath for 3-5 minutes. Stannous chloride reagent (0.5 ml) was added, mixed and the apparatus was completely assembled. Nitrogen gas was passed through the solution at a rate of 1600 ml/min. The gas flow was continued until the recorded response returned to the background value.

To the mercury depleted solution a volume of mercury standard was added and the process described above was repeated. The quantity of mercury in the sample was determined by comparison of the initial with the subsequent peak-height response.

The error associated with this procedure is 20 percent, 10 percent and 6 percent at 5, 10, and 30 ng/liter levels of concentration.

6. Vanadium by NAA (Dr. Robertson) - To accomplish this analysis the V must be separated and concentrated from the seawater matrix prior to the neutron activation. We employed a new technique, recently developed under another program, to perform these measurements. Vanadium-48 ($t_{1/2}$ = 16 days) tracer was produced by proton bombardment of a titanium foil in the University of Washington cyclotron, and carrier-free ^{48}V radiochemically separated and used as a tracer in the methods development.

To 100 ml aliquots of seawater in precleaned polystyrene beakers was added 5 mg of high purity iron solution and 250 μl of phenol red indicator

(0.1 gm per 250 ml of 0.001M NaOH). High purity 1.5M NH_4OH was then added dropwise while stirring until the first permanent color change from yellow to red occurred at a pH of about 7.8 ± 0.3. The $Fe(OH)_3$ precipitates were allowed to settle for about 20 minutes and the precipitates were then centrifuged and washed 3 times with 0.5M ammonium acetate containing 1 g/ℓ of Magnifloc.

The precipitates were then transferred to 2/5 dram pre-cleaned polyethylene snap-top vials and were dried slowly under a heat lamp. The vials were then sealed in polyethylene bags and encapsulated in 2 dram polyethylene vials for neutron activation. Vanadium standards (14.2 μg) were prepared by pipetting 10 μl of standard solution onto discs of high purity IPC filter media, drying the discs and encapsulating them in the same manner as the $Fe(OH)_3$ precipitates. The samples and standards were neutron irradiated at the Washington State University Triga reactor, one at a time, standards interspersed between samples, for 2.0 minutes each. Following the irradiation the samples were allowed to decay for 2.0 minutes and were then counted directly on a Ge(Li) diode detector for 10 minutes to measure the 1434 keV γ-ray of ^{52}V (3.8 minutes).

The chemical recovery of vanadium for this procedure was 95.6 ± 1.4%, and the precision and accuracy were estimated to be less than 10%. The average procedural blank amounted to 0.11 ± 0.03 μg/ℓ.

Biota

1. Cadmium, copper, nickel, and zinc by AA (D. C. Burrell) - Most samples were initially rinsed with DDW, stored in polyethylene bags, and freeze dried. Where applicable, shells were removed after this step, and the remaining tissue was ground to a fine powder using a mortar and pestle.

For the crab samples, only legs and claws were treated as above. Pollock and rock sole samples were partially thawed then, using a glass shard and plastic knife, the skin was removed and underlying flakes of tissue removed and freeze dried.

All glassware was cleaned with "Nochromix", 10% HCl and DDW. Approximately 1.0 g of powdered sample was weighed into a cleaned 35 ml centrifuge tube and enough DDW added to dampen the sample. Digestion was accomplished using the nitric acid, vapor phase method of Thomas and Smythe (1973).

After digestion, a volume of approximately 10 ml of solution remained. The tubes were then inserted into a custom made "furnace" which consisted of nichrome heating wires wrapped around pyrex cylinders, the whole being asbestos insulated and supplied *via* a variable power source. The solutions were slowly reduced in volume to *ca.* 1 ml and, while still warm, 50% H_2O_2 solution was added until frothing ceased to effect a final clearing of the sample solution. These latter were finally brought to volume and analysed by atomic absorption spectroscopy (AA). All standards used for the biota analysis have been prepared using a matrix prepared from digests of the same species to be analysed.

2. Chromium by GLC (T. A. Gosink) - Weighed oven dried (110°C) portions of biota supplied by other OCS investigators were digested in teflon beakers using nitric and sulfuric acids. The digests were brought to a pH near 5.5 and placed in polypropylene bottles containing buffer and Hfta (see above) solutions. Digested samples were analysed by GLC as described for seawater above.

3. Selenium by GLC (T. A. Gosink) - Samples were placed in pre-weighed teflon-lined, screw-cap, culture tubes containing 2-4 ml of 1-3 M HNO_3 on board ship. In the laboratory the acid stored samples were quantitatively transferred to Kjeldahl flasks, along with 2 ml of the acid digestion mixture and 5 ml of core HNO_3. The flask and contents were heated for 1 minute after the evolution of white fumes were evident (about 20-25 minutes). If charriin occurred at any time during the digestion procedure, the sample had to be discarded because of potential quantitative loss of selenium. After the flasks had cooled, the contents were stripped of any additional volatile interferring components by bubbling a vigorous stream of air through the digest, and then 2 ml of concentrated NH_4OH were added. The solutions were adjusted to a pH >2 with 3 M NH_4OH and then 2 ml each of EDTA, 4-NO_2 and nanograde benzene were added. After 2 hours the tubes were vigorously agitated for 1 minute to extract the piazselenol into the benzene phase. After separation in a small separatory funnel, a 2 µl portion of the benzene was subjected to immediate gas chromatographic analysis.

Sediment - total analysis

1. Manganese and vanadium by NAA (D. E. Robertson) - Haps core samples from the south Bering Sea and the northeast and northwest Gulf regions were sectioned at 2 cm intervals shipboard and stored frozen in plastic jars. In the laboratory, these sediment samples were dried, weighed, and encapsuled in polyethylene vials prior to "rabbit" irradiation and Ge(Li) gamma spectrometric determination of the heavy metals Mn and V.

2. As, Ba, Co, Cr, Fe, Sb, by NAA (D. E. Robertson) - These measurements were made by irradiating 100 to 200 mg subsamples of sediments in the WSU Triga reactor for approximately 6 hours, storing the samples for predetermined time periods to allow short-lived interferring activation products to decay, and then counting the samples on Ge(Li) diode detectors.

3. Total mercury by NAA (H. V. Weiss) - Just before preparation for analyses the samples were thawed, mixed thoroughly and separate aliquots were removed for neutron activation analyses and dry weight determination. The water content was measured by weighing sediment before and after treatment at 110°C for one hour. From 2-3 grams of sediment were placed in an irradiation vial and 3 ml of concentrated nitric acid were added.

The comparator consisted of 1.0 μg of mercury as the nitrate in 10 ml of concentrated nitric acid. The nitric acid blank was comprised of three irradiation vials each filled with 14 ml of concentrated nitric acid.

Samples, comparators and blanks were irradiated for 2 hours at a flux of 10^{12} neutron cm^{-2} sec^{-1} in a "Lazy Susan" rotated at 1 rpm about the core of the Triga reactor at the University of California, Irvine. The irradiations were made at 1,500 to 1,700 hour, and the following morning samples were processed to attain radiochemical purity.

Sediments were digested in a nitric- and sulfuric-acid mixture as described previously (Williams and Weiss, 1973). The sediment was prepared further for radiochemical purification by addition of 25 ml of concentrated ammonium hydroxide to the digest, and the mixture was filtered. If, at this stage, pebbles were detected in the residual sediment, they were removed and the sample was corrected for their weight.

Ten mg of mercury carrier was added to the water samples and the nitric-acid blanks. The nitric-acid blank was reduced in volume to about

10 ml. Water samples and blanks both received 9 ml of concentrated ammonium hydroxide and 10 mg each of potassium and sodium chloride (these quantities of chlorides were also added prior to the succeeding precipitations).

To the filtrate was added 2.5 ml of freshly prepared stannous chloride. The precipitated mercury metal was collected by centrifugation. The precipitate was dissolved in 5 ml aqua regia; 5 mg of copper (as nitrate) was added and the solution filtered. The reduction of mercury to the metal was repeated and the solid collected by filtration. The precipitate was again dissolved with 5 ml aqua regia (1 or 2 drops of concentrated phosphoric acid were added to the water samples), and the solution was neutralized with 5 ml of concentrated ammonium hydroxide. Hydrogen-sulfide gas was passed through the pH-adjusted solution and the precipitate was collected by filtration. The mercuric sulfide was of sufficient purity to permit immediate measurement. The comparator was neutralized with 9 ml of concentrated ammonium hydroxide after the addition of mercury carrier, and the mercuric sulfide was precipitated and collected for measurements.

Usually, the processed mercury samples as well as mercury carrier standards (10 mg mercury) were re-irradiated for 5 sec. Through comparison of the activity level of the samples and standards, the carrier yield was computed and the counting rate in the original irradiation was corrected for this factor. Alternatively the carrier yield has on occasion also been determined by atomic absorption spectrometry.

The radioactive measurements were made with a sodium-iodide detector coupled to a 400-channel pulse-height analyzer. The counts attributable to the 77-keV radiation of ^{197}Hg were integrated by the method of Covell (1959). The standard deviation for this analysis is less than 10%.

4. Total Fe, Mn, Zn, Ni, Cu in archived Beaufort Sea sediments (A. S. Naidu) - Splits of samples from an archived sediment suite were taken for heavy metal analyses. The archived sediment samples have been stored in a frozen state in acid rinsed polyvials, and were originally collected with the specific purpose to conduct chemical analyses on them. The middle and outer shelf samples were separated, using a teflon-coated spatula, either from the core of van Veen grabs, or from the tops of a metal-free gravity corer. A few samples represent surficial portions of short trigger core samples retrieved in plastic core liners. The sediment samples from the relatively shallow Prudhoe Bay area, were collected in the summer of 1974 by divers, who scooped a portion of undisturbed bottom surface sediments directly into acid-rinsed polyethene boxes. All these sediments were stored in a frozen state until analyses. The middle and outer shelf samples were obtained from USCGC ice breakers *Staten Island* and *Glacier* in 1969 and 1971, respectively.

Details on the techniques followed for the chemical analysis of sediments have been described by Naidu and Hood (1972). In short, gravel-free sediment samples dried at 110°C overnight were pulverized to fine powders using an agate mortar and pestle. A known weight of these powders was first ashed, and then digested in concentrated $HF-HNO_3$ acid following the procedure given by Rader and Grimaldi (1961). From the solutions thus obtained the concentrations of Fe, Mn, Cu, Ni, V and Zn were analyzed in a Model 303 Perkin-Elmer atomic absorption spectrophotometer.

Sediment - analysis of extractable fractions

1. Cadmium, copper, nickel, zinc, iron, manganese and vanadium in sediment extracts (D. C. Burrell and A. S. Naidu) - Sediment samples were

allowed to thaw and then stirred thoroughly with an acid washed Teflon rod. A portion of the sediment was then transferred to a polyethylene bag and freeze dried for 24 hours. Approximately 1.0 gram of the dried sediment was weighed into a 250 ml polypropylene bottle with a tight fitting cap and 50 ml of the acid-reducing reagent (1M hydroxylamine hydrochloride - 25% (V/V) acetic acid as described by Chester and Hughes, 1967) was added. The bottle was then placed on a mechanical shaker for four hours. After shaking the solution was allowed to settle and filtered through a Millipore type HA filter into an erlenmeyer flask calibrated to 50 ml. A 2 ml volume of ultrex grade concentrated nitric acid was added to the filtrate which was then slowly reduced in volume, by heating on a hot plate, until nitric acid fumes evolved. The sample was allowed to cool and then brought to a volume of 50 ml with distilled, dionized water and analyzed for the appropriate elements, with the exception of vanadium. For vanadium analysis, Dr. Naidu followed the neutron activation analysis, using the isotope dilution technique, described by Weiss *et al.*, (in press). All labware used was cleaned with Nochromix, 10% HCl, and distilled dionized water prior to use.

2. Chromium (T. A. Gosink) - Approximately 10 grams of surface sediment from a Haps or van Veen grab sampler was stored frozen in an all polypropylene bottle. A weighed portion of dried sediment was prepared for solution by the method of Presley *et al.* (acetic acid and hydroxylamine) as recommended on page 3-9 in the BLM-OCS Summary Recommendations of the Trace Metal and Hydrocarbon Seminars, 8-12 September 1975. The samples prepared as described above were shaken periodically over a 24 hour period. (Reaction is quantitative in approximately 2 hours at warm room temperatures, or 10-15 minutes at 55-60°C.) A 1-2 ml portion of the benzene

solution was then washed twice with 2-4 ml portions of 0.1 M NaOH in a clean teflon-lined screw-cap culture tube. A 2 μl portion was used for gas chromatographic analysis. These solutions of $Cr(fta)_3$ are quite stable for storage, but in the case of these particulate samples a 2 to 4 day period was required to destroy some of the aluminum chelate present which also formed quantitatively under the above conditions, and masked the chromium peaks.

3. Selenium (T. A. Gosink). 1 to 5 g samples of surface sediment were immediately transferred to small pre-weighed, all polypropylene bottles containing about 10 ml of 1-3 M HNO_3. These latter were then treated and analysed as described above for the biota.

4. Granulometric and clay mineral composition of sediments from the Gulf and Bering Sea (A. S. Naidu) - Granulometric composition of the sediments were analyzed by the conventional combined sieving-pipetting method. Prior to analysis, representative portions of each of the sediment samples were treated with H_2O_2 to remove organic matter. The mud fractions (<62μm) of the sediments were collected after wet-sieving the sediments through a 230-mesh sieve, and the particles in them were disaggregated into homogenous suspensions by repeated washings in double distilled water and, if necessary, by adding a few drops of Ammonium hydroxide. From these suspensions, the weight of the silt and clay sized particles were determined by following the Stoke's Law. Grain size analyses were limited to the determination of the weight percents of gravel, sand, silt, and clay sized particles in sediments.

Clay mineral analysis was performed following the method elaborated by Naidu *et al.* (1971) and Mowatt *et al.* (1974). Briefly, it consisted of first treating each of the gross subsamples with H_2O_2 to remove organic matter. The organic-free sample was then wet-sieved using a 230-mesh sieve, and the suspensions finer than 62 μm fraction were collected into long cylinders. From homogenized suspensions the less than 2 μm e.s.d. (equivalent spherical diameter) particles were separated, using Stoke's Law. After centrifugation the solids were collected and mounted with preferred orientation on glass slides, adopting the smear technique described by Gibbs (1965). X-ray diffraction patterns of each of the clay slides were obtained on a Phillips-Norelco X-ray unit having a scintillation counter. Glycol solvation, as well as fast and slow scan techniques were employed to assist in routine identification of clay minerals.

During the present contract period the less than 2 μm as well as the 1 μm (e.s.d.) fractions of 27 sediment samples from the Gulf of Alaska have been saturated separately with 1 N solutions of Mg and K, and mounted on porus porcelain plates and X-ray diffraction analyses on all of the less than 2 μm and 1 μm fractions obtained. For each of the size fractions of the above clays, at least 8 X-ray diffraction patterns have been obtained, prior and subsequent to in KCl and $MgCl_2$ solution treatments, glycolation, and heat treatments.

The < 2μm size fraction of sediment samples from the Bering Sea were also treated with in KCl and $MgCl_2$ solutions, subsequent to mounting on porous, porcelain plates, and X-rayed.

All clay mineral quantifications in this study are based on the method given by Biscaye (1965), and is at best semiquantitative. The general precision of clay mineral analyses has been better than 10 percent.

5. Accuracy and precision - The background to accuracy and precision data for soluble seawater heavy metal contents was discussed in detail in last years Annual Report. Further discussion and data are included in Section VIIA below.

As noted in the 1975-1976 report, we have little or no control over the collection or initial storage of the biota samples analysed. However, since fresh sub-samples are taken for dissolution we do not believe addition contamination to be a potential problem. NBS orchard leaf standards are taken through the entire processing and analysis stages and results for these calibration samples have been included in each quarterly report. The most recent such set of data is given here as Table XII.

Site specific studies

The comprehensive base-line survey program was operative only through FY76. In October 1976 the trace metal OCS program was continued at a considerably reduced level and from that time our brief has been to select and operate within the framework of "site specific" field areas, one from each of the major lease areas.

1. Selection of specific sites - To realise the maximum scientific return for the contribution of the program, it was determined that restricted field sites should be chosen in conjunction with the other participating disciplines. Our initial survey data had shown no anomolous regions as regards heavy metal distributions on the open shelf regions. It was clear that continued studies would be needed to determine significant pathways and processes of heavy metal transport, i.e., that the time element would become increasingly important. Since it was clearly impossible to study a large number of such processes in all the impact regions, initial efforts were devoted to selecting sites which might, in one or more oceanographic respects, serve as paradigms for each lease area. To stay within our financial restraints, it was decided that one site per lease area would only reasonably represent the major local ecological environment or could serve as a natural laboratory for some major local oceanographic characteristics. Our previous studies had reinforced the importance of

TABLE XII

ACCURACY AND PRECISION DATA FOR BIOTA ANALYSIS
(μg/g dry weight ± one standard deviation)

a. NBS Standard #1571 Orchard leaves

Element	This Study	NBS Certified
Cd	-	0.11 ± 0.02
Cu	10.5 ± 0.3	12 ± 1
Ni	1.25 ± 0.2	1.3 ± 0.2
Zn	25.1 ± 0.5	25 ± 3

b. NBS Standard #1577 Bovine liver

Element	This Study	NBS Certified
Zn	133 ± 12	130 ± 10

coastal and estuarine regions for chemical process studies. In addition, it was clear that food chain transfers and general concentration of heavy metals by the biota was an important study area. In practice it was determined that in each of the major lease areas, one particular ecological/physical system appeared to be particularly worthy of study.

The specific sites recommended in each of the lease areas are discussed in the Appendix suffixed to this report. This latter is a brief summary of the deliberations of a multi-discipline workshop convened in Fairbanks in July 1976. It was also decided at this time that the order of priority as regards the trace metal program in view of the restricted financial resources available, should be from the N.E. Gulf of Alaska working northwards. This also approximately parallels the probable resource development sequence. The following site-specific studies are suggested for immediate implmentation as discussed in Section IX.

1. A coastal estuary adjacent to the N.E. Gulf lease area.
2. Monitoring of intertidal benthic index species on a seasonal basis in Lower Cook Inlet.
3. Food chain transfer studies in the Bering Sea with initial emphasis on marine mammals.
4. Influence of Yukon River discharge zone in the N. Bering Sea-Norton Sound area.
5. A type coastal lagoon in the Bering Sea.

VI. RESULTS

Soluble Heavy Metal Contents of Seawater

The analysis program for soluble Cd, Cu, Pb, Zn, and Ni has now been completed. A number of data have been previously presented in the 1975-1976 Annual Report.

Cd, Pb, and Cu values for filtered water from the N.E. and N.W. Gulf of Alaska are given in Tables XIII and XIV. These samples were collected and treated according to the procedure outlined above and the numbers are considered to be the best obtainable from a wire-hung sampler. These data are considered in some detail in Section VII. "Free zinc" contents of filtered water from the N.E. and N.W. Gulf and of unfiltered water from the Bering Sea are given in Tables XV-XVIII. These values are for ambient seawater pH as discussed in Section VII.

Soluble Hg data for N.E. and N.W. Gulf samples - the same station as for the Cd, Pd and Cu data - are given in Tables XIX and XX. Species fractionation in the form of inorganic and total values are given.

A few Cr and Se for both filtered and unfiltered water samples taken from the Beaufort Sea (station locations given in Fig. 11) are given in Table XXI.

Soluble vanadium data from the N.E. and N.W. Gulf of Alaska and from the S. Bering Sea are given in Tables XXII, XXIII and XXIV.

Biota

Heavy metal contents of benthic species - tanner crab and *Neptunea* - collected on trawl cruises in the S. Bering Sea are given in Tables XXV and XXVI. The reader should note particularly the high levels of Cd, Cu, and Zn in the latter species. This is considered further below.

Our most complete biota sample collection to data is for the intertidal benthic species *Mytilus* and *Fucus*. Some data for the N.E. Gulf were discussed in the previous report and additional values are given in Tables XXVII and XXVIII. Data from this lease area are discussed further

TABLE XIII

N.E. GULF OF ALASKA
Discoverer Leg III 23 November-2 December 1975

Heavy metal contents of filtered (0.4 μm) water (μg/ℓ)

Station No.	Depth (m)	Cd	Pb	Cu
02	10	-	0.03	0.18
	178	-	0.02	0.16
05	10	0.02	0.045	0.26
	162	0.035	0.03	0.16
08	10	-	0.03	0.14
	276	0.035	0.04	0.37
11	10	0.02	0.06	0.14
	1350	*	*	*
15	10	0.09	0.13	0.14
	1500	*	*	*
24	10	-	-	-
	410	*	*	*
26	10	(0.08)	(0.27)	0.15
	136	-	(0.35)	(>1.0)
29	71	0.035	(0.15)	(1.0)
30	42	0.025	0.06	0.25
33	10	0.03	0.04	0.10
	205	0.03	0.45	0.20
44	10	0.02	0.045	0.45
	165	0.04	0.06	0.36
48	10	0.02	0.07	0.20
	447	0.055	0.06	0.20
49	10	0.02	0.03	0.26
	120	0.02	0.05	0.16
50	10	0.02	0.04	0.40
	167	0.02	0.04	0.21
51	10	0.025	0.04	0.28
	133	-	0.035	-

TABLE XIII (continued)

Heavy metal contents of filtered (0.4 μm) water (μg/ℓ)

Station No.	Depth (m)	Cd	Pb	Cu
52	74	0.02	0.03	0.22
53	10	-	(>1.0)	-
	284	0.04	(1.0)	(0.48)
54	10	0.02	0.06	0.23
	202	-	0.02	0.16
55	10	0.03	0.09	0.52
	110	0.025	0.03	0.21
56	58	-	0.17	0.13
57	67	-	0.06	-
58	82	0.025	0.06	0.20
59A	10	-	-	-
	370	-	-	-

TABLE XIV

N.W. GULF OF ALASKA
Discoverer Leg III 23 November-2 December 1975

Heavy metal contents of filtered (0-4 μm) water (μg/ℓ)

Station No.	Depth (m)	Cd	Pb	Cu
106	81	0.025	0.035	0.16
108	10	-	0.07	0.16
	226	0.025	0.025	0.15
110	10	0.03	0.025	0.15
	173	*	*	*

* Intercalibration station

TABLE XV

N.E. GULF OF ALASKA
Discoverer Leg III 23 November - 2 December 1975

Free zinc contents at pH 8 in filtered (0.4 μm) water.

Station No.	Depth (m)	Zn (μg/ℓ)
02	10	n.d.
	175	0.22
05	10	n.d.
	80	0.15
08	10	n.d.
	245	0.13
11	10	n.d.
	1350*	0.28
15	10	-
	1500*	0.34
24	10	-
	410*	0.48
26	10	-
	135	0.21
29	70	0.15
30	40	n.d.
33	10	0.35
	205	n.d.
44	10	0.22
	165	0.14
48	10	0.20
	500	n.d.
49	10	0.18
	120	0.45
50	10	0.20
	165	-
51	10	0.31
	135	n.d.
52	75	0.13
53	10	-
	285	0.16
54	10	0.20
	200	0.45
55	10	0.45
	110	0.70
56	65	0.20
57	60	0.24
58	81	0.60
59A	10	-
	370	-

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*Intercalibration station

TABLE XVI

N.W. GULF OF ALASKA
Discoverer 8-16 October 1975

Free zinc contents at pH 8 in filtered (0.4 μm) water (μg/ℓ).

Station No.	Depth (m)	Zn (μg/ℓ)
101	0	0.70
	80	0.30
102	0	n.d.
	100	0.25
104	0	0.28
	95	n.d.
119	0	n.d.
	240	n.d.
120	0	0.50
	280	n.d.
121	0	0.42
	220	n.d.
122	0	0.24
	40	0.20
124	0	0.40
	105	n.d.
133	0	n.d.
	65	n.d.
135	0	n.d.
	140	n.d.
137	0	0.20
	95	n.d.
145	0	n.d.
	60	n.d.
146	0	0.35
	65	n.d.
147	0	0.15
	95	n.d.
148	0	0.28
	100	n.d.
156	0	0.32
	150	0.25
157	0	0.50
	50	0.45
158	0	–
	90	n.d.
159	0	0.33
	90	n.d.
160	0	0.45
	135	0.15

TABLE XVII

N.W. GULF OF ALASKA
Discoverer Leg III 23 November - 2 December 1975

Free zinc contents at pH 8 in filtered (0.4 μm) water.

Station No.	Depth (m)	Zn (μg/ℓ)
106	80	0.17
108	10	n.d.
	220	n.d.
110	10	0.20
	175*	n.d.

---

*Intercalibration station

TABLE XVIII

S. BERING SEA
Discoverer 2-19 June 1976

Free zinc (see text) contents at pH 8 in unfiltered water (μg/ℓ)

Station No.	Depth (m)	Zn (μg/ℓ)	Station No.	Depth (m)	Zn (μg/ℓ)
02	0	0.06	21	0	-
	40	1.2	-	40	0.56
06	0	0.36	24	0	0.40
	40	0.35	-	40	1.1
08	0	0.40	26	0	0.50
	15	(4.0)	-	45	0.47
10	0	0.45	30	0	1.7
	60	0.48	-	125	-
12	-	0.88	62	0	0.19
	75	1.5	-	45	0.42
13	0	(>5)	64	80	0.20
	75	0.58	65	-	-
14	-	1.2	-	100	0.60
	130	0.57	69	0	-
17	0	0.60	-	105	1.0
	110	1.0	-	-	-
19	0	0.75	-	-	-
	65	0.40	-	-	-

TABLE XIX

N.E. GULF OF ALASKA

Discoverer Leg III 23 November-2 December 1975
H. V. Weiss, Analyst

Soluble mercury contents of filtered (0.04 μm) water (ng/l).

Station	Depth (m)	Inorganic	Total
2	178	13	32
5	162	4	5
8	276	4	2
11	10	11	12
	1350*	4	2
15	10	24	16
	1500*	22	-
24	10	7.2 ± 0.5 (a)	2
	410*	6	7
26	10	6	4
	136	3	5
33	10	7	4
	205	3	3
44	10	27	33
	165	19.8 ± 0.5 (a)	-
48	10	11	9
	447	19	11
49	10	21	23
	120	5.5 ± 1.2 (b)	4
50	10	27	33
	107	24	26
51	10	10	10
	133	8	7
52	74	4	2
53	10	5.6 ± 0.7 (a)	5
	784	5.1 ± 0.5 (a)	2
54	10	4	4
	202	4	5
55	10	3	3
	110	6	2
56	58	8.0 ± 1.5 (b)	3
57	67	2	-
58	82	16	2
59A	370	6	3

*Intercalibration stations

(a) Duplicate

(b) Triplicate

TABLE XX

N.W. GULF OF ALASKA
Discoverer Leg III 23 November-2 December 1975
H. V. Weiss, Analyst

Soluble mercury contents of filtered (0.4 μmg) water (ng/l)

Station	Depth (m)	Inorganic	Total
108	226	4	4
110	10	3.9 ± 0.4 (a)	9
	273*	9	6

*Intercalibration station

(a) Duplicate

TABLE XXI

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).

Sta.	Sta. Depth(m)	Sample Depth(m)	μg/ℓ Cr(total)	μg/ℓ Cr(filtrate)	μg/ℓ Se(total)	μg/ℓ 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 XXI

(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

TABLE XXII

N.E. GULF OF ALASKA

Discoverer Leg III 23 November - 2 December, 1975

D. E. Robertson, Analyst

Soluble vanadium contents of filtered (0.4 μm) water • (μg/kg).

Station	Depth	V
02	178	1.6
05	162	1.7
08	10	1.3
	274	1.6
15	10	1.4
	1500	1.6
26	10	1.6
	136	1.6
29	71	1.5
30	42	1.3
33	10	1.1
	205	1.6
44	10	1.2
	165	1.4
48	10	1.3
	447	1.6
52	74	1.3
53	10	1.3
	204	1.4
55	10	1.3
	110	1.2
58	82	1.4

TABLE XXIII

N.W. GULF OF ALASKA

Discoverer Leg IV 8-16 October, 1975

D. E. Robertson, Analyst

Soluble vanadium contents of filtered (0.4 μm) water • (μg/kg).

Station	Depth	V
101	1	1.2
	80	1.4
104	1	1.6
	96	1.4
108*	10	1.5
	226	1.6
119	204	1.5
121	1	1.3
	220	1.7
124	1	1.6
	105	1.7
133	1	1.3
	68	1.3
135	1	1.4
	141	1.3
137	1	1.3
	95	1.6
145	1	1.4
	63	1.5
148	1	1.3
	100	1.3
157	1	1.4
	59	1.2
160	1	1.5
	132	1.6

**Discoverer* Leg III 23 November - 2 December, 1975

TABLE XXIV

S. BERING SEA

Discoverer Leg II 2-19 June, 1975

D. E. Robertson, Analyst

Soluble vanadium contents of filtered (0.4 μm) water • (μg/kg).

Station	Depth	V
17	110	1.0
24	40	1.3
34	175	1.3
37	0	1.3
41	0	1.3
43	0	1.5
56	0	1.4
59	30	1.3
64	0	1.5
	80	1.5, 1.4

TABLE XXV

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 XXVI

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 XXVII

HEAVY METAL CONTENTS OF *MYTILUS* (μg/g DRY WEIGHT)

Intertidal Collection Summer 1976

	Cd	Cu	Ni	Zn
A. N.E. GULF				
Port Dick	11.0	8.4	2.2	80.3
Day Harbor	10.4	5.5	1.2	68.2
Katalla	6.0	10.8	4.3	90.0
Boswell Bay	2.9	6.4	1.2	39.6
La Touche Point	5.5	8.6	3.5	52.1
B. N.W. GULF AND KODIAK ISLAND				
Sundstrom Island	10.3	8.0	3.4	106.5
Cape Nukshak	9.0	9.0	3.2	81.9
C. S. BERING SEA				
Makuchin	6.0	6.0	1.4	80.7
Otter Island	24.6	6.0	1.8	156.4

TABLE XXVIII

Heavy metal contents of *Fucus* (μg/g dry weight).
Intertidal collection, summer 1976.

	Cd	Cu	Ni	Zn
A. N.E. GULF OF ALASKA				
Kayak Island	3.8	6.0	15.0	16.7
Anchor Cove (Day Harbor)	2.8	6.8	14.5	12.5
B. N.W. GULF OF ALASKA				
Cape Nukshak	4.3	7.0	9.3	14.9
C. S. BERING SEA				
Otter Island	3.1	5.0	5.1	8.1

below in Section VII (Tables XXVI and XVIII). Tables XXVII and XXVIII also include samples collected in the N.W. Gulf region and in the Bering Sea.

Some Se contents of a range of biota samples collected on the Bering Sea trawl cruise are given in Table XXIX.

Sediment

Heavy metal contents of extracts from surficial samples collected on the standard N.E. Gulf grid (see Fig. 6) on two separate cruises are given in Tables XXX and XXXI. Extract concentrations of these same metals, plus Fe and Mn, for Lower Cook Inlet are listed in Tables XXXII and XXXIII, and for the S. Bering Sea in Table XXXIV.

In Tables XXXV-XLII are given Cr, Se and Al data for sediment extracts for samples from the N.E. and N.W. Gulf, Lower Cook Inlet and the Bering and Beaufort Seas.

Total analysis of surface sediment samples for Mn and V from the N.E. and N.W. Gulf of Alaska and the S. Bering Sea are given in Tables XLIII-XLV respectively. These distributions are mapped in Figures 12 through 17.

Analyses for total As, Ba, Co, Cr, Fe and Sb in surficial N.E. Gulf sediments are given in Table XLVI and Figures 18 through 23. Equivalent data for the N.W. Gulf region are given in Table XLVII and Figures 24 through 29.

"While rock" barium and arsenic values for surface sediments collected in the S. Bering Sea are given in Table XLVIII and Figures 30 and 31.

Data for Mn, V and Al contents of suspended sediments (collected from the same localities as the bottom sediments above is expressed in Tables IL-LIV as μg/ℓ in the solid phase per unit of seawater.

TABLE XXIX

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 XXX

N.E. GULF OF ALASKA

Silas Bent 31 August - 17 September 1975

Heavy metal contents of sediment extracts.
(mg/kg)

Station	Cd	Cu	Ni	Zn	Fe	Mn
1	<0.25	13.9	12.4	37	6380	125
3	"	9.3	9.1	27	6350	116
4	"	9.3	10.4	30	6740	106
6	"	6.7	4.3	17	2210	63
7	"	5.6	4.0	23	2770	50
25	"	3.8	2.9	13	1200	48
27	"	7.6	5.5	21	2260	117
28	"	12.8	7.4	19	2590	103
31	"	14.7	9.2	23	6375	110
32	"	13.8	8.0	22	5105	89
39	"	14.0	6.7	29	4000	79
41	"	19.4	6.7	30	4420	98
42	"	15.1	9.8	24	6780	115
43	"	12.3	11.1	22	6660	88
48	"	10.0	6.2	19	3470	87
50	"	13.9	9.4	27	7250	130

TABLE XXXI

N.E. GULF OF ALASKA

Discoverer Leg III, 23 November-2 December 1975

Heavy metal contents of sediment extracts (mg/kg)

Station	Cd	Cu	Ni	Zn
2	<0.25	6.2	5.5	30.6
5	<0.25	7.1	6.4	20.6
33	<0.25	7.2	2.0	12.3
44	<0.25	10.8	3.9	12.8
49	<0.25	12.4	11.2	37.2
51	<0.25	19.5	11.0	32.6
52	<0.25	17.3	12.6	39.2
53	<0.25	10.8	8.3	21.6
54	<0.25	13.5	8.2	22.2
55	<0.25	11.9	11.1	34.5

TABLE XXXII

LOWER COOK INLET

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

Station	Cd	Cu	Ni	Zn
4	<0.25	16.8	3.7	13.7
10	<0.25	16.9	7.9	34.3
11	<0.25	17.2	5.9	17.8
12	<0.25	15.1	4.1	14.7
18	<0.25	3.6	1.8	10.5
19	<0.25	3.0	<1.2	5.2
25	<0.25	3.0	1.3	11.6
26	<0.25	11.9	2.9	10.0
30	<0.25	6.7	2.9	19.6

TABLE XXXIII

LOWER COOK INLET
Moana Wave 31 March - 15 April 1976

Heavy metal contents of sediment extracts.
(mg/kg)

Station	Fe	Mn
4	2810	176
10	3830	113
11	3685	112
12	3310	100
18	500	70
19	690	136
25	1125	40
26	1240	62
30	3230	420

TABLE XXXIV

S. BERING SEA

Discoverer 2-19 June 1975
Heavy metal contents of sediment extracts (mg/kg)

Station	Cd	Cu	Ni	Zn	Fe	Mn
6	<0.25	<2.5	<2.5	6.4	-	-
8	<0.25	7.9	6.4	21.3	-	-
10	<0.25	<2.5	<2.5	7.2	-	-
12	<0.25	<2.5	<2.5	12.2	-	-
13	<0.25	<2.5	2.5	9.3	-	-
14	<0.25	<2.5	2.5	9.5	-	-
17	<0.25	<2.5	<2.5	12.2	1920	26.0
19	<0.25	<2.5	<2.5	6.1	1920	26.0
21	<0.25	<2.5	<2.5	12.0	-	-
26	<0.25	<2.5	<2.5	6.8	-	-
28	<0.25	<2.5	2.5	9.9	1850	22.7
30	<0.25	2.5	7.3	23.9	-	-
31	0.25	<2.5	<2.5	7.1	637	9.0
41	0.25	<2.5	<2.5	6.4	1466	22.7
43	0.25	<2.5	2.5	6.3	-	-
44	0.25	<2.5	<2.5	5.9	1040	16.2
56	0.25	9.9	8.2	19.3	-	-
57	0.25	<2.5	<2.5	6.8	-	-
59	0.25	<2.5	<2.5	4.8	1555	18.2
60	0.25	<2.5	<2.5	12.0	-	-
62	0.25	<2.5	<2.5	9.7	-	-
63	0.25	<2.5	<2.5	13.3	1756	27.3
64	0.25	<2.5	<2.5	12.0	1350	20.9
65	0.25	2.5	<2.5	10.5	915	18.8
69	0.25	<2.5	<2.5	12.5	985	21.3

TABLE XXXV

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 XXXVI

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 XXXVII

N.W. GULF OF ALASKA

Discoverer Leg IV 8-16 October, 1975

T. A. Gosink, Analyst

Selenium, chromium and aluminum 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

TABLE XXXVIII

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 XXXIX

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 XL

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 XL

(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 XLI

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 amino - acetic acid extracts.

TABLE XLII

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 XLIII

N.E. GULF OF ALASKA

Discoverer Leg III, 23 November-2 December 1975
D. E. Robertson, Analyst

Total heavy metal contents of bottom sediments (mg/kg)

Station	Depth Interval (cm)	Mn	V
2	0- 2	738 ± 49	150 ± 29
	6- 8	847 ± 48	190 ± 28
	10-12	845 ± 55	173 ± 29
	14-16	995 ± 48	185 ± 29
	18-20	817 ± 46	170 ± 28
5	8-10	777 ± 48	165 ± 29
	14-16	774 ± 49	181 ± 28
26	0- 2	924 ± 51	92 ± 16
	4- 6	879 ± 48	147 ± 25
	8-10	836 ± 48	141 ± 24
	12-14	810 ± 53	135 ± 30
30	0- 2	600 ± 51	91 ± 26
33	0- 2	635 ± 45	108 ± 24
	4- 6	432 ± 40	75 ± 20
	8-10	562 ± 42	108 ± 20
44	0- 2	851 ± 43	146 ± 26
	4- 6	786 ± 18	174 ± 30
48	0- 2	799 ± 44	161 ± 27
	4- 6	812 ± 46	143 ± 27
	8-10	756 ± 56	174 ± 28
49	0- 2	776 ± 51	157 ± 28
	4- 6	746 ± 40	168 ± 27
	8-10	731 ± 41	165 ± 27
	12-14	731 ± 38	145 ± 25
	16-18	713 ± 40	166 ± 27
50	0- 2	776 ± 40	163 ± 27
	4- 6	812 ± 43	183 ± 28
	8-10	782 ± 45	169 ± 29
	12-14	740 ± 39	169 ± 26
	18-20	763 ± 40	166 ± 27

TABLE XLIII (Continued)

Total heavy metal contents of bottom sediments (mg/kg)

Station	Depth Interval (cm)	Mn	V
51	0- 2	969 ± 50	179 ± 30
	4- 6	912 ± 46	177 ± 28
52	0- 2	936 ± 41	165 ± 27
	4- 6	889 ± 46	183 ± 31
	8-10	825 ± 45	180 ± 30
	12-14	816 ± 40	166 ± 27
	14-16	852 ± 44	152 ± 29
56	0- 2	734 ± 41	138 ± 25
	4- 6	621 ± 46	158 ± 27
	8-10	933 ± 43	151 ± 27
	12-14	886 ± 45	197 ± 26
57	0- 2	878 ± 51	152 ± 26
	4- 6	747 ± 44	144 ± 27
58	0- 2	951 ± 47	176 ± 29
	4- 6	789 ± 44	149 ± 27
	8-10	779 ± 49	167 ± 29
59A	Surf.*	858 ± 57	155 ± 30

* Samples from Station 59A collected in van Veen grab.

TABLE XLIV

N.W. GULF OF ALASKA
Discoverer Leg IV, 8-16 October 1975
D. E. Robertson, Analyst

Total heavy metal contents of bottom sediments (mg/kg dry weight)

Station	Depth Interval	Mn	V
104	0- 2	846 ± 39	72 ± 19
	4- 6	546 ± 48	108 ± 24
	8-10	570 ± 42	94 ± 22
119	0- 2	991 ± 48	130 ± 29
	4- 6	802 ± 45	137 ± 27
	8-10	724 ± 47	119 ± 28
120	0- 2	1066 ± 51	164 ± 31
	4- 6	958 ± 47	123 ± 28
	8-10	997 ± 57	167 ± 32
	12-14	1074 ± 52	150 ± 30
	16-18	931 ± 49	144 ± 28
121	0- 2	782 ± 53	118 ± 26
	4- 6	690 ± 50	121 ± 29
	8-10	744 ± 44	114 ± 26
122	0- 2	312 ± 31	27 ± 15
124	0- 2	489 ± 47	83 ± 25
	4- 6	541 ± 45	88 ± 23
	8-10	464 ± 45	70 ± 22
133	Surf.	1170 ± 50	173 ± 28
134	0- 2	711 ± 54	126 ± 27
	4- 6	651 ± 52	124 ± 25
	8-10	844 ± 56	148 ± 28
	12-14	804 ± 46	147 ± 27
	16-18	742 ± 51	118 ± 30
135	0- 2	806 ± 56	129 ± 28
	4- 6	900 ± 45	140 ± 27
	8-10	906 ± 45	132 ± 27

TABLE XLV

S. BERING SEA
Discoverer 2-19 June 1975
D. E. Robertson, Analyst

Total heavy metal contents of bottom sediments (mg/kg dry weight)

Station	Depth Interval (cm)	Mn	V
8	0- 2	720 ± 38	126 ± 26
	4- 6	567 ± 36	87 ± 25
	8-10	715 ± 43	165 ± 29
	12-14	629 ± 37	90 ± 25
12	0- 3	573 ± 49	118 ± 25
19	0- 2	628 ± 43	93 ± 27
28	0- 3	524 ± 50	92 ± 25
29	0- 4	572 ± 45	77 ± 23
30	0- 4	571 ± 43	112 ± 24
	4- 8	574 ± 38	114 ± 25
	8-12	574 ± 43	106 ± 27
37	0- 2	358 ± 42	85 ± 23
	4- 6	360 ± 38	85 ± 21
41	0- 2	-	-
43	0- 2	-	-
	4- 6	-	-
56	0- 2	-	-
	4- 6	425 ± 38	83 ± 32
	8-10	427 ± 45	86 ± 23
	12-18	427 ± 49	98 ± 23
59	0- 2	366 ± 42	77 ± 22
	4- 6	393 ± 40	77 ± 20
64	0- 2	397 ± 48	82 ± 24
	4- 6	414 ± 22	87 ± 43
	8-10	403 ± 47	89 ± 23
	12-14	422 ± 45	96 ± 24
	16-20	420 ± 46	89 ± 23
	10-24	422 ± 45	89 ± 23

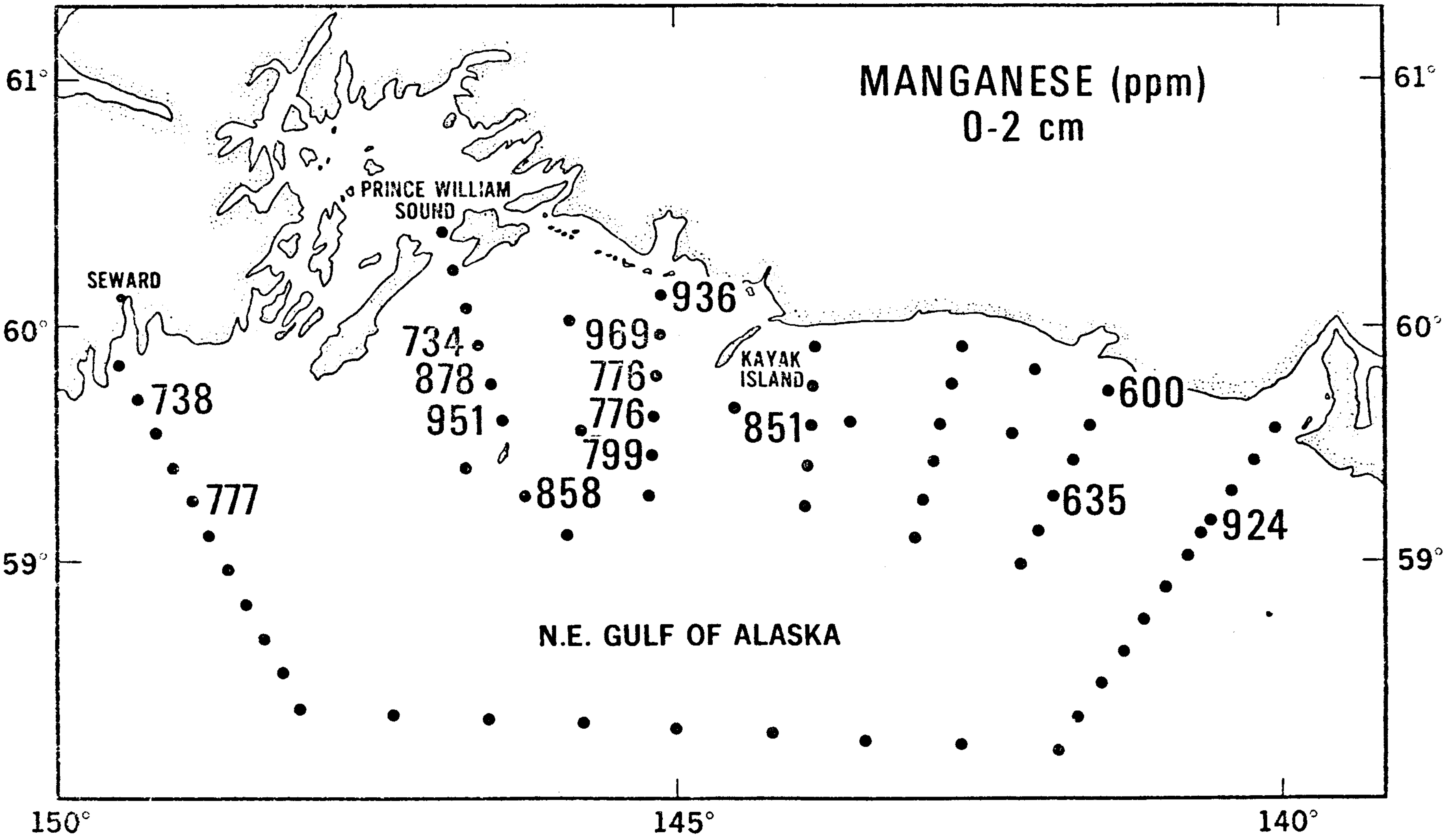

Figure 12. Total Mn content of surface sediments from N.E. Gulf of Alaska.

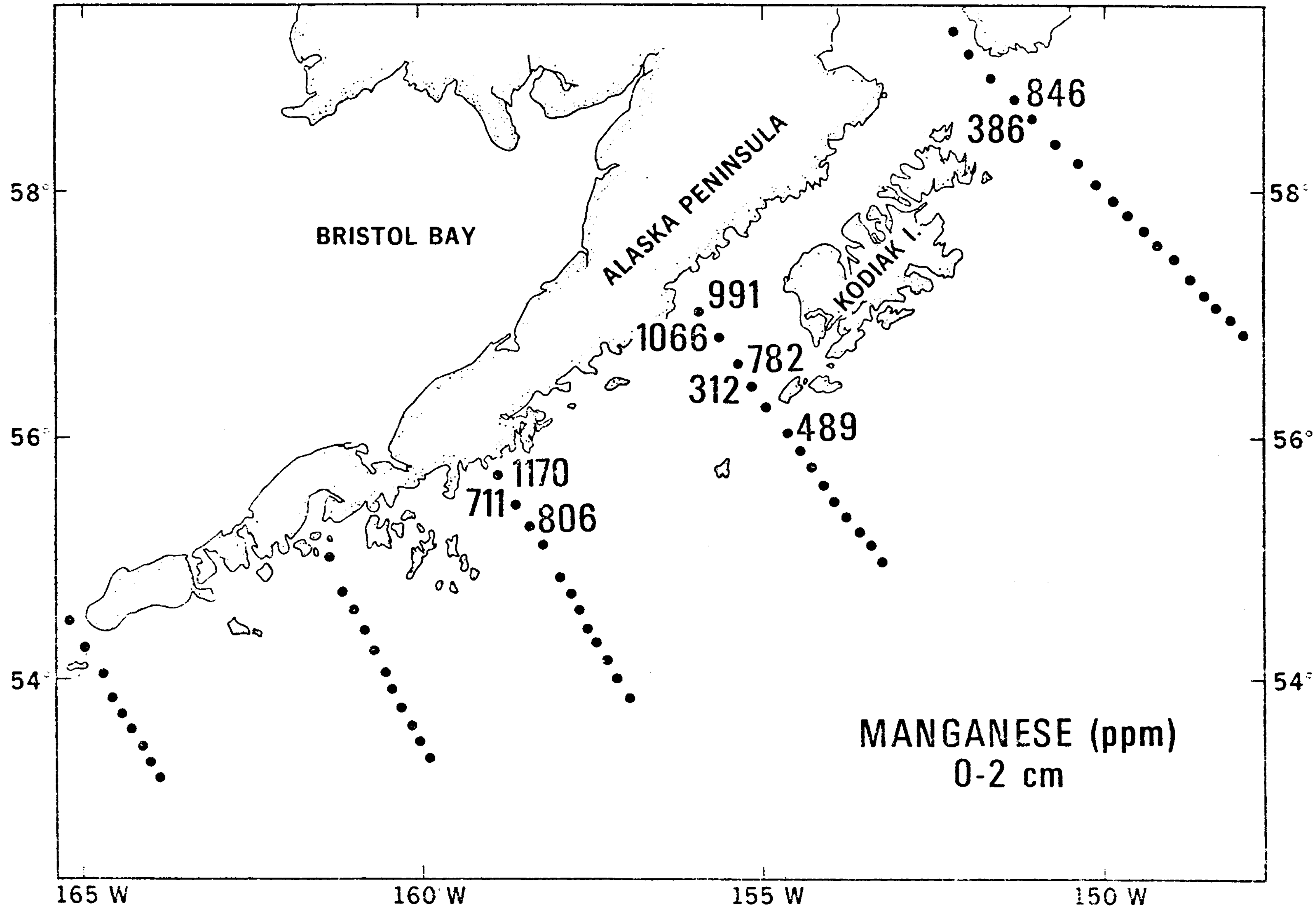

Figure 13. Total Mn contents of surface sediment from N.W. Gulf of Alaska.

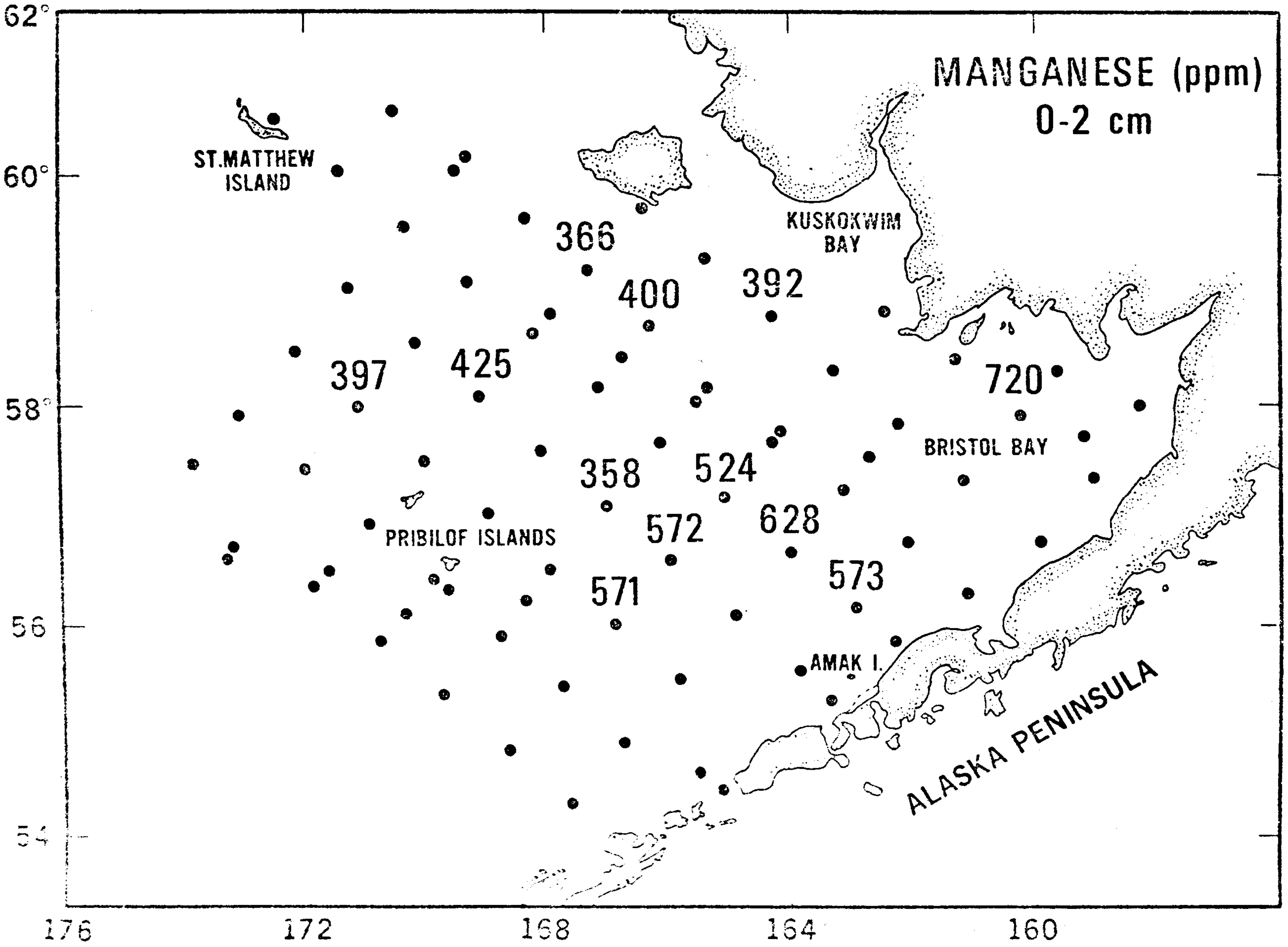

Figure 14. Total Mn contents of surface sediments from S. Bering Sea.

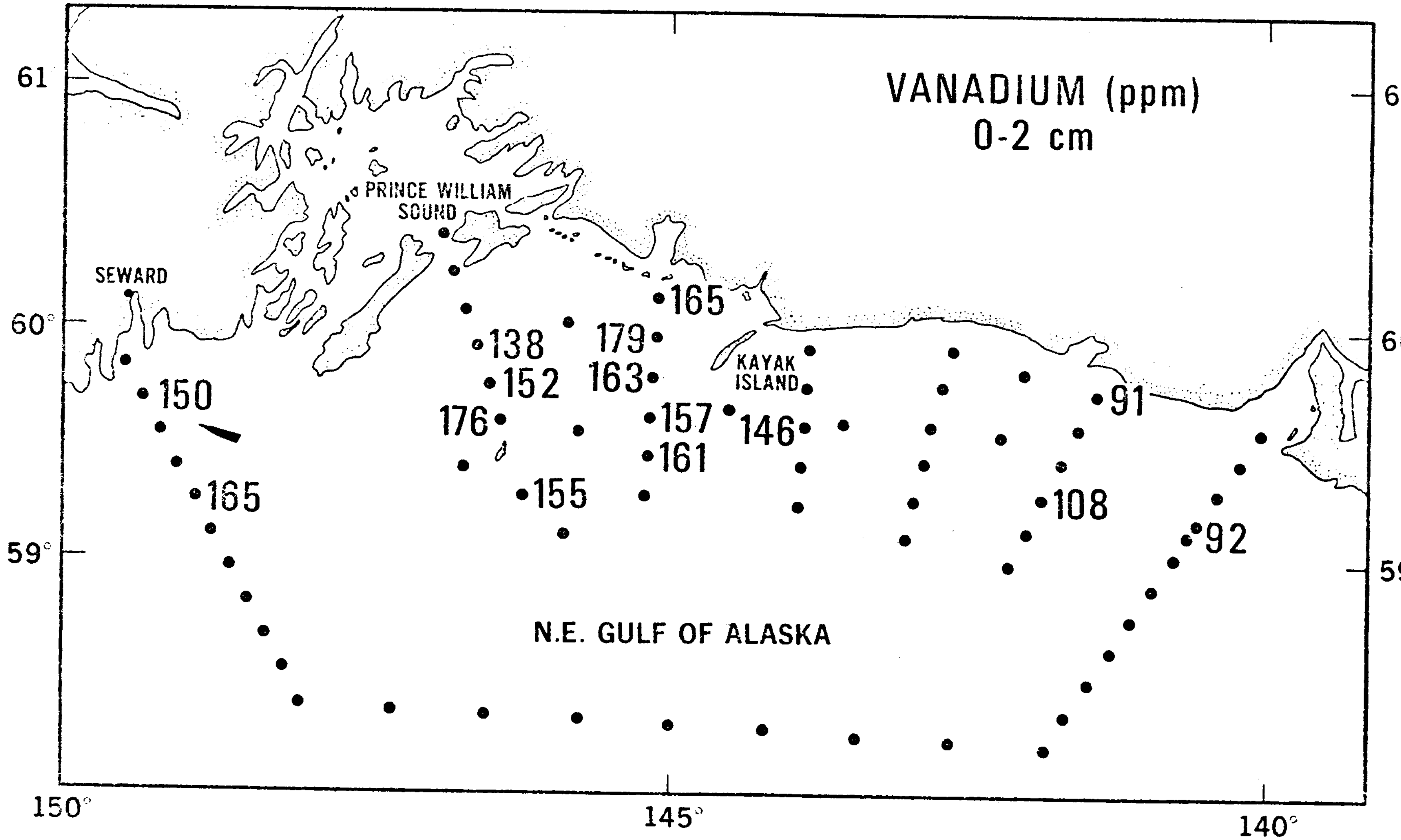

Figure 15. Total vanadium contents of sediment from N.W. Gulf of Alaska.

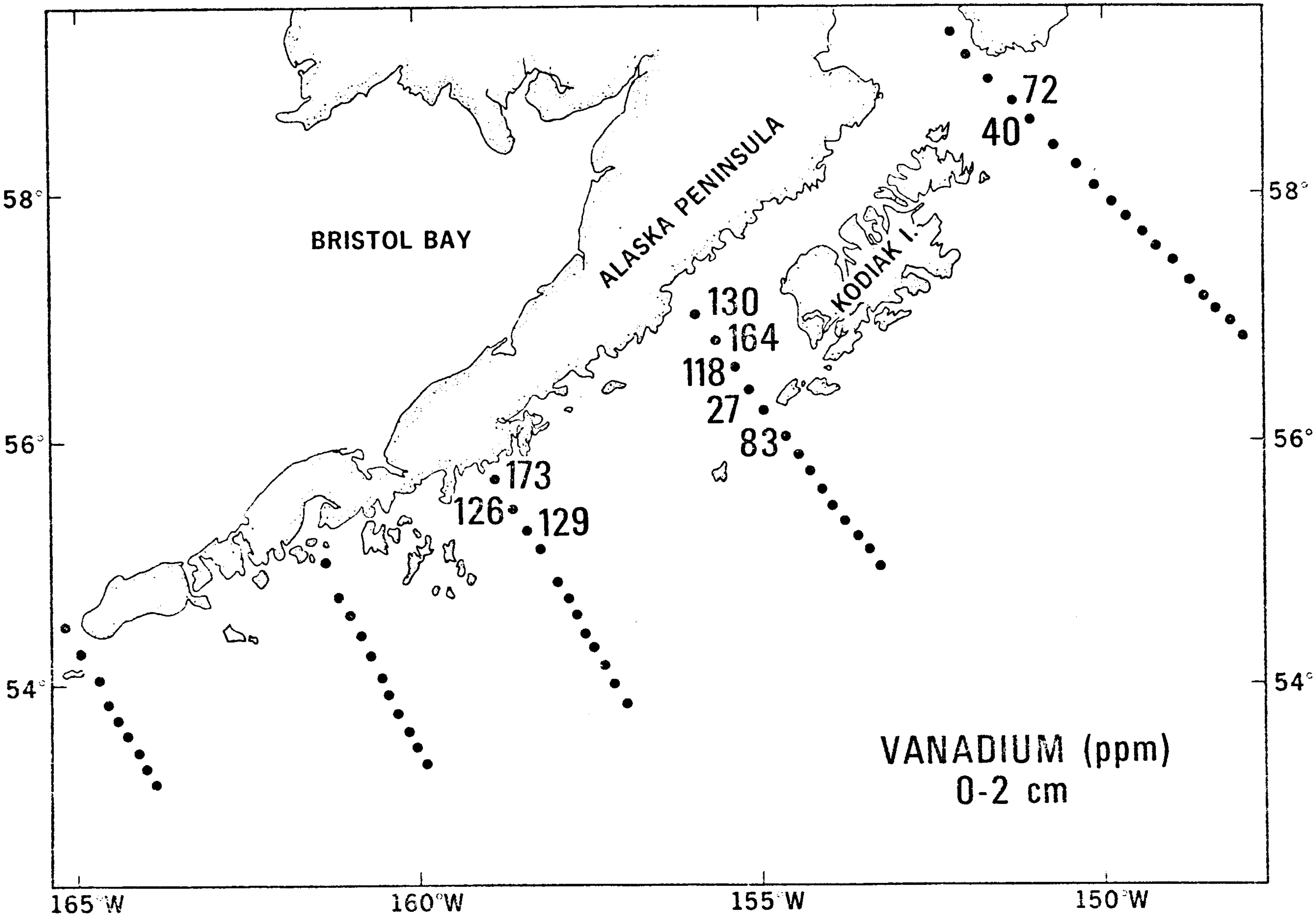

Figure 16. Total vanadium contents of sediment from N.W. Gulf of Alaska.

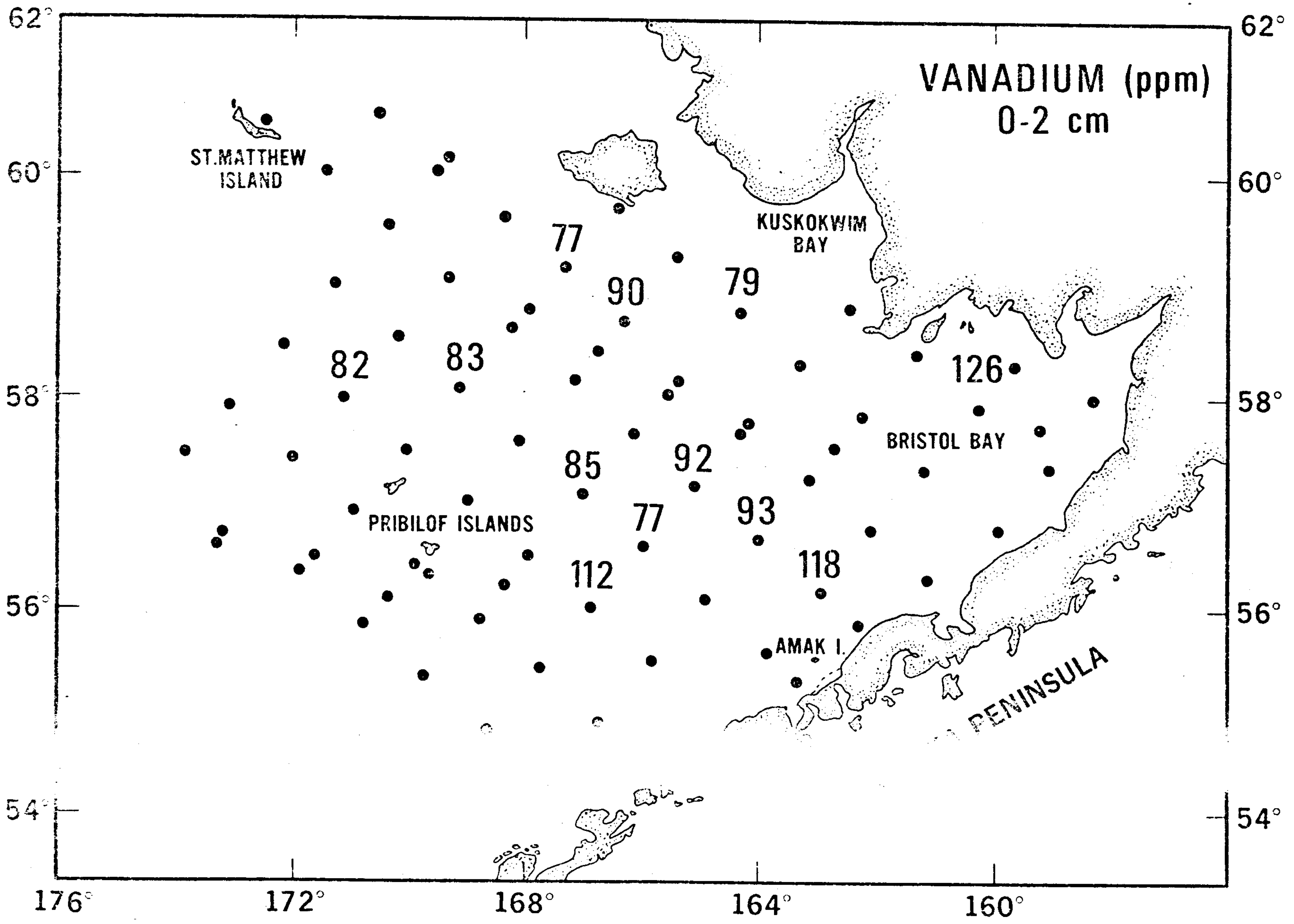

Figure 17. Total vanadium contents of sediment from S. Bering Sea.

TABLE XLVI

N.E. GULF OF ALASKA

Discoverer Leg III 23 November - 2 December, 1975

D. E. Robertson, Analyst

Total heavy metal contents of bottom sediments
(μg/g except Fe %)

Station	Interval	As	Ba	Co	Cr	Fe(%)	Sb
2	0-2	5.3	700 ± 190	16	115	4.20	0.61 ± 0.19
	6-8	7.8	930 ± 140	22	166	5.91	0.90 ± 0.16
	10-12	7.7	710 ± 130	19	134	5.02	0.71 ± 0.13
	14-16	8.0	890 ± 140	22	156	5.64	0.74 ± 0.16
	18-20	6.3	770 ± 110	19	112	4.96	0.81 ± 0.13
5	8-10	2.2	500 ± 100	20	130	5.14	0.59 ± 0.10
	14-16	9.5	720 ± 140	23	119	5.14	0.90 ± 0.15
26	0-2	1.8	540 ± 120	20	124	4.95	0.43 ± 0.11
	4-6	<2.0	460 ± 130	16	88	4.14	0.49 ± 0.12
	8-10	3.5	490 ± 120	20	126	4.98	0.57 ± 0.10
	12-14	3.1	340 ± 140	17	98	4.27	0.58 ± 0.14
30	Top 2 cm	7.2	460 ± 110	12	112	3.10	0.16 ± 0.09
51	0-2	8.7	540 ± 100	27	162	6.84	0.44 ± 0.28
	4-6	7.9	530 ± 130	20	138	4.94	0.37 ± 0.10
59A	v.v.	1.6 ± 0.6	570 ± 160	17	156	4.52	0.66 ± 25
58	0-2	2.7 ± 0.7	430 ± 160	18	145	4.80	0.35 ± 0.08
	4-6	2.3 ± 0.6	250 ± 160	17	131	4.37	0.40 ± 0.07
	8-10	2.3 ± 0.7	480 ± 170	18	153	5.19	0.45 ± 0.09
57	0-2	2.1 ± 0.6	350 ± 180	18	134	4.37	0.46 ± 0.16
	4-6	1.9 ± 0.7	490 ± 170	15	79	3.79	0.43 ± 0.09
56	0-2	2.2 ± 0.5	620 ± 140	19	116	4.23	0.24 ± 0.07
	4-6	1.9 ± 0.8	770 ± 180	12	88	2.99	0.30 ± 0.05
	8-10	3.2 ± 0.6	740 ± 160	22	171	5.73	0.56 ± 0.09
	12-14	2.7 ± 0.7	530 ± 170	18	142	4.68	0.47 ± 0.08
33	0-2	2.6 ± 0.6	450 ± 160	16	114	5.23	0.81 ± 0.07
	4-6	1.5 ± 0.7	450 ± 140	11	79	3.33	0.63 ± 0.06
	8-10	1.4 ± 0.6	350 ± 100	12	32	2.27	0.40 ± 0.05
48	0-2	2.5 ± 0.4	550 ± 130				
	4-6	2.3 ± 0.7	500 ± 120	16	104	4.41	0.51 ± 0.09
	8-10	2.1 ± 0.4	440 ± 140				

TABLE XLVI (Continued)

Station	Interval	As	Ba	Co	Cr	Fe(%)	Sb
44	0-2	2.7 ± 0.7	450 ± 120	15	112	4.36	0.42 ± 0.08
	4-6	0.8 ± 0.4	400 ± 130	16	55	2.97	0.33 ± 0.05
49	0-2	4.4 ± 0.9	350 ± 150	18	129	4.86	0.41 ± 0.10
	4-6	3.4 ± 0.4	540 ± 120	18	144	5.25	0.36 ± 0.08
	8-10	3.4 ± 0.7	530 ± 140	19	66	3.46	0.35 ± 0.06
	12-14	2.2 ± 0.3	670 ± 110	20	78	3.67	0.29 ± 0.04
	16-18	2.6 ± 0.4	380 ± 60	17	58	3.04	0.39 ± 0.06
50	0-2	3.0 ± 0.2	500 ± 70	19	74	3.44	0.26 ± 0.05
	8-10	2.4 ± 0.4	370 ± 130	12	98	2.84	<0.16
	12-14	3.2 ± 0.4	410 ± 140	20	136	5.08	0.35 ± 0.08
	18-20	2.3 ± 0.4	510 ± 110	16	110	3.76	0.28 ± 0.06
52	0-2	4.3 ± 0.5	770 ± 140	19	137	4.90	0.59 ± 0.09
	4-6	2.9 ± 0.4	720 ± 120	21	142	5.44	0.57 ± 0.25
	8-10	2.5 ± 0.5	580 ± 140	20	94	4.26	0.58 ± 0.05
	12-14	2.9 ± 0.4	520 ± 120	17	122	4.12	0.51 ± 0.08
	14-16	3.5 ± 0.5	690 ± 80	22	136	5.41	0.56 ± 0.09

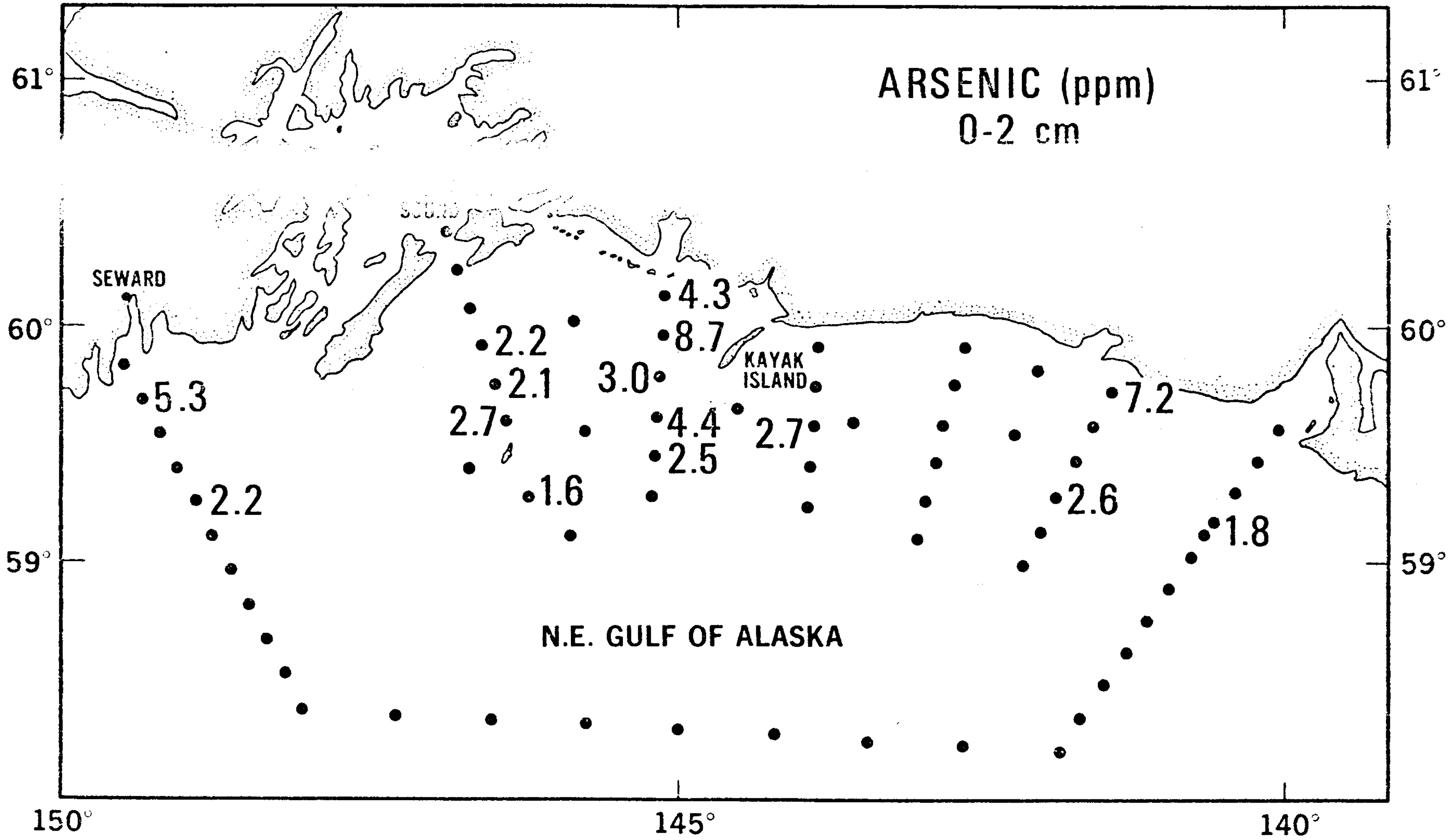

Figure 18. Total As contents of surface sediment from N.E. Gulf of Alaska.

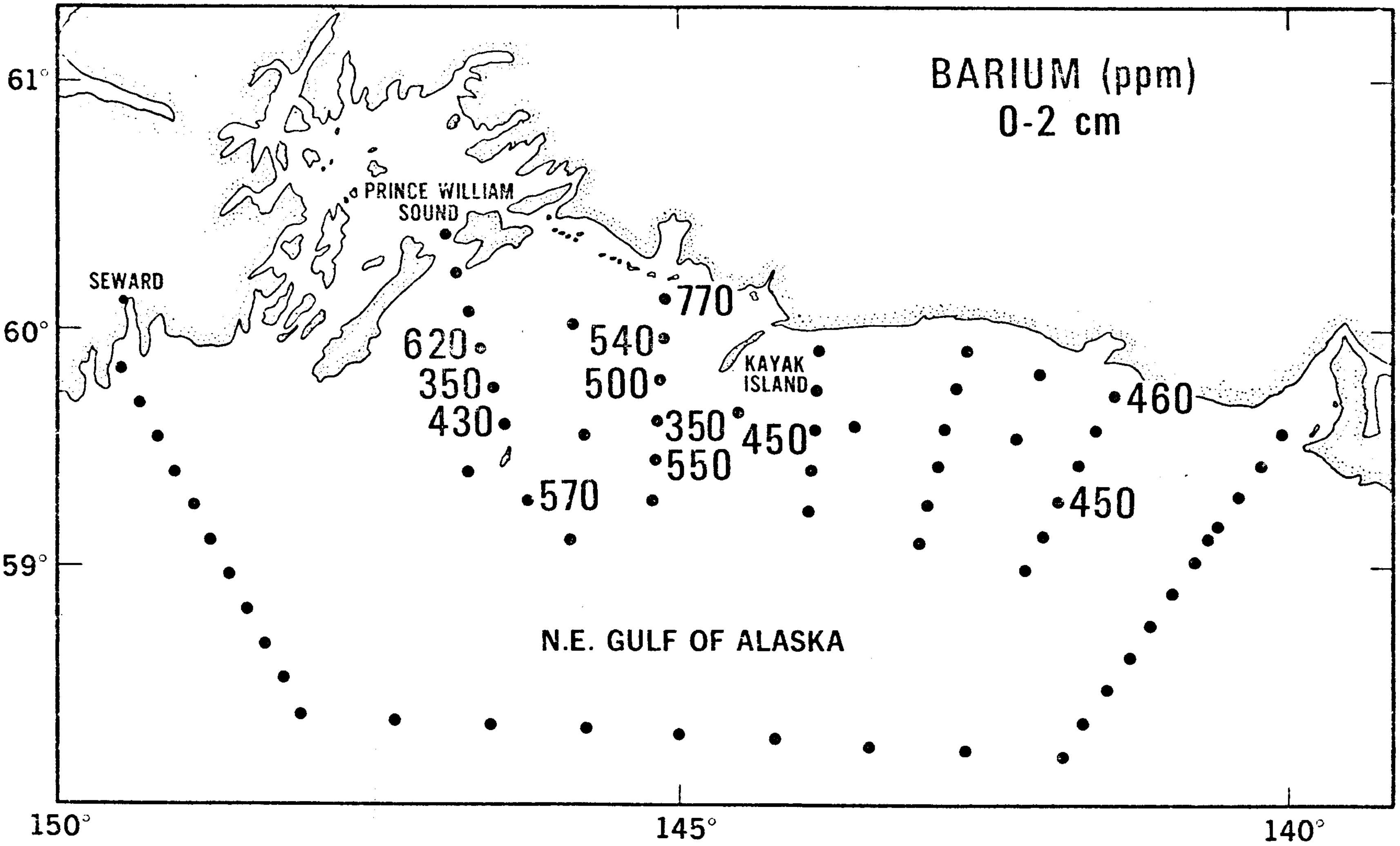

Figure 19. Total Ba contents of surface sediment from N.E. Gulf of Alaska.

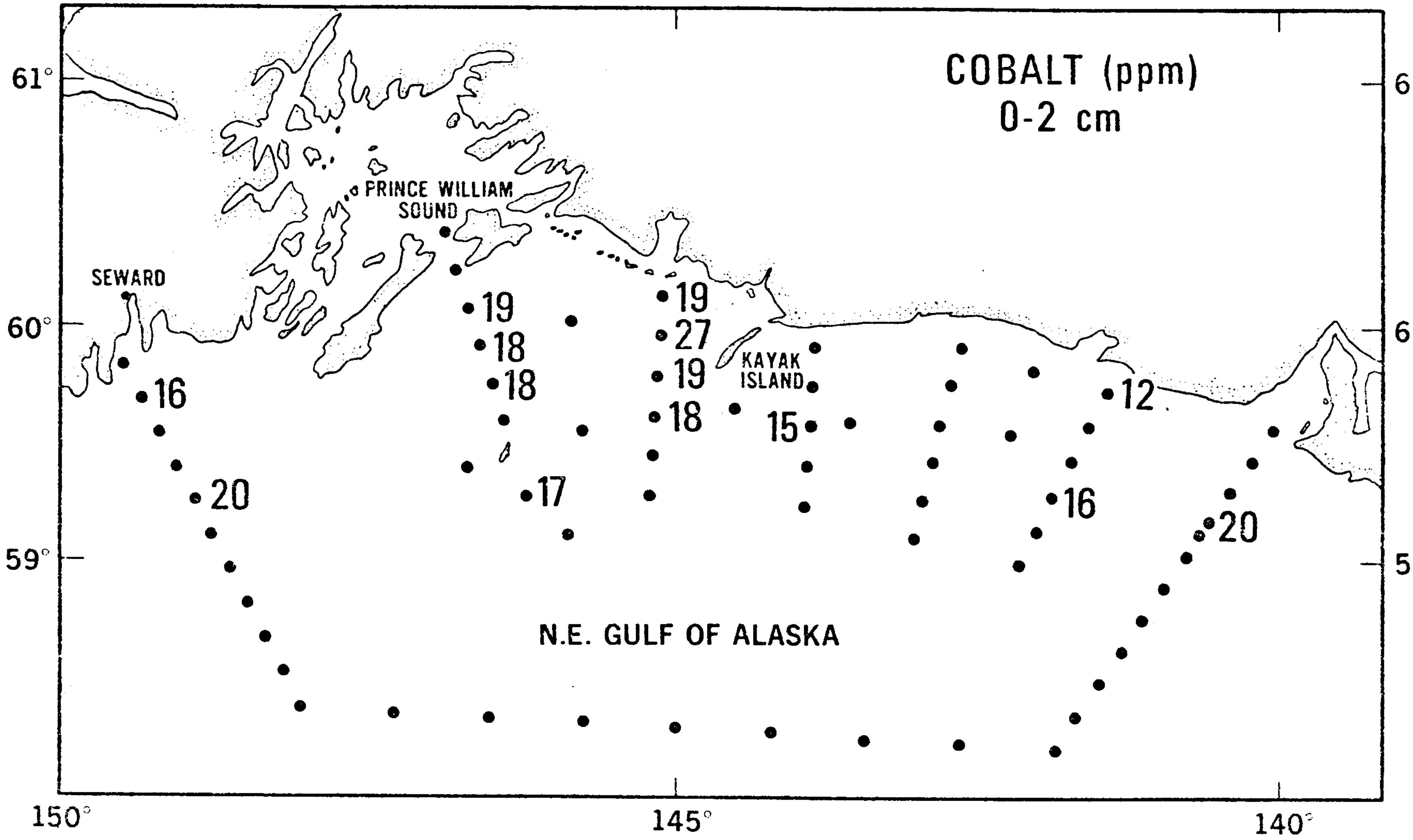

Figure 20. Total Co contents of surface sediment from N.E. Gulf of Alaska.

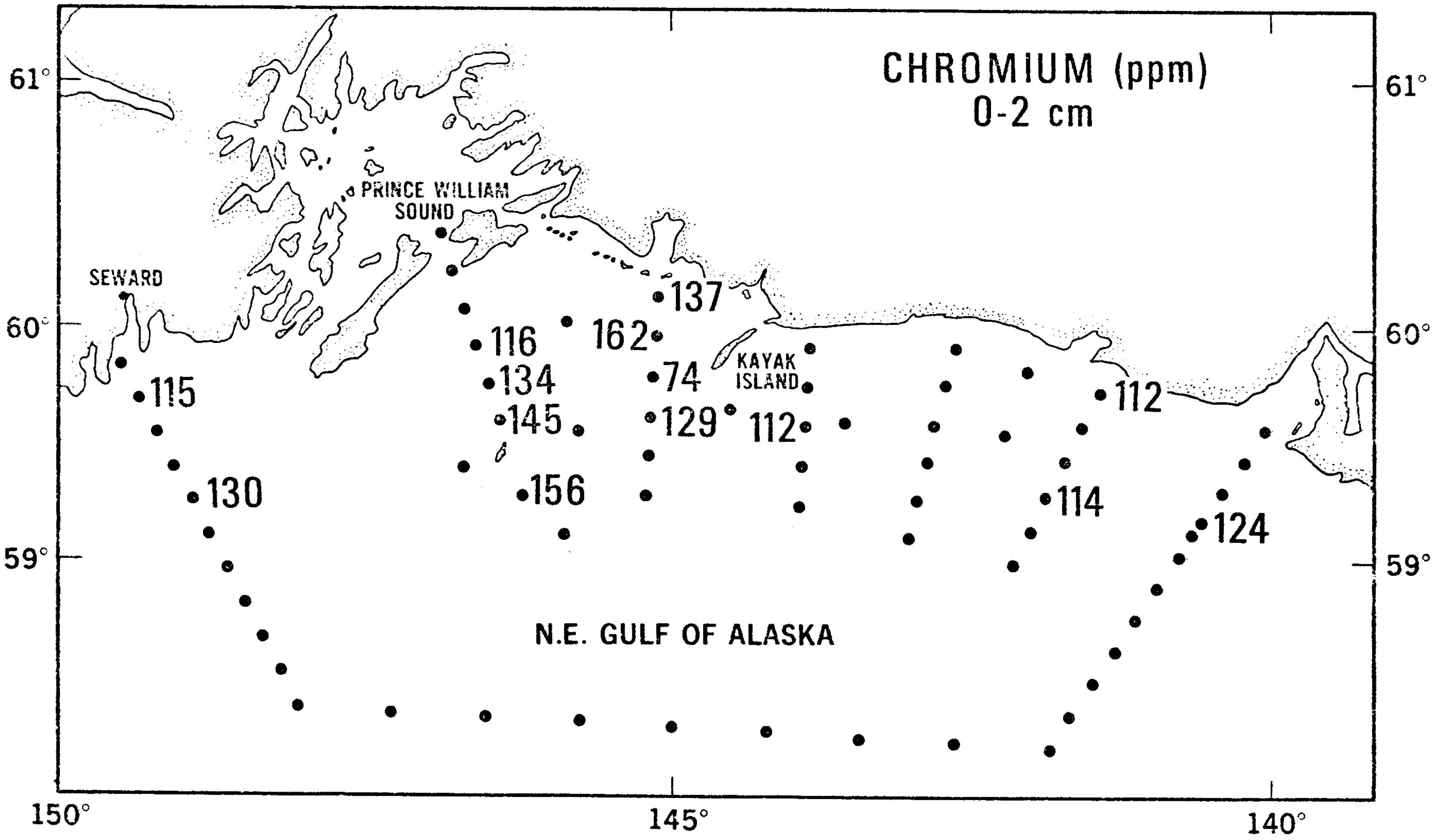

Figure 21. Total Cr contents of surface sediment from N.E. Gulf of Alaska.

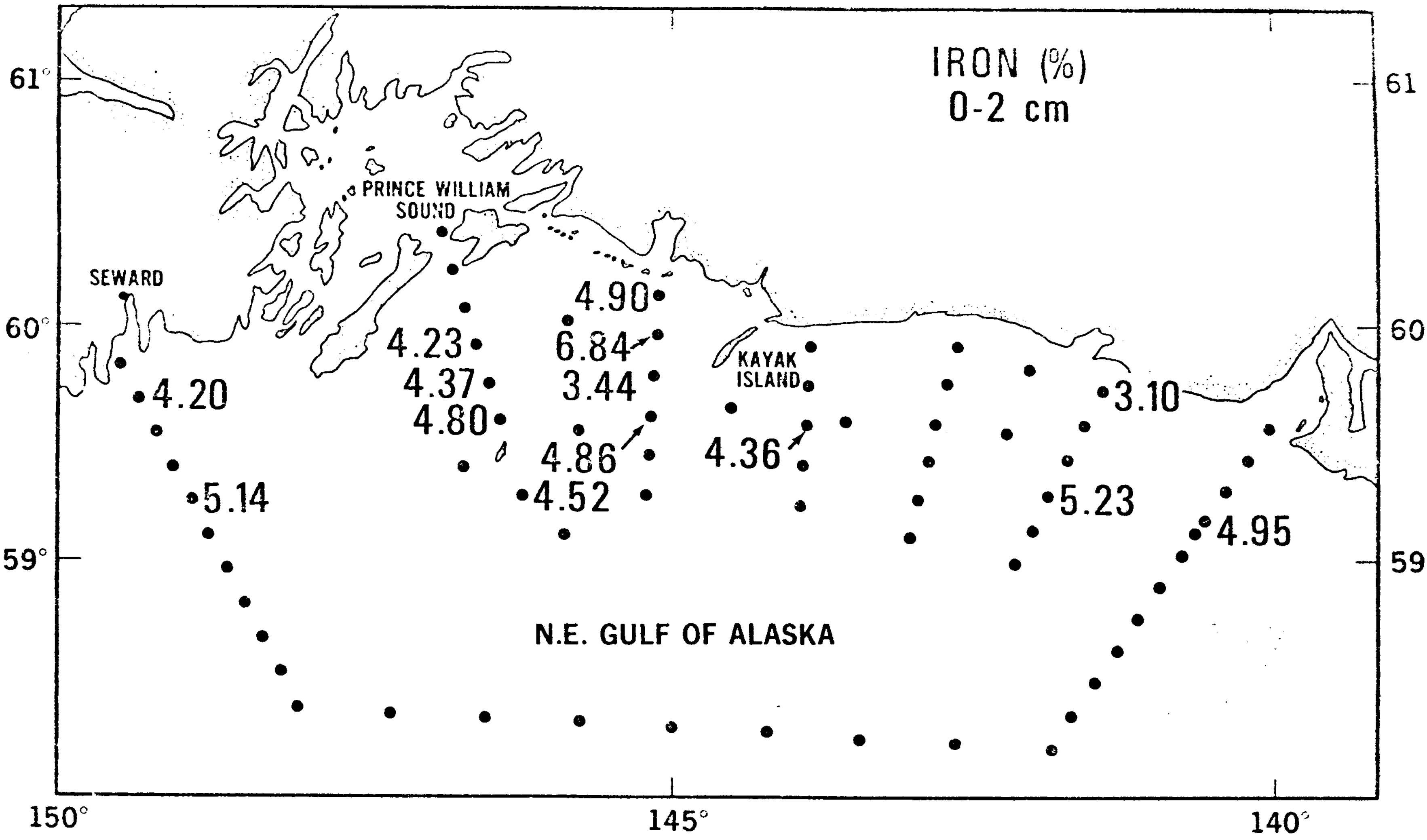

Figure 22. Total Fe contents of surface sediment from N.E. Gulf of Alaska.

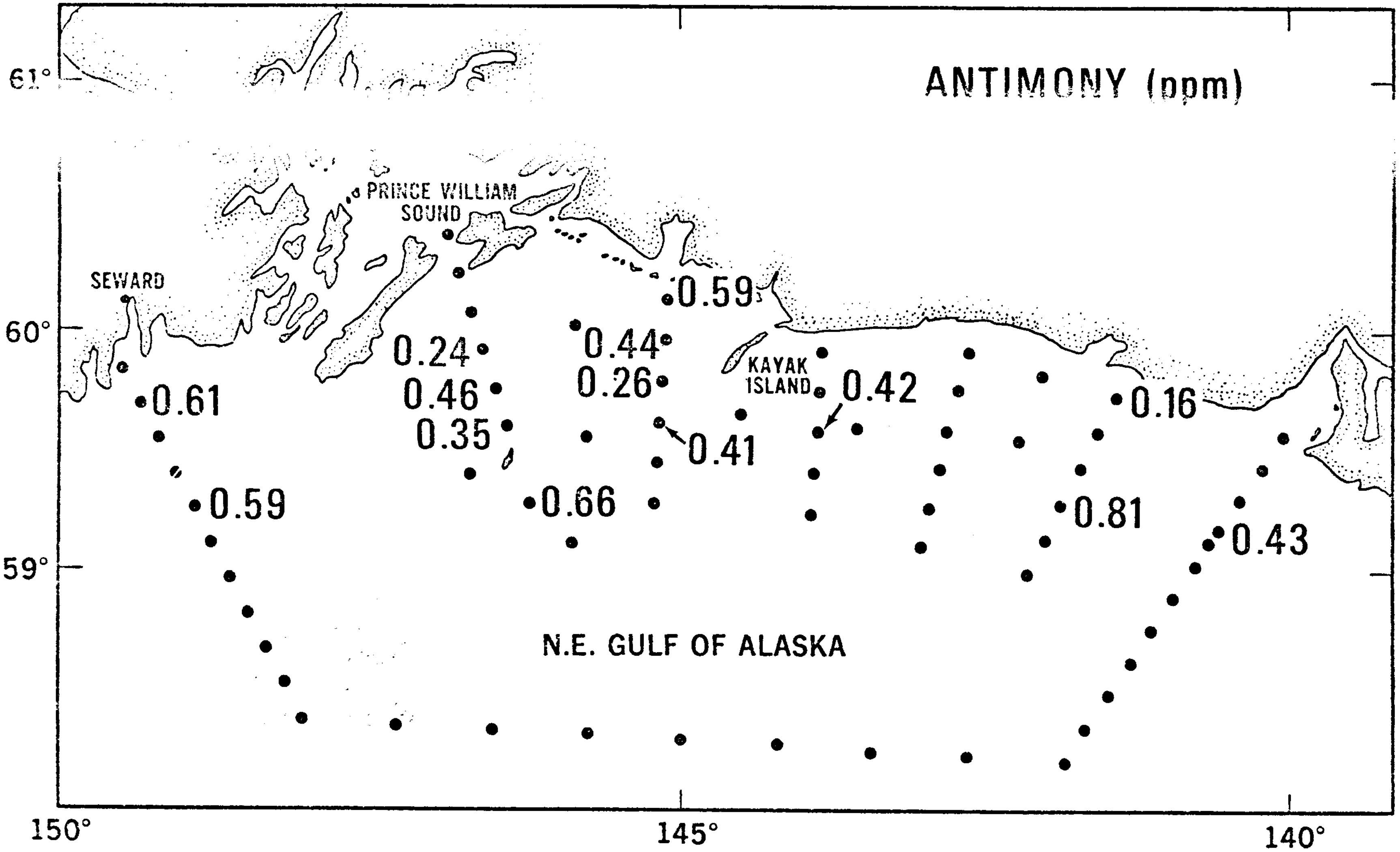

Figure 23. Total Sb contents of surface sediment from N.E. Gulf of Alaska.

TABLE XLVII

N.W. GULF OF ALASKA

Discoverer Leg IV 8-16 October, 1975

D. E. Robertson, Analyst

Total heavy metal contents of bottom sediments
(μg/g except Fe %)

Station	Interval	As	Ba	Co	Cr	Fe(%)	Sb
105	0-2	4.7	460 ± 80	5	192	1.32	0.26 ± 0.06
	4-6	1.8	560 ± 120	16	82	3.72	0.70 ± 0.08
120	4-6	2.9	670 ± 60	16	97	3.85	0.49 ± 0.10
	8-10	2.6	1100 ± 60	17	102	4.18	0.97 ± 0.12
	12-14	5.2	790 ± 80	16	100	3.96	0.96 ± 0.11
	16-18	2.6	610 ± 60	15	89	3.63	0.81 ± 0.09
121	0-2	5.4	760 ± 80	15	117	4.10	0.82 ± 0.12
	4-6	3.8	710 ± 80	15	106	3.93	0.73 ± 0.12
	8-10	5.6	670 ± 70	13	96	3.39	0.82 ± 0.09
122	0-2	2.9	260 ± 30	3	15	0.83	0.17 ± 0.06
124	0-2	2.8	630 ± 60	8	67	2.75	0.52 ± 0.10
	4-6	3.3	570 ± 70	9	61	2.73	0.43 ± 0.09
	8-10	3.7	460 ± 60	9	59	2.96	0.33 ± 0.09
133	Grab	3.8	400 ± 80	16	31	4.10	0.35 ± 0.10
134	0-2	6.6	670 ± 90	16	77	4.17	0.51 ± 0.12
	4-6	5.7	620 ± 100	15	75	4.08	0.64 ± 0.14
	8-10	7.3	820 ± 120	21	75	4.61	0.69 ± 0.14
	12-14	8.8	830 ± 110	18	75	4.73	0.73 ± 0.14
	16-18	5.1	490 ± 110	14	66	3.87	0.48 ± 0.10
135	0-2	4.3	710 ± 130	16	74	4.90	0.56 ± 0.15
	4-6	4.5	680 ± 110	15	54	4.49	0.50 ± 0.12
	8-10	5.1	250 ± 110	16	77	4.73	0.56 ± 0.13

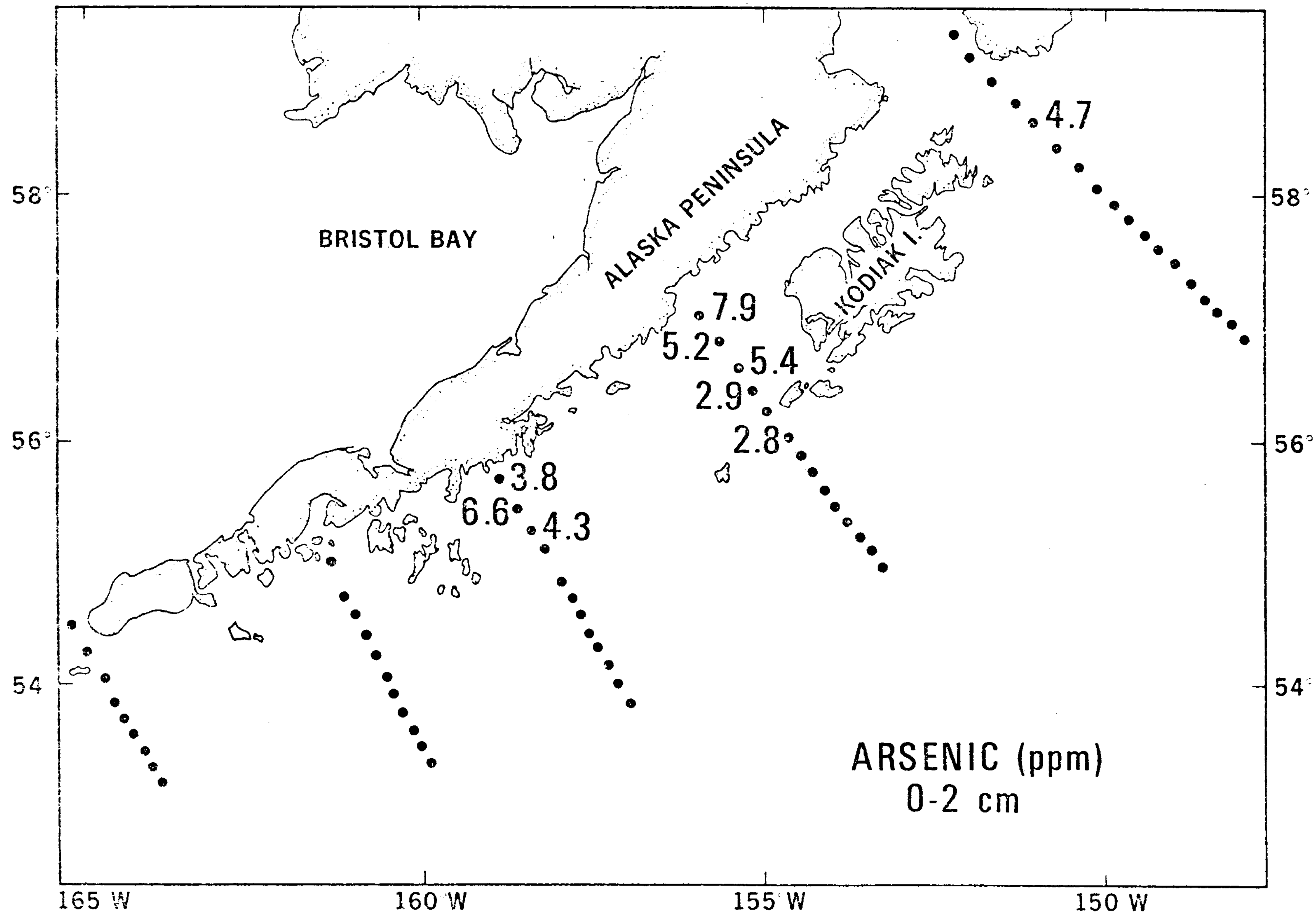

Figure 24. Total As contents of surface sediment from N.W. Gulf of Alaska.

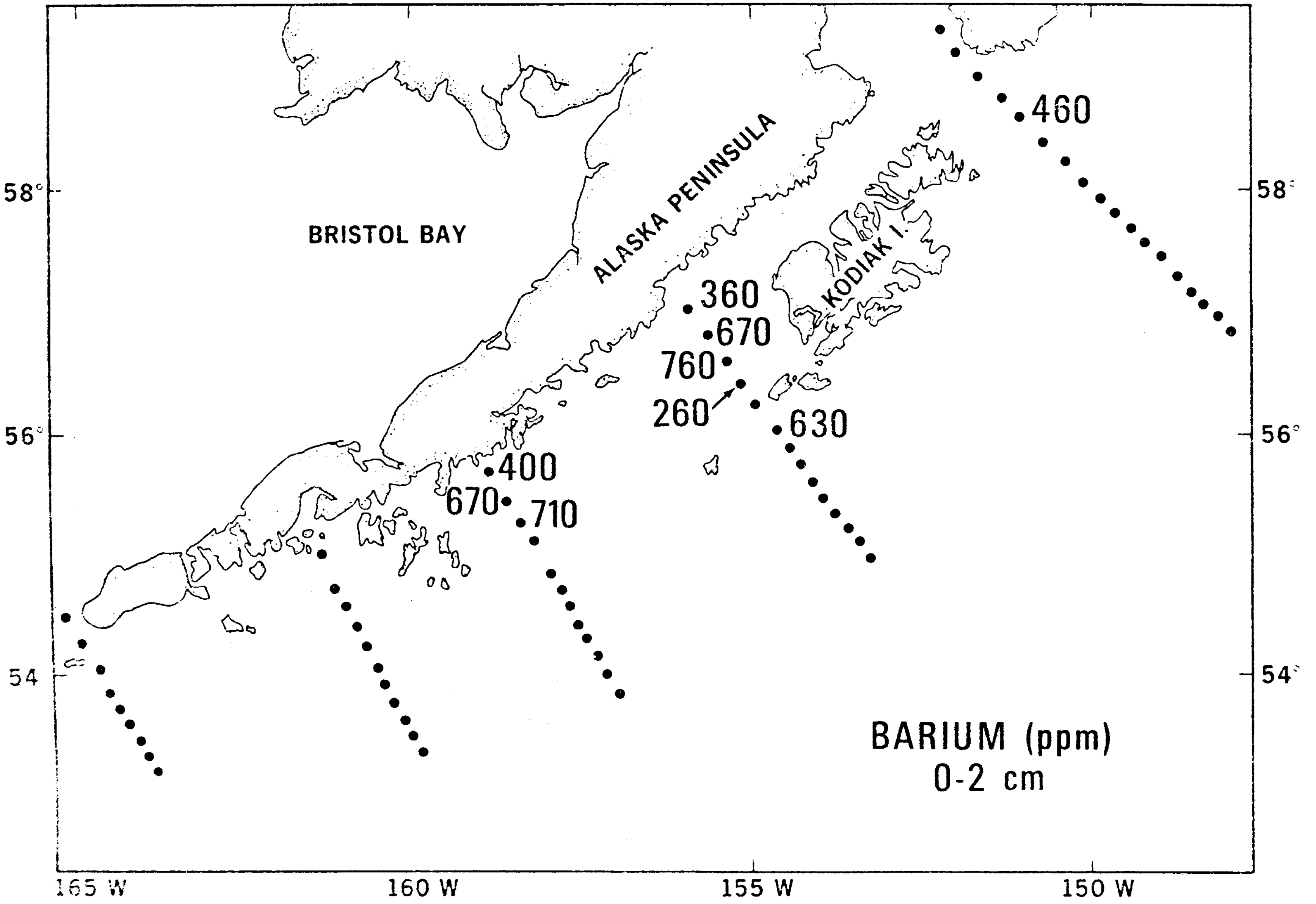

Figure 25. Total Ba contents of surface sediment from N.W. Gulf of Alaska.

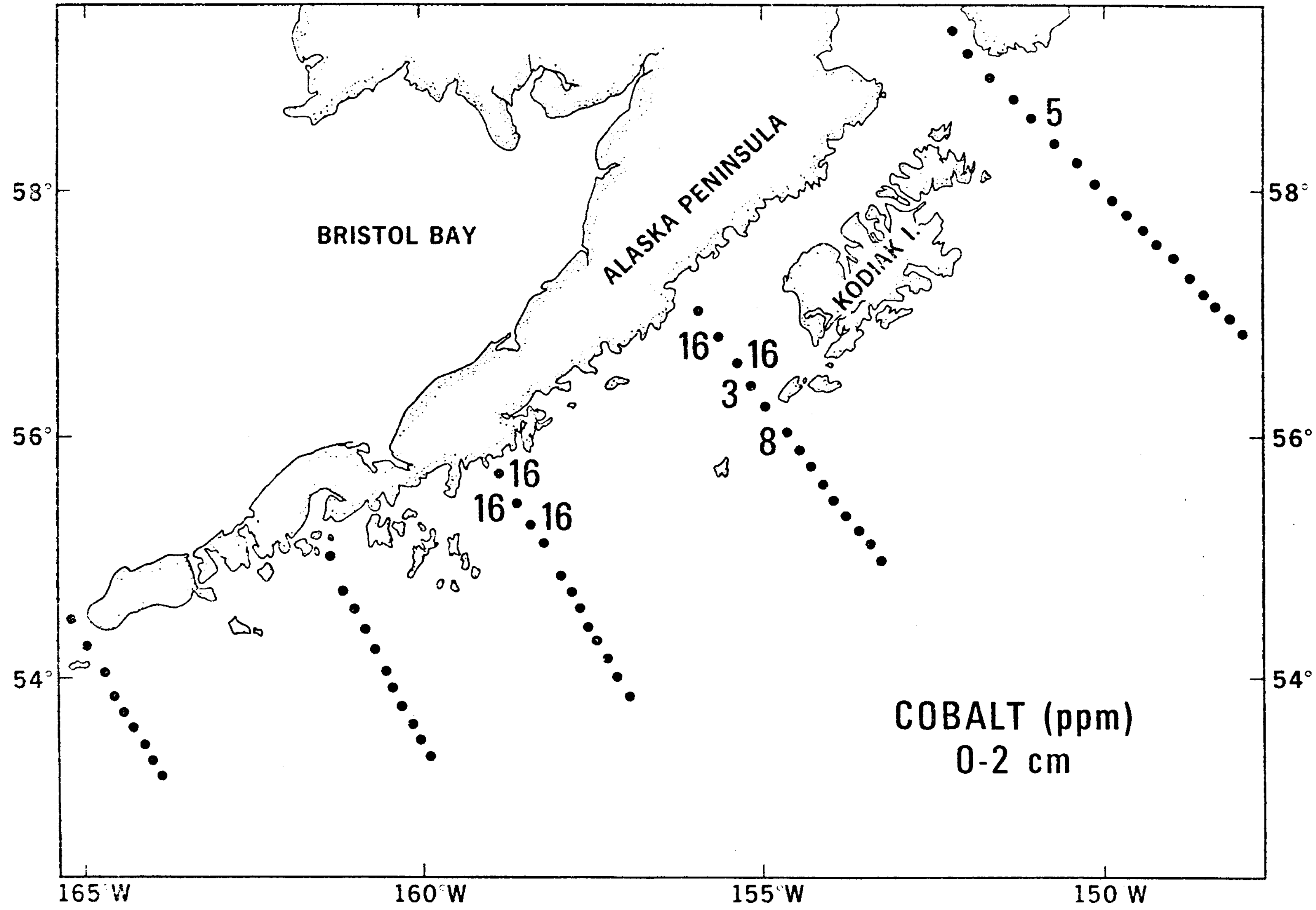

Figure 26. Total Co contents of surface sediment from N.W. Gulf of Alaska.

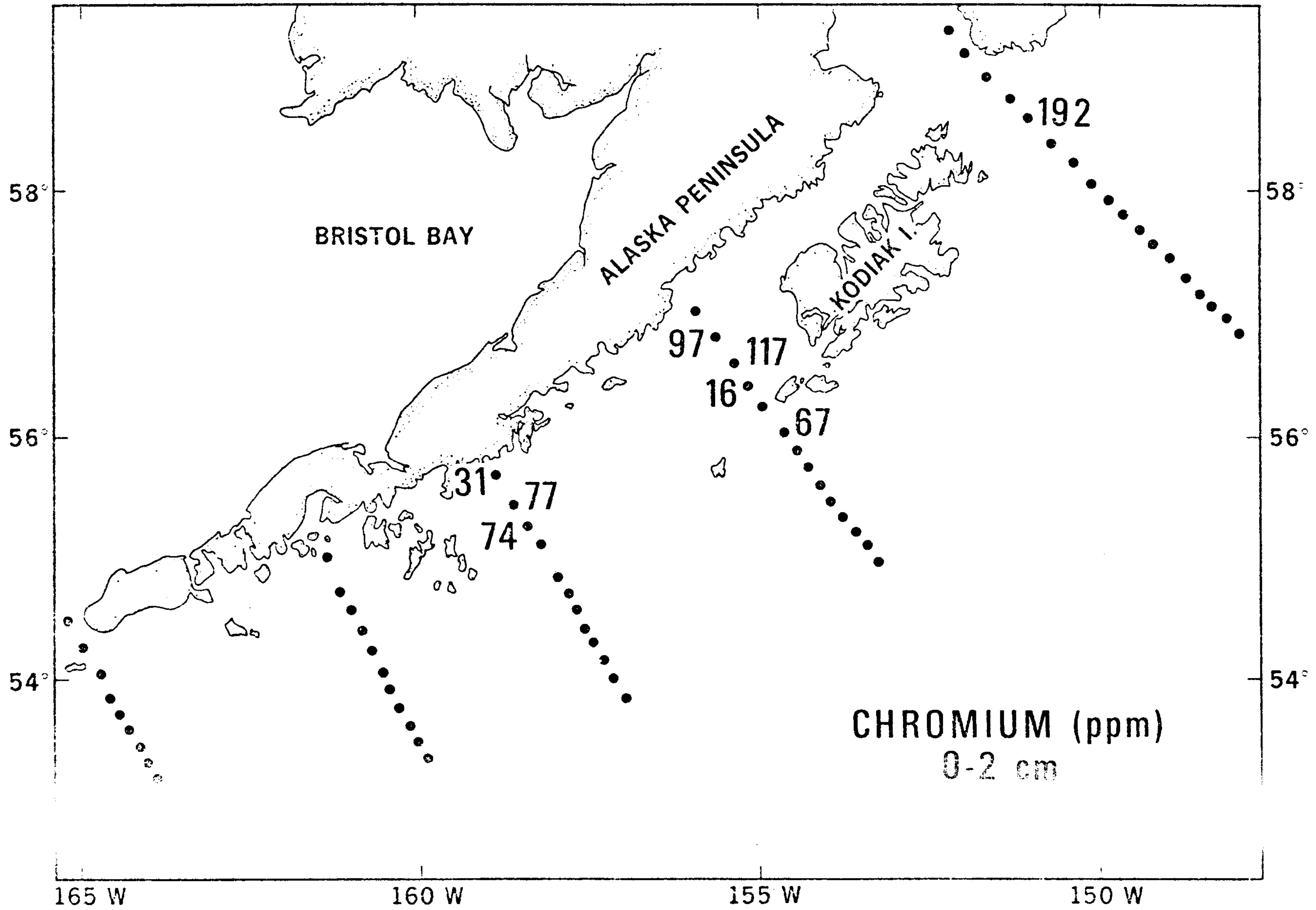

Figure 27. Total Cr contents of surface sediment from N.W. Gulf of Alaska.

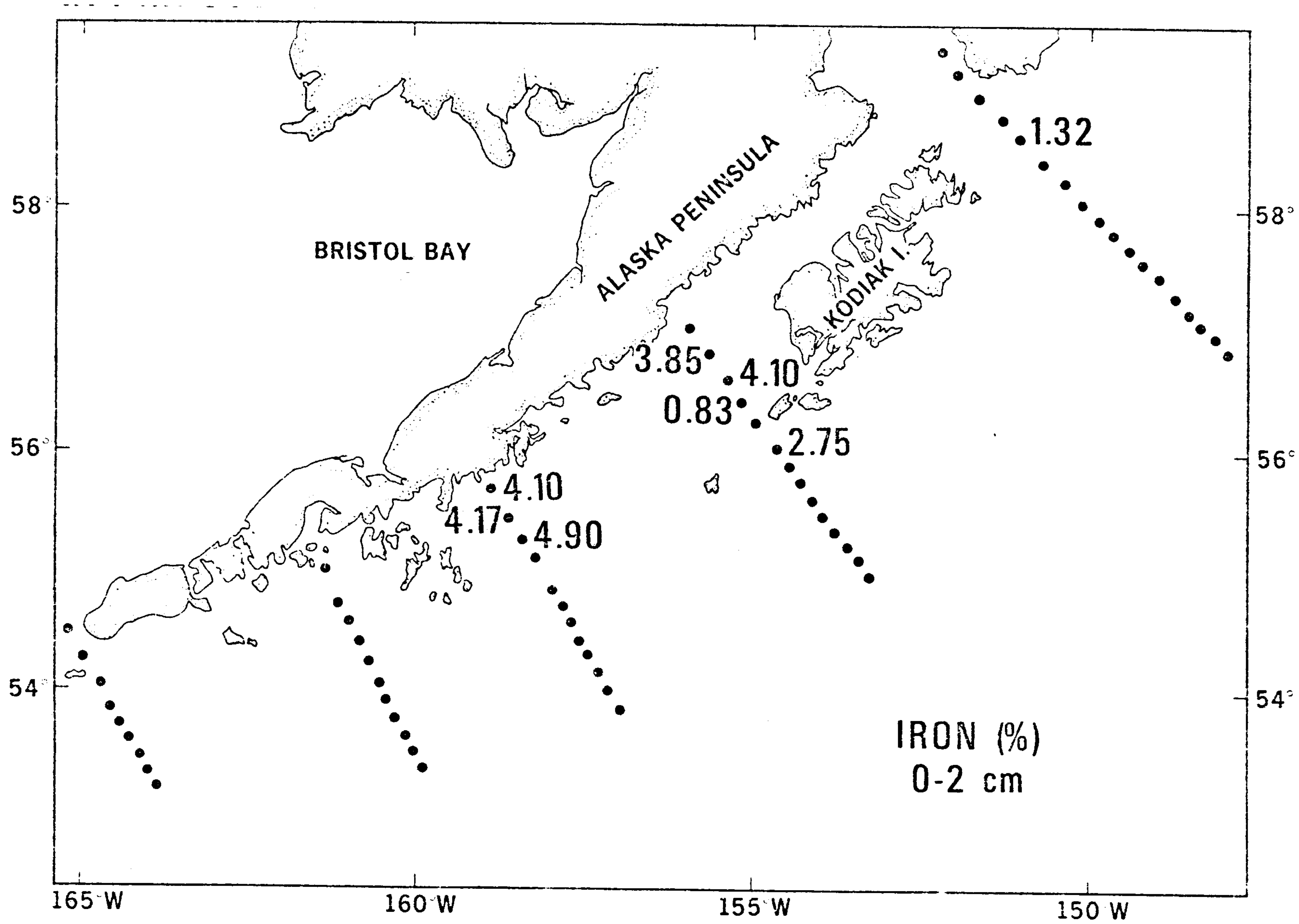

Figure 28. Total Fe contents of surface sediment from N.W. Gulf of Alaska.

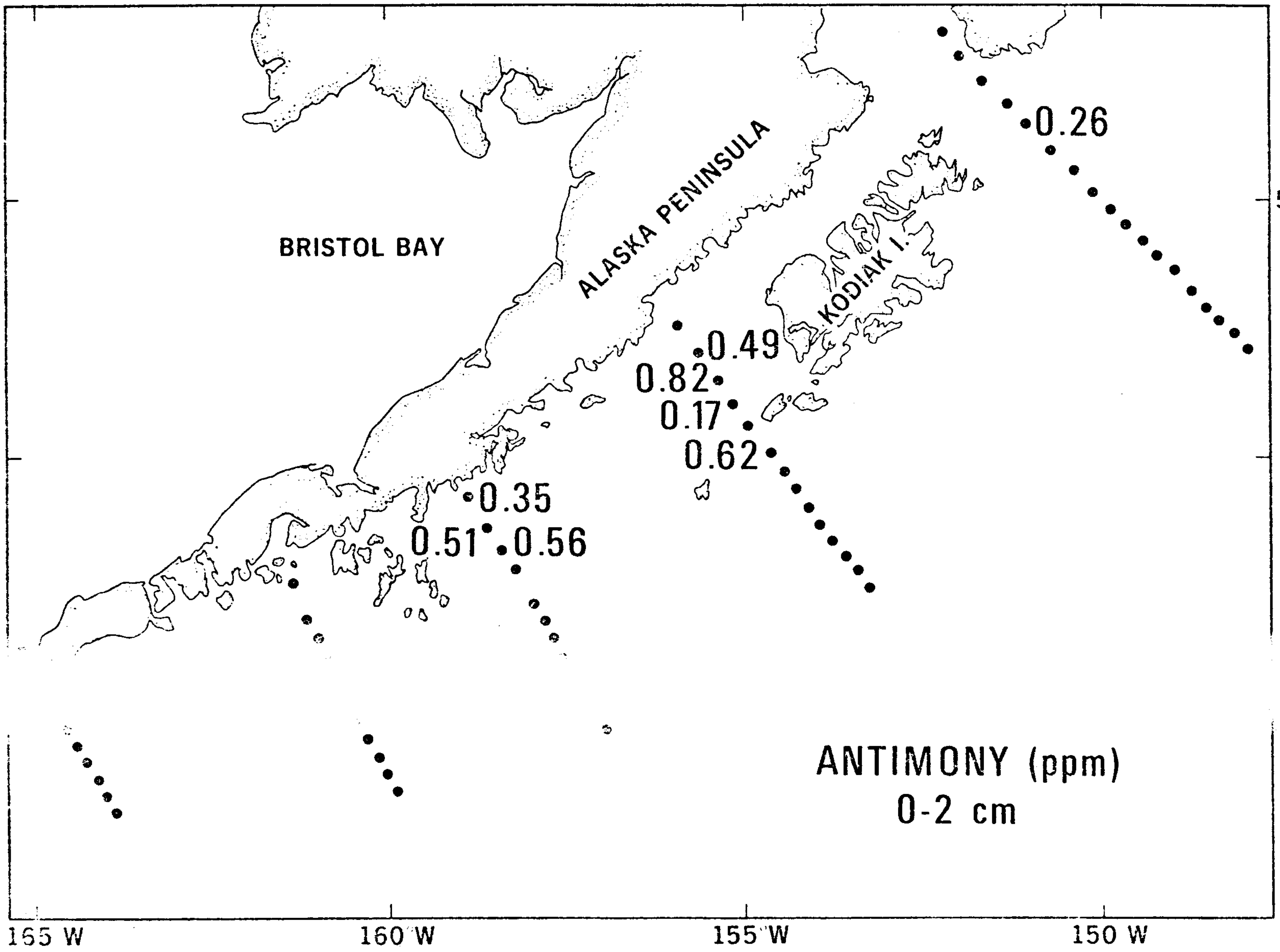

Figure 29. Total Sb contents of surface sediment from N.W. Gulf of Alaska.

TABLE XLVIII

S. BERING SEA

Discoverer 2-19 June, 1975

D. E. Robertson, Analyst

Total heavy metal contents of bottom sediments (μg/g).

Station	Interval	Ba	As
8	0-2	370 ± 230	4.1 ± 0.4
	4-6	230 ± 210	5.1 ± 0.3
	8-10	310 ± 220	4.1 ± 0.4
	12-14	<210	3.9 ± 0.4
19	0-2	440 ± 140	3.7 ± 0.4
30	0-4	200 ± 190	3.4 ± 0.6
	4-8	<260	2.1 ± 0.5
	8-12	<370	1.5 ± 0.5
37	0-2	430 ± 190	4.1 ± 0.6
	4-6	500 ± 150	3.1 ± 0.5
	8-11	750 ± 150	5.8 ± 0.4
41	0-2	480 ± 140	3.0 ± 0.4
43	0-2	<420	3.2 ± 0.5
	4-6	390 ± 200	3.5 ± 0.3
56	0-2	<260	0.7 ± 0.6
	4-6	460 ± 280	4.3 ± 0.6
	8-10	570 ± 440	2.8 ± 0.6
	12-18	<500	4.0 ± 0.7
59	0-2	1070 ± 340	4.0 ± 0.4
	4-6	<350	3.8 ± 0.4
64	0-2	1030 ± 340	2.7 ± 0.8
	4-6	500 ± 270	3.6 ± 0.6
	8-10	<280	2.9 ± 0.6
	12-14	810 ± 300	3.6 ± 0.6
	16-20	400 ± 260	4.6 ± 0.5
	20-24	600 ± 240	6.5 ± 0.4
12	0-3	650 ± 170	4.3 ± 0.5
28	0-3	490 ± 170	2.9 ± 0.5
29	0-4	530 ± 220	7.2 ± 0.5

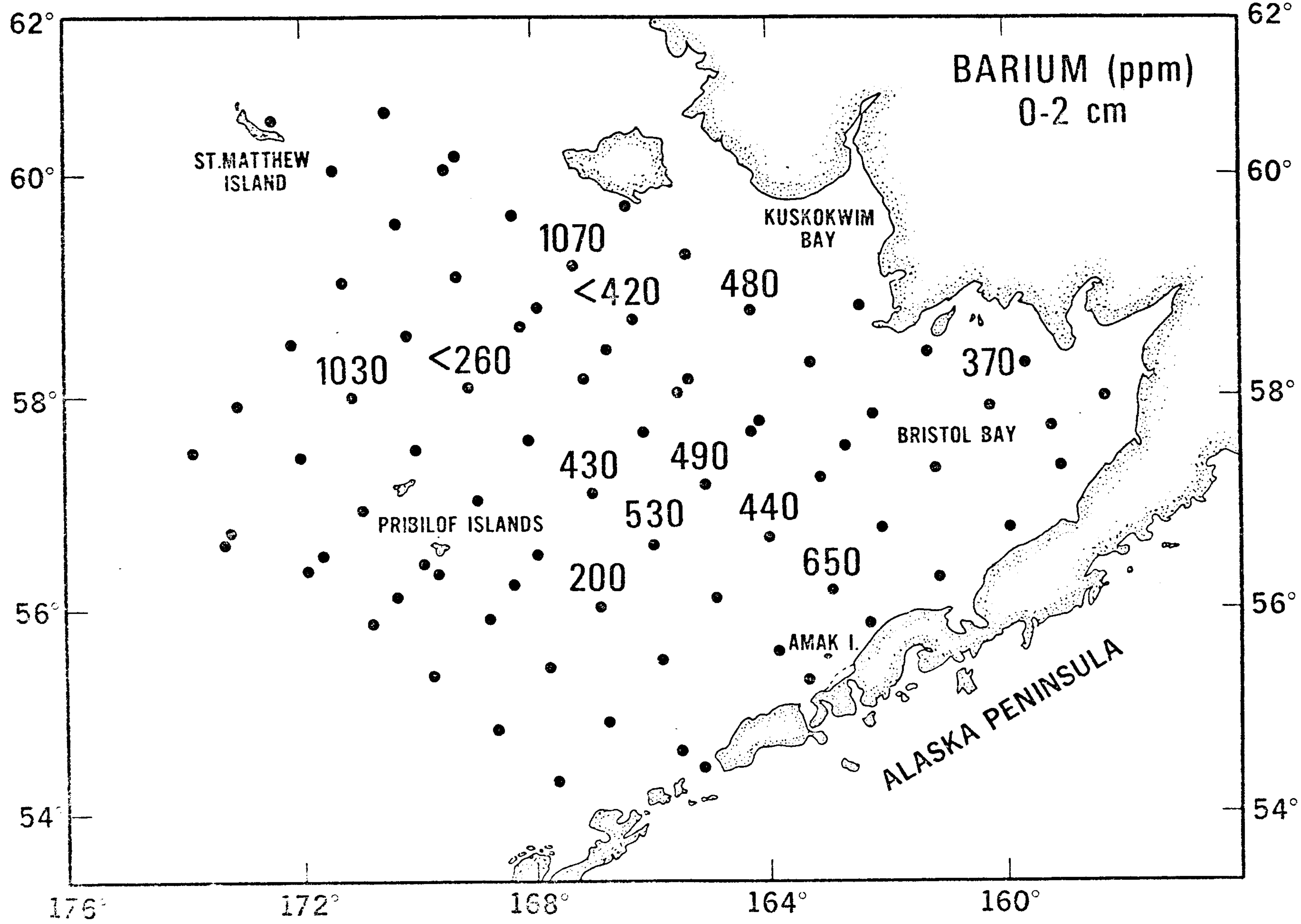

Figure 30. Total Ba contents of surface sediment from the S. Bering Sea.

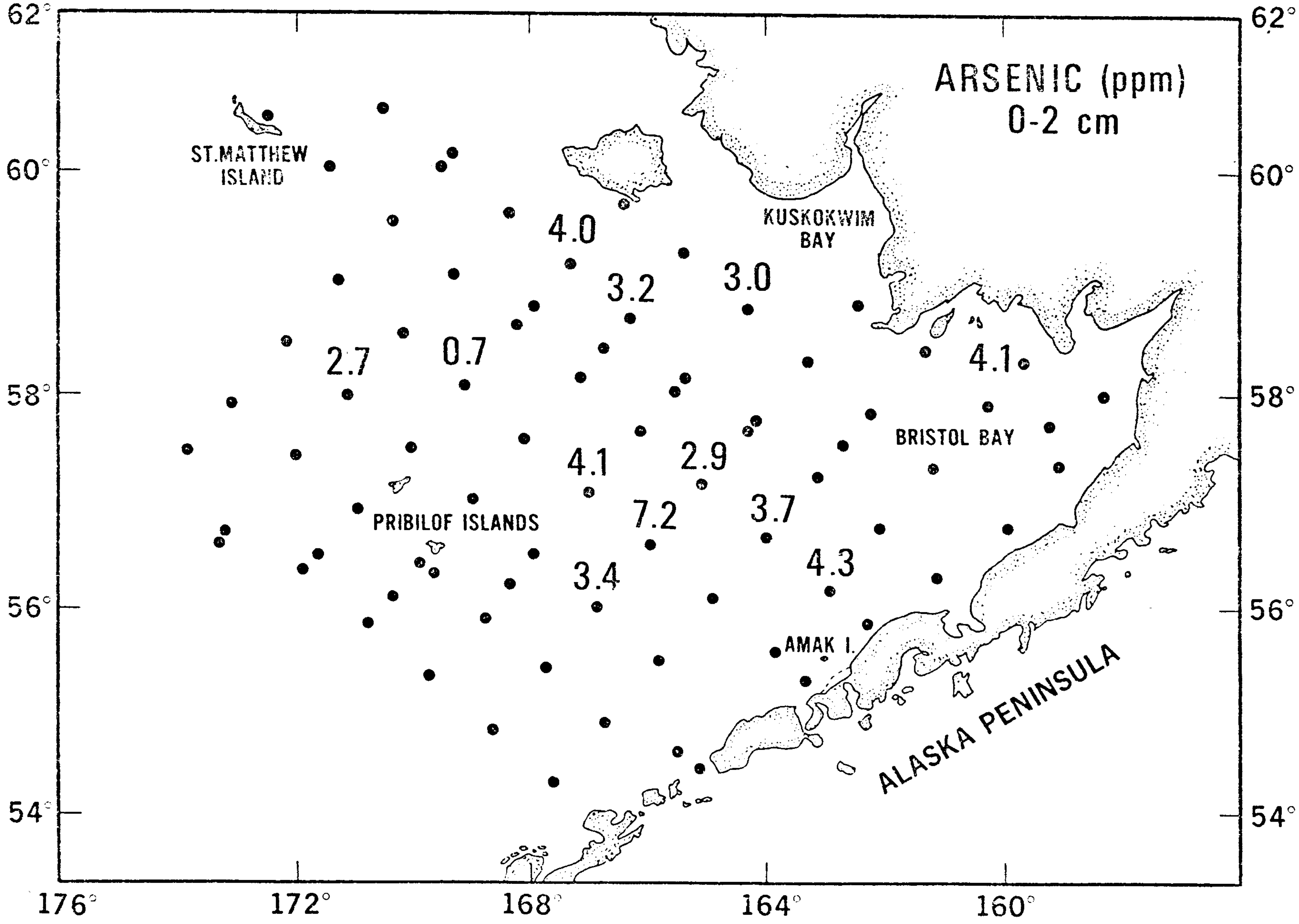

Figure 31. Total As contents of surface sediment from the S. Bering Sea.

TABLE XLIX

N.E. GULF OF ALASKA
Discoverer Leg III 23 November - 2 December 1975
D. E. Robertson, Analyst

Total heavy metal contents of suspended sediment.
(>0.4 μm; μg/ℓ)

Station	Depth	Mn	V
02	10	0.59 ± 0.12	< 0.051
	178	0.82 ± 0.13	0.063 ± 0.061
05	10	0.47 ± 0.14	< 0.070
	162	0.72 ± 0.19	< 0.091
08	10	0.27 ± 0.11	0.080 ± 0.051
	274	0.79 ± 0.21	0.16 ± 0.09
11	10	< 0.12	< 0.061
	1350	< 0.11	< 0.056
15	10	< 0.12	< 0.058
	1500	< 0.11	< 0.055
24	10	0.10 ± 0.10	< 0.044
	410	< 0.11	< 0.047
26	10	0.15 ± 0.12	< 0.057
	136	0.63 ± 0.09	0.095 ± 0.045
29	71	0.47 ± 0.11	0.11 ± 0.05
30	42	0.39 ± 0.35	0.77 ± 0.23
33	10	< 0.084	< 0.035
	205	0.24 ± 0.11	< 0.060
44	10	1.02 ± 0.20	0.20 ± 0.09
	165	0.63 ± 0.12	0.11 ± 0.07
48	10	0.11 ± 0.10	< 0.053
	447	0.33 ± 0.12	0.067 ± 0.061
49	10	1.59 ± 0.21	0.29 ± 0.10
	120	0.97 ± 0.23	0.16 ± 0.10
50	10	0.81 ± 0.18	0.12 ± 0.09
	161	0.60 ± 0.09	0.14 ± 0.04

TABLE XLIX

(Continued)

Station	Depth	Mn	V
51	10	0.59 ± 0.13	0.090 ± 0.065
	133	1.21 ± 0.21	0.15 ± 0.08
52			
	74	0.62 ± 0.12	< 0.058
53	10	0.78 ± 0.12	0.067 ± 0.065
	284	3.79 ± 0.25	0.42 ± 0.14
54	10	0.96 ± 0.22	0.11 ± 0.09
	212	1.03 ± 0.19	0.11 ± 0.09
55	10	0.97 ± 0.21	0.19 ± 0.07
	110	1.13 ± 0.20	0.15 ± 0.10
56			
	58	0.86 ± 0.12	0.16 ± 0.06
57			
	67	0.56 ± 0.12	0.13 ± 0.08
58			
	82	0.74 ± 0.19	0.21 ± 0.08
59A	10	1.02 ± 0.20	0.18 ± 0.08
	370	< 0.18	< 0.076

TABLE L

N.W. GULF OF ALASKA
Discoverer Leg IV 8-16 October 1975
D. E. Robertson, Analyst

Total heavy metal contents of suspended sediments.
(>0.4 μm; μg/ℓ)

Station	Depth	Mn	V
102	1	0.22 ± 0.02	.019 ± 0.011
	98	0.27 ± 0.02	.018 ± 0.009
103	1	0.13 ± 0.04	< 0.020
	125	0.26 ± 0.02	.021 ± 0.012
104	1	0.061± 0.010	< 0.0056
	96	0.67 ± 0.03	.059 ± 0.014
106			
	81	0.54 ± 0.12	< 0.057
108	10	0.19 ± 0.12	< 0.052
	226	0.33 ± 0.13	< 0.055
110	10	0.17 ± 0.10	< 0.046
	173	0.27 ± 0.20	< 0.080
119	1	0.68 ± 0.09	.070 ± 0.051
	204	6.48 ± 0.08	.094 ± 0.045
120	1	0.38 ± 0.07	< 0.036
	281	7.10 ± 0.09	.224 ± 0.063
121	1	0.26 ± 0.04	< 0.025
	220	2.64 ± 0.08	.148 ± 0.051
122	1	0.24 ± 0.04	< 0.036
	35	0.35 ± 0.04	.053 ± 0.024
124	1	0.28 ± 0.03	.028 ± 0.020
	105	0.30 ± 0.04	.030 ± 0.029
133	1	0.11 ± 0.04	< 0.025
	68	0.44 ± 0.04	< 0.026
135	1	0.066± 0.043	< 0.028
	141	0.36 ± 0.06	< 0.066
137	1	0.21 ± 0.05	< 0.040
	95	0.57 ± 0.06	< 0.044

TABLE L

(Continued)

Station	Depth	Mn	V
145	1	0.33 ± 0.12	< 0.090
	63	0.23 ± 0.05	< 0.029
146	1	0.23 ± 0.04	< 0.023
	63	0.35 ± 0.07	< 0.036
147	1	0.090± 0.064	< 0.069
	94	0.38 ± 0.04	.026 ± 0.023
148	1	0.15 ± 0.04	< 0.028
	100	0.26 ± 0.04	.030 ± 0.026
156	1	0.29 ± 0.05	< 0.036
	150	0.94 ± 0.15	.120 ± 0.099
157	1	0.16 ± 0.01	.021 ± 0.008
	59	0.22 ± 0.04	< 0.040
158	1	0.31 ± 0.11	< 0.093
	92	0.44 ± 0.11	< 0.081
159	1		
	96	0.28 ± 0.06	< 0.038
160	1	0.073± 0.034	< 0.020
	132	0.43 ± 0.03	< 0.024

TABLE LI

S. BERING SEA
Discoverer 2-19 June 1975
D. E. Robertson, Analyst

Total heavy metal contents of suspended sediment.
(>0.4 μm; μg/ℓ)

Station	Depth	Mn	V
02	S	0.56 ± 0.03	0.019 ± 0.014
	B	0.50 ± 0.04	0.051 ± 0.016
08	S	1.41 ± 0.02	0.072 ± 0.016
	B	2.22 ± 0.60	0.12 ± 0.03
14	S	0.096 ± 0.064	< 0.017
	B	0.17 ± 0.02	< 0.007
17	B	0.51 ± 0.02	0.085 ± 0.016
19	B	1.45 ± 0.13	0.31 ± 0.06
24	B	2.80 ± 0.03	0.12 ± 0.02
31	S	0.040 ± 0.014	< 0.007
	B	0.13 ± 0.01	0.019 ± 0.008
30	B	0.89 ± 0.05	0.18 ± 0.04
34	S	0.054 ± 0.014	< 0.008
	B	0.12 ± 0.01	0.016 ± 0.008
37	B	0.51 ± 0.02	0.030 ± 0.010
41	B	0.93 ± 0.02	0.034 ± 0.010
43	B	0.60 ± 0.02	0.028 ± 0.010
48	S	0.082 ± 0.012	0.014 ± 0.007
	B	0.14 ± 0.03	0.019 ± 0.014
53	S	0.046 ± 0.028	< 0.012
	B	0.15 ± 0.03	0.044 ± 0.014
56	B	1.48 ± 0.04	0.044 ± 0.014
59	B	0.51 ± 0.04	0.021 ± 0.019
64	B	1.00 ± 0.03	0.049 ± 0.014

TABLE LII

N.E. GULF OF ALASKA
Discoverer Leg III 23 November - 2 December 1975
D. E. Robertson, Analyst

Total major cation contents of suspended sediment.
(>0.4 μm; μg/ℓ)

Station	Depth	Al
02	10	18.7 ± 0.8
	178	32.2 ± 1.0
05	10	26.9 ± 1.2
	162	40.6 ± 1.8
08	10	16.8 ± 0.9
	274	81.5 ± 1.4
11	10	5.7 ± 1.2
	1350	7.0 ± 1.1
15	10	8.4 ± 1.1
	1500	3.9 ± 1.1
24	10	1.3 ± 0.8
	410	5.4 ± 0.9
26	10	8.9 ± 1.0
	136	34.9 ± 0.7
29	71	43.9 ± 0.8
30	42	395 ± 4
33	10	0.91 ± 0.66
	205	9.0 ± 1.1
44	10	107 ± 1
	165	46.2 ± 1.2
48	10	3.4 ± 1.1
	447	26.0 ± 1.1
49	10	141.0 ± 2.0
	120	84.9 ± 1.7
50	10	74.6 ± 1.7
	161	58.6 ± 0.5
51	10	42.6 ± 1.1
	133	83.1 ± 1.1
52	74	38.0 ± 0.9
53	10	35.9 ± 1.2
	284	222.0 ± 3.0
54	10	57.3 ± 1.6
	212	66.2 ± 1.5
55	10	83.1 ± 1.1
	110	87.8 ± 1.9
56	58	63.9 ± 1.0
57	67	44.7 ± 1.8
58	82	76.7 ± 1.3
59A	10	97.3 ± 1.3
	370	17.6 ± 1.5

TABLE LIII

N.W. GULF OF ALASKA
Discoverer Leg IV 8-16 October 1975
D. E. Robertson, Analyst

Total major cation contents of suspended sediment.
(>0.4 μm; μg/ℓ)

Station	Depth	Al
102	1	10.03 ± 0.15
	98	9.56 ± 0.08
103	1	3.79 ± 0.43
	125	7.40 ± 0.19
104	1	2.46 ± 0.08
	96	27.38 ± 0.13
106		
	81	26.3 ± 1.0
108	10	4.53 ± 0.86
	226	30.1 ± 0.8
110	10	4.42 ± 0.82
	173	17.1 ± 1.5
119	1	32.4 ± 1.0
	204	35.3 ± 0.8
120	1	16.5 ± 0.6
	281	103 ± 1
121	1	15.0 ± 0.6
	220	69.9 ± 0.8
122	1	15.1 ± 1.0
	35	28.3 ± 0.5
124	1	14.6 ± 0.4
	105	25.5 ± 0.6
133	1	5.0 ± 0.58
	68	18.3 ± 0.5
135	1	2.04 ± 0.65
	141	24.8 ± 2.1
137	1	3.73 ± 1.15
	95	20.6 ± 1.0

TABLE LIII

(Continued)

Station	Depth	Al
145	1	7.68 ± 2.19
	63	4.88 ± 0.70
146	1	3.63 ± 0.54
	63	6.79 ± 0.75
147	1	< 2.25
	94	11.0 ± 0.5
148	1	4.30 ± 0.60
	100	15.5 ± 0.6
156	1	11.0 ± 0.9
	150	56.4 ± 2.1
157	1	5.65 ± 0.16
	59	17.1 ± 1.1
158	1	4.95 ± 2.28
	92	12.2 ± 2.0
159	1	
	96	9.25 ± 0.94
160	1	1.30 ± 0.46
	132	10.3 ± 0.6

TABLE LIV

S. BERING SEA
Discoverer 2-19 June 1975
D. E. Robertson, Analyst

Total major cation contents of suspended sediment.
(>0.4 μm; μg/ℓ)

Station	Depth	Al
02	S	9.4 ± 0.2
	B	20.6 ± 0.2
08	S	64.4 ± 0.2
	B	68.0 ± 0.4
14	S	10.1 ± 0.6
	B	24.1 ± 0.2
17	B	72.2 ± 0.2
19	B	114 ± 1
24	B	77.4 ± 0.6
31	S	6.32 ± 0.20
	B	18.3 ± 0.2
30	B	102 ± 1
34	S	12.0 ± 0.2
	B	18.4 ± 0.1
37	B	28.8 ± 0.2
41	B	21.0 ± 0.2
43	B	23.0 ± 0.2
48	S	15.4 ± 0.1
	B	14.4 ± 0.1
53	S	7.34 ± 0.14
	B	14.0 ± 0.1
56	B	13.8 ± 0.1
59	B	17.2 ± 0.2
64	B	16.0 ± 0.1

Heavy metal contents of some archived samples collected in the Beaufort Sea are given in Table LV. The localities, collection and storage of these samples were discussed in the 1975-1976 Annual Report.

Deatiled clay mineralogical analyses of the < and 2 μ m fraction of Bering Sea samples are included here as Table LVI.

VII. DISCUSSION

Soluble Heavy Metal Contents in Water Column

The general survey of soluble heavy metal contents of the open-ocean lease areas is now essentially complete. Data for the Bering and Beaufort Seas have not yet been fully analysed and the following discussion relates mainly to the Gulf of Alaska. The general concentration levels and conclusions are expected to pertain for these other lease areas as well, however.

Table LVII lists means of Gulf of Alaska bottom waters for the elements analysed to date, with the exception of Cr and Se which are covered in a separate section. Also given here are the most recently published general oceanic values (Brewer, 1975). It may be seen that, almost without exception, the mean Gulf values are lower than the published data. This should not be interpreted to mean that the Gulf of Alaska is in any way atypical of open ocean waters since that would be oceanographically impossible. These data may be interpreted as follows:

1. That published world values are still generally too high. Over the last decade accepted mean values for most of the common transition and other heavy metals have been reduced by around an order of magnitude. This is a reflection of the availability of new and improved analytical techniques and, more importantly, of the difficulties to be overcome in

TABLE LV

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.

TABLE LVI

S. BERING SEA

Discoverer 2-19 June 1975

A. S. Naidu, Analyst

Clay minerology (weighted peak area percents).

Station No.	Sample Saturation	Expandable		Illite		Kaolinite		Chlorite	
		< 2 μm	< 1 μm	< 2 μm	< 1 μm	< 2 μm	< 1 μm	< 2 μm	< 1 μm
2	Glycol	-	2	-	61	-	15	-	22
	K^+ & Glycol	-	-	-	-	-	-	-	-
	Mg^{++} & Glycol	-	-	-	-	-	-	-	-
8	Glycol	45	50	10	17	17	10	28	23
	K^+ & Glycol	0	-	52	-	0	-	48	-
	Mg^{++} & Glycol	44	-	13	-	0	-	43	-
10	Glycol	43	46	19	25	12	Tr	26	29
	K^+ & Glycol	0	-	62	-	0	-	38	-
	Mg^{++} & Glycol	33	-	30	-	5	-	32	-
13	Glycol	26	36	31	26	11	10	32	28
	K^+ & Glycol	0	-	43	-	0	-	57	-
	Mg^{++} & Glycol	25	-	33	-	0	-	42	-
14	Glycol	26	35	31	32	6	8	37	25
	K^+ & Glycol	-	-	-	-	-	-	-	-
	Mg^{++} & Glycol	17	-	30	-	7	-	46	-
19	Glycol	26	40	34	20	10	7	30	33
	K^+ & Glycol	-	-	60	-	0	-	40	-
	Mg^{++} & Glycol	21	-	47	-	0	-	32	-
21	Glycol	25	35	33	29	8	9	34	27
	K^+ & Glycol	18	-	41	-	7	-	34	-
	Mg^{++} & Glycol	28	-	29	-	9	-	34	-

TABLE LVI (Continued)

Station No.	Sample Saturation	Expandable		Illite		Kaolinite		Chlorite	
		< 2 µm	< 1 µm	< 2 µm	< 1 µm	< 2 µm	< 1 µm	< 2 µm	< 1 µm
26	Glycol	24	32	38	26	10	12	28	30
	K^+ & Glycol	7	-	45	-	0	-	48	-
	Mg^{++} & Glycol	23	-	31	-	0	-	46	-
31	Glycol	25	30	35	35	11	0	29	35
	K^+ & Glycol	3	-	39	-	0	-	58	-
	Mg^{++} & Glycol	22	-	41	-	4	-	34	-
34	Glycol	28	33	33	33	12	Tr	27	34
	K^+ & Glycol	12	-	40	-	12	-	36	-
	Mg^{++} & Glycol	13	-	43	-	6	-	38	-
41	Glycol	19	28	37	31	12	9	32	32
	K^+ & Glycol	0	-	47	-	8	-	45	-
	Mg^{++} & Glycol	24	-	38	-	7	-	31	-
43	Glycol	33	36	30	33	8	8	29	23
	K^+ & Glycol	11	-	46	-	13	-	30	-
	Mg^{++} & Glycol	29	-	34	-	9	-	28	-
48	Glycol	30	36	35	36	0	4	35	24
	K^+ & Glycol	0	-	50	-	0	-	50	-
	Mg^{++} & Glycol	23	-	31	-	0	-	46	-
57	Glycol	15	29	41	38	10	8	34	25
	K^+ & Glycol	-	0	48	-	0	-	52	-
	Mg^{++} & Glycol	24	-	40	-	4	-	32	-
60	Glycol	13	21	52	43	7	14	28	22
	K^+ & Glycol	0	-	53	-	15	-	32	-
	Mg^{++} & Glycol	20	-	43	-	10	-	27	-
62	Glycol	25	25	33	42	10	8	32	25
	K^+ & Glycol	0	-	58	-	8	-	34	-
	Mg^{++} & Glycol	27	-	39	-	5	-	29	-

TABLE LVI (Continued)

Station No.	Sample Saturation	Expandable		Illite		Kaolinite		Chlorite	
		< 2 μm	< 1 μm	< 2 μm	< 1 μm	< 2 μm	< 1 μm	< 2 μm	< 1 μm
64	Glycol	22	22	45	39	Tr	10	33	29
	K^+ & Glycol	9	-	51	-	8	-	32	-
	Mg^{++} & Glycol	26	-	38	-	9	-	27	-
65	Glycol	14	27	52	40	6	5	28	28
	K^+ & Glycol	-	-	-	-	-	-	-	-
	Mg^{++} & Glycol	-	-	-	-	-	-	-	-
69	Glycol	23	25	36	42	12	5	29	28
	K^+ & Glycol	43	-	31	-	4	-	22	-
	Mg^{++} & Glycol	38	-	37	-	4	-	21	-

TABLE LVII

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 abosrption (D. C. Burrell)

[a] - Brewer (1975)

[b] - surface estuarine-fjord water

the way of sampling, storage and pre-treatments. Unless most carefully controlled, the latter processes may bias the analytical results. Such errors may be both negative and positive, systematic and non-systematic. Published compilations are also biased in favor of industrialized coastal regions and it is possible that, for some elements, values generated may not be typical of open ocean conditions.

2. It is possible, and in the case of zinc highly likely, that certain of the analytical procedures used in this study are measuring soluble chemical fractions less than total. Most instrumental techniques of necessity determine totals; other procedures are specifically designed to ensure this, and the literature values of Table LVII are presumably intended to represent totals. Such data are of limited oceanographic use, however, since the behavior of the metal in the marine environment is a function of its chemical form. Of the techniques listed in Table LVII, only voltammetry is capable of directly speciating the soluble contents, other instrumental methods require such differentiations to be accomplished prior to analysis. Chemical speciation of metals in solution in seawater is a complex and poorly understood field at present. In surveys of the type undertaken in this program it is usual to provide totals, if only to facilitate comparisons with other areas. However, in the case of zinc, the values reported are not conventional totals and the means in Table LVII are not comparable. This is considered further below.

3. For some elements, notably Se and Cr (see separate section) but probably also nickel, insufficient values have been obtained to place much confidence in the cited means.

4. The Gulf of Alaska has so far been vertually unimpacted by man and possibly these cited means, within the limits of this "meaningfulness" (see below), may be representative of the natural open ocean.

Accuracy, precision and meaningfulness of data

Comments on the precision and accuracy of the voltammetric procedures are given in a following section, together with results of intra-laboratory comparisons of test samples using both voltammetric and atomic spectrometric procedures. We have as yet received no data from NBS so cannot extend this work to include inter-laboratory calibrations. There are, of course, no seawater standards available, so ultimate accuracy tests are impossible. Indeed we are still at the stage of attempting to establish order-of-magnitude mean concentrations for many metals. It is clear, however, that major error in this field is associated with the sampling and pre-analysis processing steps and standard samples, even if available, would be of little use. Soluble concentration sampling methods can only presently be evaluated with respect to the lowest sets of values obtained; although this is itself unsatisfactory since subtraction errors, though generally less troublesome than addition or contamination errors, are quite common. At seawater pH range, sorption of hydrolysed cations is very common, and an acidification step at least is usually mandatory. (It was with the primary intention of eliminating this step - and hence to preserve ambient chemical speciation - that the filament atomic absorption procedure, referenced in the following section, was initially designed.)

The sampling and treatment scheme utilized in this program has been changed and referred from year to year. Because of unsatisfactory logistic support, the earliest data is less reliable than that produced during the present contract period, and it is these latter data that are included in the cited means. The standardized sample collection, treatment and storage procedures in use through the present contract period have been discussed above. Although the procedure generally used until recently, it is not ideal practice to collect trace metal samples using either a metallic cable or from adjacent to a metallic sampling platform. However, because of the need to collect samples from the open ocean through the year under frequently adverse conditions, it was impossible to devise any alternative, potentially cleaner method, for this survey program. As may be seen from the data presented in this and preceeding quarterly reports, it appears likely that samples collected from adjacent to the surface (nominally, at a depth of 10 m) appear to be sporadically contaminated, although in most cases this is purely subjective evaluation. For example, for a number of metals, surface values are consistently higher at the surface than at depth. This may be a real difference, possibly related to exhanced quantities of particulate material finer than the 0.4 μm cut-off at the surface. However, until such gradients can be established with certainty it seems prudent to consider only the deep water values.

It was not found to be possible to perform replicate sampling on any given station at sea so that systematic error associated with the field collections are not known. Although most error - both systematic - is considered to be generally introduced at this time, the precision need not inevitably be poor. Table LVIII, for example, lists relavent precision data for over-the-side sampling for copper in an estuary using

TABLE LVIII

Analyses of Precision of Copper Determinations by Differential Pulsed A.S.V.

INDIVIDUAL MEASUREMENT		WITHIN NISKIN BOTTLE		BETWEEN NISKIN BOTTLE	
Samples from 250 ml aged seawater pH$\sim$2.2		Samples drawn from the same Niskin bottle		Single sample drawn from the same Niskin bottle lowered to the same depth in the isolated basin over a 14 hr period	
Sample	Cu n.moles/ℓ	Sample	Cu n.moles/ℓ	Sample	Cu n.moles/ℓ
1	9.60	S_1	4.25	A_4	9.61
2	8.98	S_2	3.78	B_4	11.81
3	8.82	S_3	4.41	C_4	11.02
4	9.45	S_4	4.25	D_4	10.08
5	9.76	S_5	3.78	F_4	12.13
6	9.13	-	-	N_{16}	11.65
	$\bar{x} = 9.29$		$\bar{x} = 4.09$		$\bar{x} = 11.02$
	$\sigma = 0.38$		$\sigma = 0.30$		$\sigma = 1.00$
% Coefficient of variation = 4.0%		% Coefficient of variation = 7.3%		% Coefficient of variation = 9.2%	

the standard Niskin bottle. Analytical precision has been discussed in several previous reports and the most recently obtained set of values for Cd, Cu and Pb are listed in Table LIX. Analytical precision for the soluble Hg contents obtained by long path length atomic spectrometry is given in Tables XIX and XX, and for soluble vanadium determined by neutron activation analysis, in Tables XXII-XXIV.

Meaningfulness of the data in terms of the chemical species determined has been noted above. One further potential complication must be noted here: the use of a 0.4 μm membrane to define the soluble fraction. This is a very real problem in these sub-arctic regimes because very fine grained, mechanically weathered glacial sill constitutes a significant portion of the particulate load. In coastal regions and estiaries where the total suspended sediment load is high, the presence of significant amounts of particulate matter less than this arbitrary cut-off can be readily demonstrated. "Soluble" lead, for example, is consistently around an order of magnitude greater in the Alaskan fjords than in open ocean areas. Burrell (1975) has demonstrated fractionation of copper in fjords using progressively finer pore-size membranes.

Comments on individual elements

Silver

This heavy metal - of considerable toxicological concern in many industrial areas - has not been determined on a routine basin in the open shelf region of Alaska to date. As part of our atomic spectrometric analysis program, however, we have obtained some data for representative adjacent fjord-estuary environments. The 0.009 μg/ℓ value given in Table

TABLE LIX

PRECISION DATA (% COEFFICIENT OF VARIATION) FOR REPLICATE (n=6-15) DETERMINATIONS OF Cd, Cu AND Pb IN ONE TREATED (ACIDIFIED OR EXTRACTED) SEAWATER SAMPLE

	A		B	
	n	% c.d.	n	% c.d.
Cd	6	8.7	15	11.0
Cu	11	12.6	5	4.0
Pb	10	8.2	10	6.0

[A] This film d.c. anodic stripping voltammetry

[B] Unenclosed filament atomic spectroscopy

VLII is a mean for a vertical profile taken in Blue Fjord within Prince William Sound (S. Central Alaska). This mean is approximately half of the currently accepted oceanographic value of 0.04 μg/ℓ (Brewer, 1975). Our data may represent more recent technique; however, the fjord estuarie waters are not typical of open ocean environments. In particular the inorganic particulate load is very high and silver is likely to be strongly partitioned onto the solid phases.

Cadmium

We believe we can determine soluble concentrations of this metal with excellent precision and accuracy. It appears that Cd is less susceptible to removal from solution by sorption onto available solid surfaces. Enhancement contaminations from sampling platforms and containers are, as might be expected, considerably less of a problem for this element than for, say, lead or zinc.

Analysis of test samples in our laboratories for this metal using completely different analytical techniques - atomic spectrometric and anodic stripping voltammetry - have yielded excellent agreement (see following section). Analytical precision by anodic stripping voltammetry is around ± 15%, with single tests from separate storage bottles yielding ± 25% (coefficient of variation).

The detection limit using voltammetry and a 30-45 minute plating time onto thin-film glassy carbon electrodes is better than 0.04 μg/ℓ.

The mean for all N.E. Gulf of Alaska bottom water samples is 0.03 μg/kg; considerably lower then the generally accepted "oceanic mean" of 0.1 μg/ℓ cited by Brewer (1975). Our values are in line with those recently discussed by Martin *et al.* (1976) for California coastal waters. Of the metals determined to date in this program, cadmium is the only one to consistently show elevated soluble concentrations at depth as compared with surface waters. Such a profile for estuarine waters is given in Table LXII. In general this might be supposed to reflect regeneration from biota at depth. However, the Bering Sea values (see Table XXI in the 1975-1976 Annual Report) are for unfiltered samples and in this case (mean of bottom water date = 0.06 μg/ℓ; n=20) the increases may be due to enhanced particulate loads adjacent to the sediment floor.

Copper

We have developed considerable analytical expertise with this metal. Sampling precisions have been recorded in Table LVIII. Overall current analytical precision by dc reverse voltammetry is around 13% (coefficient of variation; Table LIX). A figure of 16% was given for pulsed stripping voltammetry in Burrell (1976). The mean N.E. Gulf of Alaska bottom water concentration in 0.4 μm filtered water is 0.2 μg/ℓ (Brewer, 1975, gives 0.5 μg/ℓ); coastal and estuarine waters generally fall in the range 0.3-0.5 μg/ℓ. Copper is strongly sorbed onto inorganic particulate sediment (Burrell, 1975) so that enhanced estuarine soluble values may reflect inclusion of glacially derived silicate particulates less 0.4 μm in size.

Recent evidence (Feeley, 1977) suggests that copper is also removed to organic solid phases in seawater. This latter fraction may be partially remobilized at the benthic boundary layer (Heggie and Burrell, 1976). Although further research on such fine gradient structure has not been an overt part of this survey program to date, it is clearly a necessary future objective since the primary impact of marine industrial development on the natural trace metal regime is likely to be enhancement or repression of such natural boundary fluxes.

As noted in the following section, we have been unable to match analysis of test samples by atomic absorption and reverse voltammetry. In our most recent series of tests, copper detered by open reservoir, atomic spectroscopy averages some 50-100% greater than by the electroanalytical techniques. It is of course possible that different fractions are being determined in each case; but this is an unlikely explanation for the discrepency. The spectrometric procedure is designed to determine that fraction which may be chelated and extracted at seawater pH. The natural inorganic form of copper in seawater is the chloro complex $CuCl_4^{2-}$ (Burrell and Lee, 1976). The voltammetric analysis is performed at pH 2.5 however and the fraction plated out and subsequently oxidized during analysis should approximate the total content.

Mercury

The total mercury content of filtered (0.4 μm) Gulf of Alaska water have been determined by ambient temperature, long path length atomic spectroscopy as described above in Section VB. Samples were acidified to pH 4 on collection and separate sub-samples were UV irradiated to further release any remaining organically bound metal. Mercury content of Gulf waters range from 2-33 ng/ℓ with a cited analytical precision of ± 1.5 (see Table XIX). Highest values were recorded for the two transects on either side of Kayak Island. With a few exception surface waters were found to be higher than for samples from adjacent to the bottom. There was no further significant release of metal following the photo-oxidation treatment.

Considering only the 18 bottom water values determined for the Gulf: there are two high values of 26 and a 32 ng/ℓ as the remainder are less than 11 ng/ℓ. This gives a mean for all 18 of 7 ng/ℓ or 4 ng/ℓ if the former two samples are omitted. Brewer (1975) cites a 30 ng/ℓ oceanic mean.

Nickel

These data have been determined only on large volume, unfiltered samples, mainly from the Bering Sea, and mainly for samples collected early in the program when inferior sampling techniques were employed. Analysis has been by conventional flame atomic absorption following APDS/M1BK chelation and extraction (Burrell, 1965) using the standardized procedure of Brooks *et al.* (1967). Analytical precision was determined to be better than 20% CV. Bottom water volume ranged from 0.3-0.9 μg/ℓ with a mean of 0.65 μg/ℓ. Surface waters were generally up to x2 higher.

Lead

It is clear that this element is particularly susceptible to non-systematic contamination, especially during the collection operations. Because of the restrictions imposed by this particular program, e.g. the necessity of obtaining samples from wire-hung containers adjacent to the ship, contamination of the surface samples would be expected, not only for this metal but probably for copper and zinc also.

We are confident that our analytical techniques do not introduce significant error since only an acidification step (using quartz redistilled acid) is involved. Complex manipulations (of the type described in the IDOE Procedure Workshop Report) are not required.

To obtain a mean value for the Gulf of Alaska, we have again arbitrarily discarded the surface (10 m) water values because of the high probability of contamination from the research vessel. For this metal, however, bottom water values > 0.1 μg/ℓ have been deleted also.

The calculated mean μg/ℓ is 0.04 μg/ℓ (Table LVII); which may be compared with Brewer's ocean mean of 0.03 μg/ℓ. Analytical precision is ± 8%.

It should be noted that even with the most careful sampling care we have been unable to obtain comparable results on test samples using this standard pulsed voltammetric method and the filament AA procedure described in the following section.

Vanadium

This metal has been determined by Dr. D. E. Robertson of Battelle Northwest Laboratory by the neutron activation procedure described above in Section VB. Results obtained for Gulf of Alaska and Bering Sea waters are given in Tables XXII-XXIV, which also indicate analytical precision. The mean for the N.E. Gulf is 1.5 ± 0.2 μg/ℓ with a range of 1.0-1.7 μg/ℓ. A possible increase of the dissolved fraction with depth is indicated.

Zinc

Given the ubiquitour contamination problems associated with this element it would probably be prudent to put little faith in any of the numbers given in this report. We would suggest that no suitable procedure has been determined for this element and that the cited "ocean mean" of 5 μg/ℓ is unreasonably high. Several good analytical techniques exist for this metal. It is, for example, determinable with particularly good sensitivity by atomic spectroscopy. However, extraordinary steps are requested to sample and treat in an uncontaminated fashion. It would be expected that these difficulties would be equally as severe as for lead.

For this element we have, for various reasons, performed the analysis at seawater pH values, with all that this implies in terms of sorption of the metal onto the electroanalytical cell. However, it should be noted that samples have been stored acidified in the usual fashion and the pH adjusted immediately prior to the plating step. Our data range for Gulf bottom waters is 0.15-0.6 with a mean of 0.3 μg/ℓ. Analytical precision is ± 25%. These data are not comparable with most other literature values since a total soluble content is not necessarily delivered here. Our standard analytical procedure involves adding a series of spikes of known ionic concentration to the seawater sample and reanalysing, so that the fraction analysed depends upon the comparative electrode behavior of the indigenous zinc species and the added metal.

Intra-Laboratory Calibration of ASV and Filament AA Techniques for Soluble Metals in Seawater

One standing aim in this laboratory has been to develop a rapid, precise method for determining the soluble concentrations of a range of trace metals in seawater using atomic absorption spectroscopy. For various reasons, but primarily because of difficulty in accomodating organic solvents in early modules, we originally rejected graphite furnace atomization in favor of unenclosed, custom designed, graphite filaments for the atomization step. The relevant theories have been considered by Burrell (1974).

The complete technique, including both sampling and analysis, was designed to utilize conveniently small quantities of sample and to incorporate the minimum of pre-analysis handling steps. The relevant stages, briefly, are:

1. Collection of large volume water samples in conventional Niskin bottles.

2. In-line syringe filtering of a series of small volume (circa 10-20 ml) sub-samples into leached glass centrifuge tubes.

3. Immediate freezing without further chemical treatment.

4. Chelation of metals at ambient seawater pH, extraction into organic solvents with approximately x10 concentration and centrifugation separation of phases.

5. Replicate syringe addition of μℓ range sample volumes into the custom manufactured (Poco graphite) open filament for atomization.

Blanks are carried through the entire process, and standard solutions through the chelation-solvent extraction-concentration stages so that extraction efficiencies are not an analytical factor. The objective of chelating at ambient pH is to facilitate chemical speciation studies; however, the technique thus assumes complexation and solubilization of ions sorbed to the container surfaces. The method has been described in detail by Burrell and Lee (1975).

Intralaboratory comparison of this filament AA procedure, and d.c. anodic stripping voltammetry (ASV) were first attempted in 1974-1975. This was considered to be an excellent comparative test since, after the initial large volume over-the-side collection, pre-analysis manipulation and the instrumental techniques are quite different. We were initially primarily interested in cadmium, and, as shown in Table LX these data compared very favorably. The values for copper and lead diverged considerably, however.

At the commencement of the first year of the OCS-NEGOA program, it was agreed that 10% of all water samples collected would be forwarded to NBS for intercalibration purposes. This program subsequently died, however, without any comparative data being generated.

For the second year of the OCS program, certain stations in the Gulf of Alaska (generally the deeper ones) were designated as intercalibration stations and multiple sampling was carried out. Splits were dispatched to NBS as previously, and other sub-samples were distributed for activation analysis. Two sets of samples were taken at this time for analysis in the Institute of Marine Science, *viz*:

1. Standard 1ℓ polyethylene bottles, from the single-purchase and leached lot as previously described, were filled with effluent water from the in-line Nuclepore filter. These samples were opened in a glove bag, acidified with Ultrex HCl, sealed and wrapped in a polyethylene bag, and frozen. These samples were returned to the laboratory for voltammetric analysis for Cd, Cu (by two separate voltammetric techniques), Pb and Zn.

2. Approximately 10 ml sub-samples from the same 10ℓ drop-top Niskin bottle as for (1) above were syringe filtered into pyrex centrifuge tubes, frozen (but untreated) and returned to the laboratory for chelation extraction and concentration and analysis by filament atomic absorption.

Comparative results for these two sets of analyses are given in Table XVI. It should be noted that these, and subsequent values presented in this section, have not yet been adjusted for precision; i.e. the significance of the final digits are presently unknown.

TABLE LX

ANALYSIS OF SOLUBLE CADMIUM IN A SUITE OF OPEN OCEAN SEAWATER SAMPLES FROM THE GULF OF ALASKA. μg/l; SAMPLES FILTERED THROUGH 0.45μ MEMBRANES

A. Filament atomic absorption spectrometry (FAA)
B. Differential pulse anodic stripping voltammetry (ASV)

Station	Z(m)	FAA	ASV
52	0	0.08	0.06
	20	0.05	0.06
51	0	0.04	0.03
	50	0.04	0.06
	100	0.10	0.07
50	0	0.05	0.05
	75	0.05	0.05
	150	0.08	0.05
49	0	0.06	--
	75	0.05	0.09
	125	0.10	0.11
48	0	0.04	0.05
	100	0.14	0.12
	175	0.06	0.09
47	0	0.08	0.10
	300	0.10	0.12
	1500	0.17	0.18

TABLE LXI

SOLUBLE TRACE METAL CONCENTRATIONS

OCS - Gulf of Alaska Intercalibration Stations

(drop-top Niskin; in-line 0.4μm filter - μg/kg;
significance of final digit undetermined)

Station number	Depth (m)	Cd		Cu			Pb	
		A	B	A	B	C	A	B
011	1350	0.15	0.04	0.75	0.13	0.17	0.55	0.08
015	1500	0.15	0.06	0.60	0.15	0.18	0.40	0.13
024	410	0.15	0.09	0.85	--	0.16	0.60	0.12
110	175	0.10	0.03	0.55	0.15	0.12	0.40	0.03

A graphite filament atomic absorption
B d.c. anodic stripping voltammetry
C differential pulse anodic stripping

It seems clear that the separate voltammetric procedures - direct d.c. and differential pulse - give closely similar values for copper. These tests used water from the same storage bottle but by different operators at different times. Data *via* filament atomic absorption is, on average, some x3 or 4 greater than the voltammetric values, even for cadmium. It appeared from these tests that the multiple handling steps necessary for the atomic spectrometric analysis contaminated the sample to an unacceptable degree.

No further open ocean intercalibration tests were possible, but intra-laboratory comparisons were continued in adjacent estuaries. Table LXII shows raw data obtained for water collected in standard Niskin bottles, filtered at 0.4 μm, and analysed as above. Again, there is a marked discrepency between copper and lead data produced by atomic spectroscopy and the stripping voltammetry; these differences are clearly unacceptable. It should be noted also that the mean values for both lead and copper are higher than for open ocean samples. It is believed that this reflects the presence of glacially derived particulate material finer than the 0.4 μm cut-off. The values for cadmium are most interesting and it is unfortunate that ASV values were not obtained. The atomic spectrometric values appear to fall in the expected range and also show a progressive increase with depth; a common characteristic of soluble Cd noted previously.

The final test in this series for which preliminary data are available is detailed in Table LXIII. Estuarine waters were again utilized in this test. These samples were however collected entirely from the sea surface from a small boat by hand. No over-the-side sampler or winch cable was used. Samples destined for both ASV and filament AA analysis

TABLE LXII

SOLUBLE TRACE METAL CONCENTRATIONS

Blue Fjord Vertical Profile

(<0.4 μm; μg/kg - Standard Niskin bottles - Replicate means - Significance of final digit not determined)

Sample depth	Cd	Cu			Pb	
(m)	A	A	B	C	A	B
0	0.04	0.08	0.15	0.20	0.75	0.10
2	0.045	1.65	0.35	--	0.50	0.15
5	0.045	0.50	0.20	--	0.40	0.30
10	0.05	0.80	0.40	0.45	0.55	0.20
15	0.05	1.25	0.75	0.75	0.45	0.15
25	0.07	1.40	0.15	0.40	0.60	0.10
50	0.07	1.15	0.20	0.35	0.75	0.20
75	0.065	1.00	0.15	0.15	0.40	0.10
100	0.10	0.90	0.30	0.10	0.70	0.65
135	0.15	1.45	0.15	0.20	0.60	0.50

A graphite filament atomic absorption
B d.c. anodic stripping voltammetry
C differential pulse anodic stripping voltammetry.

TABLE LXIII

SOLUBLE TRACE METAL CONCENTRATIONS

Resurrection Bay Surface Samples

(No sampling container - <0.4 μm - μg/ℓ;
significance of final digit not determined)

Sample number	Cd		Cu			Pb		
	A	B	A	B	C	A	B	C
S11	0.01	0.02	0.01	0.35	0.35	0.03	0.06	0.05
S12	0.04	<0.003	2.15	0.25	0.25	0.08	0.15	0.15
S13	0.01	0.03	1.80	0.45	--	0.12	0.17	--
S14	0.09	0.10	0.60	0.40	0.40	0.20	--	--
S15	0.23	0.10	0.70	0.30	0.30	<0.04	0.18	--
S31	0.08	0.02	0.45	0.35	0.55	<0.04	0.08	0.07
S32	0.07	0.02	0.61	0.35	0.30	0.04	0.15	0.10
S33	--	0.03	0.35	0.30	0.40	0.02	0.03	--

were drawn directly into leached 250 ml polyethylene bottles and wrapped in polyethylene. ASV samples were acidified; those for AA were untreated. Both sets were bugged in polyethylene, frozen and returned to the laboratory for analysis.

ASV analysis was performed directly as noted above. Sub-samples for filament analysis were chelated and extracted in the polyethylene bottles at ambient pH values. The organic layer was subsequently transferred to leached, small volume, glass centrifuge tubes prior to syringe addition of aliquots into the filament reservoir. Results of these two sets of analyses are given in Table LXIII. Some samples would appear to be contaminated; particularly for copper. However, the results for Cd and Pb, and to a lesser extent for Cu, are reasonably similar although statistical tests have not yet been applied. It may be concluded that, with most careful attention to collection methods, atomic spectrometric analysis is a suitable analytical technique for several soluble heavy metals in seawater.

Se and Cr in the Alaskan Shelf Environments by G.L.C.

[Report prepared by Dr. T. Gosink - not available in time for inclusion in this report].

Gulf of Alaska and Lower Cook Inlet

We have now had the opportunity to collect sediment samples in the N.E. Gulf of Alaska over two field seasons, but facilities were inadequate to collect water samples during the initial cruises *Fucus* and *Mytilus* samples have also been collected for us during two separate summer sampling expeditions. Samples from the N.W. Gulf region are considerably more sparse and no water or sediment samples have been collected from the Kodiak shelf *per se*. In Cook Inlet we managed to obtain a few contamination free Haps core sediments but no water or biota. Open ocean benthic sampling has been very spotty; we have elected to determine metals in crab and *Neptunea* only as offering the best coverage.

A detailed discussion of the concentrations of soluble heavy metals in the Gulf waters has been given above. Concentrations are uniform throughout the area, and uniformily low. 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. The results are given here in the same concentration units as for the soluble contents. 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 use of vanadium, where we have data for both soluble and particulate contents, the particulate fraction constitutes, on average, some 3% of the total vanadium.

Tables LXIV and LXV summarize the analytical data obtained for *Mytilus* and *Fucus* from the N.E. Gulf region. Station localities have been given previously in Figure 3. Where two sets of data are given for one locality these refer to samples collected in the summers of 1975 and 1976 respectively. No seasonal data are 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 LXVI for comparison. These latter include samples from both unpolluted (e.g. New Zealand) and presumably impacted areas (e.g. Bristol Channel of UK). How far any legitimate comparison can be made, is,

TABLE LXIV

MYTILUS

μg/g dry weight

	Cd	Cu	Ni	Zn	Hg
Port Dick					
(Gore Point)	11.0	8.5	2.0	80	--
Anchor Cove	6.0	10.5	<10.0	126	
(Day Harbor)	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	3.0	7.0	< 5.0		
(Latouche Island)	5.5	8.5	3.5	52	
Macleod Harbor	4.5	10.0	<10.0	110	0.25
(Montague Island)	4.0	9.0	< 5.0		
Zaikof Bay	4.5	9.0	<10.0	120	0.35
(Montague Island)	4.5	11.0	< 5.0		
Port Etches					
(Cape Hinchinbrook)	4.0	10.0	< 5.0		
Boswell Bay	3.0	9.5	<10.0	64	0.35
(Hinchinbrook Island)	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 LXV

FUCUS

μg/g dry weight

	Cd	Cu	Ni	Zn	Hg
Port Dick (Gore Point)	3.5	8.0	9.5	16	-
Anchor Cove (Day Harbor)	1.5	9.5	<10.0	17	0.30
	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 (Montague Island)	1.5	2.5	<10.0	5	0.45
	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 LXVI

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

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 analysis.

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.

A large number of sediment analyses have been obtained for the N.E. Gulf of Alaska, and considerably fewer from the N.W. Gulf where the bottom sediments were coarser and frequently impossible to recover in the Haps corer. This latter situation was so also in the Lower Cook Inlet region. Here, although sampling was attempted on every standard benthic station, only nine good samples were recovered.

Table LXVII lists the heavy metal contents of the sediment extracts, together with a few total analyses and the few granulometric analyses available to us. There is a clear correlation between the extract concentrations and the proportion of fine grained sediment in the sample, as would be expected. In the particular compilation the equivalent relationship between total contents and the % clay sized material is not readily apparent. However, it has been noted apparent. However, it has been noted that, in general, total heavy metal contents of the surface sediments do increase going from the Bering to the N.E. Gulf region i.e. in the direction pattern appears to hold on a large scale also. No systematic vertical variations in the cores are apparent from the total analyses. Table LXVII is grouped in transects seawards from the N.E. coast. There

TABLE LXVII

N.E. GULF OF ALASKA SEDIMENTS

	% Clay (sand &	Whole rock			Sediment extracts						
Sample	gravel)	Mn	V	Hg	Fe	Mn	Cd	Cu	Ni	Zn	Cr
01	62	-	-	-	6380	125	Tr	14	12	37	1.5
02*	-	740	150	65	-	-	Tr	6	5	31	-
03	68	-	-	-	6350	115	Tr	9	9	27	2.0
04	69	-	-	-	6740	105	Tr	9	10	30	0.5
05*	60(20)	780	165	35	-	-	Tr	7	6	21	-
06	33(44)	-	-	-	2210	65	Tr	7	4	17	1.0
07*	42(36)	-	-	50	2770	50	Tr	6	4	23	3.5
08*	-	-	-	35	-	-	-	-	-	-	-
53A	-	-	-	-	-	-	Tr	31	12	26	-
53	-	-	-	-	-	-	Tr	12	8	13	-
53*	-	-	-	45	-	-	Tr	11	8	22	-
54*	-	-	-	40	-	-	Tr	13	8	22	-
55	-	-	-	-	-	-	Tr	15	9	15	-
56	-	-	-	-	-	-	Tr	8	8	9	-
56*	-	730	140	30	-	-	-	-	-	-	-
57	-	-	-	-	-	-	Tr	14	7	13	-
57*	27(40)	880	150	60	-	-	-	-	-	-	-
58	-	-	-	-	-	-	Tr	13	5	17	-
58*	50(3)	950	180	35	-	-	-	-	-	-	-
59A*	-	860	150	60	-	-	-	-	-	-	-
52	-	-	-	-	-	-	Tr	31	12	25	-
52*	-	940	160	55	-	-	Tr	17	13	39	-
51	-	-	-	-	-	-	Tr	20	9	16	-
51*	-	970	180	50	-	-	Tr	19	11	33	1.0
50*	62	780	160	60	7250	130	Tr	14	9	27	2.0
49	-	-	-	-	-	-	Tr	26	6	18	-
49*	-	780	160	55	-	-	Tr	12	11	37	-
48	-	-	-	-	-	-	Tr	14	7	16	-
48*	31(35)	800	160	45	3470	85	Tr	10	6	19	1.5
42	-	-	-	-	-	-	Tr	19	6	16	-
42*	30(10)	-	-	-	6780	115	Tr	15	10	24	1.5

N.E. GULF OF ALASKA SEDIMENTS (Continued)

Sample	% Clay (sand & gravel)	Whole rock			Sediment extracts						
		Mn	V	Hg	Fe	Mn	Cd	Cu	Ni	Zn	Cr
43	-	-	-	-	-	-	Tr	24	6	17	-
43	60(4)	-	-	-	6660	90	Tr	12	11	22	-
44	-	-	-	-	-	-	Tr	17	6	16	-
44*	-	850	150	35	-	-	Tr	11	4	13	-
41	-	-	-	-	-	-	Tr	23	7	17	-
41	50	-	-	-	4420	100	Tr	19	7	30	-
40	-	-	-	-	-	-	Tr	23	6	17	-
40*	55	-	-	65	-	-	-	-	-	-	-
39	39	-	-	-	4000	80	Tr	14	7	29	Tr
37	-	-	-	-	-	-	Tr	9	7	16	-
30	-	-	-	-	-	-	Tr	8	4	10	-
30*	-	600	90	10	-	-	-	-	-	-	-
31	-	-	-	-	-	-	Tr	30	3	6	-
31	36(2)	-	-	-	6375	110	Tr	15	9	23	4.5
32	-	-	-	-	-	-	Tr	19	3	12	-
32	48	-	-	-	5105	90	Tr	14	8	22	1.0
33*	-	640	110	40	-	-	Tr	7	2	12	-
34	-	-	-	-	-	-	Tr	21	4	15	-
29*	-	-	-	25	-	-	-	-	-	-	-
28	40(7)	-	-	-	2590	105	Tr	13	7	19	1.0
27	-	-	-	-	2260	115	Tr	8	5	21	Tr
26*	-	920	90	30	-	-	-	-	-	-	-
25*	20(46)	-	-	30	1200	50	Tr	4	3	13	2.0
101	Tr(100)	-	-	-	-	-	-	-	-	-	-
104	15(80)	850	70	-	-	-	-	-	-	-	-
110	-	-	-	20	-	-	-	-	-	-	-

* *Discoverer* Leg III - November 23-December 2, 1975

here a suspicion of enhancement of copper in the near-shore, 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.

Extractable contents of the lower Cook Inlet sediment are much lower than from the adjacent N.E. Gulf and are more comparable in this respect with samples from the Aleutians and S. Bering Sea. Turbulent removal of fine grained sediment from this region has decreased the "sorption" capacity of the surface sediments in this locality.

Bering Sea

Data for the S. Bering Sea (primarily Bristol Bay) area are based on one sampling cruise in June 1975, on which water and bottom sediments were taken, and various trawl and intertidal collection expeditions organized by the biology investigators. Soluble Cd, Cu, Pb, and Zn values were discussed in the previous Annual Report. The comments on these elements, and also on V, given with respect to the NEGOA region (above) are relevent to the Bering Sea also. Water samples collected from the Norton Sound region have not yet been analysed, but no surprises are expected.

Analysis of the heavy metal contents of the surficial S. Bering Sea sediments is now complete. Contents of extracts have been given above; the bulk of the "whole rock" analyses are listed in the suffixed 4th Quarterly Report. There are no anomolous trends but concentrations of most heavy metals (e.g. Cd, Cu, Ni, in extracts; total Fe, Mn, V, Cr, Ci) are much reduced as compared with the eastern Gulf of Alaska. This is a direct consequence of the varying sedimentological regimes. Surficial sediments in the Bristol Bay region of the Bering Sea (and in the N.W.

Gulf area) are much coarser than the mean N.E. Gulf sediment. No size analysis has been performed on the Bering Sea sediments in this program but such data are becoming available from a cooperative study and these relationships will be discussed in more detail in a subsequent report.

Norton Sound samples were collected in September and are just now being treated and analysed. Heavy metal data for Norton Sound proper are expected to closely parallel those from Bristol Bay since this former area appears also to be swept clear of fines. The important influence of the Yukon River, and the disposition of the effluent sediment, will be studied further in 1978.

We have received far too few biota samples to permit any broad generalizations. No anomolies are shown by benthic (e.g., crab) or intertidal (*Mytilus, Fucus*) species. We wish, however, to flag our data for *Neptunea*, the giant snail. Specimens collected form the N.E. Gulf of Alaska exhibited high copper and zinc contents, and very high cadmium contents (see Table LXVIII) as noted above. When samples collected from trawls in the S. Bering Sea were prepared for analysis, the digestive tract was separated from the rest of the animal and analysed separately. The results have been given in Table XXVI. Tissue values for Cd, Cu, and Zn are still higher than in other benthic species analysed; digestive gland concentrations are considerably elevated to levels far higher than could be explained by sediment incorporated in the tracts. Since these animals are taken for food by, particularly, Japanese vessels, further study would seem to be desirable. Copper concentrations (Table XXV) in Bering tanner crab samples are generally somewhat lower than in the Gulf but not significantly so.

TABLE LXVIII

CRAB

µg/g dry weight
18 July-7 August 1975 Trawl Cruise

Sample #	Cd	Cu	Ni	Zn
1	<1.5	45.5	<5	135
3	1.5	30.0	<5	133
5	3.5	70.0	<5	82
6	2.5	132.5	<5	118
9	2.0	46.5	<5	81
25	1.5	65.0	<5	140
28	3.0	58.0	<5	128
35	<1.5	54.0	<5	149
36	2.0	65.5	<5	125

NEPTUNEA

µg/g dry weight
18July-7 August 1975 Trawl Cruise

Sample #	Cd	Cu	Ni	Zn
8	55.0	209	<5	290
18	142.5	410	<5	410
31	49.5	235	<5	357
41	86.0	245	<5	627

Heavy Metal Geochemistry of the Beaufort Sea Shelf Sediments
(By A. S. Naidu)

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 nonlithogenous 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 nonlithogenous 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

TABLE LXIX

AVERAGES OF 31 ANALYSES* OF THE TOTAL AND NONLITHOGENOUS (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)	Nonlithogenous fraction (μg/g)	% Nonlithogenous 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 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).

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 nonlithogenous 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

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	-0.3618	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	0.6821	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 metals. 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.

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 nonlithogenous 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 favorable physicochemical 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 an 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 nonlithogenous 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 nonlithogenous 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.

Summary of Sedimentology and Clay Mineralogy of Alaskan Shelves

[Summary prepared by Dr. A. S. Naidu - not available at dead-line time for this report]

VIII. CONCLUSIONS

1. Soluble contents of heavy metals in the shelf waters are as low or lower than accepted "oceanic means". Concentration values are also very uniform. No horizontal trends are apparent; more would be expected for open shelf waters. Cadmium possibly is higher at depth than at the surface. Other metals generally show the reverse trend but surface contamination from the ship should be initially suspected.

2. Particulate heavy metal concentrations are enhanced near-shore *versus* open ocean, and near-bottom *versus* surface. This reflects the particulate load distributions.

3. Biota contents show no unequivocal anomolies in their heavy metal burdens. Contents of sub and inter-tidal benthic species are, on average, as low or lower than those reported for other, generally more temperate regions. Such comparisons are best seen in the case of the commonly used intertidal index species *Mytilus* and *Fucus*. But crab contents of the common

heavy metals, because of their feeding habits, have also proved to be sensitive monitors of anthropogenic pollution. Crab samples taken from the Gulf of Alaska and the Bering Sea have uniformly low contents. The giant snail *Neptunea*, conversely, has (relatively) very high concentrations of Cd and high enrichment of Cu and Zn. However, because of a general decrease of comparative information, the significance of these data are not known at present.

4. Bottom sediments have heavy metal contents commensurate with their mineralogy and size fractionation i.e. the finer grained sediments of the N.E. Gulf of Alaska are enriched compared with surficial samples from the N.W. Gulf region, lower Cook Inlet or Bering Sea. These relationships may be best observed from the heavy metal data on chemical extracts from the sediments. There is a possible near-shore enrichment of copper but, with the limited data available, it is difficult to identify potential regional variations from those imposed by the overall character of the sediment. No systematic variations with depth have been observed from the total trace element profiles.

5. Beaufort Sea (Naidu) - In summary, it is concluded that a great bulk of the Fe, Cu, Zn, Ni, and V in the Beaufort Sea sediments are linked up with the crystal lattice of layered silicate minerals. On the other hand almost 50% of the Mn is lattice-held, and the rest of the 50% is perhaps distributed between manganic hydrate and adsorbed/exchangeable sites of layered silicate minerals. Organic matter seems to play a significant role in the fixation of most metals; however further investigations need to be pursued to define better the mechanism of the organo-metallic bonding. It is surmized that the geochemistry of the metals is largely independent of the sediment carbonate phase.

Conclusions made in this study are based to a large extent on the "circumstantial evidences" manifested by the correlation coefficient data in Table LXX, and existing knowledge on the geochemical behavior of metals. The above conclusions are, therefore, tentative and must be applied with caution while speculating the chemical impact of anthropogenic perturbations relating to oil development activities in the shelf region of Beaufort Sea.

It is recommended that more detailed inorganic and organic geochemical studies relating to the Beaufort Sea sediments be pursued on individual metals, with special reference to the physicochemical and biological conditions of the depositional environments.

6. Clay mineralogy (Naidu) - Final analysis of this work has been compiled and will be submitted in the next report.

7. Se and Cr (Gosink) - Final analysis of this work are nearing completion, and the results are not included in this report.

IX. NEEDS FOR FURTHER STUDY

The needs for further study are essentially as was proposed in the 1975-1976 Annual Report since the decision to implement these have not yet been taken. We believe that we need have a reasonable corpus of data for the distribution of heavy metals in the open shelf regions. The values obtain to date have confirmed our initial expectations that metal contents of the water and biota would be low and that of the sediments a function of the sedimentological character. It would, of course, be impossible to obtain sufficient baseline data over the entire Alaskan shelf region to satisfy every local need. It would be possible to argue that additional data would be desirable in virtually every region. However, such would be a newer ending exercise. Apart from some obvious areas which have been exceedingly short changed (such as the Beaufort Sea) or virtually neglected (such as the Kodiak shelf and Lower Cook Inlet), we tentatively conclude that additional survey data for the bulk of the lease areas would only slightly modify the basic conclusions given in the previous section, if at all.

The essential need at the present time is for work, not on static distributions, but on transfer rates and processes, and especially within the coastal zone. It is this area which is likely to receive the major impact from oil development activity and any impingement here might be expected to result in more obvious and economically damaging problems. Although the conclusions are arguable, the initial results of the NEGOA symthesis meeting, for example, was to focus attention on the sea surface and on potential coastal impact areas from Yakutat to Prince William Sound. It was considered to be unlikely that spilled oil would be transported to the deeper ocean floor in a toxic condition. Because of the rapid microbial degradation of hydrocarbon on the surface in the temperate - subarctic Gulf regions, it was suggested that major deleterious impact on the environment would occur in those areas where the water was shallow and the slick physically confined i.e. in the coastal estuaries, embayments and lagoons. In addition, and from the sepcial point of view of this chemistry program, it is the coastal regions which are the major repository for terrstially derived heavy metals (as discussed in detail in last years report). Here chemical gradients (and hence fluxes) and seasonal biological cycles are at a maximum, and perturbations of the natural biogeochemical cycles of heavy metal would be most apparent.

Open ocean areas are, of necessity, physically and chemically more uniform, and it would be expected that the effects of an oil spill or other industrial perturbation would be rapidly deluted and minimal. Future studies here should concentrate on the probably effects on biota; processes effecting the uptake of heavy metals by the biota from the water and sediment, and transfers between trophic levels. In keeping with the concept that toxic concentrations of hydrocarbons are only likely to persist (and for short periods on the surface of the water) emphasis should probably be on, say, marine birds and mammals. During this present contract period we have started work on the latter. There is some, but not much, available background information (see literature references cited in the special data report referenced in Appendix II). Some evidence exists for enhanced levels of certain metals - notably mercury - in animals taken in estuarine regions of the Bering Sea. This type of work should certainly be continued.

Clearly, it would be impossible to study the whole, or even a major portion, of the Alaskan coast. In any case, the resources available to this project have been reduced to a third of the 1975-1976 level and project areas must be chosen with the intent of extracting the maximum scientific return. In July 1976, as noted elsewhere in this report, we convened a workshop in Fairbanks to select study sites which would function, in some important respects, as paradigms for each lease area or shelf sea. A brief summary of the deliberations of this workshop are appended. Since that time our ideas have been modified as new information from other disciplines has been assimilated, particularly at the respective synthesis meetings.

The following study sites for the effect of oil on heavy metals distributions are recommended. This list includes far more than could be accomplished within the present program level. Priorities must be established elsewhere but it is presumed that the N.E. Gulf of Alaska, Lower Cook Inlet and the Bering Sea would have priority.

1. A coastal estuary on the N.E. Coast of the Gulf of Alaska. These are liable to impact both from drilling site spills and from accidents associated with staging and transportation of oil. Oil spills would be physically confined under estuarine conditions and available for toxic impact on euphotic zone, intertidal and immediately sub-tidal biota. Interaction with suspended sediment would be a major phenomenon in this environment, and perturbation of the flux of metals from the bottom sediment would likely occur.

We have previously suggested Yakutat Bay as a prime study site and, secondarily, Icy Bay. More recent information would also recommend Prince William Sound. It would be impossible to study the whole of the latter (which may itself be considered as a fjord system). Initial work should probably focus on the Hinchinbrook entrance area including inter and near sub-tidal benthos and suspended and deposited sediments from the Copper River.

2. Lower Cook Inlet is an exceedingly important commercial fisheries region. It would therefore seem highly prudent to study heavy metal uptake by one or more benthic species. Sediment-water interactions are not of importance here because of the turbulent nature of the water circulation and the consequent rapid removal of fine grained material. We propose to monitor, on a seasonal basis, heavy metal dynamics of, if possible, *Macoma, Mytilus* and *Fucus*. The former species is of particular interest in Alaskan

waters as noted in other reports. It has a widespread range and is a detritivore. The latter two species have been studied within the program to date and are widely used index species. It has been proposed to utilize the biologically rich Katchemak Bay is an easily visited primariy seasonal sampling site. Because of the nature of the water circulation and suspended sediment distribution, comparison of this area with Kamishak Bay on the opposite shore would be useful.

3. Somewhere in the Gulf or Lower Cook Inlet it might be useful to monitor heavy metal contents of surficial sediments and benthic biota in the immediate vicinity of one production platform. It would seem likely that, because of rapid dispersal and mixing, no measurable evidence of metal impact should be found unless formation waters or drilling mud are discharged very close to the sediment surface. However, this supposition should probably be researched.

4. The Bering Sea is of paramount importance to the Alaskan economy as a commercial fisheries area. It is suggested as a highly suitable area for open-ocean trophic level transfer studies. We suggested previously a tie in of the trace metal chemistry program with the PROBES program such that the necessary biological background information would be available. A second or alternative possibility would be to continue studies on marine mammal uptake of metals. Work in this field started during the current contract period and we have noted that three seal species common in the Bering Sea exhibit very different feeding habits: benthic, pisciferous, planktonic. Different heavy metal uptake patterns should pertain, and these patterns should be perturbed differently by oil development impact.

5. The primary oceanographic feature of the N. Bering Sea-Norton Sound region is the presence of massive freshwater and associated sediment discharge from the Yukon River. Potential interaction of oil and this plume should be studied.

6. Oil development in the Beaufort Sea must initially be confined to the immediate coastal zone region, shoreward of the ice shore zone. The characteristic environment here is the lagoon - barrier island complex. We have had considerable experience in this environment; notably with regard to sediment transport (see, especially Hood and Burrell, 1976). Trace metal chemistry studies within the lagoons and embayments are very sparse. One major chemical feature here might be the input of organic-rich tundra effluent waters into the coastal zone. These waters should be rich in complexed trace metals which would be deposited in the estuarine - near shore zone. Industrial impact on such natural cycles must be determined.

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X. SUMMARY OF FOURTH QUARTER OPERATIONS

This report is complete up to the time of preparation: mid-February. Data obtained after this time will be included in the next quarterly report.

XI. APPENDIX I

Summary of Specific Study Site Workshop

Wednesday 7 July 1976

Institute of Marine Science, Fairbanks

Participants:
D. C. Burrell
J. O. Colonell
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OBJECTIVES

To consider the oceanographic characteristics of the shelf and coastal regions of Alaska and to recommend suitable localities for, in particular, the long term chemical objectives of the OCSEAP program. These specific study sites were chosen also with a view to conducting physical, geological and ecological studies contemporaneously i.e., the recommendations are considered to be suitable "type areas" for a range of multi-discipline research and monitoring programs. At this time only research sites within four of the Alaskan OCS lease areas currently identified were considered: Beaufort Sea, north and south Bering Sea and the eastern Gulf of Alaska.

Beaufort Sea

In the Beaufort Sea, the lagoon-barrier island system was considered to be critical.

Important non-chemical characteristics: Dynamics of the islands; longshore currents and sea-level changes.

The Institute of Marine Science has experience in working at several localities along this Arctic Ocean coast. Practical logistic problems must be considered.

Recommended site: Prudhoe Bay.

North Bering Sea

The primary oceanographic features of this region are fresh-water discharge from the Yukon River and the general northward flow toward Bering Strait.

Important non-chemical characteristics: surface Yukon River plume; sites of deposition of Yukon sediment; local fisheries.

Chemical characteristics: Chemical gradients and reactions associated with mixing of Yukon, marine waters and particulates.

Recommended site: Yukon River plume and delta.

South Bering Sea

The eastern shelf region of the southern part of the Bering Sea - Bristol Bay and adjacent regions - is one of the most productive regions of the world. We considered this region as an entity encompassing both the St. Georges Basin and Bristol Bay lease areas.

Important non-chemical characteristics: biological productivity and associated commercial fisheries; physical and geological features associated with the shelf break and canyons.

There are biologically important lagoon complexes along the southern margin and a major fresh water discharge (Kuskokwim) along the northern. This latter flows northward along the caost and might better be considered as impacting the north Bering Sea region (above). In view of the importance of the indigenous biota a more diffuse open-ocean study site was the first choice for this region.

Recommended sites: 1. The "Golden Triangle" region

2. Izembek Lagoon as a secondary coastal site.

Gulf of Alaska

We primarily considered the northeastern Gulf lease area (including lower Cook Inlet), and, secondarily, the environment of Kodiak Island. The major impact sites in this area would be the fjord-estuaries. These latter are biologically diverse and productive and are localities where fresh water and immense quantities of particulate sediment mix with the seawater. Most of the coastal communities are located within fjords. It was considered to be of prime importance fo choose, as an intensive study site, a fjord containing one or more basins separated from the open ocean by sills. The Institute of Marine Science has demonstrated that such basins may remain unflushed over certain times of the year. Since they are also major sediment traps, maximum opportunity is afforded for reaction between marine components and chemical pollutants. Fjords located on the eastern Gulf coast are most important in this respect.

Recommended site: 1. Yakutat Bay

This is the most suitable intensive study site from a scientific point of view. It contains three well-defined basins and would serve as an excellent model for flushing, circulation and reaction studies of water and sediment. Model areas should be chosen for their inherent scientific characteristics; it is not necessary that they should themselves, be directly impacted in the event of an oil spill.

2. Port Bainbridge

Located west of Prince William Sound. This fjord would be more complex oceanographically than Yakutat, not least because of the impact of water from Prince William Sound itself rather than from the Gulf.

3. Nuka Bay and Aialik Fjord

4. Alitak Bay, S. Kodiak Island

SPECIAL DATA REPORT

NATURAL DISTRIBUTION AND ENVIRONMENTAL BACKGROUND OF TRACE HEAVY METALS IN ALASKAN SHELF AND ESTUARINE AREAS

(Title modification April 16, 1976)

Task Order #12 R.U.# 162/163/288/293/312

Contract #03-5-022-56

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January 1977

XII. APPENDIX II

A BIBLIOGRAPHY OF THE AVAILABLE LITERATURE ON RECENT SEDIMENTS OF THE CONTINENTAL SHELVES OF ALASKA

By

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PREFACE

During the past quarter of a century considerable data have been collected on recent sediments of the marginal seas of Alaska. This bibliography is a compilation of most of the available published and unpublished works of American studies in the Beaufort, Chukchi, and Bering Seas, as well as the Gulf of Alaska. An attempt has been made to include some of the important investigations that have been carried out by Russians and which have been translated into English. This bibliography has purposely omitted the studies on sediments of small inland bays and fjords which do not form a part of the open shelf regime.

This study was supported by the Bureau of Land Management through interagency agreement with the National Oceanic and Atmospheric Administration, under which a multi-year program responding to needs of Petroleum development of the Alaskan Continental Shelf is managed by the Outer Continental Shelf Environmental Assessment Program (OCEAP) Office.

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OCS COORDINATION OFFICE

University of Alaska

ENVIRONMENTAL DATA SUBMISSION SCHEDULE

DATE: March 31, 1977

CONTRACT NUMBER: 03-5-022-56 T/O NUMBER: 12 R.U. NUMBER: 162/163/288/293/312

PRINCIPAL INVESTIGATOR: Dr. D. C. Burrell

Submission dates are estimated only and will be updated, if necessary, each quarter. Data batches refer to data as identified in the data management plan.

Cruise/Field Operation	Collection Dates		Estimated Submission Dates[1]			
	From	To	Batch 1	2	3	4
Discoverer Leg II #808	6/2/75	6/19/75	*	*	None	*
Silas Bent Leg I #811	8/31/75	9/14/75	None	None	None	None
Discoverer Leg IV #812	10/8/75	10/16/75	*	*	None	*
Miller Freeman	8/16/75	10/20/75	None	None	Unknown	None
Discoverer Leg III #810	9/12/75	10/3/75	None	None	None	*
North Pacific	4/25/75	8/7/75	None	None	Unknown	None
Intertidal Biota		1975	None	None	Unknown	None
Discoverer #816	11/12/75	12/2/75	*	*	None	*
Contract 03-5-022-34	Last	Year	*	None	None	None
USCGC Glacier	8/18/76	9/3/76	*	None	None	None
Discoverer	9/10/76	9/24/76	*	None	None	None

Note: [1] Data Management Plan has been approved by M. Pelto, we await approval by the Contract Officer.

Cruise/Field Operation	Collection Dates		Estimated Submission Dates[1]			
	From	To	Batch 5	6	7	8
Discoverer Leg II 808	6/2/75	6/19/75	*	None	None	None
Silas Bent Leg I 811	8/31/75	9/14/75	None	None	None	None
Discoverer Leg IV 812	10/8/75	10/16/75	*	*	None	None
Miller Freeman	8/16/75	10/20/75	None	Lost	*	*
Discoverer Leg III 810	9/12/75	10/3/75	None	*	None	None
North Pacific	4/25/75	8/7/75	None	Lost	Lost	Lost
Intertidal Biota		1975	None	None	*	*
Discoverer 816	11/23/75	12/2/75	*	None	None	None
Contract 03-5-022-34	Last	year	*	None	*	*
Glacier	8/18/76	9/3/76	*	*	None	None

Cruise/Field Operation	Collection Dates		Estimated Submission Dates[1]	
	From	To	Batch 9	10
Discoverer Leg II 808	6/2/75	6/19/75	*	*
Silas Bent Leg I 811	8/31/75	9/14/75	*	*
Discoverer Leg IV 812	10/8/75	10/16/75	*	*
Miller Freeman	8/16/75	10/20/75	none	none
Discoverer Leg III 810	9/12/75	10/3/75	none	none
North Pacific	4/25/75	8/7/75	none	none
Intertidal Biota		1975	none	none
Discoverer 816	11/23/75	12/2/75	*	*
Contract 03-5-022-34	Last	year	*	none
Moana Wave	3/76	4/15/76	*	none
Beaufort Sea Sediments			*	*

* Suitable format for magnetic tape submission was received 3/21/77. Formating of data will proceed, delivery date is unknown at this time. These data have been submitted in tabular form in the Annual and Quarterly Reports for T/O 12 including the Final report of contract 03-5-022-34.

ANNUAL REPORT

CONTRACT #03-5-022-56
TASK ORDER #5
RESEARCH UNIT #275
REPORTING PERIOD 4/1/76-3/31/77
NUMBER OF PAGES 217

HYDROCARBONS: NATURAL DISTRIBUTION AND DYNAMICS ON THE ALASKAN OUTER CONTINENTAL SHELF

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31 March 1977

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I. SUMMARY

Results of hydrocarbon analyses of biota, water, sediment and seston are reported and discussed. In general these analyses show that the Alaskan OCS environments are free of petroleum at the present time. Petrogenic hydrocarbons were detected in intertidal sediments of the Beaufort Sea. It is not yet known to what extent, if at all, anthropogenic sources contribute to these hydrocarbons.

Efforts to understand and quantify processes by which hydrocarbons in the water column are transported to the benthic environment are described. The two such processes investigated are the association of hydrocarbons and suspended sediments and the scavenging and sedimenting of hydrocarbon droplets by zooplankton. It appears that at least for the conditions of south central Alaska the former process is not highly efficient. Results about the latter process are not yet available.

Brief descriptions of recently begun site specific studies are presented.

II. INTRODUCTION

This report describes progress made during the period April 1976 through March 1977 in a continuing study of the abundance and dynamics of hydrocarbons in Alaskan marine environments which may be impacted by petroleum development on the outer continental shelf. The period covered was one of transition between the baseline phase of this study and group of geographically and intellectually more sharply focused studies.

The baseline studies addressed the question, "What are the kinds and amounts of hydrocarbons present in various components (water, sediment, biota) of the system?" Addressing this question was a logical and necessary first step. This report and our two previous annual reports to NOAA/OCSEAP are a substantial beginning to answering that question. But rather than simply continuing to refine our answer, we have begun to address another question, "What are the processes which control the concentrations of biogenic and petrogenic hydrocarbons in the Alaskan marine environment?" Providing answers to this latter question requires more sophisticated and varied approaches to research design than is needed in the baseline phase. First, some hypotheses about important processes are needed - then plans of field measurements or laboratory experiments are needed to test the hypotheses. These are challenging and rewarding tasks. Performing them successfully gives information that has predictive value, provides a framework for interpreting the baseline data and yields more baseline data at the same time.

This report describes in detail the methods and results of our baseline measurements and discusses the site specific studies which we have begun for the purposes of eludicating processes and simultaneously gathering additional baseline data for important areas.

III. STUDY AREA

We have analysed samples from all regions of interest to NOAA/OCSEAP: the Gulf of Alaska, Cook Inlet, the Bering Sea, Norton Sound, the Chukchi Sea, and the Beaufort Sea. The details of when and where samples were collected are specified in a series of tables in Part V - Results.

IV. METHODS

Sampling

Our sampling procedures have not changed from those described in detail in our previous annual report (Shaw, 1976).

The guiding principles of our sampling are:

1. Samples are processed in the most nearly hydrocarbon free location available under field conditions.
2. Environmental materials for hydrocarbon analysis come in contact only with surfaces which have been cleaned by high heat or repeated solvent rinses.
3. Samples are processed promptly and frozen or in the case of water, chilled.
4. To the greatest extent possible, samples are collected by the person who is to analyse them.

Analytical

Biota and Sediment Samples

Frozen samples to be analysed are thawed. Specific handling prior to weighing is dependent upon material being analysed:

1. Sediment: thawed sediment is ready for weighing.
2. Plants: height measured, plants cut into lengths $\leq$ 2 cm.
3. Molluscs: if a large amount of sediment is on the shells, they are washed in redistilled water. For small molluscs, such as *Macoma*, shells are counted and included in material to be weighed and saponified, but after saponification, shells are weighed and

subtracted out to find total wet weight of soft tissues. For larger molluscs, such as *Mya* and *Mytilus*, soft tissues are removed from shells before weighing. Number and sizes of all molluscs used in samples are recorded.

4. Arthropods: plankton samples are ready for weighing when thawed. Crabs have been analysed using "entire" and "soma" portions. "Entire" indicates that the entire crab was cut into 2 cm^3 pieces, and after saponification the shell weight was subtracted to find tissue wet weight. "Soma" indicates that the carapace was removed after thawing, and only soft body tissues were weighed and saponified. For all crabs, carapace widths are recorded, and sex noted if possible.

5. Fish - some are dissected at sea and some in the lab. All fish used are measured and sexed (if possible). The following list explains terminology of fish parts that are analysed:
    a) Entire - entire fish are cut into 2 cm^3 pieces.
    b) Gills - gill arches, including rakers and filaments are removed from fish, and cut into pieces $\leq$ 1 cm in length (larger pieces caused bumping during saponification).
    c) Flesh - includes muscle tissues cut to 1 cm^3.
    d) Liver - lobes are removed and cut to 2 cm^3.
    e) Skin - epidermis, dermis, and the subcutaneous layers above the muscle tissues are removed, including those tissues between the operculum and caudal fin.
    f) Skin/Fin - pectoral, pelvic, and dorsal fins are removed along with bony fin supports and adjacent tissue layers.

This material is cut into 1 cm^3 pieces (larger pieces cause bumping).

g) Skin/Flesh - includes mid-lateral section of tissue layers from the epidermis of skin, through muscle layers, to the peritoneal lining of abdominal wall. Material is cut to 2 cm^2 segments.

Samples are weighed into clean tared flasks. For some samples, there is excess fluid in the sample jar after thawing. This fluid, or an approximate proportion for the sample used from the jar, is included with sample in flask prior to weighing.

Approximate wet weights for samples (including only soft tissues, i.e., subtracting shells as earlier noted) follows:

Sediment: 80 - 100 g

Plants: 30 - 60 g

Molluscs: 30 - 50 g

Arthropods: 20 - 80 g (25 for most plankton; 2 g is ample for plankton with a high proportion of copepods)

Fish: 40 g for flesh
10 - 20 g for other parts

Once a plant sample has been weighed, the sample is left overnight in 100 ml 4 N aqueous KOH, then 100 ml methanol and boiling chips are added (an exception is noted on Table II). After weighing sediment or animal tissues, 100 ml 1 N aqueous KOH, 100 ml methanol, and boiling chips are added, and the sample is ready for saponification (exceptions noted on Table II). Samples are saponified 24 hours.

Once cooled to room temperature the sample is liquid:liquid extracted three times with 100 ml hexane. If emulsions are created, they are broken by the addition of 5 g NaCl or 10 ml methanol. The hexane extracts are washed with 50 to 100 ml saturated aqueous NaCl, then dried overnight with Na_2SO_4. After drying the hexane extract is transferred to a clean flask and concentrated to 10 ml. A 100 µl aliquot of the hexane extract is air dried and weighed to determine total hexane extractable lipids. The sample is concentrated to 1 ml.

The amount of hexane extractable lipids determines the size of column used in column chromatography, as given in the following table:

Total mg Hexane Extractable Lipid	Column Internal Diameter	Silica for Column	Alumina for Column	Elution Volume
0 - 5	7 mm	2 g	2 g	10 ml
5 - 15	9 mm	10 ml	5 ml	20 ml
15 - 25	11 mm	20 ml	10 ml	40 ml
> 25 - use percentage of sample adequate to run in 50 ml buret, saving remainder in clean vial.				

Columns for chromatography are constructed by stopping the column with glass wool, and adding the appropriate amount of silica gel (5% deactivated) in a hexane slurry. The alumina (6% deactivated) is packed in hexane slurry above the silica.

When the hexane is used in packing, the column is drained flush with the top of the alumina, the sample is added to the top of the column. Once the sample has entered the column, an elution volume of hexane is added, and the eluate, called "Fraction 1", is collected below. When all of the hexane has entered the column, one elution volume of benzene is added to the column. The eluate of benzene collected is called "Fraction 2".

When all the benzene has entered the column, the chromatography is finished and column discarded.

The two eluates, Fractions 1 and 2, are concentrated to 1 ml, and exact volume is determined by weight (hexane = .660 g/ml; benzene = .879 g/ml).

Gas chromatographic analysis is done by injecting 5.0 μl of the sample into a Hewlett-Packard model 5710A with dual flame ionization detectors. The columns are 1/8" x 12' stainless steel packed with 3% OV-101 on Chromosorb W 100-120 AW-DMCS. The temperature program is 2 minutes at 80°C followed by 80 to 280° at 8° per minute, and 16 minutes at 280°C. The carrier gas is nitrogen or helium at 50 ml per minute.

Quantification is done with a Hewlett Packard 3380A integrator using internal and external standards.

Surface Water

A surface water sample for hydrocarbon analysis is weighed before the extraction is begun. It is then liquid:liquid extracted once by the 25 ml CCl_4 which was added during collection and once more with 25 ml CCl_4. The sample is extracted the first time in the sample bottle and the second time in another bottle which has been through the same cleaning procedure. Each bottle is additionally rinsed with 5 ml CCl_4. The extracts are combined in a 250 ml separatory funnel for removal of water. The CCl_4 extract is concentrated to about 2 ml with a rotary evaporator. For non-saponified samples, this extract is injected directly into the gas chromatograph.

In saponified samples, the solvent is changed from CCl_4 to benzene. This is accomplished by adding 10 ml benzene to the concentrated CCl_4 extract and concentrating via a rotary evaporator to 1 ml. This procedure is repeated twice (benzene is added a total of 3 times). The sample is then at a volume of 1.0 ml and the solvent is primarily benzene. The sample is saponified by refluxing for 2 hours with 10 ml benzene, 10 ml 1.0 N KOH in methanol, and 5 ml water. After saponification, the sample is extracted 3 times with 10 ml hexane, the extracts are combined and dried overnight with anhydrous Na_2SO_4.

A 7 cm column of 6% deactivated Al_2O_3 over 5% deactivated SiO_2 (1:2, v:v) is packed and the sample, which has been concentrated to 0.5 ml is placed on the column. Two 2.5 ml fractions are eluted, and collected in clean vials. The first fraction is eluted with hexane and the second is eluted with benzene. Each fraction is concentrated to 0.3 ml with a stream of ultra high purity nitrogen. These fractions of saponified samples are injected directly into the gas chromatograph.

Surface water samples were spiked intermittantly with tetradecane, tetracosane, and perylene in CCl_4. Ten microliters of spike is added to the water sample prior to sealing and storage.

Multi-gallon extractions were performed using 30 ℓ Niskin bottles. These bottles are previously rinsed with reagent solvents and lowered to the surface water immediately upon reaching the selected stations. The 25 ml CCl_4 extracts from repeated one gallon extractions are combined and stored in clean pint bottles.

The samples are analyzed on a Hewlett Packard 5710A gas chromatograph with dual flame ionization detectors. The analytical columns are 12' x 1/8" stainless steel packed with 3% OV-101 on 100 - 120 Chromosorb W (AW-DMCS). Five microliters of the sample are injected and recorded on a 3380A Hewlett Packard integrator.

The carrier gas is helium flowing at 50 ml/minute. Both the injector and detector are held at 300°. The column temperature program includes 2 minutes at 80° followed by a linear temperature rise to 280° at 8°/minute and then 16 minutes at 280°.

A SCOT capillary column was used for some of the analyses. This column, 46 m x 0.7 mm ID, was silanized with 20 ml 4% DMCS and coated with a slurry of 2% OV-101 in $CHCl_3:CH_3OH$ (4:1) on 2% Silanox 101. The carrier gas is nitrogen (ultrahigh purity) flowing at 15 ml/minute with added makeup N_2 prior to the detector at a flow of 30 ml/minute. The column temperature program includes 4 minutes at 75° followed by a linear temperature rise to 280° at 8°/minute and then 16 minutes at 280°.

Seston

Samples of seston, each collected from 740 m^2 of ocean surface were visually inspected for tar lumps which were picked out and weighed on an analytical balance.

Hydrocarbon-Sediment Interaction

Methods of collection and grain size analysis of suspended sediments for this work were reported in our last annual report (Shaw, 1976). X-ray diffraction has been used to determine the mineralogy of the sediment. Associated organics have been removed from some sediment samples by treatment with hydrogen peroxide. Both treated and untreated sediment have been tested for ability to associate with hydrocarbons. Preparations of radio-labeled biphenyl in distilled or saline water were prepared by vigorous shaking for 15 minutes or slow stirring for 16 days. The amount of biphenyl in the test water was determined by liquid scintillation counting (LSC) before sediment was added. A weighed amount of sediment was then shaken with the test water for 2 hours. Water and sediment were then separated by filtration or centrifugation and the amount of biphenyl associated with each fraction determined by LSC. In one experiment the tendency of sediment to desorb biphenyl was measured by then shaking the previously exposed sediment with clean water, separating the phases and counting. These procedures will be reported in greater detail when these experiments are completed.

Strategy for the Analysis of Aromatic Hydrocarbons

The analytical methods for biota, sediment and water are based on procedures developed about a decade ago for the measurement of aliphatic hydrocarbons. Mass spectral analyses of "Fraction 2" of numerous extracts have shown the presence of large amounts of methyl esters and other lipids but only rarely aromatic hydrocarbons. In this situation two important questions emerge about analysis for aromatics.

1. How should the procedure be changed to remove interfering lipids from Fraction 2?
2. When aromatics are detected, which compounds (or classes) should be quantified to have a useful analysis?

A good simple answer to the first question appears to have been reached based on a suggestion by R. Bieri. His modification of the present column chromatography fractionation calls for elution of aromatics with 40% benzene in hexane, a solvent mixture that does not bring esters off the column. We have defined a set of experimental conditions that make this approach work in our laboratory. As soon as we are satisfied with reproducability and recovery, we will begin to use Bieri's separation on a routine basis.

The more basic question of what to quantify has arisen in connection with some coastal Beaufort Sea sediments in which aromatics have been detected. The results obtained are reported and discussed elsewhere in this report but in the present context it should be noted that the procedure used was a time consuming one relying entirely on gas chromatography-mass spectrometry. This has produced some valuable information about the sources of the aromatics; however the method's application to a large number of samples would require a great manpower and instrumentation commitment. We are continuing to explore and evaluate analytical strategies and methods for aromatics. This work is far from complete.

V. RESULTS

Sediment and biological materials collected for hydrocarbon analysis are itemized in Table I. Results of the analyses of these materials are presented in Table II. Concentrations of hydrocarbons are reported in the units of $\mu g\ g^{-1}$ of the material analysed for two fractions and referred to as "Fraction 1" and "Fraction 2". The first of these, Fraction 1, consists of hydrocarbon eluted by hexane in the column chromatography step of sample work of which includes saturated and some olefinic hydrocarbons. Fraction 2 contains larger and more extensively unsaturated hydrocarbons, aromatic hydrocarbons (if present) and some non-hydrocarbon organic compounds. Progress toward removing the non-hydrocarbons has been described above. In addition to the total concentrations of Table II, annotated gas chromatograms are presented in Appendix 1.

TABLE I

SEDIMENT AND BIOTA COLLECTED FOR HYDROCARBON ANALYSIS

Station	Date	Depth	Species/Material	Position
Collections made during a cruise of R/V *Miller Freeman* 8/17/75 - 10/24/75				
MF 1	08/18/75	72.8 m	*Chionocetes opilio*	57°00.0'N - 167°02.9'W 47°58.0'N - 167°05.2'W
MF 2	08/18/75	72.8 m	*Theragra chalcogramma*	57°00.0'N - 167°02.9'W 47°58.0'N - 167°05.2'W
MF 3	08/18/75	75.7 m	*Theragra chalcogramma*	57°01.0'N - 167°36.3'W 57°02.0'N - 167°41.5'W
MF 4	08/18/75	75.7 m	*Chionocetes opilio*	57°01.0'N - 167°36.3'W 57°02.0'N - 167°41.5'W
MF 5	08/19/75	69.6 m	*Chionocetes opilio*	57°19.5'N - 168°53.0'W 57°20.0'N - 168°57.2'W
MF 6	08/19/75	68.3 m	*Chionocetes opilio*	57°40.4'N - 169°35.1'W 57°42.2'N - 169°34.8'W
MF 7	08/20/75	71.0 m	*Chionocetes opilio*	58°18.8'N - 179°20.5'W 58°20.1'N - 170°18.0'W
MF 8	08/20/75	81.0 m	*Chionocetes opilio*	59°39.6'N - 170°59.0'W 58°42.0'N - 171°02.8'W
MF 9	08/20/75	80.1 m	*Chionocetes opilio*	59°20.0'N - 171°46.8'W 59°19.9'N - 171°50.5'W
MF 10	08/21/75	65 m	*Chionocetes opilio*	59°59.7'N - 171°56.1'W 60°00.2'N - 171°56.1'W

TABLE I

(CONTINUED)

Station	Date	Depth	Species/Material	Position
MF 11	08/22/75	61 m	*Theragra chalcogramma*	60°21.1'N - 170°40.0'W 60°19.6'N - 170°39.8'W
MF 12	08/22/75	61 m	*Chionocetes opilio*	60°21.1'N - 170°40.0'W 60°19.6'N - 170°39.8'W
MF 13	08/22/75	50 m	*Chionocetes opilio*	60°20.0'N - 170°01.5'W 60°20.9'N - 169°59.0'W
MF 14	08/23/75	44 m	*Theragra chalcogramma*	59°59.8'N - 169°15.2'W 60°00.8'N - 169°19.0'W
MF 15	08/24/75	46 m	*Theragra chalcogramma*	59°40.8'N - 169°16.0'W 59°40.1'N - 169°12.4'W
MF 16	07/06/75	55 m	*Chionocetes bairdi*	59°44.0'N - 141°14.0'W 59°45.0'N - 141°20.0'W
MF 17	07/06/75	55 m	*Lepidopsetta bilineata*	59°44.0'N - 141°14.0'W 59°45.0'N - 141°20.0'W
MF 18	07/08/75	160 m	*Chionocetes bairdi*	59°28.0'N - 141°33.0'W 59°28.0'N - 141°27.0'W
MF 19	07/08/75	120 m	*Pandalopsis borealis*	59°37.0'N - 141°35.0'W 59°35.0'N - 141°29.0'W
MF 20	07/08/75	120 m	*Chionocetes bairdi*	59°37.0'N - 141°35.0'W 59°35.0'N - 141°29.0'W

TABLE I

(CONTINUED)

Station	Date	Depth	Species/Material	Position
MF 21	07/09/75	165 m	*Pandalopis dispar*	59°37.0'N - 142°01.0'W 59°34.0'N - 141°58.0'W
MF 22	07/09/75	152 m	*Pandalopsis borealis*	59°43.0'N - 142°04.0'W 59°41.0'N - 141°59.0'W
MF 23	07/09/75	152 m	*Pandalopsis borealis*	59°43.0'N - 142°04.0'W 59°41.0'N - 141°59.0'W
MF 24	07/10/75	68 m	*Lepidopsetta bilineata*	59°52.0'N - 141°58.0'W 59°52.0'N - 141°05.0'W
MF 25	07/10/75	68 m	*Lepidopsetta bilineata*	59°52.0'N - 141°58.0'W 59°52.0'N - 141°05.0'W
MF 26	07/10/75	68 m	*Lepidopsetta bilineata*	59°52.0'N - 141°58.0'W 59°52.0'N - 141°05.0'W
MF 27	07/12/75	167 m	*Pandalopsis hypsinotus*	59°45.0'N - 143°03.0'W 59°43.0'N - 143°03.0'W
MF 28	07/13/75	298 m	*Pandalopsis dispar*	59°42.0'N - 143°28.0'W 59°40.0'N - 143°23.0'W
MB 13	08/20/75	81 m	*Chionocetes opilio*	59°39.6'N - 170°59.0'W 58°42.0'N - 171°02.8'W
MB 16	08/20/75	80.1 m	*Chionocetes opilio*	59°20.0'N - 171°46.8'W 59°19.9'N - 171°50.5'W

TABLE I

(CONTINUED)

Station	Date	Depth	Species/Material	Position
MB 18	08/21/75	65 m	*Chionocetes opilio*	59°59.7'N - 171°56.1'W 60°00.2'N - 171°56.1'W
MB 154	07/08/75	120 m	*Chionocetes opilio*	59°37.0'N - 141°35.0'W 59°35.0'N - 141°29.0'W
MB 158	10/04/75	53 m	*Chionocetes opilio*	57°40.3'N - 163°59.0'W
Collections made during a cruise of FR/V *Miller Freeman* 5/17/76 - 6/4/76				
MB 2	05/20/76	40 m	Chaetognaths and fish larvae[1]	55°50.1'N - 162°19.4'W
MB 4	05/21/76	51 m	*Limanda aspera* (gills, liver, skin/flesh)	56°45.4'N - 159°52.9'W 56°43.9'N - 159°55.0'W
MB 5	05/21/76	40 m	Chaetognaths and fish larvae	57°21.1'N - 158°58.2'W
MB 9	05/22/76	54 m	*Paralithoides camtschatica*[1] (soma)	57°49.6'N - 160°07.3'W 57°50.6'N - 160°10.3'W
MB 10	05/23/76	66 m	*Chionocetes bairdi*[1] (soma)	57°17.9'N - 161°06.7'W 57°16.7'N - 161°09.3'W
MB 13	05/20/76	88 m	*Paralithoides camtschatica* (soma)	55°29.3'N - 163°48.1'W 55°31.1'N - 163°50.4'W
			Theragra chalcogramma (gills, liver, skin/flesh)	
MB 14	05/19/76	130 m	Zooplankton - Various taxa	54°42.6'N - 165°27.4'W

TABLE I

(CONTINUED)

Station	Date	Depth	Species/Material	Position
MB 16	05/25/76	197 m	*Chionocetes bairdi*	54°53.1'N - 166°48.7'W 54°53.5'N - 166°52.1'W
			Hipoglossus stenolepis (gills, liver)	
MB 19	05/24/76	77 m	*Limanda aspera* (gills, liver)	56°39.8'N - 163°57.1'W 56°40.9'N - 163°59.5'W
MB 22	05/23/76	46 m	*Paralithoides camtschatica*[1] (soma)	57°50.4'N - 162°15.5'W 57°48.8'N - 162°15.5'W
			Pleuronectes quadrituberculatus (gills, liver, skin/flesh, skin/fins)	
MB 25	05/23/76	37 m	*Pleuronectes quadrituberculatus* (gills, liver, skin/flesh, skin/fins)	58°19.2'N - 163°13.3'W 58°17.6'N - 163°13.2'W
MB 28	05/31/76	71 m	*Chionocetes opilio*	57°11.0'N - 165°02.4'W 57°10.0'N - 165°04.6'W
			Pleuronectes quadrituberculatus (gills, liver, skin/fin)	
MB 28	05/31/76	70 m	Chaetognaths and euphausiids	57°09.1'N - 165°06.1'W

TABLE I

(CONTINUED)

Station	Date	Depth	Species/Material	Position
MB 31	05/25/76	140 m	Copepods with some euphausiids, chaetognaths, amphipods, and terapods	55°21.4'N - 167°47.1'W
MB 37	05/29/76	76 m	Euphasiids, chaetognaths, and copepods	57°06.1'N - 166°58.3'W
MB 46	05/28/76	73 m	*Pleuronectes quadrituberculatus* (gills, liver, skin/flesh, and skin/fin)	57°34.6'N - 168°06.0'W 57°34.6'N - 168°02.5'W
MB 55	05/26/76	65 m	Amphipods, chaetognaths, 2 jellyfish, few euphausiids, and copepods	57°28.9'N - 169°60.0'W
MB 55A	05/26/76	75 m	*Limanda aspera* (gills, liver, skin/flesh, skin/fin)	57°35.9'N - 170°14.2'W 57°37.2'N - 170°15.9'W
MB 56	05/28/76	65 m	Chaetognaths, euphausiids, copepods, few amphipods	58°04.6'N - 169°03.3'W
MB 64	05/26/76	80 m	Copepods, euphausiids, and chaetognaths	57°59.9'N - 171°01.1'W
MB 69	05/27/76	117 m	*Theragra chalcogramma* (gills, liver, skin/flesh)	57°56.2'N - 173°01.0'W 57°56.3'N - 173°03.9'W
MB 70	05/27/76	90 m	Copepods, chaetognaths, some euphausiids and amphipods	58°27.0'N - 172°06.1'W

TABLE I

(CONTINUED)

Station	Date	Depth	Species/Material	Position
MB 86B	05/27/76	117 m	*Theragra chalcogramma* (gills, liver, skin/flesh)	58°40.8'N - 173°03.5'W 58°39.3'N - 173°02.6'W
MB 86B	05/27/76	117 m	Copepods, euphausiids, and some chaetognaths	58°40.7'N - 173°09.0'W
Collections made at Cottonwood Bay, Oil Bay, and Right Arm of Iniskin Bay 6/21/76 - 6/26/76				
OB 1	06/21/76	--	Water	59°40.75'N - 153°20.00'W
OB 2	06/21/76	--	Water	59°40.75'N - 153°20.00'W
OB 3	06/21/76	--	Water	59°40.5 'N - 153°19.33'W
OB 4	06/21/76	--	Water	59°40.25'N - 153°19.09'W
OB 5	06/21/76	--	Water	59°40.17'N - 153°19.17'W
OB 6	06/21/76	--	Water	59°40.33'N - 153°19.41'W
OB 7	06/21/76	--	Water	59°40.00'N - 153°18.83'W
OB 8	06/21/76	--	Water/Sea	59°40.09'N - 153°18.33'W
OB 9	06/21/76	--	Sediment	59°40.00'N - 153°18.83'W
OB 10	06/21/76	--	Sediment	59°40.00'N - 153°18.83'W

TABLE I

(CONTINUED)

Station	Date	Depth	Species/Material	Position
IB 1	06/22/76	--	*Mya arenaria*	59°43.83'N - 153°20.67'W
IB 2	06/22/76	--	Sediment sheen	59°43.70'N - 153°20.33'W
IB 3	06/22/76	--	Sediment	59°43.41'N - 153°20.00'W
IB 4	06/23/76	--	*Macoma balthica*	59°43.83'N - 153°20.67'W
IB 5	06/23/76	--	Water	59°43.75'N - 153°20.50'W
IB 6	06/23/76	--	Sediment	59°43.83'N - 153°20.67'W
IB 7	06/23/76	--	Sediment	59°43.70'N - 153°20.33'W
CB 1	06/26/76	--	*Macoma balthica*	59°37.67'N - 153°40.00'W
CB 2	06/26/76	--	*Mya arenaria*	59°37.67'N - 153°40.00'W
CB 3	06/26/76	--	Sediment	59°37.67'N - 153°40.00'W
CB 4	06/26/76	--	*Fucus distichus*	59°37.67'N - 153°40.00'W

Collections made at Katalla Bay, Simpson Bay, Resurrection Bay at Seward, and Izembek Lagoon at Cold Bay 7/19/74 - 11/7/76

KT	04/24/75	--	*Fucus distichus*	60°11.75'N - 144°30.95'W
RB	09/10/76	--	*Fucus distichus*	60°07.33'N - 149°22.40'W

TABLE I

(CONTINUED)

Station	Date	Depth	Species/Material	Position
SB	07/19/74	--	*Mytilus edulis*	60°38.00'N - 145°51.50'W
IL	11/07/76[2]	--	*Zostera marina*	55°16.00'N - 162°53.00'W
Collections made in the Beaufort Sea at Iko Bay, Smith Bay West, Cape Simpson, and Dease Inlet 8/23/76 - 8/27/76				
IK		--	Sediment	71°10.9'N - 156°02.0'W
SBW		--	Sediment	70°58.3'N - 154°34.0'W
CS 1		--	Sediment from lake near oil seep	71°02.0'N - 154°51.0'W
CS 2		--	Sediment from oil seep	70°59.4'N - 154°36.8'W
DI 1		--	Sediment in water	71°00.7'N - 155°14.2'W
DI 2		--	Sediment from beach	71°00.7'N - 155°14.2'W

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[1] Methanol added to some samples before freezing.

[2] Not frozen immediately after collection. Sample carried in plastic bag to aquarium in lab. Removed from aquarium for hydrocarbon analysis 11/16/76.

TABLE II

CONCENTRATIONS OF HYDROCARBONS IN SEDIMENT AND BIOTA.

Sample	Material/Species	Hydrocarbon Concentration µg/g Fraction 1	 Fraction 2
SEDIMENT			
CB 3	Sediment	1.0	.72
IB 2	Sediment	.16	.50
IB 3	Sediment	.49	.16
IK	Sediment	2.4	2.8
DI 1	Sediment in Water	20.	2.7
DI 2	Sediment from Beach	15.	9.7
CS 1	Sediment near Oil Seep	18.	2.3
PLANTS			
CB 4	*Fucus distichus*	13.	70.
CB 4	*Fucus distichus*[1]	10.	48.
KT	*Fucus distichus*	17.	5.0
RB	*Fucus distichus*	5.3	21.
IL	*Zostera marina* - leaves[2]	33.	7.5
IL	*Zostera marina* - entire plants[2]	17.	6.1
IL	*Zostera marina* - roots[2]	1.7	1.2

TABLE II

(CONTINUED)

Sample	Material/Species	Hydrocarbon Concentration µg/g Fraction 1	Fraction 2
MOLLUSCS			
CB 1	*Macoma balthica*	4.7	4.3
IB 4	*Macoma balthica*	13.	5.7
CB 2	*Mya arenaria*	.88	.87
IB 1	*Mya arenaria*	3.9	3.0
Unimak Island[3] (Sennett Pt.)	*Mytilus edulis*	<.01	4.3
Unimak Island[3] (Cape Lupin)	*Mytilus edulis*	0.4	5.2
Unalaska Island[3] (Eider Pt.)	*Mytilus edulis*	0.6	7.3
Sitkalidek Lagoon[3]	*Mytilus edulis*	0.4	5.5
SB	*Mytilus edulis*	0.4	3.0
SB	*Mytilus edulis*	.07	.61
ARTHROPODS			
MB 64	Copepods, euphausiids, and chaetognaths[4]	520.	<.01
MB 86B	Copepods, euphausiids, some chaetognaths	1700.	-
MB 31	Copepods with some euphausiids, chaetognaths, amphipods, and terapods	1600.	-
MB 31	Copepods with some euphausiids, chaetognaths, amphipods, and terapods	1100.	-

TABLE II

(CONTINUED)

Sample	Material/Species	Hydrocarbon Concentration µg/g Fraction 1	 Fraction 2
MB 31	Copepods with some euphausiids, chaetognaths, amphipods, and terapods	1500.	-
MB 31	Copepods with some euphausiids, chaetognaths, amphipods, and terapods[5]	1900.	<.01
MB 31	Copepods with some euphausiids, chaetognaths, amphipods, and terapods[6]	2900.	<.01
MB 56	Chaetognaths, euphausiids, copepods, few amphipods	66.	39.
MB 13	*Chionocetes opilio* - entire	0.2	2.1
MB 16(1)	*Chionocetes opilio* - entire	3.1	3300.
MB 16(2)	*Chionocetes opilio* - entire	1.0	330.
MB 18	*Chionocetes opilio* - entire	0.1	18.
MB 154	*Chionocetes opilio* - entire	0.8	62.
MB 158	*Chionocetes opilio* - entire	0.5	45.
MF 13	*Chionocetes opilio* - soma	<.01	.27
MB 9(1)	*Paralithoides camtschatica* - soma	<.01	8600.
MB 9(2)	*Paralithoides camtschatica* - soma	0.9	2000.
FISH			
MB 16	*Hipoglossus stenolepis* - gills	6.6	130.
MB 16	*Hipoglossus stenolepis* - liver	6.9	1.9

TABLE II

(CONTINUED)

Sample	Material/Species	Hydrocarbon Concentration µg/g Fraction 1	 Fraction 2
MB 19	*Limanda aspera* - gills	33.	.28
MB 19	*Limanda aspera* - liver	4.0	2.9
MB 25	*Pleuronectes quadrituberculatus* - gills	<.01	1.9
MB 28	*Pleuronectes quadrituberculatus* - skin/fin	<.01	3.6
MB 28	*Pleuronectes quadrituberculatus* - skin/fin	<.01	6.5
MB 28	*Pleuronectes quadrituberculatus* - skin/fin	<.01	4.1
MB 46	*Pleuronectes quadrituberculatus* - skin/flesh	<.01	3.4
MB 25	*Pleuronectes quadrituberculatus* - skin/flesh	<.01	2.2
MF 11	*Theragra chalcogramma* - entire fish	.62	4.1
MF 20	*Theragra chalcogramma* - flesh	.36	3.0
MF 2 and 21	*Theragra chalcogramma* - gills	8.9	12.
MF 30 and 34	*Theragra chalcogramma* - gills	1.7	14.
MF 69	*Theragra chalcogramma* - gills	0.9	6.8
MB 86B	*Theragra chalcogramma* - gills	1.0	9.1
MF 2 and 21	*Theragra chalcogramma* - liver	1800.	300.
MF 30 and 34	*Theragra chalcogramma* - liver	49.	160.
MB 86B	*Theragra chalcogramma* - liver	19.	170.
MB 86B	*Theragra chalcogramma* - liver	17.	300.
MB 86B	*Theragra chalcogramma* - liver	-	470.
MB 86B	*Theragra chalcogramma* - liver	21.	590.

TABLE II

(CONTINUED)

Sample	Material/Species	Hydrocarbon Concentration μg/g Fraction 1	Fraction 2
MF 2 and 21	*Theragra chalcogramma* - skin	7.3	30.
MF 20, 30 and 34	*Theragra chalcogramma* - skin	3.5	12.
MB 86B	*Theragra chalcogramma* - skin/flesh	.12	2.3
MB 86B	*Theragra chalcogramma* - skin/flesh	.12	47.
MB 69	*Theragra chalcogramma* - skin/flesh	.06	-

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[1] Virtis homogenized sample, added 100 ml 1 N aq. KOH, 100 ml methanol, boiling chips, and immediately saponified.

[2] Not frozen immediately after collection. Samples carried in plastic bag to aquarium in lab. Removed from aquarium for hydrocarbon analysis 11/16/76.

[3] Collected 5/20/76 to 6/17/76 by S. Zimmerman.

[4] Groups of plankton listed in order of major components in the sample.

[5] 200 ml 2 N KOH, no methanol for saponification.

[6] 100 ml 2 N KOH, 100 ml ethanol for saponification.

Stations of which surface water samples for hydrocarbon analysis were taken are listed in Table IIIa-e. Table IVa-e reports concentrations of hydrocarbons found in water in the units of $\mu g\ kg^{-1}$. The meaning of "Fraction 1" and "Fraction 2" are the same as for biota and sediment. Annotated gas chromatograms are presented in Appendix 2.

Stations sampled for tar in seston and the results obtained are listed in Table V.

Preliminary results concerning the association of Gulf of Alaska suspended sediment with biphenyl are shown in Table VI. A single experiment indicates that of the biphenyl which associates with the sediment particles, 80-90% is rapidly desorbed when the sediment comes into contact with clean water.

VI. DISCUSSION

Biota

Samples of a total of eleven identified species have been investigated. These include two species of plants, three species of mollusc, two species of crab, mixed collections of zooplankton, and four species of fish.

Both of the plant species investigated are benthic macrophytes, *Fucus distichus* and *Zostera marina*, which support important detritus food webs. Both species are common in intertidal and shallow subtidal zones of Alaska and elsewhere. *Fucus distichus* is found in rocky areas while *Z. marina* grows in silty sediments. The major hydrocarbons in *F. distichus* include pentadecane, heptacosane, the 21:5, 21:6 and 25:4 polyolefins and squalene. For all of the analyses reported here, pentadecane constituted less than half of the total hydrocarbon content. Youngblood *et al.* (1971) found that 98% of the hydrocarbon content of *F. distichus* was pentadecane. These two results become compatable in light of the observation we have made during

TABLE IIIa

STATION LOCATIONS OF HYDROCARBON SURFACE WATER SAMPLING IN THE GULF OF ALASKA BY THE R/V *MOANA WAVE* 24 FEB - 29 FEB 1976

		Position	
Station	Date Taken	Latitude	Longitude
GASS 01	2/21/76	59°50.2'	149°30.5'
GASS 02	2/21/76	59°41.5'	149°22.0'
GASS 03	2/21/76	59°33.0'	149°13.2'
GASS 04	2/21/76	59°24.5'	149°04.9'
GASS 05	2/22/76	59°16.0'	148°56.0'
GASS 06	2/22/76	59°07.2'	148°47.5'
GASS 07	2/22/76	58°58.7'	148°38.7'
GASS 08	2/22/76	58°49.7'	148°30.0'
GASS 09	2/22/76	58°41.1'	148°21.6'
GASS 10	2/23/76	58°32.3'	148°13.2'
GASS 11	2/24/76	58°23.2'	148°04.8'
GASS 15	2/24/76	58°18.1'	145°00.5'
GASS 24	2/25/76	58°54.3'	141°00.5'
GASS 29	2/26/76	59°34.6'	140°06.0'
GASS 37	2/27/76	59°16.2'	142°59.2'
GASS 39	2/27/76	59°35.7'	142°49.5'
GASS 41	2/27/76	59°55.1'	142°39.5'
GASS 47	2/29/76	59°17.5'	145°13.0'
GASS 50	2/27/76	59°47.7'	145°09.0'
GASS 52	2/28/76	60°07.6'	145°06.5'
GASS 53	2/29/76	60°23.0'	146°54.0'
GASS 57	2/29/76	59°45.6'	146°31.0'
GASS 58	2/29/76	59°36.2'	146°25.5'
GASS 59A(75)	2/29/76	59°17.1'	146°14.0'

TABLE IIIb

STATION LOCATIONS OF HYDROCARBON SURFACE WATER SAMPLING IN THE GULF OF ALASKA BY THE R/V *MOANA WAVE* 20 APRIL - 2 MAY 1976

Station	Date Taken	Position	
		Latitude	Longitude
GASS 02	4/20/76	59°41.5'	149°22.0'
GASS 06	4/20/76	59°07.2'	148°47.5'
GASS 15	4/21/76	58°18.1'	145°00.5'
GASS 24	4/22/76	58°54.3'	141°00.5'
GASS 30	4/22/76	59°44.1'	141°27.9'
GASS 37	4/23/76	59°16.2'	142°59.2'
GASS 39	4/23/76	59°35.7'	142°49.5'
GASS 41	4/23/76	59°55.1'	142°39.5'
GASS 47	4/24/76	59°17.5'	145°13.0'
GASS 50	4/24/76	59°47.7'	145°09.0'
GASS 52	4/24/76	60°07.6'	145°06.5'
PWS 70	4/25/76	58°59.7'	151°47.0'
GASS 101	4/28/76	59°19.8'	152°24.1'
GASS 107	4/28/76	58°18.6'	150°28.0'
GASS 115	4/29/76	57°20.6'	148°38.7'
GASS 118	4/29/76	57°00.0'	148°00.0'
GASS 125	4/30/76	55°58.9'	154°28.5'
GASS 128	4/30/76	55°35.3'	153°56.7'
GASS 131	4/30/76	55°10.7'	153°25.7'

TABLE IIIc

STATION LOCATIONS OF HYDROCARBON SURFACE WATER SAMPLING IN COOK INLET BY R/V *ACONA* 25 JUNE - 27 JUNE 1976

Station	Date Taken	Position	
		Latitude	Longitude
CI 01	6/27/76	59°03.1'N	151°52.4'W
CI 02	6/27/76	59°03.25'N	152°41.2'W
CI 03	6/27/76	59°03.1'N	153°23.4'W
CI 04	6/26/76	59°17.7'N	152°07.7'W
CI 05	6/27/76	59°17.2'N	152°41.1'W
CI 06	6/27/76	59°17.2'N	153°14.1'W
CI 07	6/27/76	59°42.7'N	151°07.4'W
CI 08	6/27/76	59°34.2'N	151°25.4'W
CI 09	6/27/76	59°33.2'N	151°36.4'W
CI 10	6/27/76	59°35.4'N	151°49.7'W
CI 11	6/25/76	59°35.3'N	152°09.8'W
CI 12	6/25/76	59°35.25'N	152°29.8'W
CI 13	6/25/76	59°35.25'N	152°49.8'W
CI 14	6/26/76	59°35.2'N	153°16.7'W
CI 15	6/26/76	59°46.2'N	152°08.7'W
CI 16	6/25/76	59°46.3'N	152°45.3'W
CI 17	6/26/76	60°01.2'N	151°53.2'W
CI 18	6/26/76	60°01.2'N	152°01.9'W
CI 19	6/26/76	60°01.3'N	152°21.1'W
CI 20	6/26/76	60°01.2'N	151°31.4'W

TABLE IIId

STATION LOCATION OF HYDROCARBON SURFACE WATER SAMPLING IN NORTON SOUND BY USNOSS *DISCOVERER* 10 SEPT - 24 SEPT 1976

Station	Date Taken	Position	
		Latitude	Longitude
N 04	9/13/76	63°19.2'N	165°30.2'W
N 07	9/12/76	63°38.2'N	163°30.3'W
N 22	9/11/76	64°34.2'N	162°00.2'W
N 24	9/14/76	64°30.0'N	167°30.0'W
N 26	9/14/76	64°30.2'N	166°31.5'W
N 30	9/15/76	65°28.7'N	168°28.4'W
C 3	9/22/76	66°28.4'N	166°59.8'W
C 6	9/17/76	66°23.2'N	162°14.8'W
C 10	9/16/76	67°00.0'N	167°01.7'W
C 12	9/22/76	67°27.2'N	168°18.5'W
C 20	9/20/76	68°27.2'N	167°02.3'W
C 21	9/21/76	69°00.2'N	168°19.2'W

TABLE IIIe

STATION LOCATION OF HYDROCARBON SURFACE WATER SAMPLING IN THE BEAUFORT SEA BY USCGC *GLACIER* 23 AUG - 2 SEPT 1976

		Position	
Station	Date Taken	Latitude	Longitude
BS 1	8/23/76	70°36.0'N	148°11.0'W
BS 2	8/24/76	70°36.65'N	148°21.43'W
BS 3	8/25/76	70°31.28'N	147°31.22'W
BS 4	8/26/76	70°39.03'N	147°40.54'W
BS 5	8/27/76	70°47.59'N	149°04.35'W
BS 6	8/27/76	70°57.31'N	149°31.81'W
BS 7	8/28/76	71°07.99'N	151°19.45'W
BS 8	8/29/76	71°43.16'N	151°46.72'W
BS 9	8/30/76	71°34.99'N	152°16.60'W
BS 10	8/30/76	71°22.14'N	152°20.09'W
BS 11	8/31/76	71°19.04'N	152°32.40'W
BS 12	9/1/76	71°07.63'N	152°57.97'W
BS 13	9/2/76	71°23.5'N	154°23.0'W
BS 14	9/2/76	71°34.6'N	155°35.2'W

TABLE IVa & b

HYDROCARBON CONCENTRATIONS IN WATER FROM THE GULF OF ALASKA, 1976

GASS	Date	µg/Kg Fraction 1	µg/Kg Fraction 2	Date	µg/Kg Fraction 1	µg/Kg Fraction 2
01	2/21	0.11	ND	-	-	-
02	2/21	0.07	ND	4/20	ND	0.08 NB
03	2/21	0.17	0.02	-	-	-
04	2/21	0.32	0.02	-	-	-
05	2/22	0.03	ND	-	-	-
06	2/22	0.02	ND	4/20	1.53*	0.16
07	2/22	0.04	ND	-	-	-
08	2/22	0.12	0.10	-	-	-
09	2/22	ND	0.09	-	-	-
10	2/23	0.11	0.24	-	-	-
11	2/24	0.15	0.22	-	-	-
15	2/24	0.09	0.15	4/20	1.00*	0.95
24	2/25	0.17	ND	4/22	0.54*	0.33
29	2/26	0.56	0.16	-	-	-
30	-	-	-	4/22	0.86*	0.59
37	2/27	0.04	0.08	4/23	0.86*	0.19
39	2/27	0.06	0.07	4/23	0.37*	0.14
41	2/27	0.18	0.03	4/23	1.81*	7.72
47	2/29	1.51	0.04	4/24	1.02*	0.36
50	2/27	0.05	ND	4/24	2.06 NB*	0.08 NB
52	2/28	0.05	ND	4/24	0.58*	0.55
53	2/29	0.11	0.08	-	-	-
57	2/29	0.19	0.07	-	-	-
58	2/29	0.18	0.05	-	-	-
59A(75)	2/29	0.06	0.33	-	-	-
70	4/25	0.49*	0.36	-	-	-
101	4/28	0.66 NB*	0.16 NB	-	-	-
107	4/28	0.85*	0.59	-	-	-
115	4/29	0.55 NB*	0.10 NB	-	-	-
118	4/29	0.40*	1.23	-	-	-

TABLE IVa & b

CONTINUED

GASS	Date	µg/Kg Fraction 1	µg/Kg Fraction 2	Date	µg/Kg Fraction 1	µg/Kg Fraction 2
125	4/30	0.60*	0.40	-	-	-
128	4/30	0.08*	0.09	-	-	-
131	4/30	0.13*	0.14	-	-	-

µg/Kg = µg of sample detected per Kg surface water extracted

ND = None detectable < 0.02 µg/Kg

NB = Niskin bottle extraction was performed

* = Adjusted value from 85% recovery of PHR spike added

TABLE IVc

HYDROCARBON CONCENTRATIONS IN WATER FROM COOK INLET, ALASKA, 1976

Station	Date	μg/Kg Fraction 1	μg/Kg Fraction 2
CI 01	6/27	0.17*	0.05
CI 02	6/27	0.71*	0.41
CI 03	6/27	0.46*	0.21
CI 04	6/26	0.14*	0.04
CI 05	6/27	0.02*	0.29
CI 06	6/27	0.12* NB	0.10 NB
CI 07	6/27	0.33*	0.04
CI 08	6/27	0.50*	0.61
CI 09	6/27	0.25*	L
CI 10	6/27	0.52*	0.20
CI 11	6/25	0.30*	0.39
CI 12	6/25	0.38*	0.26
CI 13	6/25	L	L
CI 14	6/26	1.02*	0.44
CI 15	6/26	0.76*	ND
CI 16	6/25	0.41*	0.13
CI 17	6/26	0.11*	0.91
CI 18	6/26	0.15* NB	0.16 NB
CI 19	6/26	0.20*	0.15
CI 20	6/26	L	L

L = Lost during sample preparation

μg/Kg = μg of sample detected per Kg surface water extracted

NB = Niskin bottle extraction was performed

* = Adjusted from 61.52% recovery of PHR spike added, standard deviation 18.24

ND = None detectable

TABLE IVd

HYDROCARBON CONCENTRATIONS IN SURFACE WATER FROM NORTON SOUND AND CHUKCHI SEA

Station	Date	μg/Kg
N 04	9/13/76	L
N 07	9/12/76	1.36*
N 22	9/11/76	0.64**
N 24	9/14/76	0.60
N 26	9/14/76	0.34
N 30	9/15/76	0.68*
C 3	9/22/76	1.02**
C 6	9/17/76	0.13
C 10	9/16/76	0.88**
C 12	9/22/76	0.86
C 20	9/20/76	0.27**
C 21	9/21/76	1.41*

μg/Kg = μg of sample detected per Kg surface water extracted

L = Lost during sample preparation

* = Adjusted value from 48.2% recovery of PHR spike added

** = Adjusted value from 59.1% recovery of PHR spike added

TABLE IVe

HYDROCARBON CONCENTRATIONS IN SURFACE WATER FROM BEAUFORT SEA

Station	Date	µg/Kg Fraction 1	µg/Kg Fraction 2
BS 1	8/23/76	27.16	0.43
BS 2	8/24/76	6.92	0.08
BS 3	8/25/76	0.17	0.19
BS 4	8/26/76	1.49	0.10
BS 5	8/27/76	0.27	0.20
BS 6	8/27/76	0.41	0.90
BS 7	8/28/76	0.17	0.07
BS 8	8/29/76	0.14	0.25
BS 9	8/30/76	0.48	0.28
BS 10	8/30/76	0.42	0.04
BS 11	8/31/76	0.42	0.69
BS 12	9/1/76	0.11	0.45
BS 13	9/2/76	0.05	0.83
BS 14	9/2/76	0.18	0.14

µg/Kg = µg of sample detected per Kg surface water extracted

TABLE V

SESTON COLLECTIONS FOR FLOATING TAR

Station	Date Taken	Location Latitude	 Longitude	Tar (mg)
GASS 02	4/20/76	59°49.5'N	149°22.0'W	-
GASS 06	4/20/76	59°07.2'N	148°47.5'W	115.8
GASS 15	4/21/76	58°18.1'N	145°00.5'W	-
GASS 24	4/22/76	58°54.3'N	141°00.5'W	-
GASS 30	4/22/76	59°44.1'N	141°36.8'W	-
GASS 37	4/23/76	59°16.2'N	142°59.2'W	-
GASS 39	4/23/76	59°35.7'N	142°49.5'W	-
GASS 41	4/23/76	59°55.1'N	142°39.5'W	4.6
GASS 47	4/24/76	59°17.5'N	145°13.0'W	-
GASS 50	4/24/76	59°47.7'N	145°09.0'W	-
GASS 52	4/24/76	60°07.6'N	145°06.5'W	-
GASS 101	4/28/76	59°19.8'N	152°24.1'W	-
GASS 107	4/28/76	58°18.6'N	150°28.0'W	-
GASS 115	4/29/76	57°20.6'N	148°38.7'W	-
GASS 118	4/29/76	57°00.0'N	148°00.0'W	-
GASS 121	5/1/76	56°43.2'N	155°27.9'W	-
GASS 125	4/30/76	55°58.9'N	154°28.5'W	-
GASS 128	4/30/76	55°35.3'N	153°56.7'W	-
GASS 131	4/30/76	55°10.7'N	153°25.7'W	2.0
PWS 70	4/25/76	58°59.7'N	151°47.0'W	-
AH 11	10/25/76	52°20.0'N	158°00.0'W	31.8
AH 26	10/27/76	47°20.0'N	158°00.0'W	75.5
AH 31	10/28/76	45°40.0'N	158°00.0'W	46.5
AH 35	10/28/76	44°20.0'N	158°00.0'W	23.3
AH 44	10/30/76	41°20.0'N	158°00.0'W	3.0
AH 45	10/30/76	41°00.0'N	158°00.0'W	13.6
AH 49	10/31/76	39°40.0'N	158°00.0'W	72.8
AH 52	10/31/76	38°40.0'N	158°00.0'W	158.9
AH 56	11/1/76	37°20.0'N	158°00.0'W	136.5
AH 59	11/1/76	36°28.0'N	158°00.0'W	34.3

TABLE V

CONTINUED

Station	Date Taken	Location		Tar (mg)
		Latitude	Longitude	
AH 63	11/2/76	35°00.0'N	158°00.0'W	64.9
AH 66	11/2/76	33°30.0'N	158°00.0'W	201.4
AH 69	11/3/76	31°59.2'N	158°00.0'W	931.3
AH 70	11/3/76	31°30.0'N	158°00.0'W	114.2
AH 72	11/3/76	30°30.0'N	158°00.0'W	116.3
AH 76	11/4/76	28°30.0'N	158°00.0'W	214.4
AH 80	11/4/76	26°29.5'N	158°00.0'W	19.1
AH 82	11/5/76	25°30.0'N	158°00.0'W	243.5
AH 85	11/5/76	24°00.0'N	158°00.0'W	5.9
AH 88	11/6/76	22°30.0'N	158°00.0'W	47.4
N 01	9/13/76	63°59.4'N	165°31.3'W	-
N 03	9/13/76	63°38.4'N	164°31.0'W	-
N 04	9/13/76	63°19.2'N	165°30.2'W	-
N 06	9/12/76	63°38.4'N	164°31.0'W	-
N 07	9/12/76	63°38.2'N	163°30.3'W	-
N 11	9/14/76	64°01.0'N	167°31.6'W	-
N 13	9/13/76	63°59.7'N	165°29.7'W	-
N 16	9/12/76	64°00.0'N	162°30.0'W	-
N 18F	9/22/76	67°57.3'N	165°47.8'W	-
N 20	9/12/76	64°20.4'N	163°32.7'W	-
N 22	9/11/76	64°34.2'N	162°00.2'W	-
N 26	9/14/76	64°30.2'N	166°31.5'W	-
N 28	9/15/76	65°00.0'N	167°32.7'W	-
C 3	9/22/76	66°28.4'N	166°59.8'W	-
C 6	9/17/76	66°23.2'N	162°14.8'W	-
C 7	9/16/76	66°43.8'N	163°18.9'W	-
C 9	9/16/76	66°59.9'N	167°01.9'W	-
C 10	9/16/76	67°00.0'N	167°01.7'W	-
C 11	9/16/76	66°59.7'N	165°42.0'W	-
C 12	9/22/76	67°27.2'N	168°18.5'W	-

TABLE V

CONTINUED

Station	Date Taken	Location		Tar
		Latitude	Longitude	(mg)
C 13	9/20/76	67°31.8'N	167°00.8'W	-
C 16	9/21/76	68°30.0'N	168°22.0'W	-
C 18	9/20/76	67°57.3'N	165°47.8'W	-
C 20	9/20/76	68°27.2'N	167°02.3'W	-
C 21	9/21/76	69°00.2'N	168°19.2'W	-
CI 01	6/27/76	59°03.1'N	151°52.4'W	-
CI 02	6/27/76	59°03.25'N	152°41.2'W	-
CI 03	6/27/76	59°03.1'N	153°23.4'W	-
CI 04	6/26/76	59°17.1'N	152°07.7'W	-
CI 05	6/27/76	59°17.2'N	152°41.1'W	-
CI 06	6/27/76	59°17.2'N	153°14.1'W	-
CI 07	6/27/76	59°42.7'N	151°07.4'W	-
CI 08	6/27/76	59°34.2'N	151°25.4'W	-
CI 09	6/27/76	59°33.2'N	151°36.4'W	-
CI 10	6/27/76	59°35.4'N	151°49.7'W	<.1
CI 11	6/25/76	59°35.3'N	152°09.8'W	-
CI 12	6/25/76	59°35.25'N	152°29.8'W	-
CI 13	6/25/76	59°35.25'N	152°49.8'W	-
CI 14	6/26/76	59°35.2'N	153°16.7'W	-
CI 15	6/26/76	59°46.2'N	152°08.7'W	-
CI 16	6/25/76	59°46.3'N	152°45.3'W	-
CI 17	6/26/76	60°01.2'N	151°53.2'W	-
CI 18	6/26/76	60°01.2'N	152°01.9'W	-
CI 19	6/26/76	60°01.3'N	152°21.1'W	-
CI 20	6/26/76	60°01.2'N	151°31.4'W	-
GASS 01	2/21/76	59°50.2'N	149°30.5'W	-
GASS 06	2/22/76	59°07.2'N	148°47.5'W	1.1
GASS 15	2/24/76	58°18.1'N	145°00.5'W	-
GASS 24	2/25/76	58°54.3'N	141°00.5'W	-
GASS 29	2/26/76	59°34.6'N	140°06.0'W	-

TABLE V

CONTINUED

Station	Date Taken	Location		Tar (mg)
		Latitude	Longitude	
GASS 37	2/27/76	59°16.2'N	142°59.2'W	-
GASS 39	2/27/76	59°35.7'N	142°49.5'W	-
GASS 41	2/27/76	59°55.1'N	142°39.5'W	<.1
GASS 47	2/29/76	59°17.5'N	145°13.0'W	-
GASS 50	2/27/76	59°47.7'N	145°09.0'W	-
GASS 52	2/28/76	60°07.6'N	145°06.5'W	-
GASS 53	2/29/76	60°23.0'N	146°54.0'W	-

TABLE VI

PARTITION OF BIPHENYL BETWEEN WATER AND SUSPENDED SEDIMENT

% Saturation of biphenyl in test water*	S°/oo	Sediment[†] type	% of biphenyl present		
			on sediment	in water	on filter
3.7	0	+	0.16	81.5	0.016
30.7	0	+	0.15	82.3	0.013
101.3	0	+	1.37	80.7	0.067
3.7	35	+	0.86	98.0	0.114
30.7	35	+	0.79	99.6	0.116
101.3	35	+	20.10	51.8	1.41
2.7	0	-	1.79	78.5	0.180

* based on 7.5 mg/ℓ for biphenyl at saturation

[†] + = sediment treated with H_2O_2; - = untreated sediment

the analysis of other samples of Alaskan *F. distichus* that our results reported here apply to samples collected in summer, but that in winter pentadecane is the chief hydrocarbon. Youngblood and Blumer (1973) have also reported the presence of a 21:6 polyene in *F. distichus*. One of the *F. distichus* samples (RB) contains an array of linear alkanes centered at nonacosane. Similar arrays have been noted by several workers in seawater samples. However, their origin (biogenic, petrogenic, or artifact) remains unknown. These and other analyses of *F. distichus* show that, although the variability of biogenic hydrocarbon composition is less than for animals with variable dietary inputs, distinct hydrocarbon changes occur as a result of seasonal, growth and reproductive cycles. The dominant hydrocarbons of *Zostera marina* include pentadecane, heptadecane, nonadecane, and heneicosane. In the single sample of this species analysed, these compounds are more abundant and in different proportions in the leaves than in the roots.

Three species of bivalve molluscs, *Macoma balthica, Mya arenaria* and *Mytilus edulis* have been analysed. Reports of the ability of *M. balthica* to take up petroleum and of the effects of oil on this species have recently appeared (Shaw *et al.*, 1976, 1977). The two analyses reported here are of samples collected in the Kamishak Bay area of Cook Inlet, a region with several reported coastal oil seeps (Blasko, 1976). However, petroleum hydrocarbons are not evident. Two samples of *M. arenaria* from the same region also shows only biogenic hydrocarbons. The six samples of *M. edulis* analyses show very low hydrocarbon levels. These organisms came from the Aleutian Islands (kindly provided by S. Zimmerman) and from Prince William Sound. In other environments, *M. edulis* has been shown to accumulate petroleum hydrocarbons (Clark and Finley, 1973). The absence of petroleum from these deposit and filter feeding molluscs is a general indication of the absence of oil from their environment.

The two species of crab which have been investigated, *Chionecetes opilio* (snow crab) and *Paralithoides camtschatica* (King crab) each show low levels of hydrocarbons. Most of these samples contain large amounts of methyl esters in their benzene eluates of column chromatography ("fraction 2"). It seems clear that these species now have a negligable hydrocarbon burden. However, it is not known to what extent they can be expected to take up petroleum from their environment or how efficiently oil would be transfered to their benthic habitat.

Analyses of mixed zooplankton from four hauls made in the Bering Sea indicate that these animals are rich in hydrocarbons. Pristane is the chief hydrocarbon with lesser amounts of nonadecane, eicosane and one or more of the 21:6 polyolefins. Wax esters are so abundant in the benzene eluates that no hydrocarbons can be detected in those fractions. Only general taxonomic characterizations of the animals present in each haul were possible. These have been noted on the chromatograms in Appendix I. Replicate analyses of one haul (MB31) indicate reasonable homogenity of the samples. None of the plankton analyses show evidence of petrogenic hydrocarbons. The available literature (Conover, 1971) indicates that zooplankton ingest petroleum droplets which are dispersed through the water column following an oil spill.

Hydrocarbon analyses have been carried out on four Alaskan species of fin-fish: *Hipoglossus stenolepis* (halibut), *Limanda aspera* (yellowfin sole), *Pleuronectes guadrituberculatus* (Alaska plaice), and *Theragra chalcogramma* (Alaska pollock). Seven different tissues or groups of tissues were analysed:

1. Entire fish: This is not a preferred approach and was used only when necessitated by small sample size.

2. Flesh: This tissue's contamination would have direct public health consequences. However, petroleum residues in flesh would probably not be as high as in other organs. Thus flesh is not a sensitive indicator.
3. Gills: This tissue is expected to show rapid but probably short term uptake of dissolved petroleum from the water column since the gills natural function is to provide for exchange of non-polar molecules (gases) between the fish and the water.
4. Liver: One of this complex organ's functions is to remove unwanted substances from the blood. Thus, hydrocarbons which enter through the gills are likely to be concentrated in the liver where they are stored or excreted slowly.
5. Skin, Skin/Fin, and Skin/Flesh: These three tissue groups all contain subcutaneous fat storage areas which may be sites of hydrocarbon deposition within the animals. The skin/flesh samples consist of the abdominal wall, including the dermis, muscle and peritoneum. The skin/fin samples include the dermis and tissues around the basal bones.

Several points emerge from these analyses. Most generally, none of the materials analysed shows evidence of petrogenic hydrocarbons. Aliphatic hydrocarbons were undetectably low in *P. quadritubercalatus* for all tissues examined. In gill and liver of *H. stenolepis* and *L. aspera* low to moderate levels of squalene were found. However, it should be noted that analytical recoveries of squalene are eratic (probably because of the ease of isomerization and polymerization of this polyene). Pristane is ubiquitous in all tissues of *T. chalcogramma*. However, the concentration of pristane in the livers of individuals of this species was found to vary over two orders of magnitude. A major unanswered question is the extent to which the mechanisms of hydrocarbon entry and storage hypothesized above would actually operate in the event of the introduction of oil into the environment.

Water

Our analyses of water for hydrocarbons are not sufficiently precise to allow detailed interpretation of the results for individual samples. However, the results as a group indicate the general condition of this environmental component.

Three (BS-1, BS-2 and BS-3) of 14 surface water samples collected in the Beaufort Sea showed arrays of petrogenic hydrocarbons characteristic of distillate fuel oil. The most likely source of this oil is the diesel fuel of the ship from which the samples were collected. These data have been included in this report to emphasize the difficulty of collecting uncontaminated samples from ice choked waters where even an ice breaker's headway can be insufficient to stay ahead of her own pollution. Eleven other water samples from the Beaufort Sea reveal no evidence of petrogenic hydrocarbons. The analysis of surface water hydrocarbons from the Chukchi Sea and Norton Sound did not include saponification or column chromatography. Total extractables were analysed by gas chromatography and ubiquitous components identified by mass spectrometry. The results obtained in this way do not appear markedly different from those for other areas: total concentrations are generally one $\mu g\ kg^{-1}$ or less and the compounds present appear to be biogenic. The same is true for samples from Lower Cook Inlet. For nine of the eleven Gulf of Alaska stations sampled in both February and April, the spring samplings show higher hydrocarbon concentrations. This association with the spring bloom would appear to reinforce the idea of biogenic origin. Several samples (e.g., GASS101) show the puzzling array of normal alkanes discussed above in connection with an analysis of *Fucus distichus*. Marty and Saliot (1976) have reported a similar array in seawater surface micro-layer samples. Yet the processes responsible for this kind of distribution are unclear.

Sediments

Only a small number of intertidal sediments have been analysed as part of this project. Extensive investigations of the hydrocarbon contents of subtidal sediments have been carried out by another NOAA/OCSEAP investigator.

Three sediment samples from Cottonwood Bay and Iriskin Bay, both in the Kamishak Bay area of Cook Inlet show no petrogenic hydrocarbons and confirm the conclusion drawn from the analyses of molluscs and plants of the area that petroleum from seeps in the region is not generally accumulating in the intertidal environment.

Analyses of sediments from Iko Bay, Dease Inlet and Cape Simpson in the Beaufort Sea show a dominance of normal alkanes of odd chain lengths characteristic of terrestrial plants, in this case probably tundra. The Iko Bay sample also contains phytane, a petrogenic compound (Blumer and Snyder, 1965) as do several sediment samples previously collected in and around Prudhoe Bay. After noting the presence of phytane we investigated the aromatic hydrocarbons present in considerable detail to try to determine the origin of these petrogenic components.

Youngblood and Blumer (1975) have discussed possible sources of polycyclic aromatic hydrocarbons (PAH) in recent sediments. These sources include biosynthesis, fossil hydrocarbons, and pyrolysis. Biosynthesis of PAH has been reported by several investigators. However, recent work of Hase and

Hites (1976) indicates that previous studies may have observed bioaccumulation and bio-magnification rather than biosynthesis. While biosynthesis cannot be excluded entirely, it presently appears that enzymatically directed reactions would not lead to the complex mixture of many PAH in comparable concentrations which has been observed (Table VII).

Youngblood and Blumer (1975) have shown that distinct differences exist in the relative amounts of an unsubstituted PAH and its alkyl homologs between fossil fuels and ancient sediments on one hand and pyrolysis products on the other. Low temperature formation of petroleum leads to PAH mixtures rich in alkyl substitution; C_1-C_3 homologs are usually substantially more abundant than their unsubstituted parent. High temperature pyrolysis of wood leads predominantly to unsubstituted PAH; alkyl homologs are present only in rapidly decreasing amounts. Urban air particulates, whose PAH are presumed to be mainly the result of pyrolysis of fossil fuels during incomplete combustion, present a more complex picture. Lao *et al.* (1973) report ratios of near unity for anthracene and phenanthrene and their C_1 and C_2 homologs. However, the same workers report rapidly declining amounts of flouranthene plus pyrene and their C_1 and C_3 homologs.

Interpreting the data of Table VIII in light of the above discussion suggests that the PAH of Iko Bay, Prudhoe Bay, and Gull Island (in the mouth of Prudhoe Bay) are of fossil origin or possibly the result of pyrolysis of fossil fuels but are not products of the pyrolysis of modern plant material. The absence of human activity at Iko Bay would seem to rule out pyrolysis of fossil fuels as the source at that location. Although no natural oil seeps have been reported at Iko Bay, a region of seeps is known at Cape Simpson about 60 km to the east (Leffingwell, 1919). It is also possible that undiscovered seeps exist nearshore in the Beaufort Sea. The Meade River,

TABLE VII

AROMATIC HYDROCARBONS FOUND IN PRUDHOE BAY SEDIMENTS AND CRUDE OIL. MASSES ARE OF PARENT MOLECULE PLUS HYDROGEN GENERATED BY CHEMICAL IONIZATION USING METHANE AS REAGENT GAS. THE CONSISTENT STRUCTURE "NAPHTHALENE +C_2H_4" INCLUDES THE TWO ISOMERS OF ETHYLNAPHTHALENE AND THE TWELVE ISOMERS OF DIMETHYLNAPHTHALENE. OTHER CONSISTENT STRUCTURE ENTRIES ARE TO BE INTERPRETED ANALOGOUSLY.

Mass	Consistent Structure	Percent of Aromatics In Sediment	In Crude
129	naphthalene	1.4	9.2
143	naphthalene +CH_2	11.2	25.8
157	naphthalene +C_2H_4	20.2	30.5
171	naphthalene +C_3H_6	19.5	19.2
179	anthracene or phenanthrene	8.3	2.5
193	anthracene or phenanthrene +CH_2	14.6	5.1
207	anthracene or phenanthrene +C_2H_4	8.8	4.8
221	anthracene or phenanthrene +C_3H_6	4.9	2.4
229	naphthacene or isomer	1.8	0.2
243	naphthacene or isomer +CH_2	2.1	0.3
253	perylene or isomer	7.3	0
		100	100

TABLE VIII

RELATIVE CONCENTRATIONS OF ANTHRACENE PLUS PHENANTHRENE AND THEIR ALKYL HOMOLOGS WITHIN BEAUFORT SEA SEDIMENTS AND PRUDHOE BAY CRUDE OIL. VALUES WITHIN EACH COLUMN HAVE BEEN SEPARATELY NORMALIZED. SEE TABLE I FOR EXPLANATION OF "MASS" AND "CONSISTENT STRUCTURE".

Mass	Consistent Structure	Iko Bay	Cape Simpson	Prudhoe Bay	Gull Island	Crude Oil
179	anthracene or phenanthrene	0.5	1.0	0.3	0.4	0.5
193	anthracene or phenanthrene $+CH_2$	0.8	0.0	0.3	1.0	1.0
207	anthracene or phenanthrene $+C_2H_4$	1.0	0.0	1.0	1.0	0.9
221	anthracene or phenanthrene $+C_3H_6$	-	0.0	0.6	0.8	0.5

which enters Dease Inlet about 20 km east of Iko Bay has been reported to contain floating fragments of oil shale and to have coal beds exposed along its banks (Smith and Mertie, 1930). Other rivers further to the east (the Sagavanirktok, the Canning and the Mackenzie) also drain regions in which fossil hydrocarbons are exposed at the surface. The longshore currents toward the west could carry materials from any of these rivers into Iko Bay. However, the idea of a general supply of fossil hydrocarbons fails to explain the fact that sediment from Cape Simpson contained anthracene plus phenanthrene at a concentration two orders of magnitude lower than Iko Bay.

Table VIII shows that the PAH homolog distributions at Gull Island and Prudhoe Bay are not dramatically different from that at Iko Bay. Neither are the total concentrations greatly different, Gull Island and Prudhoe Bay having about 5 and 3 times respectively the concentrations of three ring PAH as Iko Bay. Gull Island and Prudhoe Bay are subject to the same kinds of natural sources of fossil hydrocarbons as Iko Bay (Leffingwell, 1919) and in addition to anthropogenic inputs of petroleum and its pyrolysis products, the latter largely through the exhaust of diesel engines. However, our data is so limited and the hints of complexity of sources so clear that we feel that it would be premature and simplistic to conclude that human activities at Prudhoe Bay have raised the sedimentary PAH load about four fold. However, the available data indicate that petroleum hydrocarbons are present in the sediments of the Prudhoe Bay area at concentrations comparable to or greater than those at undeveloped sites on the Beaufort Sea coast.

Seston

Seventy-seven seston tows of 740 m^2 of sea surface each, showed an arimethic mean concentration of tar of 2.17×10^{-3} mg m^{-2}. This does not appear strikingly different that the mean value of 6.6×10^{-4} mg m^{-2} reported in our previous report to OCSEAP (Shaw, 1976). The agreement appears particularly good when one notes that this year's mean is raised by a single high value (Table V). These tar concentrations are quite low by world standards. A detailed discussion of the reasons for this low tar concentration has already been presented (Shaw, 1976) and will not be repeated here. It should be noted, however, that one research cruise to the Gulf of Alaska terminated not at an Alaskan port but at Honolulu, providing an opportunity to sample seston across the north Pacific. Twenty seston collections showed a mean tar concentration of 0.17 mg m^{-2} with some recognizable tar in every tow.

Hydrocarbon Sorption by Sediment

Table VI shows that under experimental conditions, suspended sediment took up at most 20.1% and more commonly less than 1% of the biphenyl from the water. Increasing the concentration of biphenyl in water increased the percentage associated with sediment only when the biphenyl was present in excess of its solubility. Under these conditions some biphenyl particles must have been present and their association properties are probably quite different than dissolved biphenyl. Most of the reported experiments used sediment which had been treated with H_2O_2 to remove adhering organics. Untreated sediment, which was used in one experiment, probably had an unrealistically high level of associated organics as a result of contamination from plankton when the sediment was obtained by centrifugation. This untreated sediment had a greater affinity for biphenyl than the treated sediment indicating that hydrocarbons may associate with organics which associate with minerals more readily than hydrocarbons associate directly with minerals.

If this observation is substantiated by further experiments it will be of major importance in south central Alaska where most sediments are glacial and reach the sea with few associated organics compared to sediments of lower latitudes. The effect of increased salinity appears to be to increase the percentage of biphenyl which associates with sediment. This is probably a consequence of the salting out of the biphenyl from the water.

Our finding of slight association between biphenyl and suspended sediment is in concert with that of Button (1976) who detected no loss of dodecane from aqueous solution in the presence of several mineral phases. Differences in experimental approaches make direct comparison of the two sets of data difficult. However, it is important to understand that the π electron cloud of biphenyl has a greater tendency to have bonding interactions with polar and ionic substances than does dodecane. Thus the expectation is that biphenyl would associate directly with minerals to a greater extent than would dodecane. The available data are consistent with this expectation. The ease with which biphenyl is desorbed from sediment in the presence of clean water indicates that this association is a reversible process rather than a unidirectional path that necessarily transports hydrocarbons to the benthos as suspended sediments settle out of the water column.

Bio-Sedimentation

The inefficiency of hydrocarbon suspended sediment association as a mechanism of transporting petroleum from the water column to benthos, does not mean that this transport does not efficiently occur by some other mechanism. Another potential mechanism previously noted in the literature is the ingestion of oil droplets by zooplankton and their subsequent deposition as larger, denser, faster sinking fecal pellets (Conover, 1971). We have begun as investigation of the importance of this transport process under the conditions of the spring plankton bloom in the Bering Sea. Our objective is to determine the extent to which numerically important zooplankton ingest and excrete oil droplets of various size classes. Work to date has concerned developing techniques for producing size characterized oil in water dispersions. These dispersions will be used in feeding experiments with plankton of the Bering Sea during a cruise of the USNOSS *Discoveror* in the spring of 1977.

Site Specific Studies

Two primary sites for intensive hydrocarbon studies have been selected, Cook Inlet and the Bering Sea.

Cook Inlet, because of its comparatively easy year round accessability, its established petroleum operations and its fisheries importance is a logical choice for study on a seasonal basis. In the lower Inlet a comparative study is being carried out between the intertidal and shallow subtidal environments of Kachemak Bay on the Kenai Peninsula and Kamishak Bay on the Alaska Peninsula. The former is bathed by waters entering the Inlet from the Gulf of Alaska while the latter receives water that has passed through the Inlet and thus would contain whatever petroleum residues might result from oil development in the Inlet. Further work to identify good monitoring species and to elucidate the pathways of hydrocarbon transfer through the important detritus based food web of area is underway. This work should result in ability to predict the extent to which hydrocarbons entering the food web at various points would impact species of fisheries or ecologic importance.

Whereas the food webs in Cook Inlet which lead to economically important species are largely benthic, similarily important food webs in the Bering Sea are predominately pelagic. The biology of this pelagic community is already being studied in detail by OCSEAP, PROBES and other research teams. Working with these on-going investigations and in the laboratory is making possible a study of hydrocarbon transfer in this pelagic food web which will complement the work done in Cook Inlet. The Bering Sea work is focusing on the food webs which support the economically important Alaska pollock and the aesthetically important seal populations of the area.

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VII. QUARTERLY ACTIVITY SUMMARY

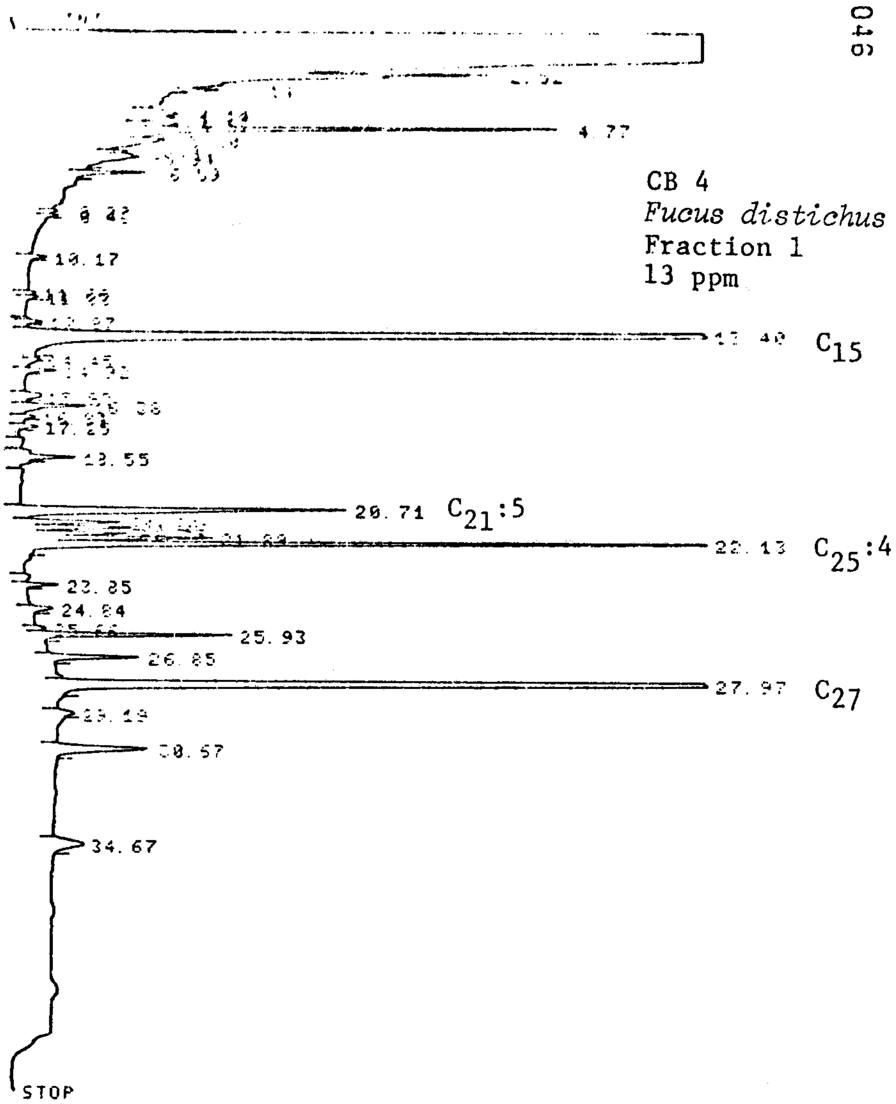
A. Field Activities: none

B. Laboratory Activities

Analyses of materials collected in previous quarters have continued without major problems. A substantial diversion of effort has been required for the preparation of our annual report.

VIII. APPENDIX I

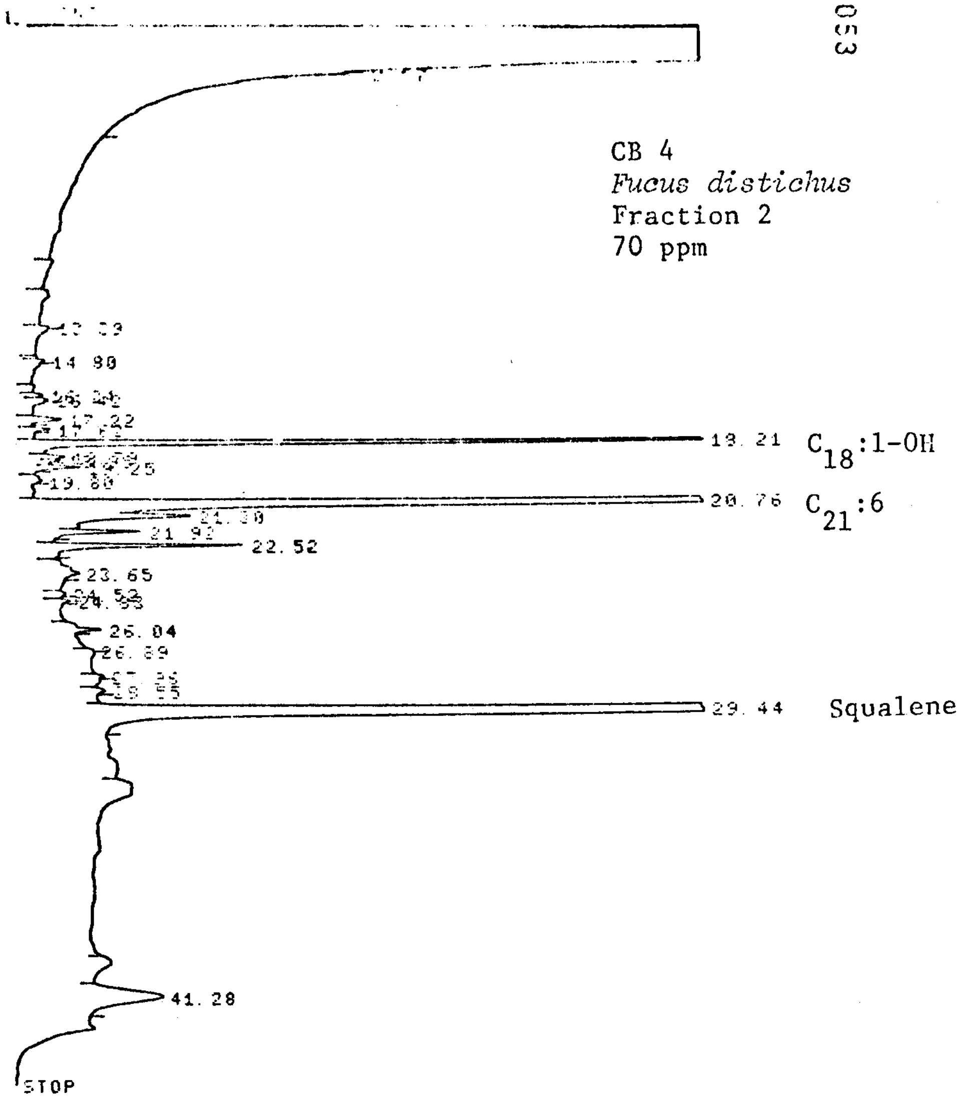
ANNOTATED GAS CHROMATOGRAMS OF BIOTA AND SEDIMENT



CB 4
Fucus distichus
Fraction 1
13 ppm

```
                        AREA %
   RT    TYPE     AREA
R [illegible]
R [illegible]
R [illegible]
R [illegible]
R [illegible]
R [illegible]
R [illegible]
R [illegible]
R [illegible]
R [illegible]
R [illegible]
R [illegible]
R [illegible]
R [illegible]
 11.83    M        512              .112 9
 12.87             577              .127 3
 13.40          194999            43.01
 14.45             189              .041 69
 14.92            1104             [illegible]
 [illegible]
 [illegible]
 [illegible]
S [illegible]
 18.55            [illegible]       .557 2
 20.71           21395             4.719
 21.24    M       [illegible]      1.049
 21.46    M       [illegible]      1.179
 21.70    M       [illegible]      1.053
 [illegible] M    [illegible]      [illegible]
 22.13    M       [illegible]      [illegible]
 23.85            [illegible]       .321
 [illegible]
 [illegible]
 [illegible] M    [illegible]      [illegible]
 [illegible]
 [illegible]
 [illegible]
 [illegible]
 34.67            [illegible]      [illegible]
```

053



CB 4
Fucus distichus
Fraction 2
70 ppm

C_{18}:1-OH

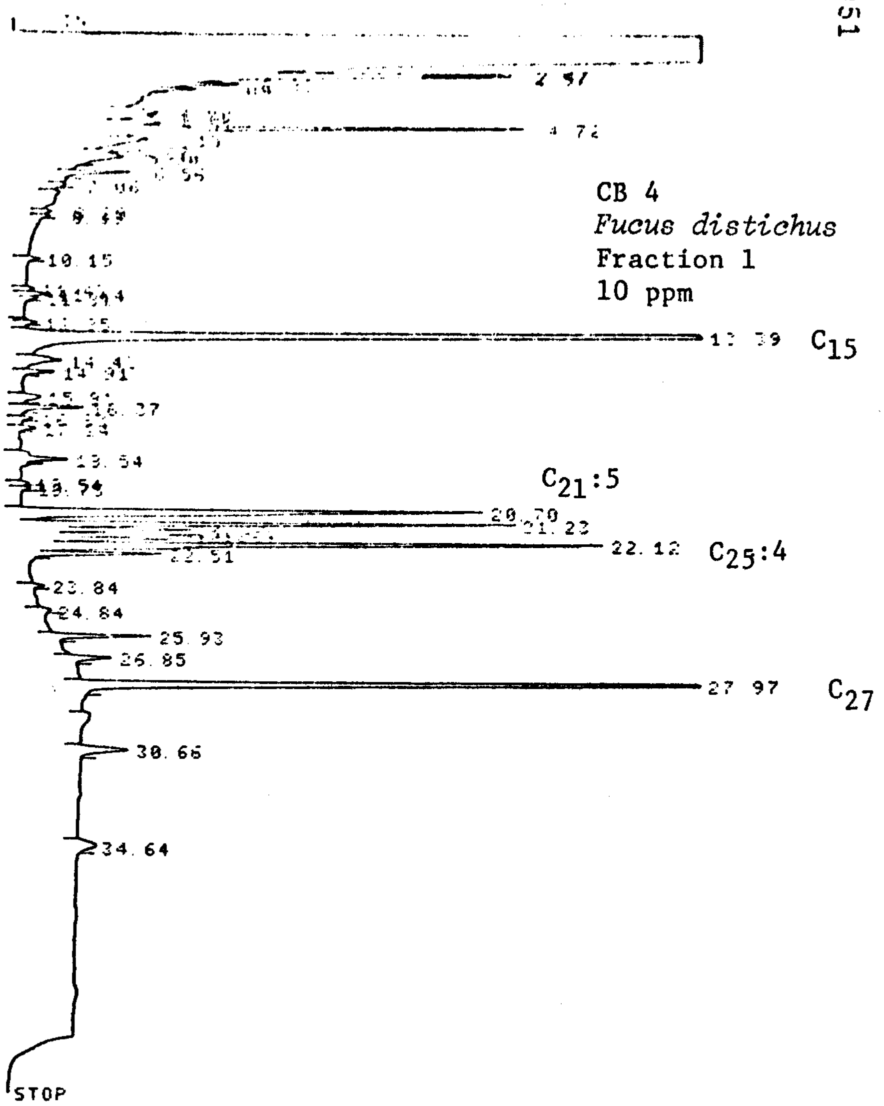
C_{21}:6

Squalene

```
                        AREA %
      RT    TYPE      AREA
R ~~[illegible]~~
    13.79              174              .019 79
    14.80              261              .029 68
    16.24              223              .025 36
    16.42    M         261              .029 58
S ~~[illegible]~~
    17.62              815              .092 68
A ~~[illegible]~~
S ~~[illegible]~~
    18.95    N         499              .056 75
    19.25             1880              .213 8
    19.80              817              .092 91
    20.76           399360            45.3
    21.30    M       16799             1.91
    21.92    N        5138              .584 3
    22.52             9916             1.129
    23.65             2942              .334 6
    [illegible]
    [illegible]
    26.04           [illegible]         [illegible]
    26.89              165              .018 76
    27.94              318              .036 16
    28.55              642              .073 01
    29.44           374069            42.57
R ~~[illegible]~~

[illegible]
[illegible]
```

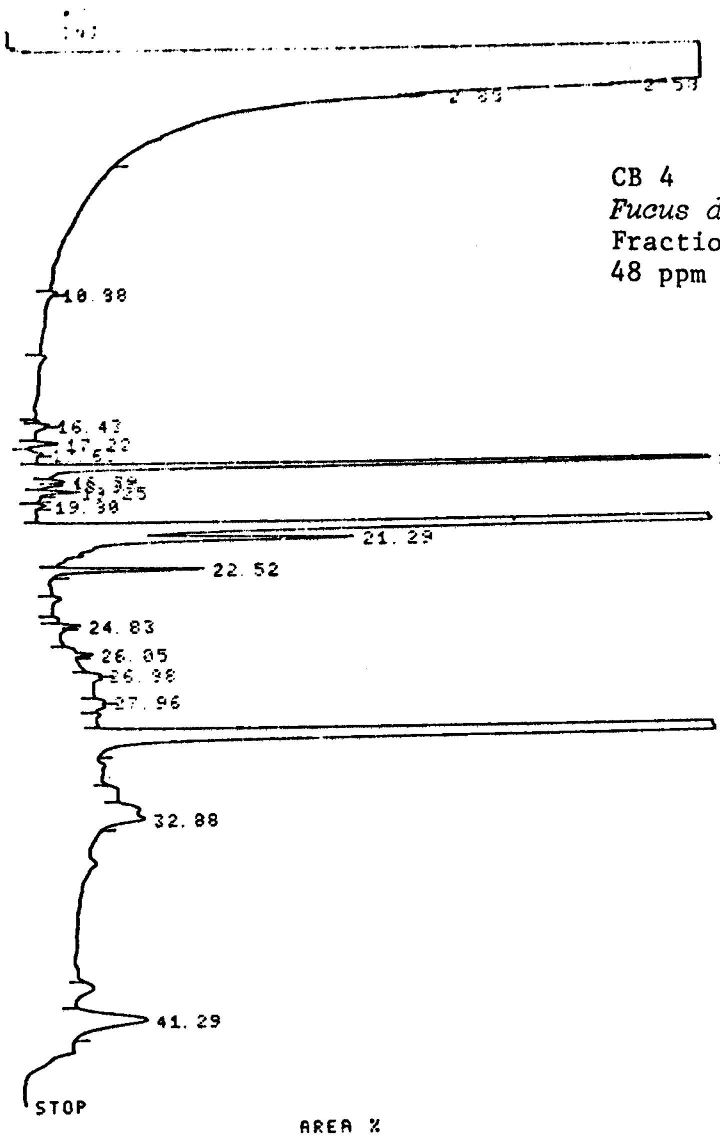
054



CB 4
Fucus distichus
Fraction 1
10 ppm

```
                             AREA %
     RT    TYPE       AREA
R  ~~[illegible]~~
R  ~~[illegible]~~
R  ~~[illegible]~~
R  ~~[illegible]~~
R  ~~[illegible]~~
R  ~~[illegible]~~
R  ~~[illegible]~~
R  ~~[illegible]~~
R  ~~[illegible]~~
R  ~~[illegible]~~
R  ~~[illegible]~~
R  ~~[illegible]~~
R  ~~[illegible]~~
R  ~~[illegible]~~
R  ~~[illegible]~~
R  ~~[illegible]~~
R  ~~[illegible]~~
R  ~~[illegible]~~
    11.31   M          607              .130 8
    12.85              783              .092 55
    13.39           212268            45.75
    14.43   M         7250              .786 7
    14.91   M   [illegible]         [illegible]
    [illegible]
    [illegible]
    16.[illegible]     [illegible]      .110 1
S  ~~[illegible]~~
    18.54      [illegible]              .573 9
    19.54      [illegible]              .059 27
    19.75      [illegible]              .063 4
    20.70      [illegible]             6.305
    21.23   M  [illegible]             4.[illegible]
    21.47   M  [illegible]             1.[illegible]
    21.[illegible]  M  [illegible]     1.[illegible]
    21.[illegible]  M  [illegible]     1.[illegible]
    22.12   M  [illegible]             [illegible]
    22.51   M  [illegible]             1.[illegible]
    23.84      [illegible]              .11[illegible]
    24.84      [illegible]              .1[illegible] 1
    25.93      [illegible]              [illegible]
    26.85      [illegible]              [illegible]
    27.97      [illegible]            11.[illegible]
```

043



CB 4
Fucus distichus
Fraction 2
48 ppm

C_{18}:1-OH

C_{21}:6

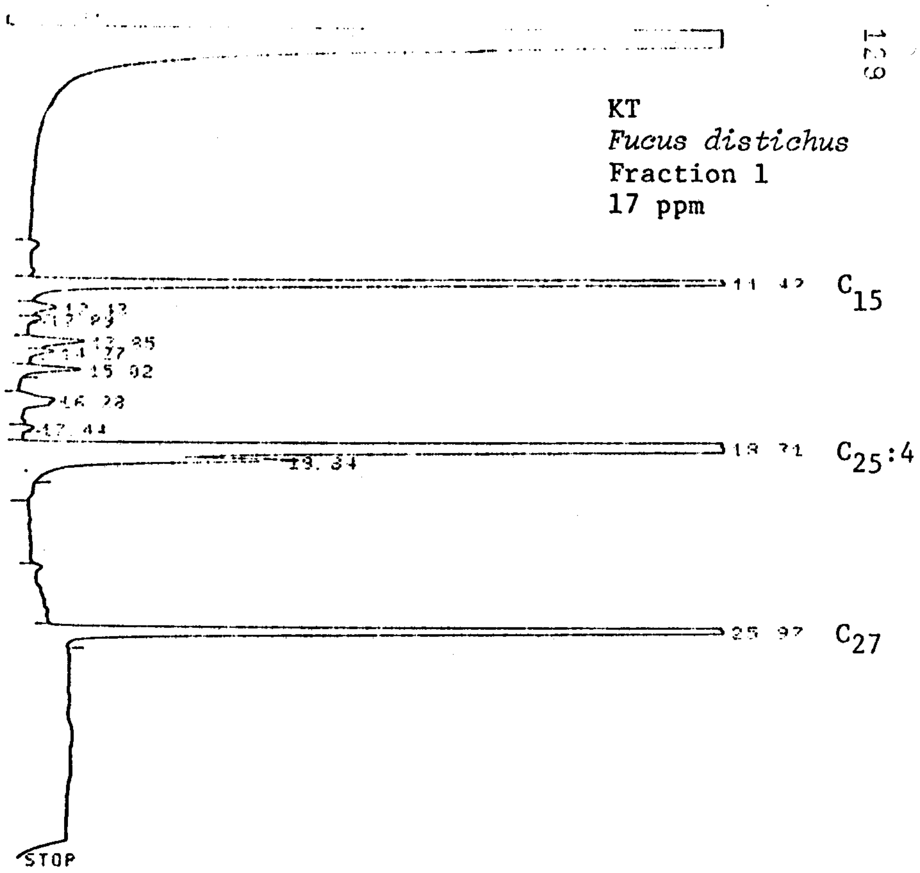
Squalene

049

```
                          AREA %
     RT    TYPE       AREA
R  [illegible]
R  [illegible]
R  [illegible]
   16.4?              265                     .022 37
S  [illegible]
   17.63    ?         565                     .048 33
A  [illegible]
S  [illegible]
   18.95   TM         845                     .072 16
   19.25   TM        1532                     .130 8
   19.80              536                     .050 04
   20.76           529081                   45.19
   21.29    M       33895                    2.895
   22.52    M        7805                     .666 5
   24.83              854                     .073 78
   26.05             1398                     .119 4
   [illegible]
R  [illegible]

HP 3390A
[illegible]           STOP 45           REJECT   100
[illegible]           ATTN   4
```

129



KT
Fucus distichus
Fraction 1
17 ppm

C_{15}

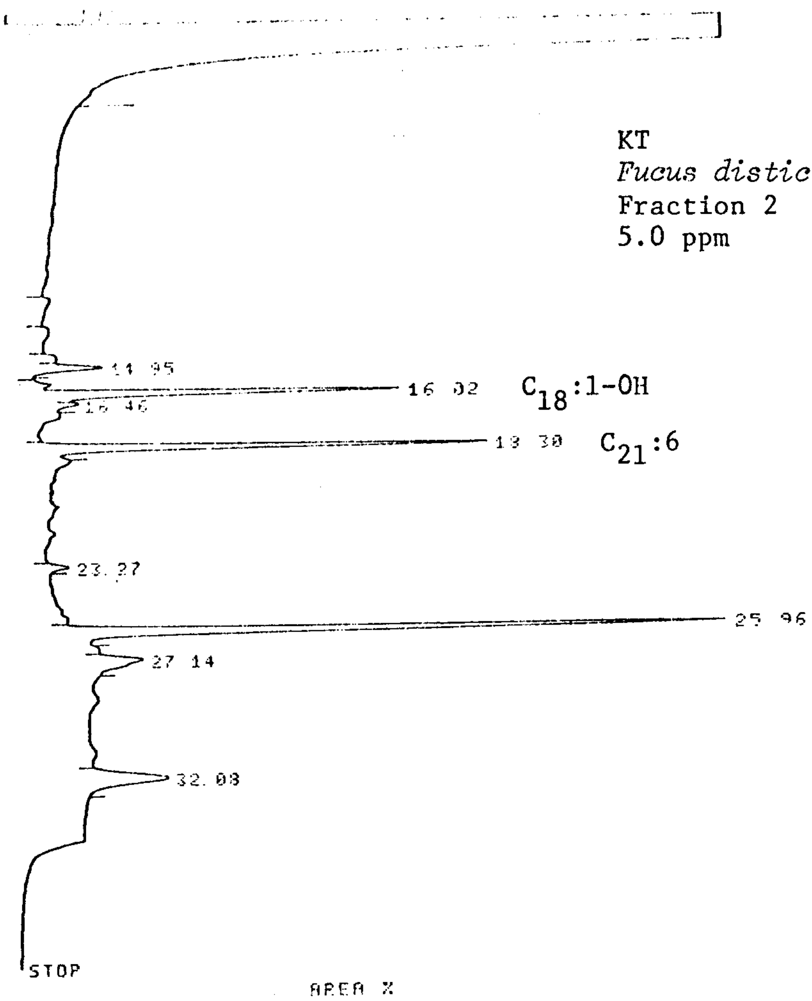
C_{25}:4

C_{27}

```
                        AREA %
     RT    TYPE     AREA
  11 42            127845           12.58
  12.43     M        2145             .211
  12 89               671             .066 01
  13 85              5652              556
  14.27     M        2165             .213
S 15 02              4104             .403 7
  16.28               314             .029 07
  17 44               650             .06, 94
  18 71            714129           70 25
  18 64     M       27499            2.705
  25 97            130918           12 88

HP 3390A
DLY  4.            STOP 45            REJECT   100
MV/M  .30          ATTN      4
```

KT
Fucus distichus
Fraction 2
5.0 ppm



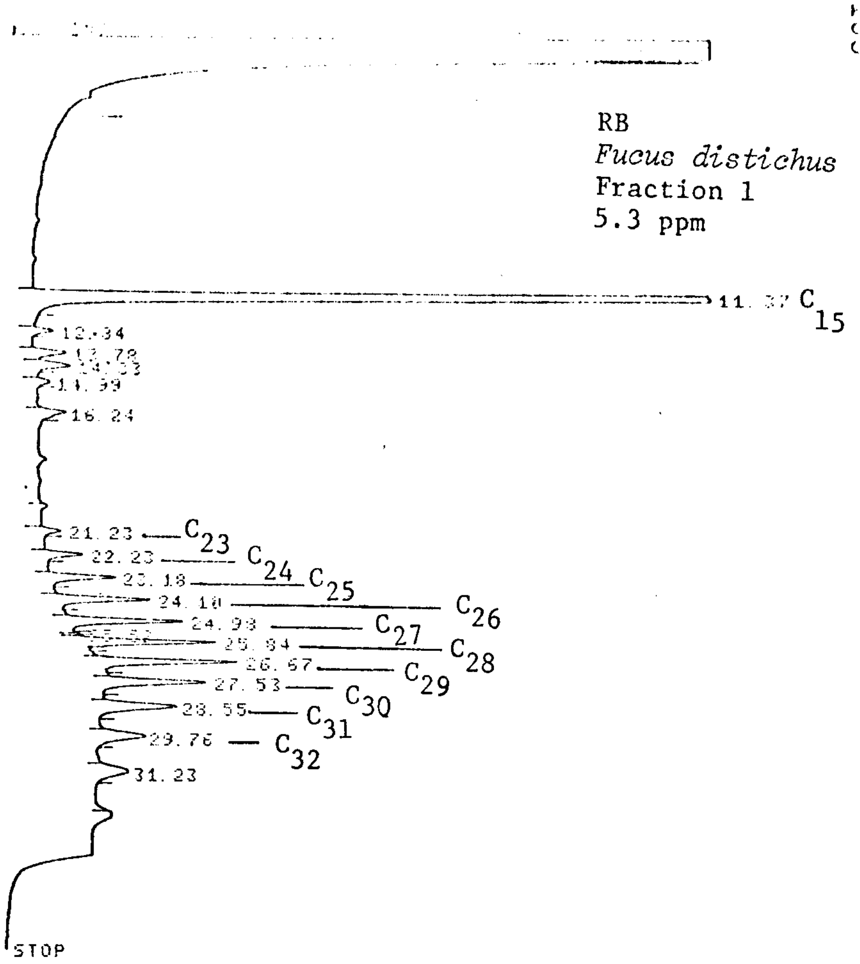
C_{18}:1-OH

C_{21}:6

Squalene

```
                        AREA %
     RT    TYPE      AREA
C-~~14.95               [illegible]              [illegible]~~
A ~~16.02               26285                   19.63~~
C ~~16.46              2089                     1.56~~
  18.30                 30269                   22.61
C ~~23.27               [illegible]              [illegible]~~
* 25.96                 48070-1000              35.9
  27.14                  6440                    4.81
  32.08                 14253                   10.65

HP 3380A
DLY  4.             STOP 45           REJECT    100
MV/M   30           ATTN      4
```

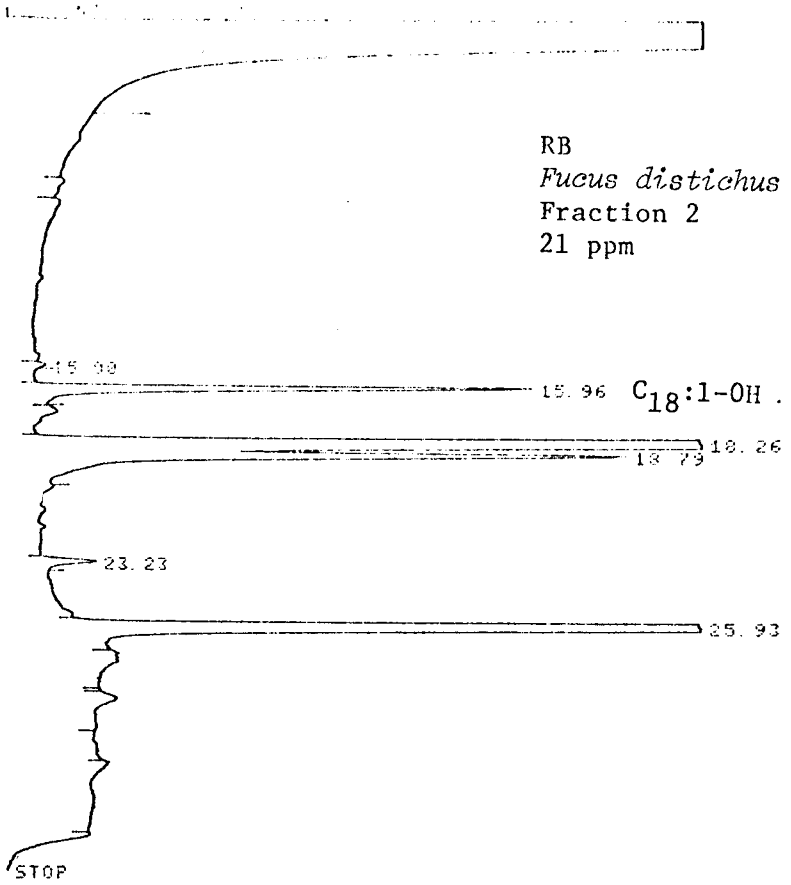


RB
Fucus distichus
Fraction 1
5.3 ppm

```
                                AREA %
      RT    TYPE      AREA
    11.37            178692               68.67
S ~~12.34             [illegible]             .522~~
    13.78              2748                1.056
    14.33    M         3211                1.234
S ~~14.99             [illegible]             .494~~
S ~~16.24             [illegible]             [illegible]~~
    21.23              1307                 .502 2
    22.23              2638                1.014
    23.18              4951                1 903
    24.10              6871                2.64
    24.93              8591                3.301
    25.84             10183                3.912
    26.67             10509                4 038
    27 53              9045                3.477
    28.55              7606                2.923
    29 76              5312                2.041
R ~~31.23              4592                1.765~~

HP 3380A
DLY  4             STOP 45            REJECT   100
MV/M   10          ATTN      4
```

RB
Fucus distichus
Fraction 2
21 ppm



C_{18}:1-OH .

C_{21}:6

Squalene

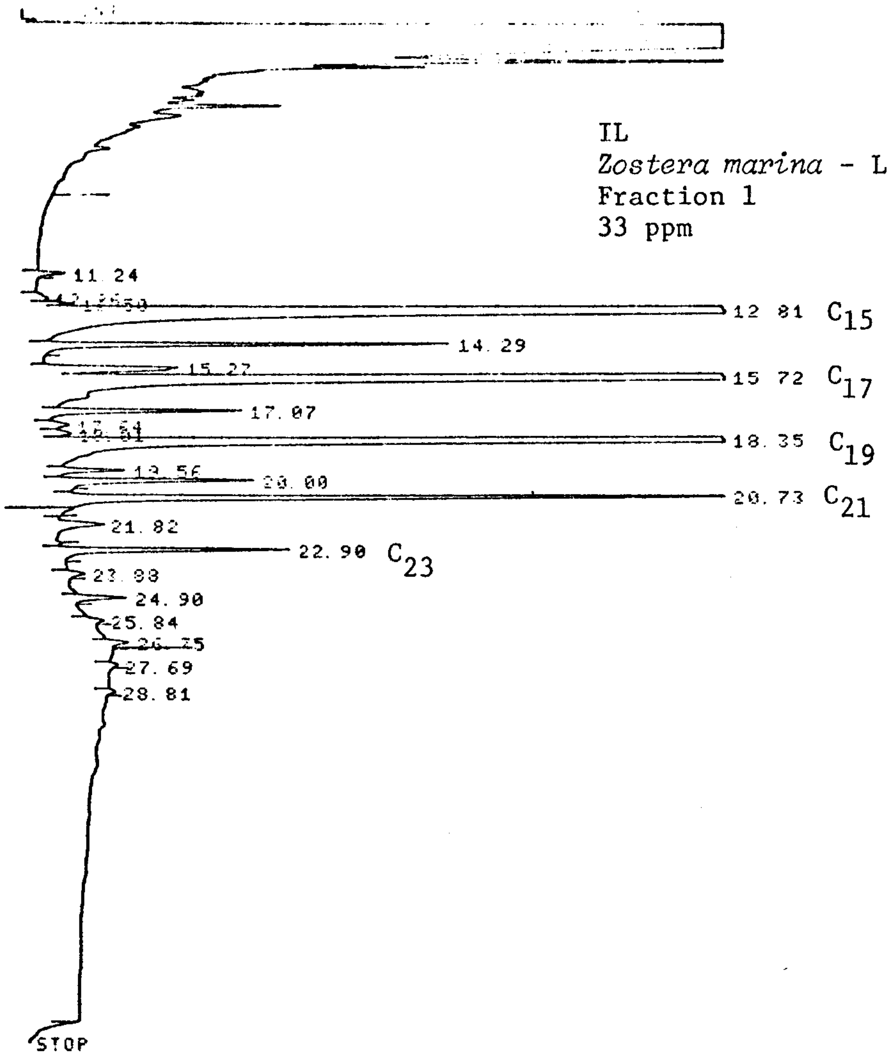
AREA %

RT TYPE AREA

S ~~15.90 542 332.44~~
A ~~15.96 36505 1.551~~
18.26 438099 55.17
18.79 H 60335 7.82
C ~~23.23 512.3~~
25.93 233578 30.72

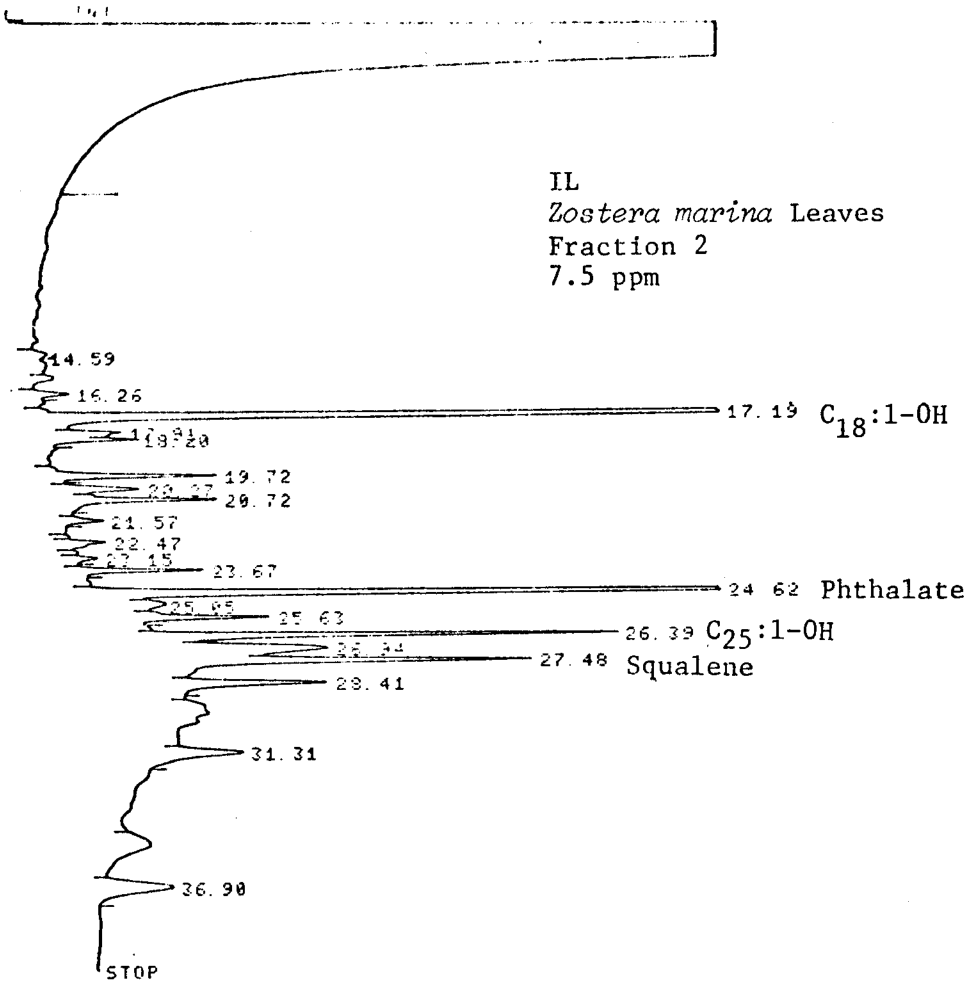
HP 3380A
DLY 4. STOP 45 REJECT 100
MV/M .30 ATTN 4

IL
Zostera marina - Leaves
Fraction 1
33 ppm



```
                          AREA %
      RT    TYPE      AREA
R ~~11.24                 1439                          .077 01~~
  12.26                    406                          .021 73
  12.50                   1275                          .068 23
  12.81      M          982796                        52.59
  14.29      T           19415                         1.039
  15.27      T           11541                          .617 6
  15.72      TM         485342                        25.97
  17.07      TM           9903                          .530 3
  17.64      TM           1393                          .074 54
  18.01      TM           1538                          .082 3
  18.35      TM         257844                        13.8
  19.56      TM           3589                          .192 1
  20.00      TM          10353                          .554 6
  20.73                  45226                         2.42
  21.82                  17171                          .919
  22.90                  12353                          .661 4
C ~~[illegible]~~
C ~~[illegible]~~
C ~~[illegible]~~
C ~~[illegible]~~
C ~~[illegible]~~
C ~~[illegible]~~

HP 3380A
[illegible]                 STOP 45              REJECT     100
[illegible]                 [illegible]      4
```

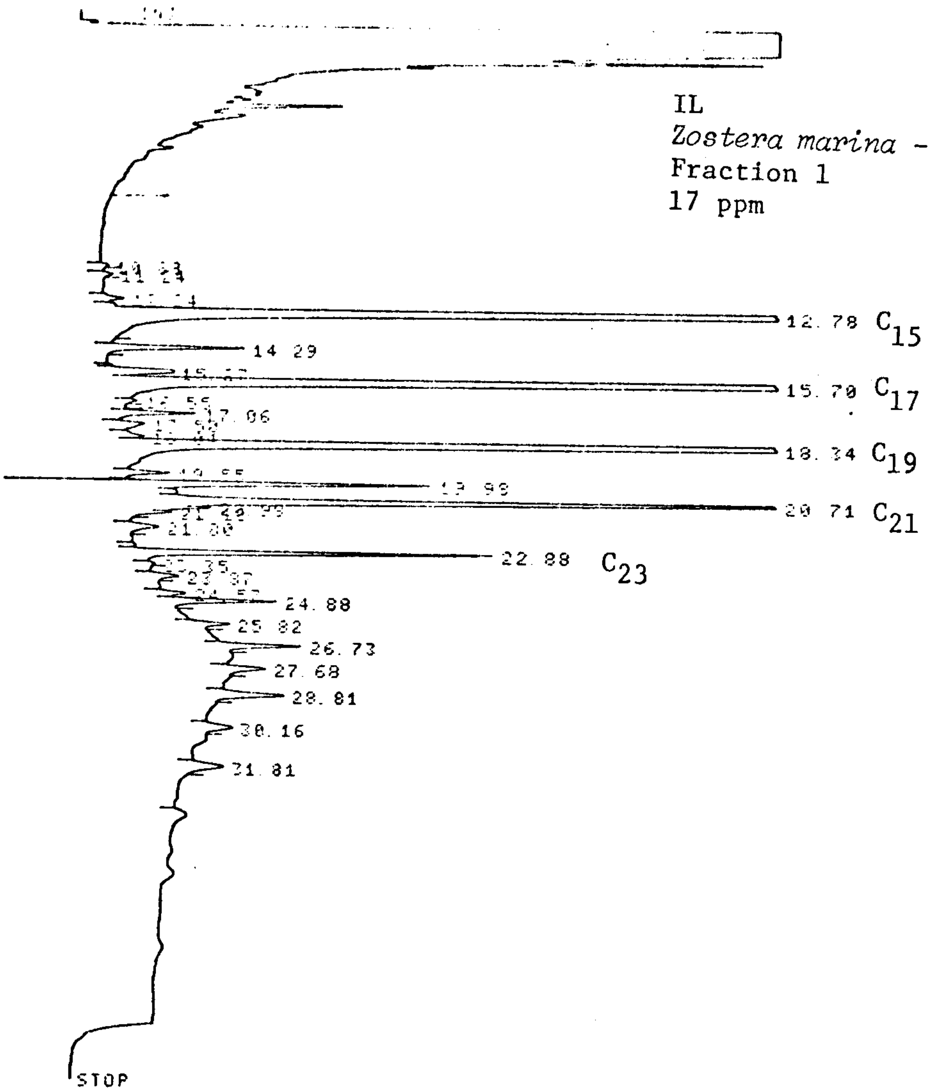


IL
Zostera marina Leaves
Fraction 2
7.5 ppm

```
                        AREA %
    RT    TYPE       AREA
  14.59               836                 .247 5
S ~~[illegible]       [illegible]         .531 3~~
A ~~[illegible]       [illegible]       [illegible]~~
  17.91     M        7258                2.149
  18.20     M        4904                1.452
  19.72              9125                2.702
  20.27              5913                1.751
  20.72     M       10558                3.126
  21.57              2475                 .732 8
  22.47              2410                 .713 6
  23.15              1147                 .339 6
  23.67              6446                1.909
A ~~[illegible]       [illegible]       [illegible]~~
  25.05     M        6558                1.942
  25.63     M        9304                2.755
A ~~[illegible]       [illegible]       [illegible]~~
  26.94     M       24198                7.162
  27.48     M       32163                9.523
  28.41     M       13166                3.899
  31.31              8693                2.574
R ~~[illegible]       [illegible]       [illegible]~~

HP 3380A
DLY   8         STOP 45        REJECT   100
PK.WD .30       ATTN     4
```

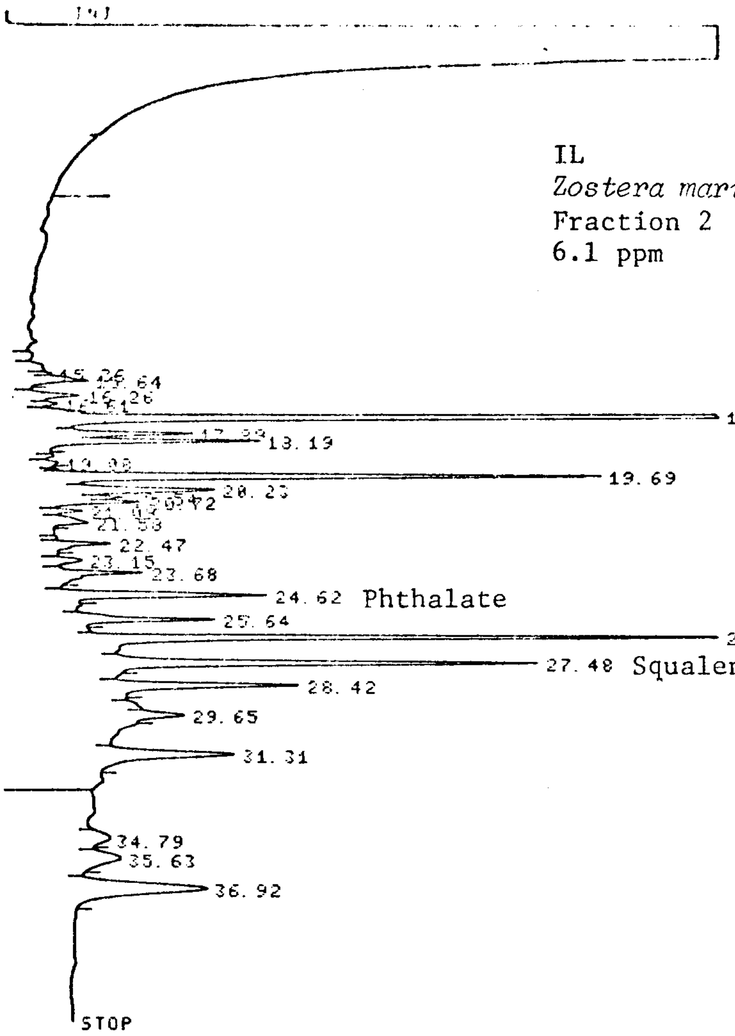
IL
Zostera marina - Entire plants
Fraction 1
17 ppm



AREA %

	RT	TYPE	AREA	
R	~~[illegible]~~		~~[illegible]~~	~~[illegible]~~
R	~~[illegible]~~		~~[illegible]~~	~~[illegible]~~
	12.24		1238	.144 6
	12.78	M	306476	35.79
	14.29		6580	.768 3
	15.27		5226	.610 2
	15.70	M	212994	24.87
	16.55	T	493	.058 27
	[illegible]		3949	.461
	17.50	M	2153	.251 4
	18.04	M	1971	.218 5
	18.34	M	188295	21.99
	18.55	M	2427	.283 4
	19.98	M	17631	2.059
	20.71	M	50856	5.938
	20.93	M	4045	.472 [illegible]
	21.18	M	2276	[illegible] 4
	21.80		2207	.263 4
	22.88		17993	2.101
	[illegible] 15	M	362	.042 [illegible]
C	~~[illegible]~~		~~[illegible]~~	~~[illegible]~~
	24.57		1247	.145
C	~~[illegible]~~		~~[illegible]~~	~~[illegible]~~
C	~~[illegible]~~		~~[illegible]~~	~~[illegible]~~
C	~~[illegible]~~		~~[illegible]~~	~~[illegible]~~
C	~~[illegible]~~		~~[illegible]~~	~~[illegible]~~
C	~~[illegible]~~		~~[illegible]~~	~~[illegible]~~
C	~~[illegible]~~		~~[illegible]~~	~~[illegible]~~
C	~~[illegible]~~		~~[illegible]~~	~~[illegible]~~

[illegible]



IL

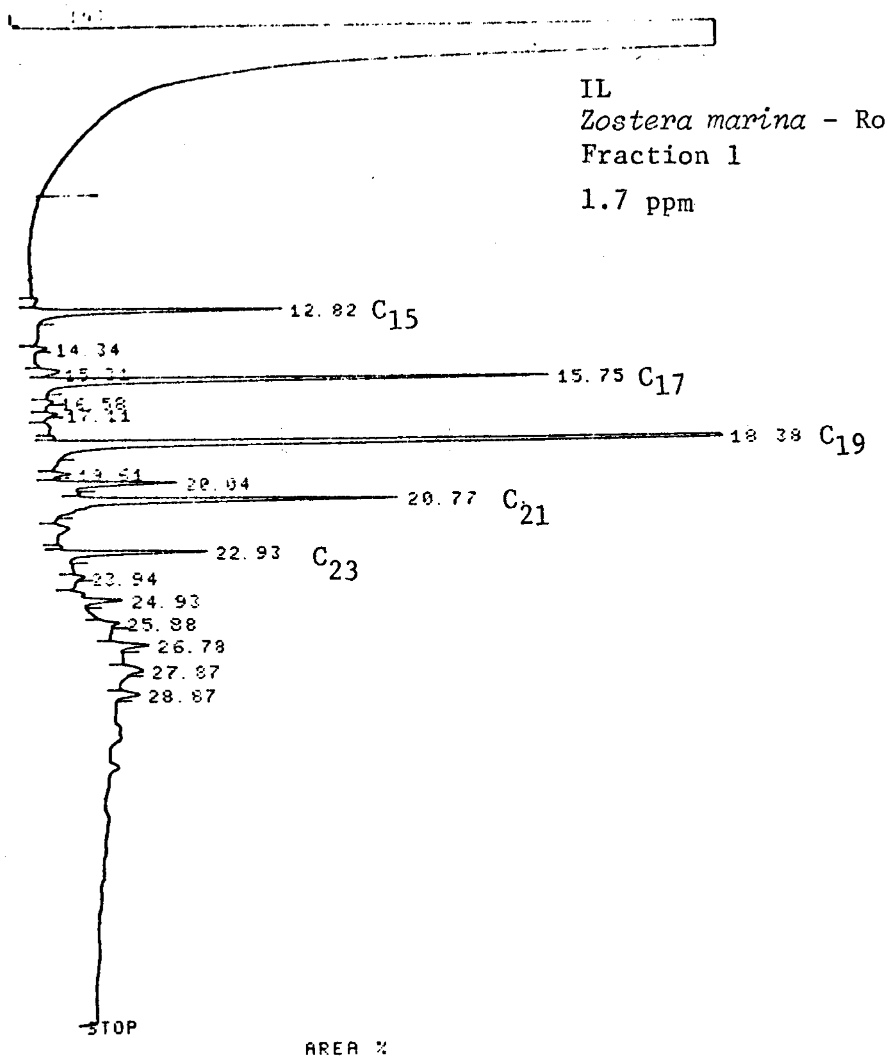
Zostera marina - Entire plants

Fraction 2

6.1 ppm

```
                               AREA %
     RT     TYPE        AREA
  15 36                  362             .099 35
  15 64      M          3903            1.077
S 16 26                 [illegible]      [illegible] 5
  16 61      M          1517             .418 4
A 17 19      M          9[illegible]    25.[illegible]
  17 89      M         10725            2 958
  18 19      M         12793            3 529
  19 08                  500             137 9
  19 69                36902           10.18
  20.23      M         13707            3.781
  20 54      M          3567             983 9
  20 72      M          4924            1.358
  21 09      M          1301             .358 9
  21 58      M          3371             .929 9
  22 47                 3334             .919 6
  23 15                 1811             .499 5
  23 68      M          6170            1.702
A 24 62                16[illegible]    4.4[illegible]
Ce 25 64                [illegible]-110  2 434
A 26 39                [illegible]      11.[illegible]
  27 48      M          [illegible]     3 47[illegible]
  28 42                 13[illegible]   [illegible]
  29 65                 40[illegible]   1 111
  31 31                157[illegible]   4 [illegible]
```

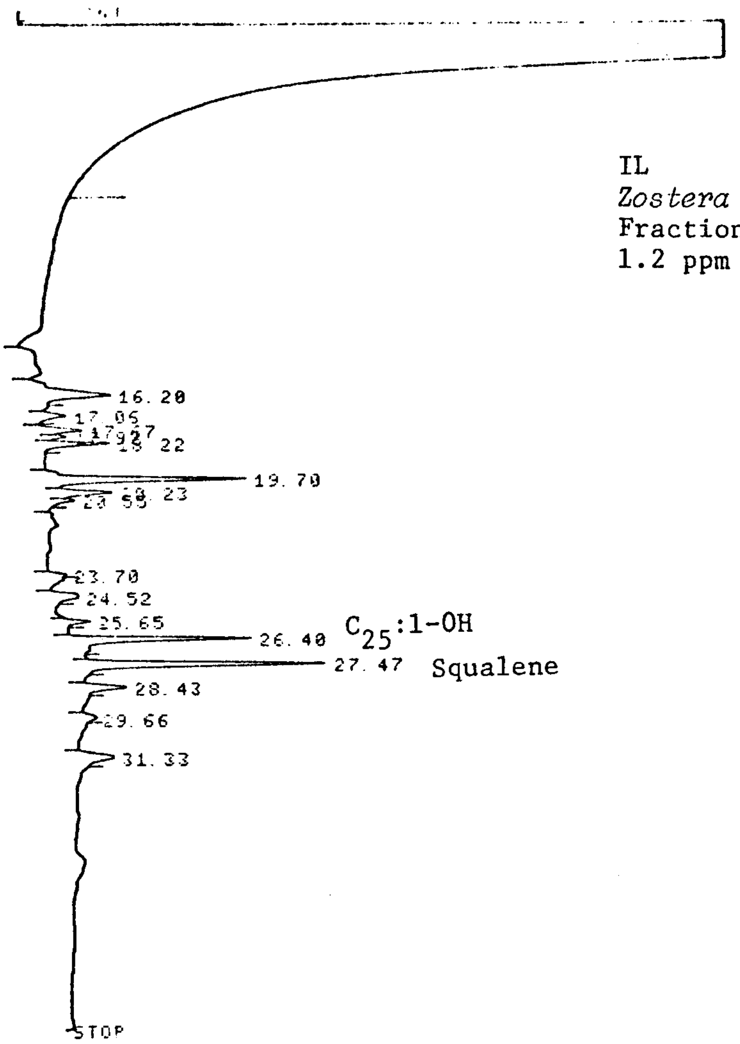
IL
Zostera marina - Roots
Fraction 1
1.7 ppm



```
                         AREA %
   RT    TYPE      AREA
 12. 82            13772           9. 313
 14. 34              617             417  2
 15. 31             1853           1. 253
 15. 75    M       26921          18. 2
 16. 58              385            . 260  3
 17. 11              519            . 351
 18. 38            58407          39. 5
 19. 61              878            . 593  7
 20. 04             6038           4. 117
 20  77            20228          13. 69
 22  93             7675           5  192
C
C
C
C
C
C

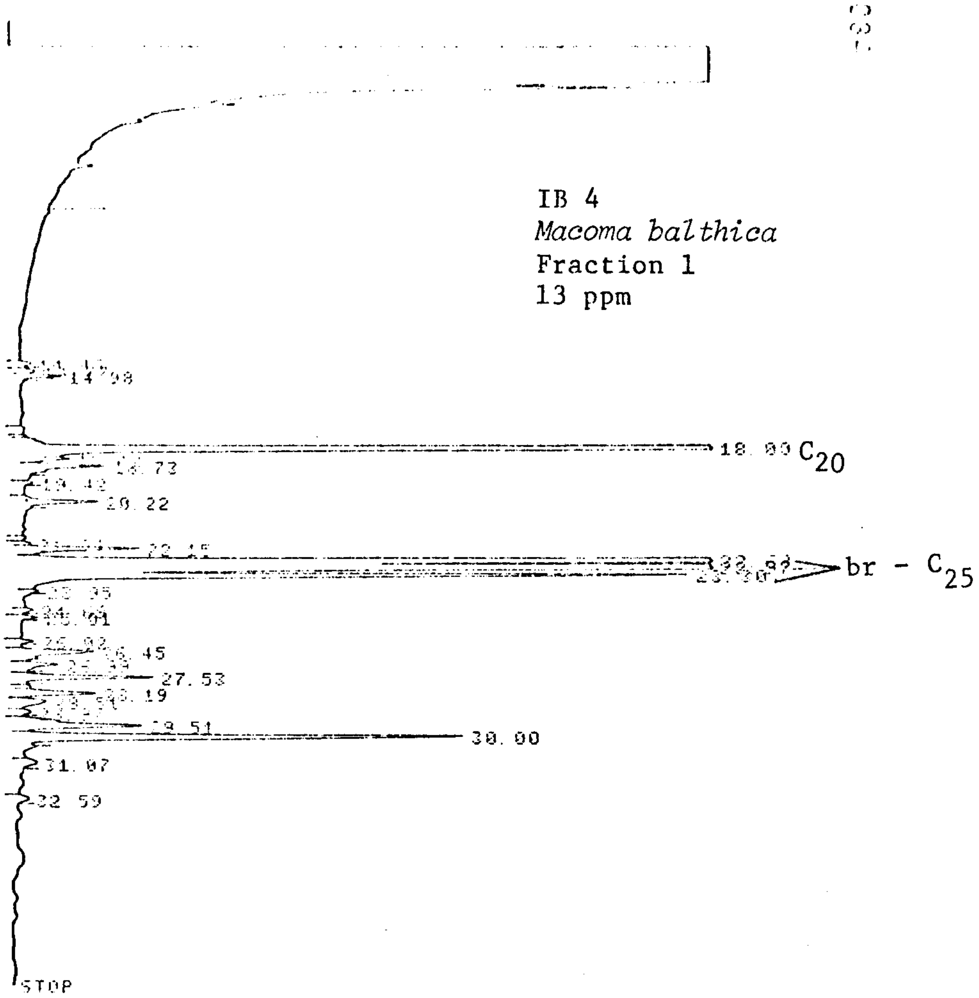
HP 3380A
ZERO  6            SLP  45            REJECT    100
PK WD  .10         ATTN       4
```

IL
Zostera marina - Roots
Fraction 2
1.2 ppm



```
                              AREA %
     RT    TYPE       AREA
S[illegible]                  [illegible]                [illegible]
  17.05               2033                    2.387
S[illegible]                  [illegible]                [illegible]
  17.92     M         1562                    1.934
  18.22     M         4418                    5.197
  19.70              14804                   17.38
  20.23     M         5573                    6.543
  20.55     M         1933                    2.269
  23.70                397                     .466 1
C[illegible]                  [illegible]                [illegible]
C[illegible]                  [illegible]                [illegible]
A[illegible]                  [illegible]                [illegible]
C*27.47              16644-4191              19.54
  28.40               3368                    3.954
  29.66               1258                    1.477
  31.33               3909                    4.589

HP 3380A
DLY  8             STOP 45          REJECT    100
MV/M  30           ATTN      4
```

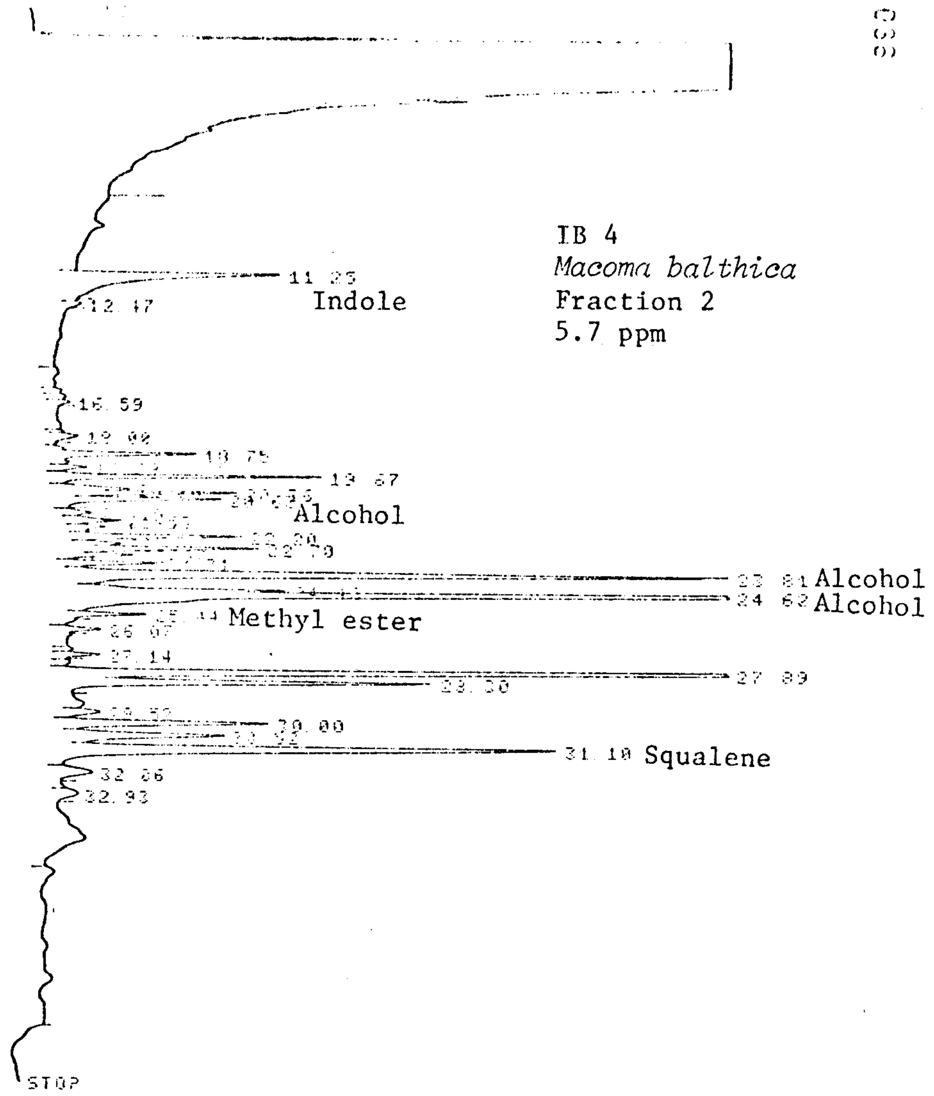


IB 4
Macoma balthica
Fraction 1
13 ppm

```
                         AREA %
    RT    TYPE     AREA
  14.45             563            .087 73
  14.77             642            .1
  14.98    M       1767            .275 4
  18.00          139824          21.79
  18.42    M       2244            .349 7
 *18.73    M       5052            .787 3
  19.42             342            .053 3
 *20.22            3315            .534 5
  21.94             373            .058 44
  22.15    M       6601           1.029
  22.65    M     121414          18.92
  22.97    M     259023          40.36
  23.30    M      20784           3.217
  23.95    M        449            .069 57
  24.69             542            .084 46
  25.01             894            .136 6
  26.02             561            .087 42
  26.45            5302            .825 6
  26.99    M       1810            .282 1
  27.53            6658           1.042
  28.19            4007            .624 4
  28.51    M       1657            .258 2
  28.97    T        519            .080 88
  29.51            9376           1.461
  30.00    M      28422           4.429
  31.07            1616            .251 9
  32.59            1049            .163 5

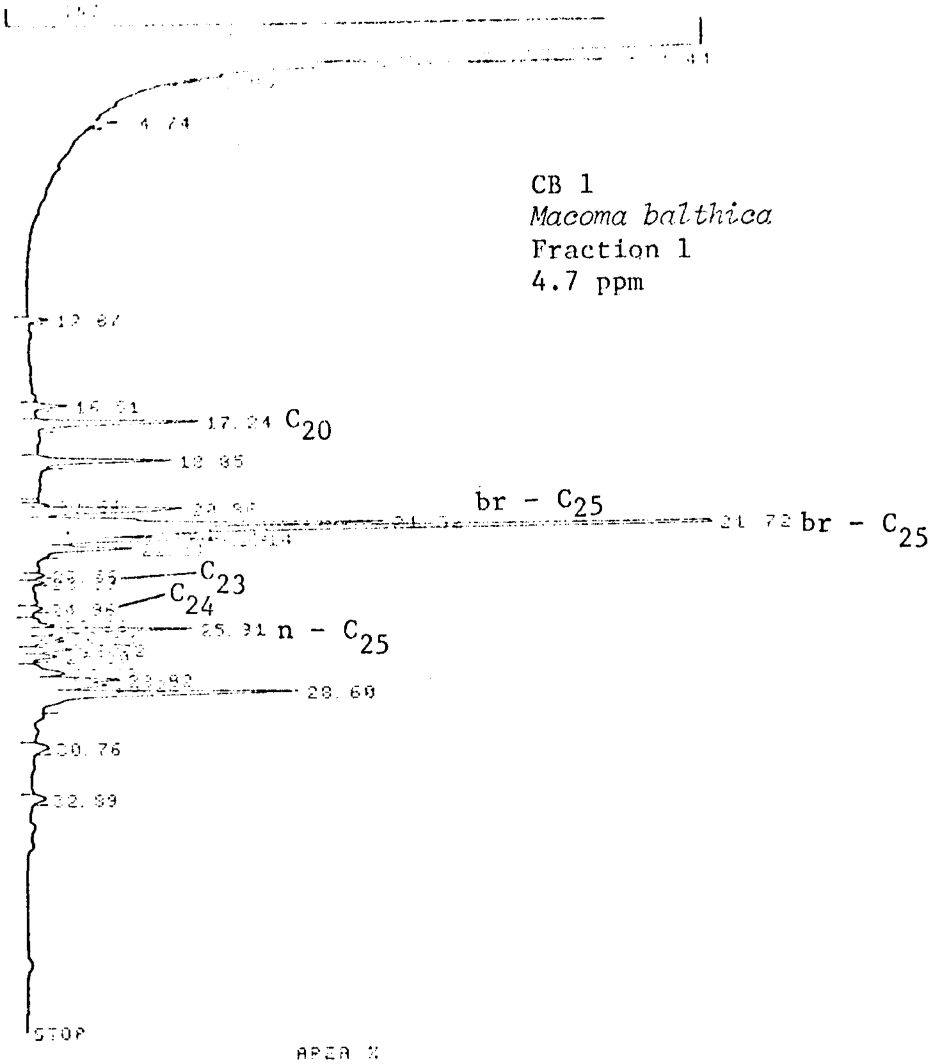
NO 7726
DLY  2            SLOPE  45          REJECT    100
MAXM    0         ATTN       4
```

035



IB 4
Macoma balthica
Fraction 2
5.7 ppm

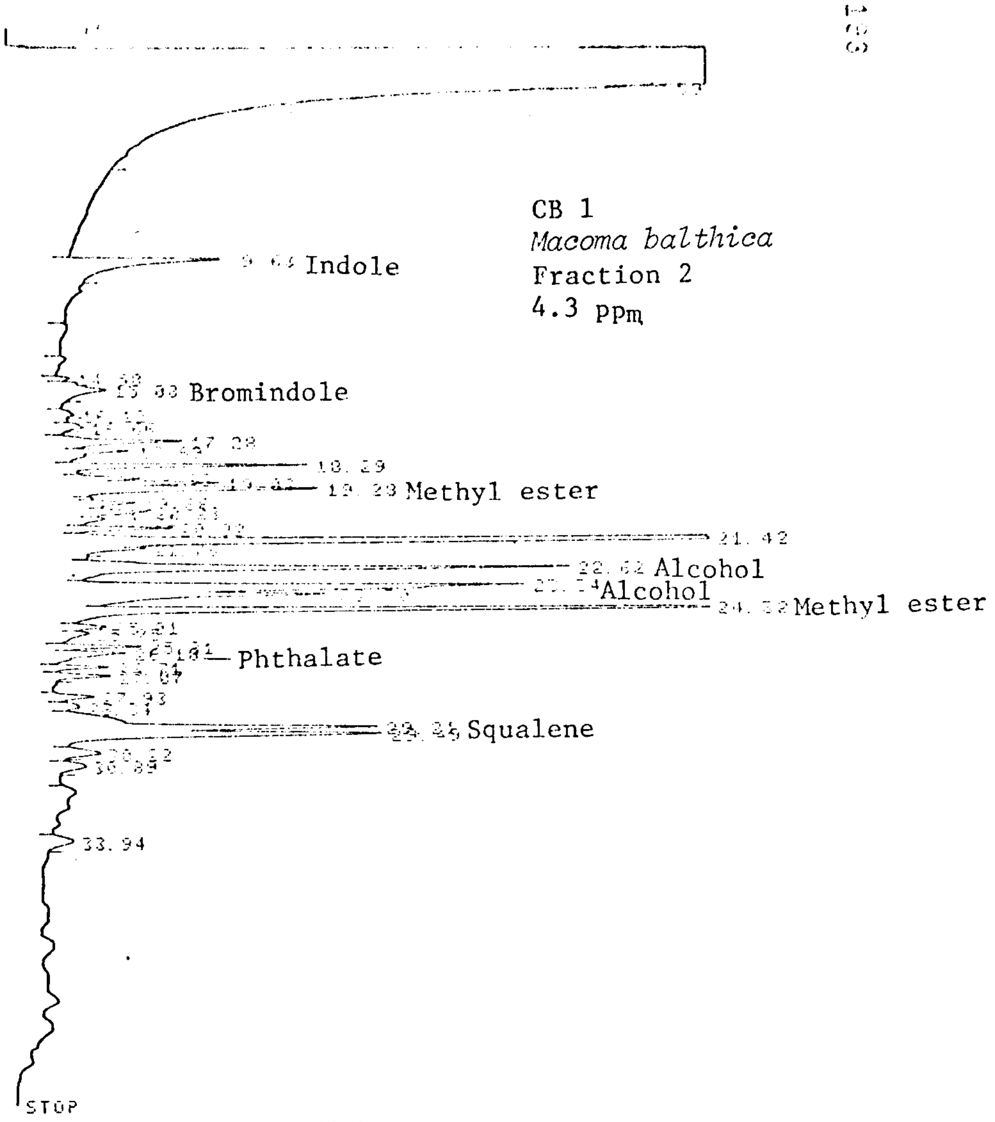
```
                                   AREA %
        RT     TYPE      AREA
A,R [illegible]                [illegible]                5.482
R   [illegible]                [illegible]                 [illegible]
     16.59                  434                     .111
     18.08                 1075                     .262 5
C*   18.75                 7296                   1.789
     19.25                  989                     .241 3
     19.67      M         11908                   2.907
C*   [illegible] M     [illegible]                .773
     [illegible] M     [illegible]7               2.053
A    [illegible]
     21.18             [illegible]                 .271
     [illegible] M     [illegible]6               [illegible]
     [illegible] M     [illegible]                 .292
     [illegible]       [illegible]45              1.[illegible]9
                M      [illegible]                 .471 6
                M      [illegible]41              2.[illegible]
                M      [illegible]                 .71[illegible]
                M      [illegible]                1.[illegible]
A    [illegible]
     [illegible] M     [illegible]                 [illegible]
A    [illegible]
A    [illegible]
     [illegible]       [illegible]                 [illegible]
C    [illegible]
     [illegible] M     [illegible]                 [illegible]
     [illegible] M     [illegible]                 [illegible]
     [illegible] M     [illegible]                 [illegible]
C*   [illegible] M     [illegible]                 [illegible]
     [illegible] M     [illegible]                 [illegible]
```



CB 1
Macoma balthica
Fraction 1
4.7 ppm

AREA %

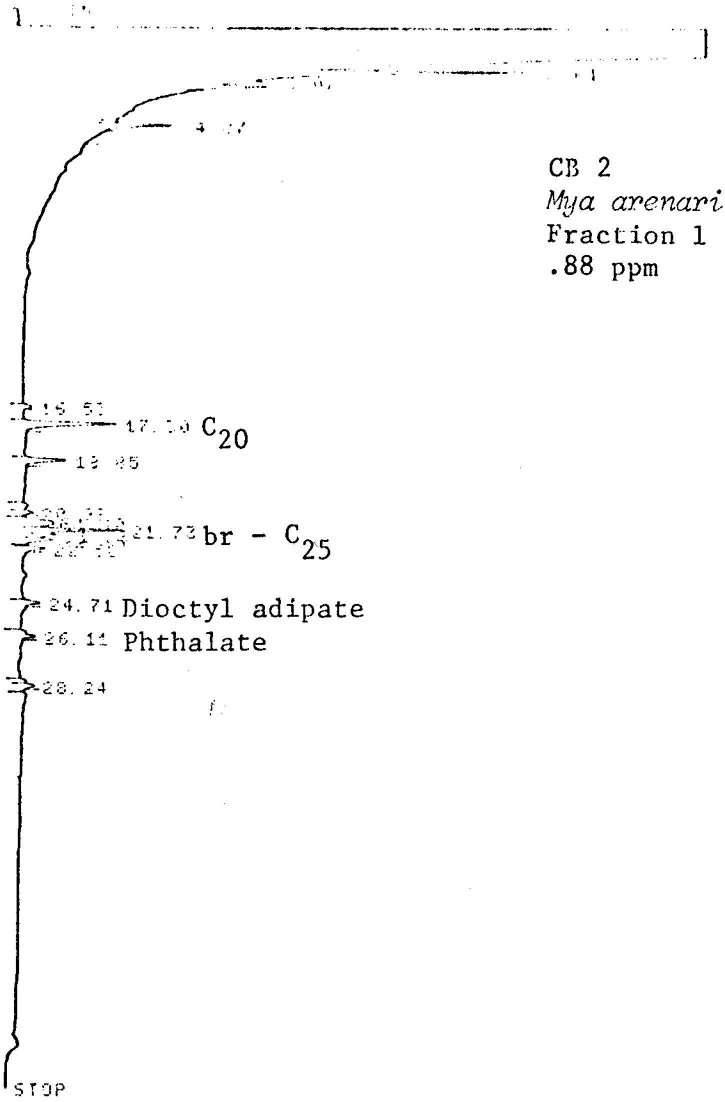
	RT	TYPE	AREA	AREA %
SOL	~~[illegible]~~	~~[illegible]~~	~~[illegible]~~	~~[illegible]~~
SOL	~~[illegible]~~	~~[illegible]~~	~~[illegible]~~	~~[illegible]~~
SOL	~~[illegible]~~	~~[illegible]~~	~~[illegible]~~	~~[illegible]~~
	[illegible] 67		[illegible]	514 9
	[illegible] 51		1211	219 6
SPT	~~[illegible]~~		~~[illegible]~~	~~[illegible]~~
	[illegible]		[illegible]	[illegible] 049
SPT	~~[illegible]~~		~~[illegible]~~	~~[illegible]~~
	[illegible]	[illegible]	[illegible]	5 [illegible]
	21 52	[illegible]	[illegible]	11 [illegible]
	21 72	[illegible]	[illegible] 156	[illegible]
	21 92	[illegible]	[illegible]	[illegible] 241
	[illegible] 14	[illegible]	13474	5 [illegible]
	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]		[illegible]	[illegible]
	[illegible]		[illegible]	[illegible]
	[illegible]		[illegible]	[illegible]
	[illegible]		[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]
SPT	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]
SPT	[illegible]	[illegible]	[illegible]	[illegible]
SPT	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]		[illegible]	[illegible]
	[illegible]		[illegible]	[illegible]



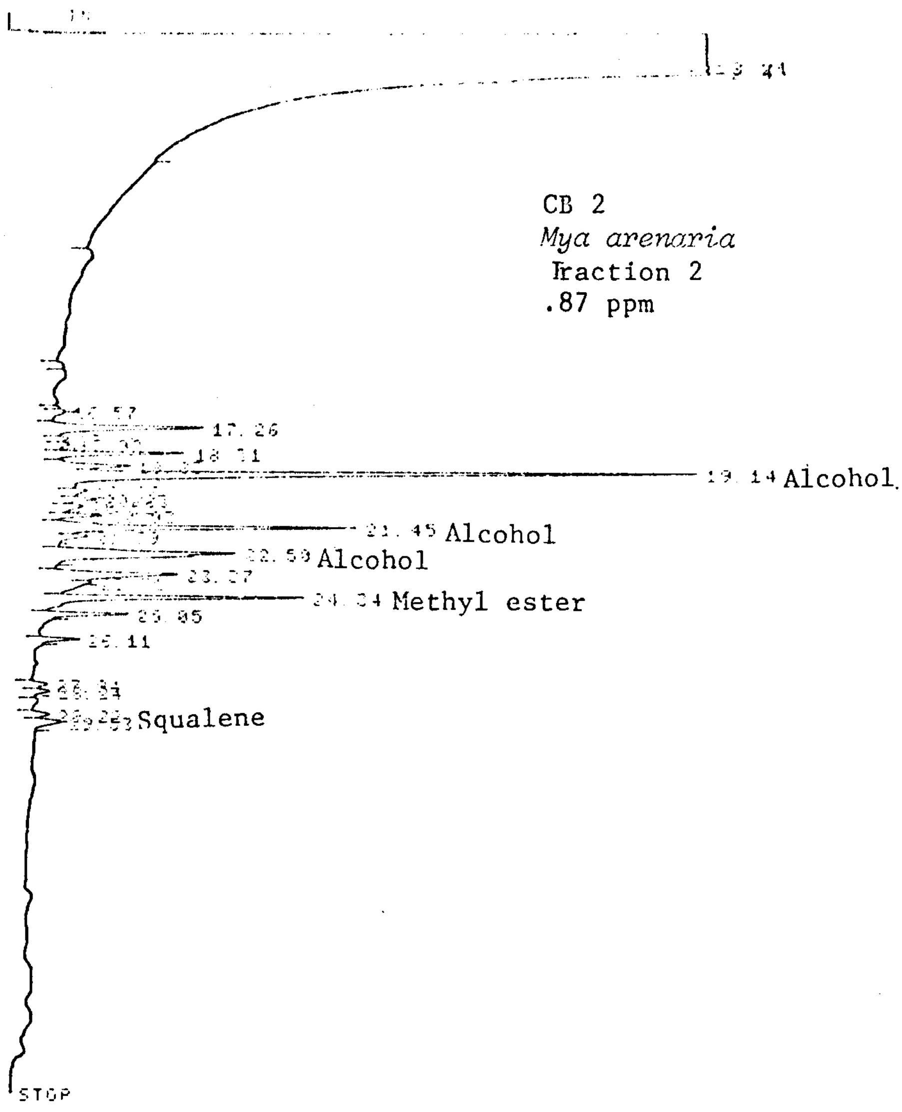
CB 1
Macoma balthica
Fraction 2
4.3 ppm

```
                                   AREA %
          RT    TYPE      AREA
SOL  [illegible]
A, R [illegible]
     [illegible] 50              515                [illegible]
A    [illegible]
     [illegible] 12              868                [illegible]
     [illegible]                1277                [illegible]
SPT  [illegible]
     [illegible]        M       [illegible]          [illegible]
     [illegible] 29             [illegible]          [illegible]
SPT  [illegible]
     [illegible]                [illegible]          [illegible]
MC   [illegible]
     [illegible]                [illegible]          [illegible]
     [illegible]        M       [illegible]          [illegible]
     [illegible] 51             [illegible]          [illegible]
     [illegible]                [illegible]          [illegible]
A
M
A, SPT
A
     [illegible]
M
     [illegible]
CNT  [illegible]
     [illegible]
```

CB 2
Mya arenaria
Fraction 1
.88 ppm

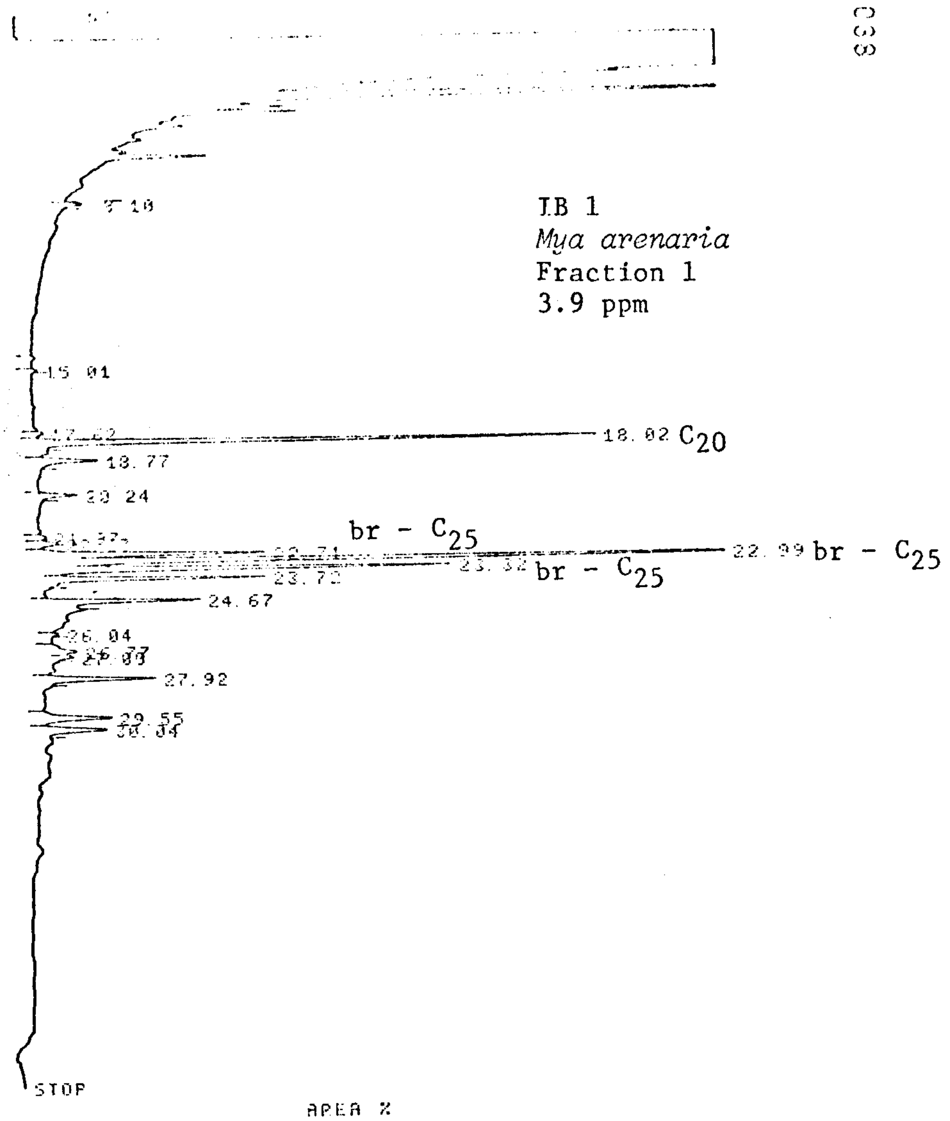


```
                                   AREA %
     RT     TYPE        AREA
SOL
SOL
SOL
SOL
  15.57                  507                     1.774
  17.10                 [illegible]              16.27
  18.85                 2?17                      7.27
  20.33                  501                      1.4
  21.40                  280                       .924
  21.73                 [illegible]42             10.76
  21.93                 1?02
  22.15                 1?54
CNT
CNT
STD
```



CB 2
Mya arenaria
Fraction 2
.87 ppm

```
                          AREA %
   RT     TYPE     AREA
SOL
SOL
[illegible].57             117                 .373   51
SPT
17.69      M       323                 .219   5
17.92              452                 .307   2
[illegible]             5734                4 [illegible]
SPT
A
[illegible]             [illegible]                1 [illegible]
[illegible]              2091                1 .421
[illegible]     M      [illegible]                 .138
[illegible]              [illegible]                1 [illegible]
A
[illegible]              [illegible]                  [illegible]
A
A
                                                1[illegible]
A
CNT
SPT
CNT
```



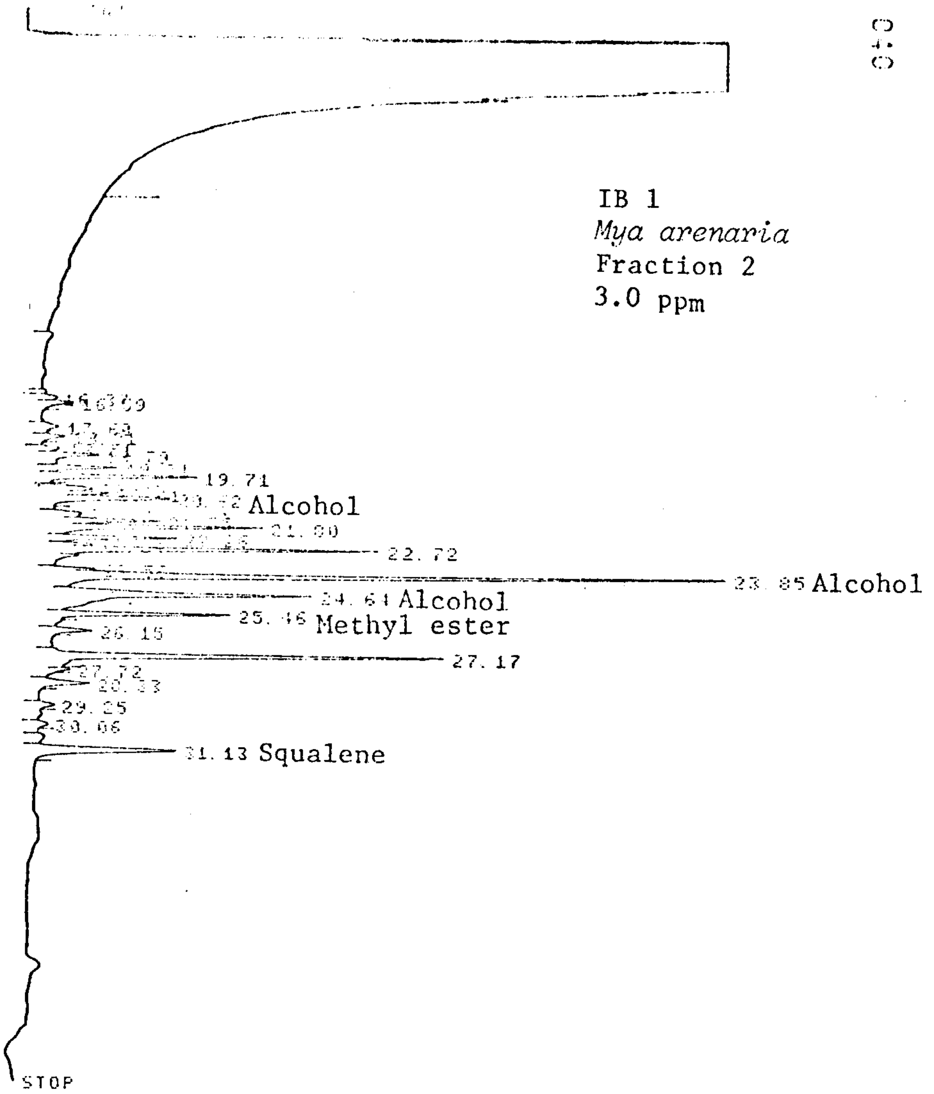
IB 1
Mya arenaria
Fraction 1
3.9 ppm

```
                        AREA %
    RT     TYPE      AREA
R ~~[illegible]~~
  15.01                241            .1726
  17.62                271            .1952
  18.02              24520          17.67
SPT ~~[illegible]~~
SPT ~~[illegible]~~
  ~~[illegible]~~
  22.13                986            .7101
  22.71     M        13549           9.757
  22.99     M        38062          27.41
  23.32     M        20559          14.81
  23.72     M        11069           7.972
  24.67               5658           4.074
  26.04                277            .1995
  26.77               1782           1.283
  27.00     M          901            .6489
  27.92               5894           4.245
  29.55               4925           3.547
  30.04     M         4106           2.95

HP [illegible]
[illegible]            [illegible] 45        REJECT    100
[illegible]    30      ATTN      4
```

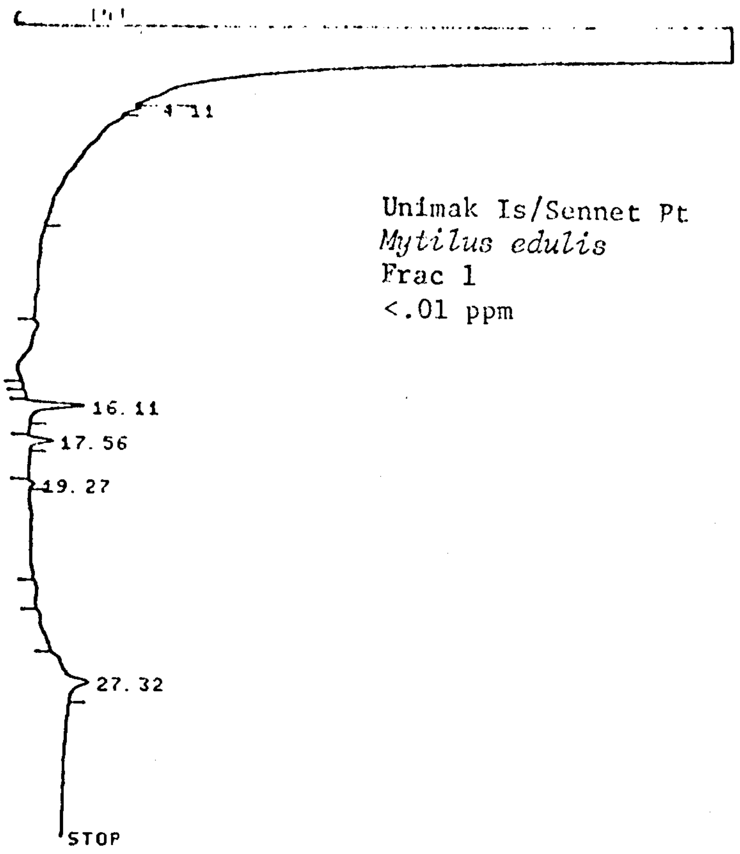
040

IB 1
Mya arenaria
Fraction 2
3.0 ppm



```
                         AREA %
      RT    TYPE      AREA
   15 37                802                 .443 8
   16 59     M         1976                1.094
   17 60               1125                 .622 6
   18 01               1050                 .581 1
   18.51               1000                 .553 4
C* 18.79     M         4397                2.431
   19 71     M         7532                4.955
   19 71     M         7377                4.087
C* 20 [illegible]      2787                1.54
   20 41     M         2791                1.545
A  [illegible]
   21.24               1299                 .718 9
   21 [illegible] M    6155                3.413
   21 [illegible] M   10270                5.729
   22.26     M         4853                2.686
   22 54     M          812                 .449 4
   22 72     M        13843                7.661
   22 86               1543                 [illegible] 8
A  [illegible]
A  [illegible]
Me [illegible]
   [illegible]         [illegible]         1.[illegible]8
C* 27 1[illegible]     [illegible]        10 [illegible]
   [illegible]         [illegible]          [illegible] 2
   [illegible]         [illegible]         1.[illegible]
   [illegible]         [illegible]          [illegible] 6
   [illegible]         [illegible]          [illegible] 2
   [illegible]         [illegible]         [illegible]
```

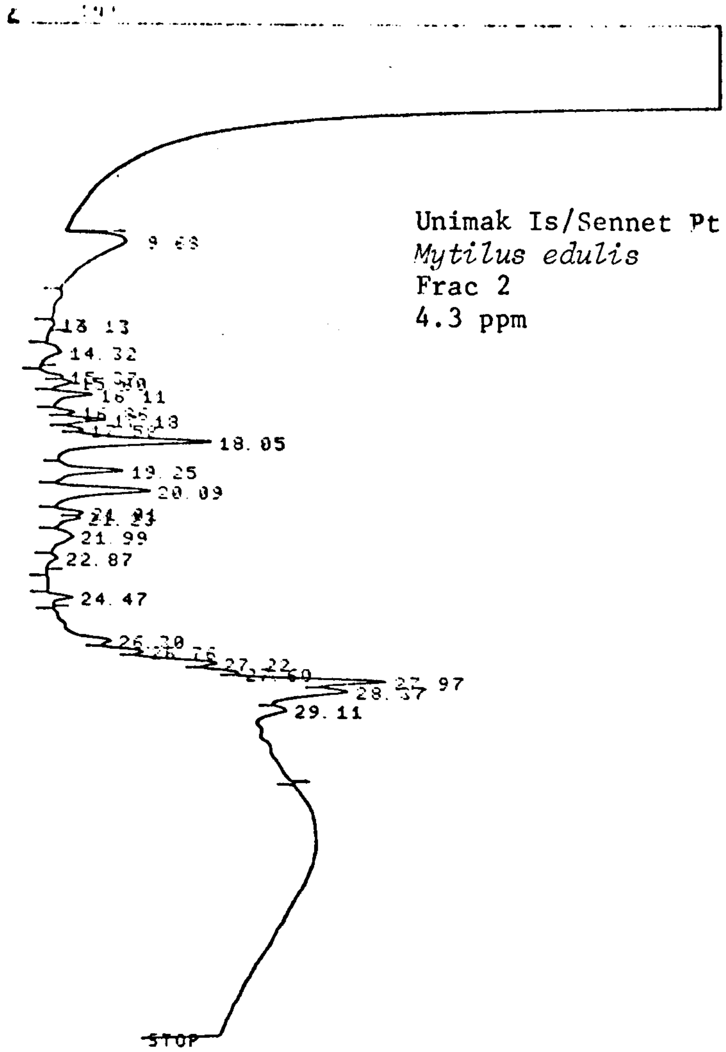
041



Unimak Is/Sennet Pt
Mytilus edulis
Frac 1
<.01 ppm

```
                                AREA %
     RT     TYPE        AREA
•   4.11     T           451                3.234
s  16.11                5051               35.99
s  17.56                1919               13.71
s  19.27                 447                3.194
s  27.32                6117               43.71


HP 3380A
DLY  4.         STOP 45           REJECT    100
MV/M  .10       ATTN      4
```

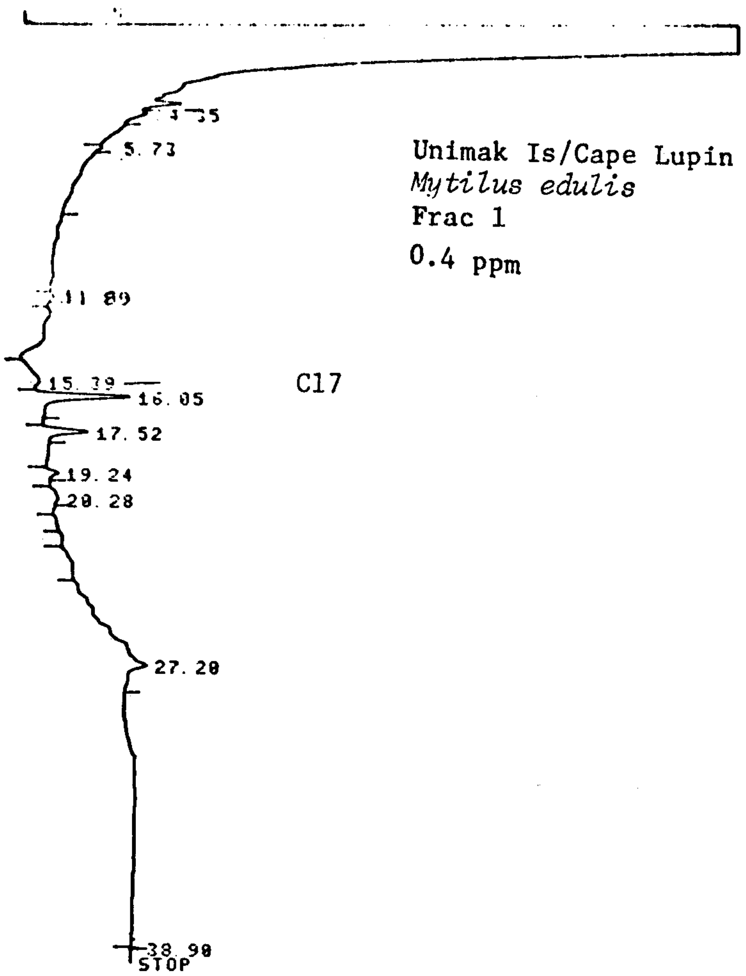


Unimak Is/Sennet Pt
Mytilus edulis
Frac 2
4.3 ppm

AREA %

	RT	TYPE	AREA	
O	~~9.63~~	~~T~~	~~[illegible]~~	~~12.[illegible]~~
	13.13	T	409	[illegible] 5
	14.32	T	2694	1.[illegible]
	15.37	T	1670	851 7
	15.60	TM	3473	1.771
S	~~16.11~~	~~TM~~	~~5159~~	~~[illegible].141~~
	16.86	TM	3050	1.555
	17.18	TM	6023	3.072
S	~~17.59~~	~~TM~~	~~3213~~	~~1.639~~
	18.05	TM	23899	12.19
	19.25	TM	11519	5.875
	20.09	TM	15407	7.858
	21.01	TM	3365	1.716
	21.23	TM	4156	2.1[illegible]5
	21.99	TM	5741	2.[illegible]
	22.87	TM	1403	715 5
C	~~24.47~~	~~T~~	~~[illegible]~~	~~[illegible]~~
	26.76	[illegible]	1980	1.01
	27.22	[illegible]	8809	4.4[illegible]
	27.60	[illegible]	7464	3.[illegible]
	27.97	TM	25611	13.06
	28.37	TM	25375	12.94
	29.11	TM	9351	4.769

```
HP 3390A
[illegible]  4          STOP 45          REJECT   100
MV/M    10          ATTN       4
```

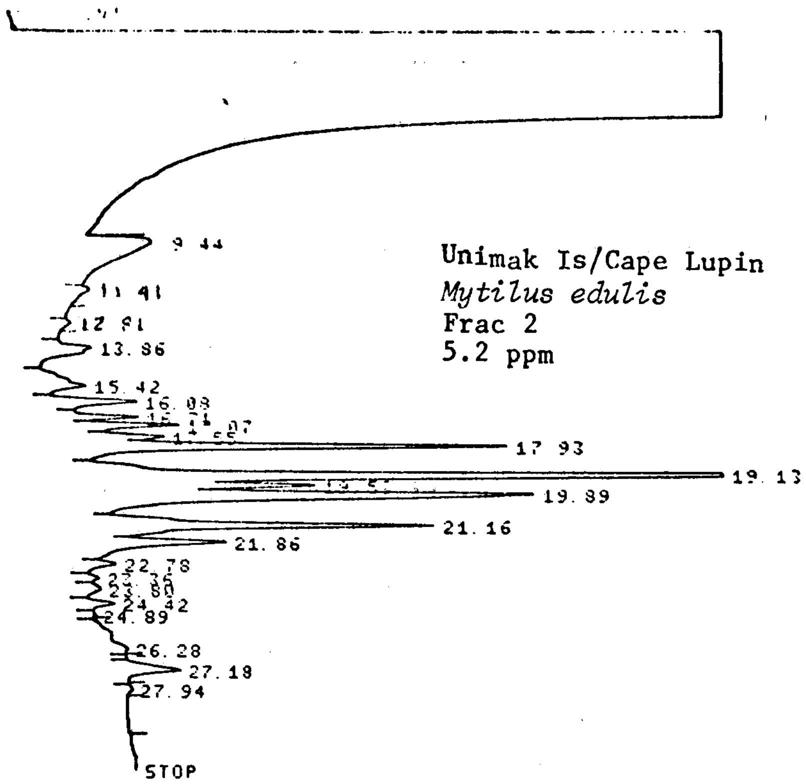


Unimak Is/Cape Lupin
Mytilus edulis
Frac 1
0.4 ppm

C17

```
                                AREA %
   RT     TYPE       AREA
 ~~4.35     TM        783              2.055~~
 ~~5.73     T         232               .598 9~~
11.89                 476              1.249
15.39                2524              6.624
16.05       M        9421             24.7[illegible]
17.52                3562              9.[illegible]
19.24                 902              2.[illegible]
20.28                1083              2.842
27.20               19100             50.13

HP 3380A
DLY  4.            STOP 45          REJECT   100
MV/M  .10          ATTN     4
```

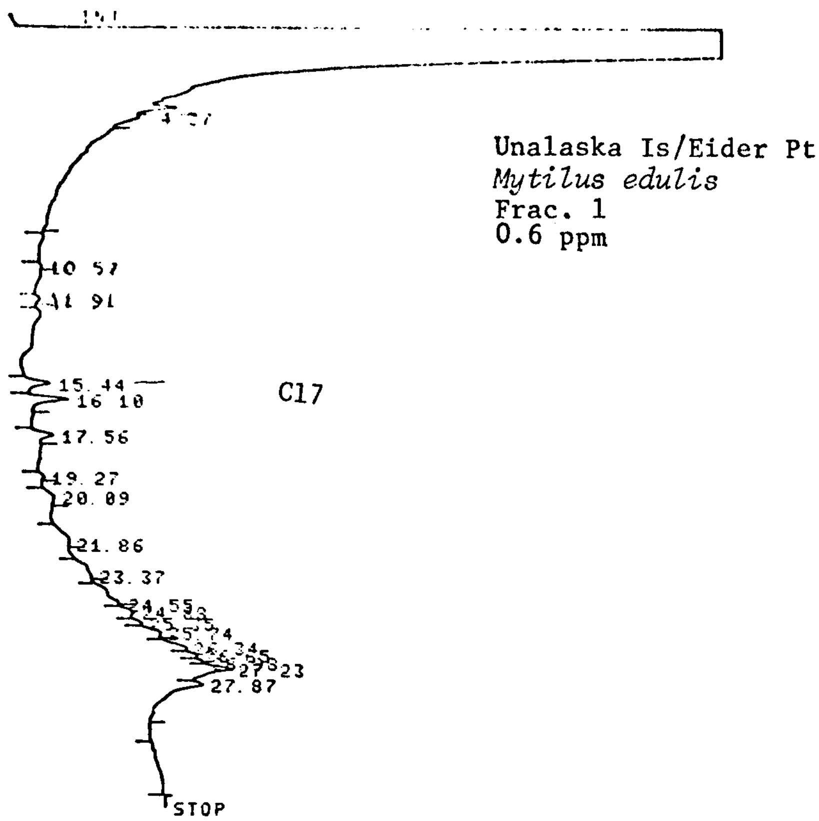


Unimak Is/Cape Lupin
Mytilus edulis
Frac 2
5.2 ppm

AREA %

	RT	TYPE	AREA		
C	~~9.44~~	~~T~~	~~23651~~	~~6.146~~	
	11.41	TM	2359	.613	
	12.81	T	838	.217	8
	13.86	T	6181	1.606	
	15.42	TM	6868	1.785	
S	~~16.03~~	~~TM~~	~~8911~~	~~2.316~~	
	16.71	TM	8403	2.184	
	17.07	TM	12100	3.144	
	17.55	TM	10479	2.723	
	17.93	TM	44437	11.55	
	19.13	TM	87737	22.8	
	19.53	TM	20618	5.358	
	19.89	TM	67540	17.55	
	21.16	TM	45375	11.79	
	21.86	TM	21740	5.65	
	22.78	TM	4089	1.062	
	23.26	TM	1396	.362	8
	23.80	TM	2159	.561	1
C	~~24.42~~	~~TM~~	~~2022~~	~~.525~~	~~5~~
	24.89	TM	296	.076	92
	26.28	T	1089	.283	
	27.18	T	6106	1.587	
	27.94	T	411	.106	9

HP 3380A
DLY 4 STOP 45 REJECT 100
MV/M .10 ATTN 4

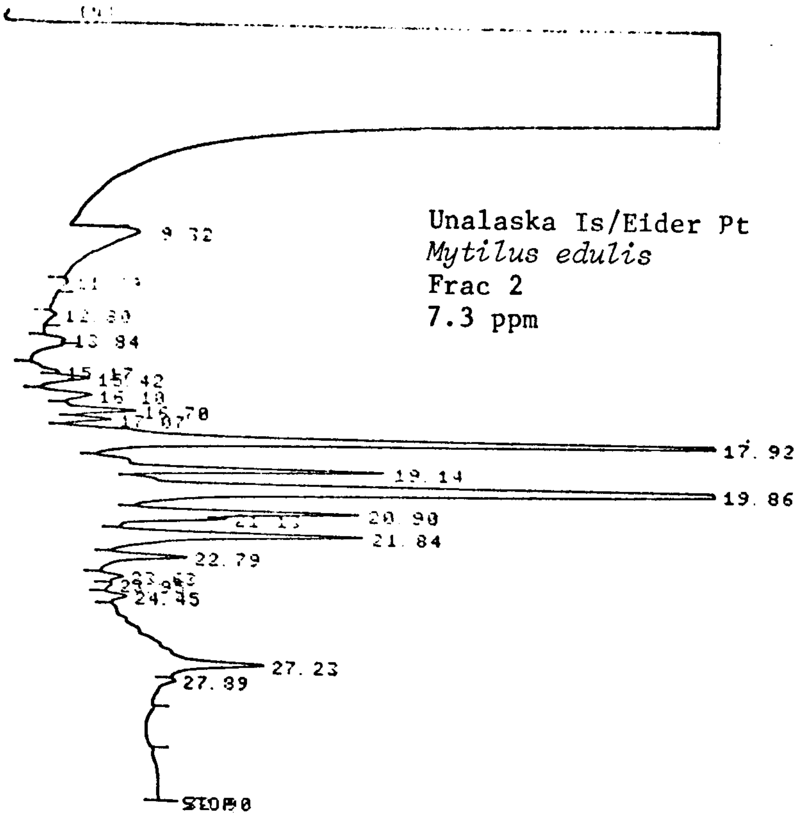


Unalaska Is/Eider Pt
Mytilus edulis
Frac. 1
0.6 ppm

AREA %

	RT	TYPE	AREA		
o	~~4.37~~	~~TM~~	~~396~~	~~.859~~	~~1~~
o	~~10.57~~		~~215~~	~~.466~~	~~6~~
	11.91		391	.848	6
	15.44		2167	4.703	
s	~~16.10~~	~~M~~	~~3115~~	~~6.76~~	
s	~~17.56~~		~~1340~~	~~2.908~~	
s	~~19.27~~		~~300~~	~~.651~~	~~1~~
	20.09		861	1.869	
	21.86		1158	2.513	
	23.37		945	2.051	
	24.55		683	1.482	
	24.88		573	1.244	
	25.35	M	155	.338	6
	25.74	M	605	[illegible]	
	26.34		2675	[illegible]	
	26.65	M	3021	6.51	
	26.98	M	3608	7.83	
s	~~27.23~~	~~M~~	~~13446~~	~~29.18~~	
	27.87	M	9522	20.67	

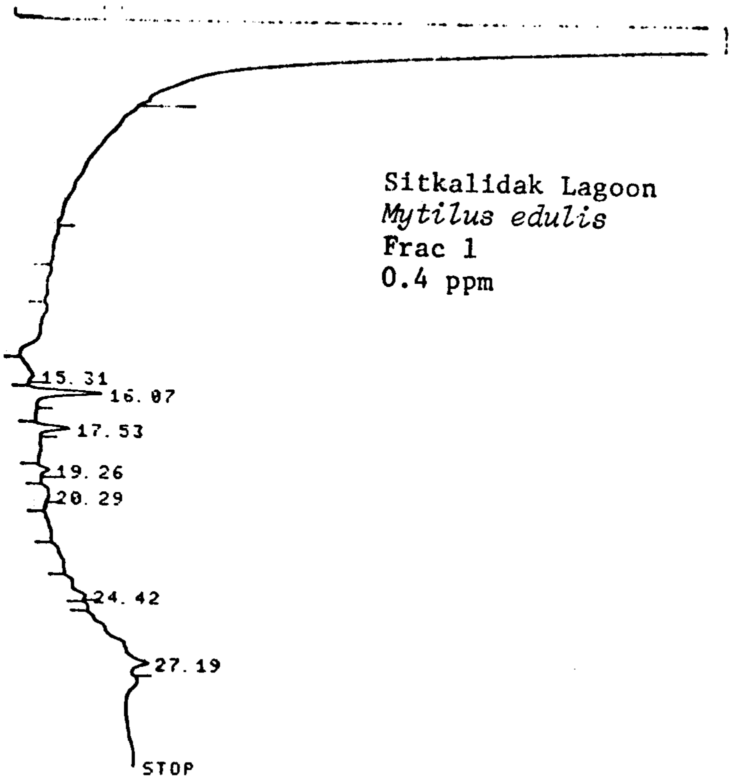
```
HP 3380A
DLY   4.          STOP 45          REJECT    100
MV/M  .10         ATTN      4
```



Unalaska Is/Eider Pt
Mytilus edulis
Frac 2
7.3 ppm

	RT	TYPE	AREA	AREA %
o	~~9.32~~	~~T~~	~~23730~~	~~5.774~~
	11.39	TM	1045	.254 3
	12.80	T	803	.195 4
	15.17	T	1995	.485 4
	15.42	TM	5135	1.25
s	~~16.10~~	~~TM~~	~~5383~~	~~1.31~~
	16.70	TM	8339	2.029
	17.07	TM	5171	1.258
	17.92	TM	36995	21.17
	19.14	TM	34528	8.402
	19.86	TM	111907	27.23
	20.90	TM	25093	5.126
	21.13	TM	11189	2.965
	21.84	TM	15531	3.365
	22.79	TM	9452	2.3
	23.63	TM	1737	.422 7
	23.95	TM	651	.158 4
C	~~24.45~~	~~TM~~	~~1374~~	~~.334 3~~
S	~~27.23~~	~~TM~~	~~33249~~	~~3.091~~
	27.89	TM	5215	1.269
	32.90	I	371	.090 28

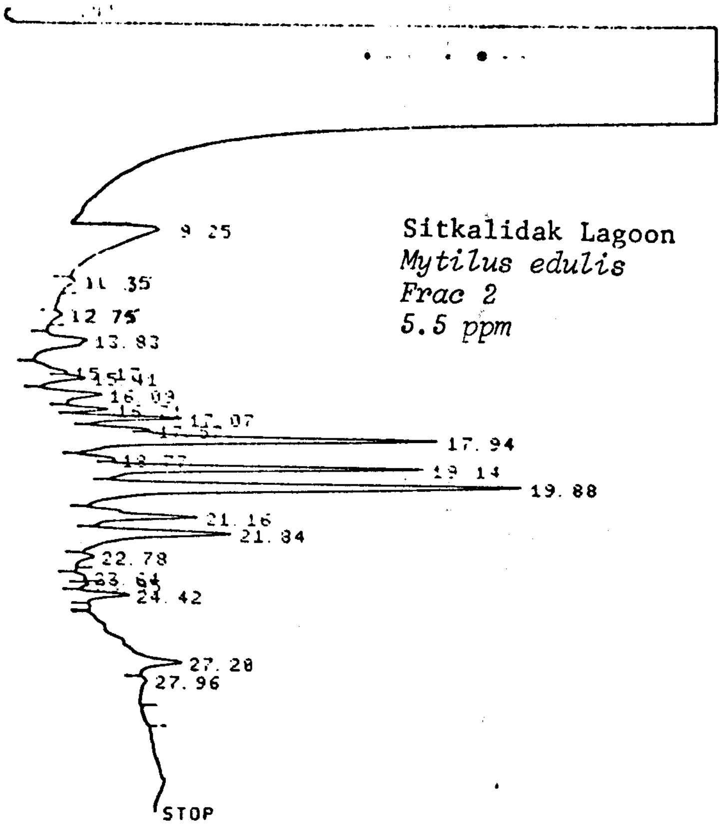
```
HP 3380A
DLY  4.          STOP 45         REJECT   100
MV/M   10        ATTN     4
```



Sitkalidak Lagoon
Mytilus edulis
Frac 1
0.4 ppm

```
                        AREA %
   RT    TYPE      AREA
 15.31             1430          7.299
~~16.07             5835         29.78~~
~~17.53             2406         12.28~~
~~19.26              776          3.961~~
 20.29             1068          5.451
 24.42              601          3.067
 27.19             7477         38.16

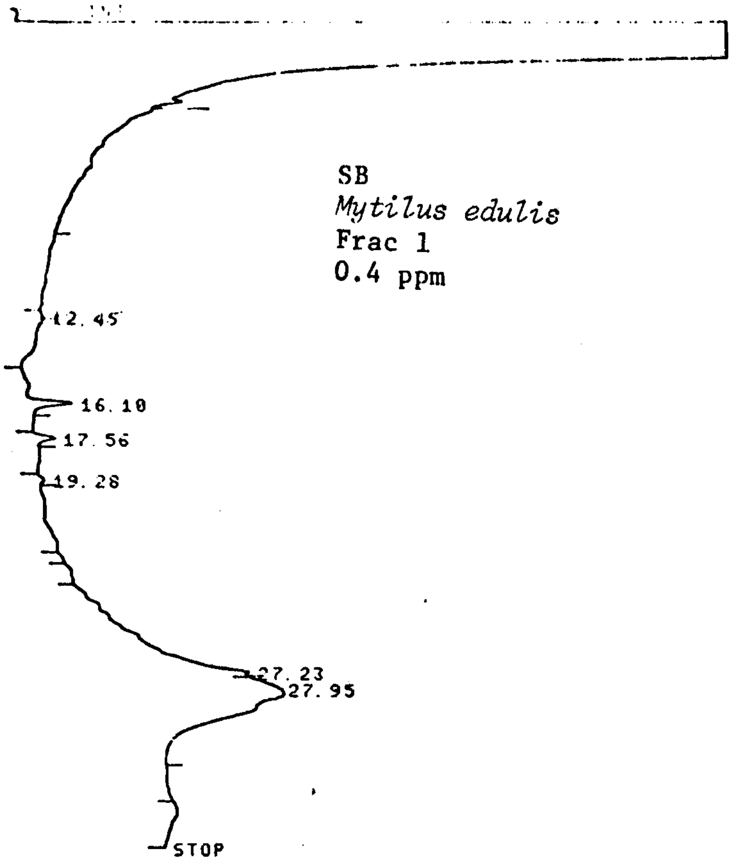
HP 3390A
DLY   4.          STOP 45          REJECT   100
MV/M  .10         ATTN     4
```



Sitkalidak Lagoon
Mytilus edulis
Frac 2
5.5 ppm

```
                                       AREA %
       RT     TYPE       AREA
O ~~  9.25     T         39142                     10.2~~
     11.35     TM         1580                      .534 6
     12.75     T          1156                      .391 2
     13.83     T          6971                     2.359
     15.17     TM         2822                      .954 9
     15.41     TM         4677                     1.583
S ~~ 16.09     TM         7000                     2.369~~
     16.71     TM         6069                     2.054
     17.07     TM        12113                     4.099
S ~~ 17.57     TM         7476                     2.53~~
     17.94     TM        45537                    15.41
     18.77     TM         5857                     1.981
     19 14     TM        36103                    12.22
     19 88     TM        60607                    20.51
     21.16     TM        17500                     5.922
     21.84     TM        22942                     7.763
     22.78     TM         1963                      .664 2
     23.64     T           321                      .108 6
     23.95     T           216                      .073 09
C ~~ 24.42     TM   [illegible]                    4.143~~
     27.20     T         17122                     5.794
     27 96     TM         3761                     1.273

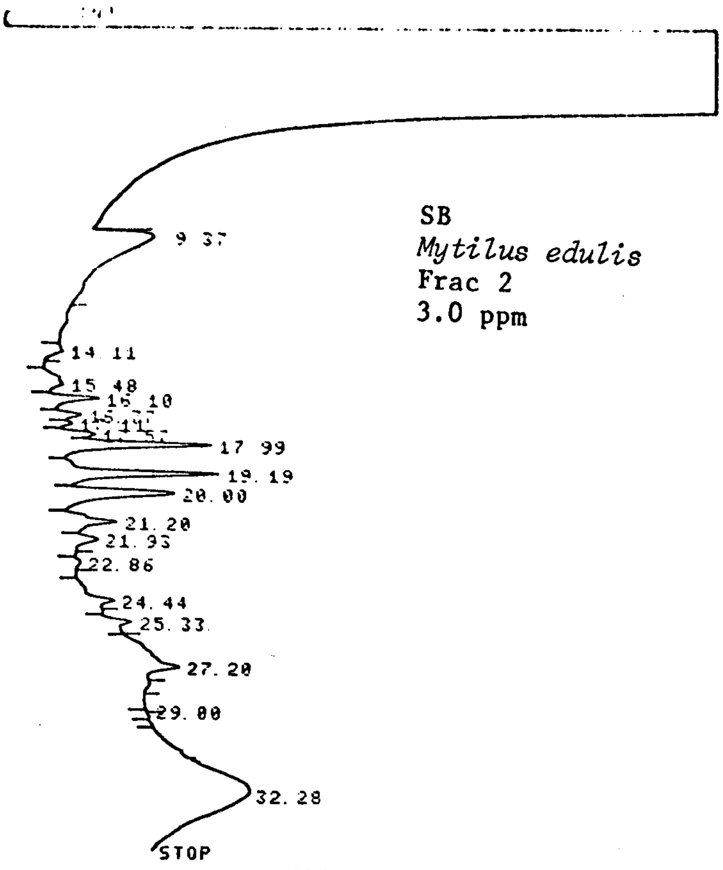
 HP 3380A
 CLV   4             STOP 45              REJECT    100
 MV/M    10          ATTN       4
```



SB
Mytilus edulis
Frac 1
0.4 ppm

```
                         AREA %
     RT    TYPE      AREA
   12.45              194               .331 4
s ~~16.10                3815              16.35~~
s ~~17.56                1537              6.587~~
s ~~19.28                 487              2.087~~
   27.95            17302              74.15

HP 3380A
DLY  4.          STOP 45          REJECT   100
MV/M  .10        ATTN     4
```

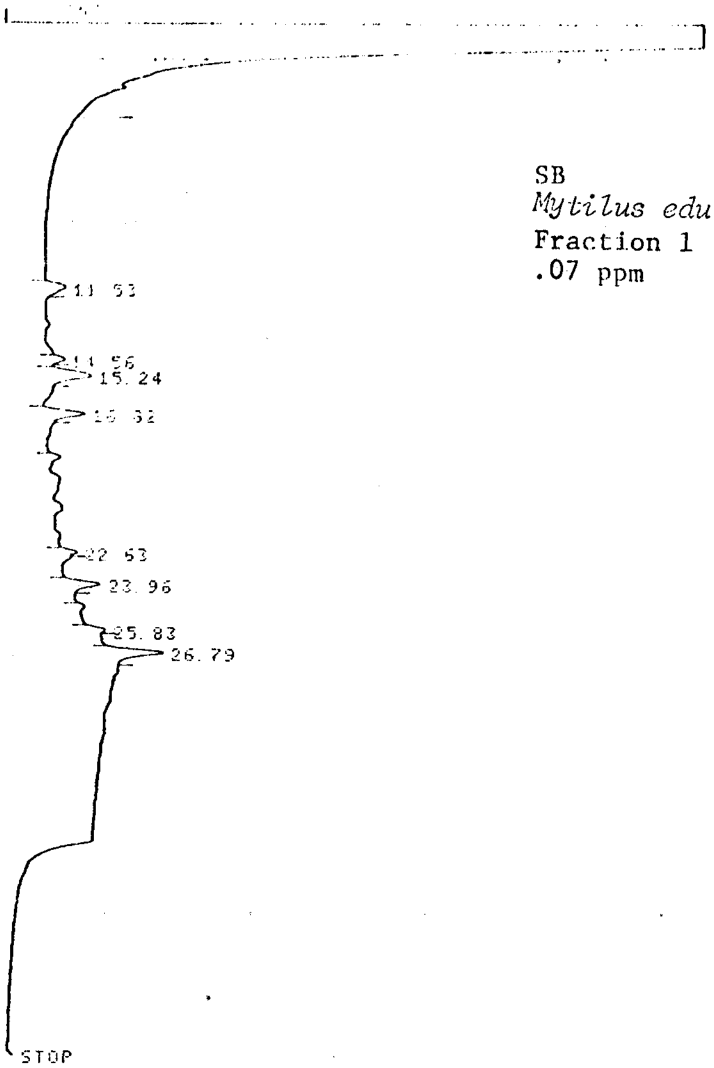


SB
Mytilus edulis
Frac 2
3.0 ppm

```
                                 AREA %
         RT     TYPE       AREA
0   ~~9. 37      T        25991                  13. 17~~
    14. 11       T         1308                    . 662 8
    15. 48       T         3193                   1. 618
S   ~~16. 10     TM        4939                   2. 452~~
    16. 77       TM        2821                   1. 43
    17. 11       TM        1707                    . 865
S   ~~17. 57     TM        5954                   2. 904~~
    17. 99       TM       16979                   8. 604
    19. 19       TM       17884                   9. 063
    20. 00       TM       14998                   7. 6
    21. 20       TM        6352                   3. 219
    21  93       TM        2850                   1. 444
    22  96       T          592                   [illegible]
    24. 44       T          641                    . 324 8
    25. 33       T         1178                    . 596 9
    27. 20       T         9304                   4. 715
    32. 28     I          82749                  41. 93

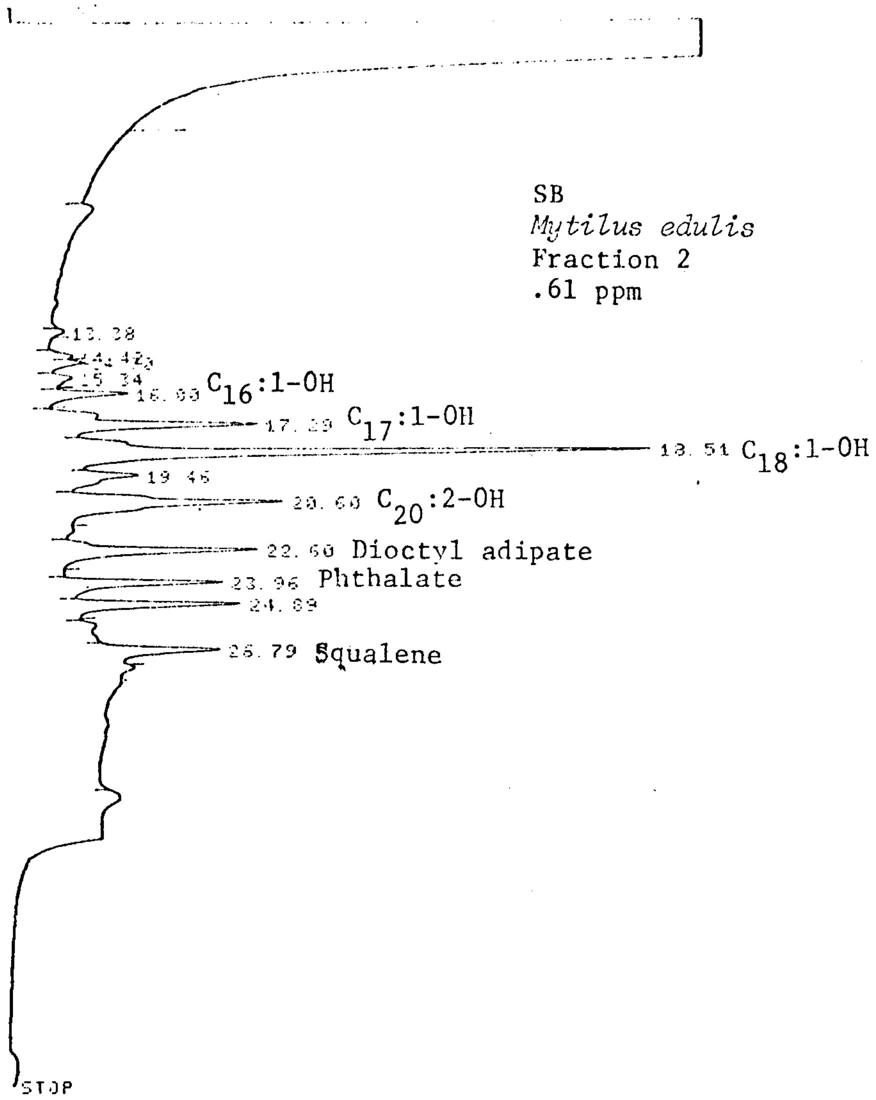
HP 3380A
DLY  4.            STOP 45              REJECT   100
MV/M  . 10         ATTN      4
```

SB
Mytilus edulis
Fraction 1
.07 ppm



```
                         AREA %
    RT    TYPE      AREA
  11 53             2750              11.75
  14.56             1016               4.341
S ~~[illegible]~~
S ~~[illegible]~~
C ~~[illegible]~~
C ~~[illegible]~~
 .25.83              450               1 323
C ~~[illegible]~~

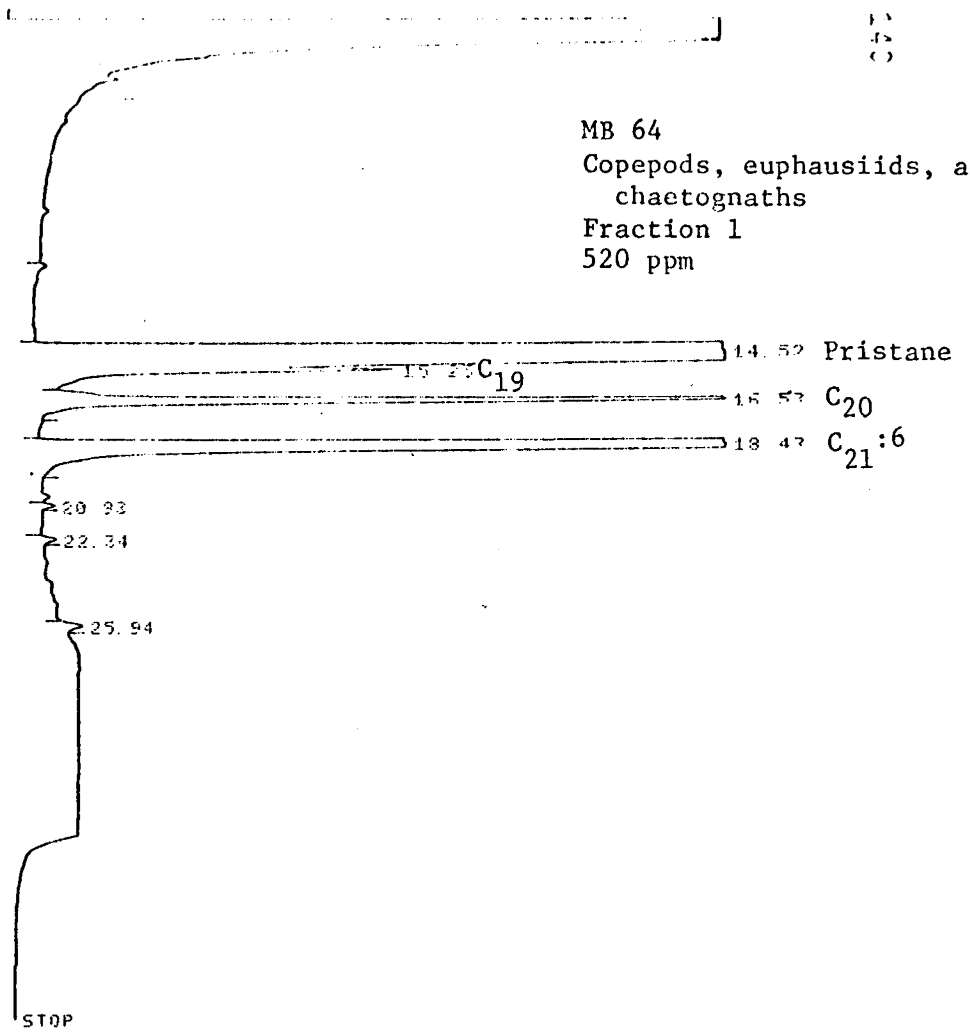
 HP 3380A
 DLY  4.            STOP 45          REJECT   100
 MV/M   30          ATTN      4
```



SB
Mytilus edulis
Fraction 2
.61 ppm

```
                    AREA %
    RT    TYPE     AREA
  13.38            1577            .716 3
  14.42             376            .170 3
S [illegible]
A [illegible]
A [illegible]
A [illegible]
  19.46    P      12708           5.776
A [illegible]
A [illegible]
A [illegible]
  24.89    M      15442           7.019
C [illegible]

HP 3390A
DLY  4           SLOP 45          REJECT    100
MV/M   10        ATTN      4
```

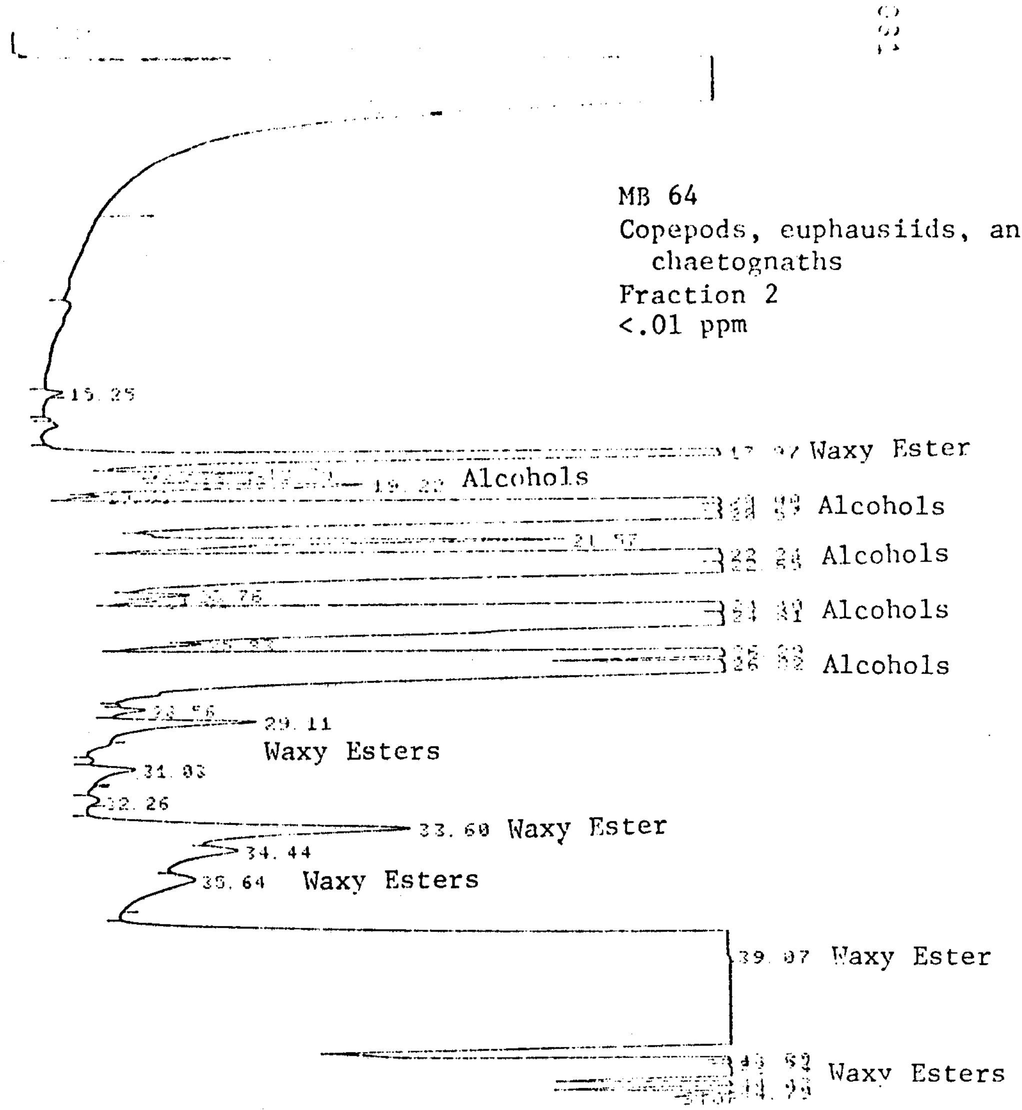


MB 64
Copepods, euphausiids, and
chaetognaths
Fraction 1
520 ppm

```
                         AREA %
    RT    TYPE      AREA
 14.52            7916373           92.63
 15.25     M        34147             .399 6
 16.53     M        68364              796 4
 18.43             521114            6 103
 20.93                871              010 19
 22.34               1080             .012 64
 25.94               1646              019 26


HP 3380A
DIV  4            STOP 45          REJECT    100
HV/M    30        ATTN       4
```

MB 64
Copepods, euphausiids, and
chaetognaths
Fraction 2
<.01 ppm



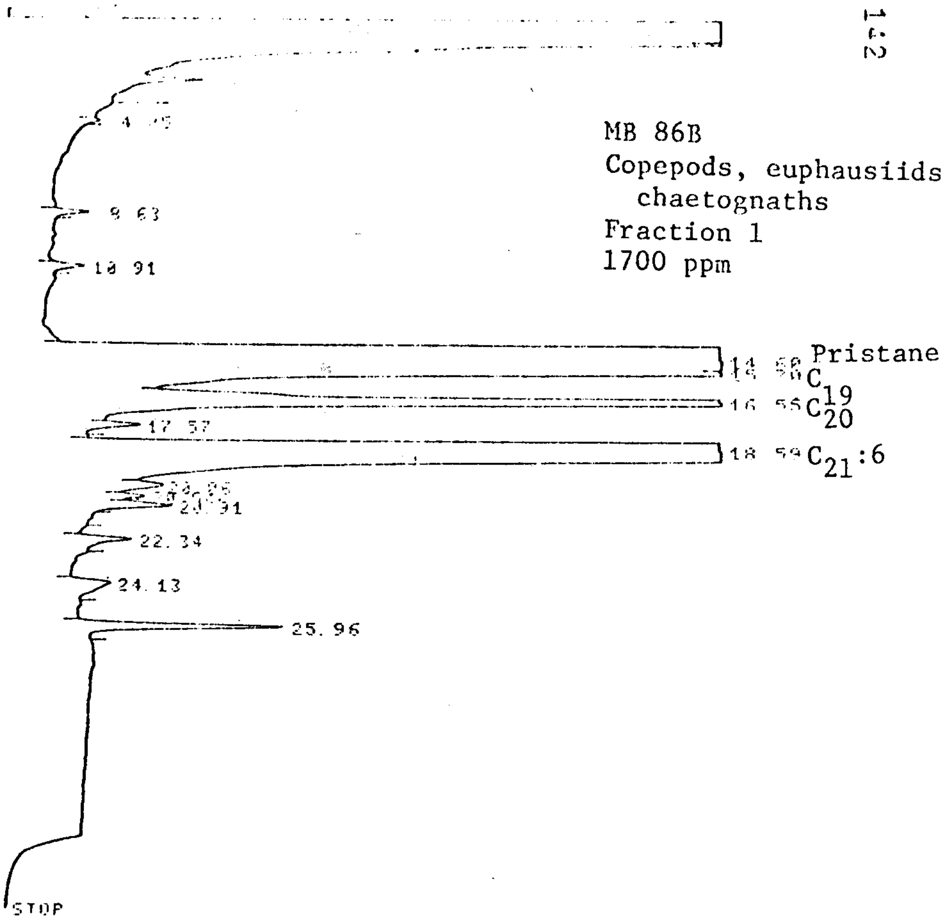
AREA %

RT TYPE AREA

C62

142

MB 86B
Copepods, euphausiids, some chaetognaths
Fraction 1
1700 ppm

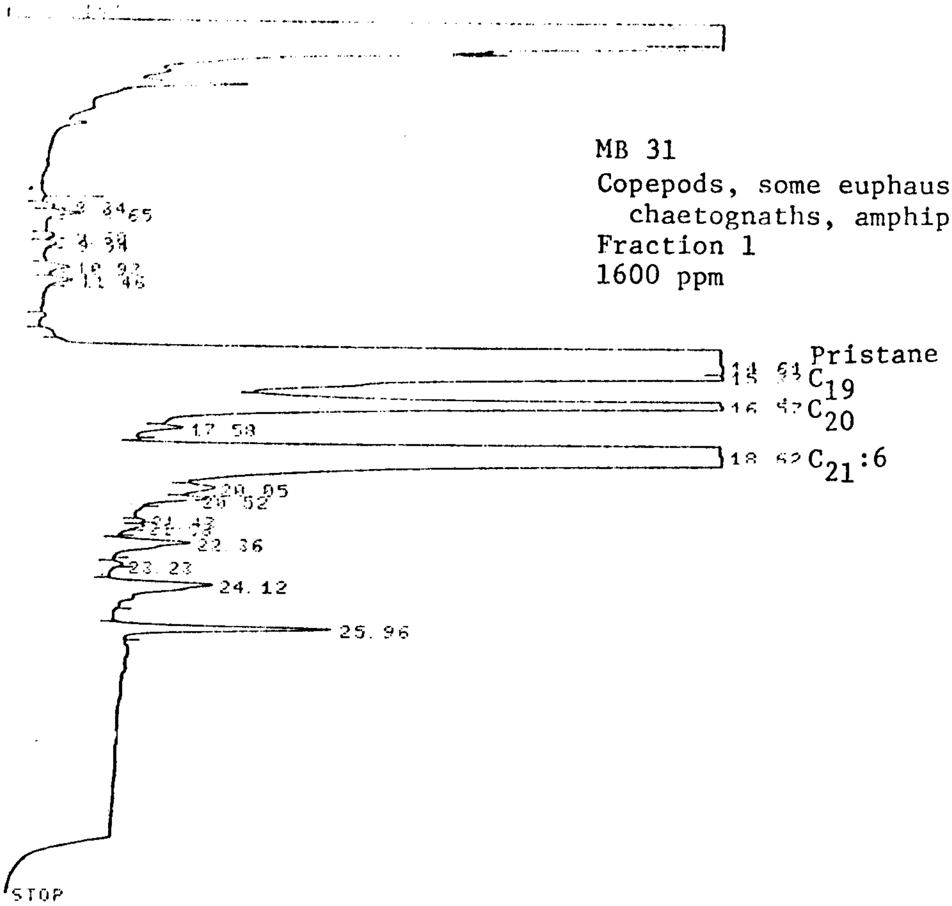


```
                                   AREA %
     RT    TYPE       AREA
R  [illegible]
R  [illegible]
  10 91                2834                     009 062
  14.60     *      22839977              71.77
  15 30     M        117493                     369 2
  16.55     M        206198                     647 9
  17.57     M          5483                    .017 23
  18 59             8614926              27.07
  20 06     T          3130                     009 835
  20.54     TM         1211                     003 805
  20 91     T          4347                    .013 66
  22.34                4430                     013 92
  24 13                5544                    .017 42
  25 96               16296                    .051 21

HP 3380A
SLP   4              STOP 45            REJECT    100
HVZM   20            ATTN      4
```

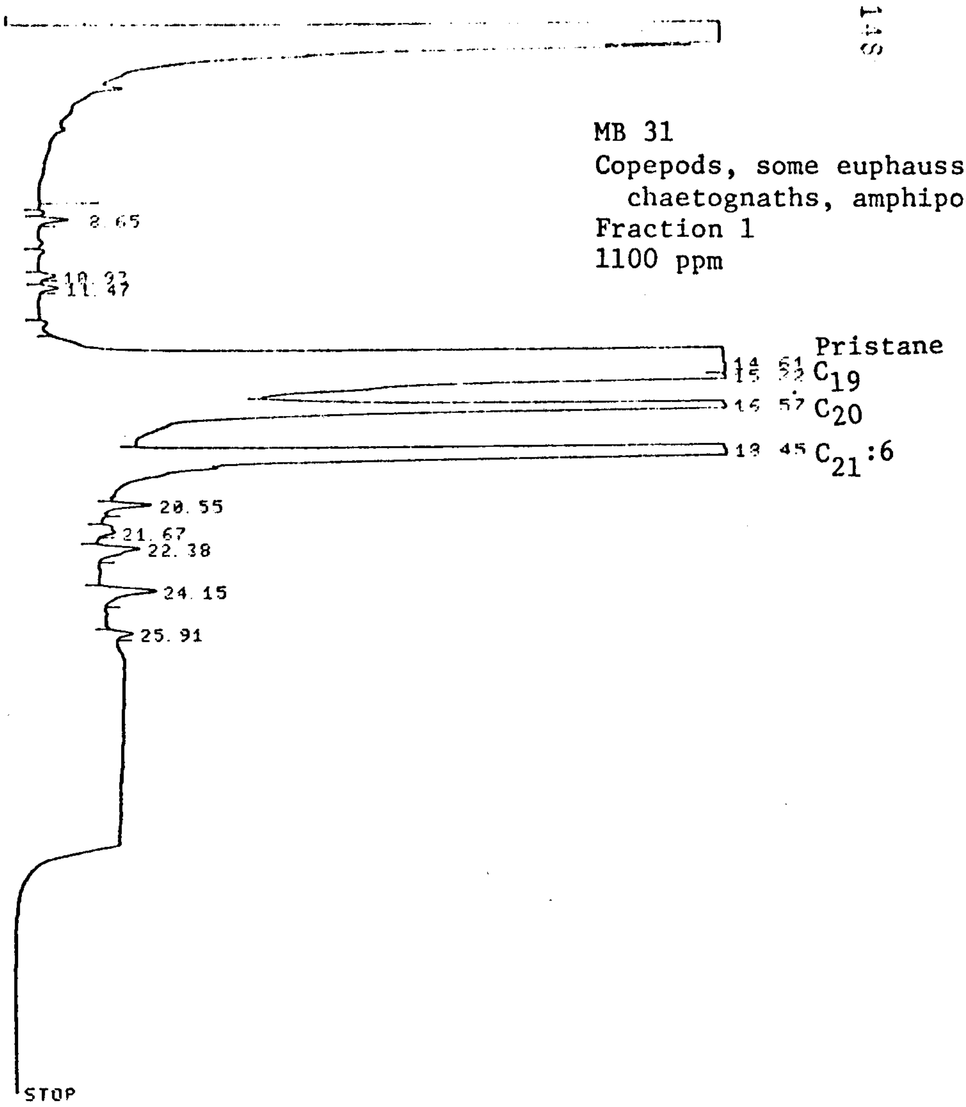
143

MB 31
Copepods, some euphausiids,
chaetognaths, amphipods, and terapods
Fraction 1
1600 ppm



```
                                      AREA %
      RT     TYPE        AREA
R [illegible]
R [illegible]
R [illegible]
    9 94                  579                    001 792
   10 93                 1910                    005 013
   11 45                 1775                    004 659
   14 61      *      27667423             72 62
   15 33      M        169205                    444 1
   16 57      M        [illegible]               715 4
   17 58      M          4986                    017 09
   18 62              9327772             25 06
   20.05      T          4215                    011 06
   20.52      TM         3812                    01
   21.43      T           247                    000 648 3
   21 63      T           575                    001 569
   22 36                 8304                    022 32
   23.27                  583                    001 53
   24 12                15764                    044
   25.96                17271                    045 23

HP 3380A
DLY   8.            STOP 45           REJECT   100
MV/M    30          ATTN      4
```

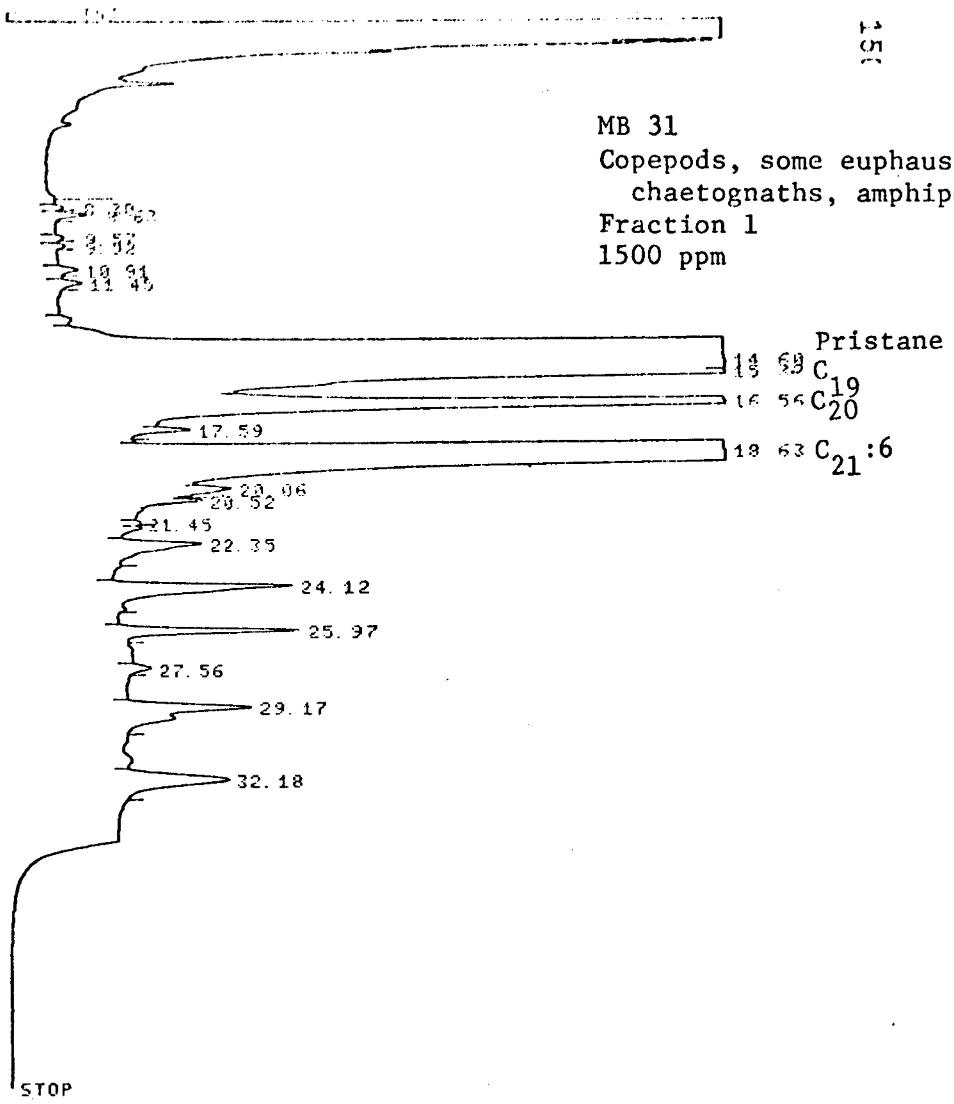


MB 31
Copepods, some euphaussids,
chaetognaths, amphipods, and terapods
Fraction 1
1100 ppm

```
                         AREA %·
   RT    TYPE      AREA
R ~~8.65             1947               .007 992~~
 10.93               1177               .004 527
 11.47               1301               .005
 14 61    *      24893987           ·95.67
 15.32    M        177737               .683 1
 16.57    M        265320              1 02
 18 45    M        659153              2 573
 20.55    M          4956               019 05
 21.67               1963               007 544
 22 38               5076               019 51
 24 15               6837               026 27
 25.91               1745               006 706

HP 3380A
DLY  3.            STOP 45           REJECT   100
MV/M   30          ATTN      4
```

MB 31
Copepods, some euphausiids
chaetognaths, amphipods, and terapods
Fraction 1
1500 ppm

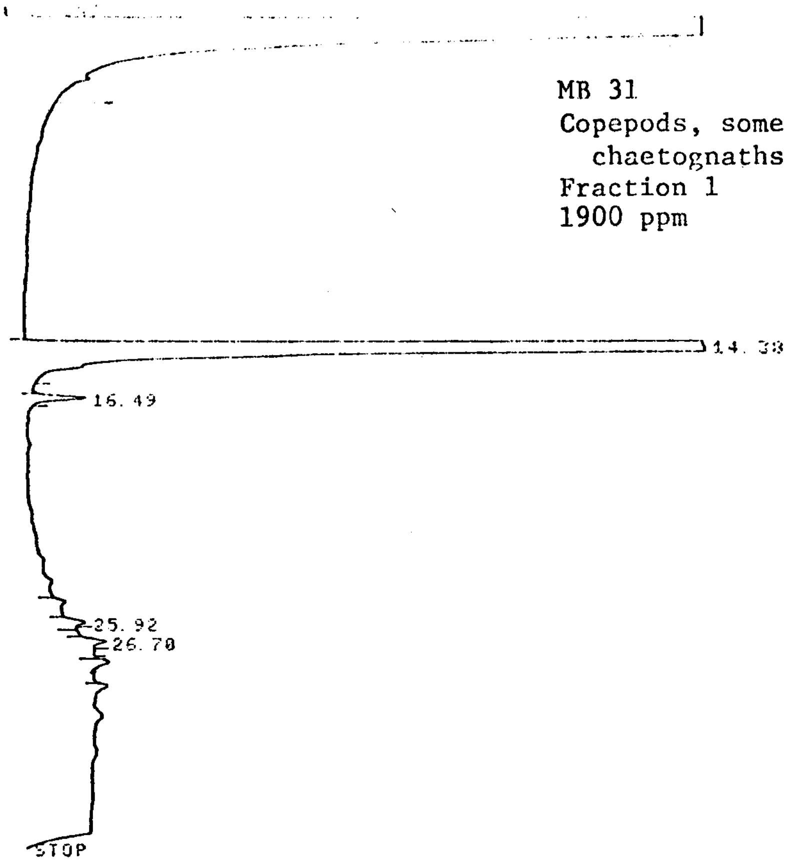


151

```
                              AREA %
     RT    TYPE       AREA
R [illegible]
R [illegible]
R [illegible]
    9.92                577                  001  52
   10.91               1337                 .003  521
   11.45               1634                 .004  304
   14.60    *      26484485              69.76
   15.32    M        151295                  398  5
   16.56    M        239067                 [illegible]
   17.59    M          5524                  014  55
   18.63           10983747              28  93
   20.06    T          4212                  011  09
   20.52    T          1455                 .003  872
   21.45    T           214                 .000  567 6
   22.35              10772                  028  37
   24.12              23965                 .063  12
   25.97              14648                  038  53
   27.56               1872                  004  925
   29.17              21714                  056  14
R [illegible]

HP [illegible]
DLY  8              STOP 45           REJECT    100
MV/M   30           ATTN      4
```

151

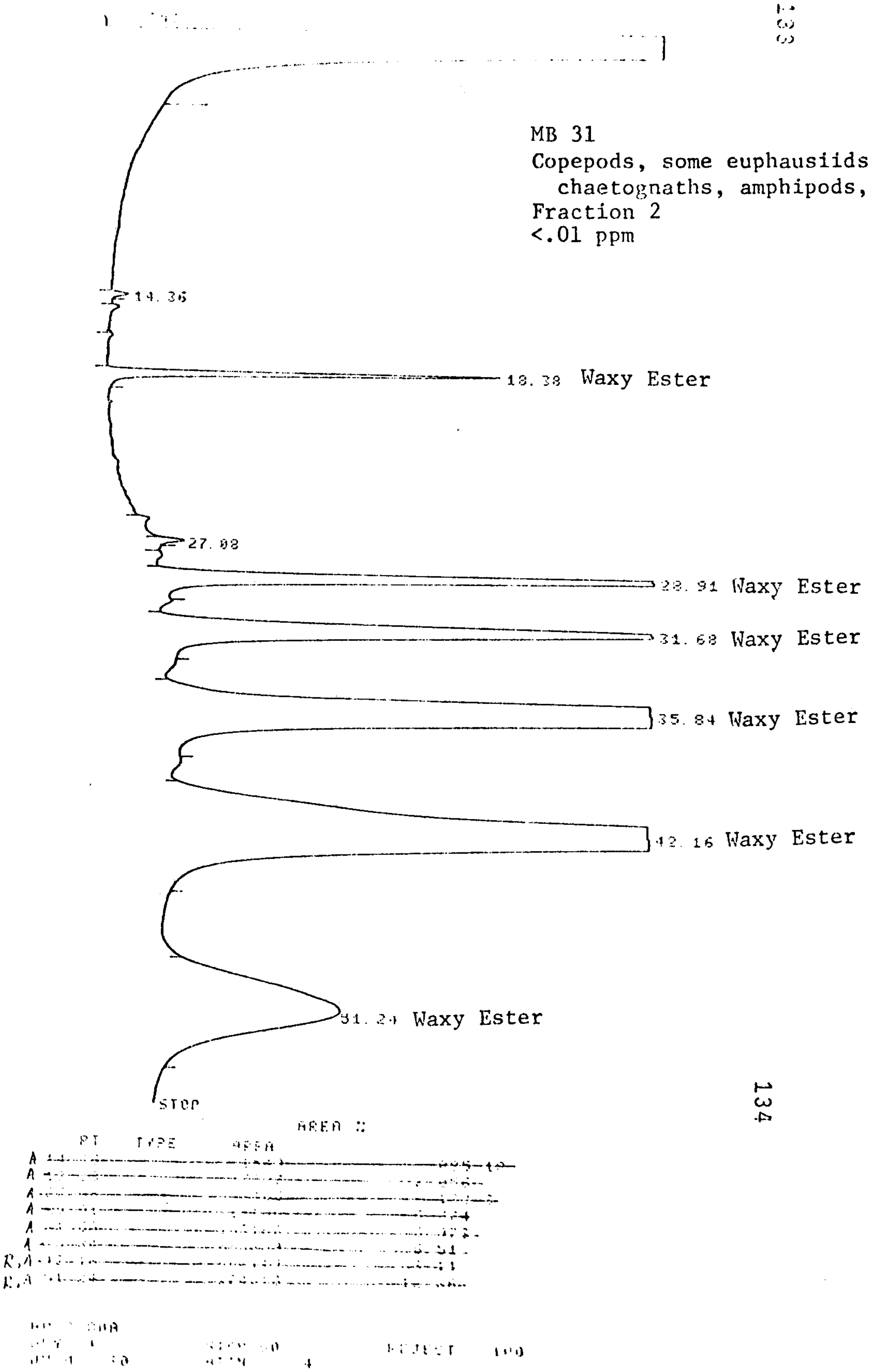


MB 31
Copepods, some euphausiids,
chaetognaths, amphipods, and terapods
Fraction 1
1900 ppm

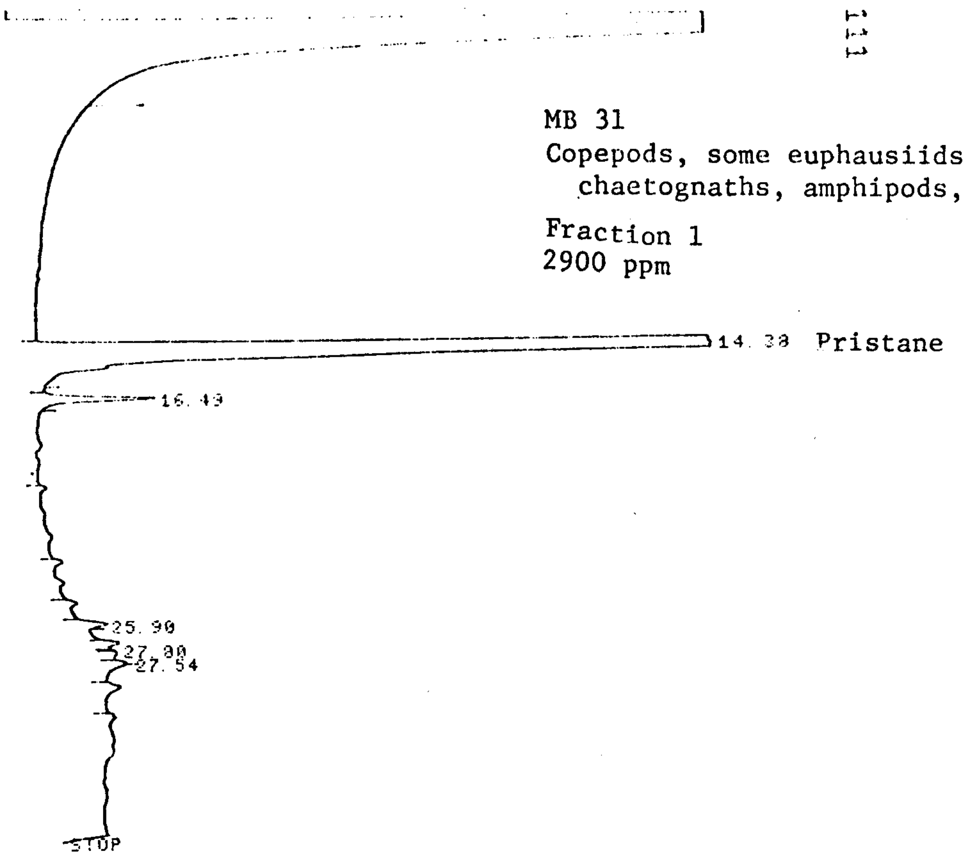
Pristane

```
                                AREA %
    RT    TYPE      AREA
 14.38             1099745                99.47
 16.49                3488                  .318 4
C ~~25.92              1443                  .131 6~~
C ~~26.70              1237                  .112 9~~


HP 3390A
DLY  4.             STOP 45            REJECT    100
MV/M   30           ATTN      4
```



MB 31
Copepods, some euphausiids,
chaetognaths, amphipods, and terapods
Fraction 2
<.01 ppm

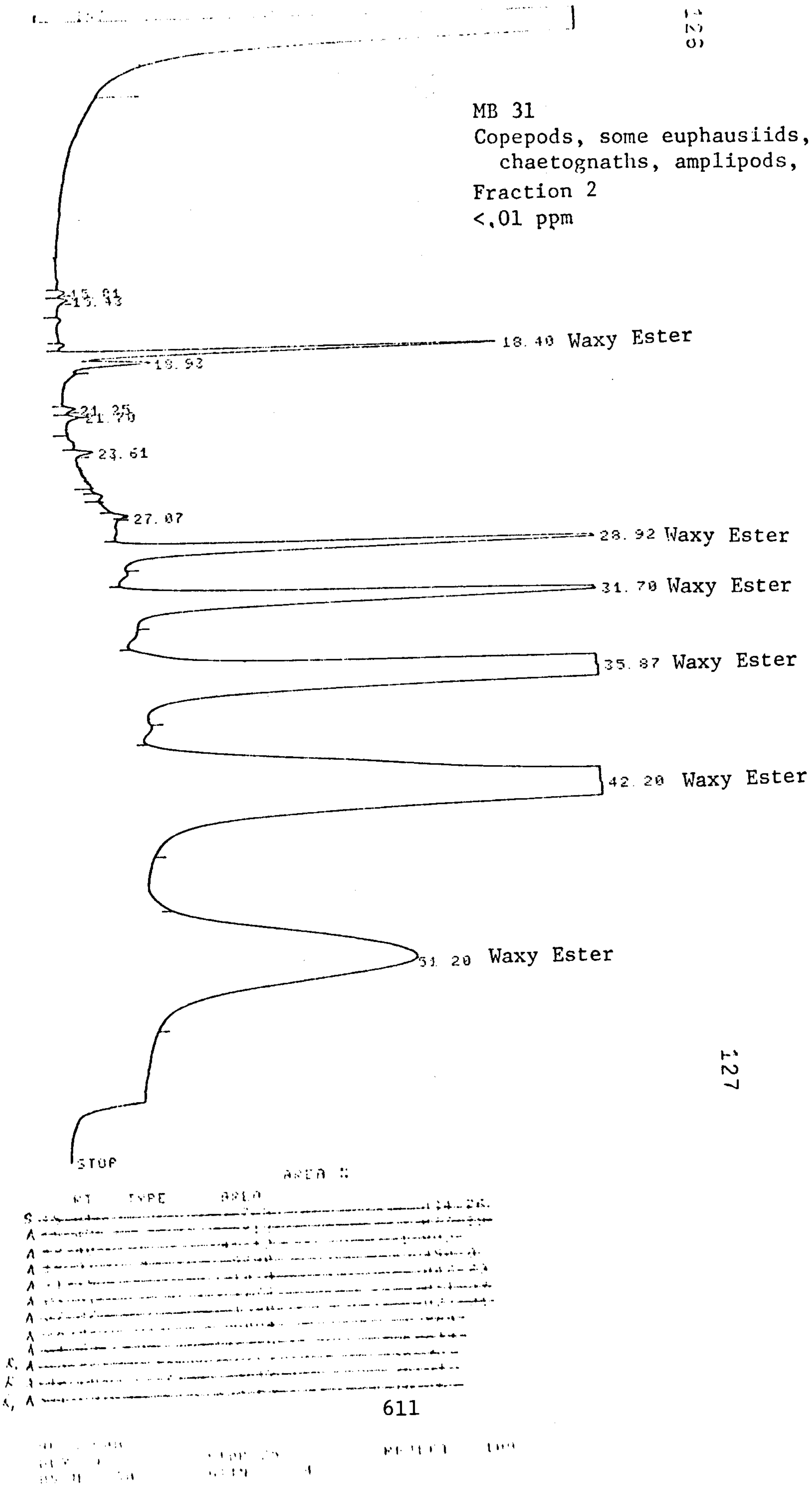


MB 31
Copepods, some euphausiids,
chaetognaths, amphipods, and terapods

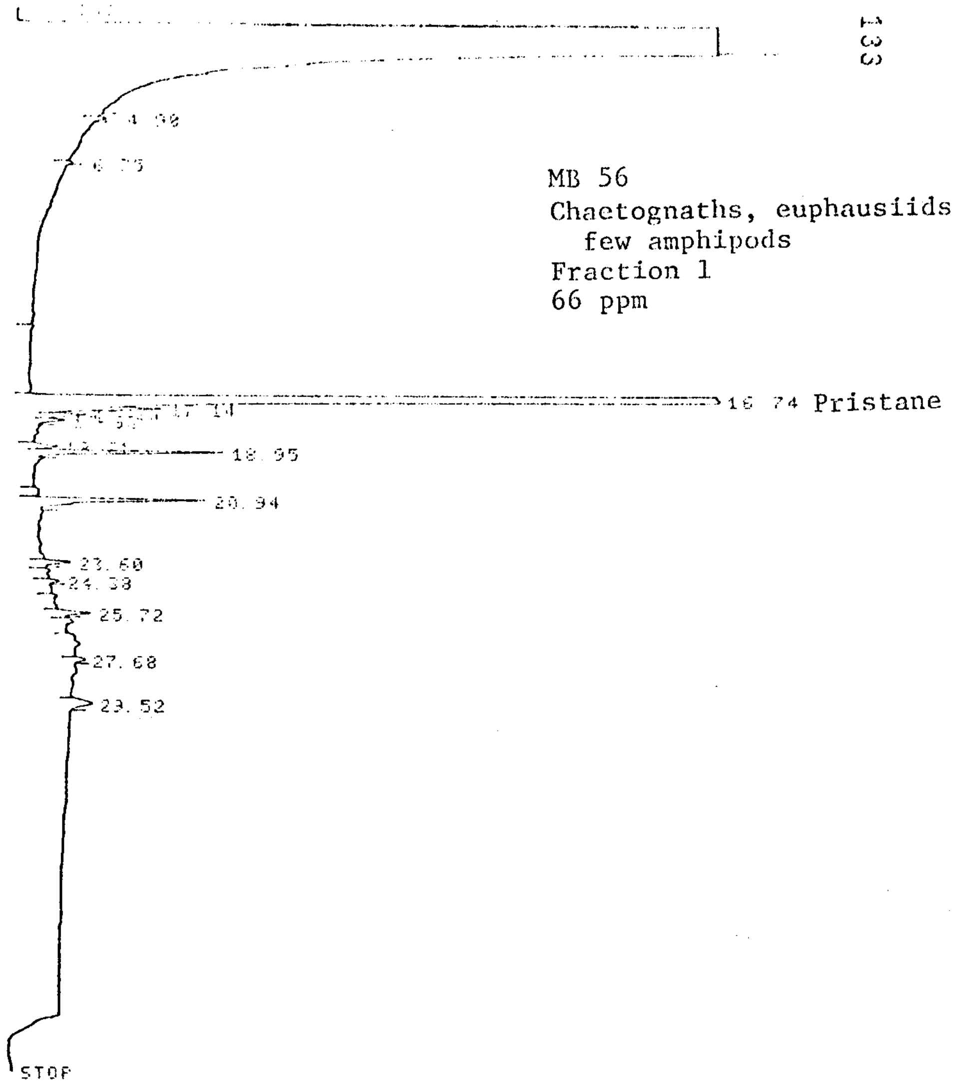
Fraction 1
2900 ppm

```
                          AREA %
     RT    TYPE      AREA
  14.38            1474550           99.26
  16.49               8906            .599 5
C ~~25.90               1879            .125 4~~
C ~~27.54                277            .018 65~~


HP 3380A
DLY  4.           STOP 45          REJECT   100
MV/M  .30         ATTN      4
```



MB 31
Copepods, some euphausiids,
chaetognaths, amplipods, and terapods
Fraction 2
<.01 ppm

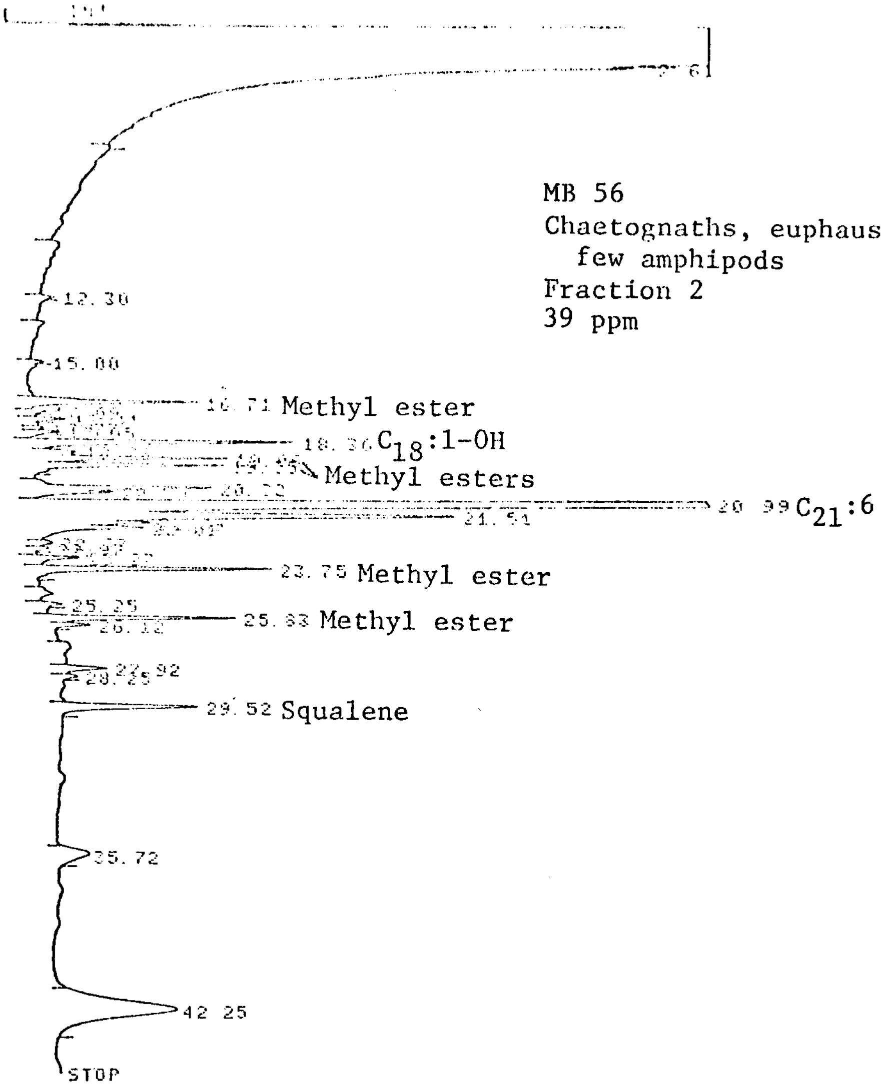


MB 56
Chaetognaths, euphausiids, copepods
few amphipods
Fraction 1
66 ppm

```
                        AREA %
  RT    TYPE      AREA
~~4.98~~              478             .054 92
~~6.75~~              270             .031 55
 16.74             319276        95.73
 17.14     "         7082             .827 5
~~17.40~~   4          2956             .299 6
 17.62     "         1355             .163
 18.71               1126             .171 5
 18.95     "         8274             .966 8
 20.94               9933             .12
 23.60               1207             .140 6
 24.38                519             .060 64
 25.72               1197             .172 0
 27.68                542             .075 92
 28.52               1900             .224 4

MF 1350A
CLV  2          STOP 45         REJECT   100
SM.H   30       ATTN      4
```

134



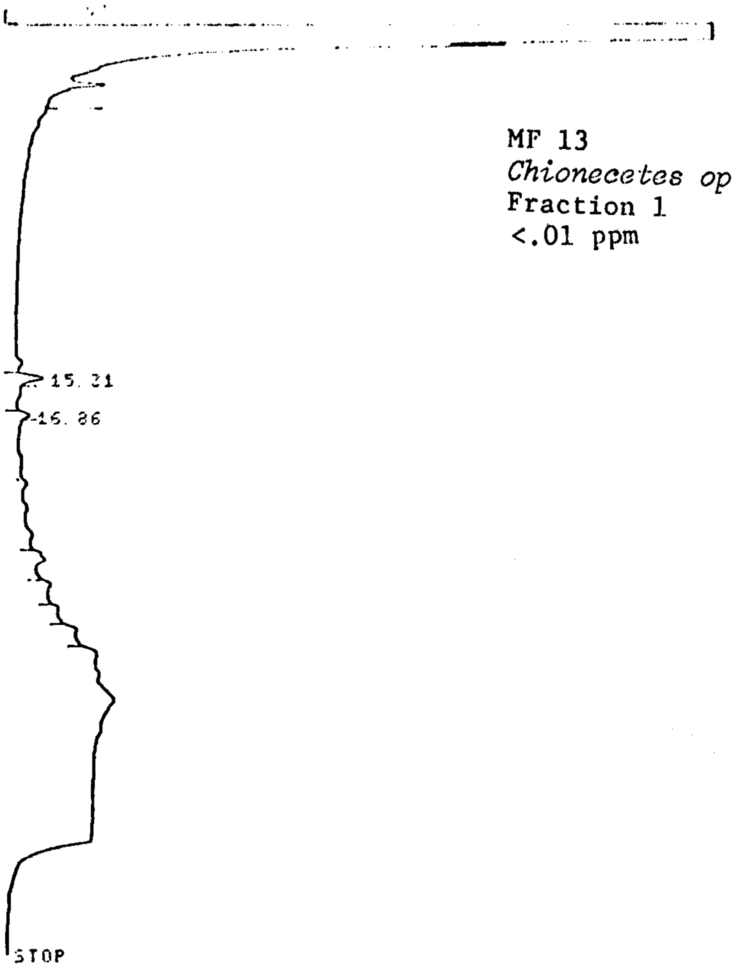
MB 56
Chaetognaths, euphausiids, copepods,
few amphipods
Fraction 2
39 ppm

AREA %

	RT	TYPE	AREA		
	~~2.61~~	~~T~~	~~1602~~	~~.241~~	
	12.30		503	.075	66
	15.00		505	.075	96
ME	~~16.71~~		~~8963~~	~~1.348~~	
	17.09	M	531	.079	87
S	~~17.41~~		~~1195~~	~~.179~~	~~9~~
	17.77		304	.045	72
	17.95	M	1279	.192	4
OH	~~18.36~~	~~M~~	~~14963~~	~~2.251~~	
	19.78	T	1221	.183	6
ME	~~19.66~~	~~M~~	~~9834~~	~~1.479~~	
ME	~~19.85~~	~~M~~	~~9557~~	~~1.437~~	
	20.32		9994	1.503	
	20.50	M	4146	.623	6
	20.99	M	471672	70.94	
	21.51	M	32580	4.9	
	21.79	M	6385	.960	4
	22.01	M	8739	1.314	
	22.63	M	1213	.182	4
	22.87	M	804	.120	9
	23.27		2594	.390	2
ME	~~23.75~~	~~M~~	~~[illegible]~~	~~1.[illegible]~~	
	25.25		775	.116	6
ME	~~25.83~~		~~9262~~	~~1.393~~	
B	~~26.12~~	~~M~~	~~1.54~~	~~.230~~	
	27.92		2448	.368	2
	28.25	M	799	.12	
	29.52		9819	1.477	
	35.72		[illegible]	.741	
	~~42.25~~		~~[illegible]~~	~~[illegible]~~	

[illegible] 30 A
[illegible] REJECT [illegible]

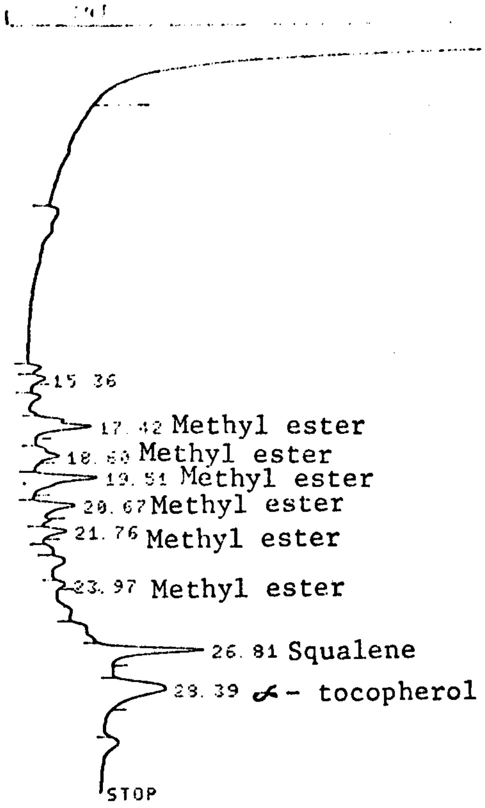
MF 13
Chionecetes opilio - Soma
Fraction 1
<.01 ppm



```
                              AREA %
     RT   TYPE       AREA
S [illegible]
S [illegible]

HP 3380A
DLY  4.          STOP 45          REJECT   100
HV/M  .30        ATTN      4
```

MF 13
Chionecetes opilio - Soma
Fraction 2
.27 ppm



AREA %

RT TYPE AREA

S ~~15.36 1152~~

~~2.213~~

ME ~~17.42 5065 17.08~~

ME ~~18.60 1773 5.25~~

ME ~~19.51 [illegible] 14.52~~

ME ~~20.67 [illegible] 6.755~~

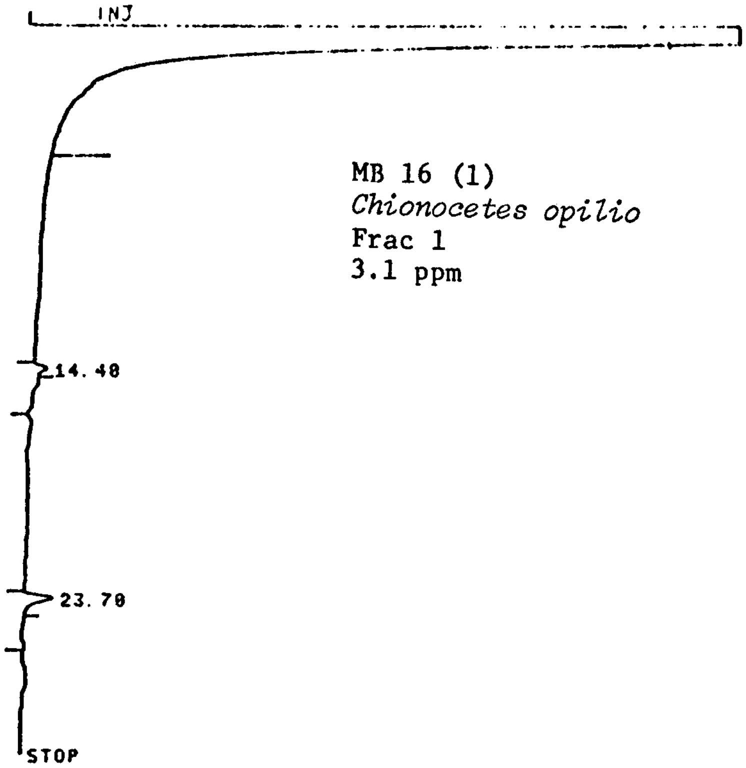
ME ~~21.76 [illegible] 4.672~~

ME ~~23.97 [illegible] 1.375~~

* 26.81 11872-5342 22.8

A ~~28.39 12380 24.70~~

HP 3380A
DLY 4.　　STOP 45'　　REJECT 100
MV/M .30　　ATTN 4

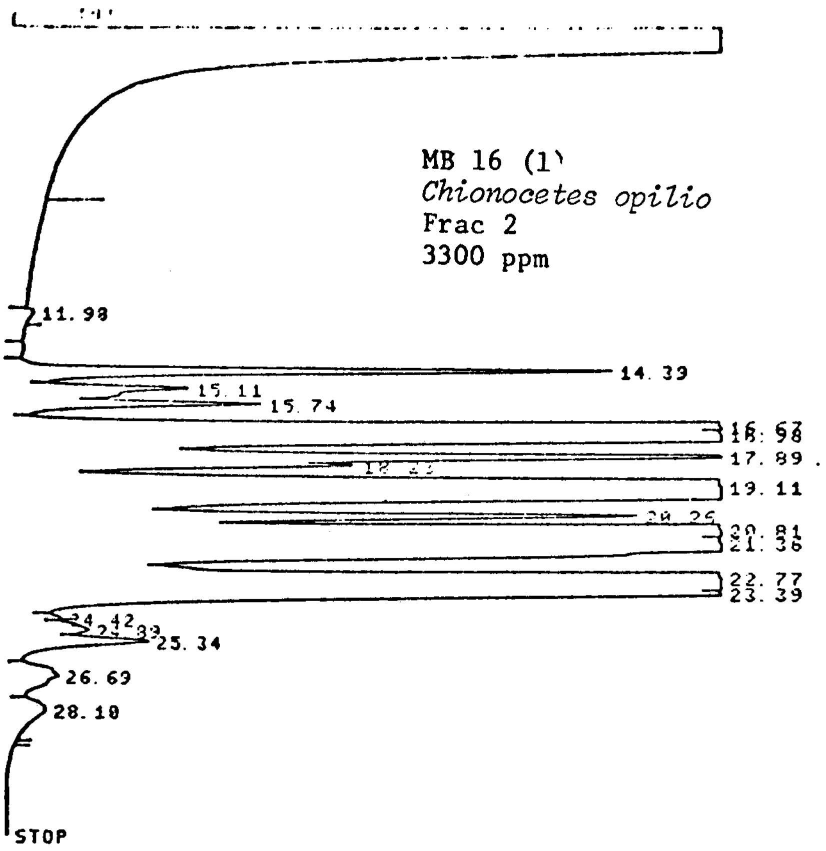


MB 16 (1)
Chionocetes opilio
Frac 1
3.1 ppm

AREA %

RT	TYPE	AREA	
S~~14.40~~		~~949~~	~~21.83~~
23.70		3399	78.17

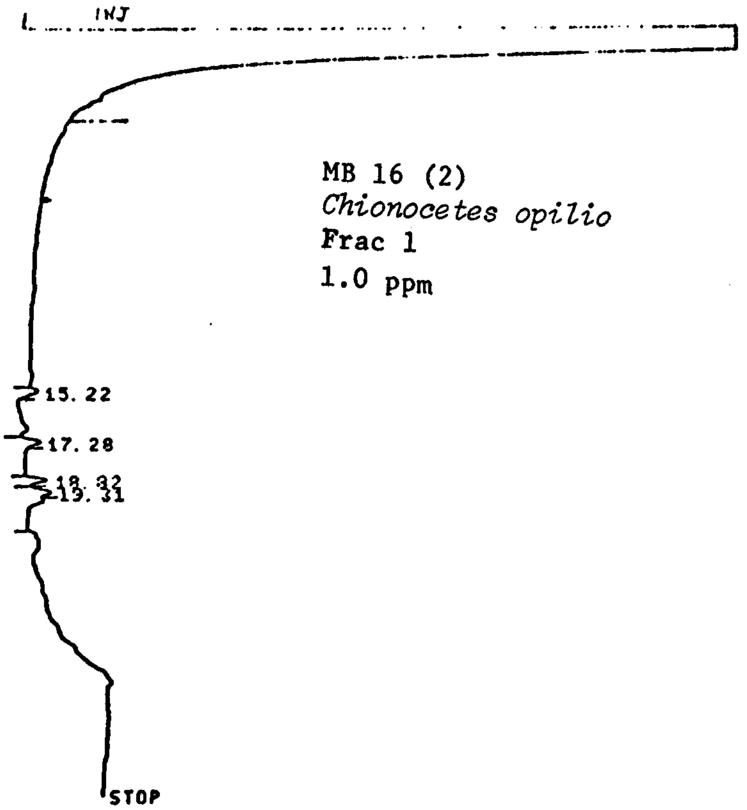
```
HP 3380A
DLY  4.         STOP 45         REJECT    10
MV/M  .10       ATTN     4
```



MB 16 (1)
Chionocetes opilio
Frac 2
3300 ppm

```
                              AREA %
      RT    TYPE      AREA
   11.98               .1065                 .021 56
   14.39               52192                1.057
   15.11     M         22979                 .465 2
   15.74     M         22313                 .451 7
   16.67     M        472873                9.574
   16.98     M        727559               14.73
   17.89     M         85725                1.736
   18.23     M         27720                 .561 2
ME 19.11     M       1577076 ------------~~31.93~~----
   20.26     M         62421                1.264
   20.81     M        600164               12.15
   21.36     M        702954               14.23
   22.77     M        442523                8.959
   23.39     M        101413                2.053
   24.42     M           210                 .004 252
   24.89                5001                 .101 2
   25.34     M         13971                 .282 8
   26.69     M         13696                 .277 3
   28.10     T          7516                 .152 2

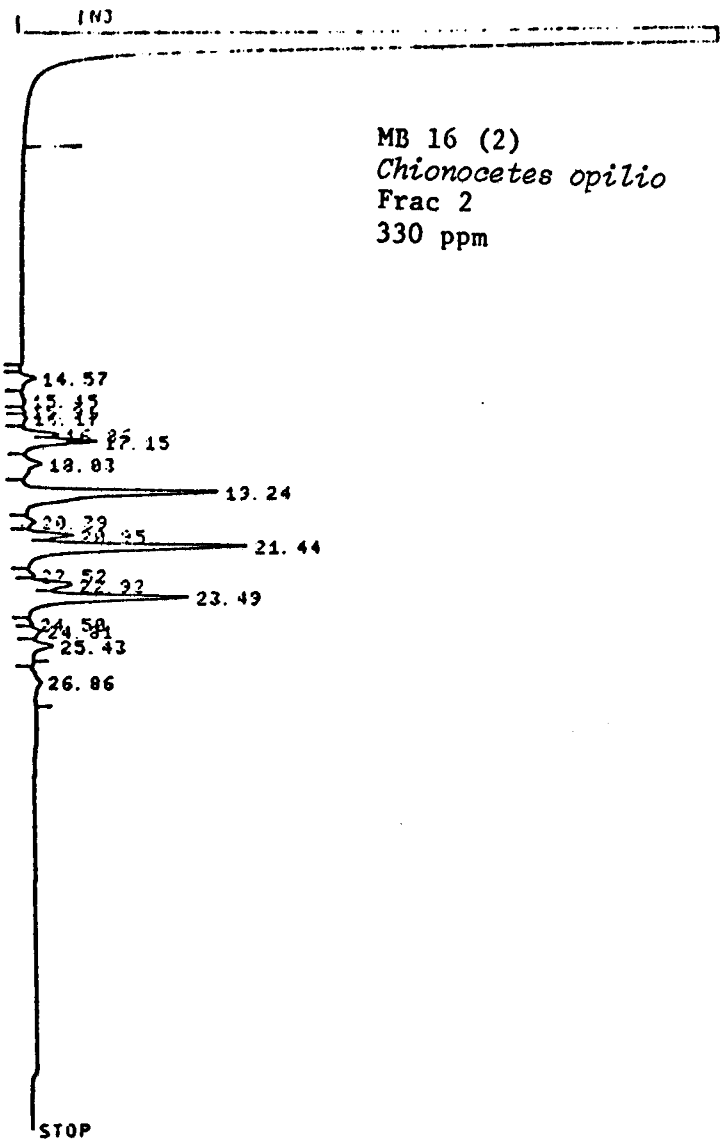
HP 3390A
SLP  4           STOP 45          REJECT    10
MV/M   10        ATTN      4
```



MB 16 (2)
Chionocetes opilio
Frac 1
1.0 ppm

```
                                AREA %
      RT    TYPE      AREA
S~~15.22              1385              25.07~~
 17.23                1480              26.79
 18.82                1391              25.18
 19.31                1269              22.97


HP 3380A
DLY  4.         STOP 45          REJECT     10
MV/M  .30       ATTN      4
```

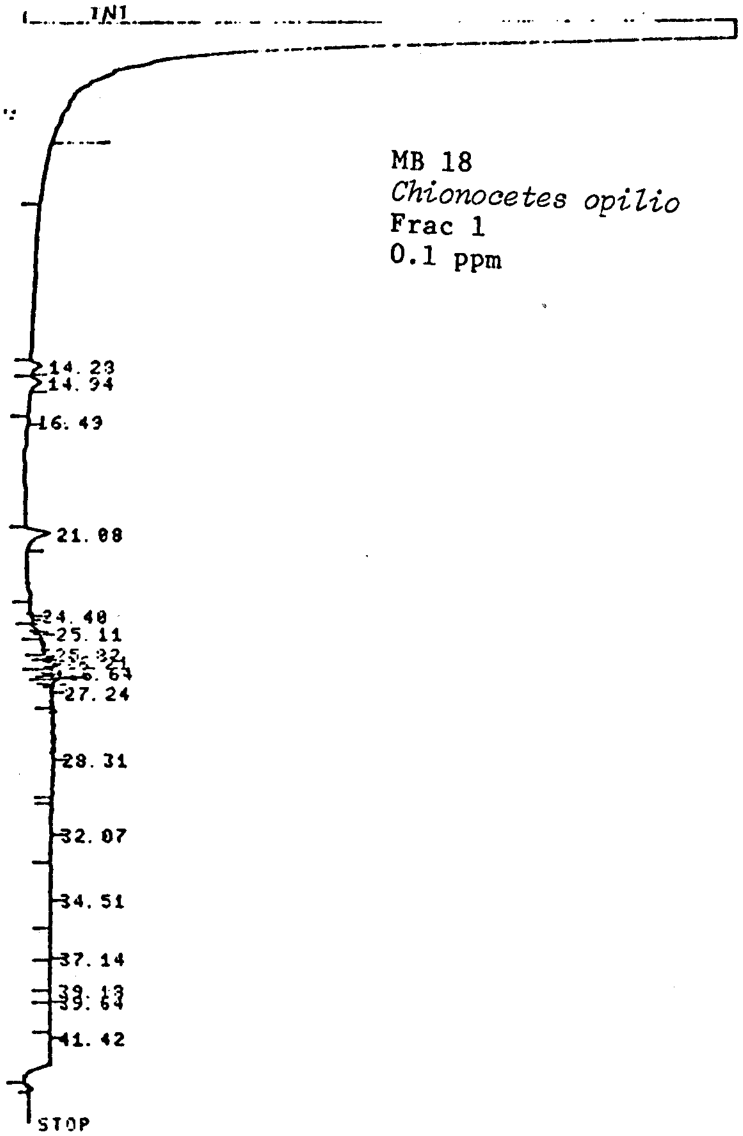


MB 16 (2)
Chionocetes opilio
Frac 2
330 ppm

```
                    AREA %
   RT    TYPE      AREA
 14.57              17394              1.175
S~~15.45   M         4765               .321~~ 0
 15.91     M         2512·              .169 7
 16.17     M         5344·              .361
 16.86     M        44854.             3.03
 17.15     M       107191·             7.24
 18.03     M        40004·             2.702
 19.24     M       344691·            23.28
 20.39     M        16196·             1.094
 20.95     M        67526·             4.561
 21.44     M       376351·            25.42
 22.52     M         9190'              .620 7
 22.92     M        86515.             5.844
 23.49     M       273352.            18.5
 24.50     M         3807·              .257 1
 24.01     M        19512'             1.318
 25.43     M        37843.             2.556
 26.86              22982              1.552

HP 3380A
DLY  4.            STOP 45            REJECT    10
MV/M   30          ATTN    64
```

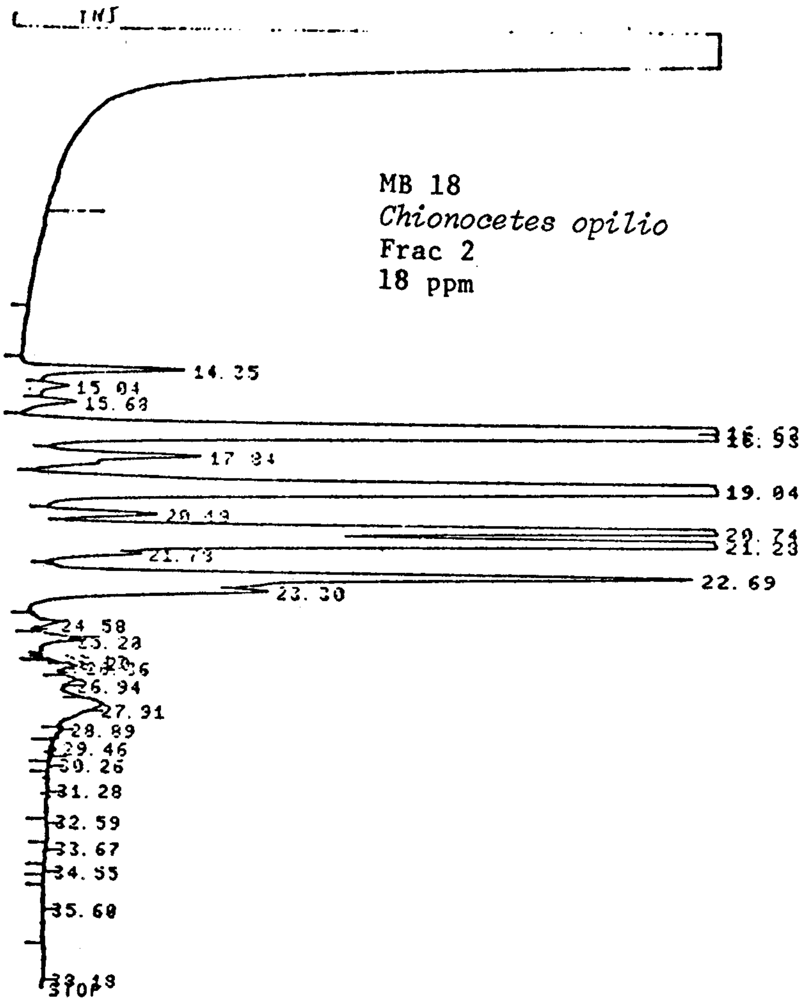
004



MB 18
Chionocetes opilio
Frac 1
0.1 ppm

			AREA %
RT	TYPE	AREA	
14.29		825	5.034
S~~14.94~~		~~1038~~	~~6.334~~
16.49		234	1.428
~~21.08~~		~~2899~~	~~17.69~~
N~~24.40~~		~~243~~	~~1.483~~
N~~25.11~~		~~406~~	~~2.477~~
N~~25.82~~		~~1203~~	~~7.341~~
N~~26.21~~	~~H~~	~~2457~~	~~14.99~~
N~~26.64~~	~~H~~	~~1766~~	~~10.78~~
N~~27.24~~	~~H~~	~~2645~~	~~16.14~~
N~~28.31~~		~~849~~	~~5.181~~
N~~32.07~~		~~393~~	~~2.398~~
N~~34.51~~		~~528~~	~~3.222~~
N~~37.14~~		~~700~~	~~4.271~~
N~~39.13~~		~~422~~	~~2.575~~
N~~39.64~~	~~H~~	~~111~~	~~.6774~~
N~~41.42~~		~~68~~	~~.415~~

```
HP 3380A
PLV  4          STOP 45          REJECT    10
HV.M   10       ATTN      4
```

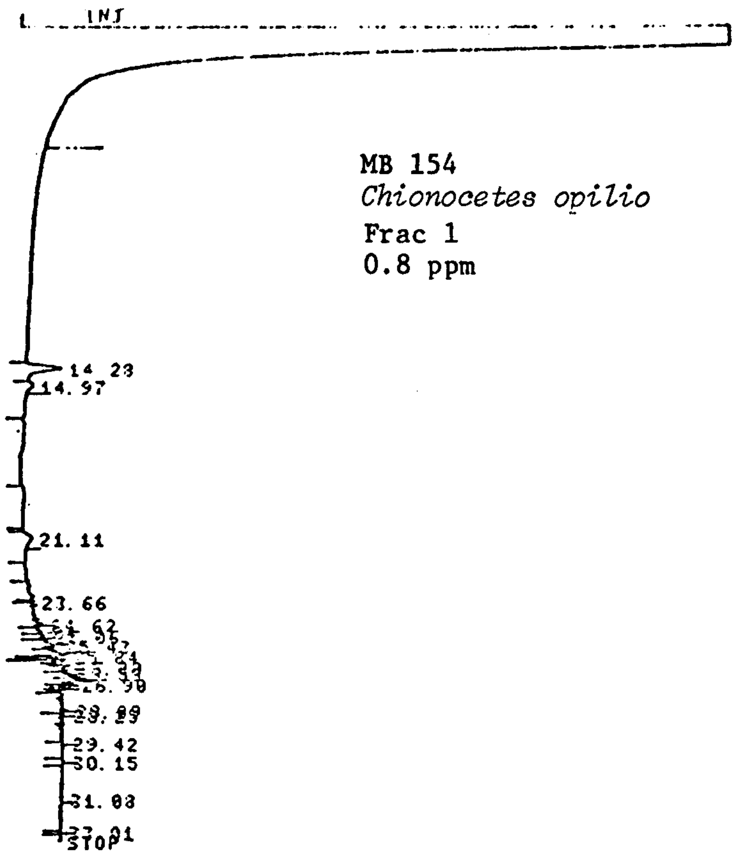


MB 18
Chionocetes opilio
Frac 2
18 ppm

AREA %

	RT	TYPE	AREA	
	14.35		15489	1.537
S	15.04	M	6592	.654 1
	15.68	M	6209.	.616 1
ME	~~[illegible]~~	~~M~~	~~[illegible]~~	~~[illegible]~~
ME	~~[illegible]~~		~~[illegible]~~	~~[illegible]~~
	17.84	M	26265.	2.606
ME	~~19.04~~	~~M~~	~~292982~~	~~29.04~~
	20.19	M	13915.	1.381
ME	~~20.74~~	~~M~~	~~125913~~	~~12.50~~
ME	~~21.23~~	~~M~~	~~149141~~	~~14.[illegible]~~
	21.73	M	11362	1.127
	22.69	M	90284	8.959
	23.30	M	29156.	2.893
N	24.58	M	3366	.334
N	[illegible]		[illegible]	.241 5
N	[illegible]		[illegible]	.014 23
N	[illegible]	M	[illegible]	.029 06
N	[illegible]	M	2376	.235 8
	26.94		1373.	.136 2
	27.91		2351.	.233 3
N	[illegible]		[illegible]	.009 625
N	[illegible]		1006	.099 87
N	30.26		160	.015 88
N	31.28		464	.046 04
N	32.59		61	.006 028
N	33.67		194	.019 25
N	34.55		145	.014 39
N	35.60		[illegible]	.011 [illegible]
N	[illegible]		[illegible]	[illegible] 04

HP 3390A
DLY 4 STOP 45 REJECT 10
[illegible] 10 [illegible] 4

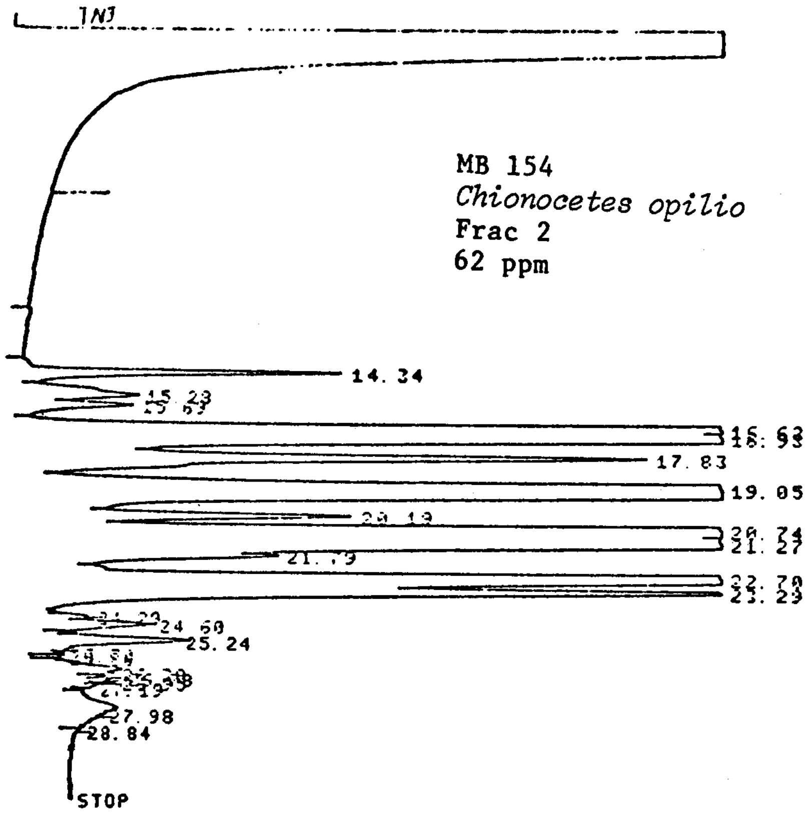


MB 154
Chionocetes opilio
Frac 1
0.8 ppm

150

```
                          AREA %
       RT    TYPE      AREA
     14.28             3213              18.26
   S14.97     M         870               4.945
   S21.11               311               1.79
   N23.66                61                .346 7
   N24.62     M        1117               6.349
   N24.91               233               1.324
   N25.96               383               2.177
   N26.47              1556               8.844
   N25.24     M        2715              15.43
   N[illegible]     M        1[illegible]               [illegible]
   N[illegible]               [illegible]                .551 4
   N[illegible]              20[illegible]              11.[illegible]
   N[illegible]              14[illegible]               8.[illegible]
   N28.25               143                .[illegible]
   N29.42                65                .[illegible] 1
   N30.15               153                .631
   N31.08               895               5.085
   N33.01                27                .153 5

   HP 3380A
   DLY   4             STOP 45          REJECT    10
   MV/M    10          ATTN      4
```

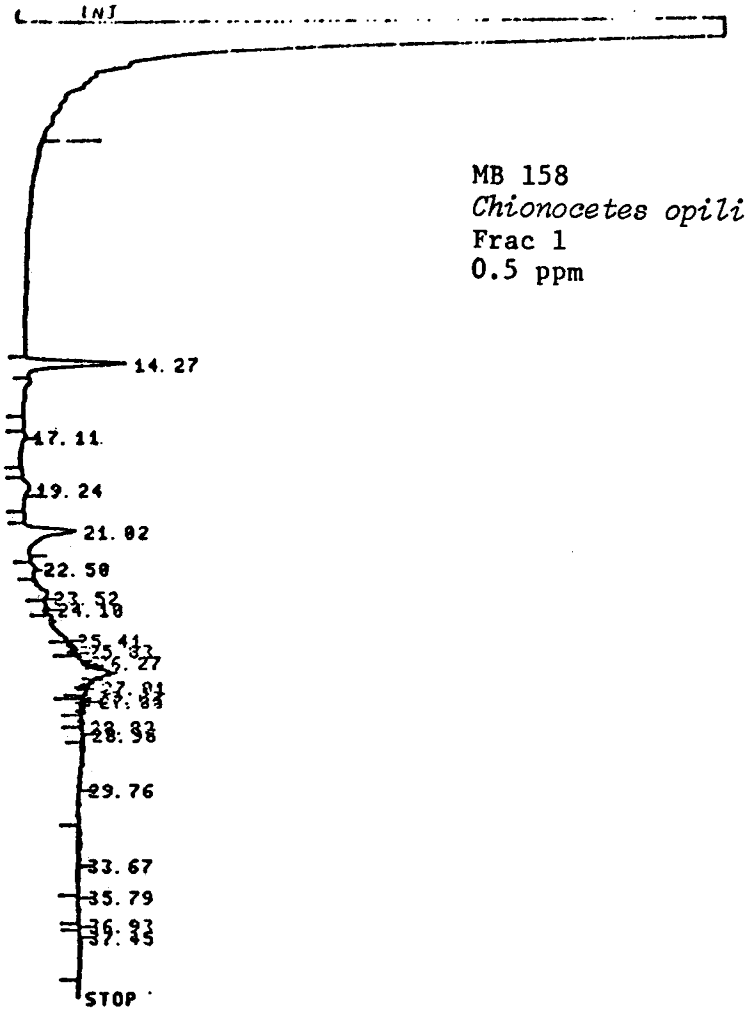


MB 154
Chionocetes opilio
Frac 2
62 ppm

```
                              AREA %
       RT    TYPE        AREA
    14.34               23636              1.302
    15.28     M         16531               .751 6
    15.69     M         10692               .486 1
 ME~~16.62     M        215119              9.791~~
 ME~~16.93     M        327033             14.87~~
    17.83     M         62239              3.739
 ME~~19.05     M        541215             29.16~~
    20.19     M         32947              1.498
 ME~~20.74     M        224176             10.13~~
   ~~21.27     M        283596             12.89~~
    21.79     M         24085              1.095
 ME~~22.70     M        189802              8.63~~
    23.29     M         69377              3.927
    24.29     M            62               .002 819
    24.60                6944               .315 7
    25.24     M         15232               .692 6
  -N~~25.70     M          1061               .048-24~~
 --N 25.86    M           665               .030-24
   N 26.39    M          6370               .289 6
  -N~~26.78~~    M           774               .035 19
 --N 27.19    T          1112               .050 56
    27.98     M          4479               .203 7
 --N28.84                 177               .008 048

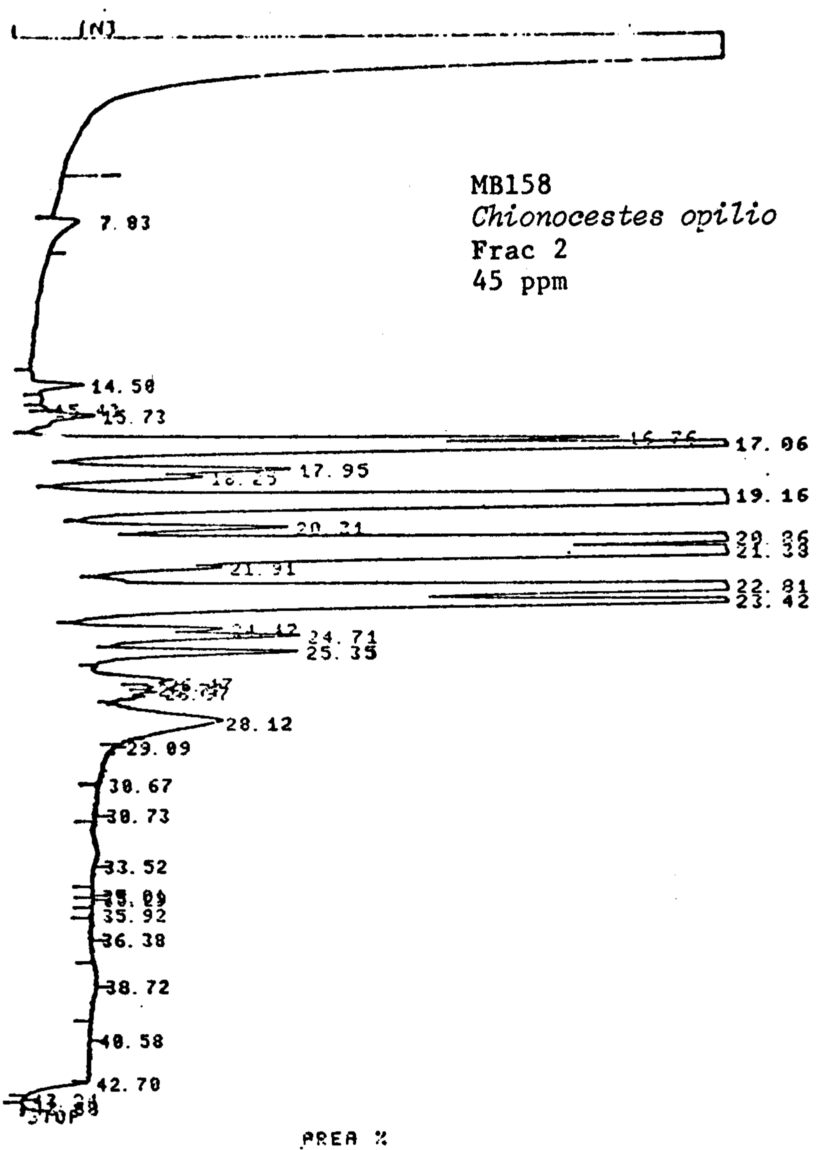
   HP 3390A
   OLV   4          STOP 45          REJECT    10
   MV/M  .10        ATTN     4
```

MB 158
Chionocetes opilio
Frac 1
0.5 ppm



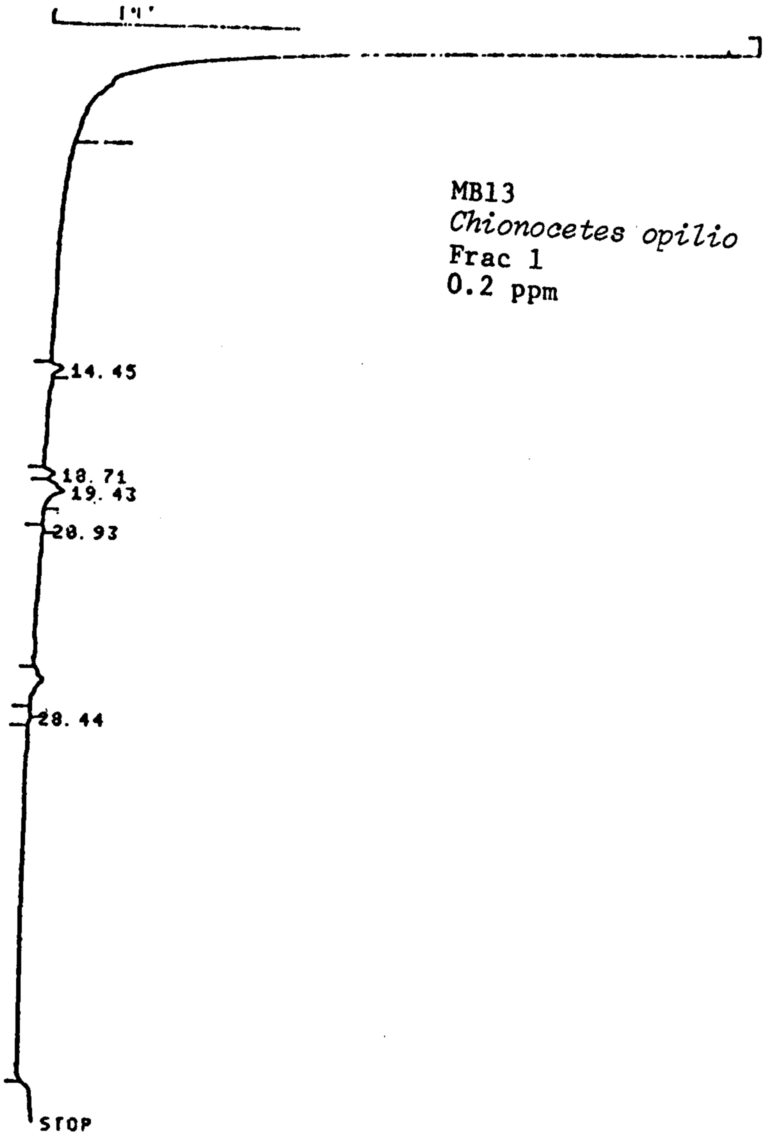
```
                              AREA %
     RT    TYPE       AREA
   14.27              8540             36.33
   17.11               240              1.021
   19.24              1093              4.65
 S ~~21.02            [illegible]      25.[illegible]~~
   22.50               317              1.349
   23.52               814              3.463
 N ~~24.10             437              1.859~~
 N ~~25.41             404              1.719~~
 N ~~25.63             904              3.846~~
 N ~~26.27             574              2.442~~
 N ~~27.01             495              2.[illegible]~~
 N ~~27.[illegible]    429              1.825~~
 N ~~27.[illegible] M  [illegible]      1.23[illegible]~~
 N ~~28.02             544              2.314~~
 N ~~28.96             259              1.[illegible]~~
 N ~~29.76             77[illegible]    3.[illegible]~~
 N ~~33.67             11[illegible]    4.[illegible]~~
 N ~~35.79              43               .182  9~~
 N ~~36.93              34               .144  6~~
 N ~~37.45             11[illegible]     .[illegible]5~~

HP 3390A
DLY  4.           STOP 45          REJECT    10
MV/M  .10         ATTN     4
```


MB158
Chionocestes opilio
Frac 2
45 ppm

```
                           AREA %
   RT     TYPE      AREA
   7.83             [illegible]             [illegible]
  14.50              3499                .224 2
  15.43               132                .008 837
  15.73              5904                .395 2
  16.76    M        41734               2.794
  17.06    M       129344               8.659
  17.95    M        27035               1.81
  18.25    M        14764                .988 4
  19.16    M       423415              28.75
  20.21    M        24916               1.669
ME20.86    M       [illegible]         10.55
ME21.33    M       [illegible]         16
  21.91    M        15032               1.006
ME22.81    M       199887              12.78
ME23.42    M       [illegible]          7.[illegible]
  24.42    M        11390                .762 5
  24.71    M        23434               1.569
  25.35    M        21238               1.422
N 26.47    M         7275                .487
N 26.77    M         3257                .218
N 26.97    M         5073                .339 6
  28.12    M        25420               1.702
N 29.09              [illegible]         .012
N [illegible]
N [illegible]
N [illegible]
N [illegible]
N [illegible]
```

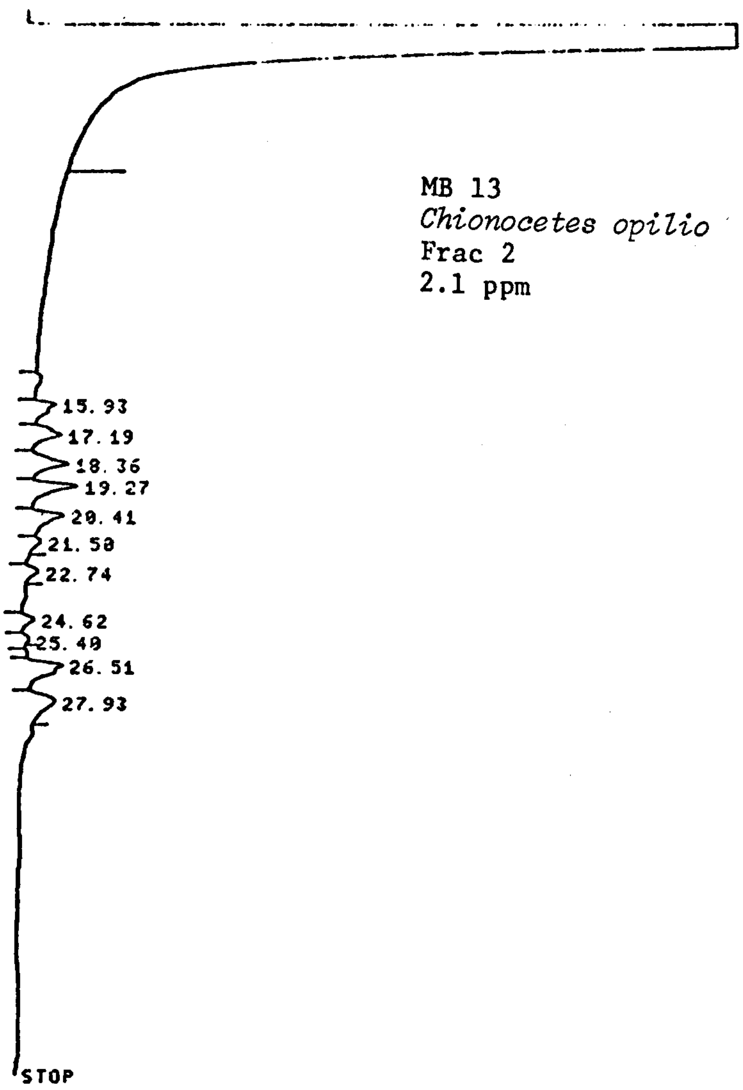
```
HP [illegible]
[illegible]          STOP [illegible]          REJECT      10
```



MB13
Chionocetes opilio
Frac 1
0.2 ppm

```
                        AREA %
  RT   TYPE     AREA
S~~14.45          1249               19.83~~
 18.71             916               14.65
 19.43    M       3732               59.69
 20.93             243                3.887
 28.44             121                1.935

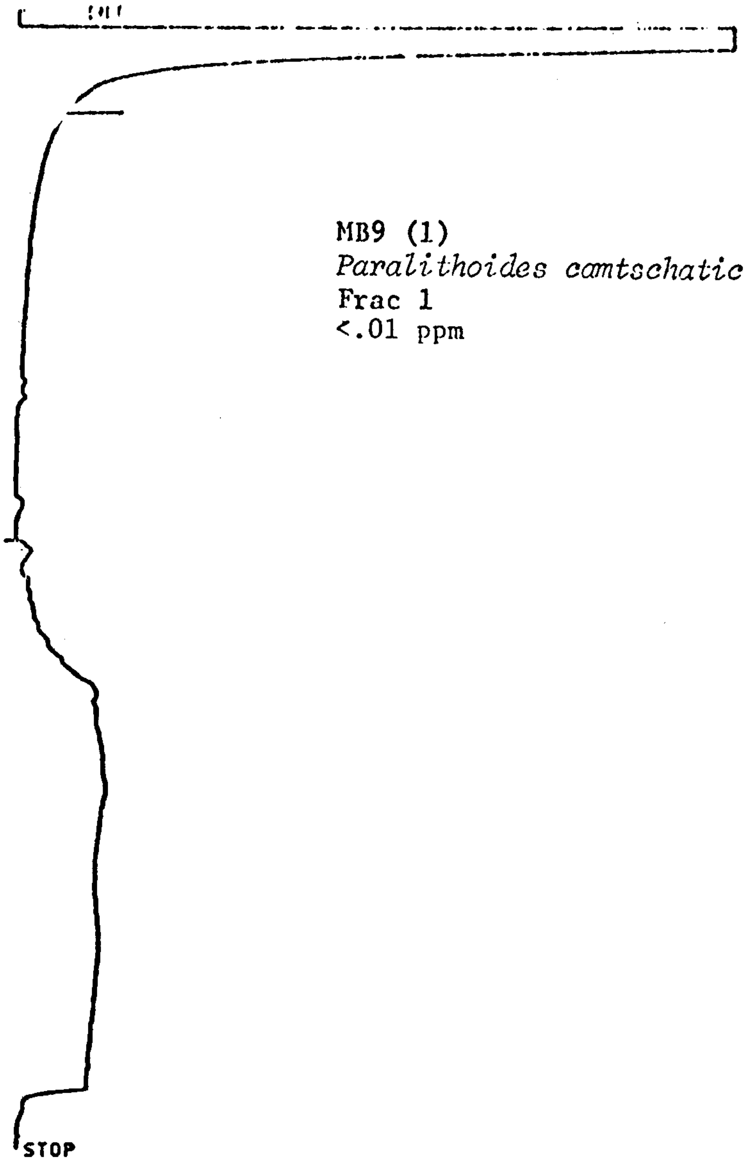
HP 3380A
DLY  4.            STOP 45            REJECT     10
MV/M   10          ATTN      4
```



MB 13
Chionocetes opilio
Frac 2
2.1 ppm

```
                          AREA %
   RT   TYPE     AREA
 15 93           3168           7.257
 17 19    M      4486          10.28
 18.36    M      5692          13.04
 19.27    M      6164          14.12
 20.41    M      5750          13.17
 21.50    M      1835           4.203
 22.74           1695           3.86
 24.62           1519           3.479
 25.40    M       734           1.681
 26.51           6525          14.95
 27.93    M      6098          13.97

HP 3390A
DLY  4.           STOP 45           REJECT    10
MV/M   10         ATTN      4
```

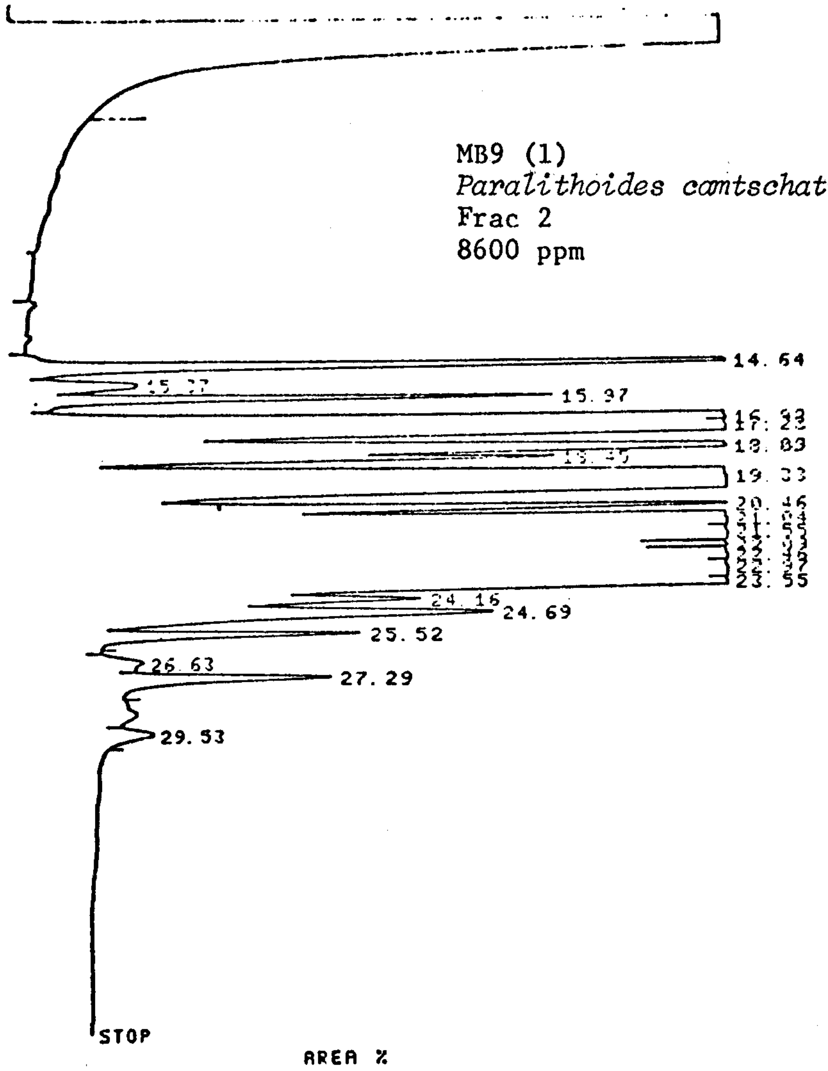


MB9 (1)
Paralithoides camtschatica - soma
Frac 1
<.01 ppm

198

```
                    AREA %
                            NO PEAKS

HP 3330A
DLY  4.         STOP 45          REJECT    10
MV/M  .30       ATTN     4
```

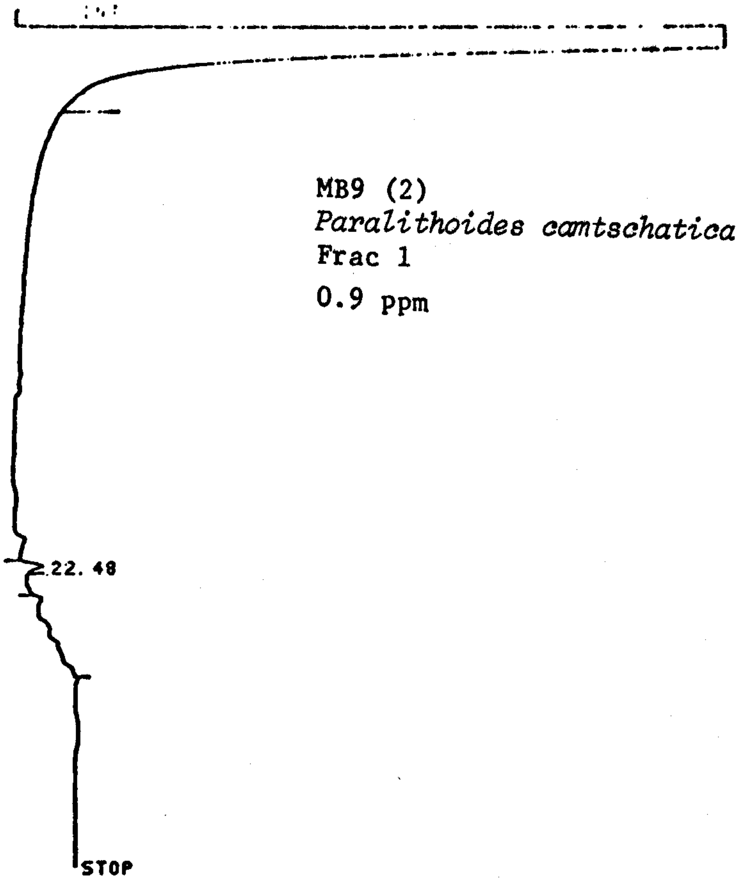


MB9 (1)
Paralithoides camtschatica - soma
Frac 2
8600 ppm

199

```
                        AREA %
   RT     TYPE       AREA
 14.64               77404             .934 9
 15.27      M        15263.            .184 3
 15.97      M        40664             .491 1
 16.92      M       375844.           4.539
 17.22      M       834011.          10.07
 18.09      M       114915            1.388
 18.45      M        41552.            .501 9
MS ~~19.33      M      2119366          25.6~~
 20.46      M        68624.            .828 8
 21.04      M      1740651.          21.02
 21.55      M       899980.          10.87
 22.09      M        60731.            .733 5
 22.46      M       430297.           5.198
 22.97      M      1147197.          13.36
 23.55      M       147231.           1.778
 24.16      M        39335.            .481 7
 24.69      M        62352.            .753 1
 25.52      M        25203.            .305 6
 26.63                5979             .071 01
 27.29      M        26548             .320 6
 29.53                5691             .068-74

HP 3390A
DLY  4             STOP 45         REJECT     10
MV/M   20          ATTN     4
```

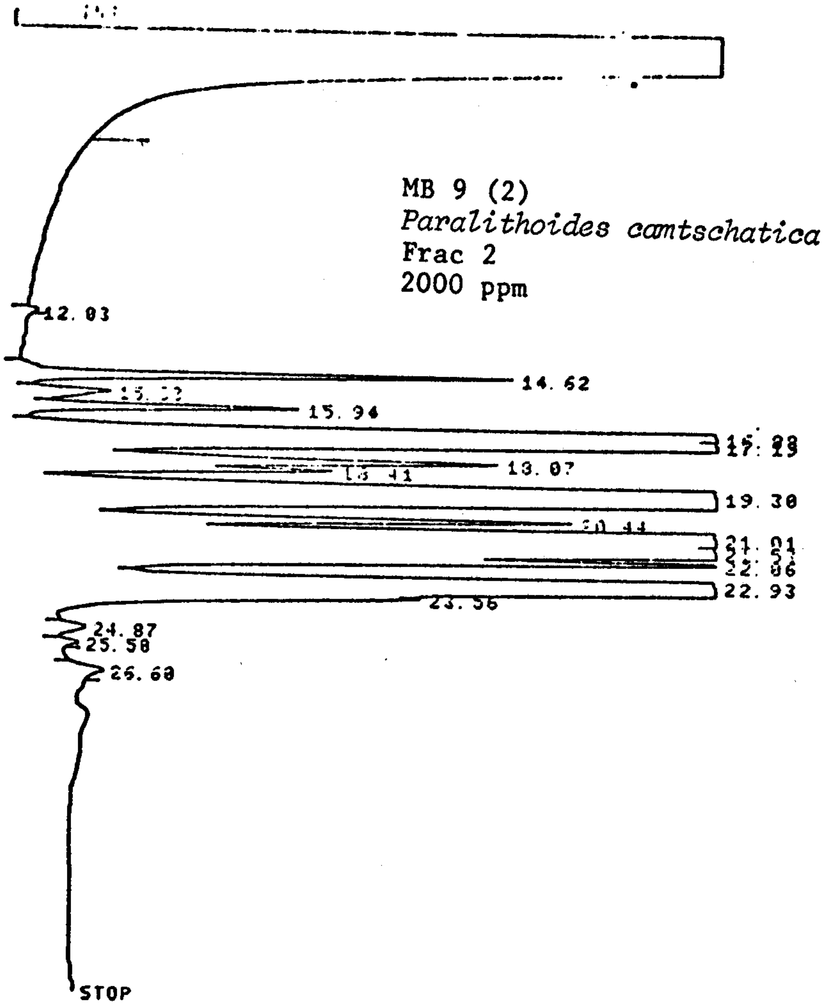


MB9 (2)
Paralithoides camtschatica - soma
Frac 1
0.9 ppm

196

```
                AREA %
   RT   TYPE     AREA
 22.48            1761         100.

HP 3380A
DLY  4.        STOP 45        REJECT    10
MV/M  .30      ATTN     4
```

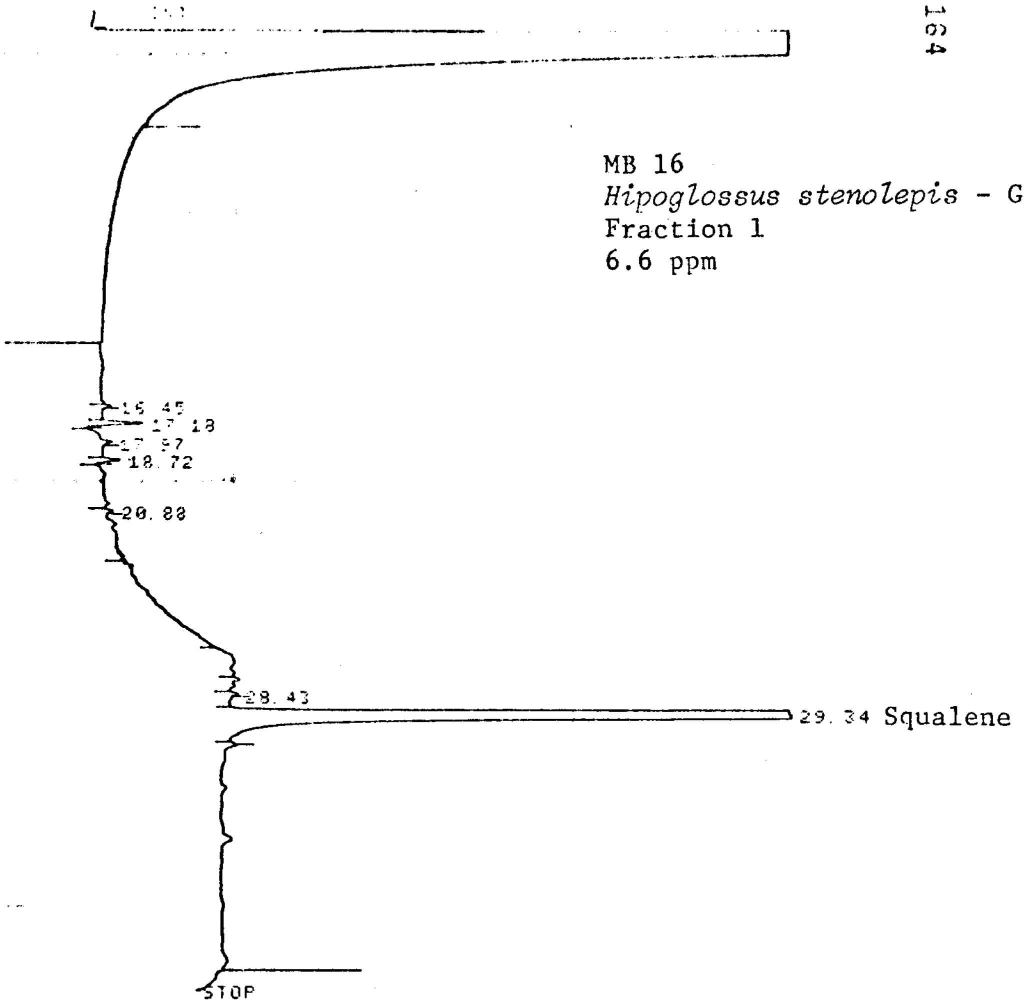


MB 9 (2)
Paralithoides camtschatica - soma
Frac 2
2000 ppm

```
                              AREA %
       RT    TYPE      AREA
    12.03                 756              .014 45
    14.62               39634              .757 7
    15 33     M         10933              .289
    15.94     M         22478              .429 7
    16.98     M        336796             6.439
    17 13     M        495646             9.475
    18.07     M         54420             1.04
    18.41     M         25994              .496 9
 ME ~~19.30     M       1414543            27.04~~
    20.44     M         50803              .971 2
    21.01     M       1390914.           26.59
    21.53     M        504355             9.642
    22.06     M         71492             1.367
    22.93     M        765003.           14.63
    23 55     M         35677.             .682
    24.87     M          3481.             .066 54
    25.50     M          1545              .029 54
    26.60                3603              .063 58

HP 3390A
DLY   4           STOP 45          REJECT    10
PK/M    30        ATTN       4
```

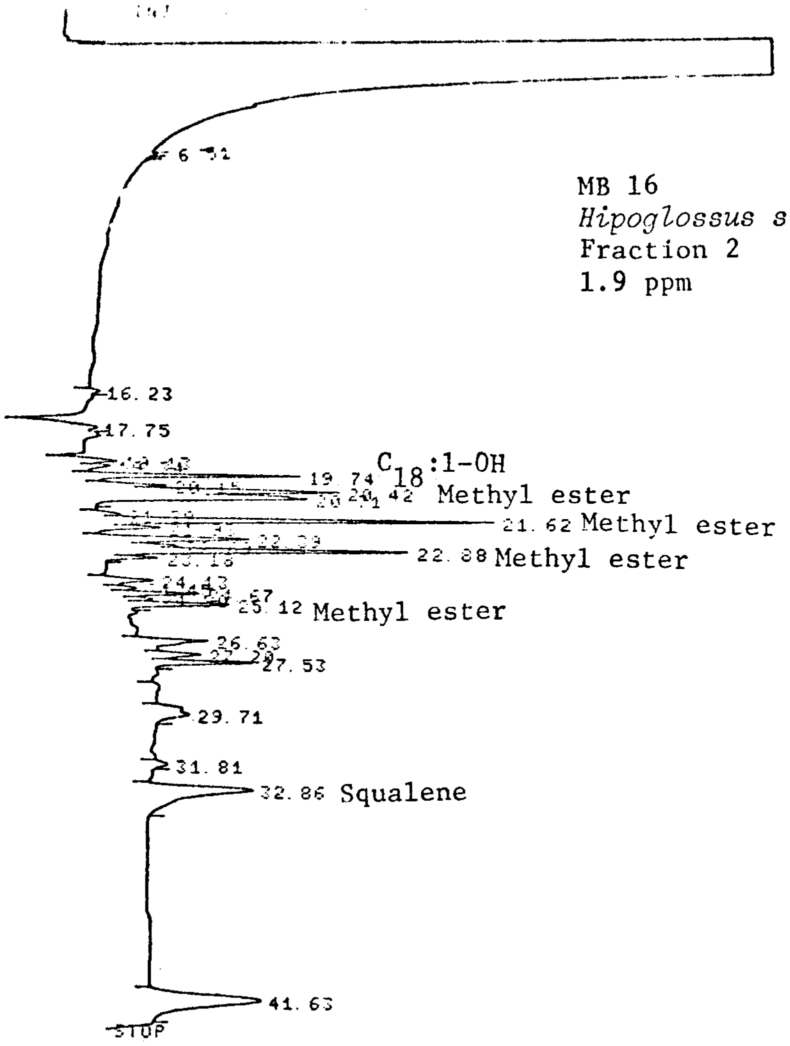
MB 16
Hipoglossus stenolepis - Gills
Fraction 1
6.6 ppm



```
                    AREA %
    RT    TYPE        AREA
S ~~[illegible]                [illegible]            .078 74~~
S ~~[illegible]                [illegible]            .646 6~~
  17 97                 1627               .457 7
S ~~18 72               [illegible]            .271 5~~
  20 88                  365               .102 1
  28.43                  313               .087 52
  29.34               351774             98.36

HP 3380A
DLY  4.           STOP 45          REJECT   100
MV/M   30         ATTN      4
```

MB 16
Hipoglossus stenolepis - Gills
Fraction 2
1.9 ppm

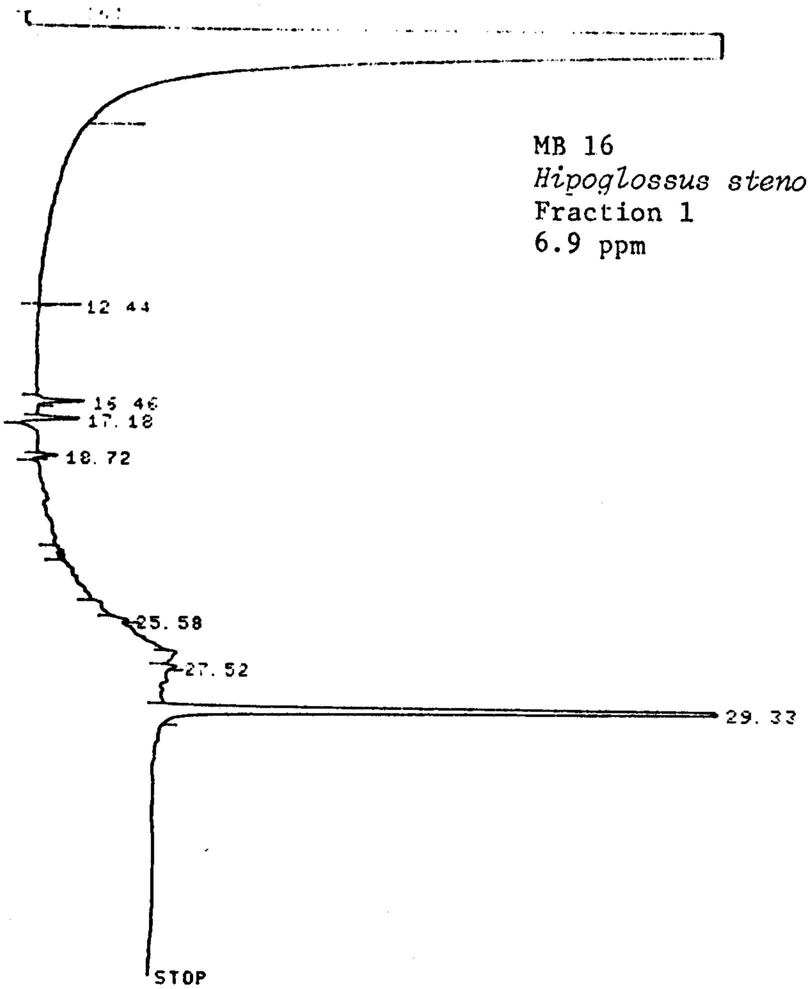


```
                             AREA %
     RT     TYPE       AREA
R ~~6 51     T          [illegible]                 .162 5~~
S ~~16.23               [illegible]                 [illegible]~~
S ~~17.75               [illegible]                1.137~~
  19.13                 3607                       1.782
  19 34      M          3143                       1 553
A ~~19.74    M          [illegible]                [illegible]~~
  20.15      M          4625                       2.285
ME ~~20 42   M          17692                      [illegible]~~
ME ~~20.71   M          [illegible]                [illegible]~~
  21.29                 1258                        .621 5
  21.62      M          22327                     11.03
  21.93      M          3634                       1 795
  22.39      M          9375                       4 632
  22.53      M          3730                       1.873
ME ~~22.88   M          [illegible]                [illegible]~~
  23.18      M          2658                       1.313
  24 13                 2787                       1.377
  24 45      M          1179                        .582 5
  24 57      M          3999                       1.976
  24 90      M          1427                        705
ME ~~25 12   M          [illegible]                [illegible]~~
  26 63                 5273                       2 605
  27 29      M          4510                       2 228
C ~~27.53    M          [illegible]                [illegible]~~
  29 71                 5358                       2 647
  31 81                 1112                        554 8
  32 86                 17360                      8 676
R ~~41 63               [illegible]               [illegible]~~

HP 3390A
ATT 2               STOP 45             AR REJ    100
PK WD   .04         THRSH      4
```

163

MB 16
Hipoglossus stenolepis - Liver
Fraction 1
6.9 ppm

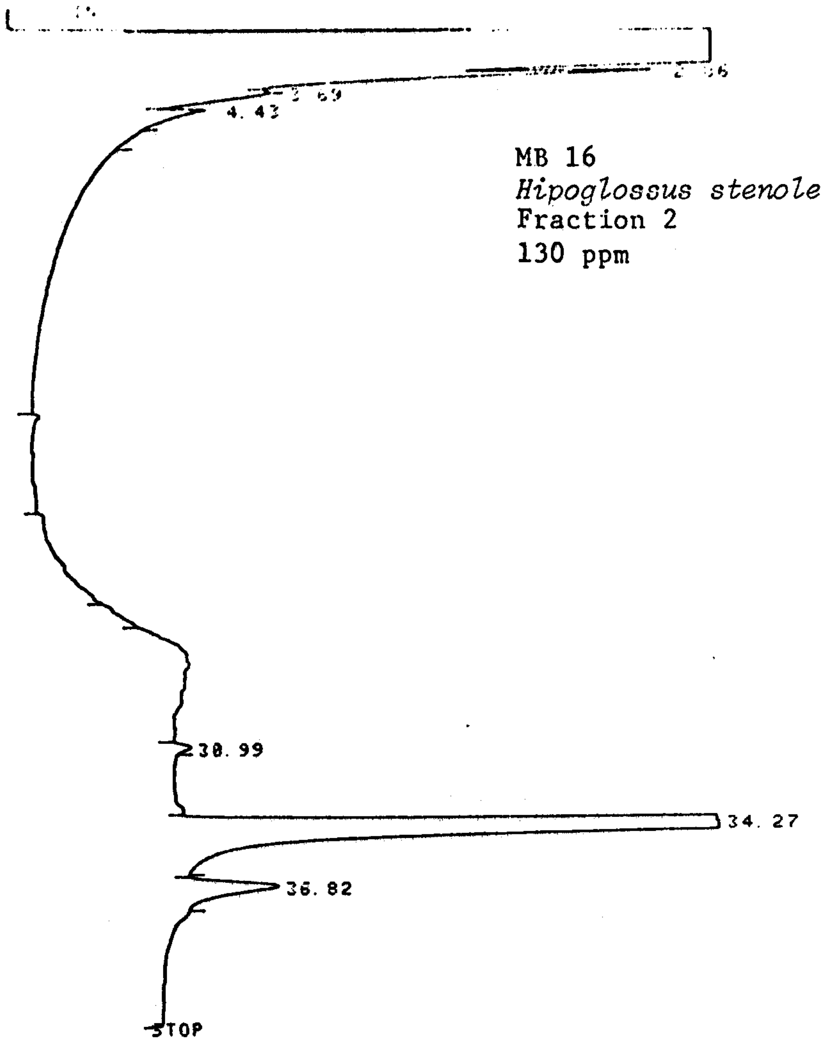


Squalene

```
                    AREA %
  RT   TYPE     AREA
 12.44           232          .351 4
S~~15.46~~      ~~2342~~        ~~3.547~~
S~~17.18~~      ~~2193~~        ~~3.320~~
S~~18.72~~      ~~[illegible]~~     ~~[illegible]~~
 25.58           516          .781 6
 27.52           561          .849 7
 29.33         58899        89.21

HP 3380A
DLY  4          STOP 45          REJECT   100
MV/M   30       ATTN      4
```

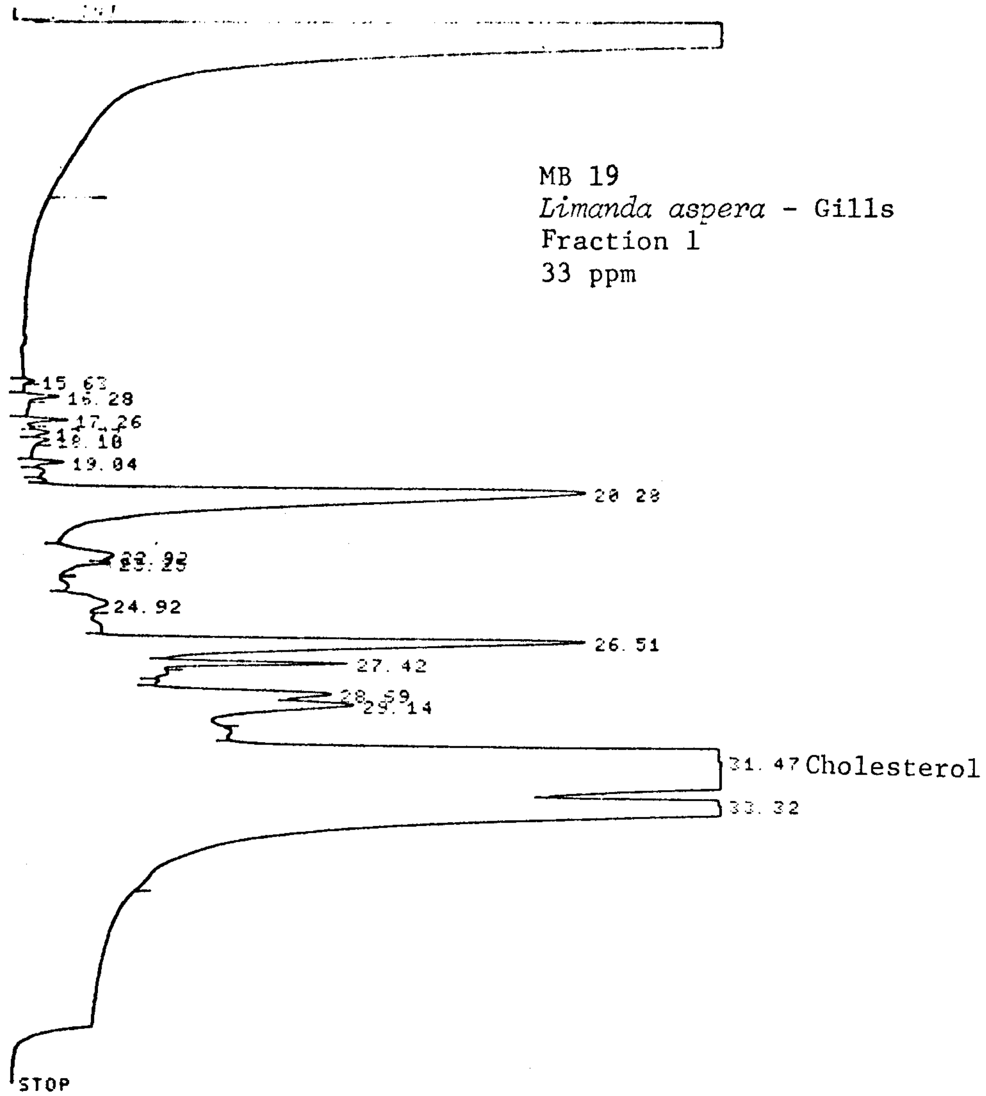
MB 16
Hipoglossus stenolepis - Liver
Fraction 2
130 ppm



Squalene

```
                    AREA %
 RT    TYPE      AREA
R2.36    T       13339             3.459
R3.69    T+       1[illegible]               .043 35
R4.43    T        5424             1.354
 30.99            1813              .454 1
 34.27          360457            90.29
 36.82           17533             4.392

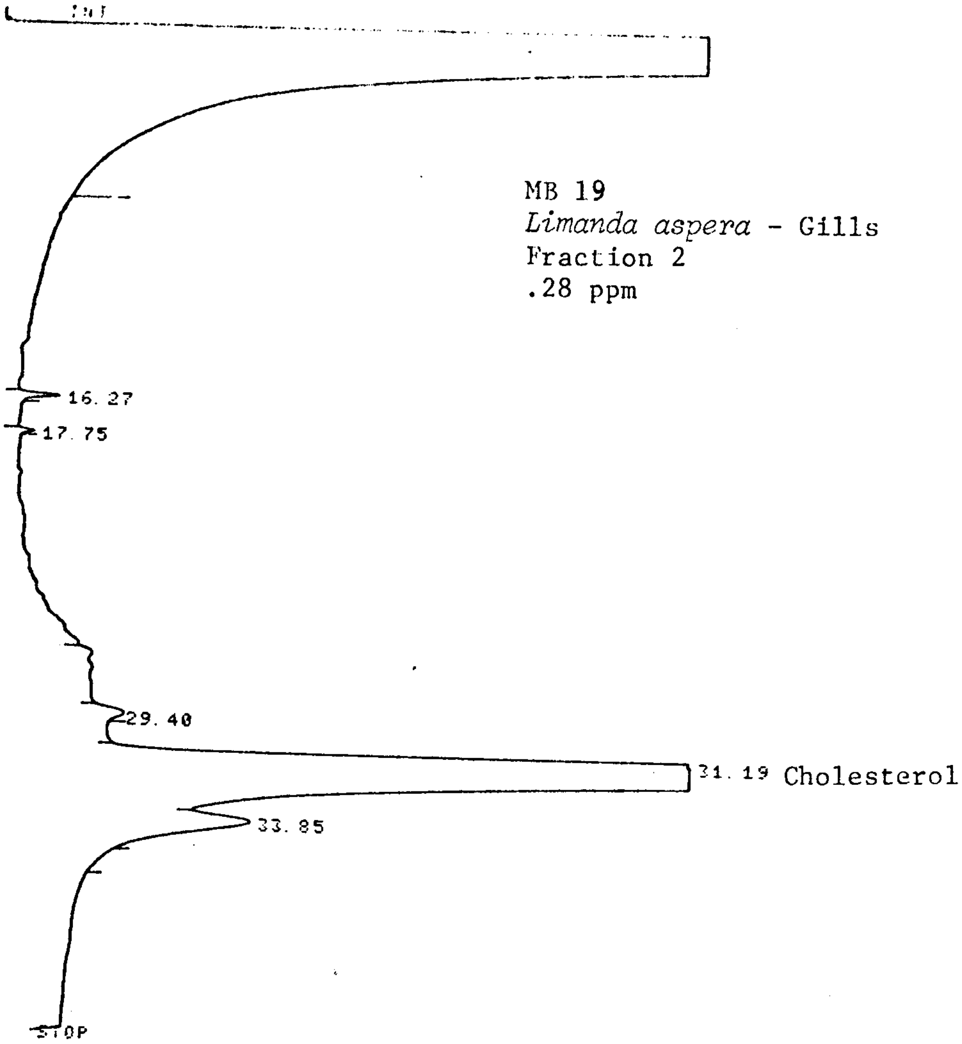
HP 3380A
DLY  2.          STOP 45          REJECT   100
MV/M  .30        ATTN     4
```



MB 19
Limanda aspera - Gills
Fraction 1
33 ppm

```
                              AREA %
   RT   TYPE      AREA
  15.63            624              .009 059
9 ~~16.28          [illegible]      [illegible]~~
  17.25           2140              .031 07
S ~~17.77          [illegible]      [illegible] 15~~
  18.10   M       1177              .017 09
  19.04           1620              .023 56
  20.28         147247             2.138
  22.92   T       8592              .124 7
  23.25   TM      4626              .067 16
  24.92           4808              .069 8
  26.51          76645             1.113
  27.42   M      11934              .173 3
  28.69          19734              .286 5
  29.14   M      25613              .371 8
A ~~31.47          [illegible]     [illegible]~~
R ~~33.32  M       [illegible]     1.[illegible]~~

HP 3380A
DLY  3.          STOP 45          REJECT   100
MV/M   20        ATTN     4
```



MB 19
Limanda aspera - Gills
Fraction 2
.28 ppm

```
                              AREA %
      RT    TYPE      AREA
S ~~16.27             [illegible]           [illegible]~~
S ~~17.75             [illegible]           [illegible]~~
   29.40              3157                   353 7
A ~~31.19             [illegible]           [illegible]~~
R ~~33.85             [illegible]           [illegible]~~

HP 3380A
DLY   8.
MV/M   .30        STOP 45            PEJECT    100
                  ATTN       4
```

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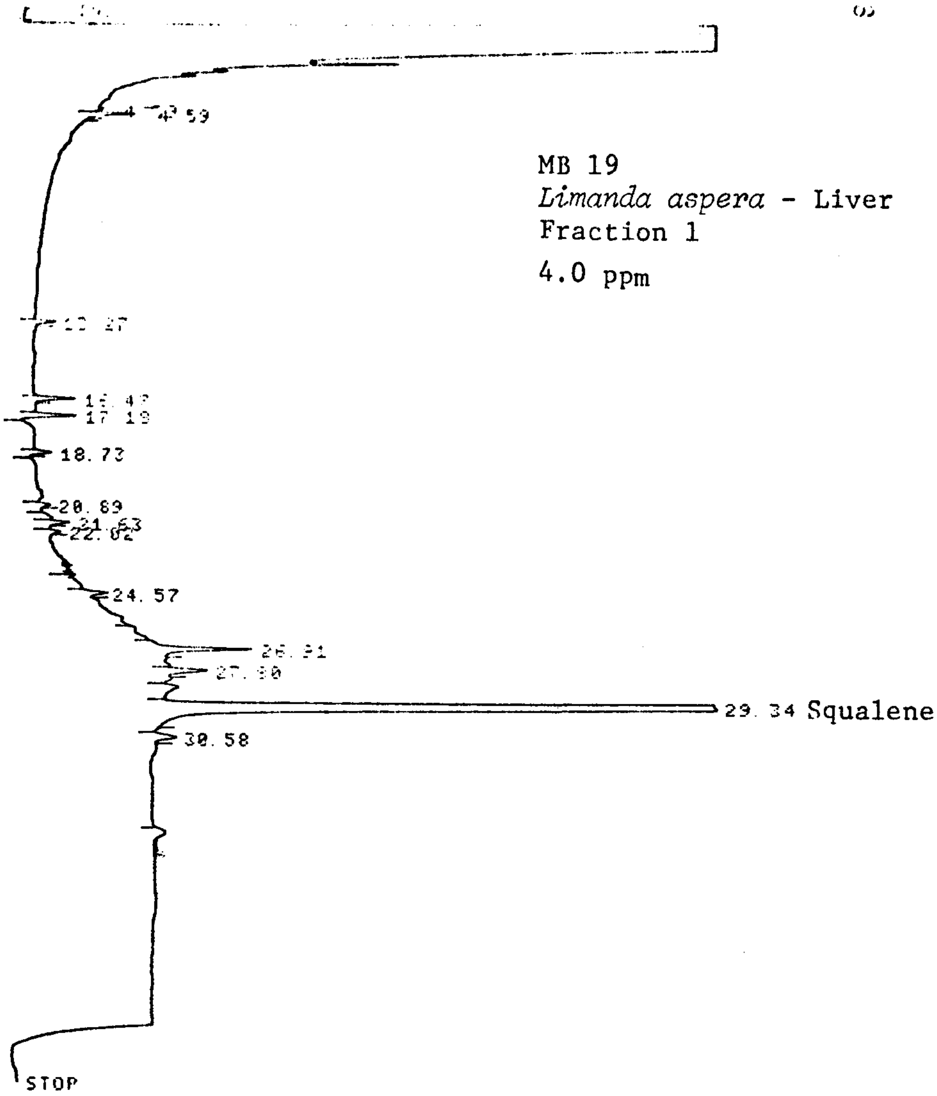
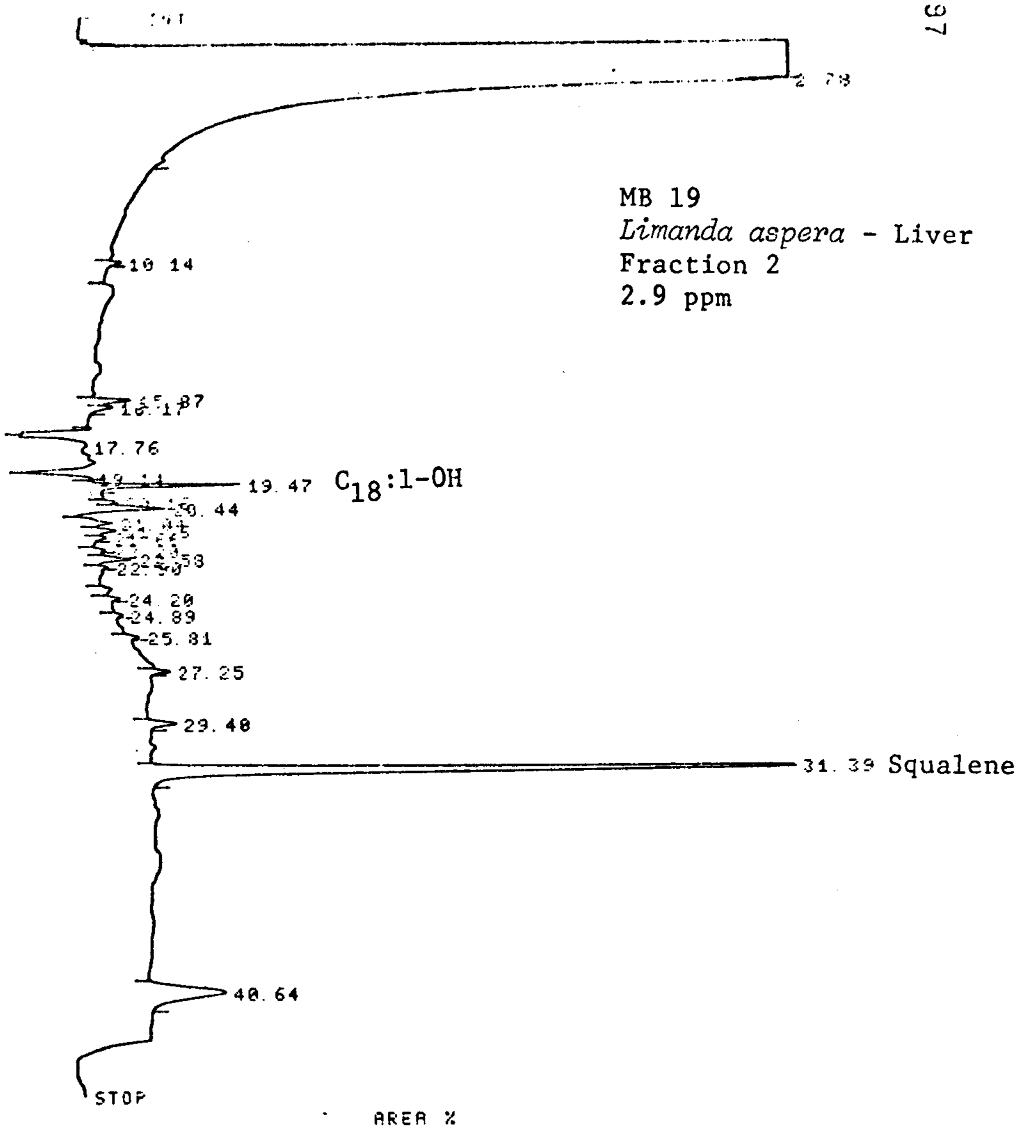
MB 19
Limanda aspera - Liver
Fraction 1
4.0 ppm



AREA %

RT	TYPE	AREA		
R ~~[illegible]~~	~~I~~	~~[illegible]~~	~~.165~~	~~9~~
R ~~[illegible]~~	~~IN~~	~~[illegible]~~	~~1.044~~	
13.27		799	.484	8
S ~~15.47~~		~~[illegible]~~	~~1.324~~	
S ~~17.19~~		~~[illegible]~~	~~1.377~~	
S ~~18.73~~		~~[illegible]~~	~~[illegible]~~	~~2~~
20.89		519	.315	3
21.63		822	.499	4
22.02		494	.300	1
24.57		1077	.654	3
26.91		4971	3.02	
27.80		2352	1.429	
29.34		144959	88.01	
~~30.58~~		~~[illegible]~~	~~.947~~	~~1~~

159

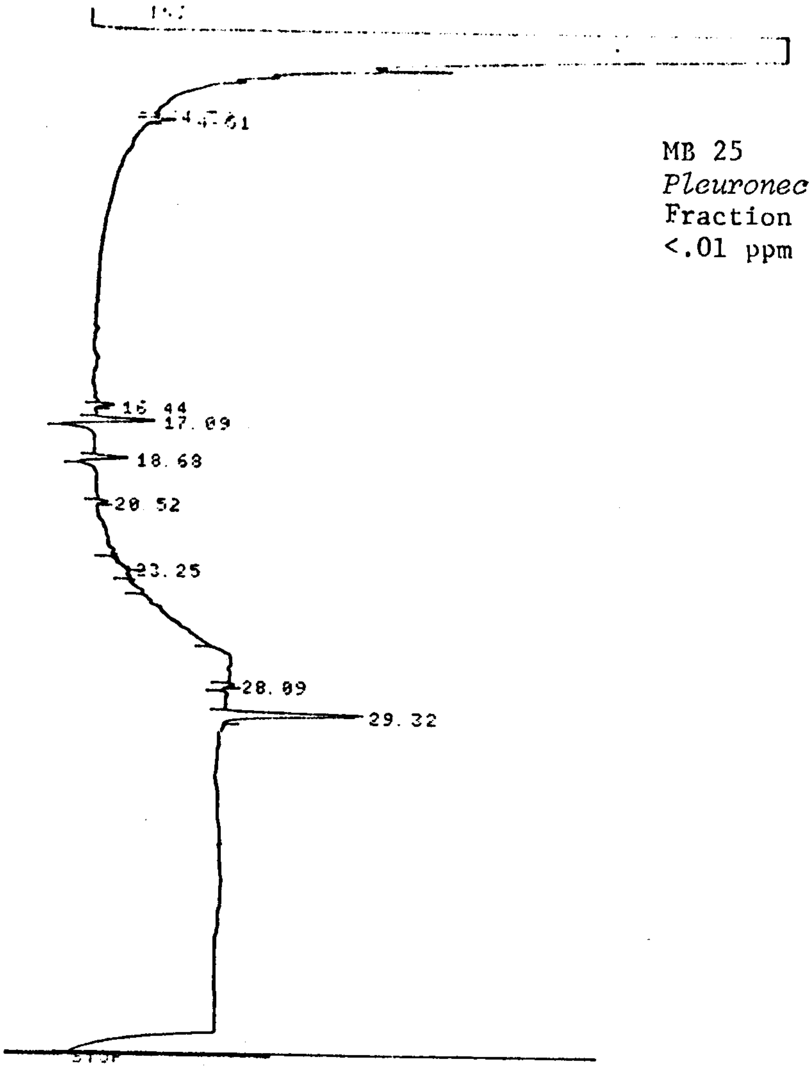


MB 19
Limanda aspera - Liver
Fraction 2
2.9 ppm

```
                       AREA %
     RT    TYPE      AREA
R    2.78             2023                   1.274
R   10.14                                     .335 3
    15.87             2540                   1.588
S   16.17    M                                .674 4
S   17.76            13267
    19.14    M        1403                    .880 4
A
ME                                            .857 8
ME           M
    21.04    M        2563                   1.603
    21.36    M        2429                   1.519
    21.66    M        1045                    .654
    22.20              299                    .131 3
ME  22.58                                    1.284
    22.90    M         355                    .222
    24.20              493                    .312
    24.89              368                    .230 1
    25.81              605                    .378 3
C   27.25                                     .546 2
    29.40             1965                   1.229
    31.39                                    37.34
R   40.64

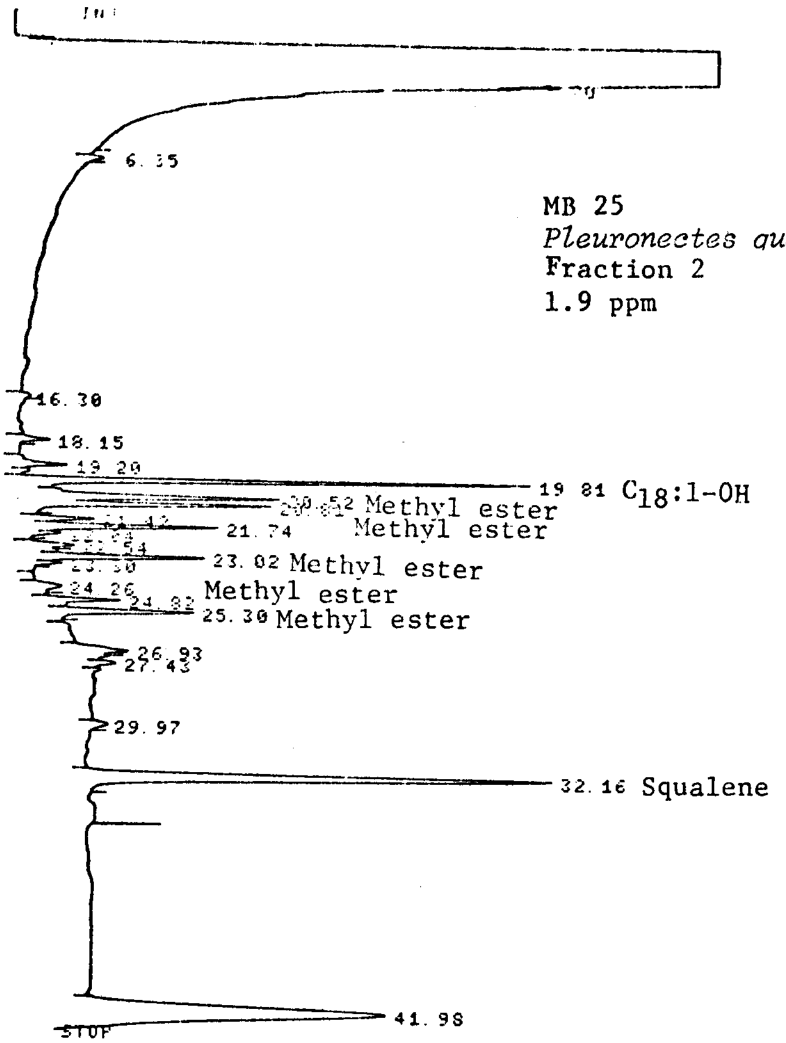

HP 3380A
PLT  2                STOP 45             REJECT    100
S  M      0           ATTN      4
```

MB 25
Pleuronectes quadrituberculatus - Gills
Fraction 1
<.01 ppm



```
                                         AREA %
      RT     TYPE         AREA
R ~~[illegible]~~
R ~~[illegible]~~
S ~~[illegible]~~
S ~~[illegible]~~
S ~~[illegible]~~
C ~~[illegible]~~
C ~~[illegible]~~
C ~~[illegible]~~
C ~~[illegible]~~

HP 3380A
DLY  4.               STOP 45            REJECT    100
MV/M  .30             ATTN      4
```



MB 25
Pleuronectes quadrituberculatus - Gills
Fraction 2
1.9 ppm

```
                              AREA %
       RT    TYPE     AREA
R  ~~3 22  [illegible]  1166            [illegible] 4~~
R  ~~[illegible]       [illegible]      [illegible]~~
   16.30               484              .210 8
   18.15               1725             .755 6
   19 20               2457            1.07
A  ~~[illegible]       [illegible]    11.[illegible]~~
ME ~~[illegible]    M  [illegible]     [illegible]~~
ME ~~[illegible]    M  [illegible]     [illegible]~~
   21 42               [illegible]     1.767
   21 74    M          11503           5 053
   22 04    M          1807             .786 9
   22.54               1553             .676 2
ME ~~[illegible]       [illegible]      [illegible]~~
   23.30    M          968               421 5
   24 26               1614              702 9
ME ~~[illegible]       [illegible]    1.[illegible]~~
ME ~~[illegible]    M  [illegible]      [illegible]~~
   26 93               2117              952 4
C  ~~[illegible]       [illegible]      [illegible]~~
   29 97               1410              644 5
   32 16               44029           19 2
R  ~~[illegible]       [illegible]      [illegible]~~

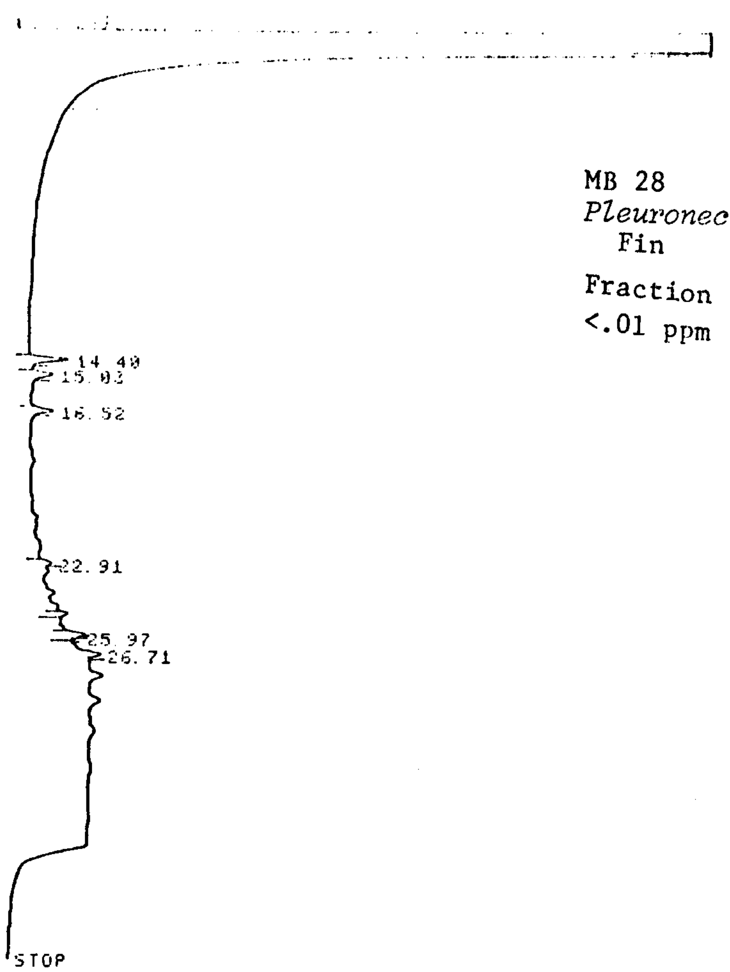
HP 3390A
CHT SP 2.              STOP 45          REJECT   100
PK WD  30              ATTN      4
```

MB 28

Pleuronectes quadrituberculatus - Skin/ Fin

Fraction 1

<.01 ppm



AREA %

RT TYPE AREA

C ~~14.40 2581 27.09~~

S ~~15.03 1541 16.2~~

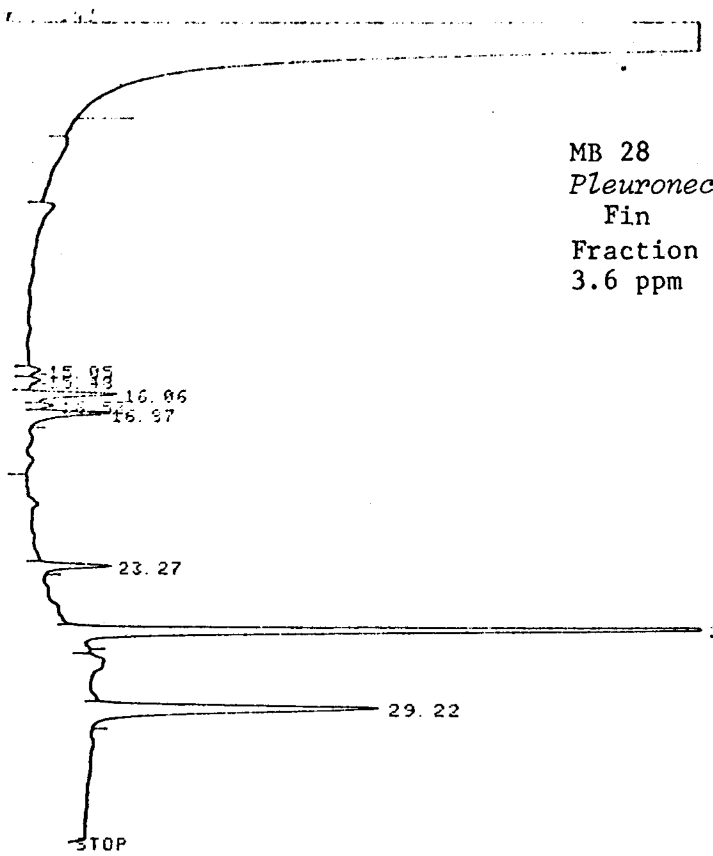
S ~~16.52 [illegible] 18.52~~

C ~~22.91 611 6.425~~

C ~~25.97 [illegible] 12.57~~

C ~~26.71 [illegible] 18.52~~

HP 3380A
DLY 4. STOP 45 REJECT 100
MV/M .30 ATTN 4



Squalene

MB 28
Pleuronectes quadrituberculatus - Skin/
Fin
Fraction 2
3.6 ppm

```
                              AREA %
      RT    TYPE      AREA
S ~~15.05                1873                  .762 2~~
  15.48                   712                  .621 7
  16.06                  6743                 5.888
C ~~16.57      M          1906                 1.651~~
  16.97      N           7456                 6.51
  23.27                  5096                 4.449
  25.97                 58783                51.33
  29.22                 32961                28.78

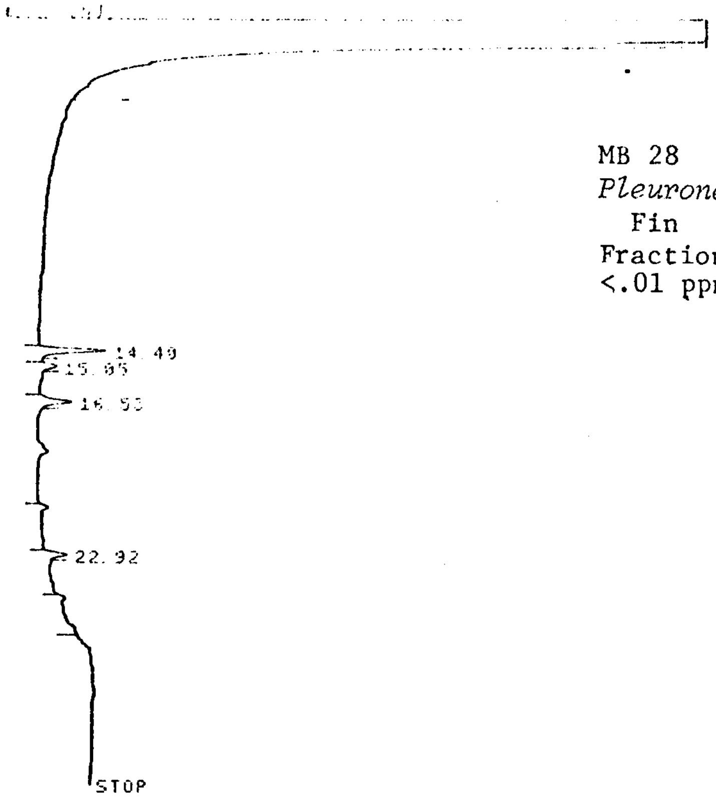
 HP 3380A
 DLY  4.          STOP 45          REJECT   100
 MV/M  .30        ATTN     4
```

MB 28

Pleuronectes quadrituberculatus - Skin/
  Fin

Fraction 1

<.01 ppm



AREA %

RT TYPE AREA

C ~~14.49 4537 46.09~~

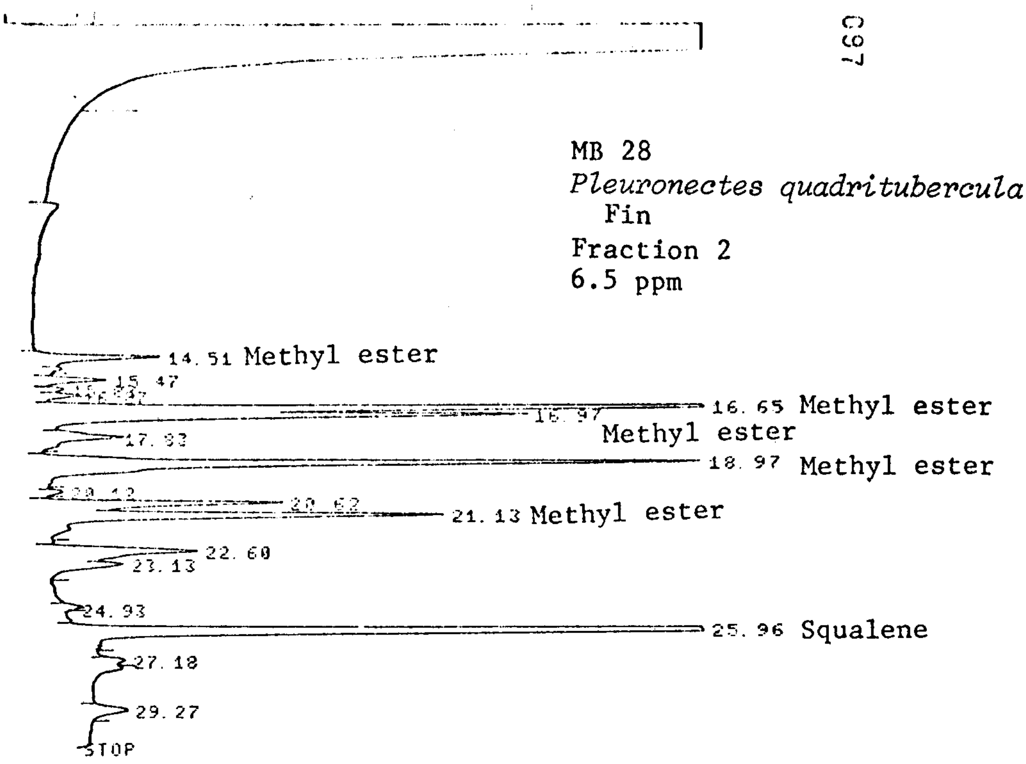
S ~~15.95 1164 11.87~~

S ~~16.53 2622 26.9~~

C ~~22.92 1417 14.45~~

```
HP 3380A
DLY  4.          STOP 45          REJECT   100
HV/M   30        ATTN      4
```

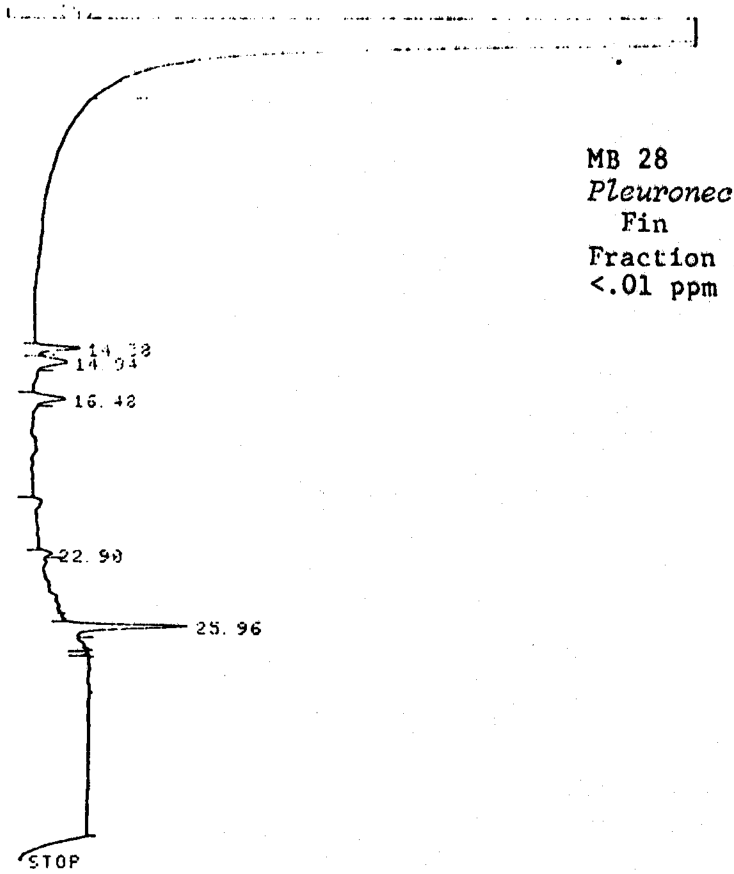
MB 28
Pleuronectes quadrituberculatus - Skin/
Fin
Fraction 2
6.5 ppm



AREA %

RT	TYPE	AREA	
ME ~~14.51~~		~~[illegible]~~	~~2.869~~
15.47		3812	1.021
15.83	M	885	.237 1
16.07	M	2068	.554 .1
ME ~~16.65~~	~~M~~	~~[illegible]~~	~~16.42~~
ME ~~16.97~~	~~M~~	~~[illegible]~~	~~13.38~~
17.83	M	10206	2.735
ME ~~18.97~~		~~[illegible]~~	~~16.88~~
20.12		684	.183 3
20.62		19304	5.172
ME ~~21.13~~	~~M~~	~~[illegible]~~	~~10.01~~
22.60		18816	5.042.
23.13	M	8950	2.398
24.93		1194	.319 9
25.96		91432	24.5
27.18		849	.227 5
29.27		3824	1.025

```
HP 3380A
DLY  4.          STOP 45          REJECT   100
MV/M  .30        ATTN     4
```



MB 28
Pleuronectes quadrituberculatus - Skin/Fin
Fraction 1
<.01 ppm

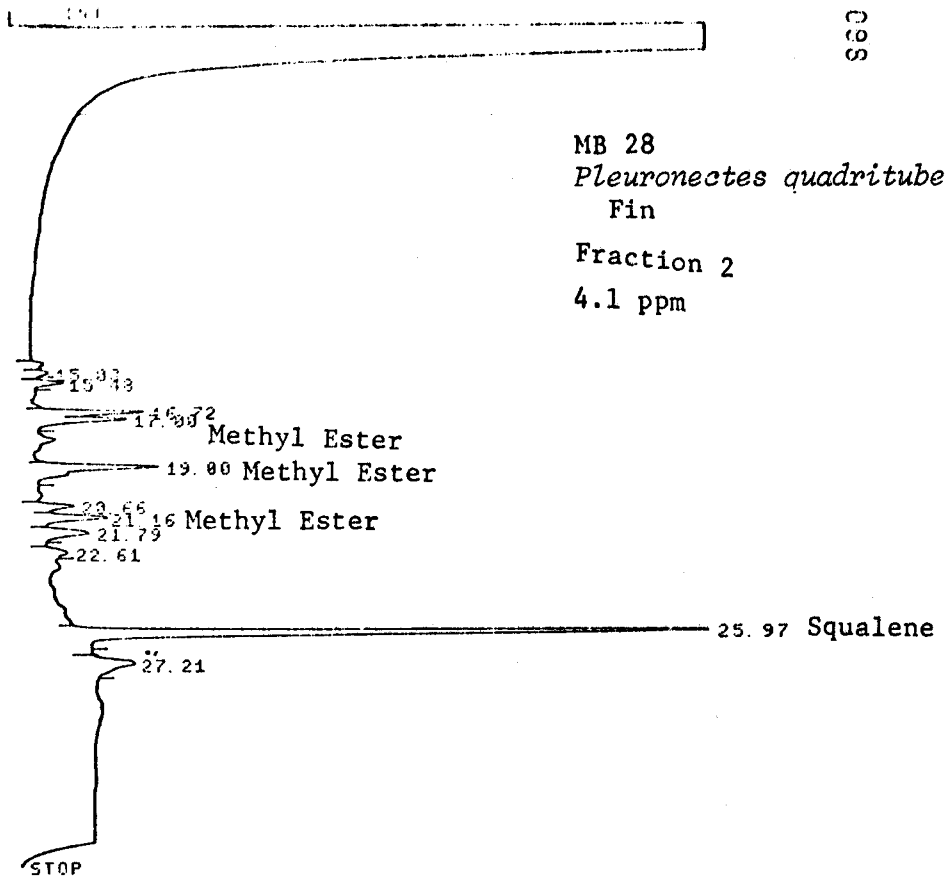
	PT	TYPE	AREA	AREA %
C	~~[illegible]~~		~~[illegible]~~	~~15.43~~
S	~~[illegible]~~		~~[illegible]~~	~~16.27~~
S	~~[illegible]~~		~~[illegible]~~	~~15.21~~
C	~~[illegible]~~		~~[illegible]~~	~~[illegible]~~
C	~~[illegible]~~		~~[illegible]~~	~~49.81~~

```
HP 3380A
DLY  4.          STOP 45           REJECT   100
MV/M  .30        ATTN      4
```

MB 28
Pleuronectes quadrituberculatus - Skin/
Fin

Fraction 2

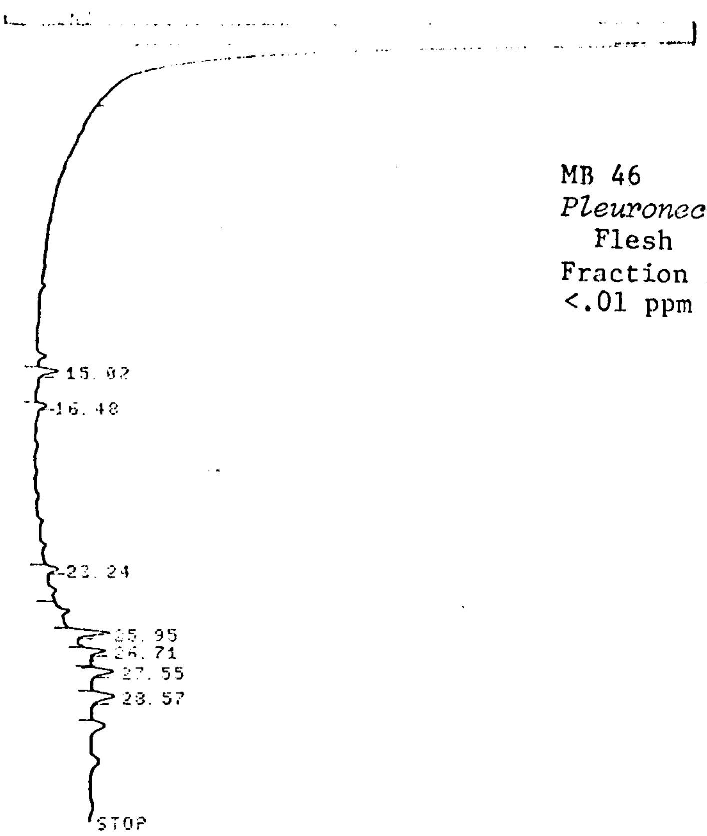
4.1 ppm



	RT	TYPE	AREA	AREA %
S	~~15.03~~		~~721~~	~~.7288~~
	15.48		1936	1.957
	16.72		7552	7.634
ME	~~17.00~~	~~M~~	~~6949~~	~~7.025~~
ME	~~19.00~~		~~11027~~	~~11.15~~
	20.56		2972	3.004
ME	~~21.16~~	~~M~~	~~6072~~	~~6.138~~
	21.79	M	5055	5.11
	22.61		1663	1.681
	25.97		48551	49.08
	27.21		6426	6.496

```
HP 3380A
DLY  4.          STOP 45          REJECT   100
MV/M  .30        ATTN      4
```

MB 46
Pleuronectes quadrituberculatus - Skin/
Flesh
Fraction 1
<.01 ppm

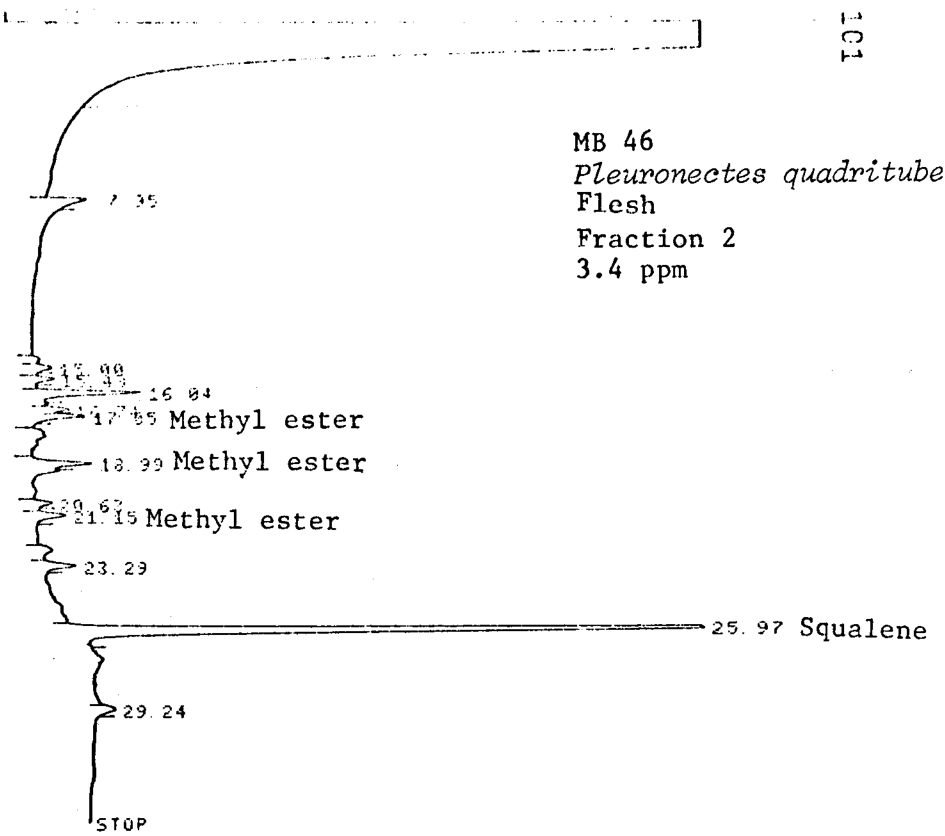


```
                          AREA %
     RT    TYPE       AREA
S ~~15.02                 [illegible]            [illegible]~~
S ~~16.48                 [illegible]            [illegible]~~
C ~~23.24                 [illegible]            [illegible]~~
C ~~25.95                 [illegible]            [illegible]~~
C ~~26.71                 [illegible]            [illegible]~~
C ~~27.55                 [illegible]            [illegible]~~
C ~~28.57                 [illegible]            [illegible]~~

HP 3390A
DLY  4.           STOP 45           REJECT    100
MV/M  .30         ATTN      4
```

1C1

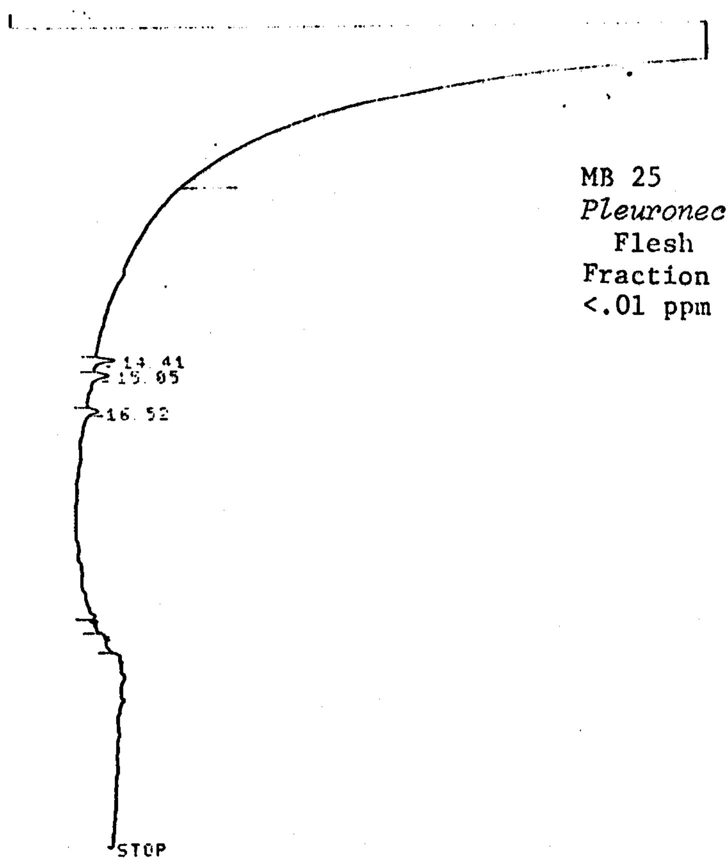
MB 46
Pleuronectes quadrituberculatus - Skin/
Flesh
Fraction 2
3.4 ppm



	RT	TYPE	AREA	AREA %
R	~~7.95~~		~~1090~~	~~1.259~~
S	~~15.00~~		~~1172~~	~~1.356~~
	15.48		1246	1.442
	16.04		6810	7.879
	16.74		1005	1.163
ME	~~17.55~~		~~1735~~	~~1.573~~
ME	~~18.99~~		~~3117~~	~~3.607~~
	20.63		1183	1.369
ME	~~21.15~~		~~2388~~	~~2.763~~
	23.29		2435	2.817
	25.97		59773	69.16
	29.24		1838	2.127

```
HP 3380A
DLY  4             STOP 45          REJECT   100
MV/M  .30          ATTN      4
```

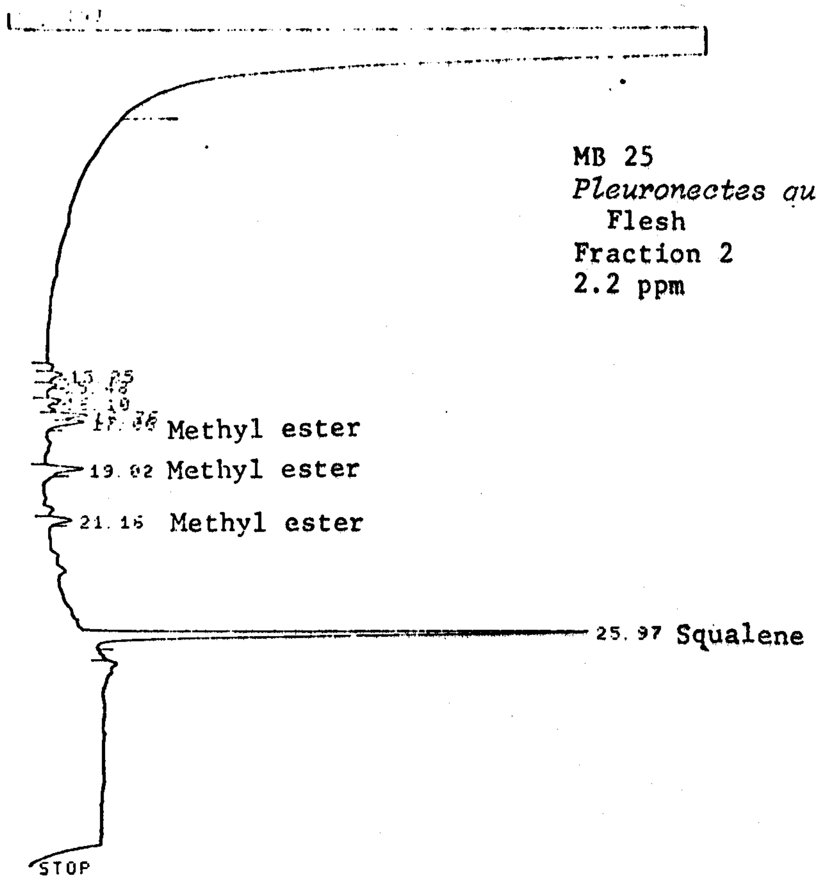
086



MB 25
Pleuronectes quadrituberculatus - Skin/
Flesh
Fraction 1
<.01 ppm

	RT	TYPE	AREA	AREA %
C	~~14.41~~		~~1172~~	~~38.77~~
S	~~15.35~~		~~[illegible]~~	~~33.13~~
S	~~16.52~~		~~[illegible]~~	~~28.1~~

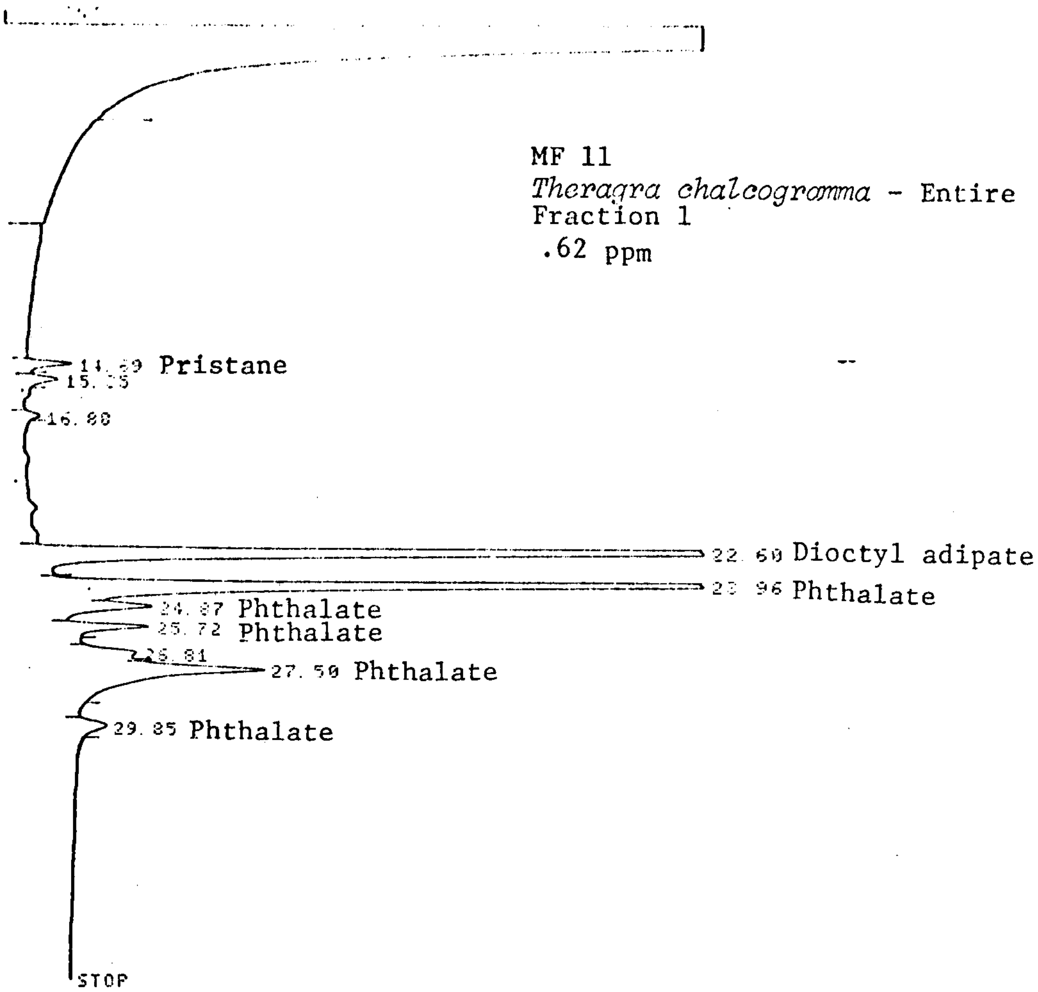
```
HP 3380A
DLY  4.            STOP 45          REJECT   100
MV/M  .30          ATTN     4
```



MB 25
Pleuronectes quadrituberculatus - Skin/
Flesh
Fraction 2
2.2 ppm

	RT	TYPE	AREA	AREA %
S	~~15.05~~		~~[illegible]~~	~~1.706~~
	15.48		531	1.108
	16.10		762	1.59
	16.76		2143	4.472
ME	~~17.36~~	~~M~~	~~[illegible]~~	~~5.635~~
ME	~~19.02~~		~~[illegible]~~	~~3.763~~
ME	~~21.16~~		~~[illegible]~~	~~2.754~~
	25.97		36450	76.07

```
HP 3380A
DLY  4.          STOP 45          REJECT   100
MV/M  .30        ATIN      4
```

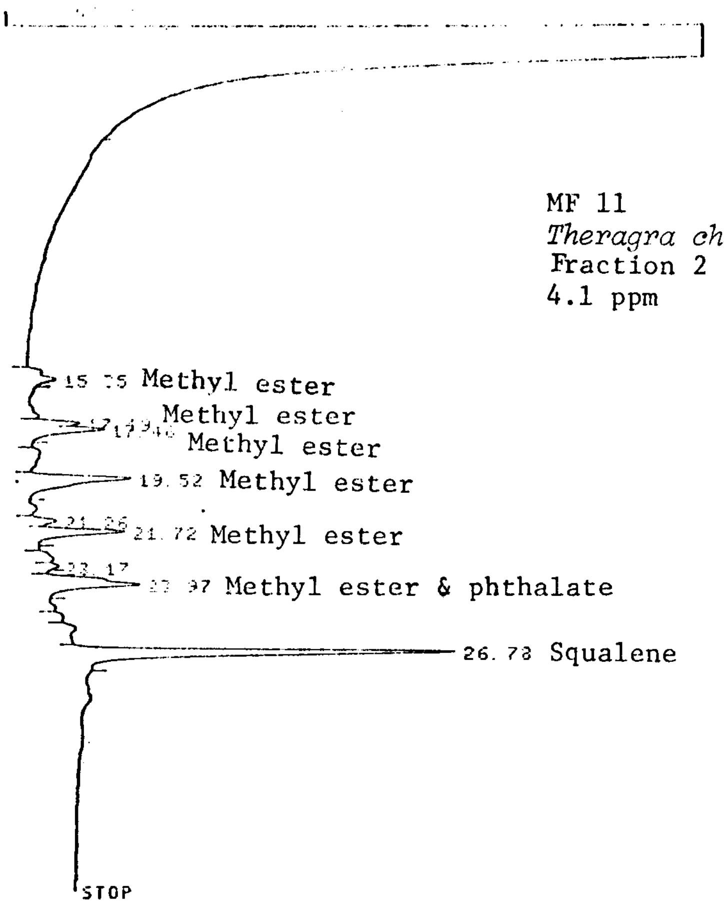


MF 11
Theragra chalcogramma - Entire
Fraction 1
.62 ppm

```
                         AREA %
   RT     TYPE      AREA
 14.69              3728          1.353
S~~15.35          [illegible]   [illegible]~~
S~~16.80          [illegible]   [illegible]~~
A~~22.60          [illegible]   [illegible]~~
A~~23.96          [illegible]   [illegible]~~
A~~24.87          [illegible]   [illegible]~~
A~~25.72          [illegible]   [illegible]~~
 26 81               691           250 7
A~~27.50          [illegible]   [illegible]~~
A~~29.85          [illegible]   [illegible]~~

HP 3380A
DLY  4.          STOP 45        REJECT   100
MV/M  .30        ATTN     4
```

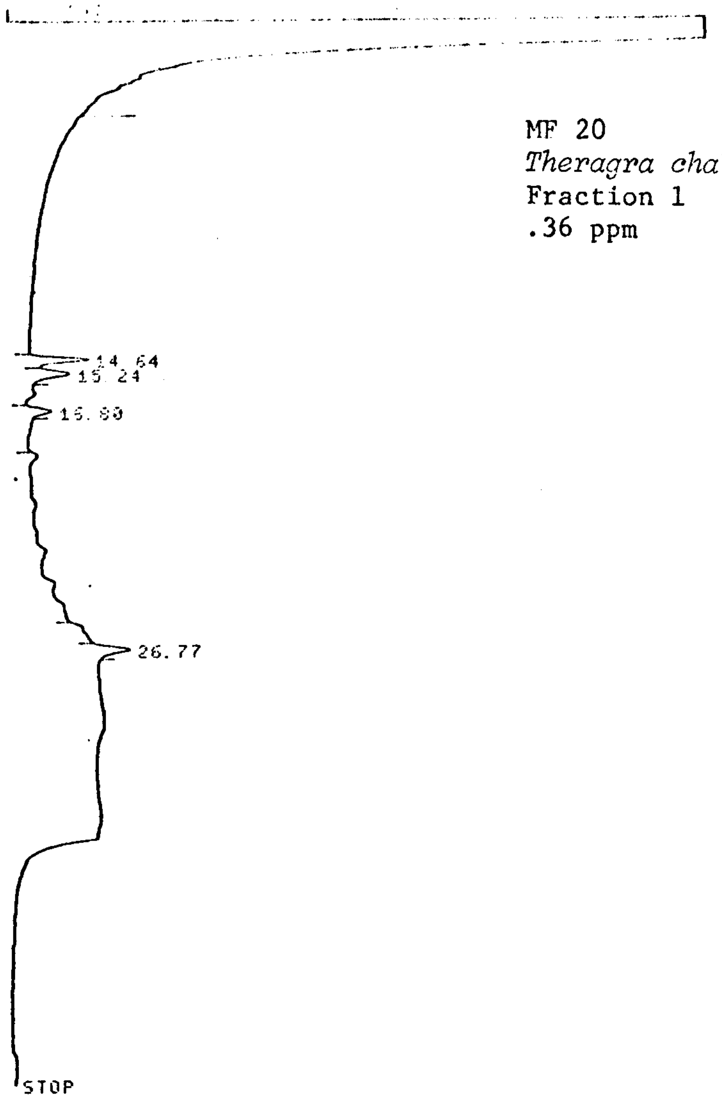
MF 11
Theragra chaleogramma - Entire
Fraction 2
4.1 ppm



	RT	TYPE	AREA	AREA %
ME+S	~~15.25~~		~~2639~~	~~4.314~~
ME	~~17.19~~		~~2073~~	~~3.37~~
ME	~~17.46~~		~~2126~~	~~3.338~~
ME	~~19.52~~		~~12243~~	~~15.44~~
	21.26		2189	2.414
ME	~~21.72~~		~~9274~~	~~13.52~~
	23.17		689	.781 4
ME+A	~~23.97~~		~~13193~~	~~14.96~~
*	26.78		35442-5929	40.19

```
HP 3380A
DLY  4.          STOP 45          REJECT   100
MV/M  .30        ATTN
```

MF 20
Theragra chalcogramma - Flesh
Fraction 1
.36 ppm

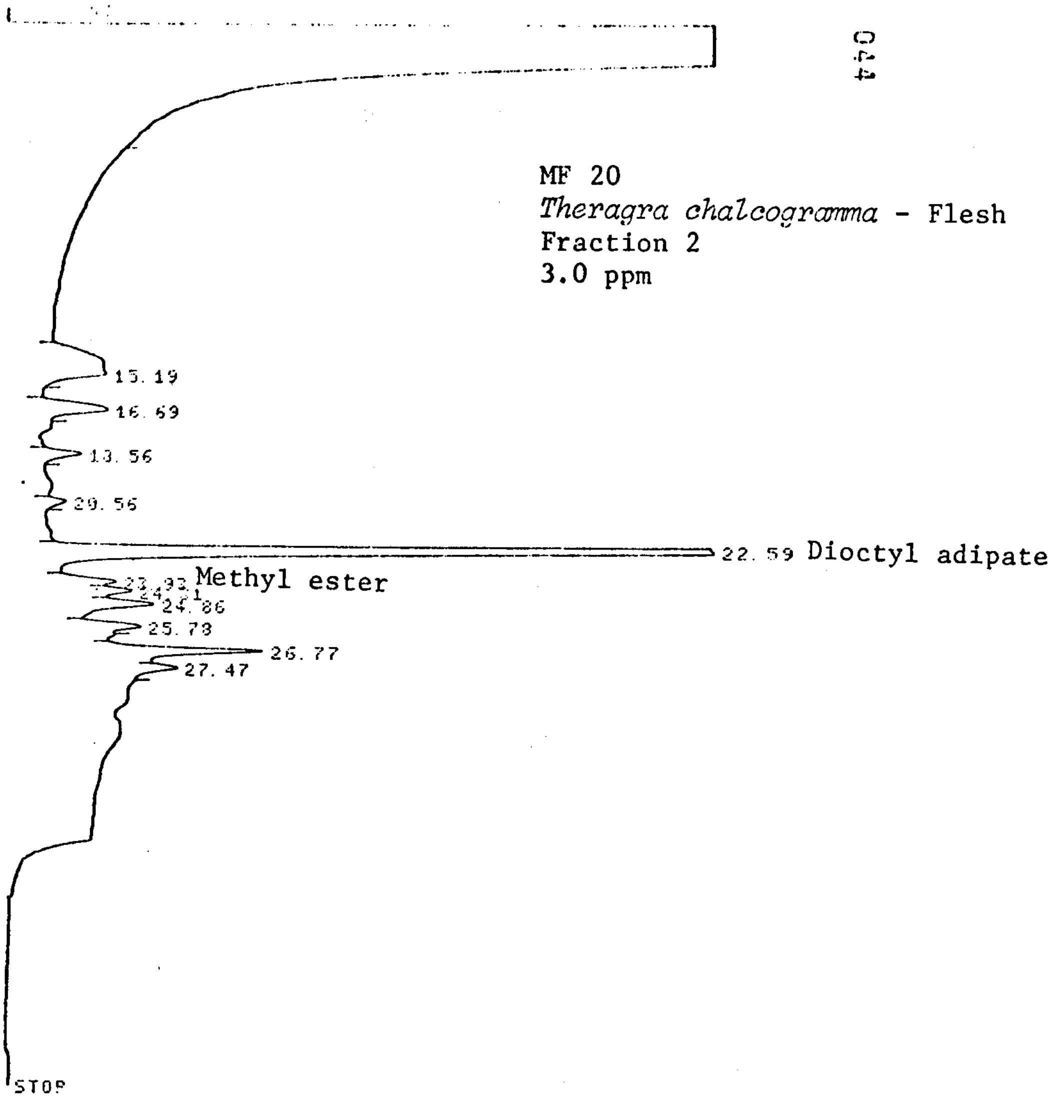


AREA %

RT TYPE AREA
14.64 5215 32.07
S ~~15.24 H [illegible] 22.49~~
S ~~15.80 [illegible] 20.42~~
26.77 4069 . 25.02

HP 3380A
DLY 4. STOP 45 REJECT 100
HV/M .30 ATTN 4

044

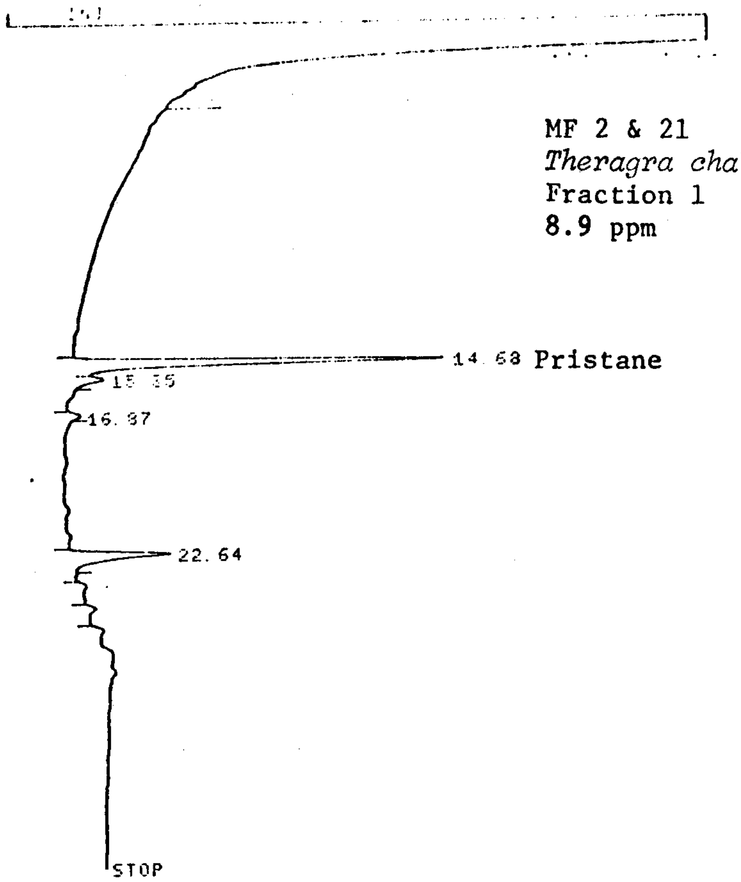


MF 20
Theragra chalcogramma - Flesh
Fraction 2
3.0 ppm

```
                                   AREA %
      RT    TYPE        AREA
   15.19               25531              11.25
   16.69               10206               4.497
   18.56                4392               1.935
   20.56                2017                .888  8
A  ~~22.59              [illegible]        57.?7~~
ME ~~23.93   M          3449               2.?07~~
   24.31     M          8093               3.566
   24.86     M         11310               4 984
   25.78     M          4116               1.814
 ✱ 26.77               17176-5463          7.568
   27.47     M          7776               3.426

HP 3380A
DLY  4              STOP 45            REJECT   100
MV/M  .30           ATTN      4
```

045



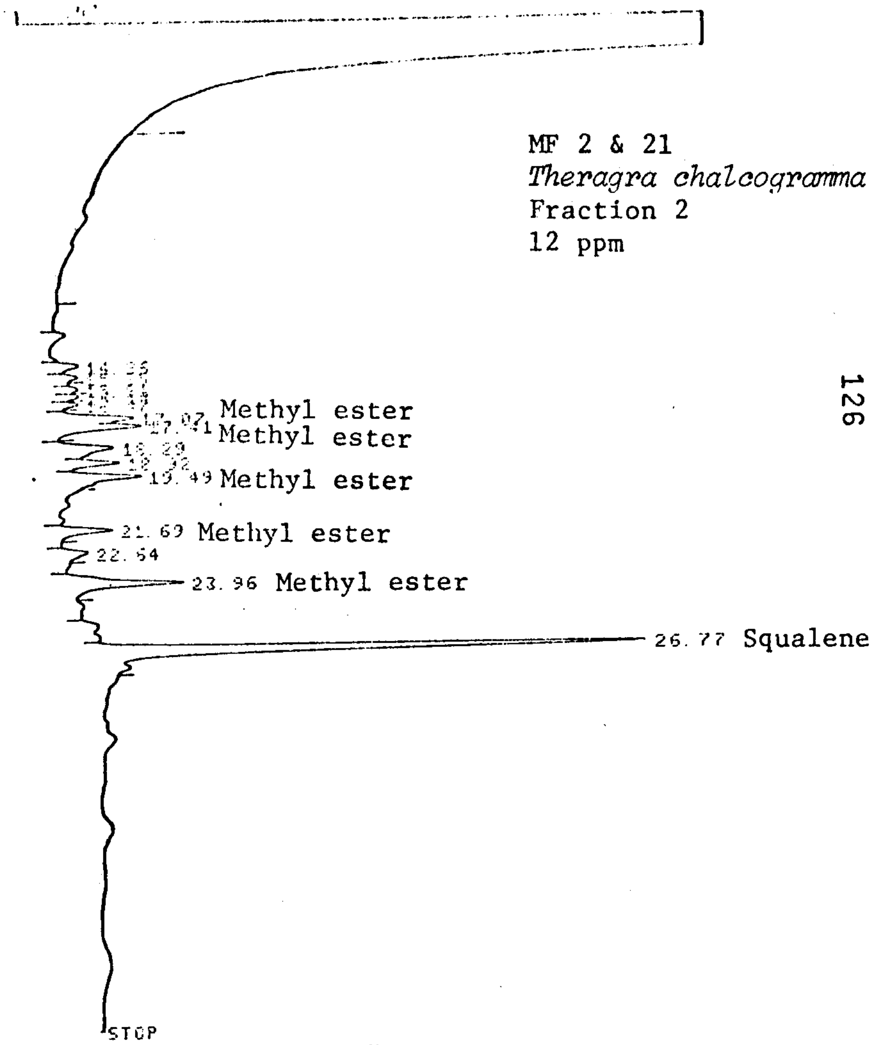
MF 2 & 21
Theragra chaleogramma - Gills
Fraction 1
8.9 ppm

AREA %

RT	TYPE	AREA	
14.68		33318	67.32
S ~~15.35~~		~~[illegible]~~	~~[illegible]~~
S ~~16.87~~		~~1167~~	~~[illegible]~~
22.64		11625	23.49

```
HP 3380A
DLY  4.          STOP 45          REJECT   100.
MV/M  .30        ATTN      4
```

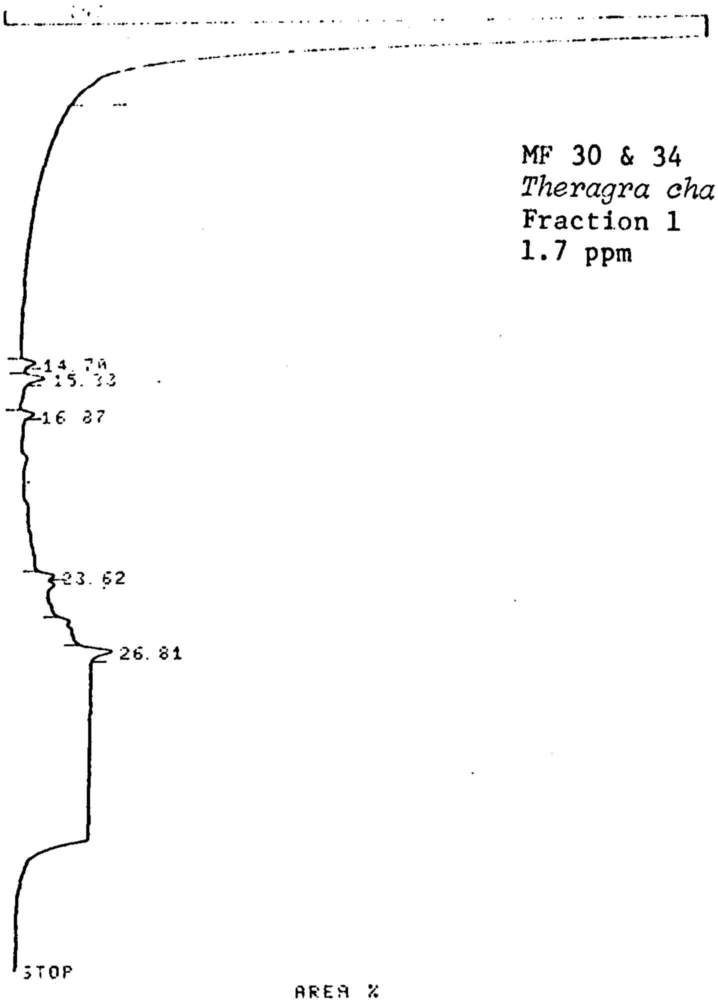
MF 2 & 21
Theragra chalcogramma - Gills
Fraction 2
12 ppm



```
                    AREA %
   RT   TYPE     AREA
 14.86          2139              1.884
S~~[illegible]~~  H   ~~[illegible]~~          ~~[illegible]~~ 4
 15.81           513              .451 8
 16.12           585              .515 2
 16.47           808              .711 5
ME~~17.07~~         ~~[illegible]~~          ~~[illegible]~~
ME~~[illegible]~~         ~~[illegible]~~          ~~[illegible]~~
 18.29          6971              6.139
 18.92   H      4460              3.928
ME~~[illegible]~~         ~~[illegible]~~          ~~[illegible]~~
ME~~[illegible]~~         ~~[illegible]~~          ~~[illegible]~~
 22.64          2507              2.208
ME~~[illegible]~~         ~~[illegible]~~          ~~[illegible]~~
* 26.77         52203-6007       46.

HP 3380A
DLY  4.          STOP 45        REJECT   100
HV/H  .30        ATTN    4
```

MF 30 & 34
Theragra chalcogramma - Gills
Fraction 1
1.7 ppm

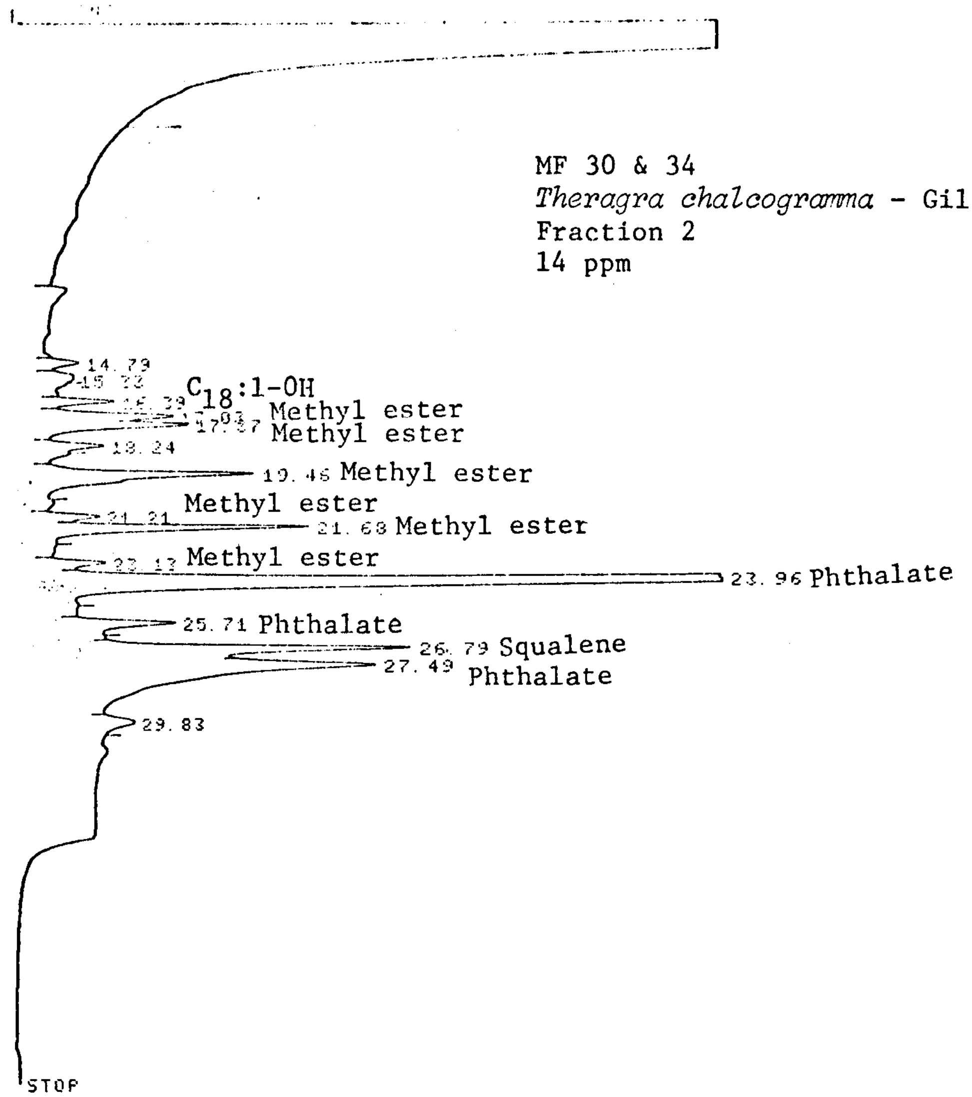


```
                          AREA %
    RT    TYPE      AREA
 14.70              1119            13.44
S ~~15.33           [illegible]     23.37~~
S ~~16.87           [illegible]     12.56~~
 23.62               677             8.129
 26.81              3482            41.81

HP 3380A
DLY  4.          STOP 45         REJECT   100
MV/M  .30        ATTN     4.
```

036

MF 30 & 34
Theragra chalcogramma - Gills
Fraction 2
14 ppm

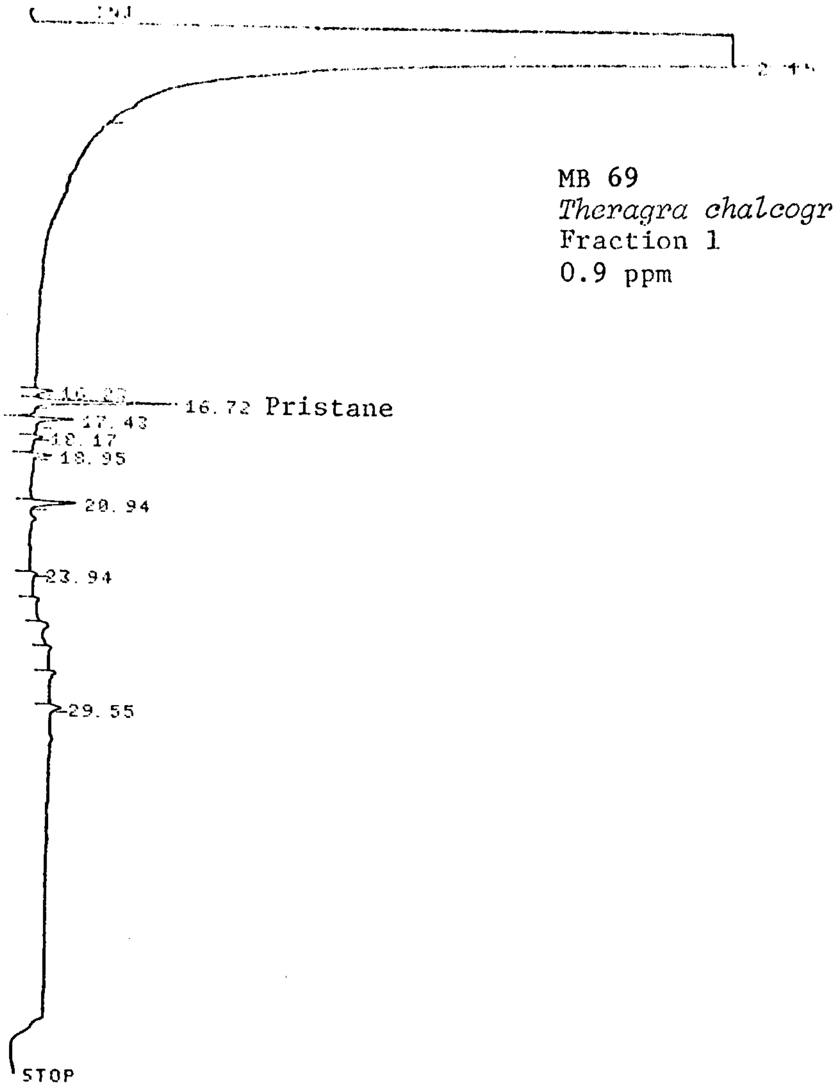


```
                              AREA %
      RT     TYPE      AREA
     14.79               3143                     .734 3
S    ~~[illegible]~~
A, S ~~[illegible]~~
ME   ~~[illegible]~~
ME   ~~[illegible]~~
     18.24    M          3535                     .825 9
ME   ~~[illegible]~~
ME   ~~[illegible]~~
ME   ~~[illegible]~~
ME   ~~[illegible]~~
A    ~~[illegible]~~
A    ~~[illegible]~~
*    26.79               35302-4854              8.247
A    ~~[illegible]~~
     29.83    T          5023                    1.177

HP 3380A
SLY   4              STOP 45            REJECT   100
MV/M   30            ATTN     4
```

037

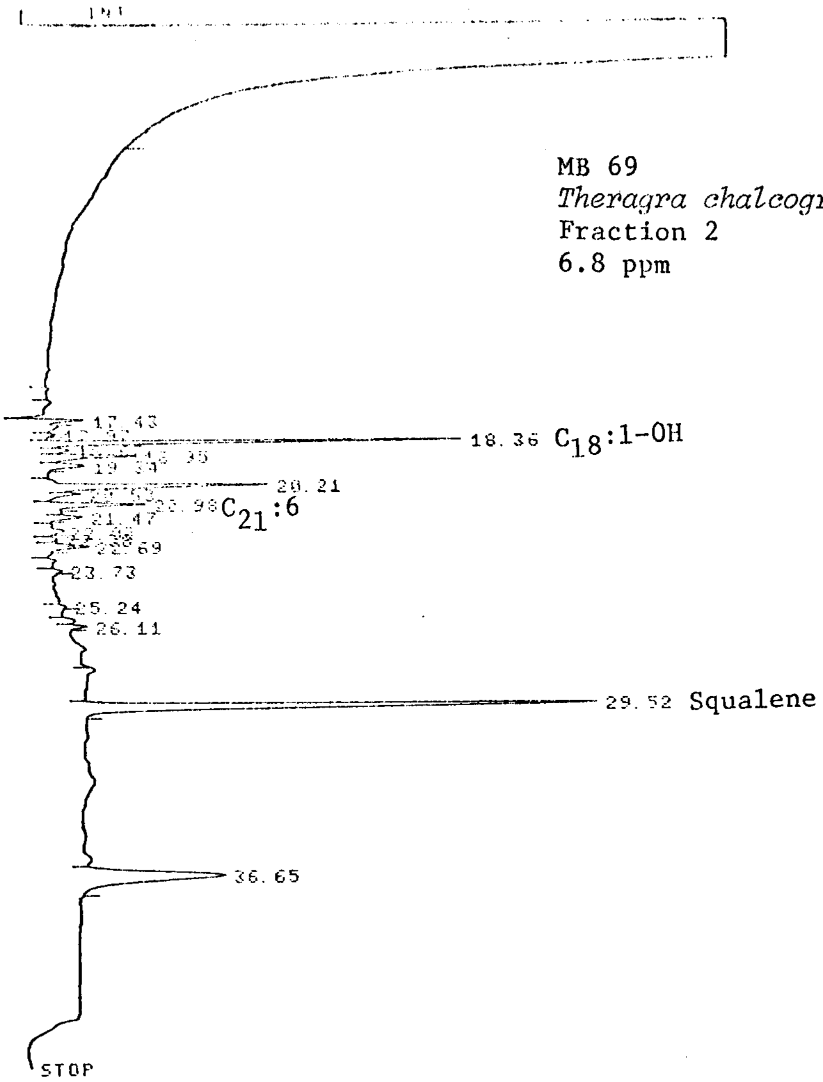
MB 69
Theragra chalcogramma-Gills
Fraction 1
0.9 ppm



```
                                AREA %
     RT     TYPE       AREA
  ~~2.15      T         2525                  14.49~~
  16.23                  917                   5.263
  16.72                 6425                  36.87
5 ~~17.43                 2657                  15.25~~
  18.17                  418                   2.399
5 ~~18.95                 1011                   5.802~~
  20.94                 2482                  14.24
8 ~~23.94                  288                   1.653~~
  29.55                  701                   4.023

HP 3380A
DLY  2.              STOP 45             REJECT    100
MV/M  .30            ATTN       4
```

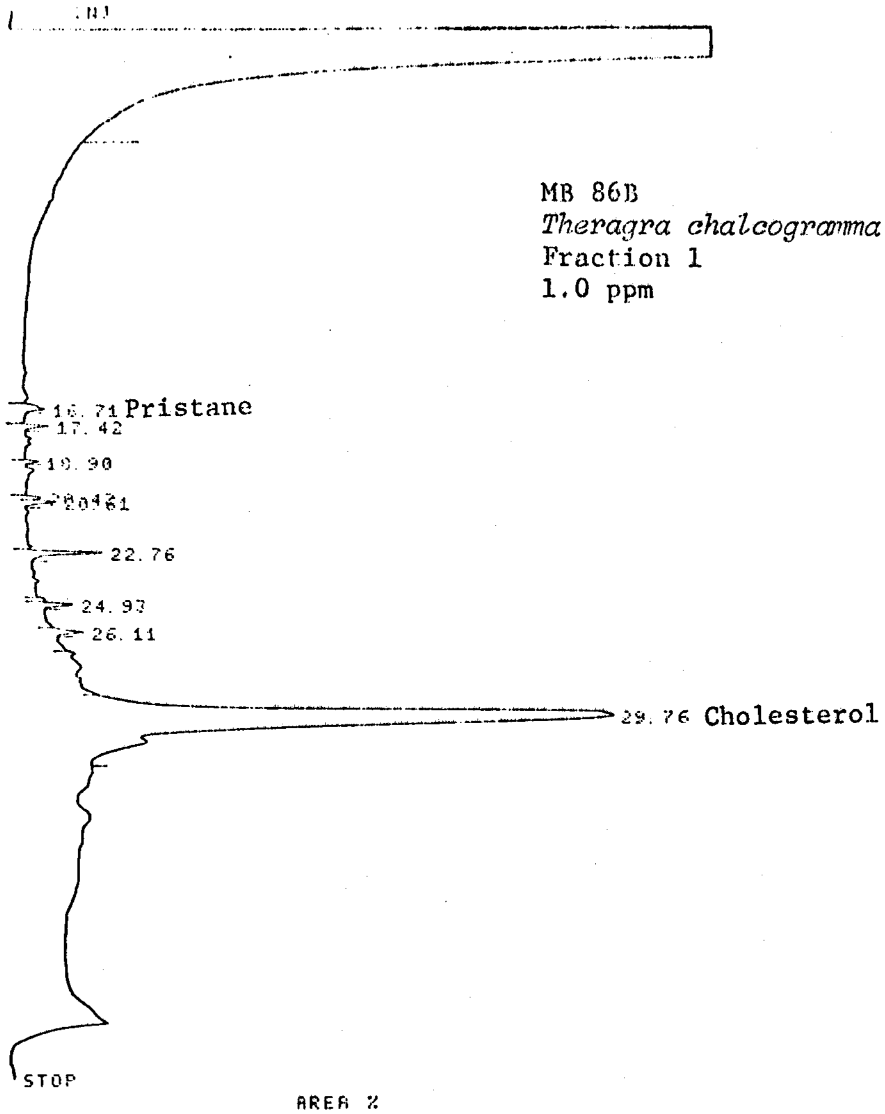
MB 69
Theragra chalcogramma - Gills
Fraction 2
6.8 ppm



	RT	TYPE	AREA	AREA %
5	~~17.43~~		~~2062~~	~~1.848~~
	17.97		334	.299 4
OH	~~18.36~~		~~17863~~	~~16.01~~
	18.67	M	1413	1.267
	18.95	M	5108	4.578
6	~~19.34~~	~~M~~	~~2443~~	~~2.19~~
	20.21		12553	11.25
	20.53	M	1786	1.601
	20.98	M	4420	3.962
6	~~21.47~~		~~1203~~	~~1.078~~
	22.03		1089	.976 1
	22.38		300	.268 9
	22.69		2229	1.998
5	~~23.73~~		~~407~~	~~.364~~ 8
	25.24		270	.242
6	~~26.11~~		~~686~~	~~.614~~ 9
	29.52		36000	32.27
	36.65		21399	19.18

```
HP 3380A
DLY  2              STOP 45           REJECT    100
MV/M   30           ATTN     4
```

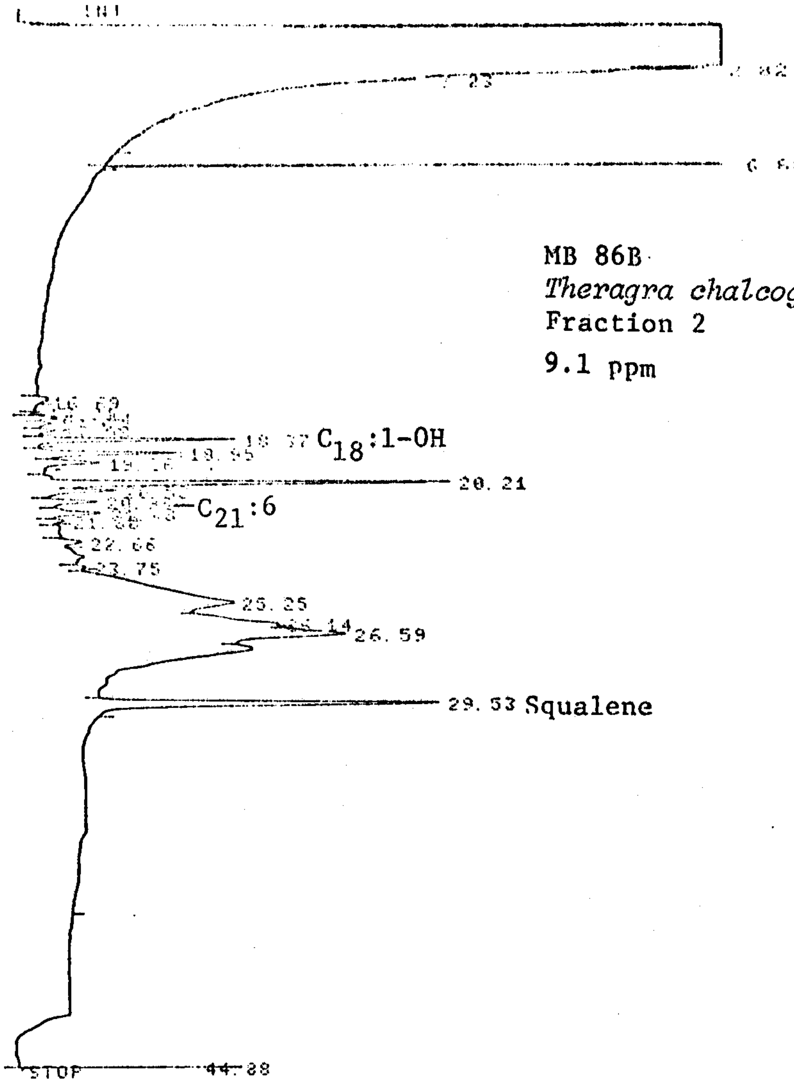
MB 86B
Theragra chalcogramma - Gills
Fraction 1
1.0 ppm



```
                            AREA %
   RT    TYPE       AREA
 16.71              1501                .931 3
~~17.42              1104                .685~~
~~18.90               374                .356 1~~
 20.43               727                .451 1
 20.61     M        1712               1.062
 22.76              3685               2.286
 24.93              1405                .871 7
 26.11              1520                .943 1
 29.76            148348              92.41

HP 3380A
SLP  2.            STOP 45           REJECT    100
MV/M  .30 ..       ATTN       4
```

MB 86B
Theragra chalcogramma - Gills
Fraction 2
9.1 ppm



C_{18}:1-OH

C_{21}:6

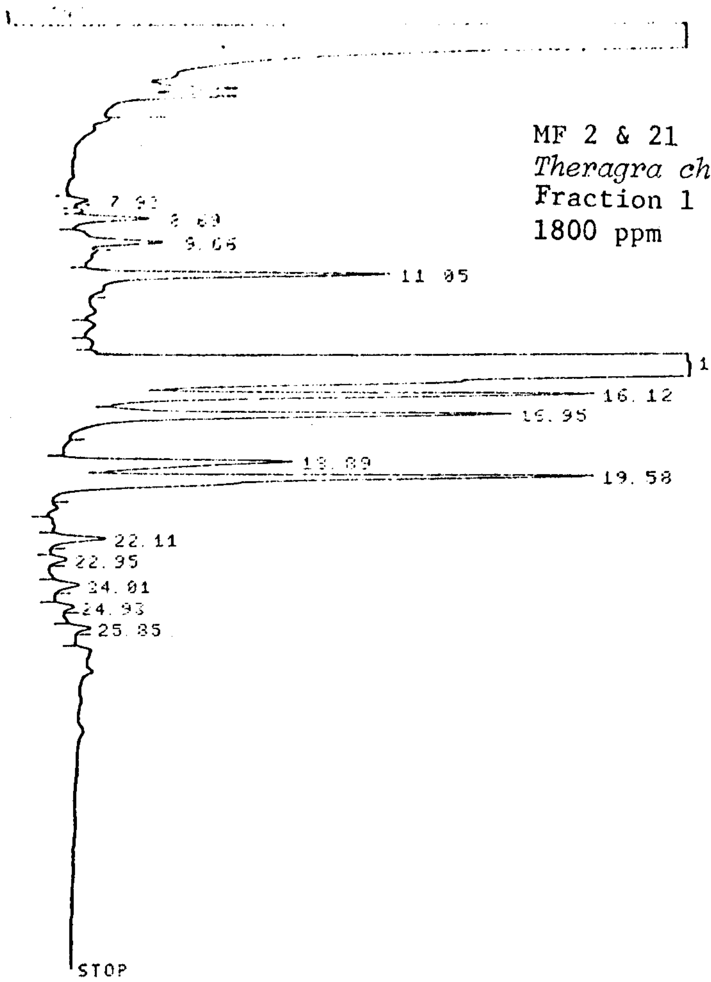
Squalene

AREA %

RT	TYPE	AREA		
~~2.82~~	~~T~~	~~4808~~	~~3.474~~	
~~3.23~~	~~T~~	~~573~~	~~.414~~	~~4~~
~~6.89~~		~~22444~~	~~16.22~~	
16.69		943	.681	4
S ~~17.44~~		~~1151~~	~~.831~~	~~7~~
17.67	M	1175	.849	1
17.98	M	971	.701	6
OH ~~18.37~~		~~8646~~	~~6.248~~	
18.95		8020	5.795	
19.76	M	3758	2.716	
20.21		21470	15.49	
20.53	M	3821	2.761	
20.98	M	2762	1.996	
21.48	M	3222	2.329	
21.80	M	433	.312	9
22.66		1220	.881	6
23.75		296	.213	9
25.25		17915	12.95	
26.59		9060	6.547	
29.53		24552	17.74	
~~44.35~~		~~[illegible]~~	~~.259~~	~~4~~

```
HP 3380A
FLV  2            STOP 45           REJECT   100
PK.W  .20         [illegible]    4
```

MF 2 & 21
Theragra chalcogramma - Liver
Fraction 1
1800 ppm

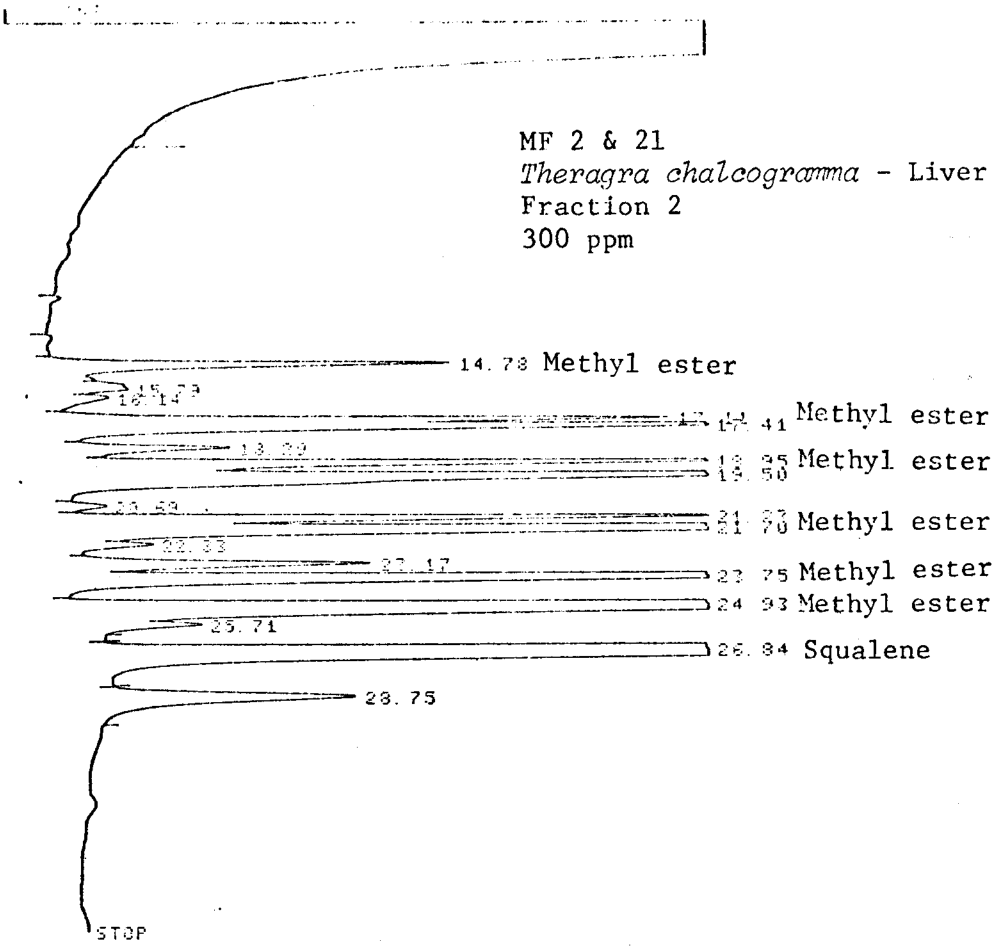


```
                     AREA %
    RT    TYPE       AREA
R ~~7.93             1450                   .017 94~~
R ~~8.69             [illegible]            [illegible]~~
R ~~9.66   M         [illegible]            [illegible]~~
  11.05              27730                  .333 8
  14.81            8074399            97.2
  16.12    M         47158                  .567 7
  16.95    M         43843                  .527 8
  18.89              27709                  .333 5
  19 58    M         59183                  .712 4
  22 11               5073                  .061 07
C ~~22.95             1743                  [illegible]~~
  24.01               3276                  .039 44
  24 93               1400                  .016 85
  25.85               1592                  .019 16

HP 3390A
DLY  4.          STOP 45   .      REJECT   100
MV/M   30        ATTN      4
```

130

MF 2 & 21
Theragra chalcogramma - Liver
Fraction 2
300 ppm



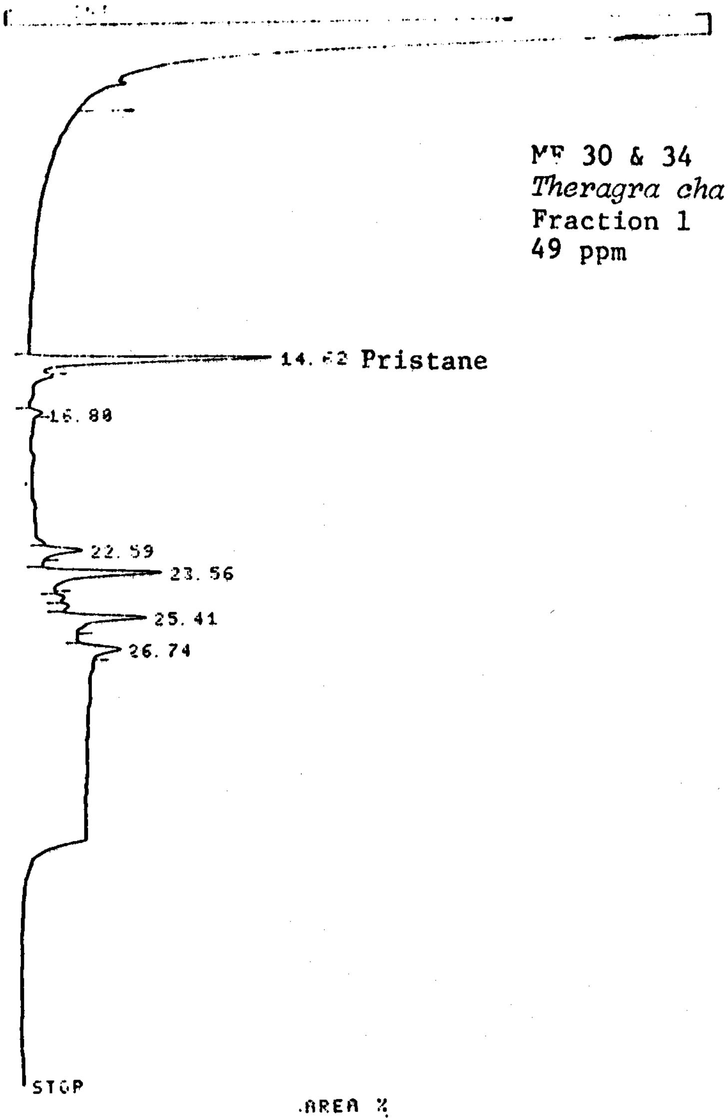
AREA %

	RT	TYPE	AREA		
ME	~~14.78~~		~~38392~~	~~2.246~~	
	15.79	M	14860	.869	6
	16.14	M	8043	.470	7
ME	~~17.11~~	~~M~~	~~47093~~	~~2.293~~	
ME	~~17.41~~	~~M~~	~~79123~~	~~4.63~~	
	18.29	M	20811	1.218	
	18.95	M	67721	3.963	
ME	~~19.50~~	~~M~~	~~122294~~	~~7.145~~	
	20.69	M	4849	.283	8
ME	~~21.23~~	~~M~~	~~51226~~	~~3.3~~	
ME	~~21.70~~	~~M~~	~~165340~~	~~9.706~~	
	22.73	M	9830	.575	2
ME	~~23.17~~	~~M~~	~~35357~~	~~2.070~~	
ME	~~23.75~~	~~M~~	~~140393~~	~~8.251~~	
	24.93	M	197042	11.53	
	25.71	T	3757	.219	9
	26.84		656112	38.39	
	28.75		39236	2.296	

```
HP 3390A
OLY   4.            STOP 45            REJECT    100
MV/M  .20           ATTN       4
```

133

MF 30 & 34
Theragra chalcogramma- Liver
Fraction 1
49 ppm

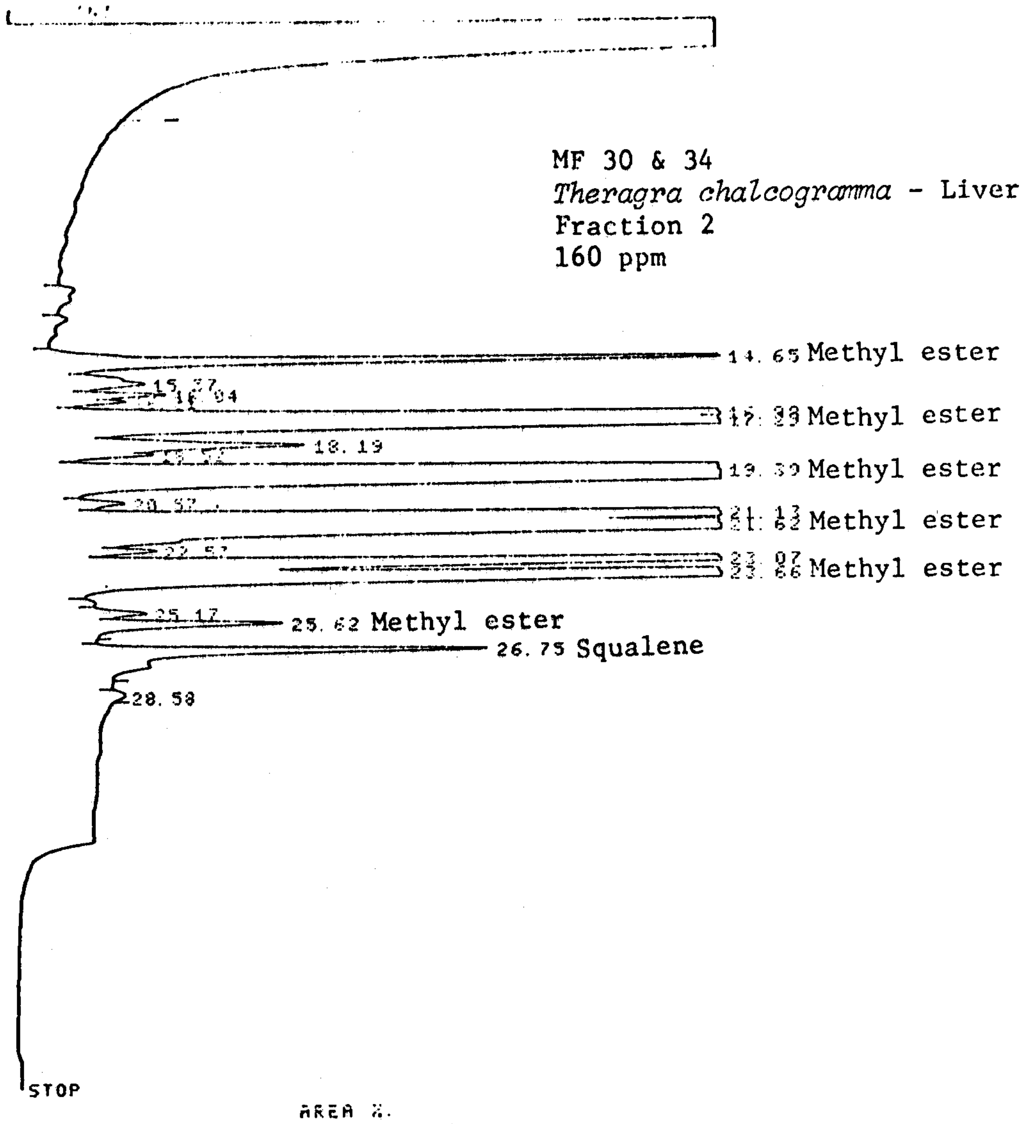


```
                          .AREA %
    RT    TYPE       AREA
  14.62              20334              41.82
S [illegible]
  22.59               3460               7.046
  23.56              11017              24.06
  25.41               8118              16.53
  26.74               4204               8.561

HP 3380A
OLY  4.             STOP 45             REJECT    100
MV/M  .30           ATTN      4
```

052

MF 30 & 34
Theragra chalcogramma - Liver
Fraction 2
160 ppm



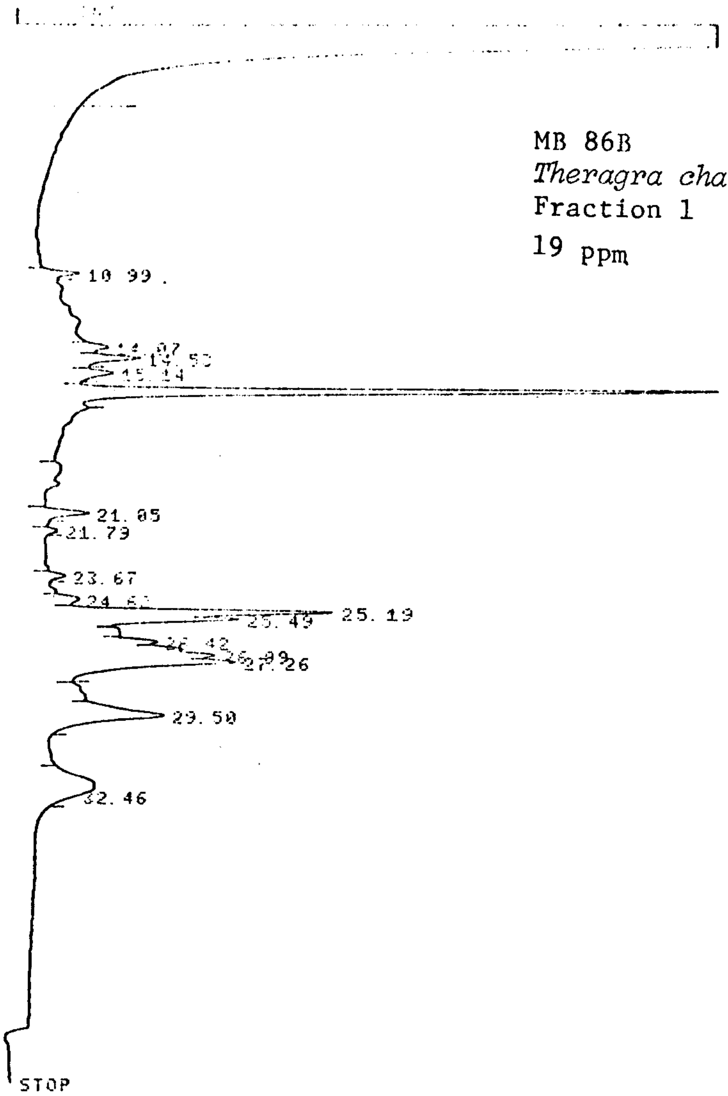
AREA %.

	RT	TYPE	AREA		
ME	~~14.65~~		~~[illegible]~~	~~3.147~~	
	15.57	M	16377	.729	1
	16.04	M	9131	.406	5
	16.31	M	5461	.243	1
ME	~~[illegible]~~	~~M~~	~~[illegible]~~	~~6.614~~	
ME	~~[illegible]~~	~~M~~	~~[illegible]~~	~~11.6~~	
	18.19	M	31382	1.397	
	18.52	M	7273	.323	8
ME	~~[illegible]~~	~~M~~	~~[illegible]~~	~~25.18~~	
	20.57	M	5814	.258	8
ME	~~[illegible]~~	~~M~~	~~[illegible]~~	~~7.251~~	
ME	~~[illegible]~~	~~M~~	~~[illegible]~~	~~21.34~~	
	22.57	M	7622	.339	3
ME	~~[illegible]~~	~~M~~	~~[illegible]~~	~~5.741~~	
ME	~~[illegible]~~	~~M~~	~~[illegible]~~	~~12.5~~	
	25.17		4701	.209	3
ME	~~[illegible]~~	~~M~~	~~[illegible]~~	~~[illegible]~~	
	26.75		45402	2.021	
	28.58		1773	.079	16

```
HP 3380A
DLY  4             SLOP 45           REJECT   100
HV/H  .78          ATTN      4
```

053

MB 86B
Theragra chalcogramma - Liver
Fraction 1
19 ppm

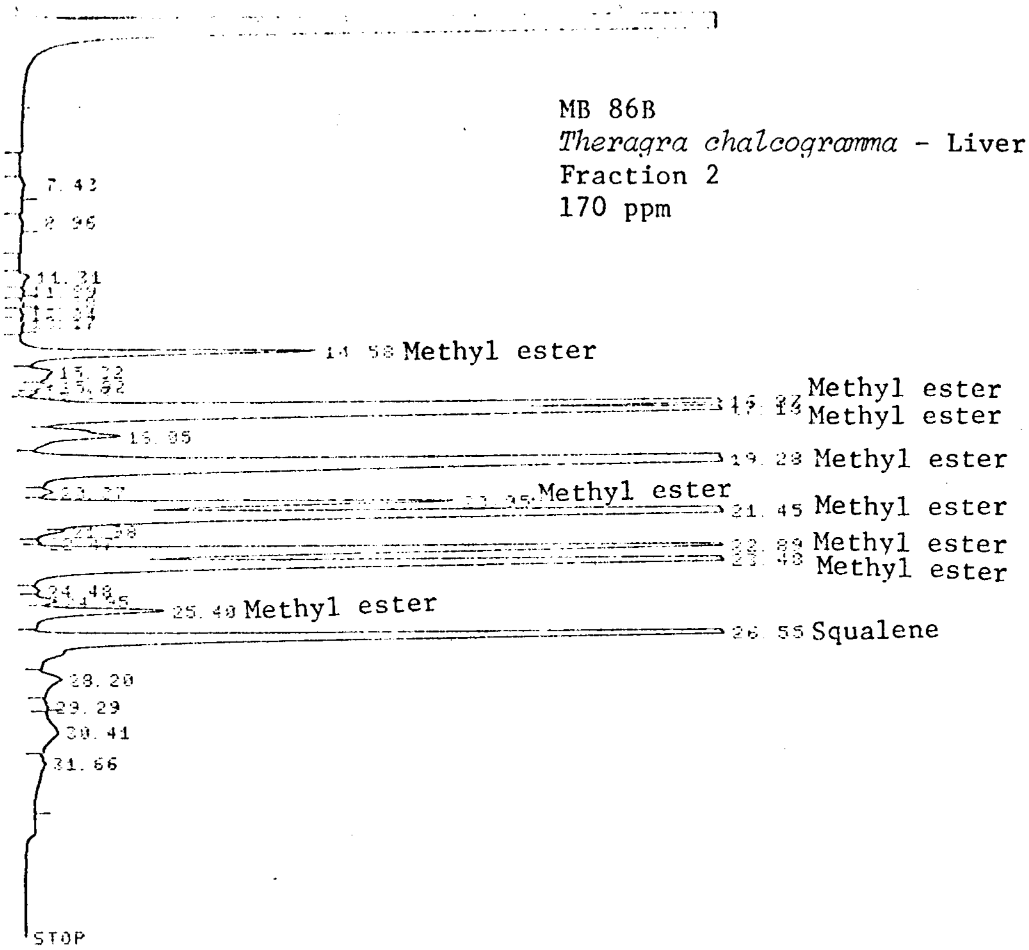


Pristane

```
                              AREA %
    RT     TYPE      AREA
 10.99               1982              1.105
 14.07               3184              1.776
 14.53      M        5149              2.972
 15.14               2611              1.456
 15.91              52416             29.24
 21.05               4005              2.234
 21.79                915               .510  4
 23.67               1367               .762  5
 24.62               1396               .778  6
 25.19      M       21428             11.95
 25.49      M       11152              6.22
 26.42               3323              1.853
 26.99      M       16942              9.45
 27.26      M       17317              9.659
 29.50              18874             10.53
R ~~32.46           [illegible]        [illegible]~~

HP 3390A
DLY  4            STOP 45          REJECT     10
MV/M   30         ATTN      4
```

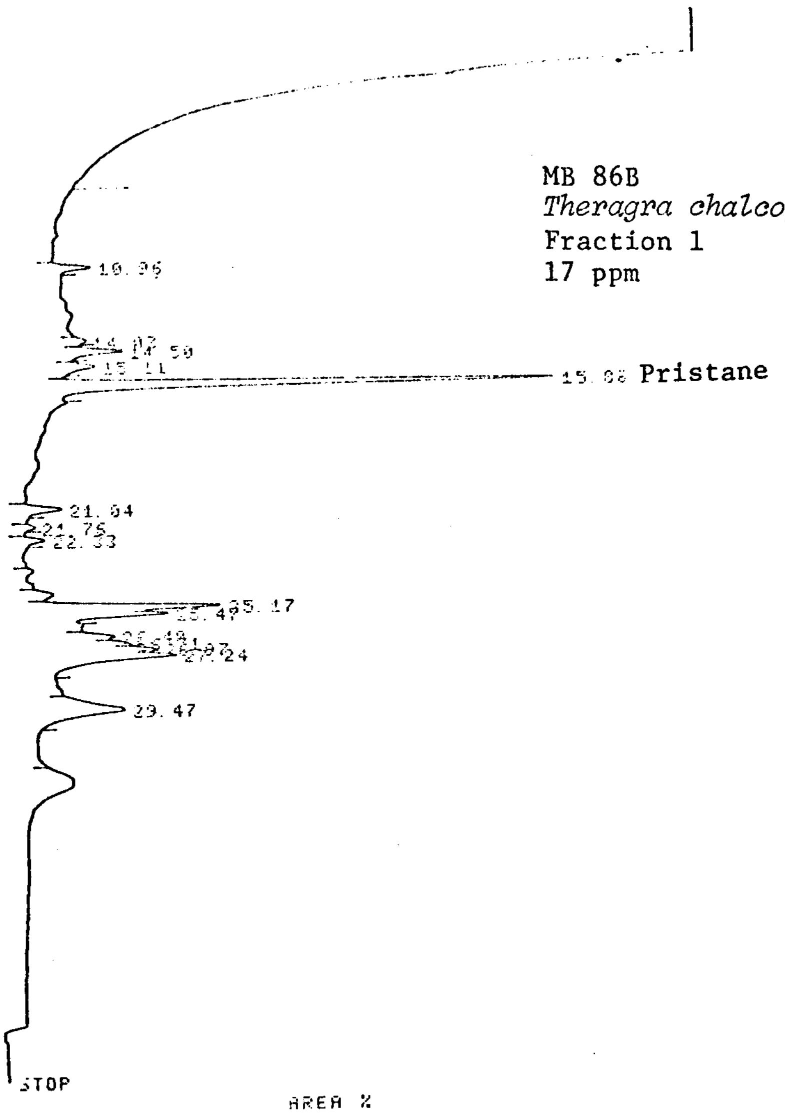
MB 86B
Theragra chalcogramma - Liver
Fraction 2
170 ppm



AREA %

	RT	TYPE	AREA	
R	~~7.43~~		~~7017~~	~~.047 47~~
R	~~8.96~~		~~[illegible]~~	~~[illegible]~~
	11.31		12905	.094 91
	11.39	T	1118	.007 356
	12.38		1192	.007 842
	12.84		1658	.010 91
	13.17	M	3167	.020 84
ME	~~14.58~~		~~[illegible]5129~~	~~2.665~~
	15.32	M	73878	.525 5
	15.92	M	39158	.257 6
	16.13	M	13386	.088 07
ME	~~[illegible]~~	~~M~~	~~[illegible]~~	~~[illegible]~~
ME	~~[illegible]~~	~~M~~	~~[illegible]~~	~~[illegible]~~
ME	~~[illegible]~~	~~M~~	~~[illegible]~~	~~[illegible]~~
ME	~~[illegible]~~	~~M~~	~~[illegible]~~	~~[illegible]~~
	20.27	M	42173	.277 5
ME	~~[illegible]~~	~~M~~	~~[illegible]~~	~~[illegible]~~
ME	~~[illegible]~~	~~M~~	~~[illegible]~~	~~[illegible]~~
	21.90	M	41932	.275 2
	22.47	M	9927	.065 31
ME	~~[illegible]~~	~~M~~	~~[illegible]~~	~~[illegible]~~
ME	~~[illegible]~~		~~[illegible]~~	~~[illegible]~~
	24.48	M	7140	.046 96
	[illegible]	M	34497	.227
ME	~~[illegible]~~	~~M~~	~~[illegible]~~	~~[illegible]~~
	26.55	M	[illegible]22021	9.872
	28.20	M	48803	.321 1
	29.29	M	2137	.014 06
	30.41		62670	.412 4
R	~~31.66~~	~~M~~	~~[illegible]~~	~~[illegible]~~

HP 3390A
DLY 4 STOP 45 REJECT 10
DELAY 30 ATTN 64

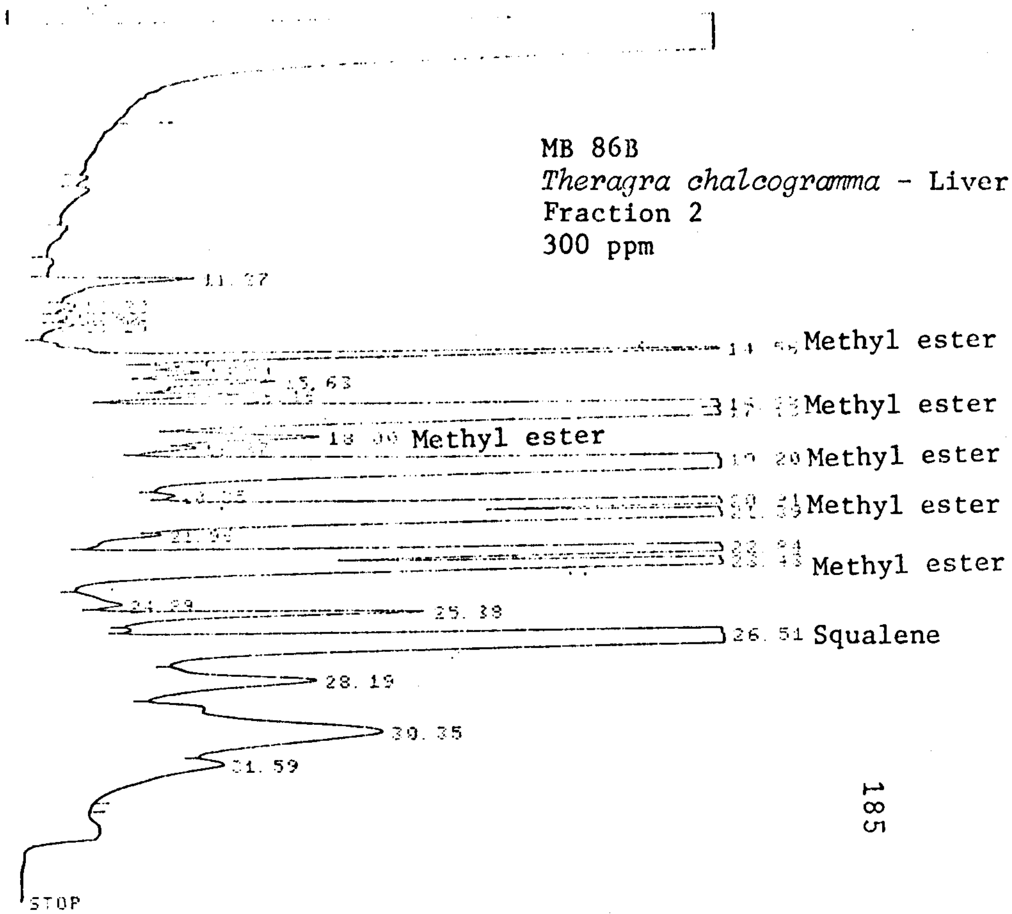


MB 86B
Theragra chalcogramma - Liver
Fraction 1
17 ppm

```
                      AREA %
   RT    TYPE      AREA
                                   2.675
10.96               2794
14.03                832            .796 5
14.50               3698           3.54
15.11               2550           2.441
15 88              40346          38.63
21.04               3324           3.182
21 76                750            .718
22.33               1540           1.462
25.17              14618          13.99
25.47     M         8286           7.933
26.40                878            .840 5
26.71     M          293            .280 5
26.97               2825           2.705
27.24     M         6808           6.518
29 47              14903          14.27

HP 3380A
DLY  4.               STOP 45            REJECT     10
MV/M  .50             ATTN       4
```

182

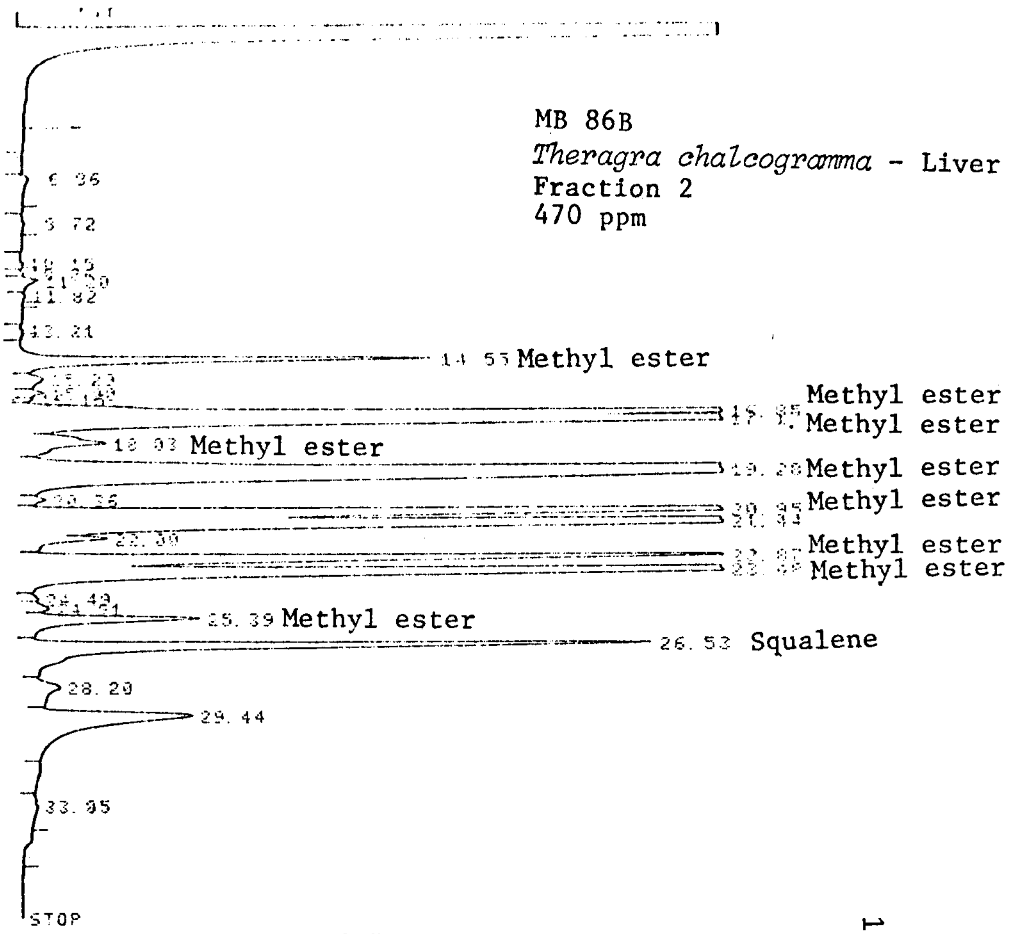


MB 86B
Theragra chalcogramma - Liver
Fraction 2
300 ppm

```
                          AREA %
     RT    TYPE      AREA
   11.27             18011                     .473 1
   12.33    T         1306                     .034 31
   12.[illegible]               787                     .020 67
   13.15              1369                     .035 72
ME [illegible]
   14.55    M         9509                     .249 8
   15.21    M        15385                     .404 1
   15.63    M        30642                     .804 9
   16.13    M        16838                     .442 3
ME [illegible]
ME [illegible]
ME [illegible]
   18.[illegible]   M        13117                     .337 1
ME [illegible]
   20.[illegible]   M        12011                     .316
MF [illegible]
ME [illegible]
   21.95    M        11313                     .297 2
   22.94    M       174990                    4.596
NC [illegible]
   24.89    M         [illegible]                     .107 7
ME [illegible]
   26.51           [illegible]                    39.18
   28.19    T        [illegible]                     .785 1
   30.35    TM       [illegible]                    2.821
R  [illegible]

[illegible]
[illegible]              STOP 45          REJECT   [illegible]
[illegible]              ATTN     4
```

185

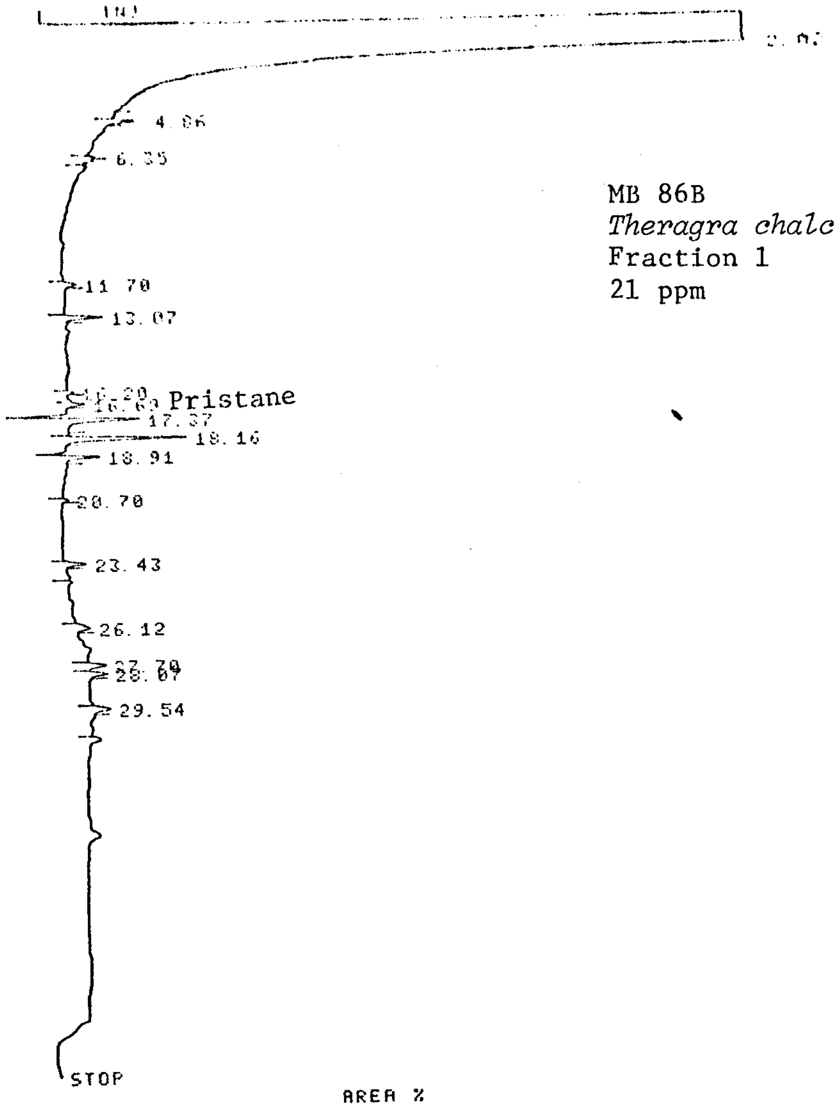


MB 86B
Theragra chalcogramma - Liver
Fraction 2
470 ppm

```
                          AREA %
      RT    TYPE      AREA
R  ~~[illegible]~~                                  
R  ~~[illegible]~~
   10.15             2623               .012 73
   10.86             1015               .004 927
   11 20     M      29143               .141 5
   11.82     T       2113               .010 26
   13 21             1098               .005 33
ME ~~[illegible]~~
   15.29     M      59304               .287 9
   15.90     M      32396               .157 3
   16 15     M      11762               .057 1
ME ~~[illegible]~~
ME ~~[illegible]~~
ME ~~[illegible]~~
ME ~~[illegible]~~
   20 36     M      43814               .212 7
ME ~~[illegible]~~
ME ~~[illegible]~~
   22.00     M     156319               .759 9
ME ~~[illegible]~~
ME ~~[illegible]~~
   24 49     M      29786               .144 6
   24 91     M      59841               .290 5
   25 39     M     342109              1 662
ME ~~[illegible]~~
   28 20     M     192531               .934 8
   29 44     M    1005601              4 881
R  ~~[illegible]~~

HP 3380A
DLY  4.          STOP 45           REJECT     10
HVPM   30        ATTN     64
```

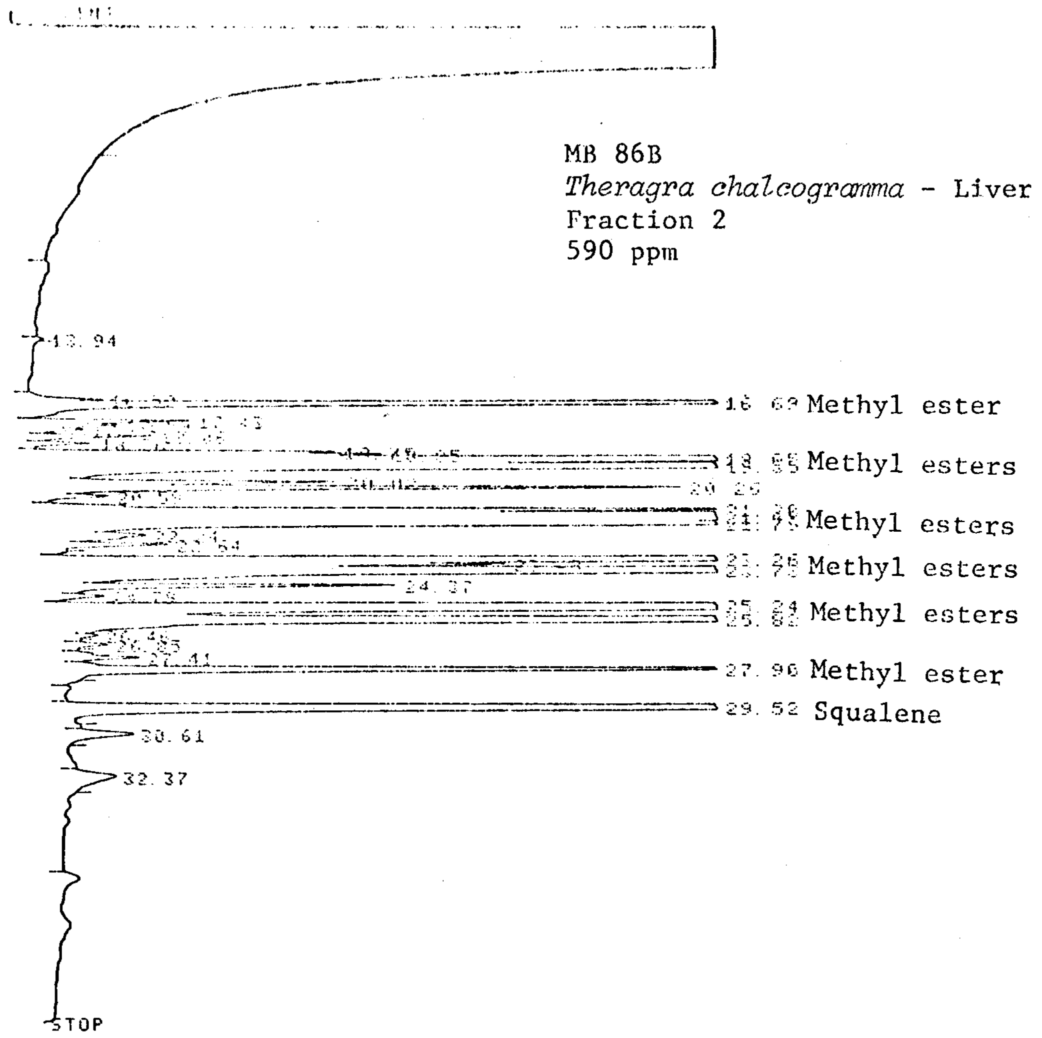
MB 86B
Theragra chalcogramma - Liver
Fraction 1
21 ppm



AREA %

RT	TYPE	AREA		
~~2.02~~	~~T~~	~~3718~~	~~13.32~~	
~~4.86~~		~~1033~~	~~3.7~~	
~~6.35~~		~~186~~	~~.666~~	~~3~~
11.70		645	2.311	
13.07		1656	5.932	
16.20		274	.981	5
16.69		580	2.078	
S ~~17.37~~		~~7100~~	~~25.43~~	
18.16		5294	18.96	
S ~~18.91~~		~~1940~~	~~6.949~~	
20.70		264	.945	7
23.43		1115	3.994	
26.12		1028	3.682	
27.70		1050	3.761	
28.07	M	940	3.367	
29.54		1093	3.915	

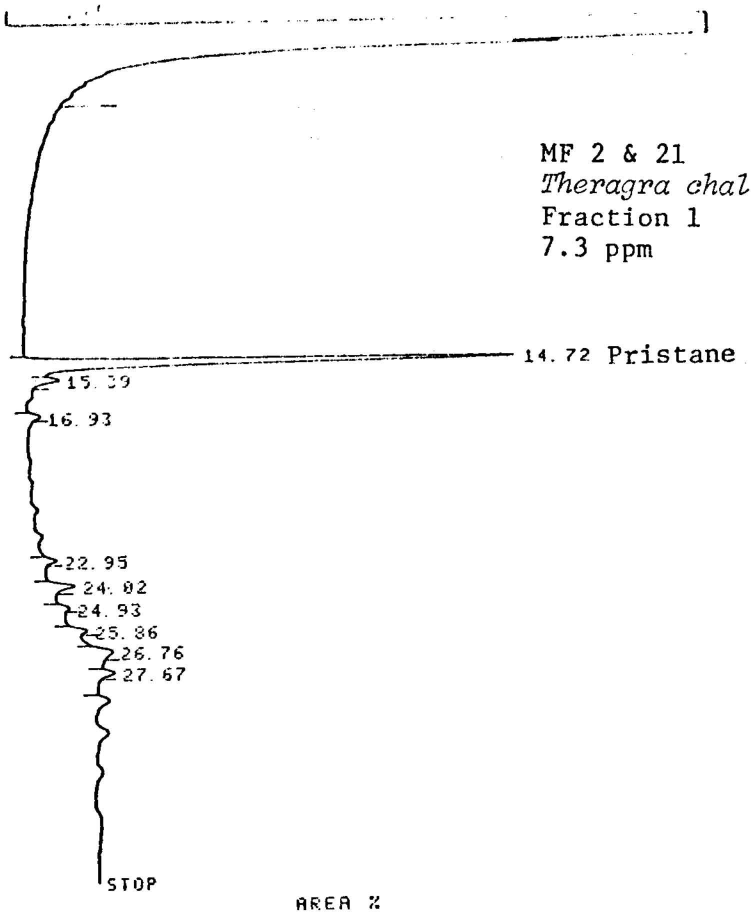
```
HP 3380A
DLY  2.            STOP 45          REJECT   100
MV/M  .70          ATTN      4
```



MB 86B
Theragra chalcogramma - Liver
Fraction 2
590 ppm

```
                         AREA %
    RT    TYPE      AREA
  13.94              293               .007 79
  16.52             3239               .086 12
ME~~16.69   M      99365              2.656~~
 S~~17.43   M       6873               .182 7~~
  17.59     M       4146               .110 2
  17.78     M       2672               .071 04
  18.06     M       5675               .150 9
  18.36     M       2616               .069 55
  18.75     M      10151               .269 9
  19.85     M      12514               .333 5
ME~~19.55   M     [illegible]         7.415~~
ME~~19.65   M     [illegible]         10.29~~
  20.02     M      15705               .417 6
  20.26     M      34122               .907 2
  20.59     M       2320               .101 6
ME~~21.20   M     [illegible]         [illegible]~~
ME~~21.49   M     [illegible]         [illegible]~~
ME~~21.79   M     [illegible]         [illegible]~~
  22.24     M       8767               .232 1
  22.64     M       5760               .153 1
ME~~23.26         [illegible]         [illegible]~~
  23.48     M      17034               .452 9
  23.73     M     [illegible]        15.66
  24.37     M     [illegible]          487 9
  24.79     M       2763               073 45
ME~~25.24   M     [illegible]         [illegible]~~
ME~~25.82   M     [illegible]         [illegible]~~
  26.46     M     [illegible]         [illegible] 1
  26.85           [illegible]         [illegible]
  27.41           [illegible]         [illegible]
ME~~27.90   M     [illegible]         [illegible]~~
  29.52           [illegible]         [illegible]
  30.61           [illegible]         [illegible]
  32.37           [illegible]         [illegible] 1
```

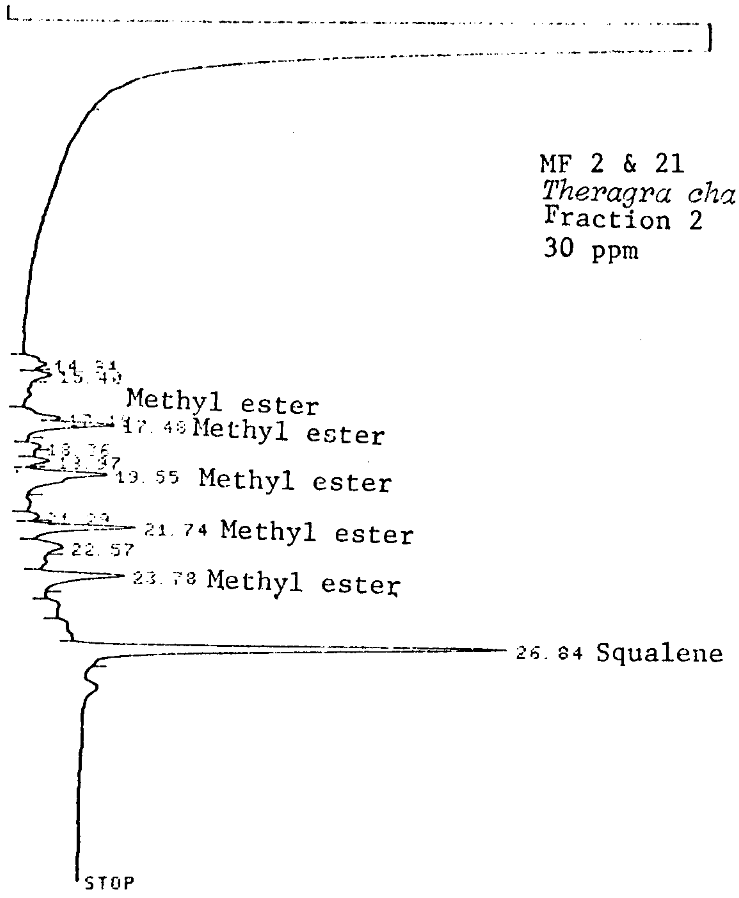
MF 2 & 21
Theragra chaleogramma - Skin
Fraction 1
7.3 ppm



```
                         AREA %
    RT    TYPE      AREA
  14.72             41755              76.38
S [illegible]
S [illegible]
C [illegible]
C [illegible]
C [illegible]
C [illegible]
  [illegible]
C [illegible]

HP 3380A
DLY  4.           STOP 45          REJECT   100
MV/M  .30         ATTN     4
```

MF 2 & 21
Theragra chaleogramma - Skin
Fraction 2
30 ppm

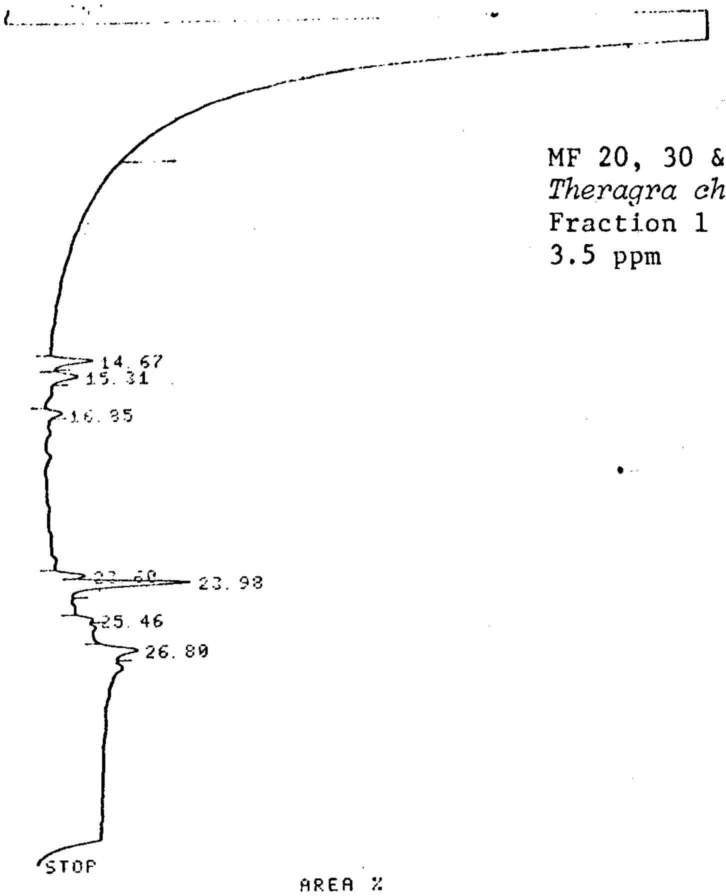


```
                          AREA %
     RT    TYPE      AREA
  14 94              1683              1. 873
S 15 40              [illegible]       [illegible]
ME 17 15             7317              7. 91
ME 17 48             [illegible]       [illegible]
  18. 36              720               . 801  4
  18. 97             1722              1. 471
ME 19 55             [illegible]       12. 15
  21. 23              635               . 706  7
ME 21 74             [illegible]       13. 44
  22 57     M        2717              3. 024
MC 23 78             [illegible]       [illegible]
*26. 84              39266-5291        43. 81

HP 3380A
DLY   4          STOP 45          REJECT   100
MV/M   30        ATTN      4
```

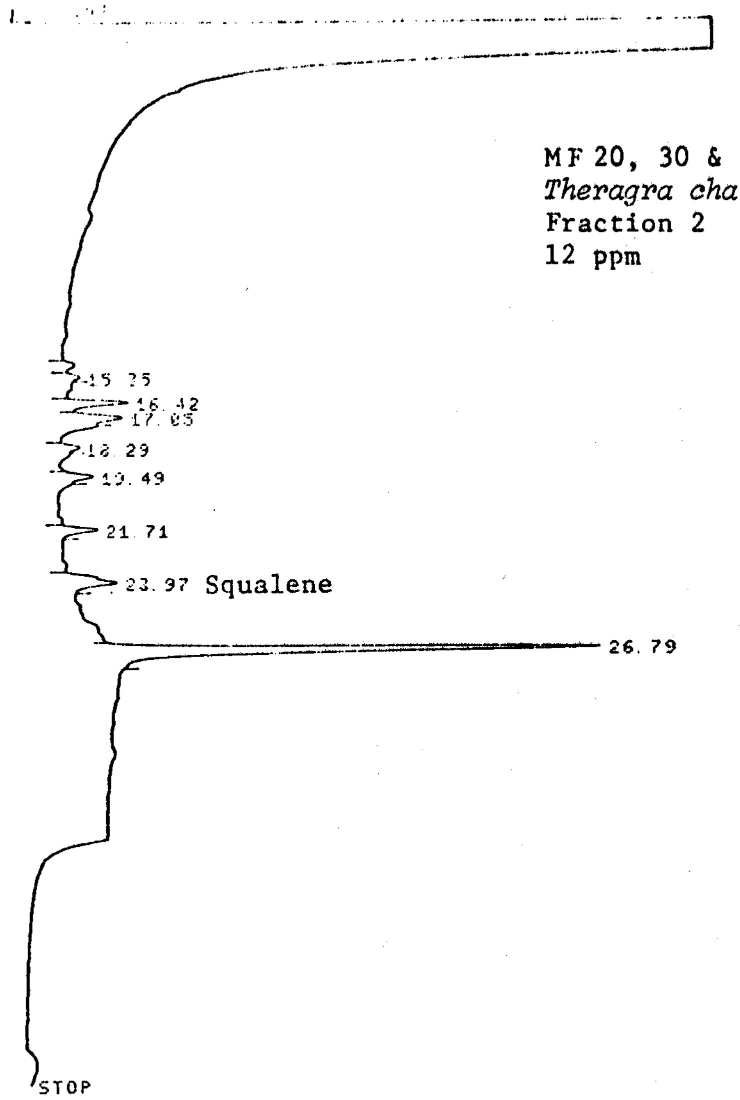
MF 20, 30 & 34
Theragra chalcogramma - Skin
Fraction 1
3.5 ppm

039



```
                          AREA %
     RT    TYPE       AREA
  14.67               3537                13.66
S ~~15.31               2510                 9.696~~
S ~~16.85               [illegible]                 5.115~~
  23.60               1983                 7.661
  23.98     M        12383                47.84
  25.46                604                 2.333
  26.80               3545                13.69

HP 3380A
DLY  4.            STOP 45           REJECT   100
MV/M  .30          ATTN
```



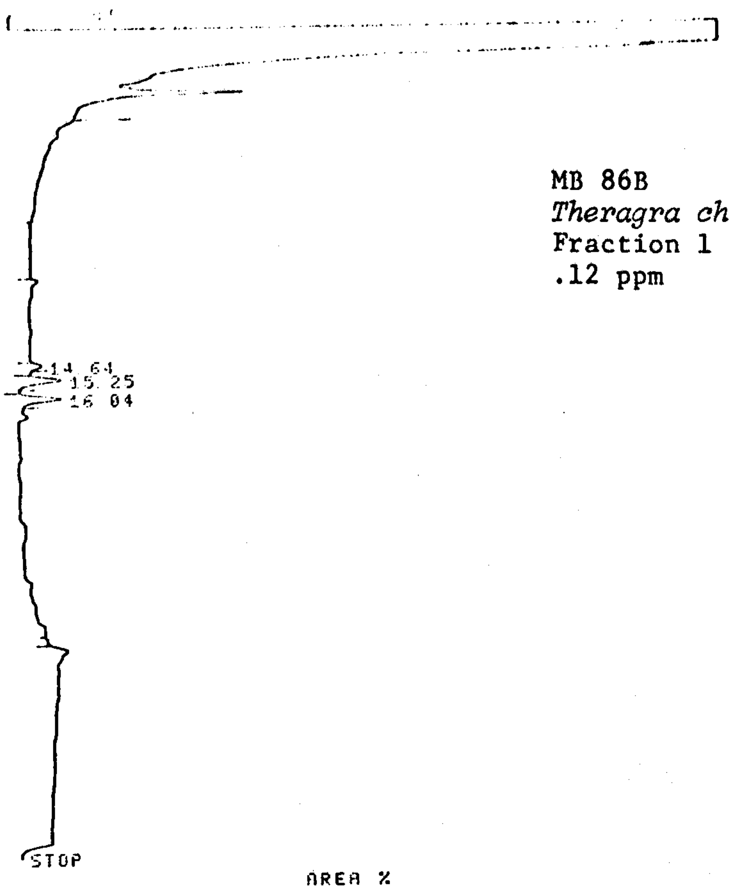
MF 20, 30 & 34
Theragra chalcogramma - Skin
Fraction 2
12 ppm

040

```
                              AREA %
    RT     TYPE        AREA
~~15.25                 889                1.276~~
  16.42                4563                6.551
  17.05     M          3247                4.662
  18.29                1251                1.796
  19.49                2609                3.746
  21.71                3353                4.814
 *23.97                6602-2410           9.478
  26.79               47140               67.68

HP 3380A
CLY  4.            STOP 45            REJECT    100
MV/M  .30          ATTN      4
```

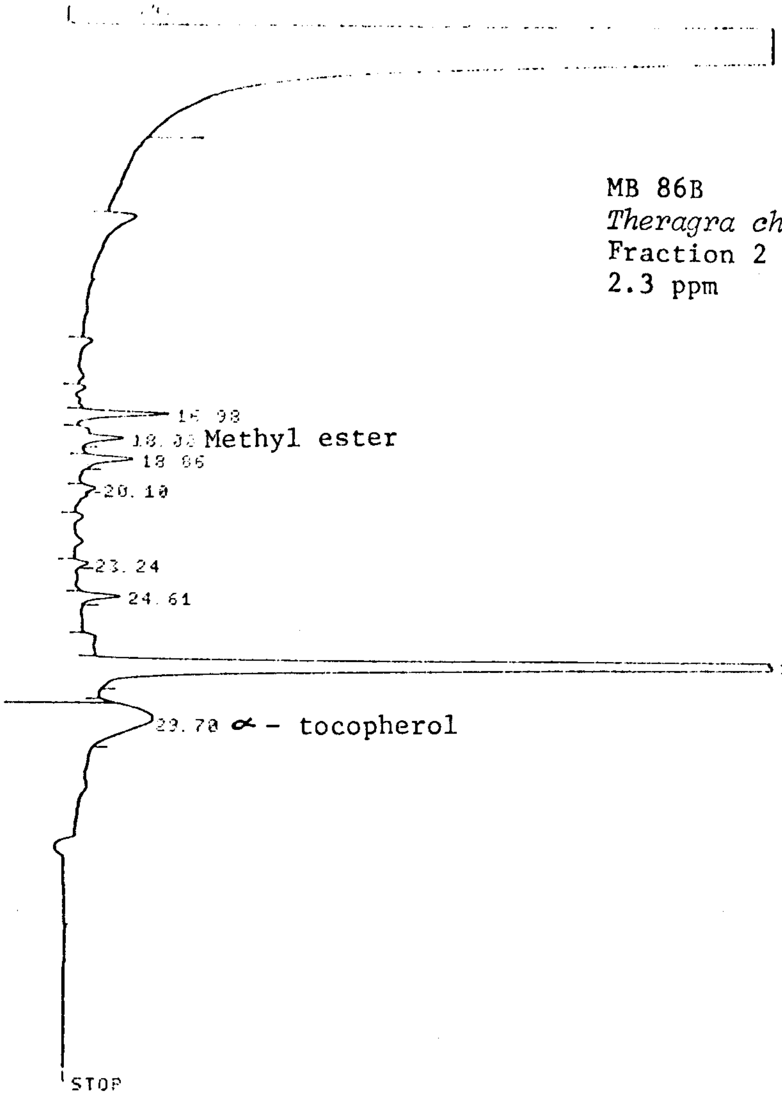
MB 86B
Theragra chalcogramma - Skin/Flesh
Fraction 1
.12 ppm



```
                      AREA %
   RT   TYPE      AREA
 14.64              983          12.53
 15.25             3324          42.38
 16.04             3537          45.09


HP 3380A
DLY  4.         STOP 45          REJECT    10
MV/M  :30       ATTN      4
```

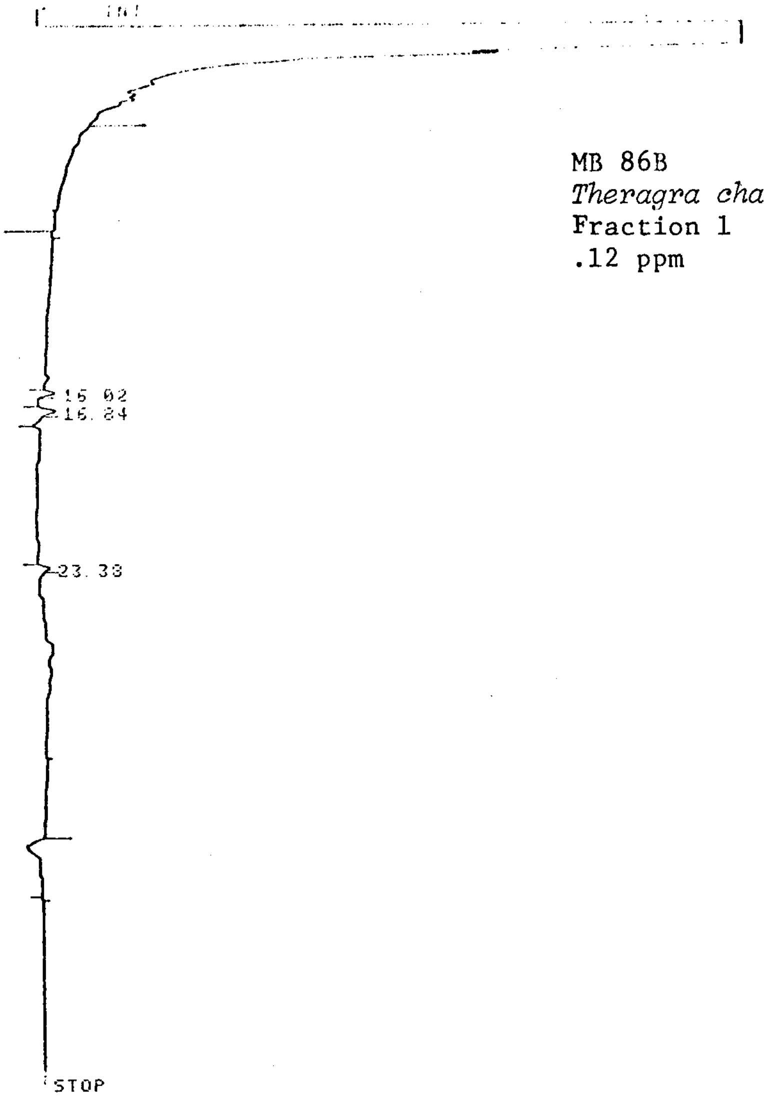
MB 86B
Theragra chalcogramma - Skin/Flesh
Fraction 2
2.3 ppm



```
                              AREA %
      RT    TYPE      AREA
   15.93              7117             3.316
ME ~~[illegible]  [illegible]  [illegible]  [illegible]~~
   18.86              4503             2.098
   20.10              1056              .432  1
   23.24              1004              .467  9
   24.61              3815             1.778
   27.49            170913            79.6
A  ~~[illegible]  [illegible]  [illegible]~~

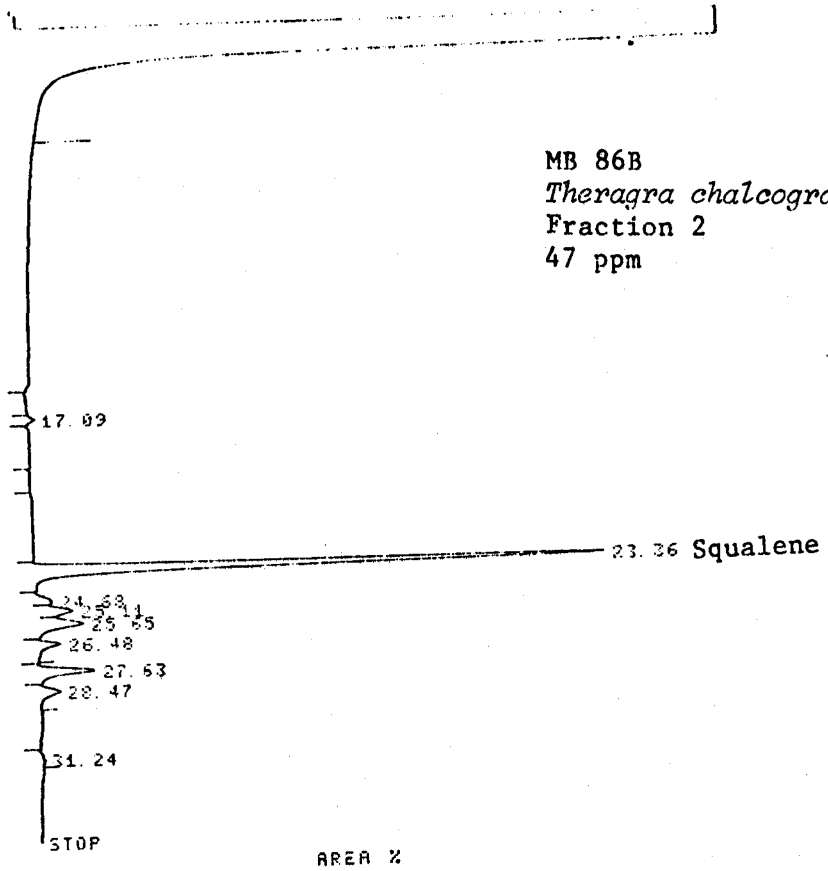
HP 3380A
DLY   4           STOP 45          REJECT    10
MV/M  10          ATTN      4
```

MB 86B
Theragra chalcogramma - Skin/Flesh
Fraction 1
.12 ppm



```
                      AREA %
   RT    TYPE      AREA
 16.02             1030           34.53
 16.84             1196           40.09
 23.38              757           25.38

HP 3380A
DLY   4           STOP 45           REJECT     10
MV/M  .30         ATTN     4
```



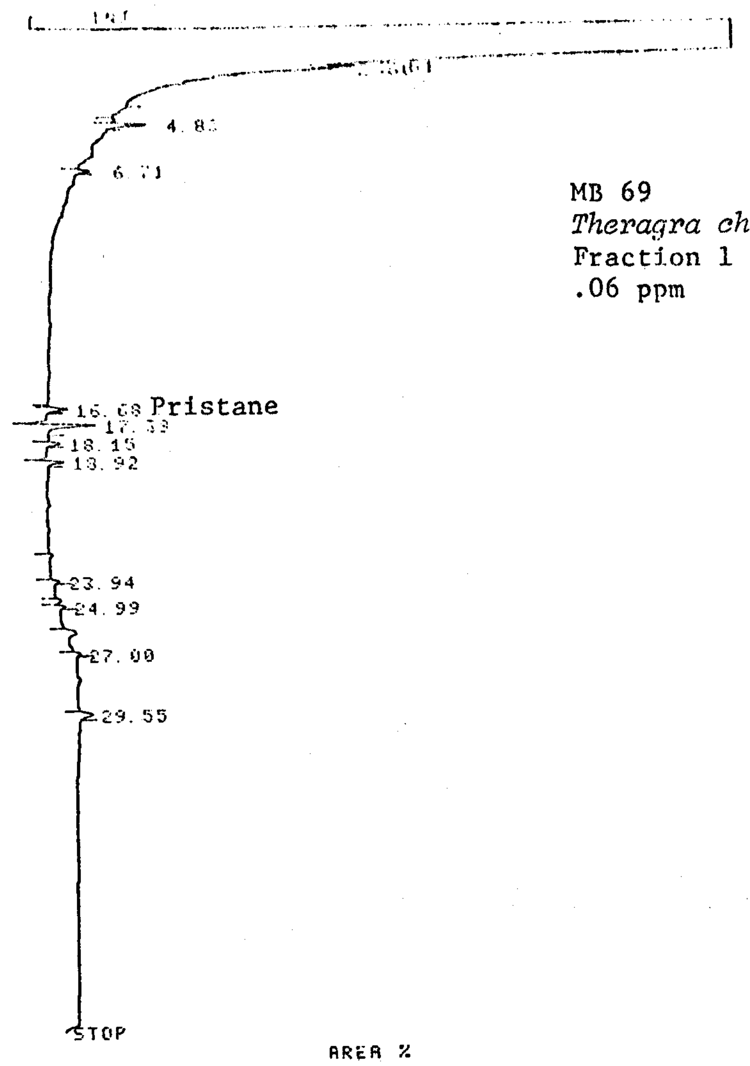
MB 86B
Theragra chalcogramma - Skin/Flesh
Fraction 2
47 ppm

```
                         AREA %

    RT    TYPE       AREA
                      3378             .672 4
 17. 09              373650         64. 79
 23. 36               16237           2. 815
 24. 68     M          37918           6. 574
 25. 11     M          54191           9. 396
 25. 65     M          19534           3. 387
 26. 48     M          47371           8. 213
 27. 63                20587           3. 569
 28. 47     M
R ~~31. 24              3387            .597 3~~


HP 3380A                                  REJECT     10
DLY  4.               STOP 45
MV/M  .30             ATTN    32
```

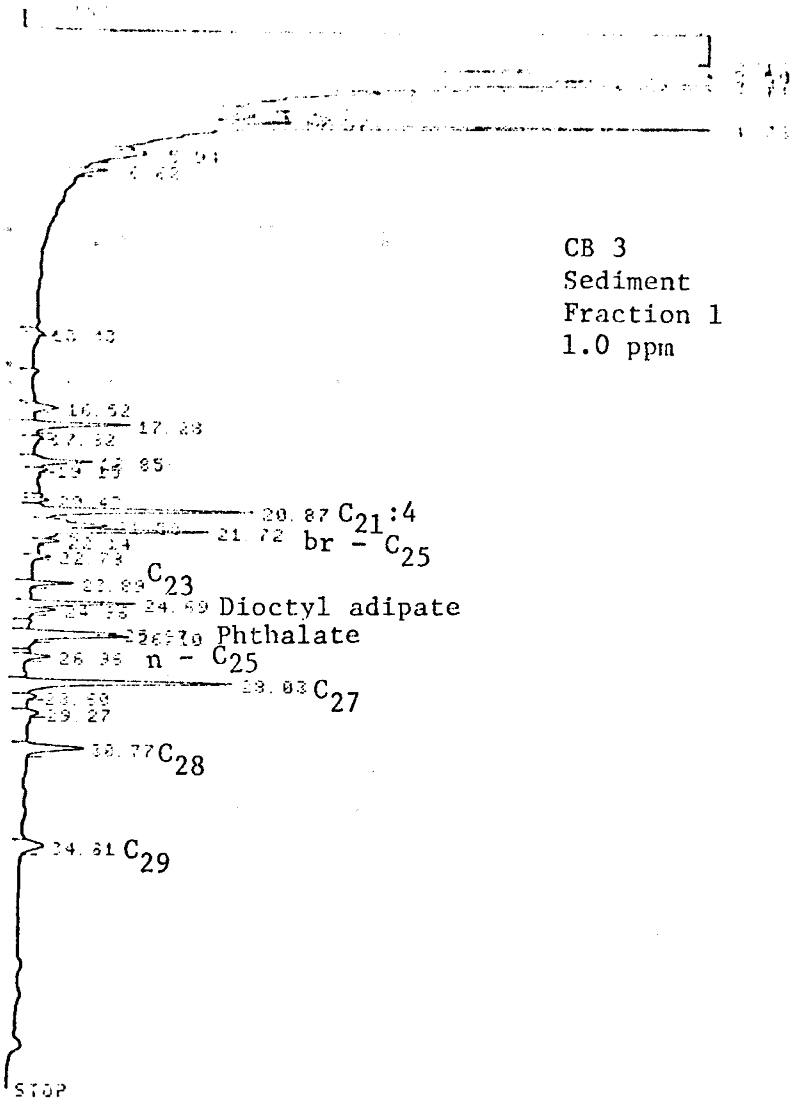
MB 69
Theragra chalcogramma - Skin/Flesh
Fraction 1
.06 ppm



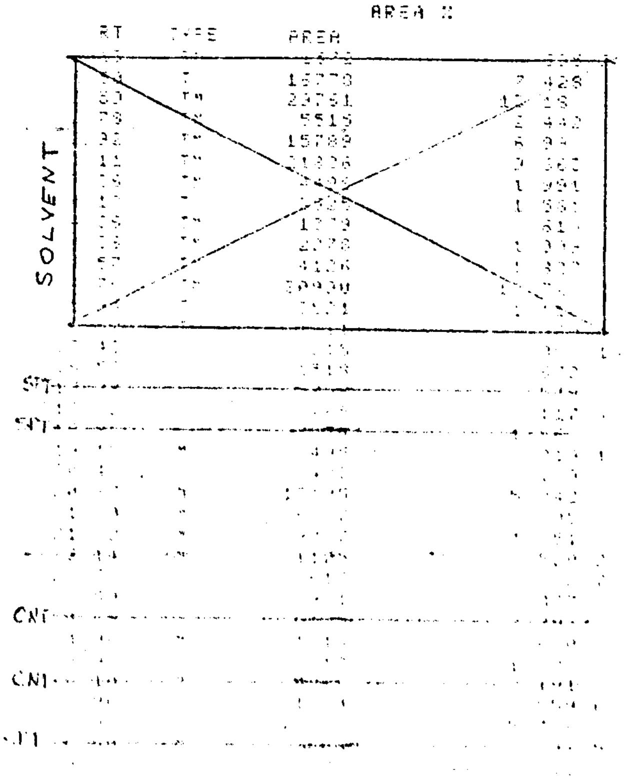
AREA %

RT	TYPE	AREA	
~~2.51~~	~~T~~	~~1352~~	~~10.71~~
~~2.60~~	~~TM~~	~~1802~~	~~14.28~~
~~4.83~~		~~1567~~	~~12.41~~
~~6.71~~		~~593~~	~~4.697~~
16.68		685	5.426
S ~~17.39~~		~~3337~~	~~26.43~~
18.15		610	4.832
S ~~18.92~~		~~912~~	~~7.224~~
B ~~23.94~~		~~282~~	2.234
B 24.99		~~316~~	~~2.503~~
B ~~27.00~~		~~281~~	2.226
29.55		886	7.018

```
HP 3380A
DLY  2.           STOP 45          REJECT   100
MV/M  .30         ATTN     4
```

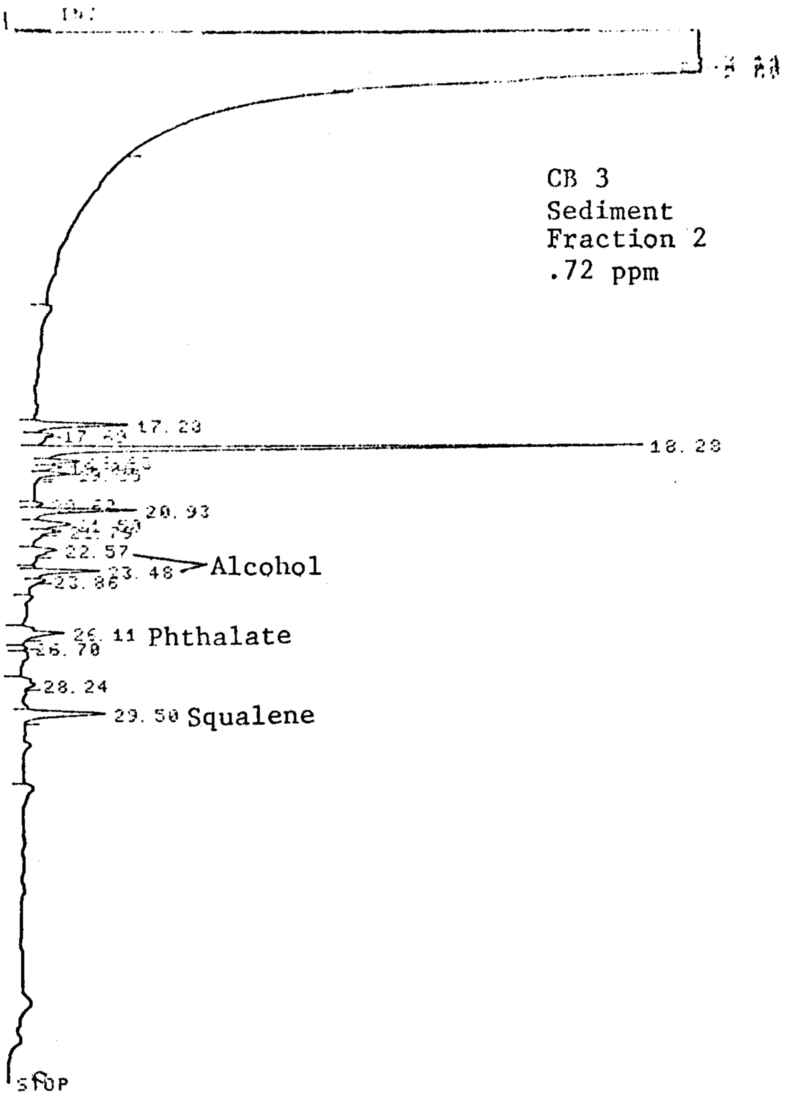


CB 3
Sediment
Fraction 1
1.0 ppm



AREA %

RT	TYPE	AREA	AREA %
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	7.428
[illegible]	[illegible]	23751	[illegible]
[illegible]	[illegible]	5515	2.442
[illegible]	[illegible]	15789	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]



CB 3
Sediment
Fraction 2
.72 ppm

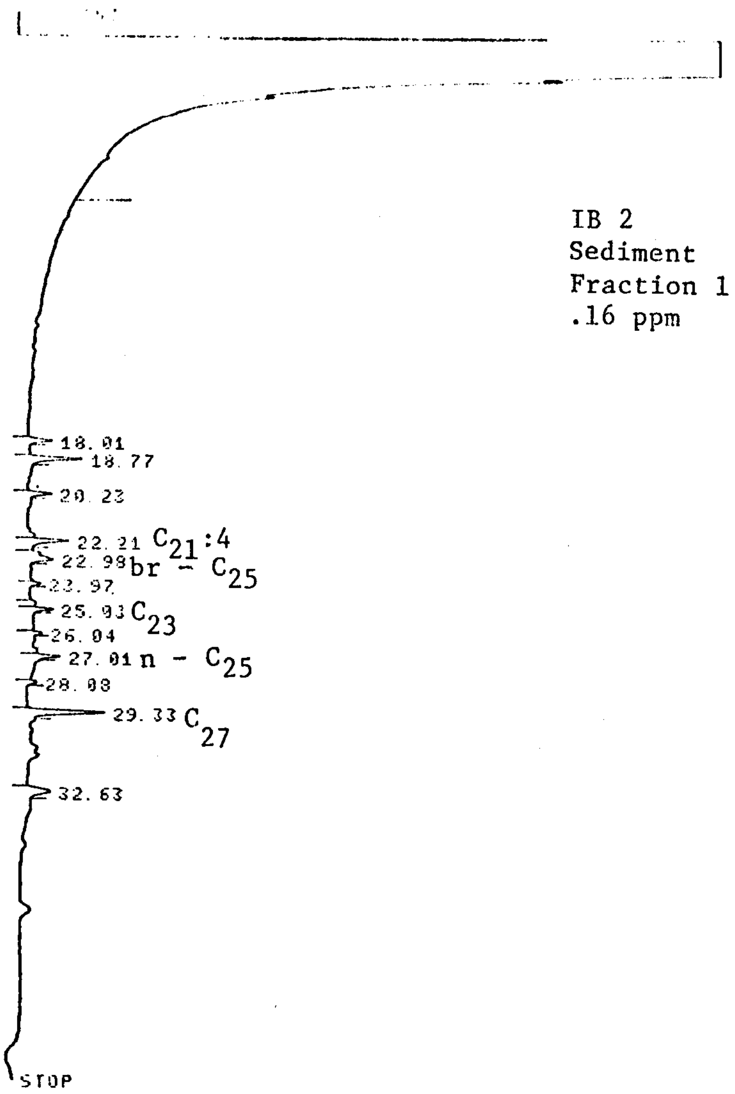
Alcohol

Phthalate

Squalene

```
                                       AREA %
     RT     TYPE       AREA
SOL ~~[illegible]                                     7.122~~
SOL ~~[illegible]                                     [illegible]~~
SOL ~~[illegible]                                     [illegible]~~
SOL ~~[illegible]                                     1.342~~
SFT ~~[illegible]                                     [illegible]~~
     17.69   M          513                            .594 5
     18.28            32225                        37.1
SFT ~~[illegible]                                     [illegible]~~
     19.06   TM         937                           1.075
     19.35   TM        1619                           1.858
SFT ~~[illegible]                                     .521~~ 1
     20.93   M         5515                           6.[illegible]
     21.50   M         2372                           2.723
     21.79   M         1164                           1.336
A   ~~[illegible]~~
A   ~~[illegible]~~
     [illegible]   M    614                            .704 7
CNT ~~[illegible]~~
     [illegible]                                       .258 2
SFT ~~[illegible]~~
CNT ~~[illegible]~~

AF [illegible]
DLY 2             [illegible]                REJECT  100
MVTH .20          ATTN      4
```



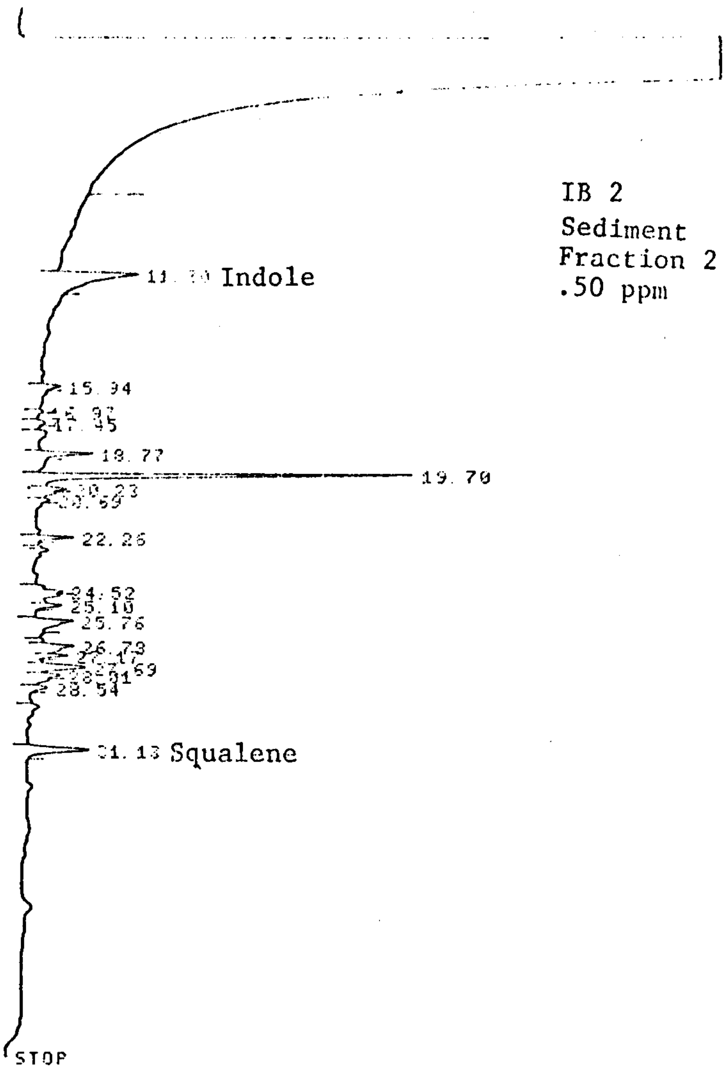
IB 2
Sediment
Fraction 1
.16 ppm

AREA %

	RT	TYPE	AREA	
	18.01		1276	6.614
SPT	~~18.77~~		~~2814~~	~~14.59~~
SPT	~~20.23~~		~~1181~~	~~6.122~~
	22.21		1930	10.
	22.98		2153	11.16
	23.97		707	3.665
	25.93		823	4.266
	26.04		406	2.105
	27.01		1023	5.303
	28.08		480	2.488
	29.33		4393	22.77
	32.63		2105	10.91

```
HP 3390A
DLY  9              STOP 45          REJECT    100
MV/M    30          ATTN       4
```

043

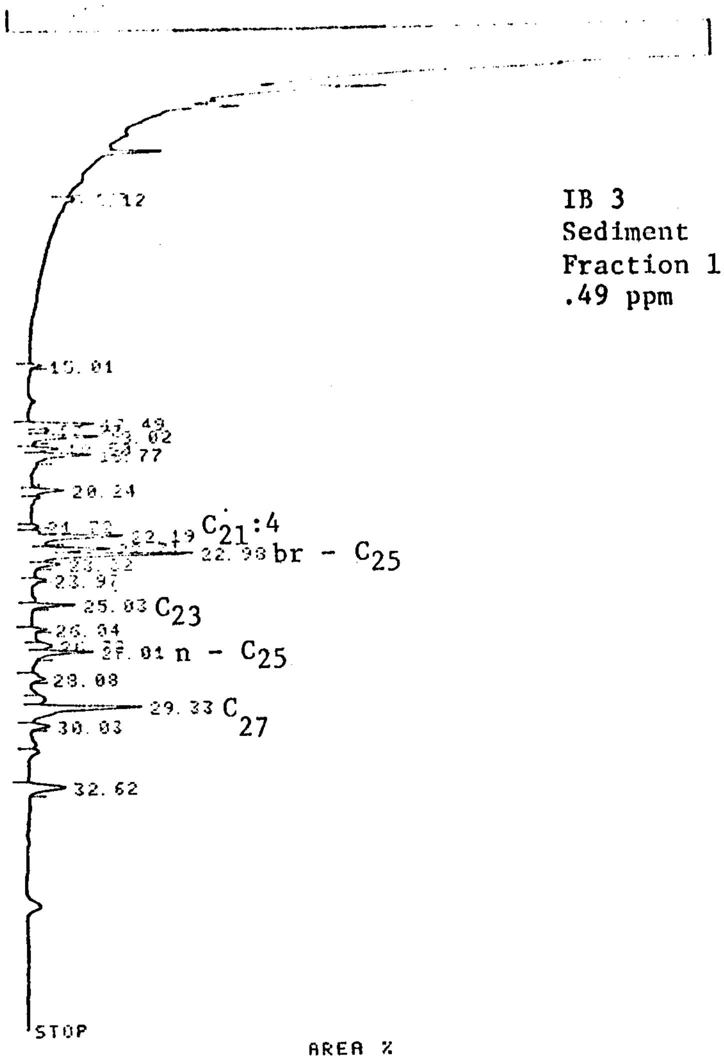


IB 2
Sediment
Fraction 2
.50 ppm

```
                                AREA %
       RT    TYPE      AREA
     11.30            10546              20.28
     15.94              816              1.559
     16.97              190               .365 4
     17.45              473               .919 3
SPT  18.77             2571              [illegible]
     19.70            17134            . 32.95
SPT  20.23    H         652              1.254
     20.69              342               .657 7
     22.25             1672              3.215
     24.52              383               .736 6
     25.10              960              1.846
     25.76             2391              4.598
     26.73             2611              5.022
 €   27.17    H        [illegible]       [illegible]
     27.69             3450              6.625
     28.01    H         669              1.287
     28.54              843              1.621
   · 31.13             4900              9.424

   HP 3390A
   [illegible]        STOP 45            REJECT    100
   [illegible]        ATTN      4
```

045



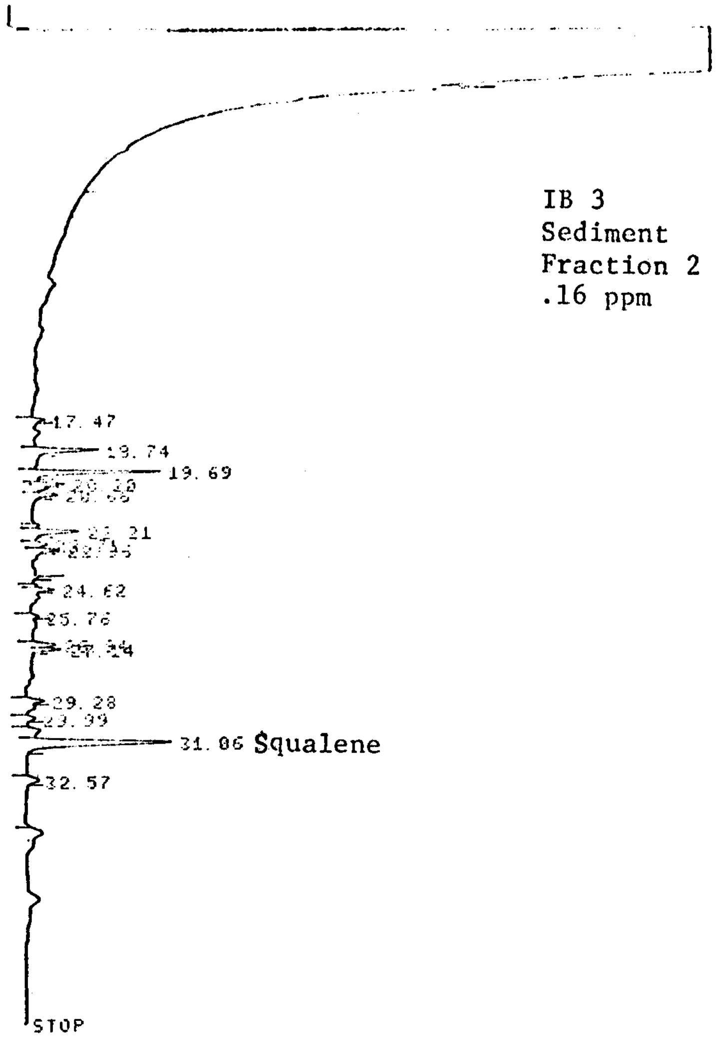
IB 3
Sediment
Fraction 1
.49 ppm

```
                       AREA %
    RT     TYPE      AREA
   8.12               432            .745 2
  15.01               629           1.166
  17.49              3256           6.036
  17.73     M         995           1.844
  18.02     M        4035           7.48
  18.50              1226           2.273
SPT 19.77             [illegible]   [illegible]
SPT 20.24             [illegible]   [illegible]
  21.72               264            .489 4
  22.19              4671           8.659
  22.71              3605           6.682
  22.98     M        7931          14.70
  23.32     M        1307           2.423
  23.97               490            .908 3
  25.03              1761           3.264
  26.04               593           1.099
  26.72              1343           2.489
  27.01     M        3132           5.806
  28.08              1213           2.249
  29.33              7490          13.88
  30.03     M        1194           2.213
  32.62              3455           6.404

[illegible]                                REJECT   100
[illegible]             STOP 45
[illegible]             ATTN      4
```

C47

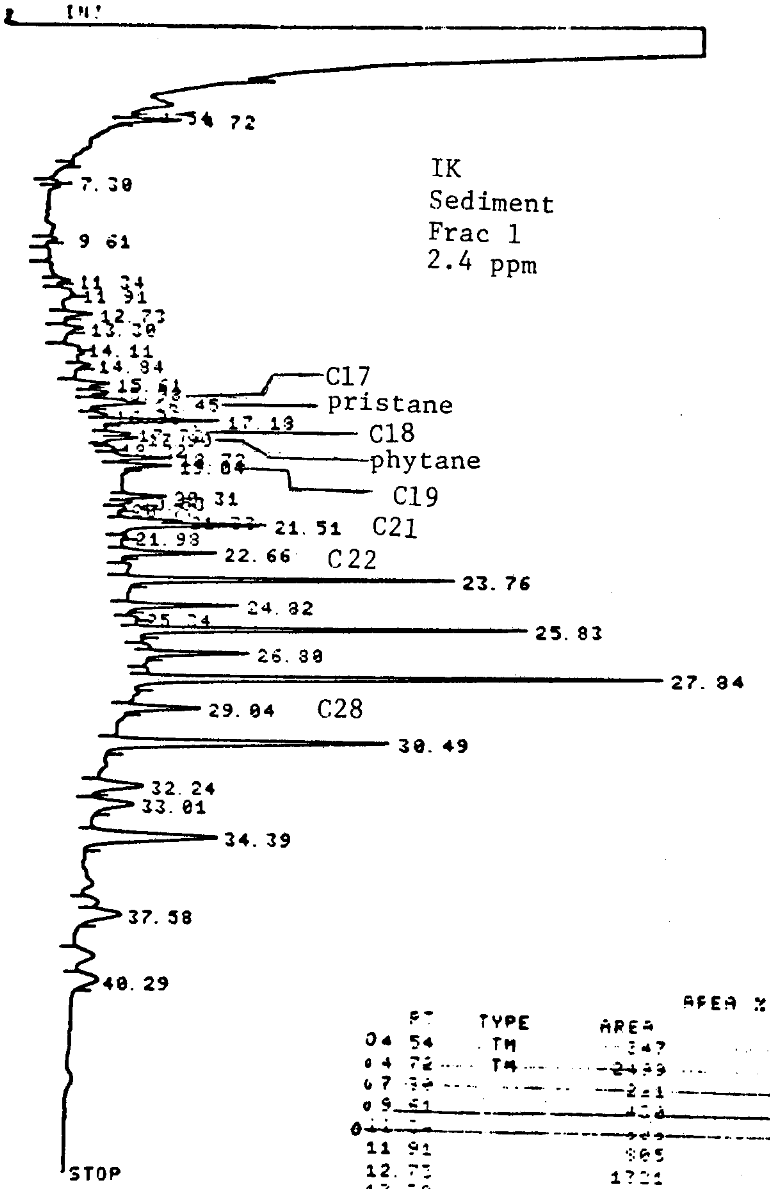
IB 3
Sediment
Fraction 2
.16 ppm



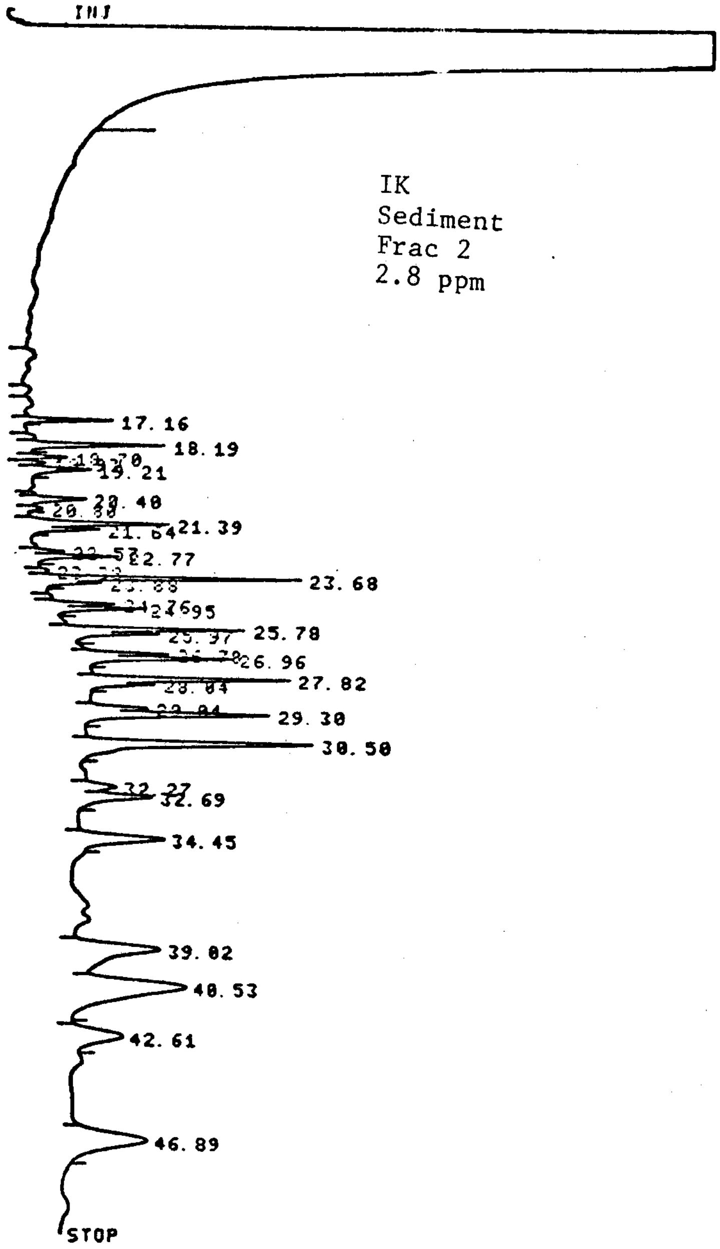
Squalene

```
                              AREA %
      RT    TYPE      AREA
  17 47                555             1.661
SPI~~[illegible]       [illegible]     [illegible]~~
  19.69               5076            13.18
SPI~~[illegible]       [illegible]     [illegible]~~
  20.65               1048             3.136
  22.21               2400             7.182
  22 71                644             1.927
  22 95                967             2.894
  24.62                759             2.271
  25  6                392             1.173
  26 94               1127             3.371
C ~~[illegible]        [illegible]     [illegible]~~
  29.28                789             2.358
  29 99                604             1.807
C ~~[illegible]        [illegible]     [illegible]~~
  32.57               1107             3.312


HP 3390A
DIV .6               STOP 45               REJECT   100
MV.M   70            ATTN      4
```



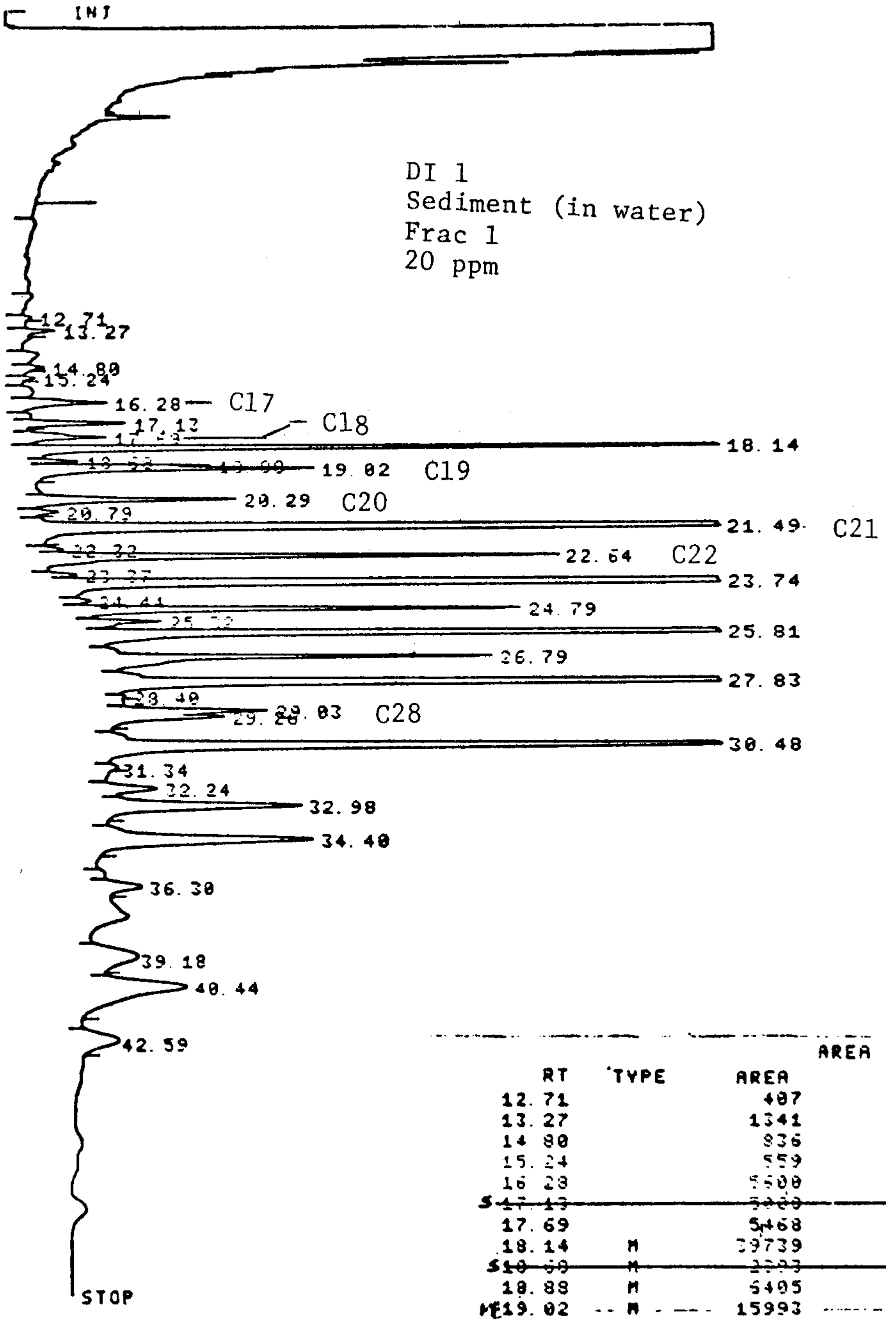
			AREA %
RT	TYPE	AREA	
04 54	TM	347	.192 4
04 72	TM	2499	1.386
~~07 30~~		~~221~~	~~.122 5~~
~~09 61~~		~~428~~	~~.238 4~~
0 ~~11 34~~		~~[illegible]~~	~~[illegible]~~
11 91		805	.446 3
12.73		1302	.722 4
13 30		1107	.613 8
14 11		456	.258 4
14.84		535	.296 6
15 61		1247	.691 4
15 98		746	.413 6
16.45		4133	2.292
16.96		695	.385 3
S ~~17.18~~	~~M~~	~~5315~~	~~2.947~~
17.72		1090	.604 4
17.90	M	1640	.909 3
18.32		207	.114 8
S ~~18.72~~		~~2739~~	~~1.519~~
19 04	M	2319	1.286
20.31		2185	1.211
S ~~20.53~~	~~M~~	~~597~~	~~.331~~
20 77	M	420	.232 9
21.33		3512	1.947
21.51	M	8055	4.456
21.98	M	371	.205 7
22.66		4703	2.608
23.76		15234	8.447
24.82		5771	3.2
25.34		297	.164 7
25.83		17989	9.974
26.80		4938	2.738
27.84		27625	15.32
29 04		4724	2.619
30.49		21644	12.
32.24		4821	2.673
33 01		4617	2.56
34 39		16081	8.916
~~037.58~~		~~4544~~	~~2.447~~
~~040.29~~		~~3960~~	~~2.196~~



IK
Sediment
Frac 2
2.8 ppm

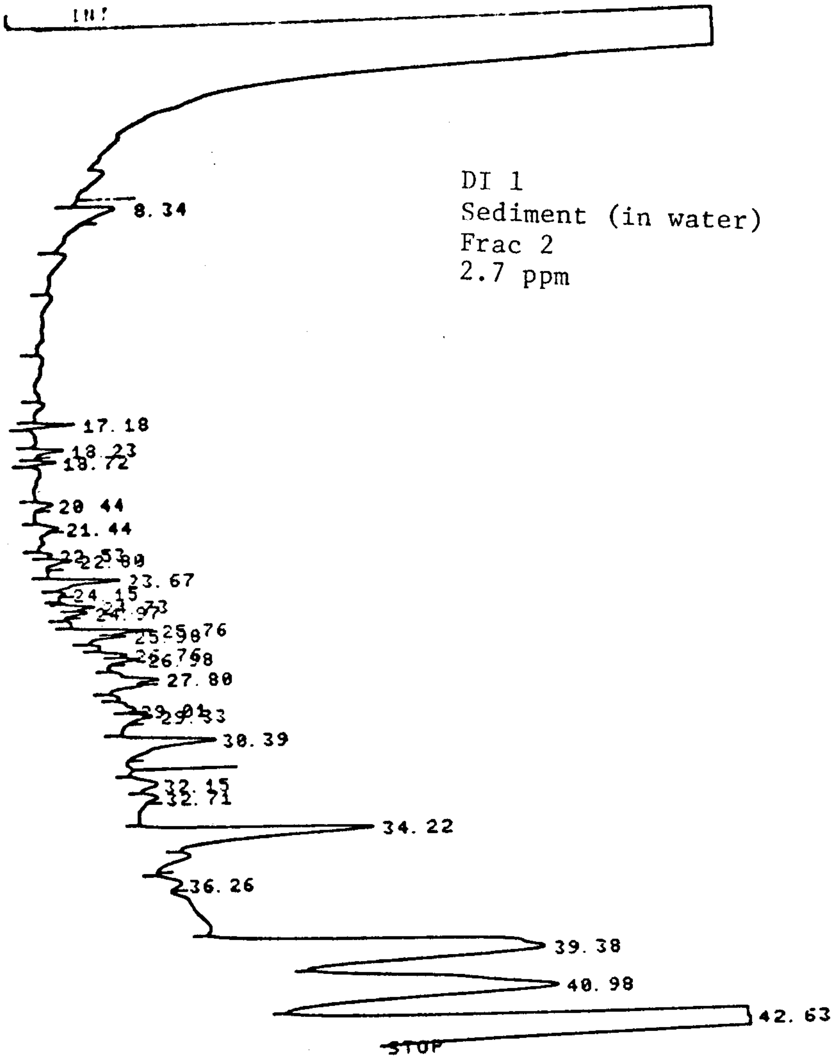
077

	RT	TYPE	AREA	AREA %	
S	~~17.16~~		~~4006~~	~~1.66~~	
	18.19		6808	2.821	
S	~~18.70~~		~~1810~~	~~.750~~	~~1~~
	18.93	M	971	.402	4
	19.21	M	4346	1.801	
	20.40		3087	1.279	
	20.80	M	682	.282	6
	21.39		7744	3.209	
	21.64	M	4014	1.663	
	22.57		1290	.534	6
	22.77	M	4252	1.762	
MS	~~23.33~~		~~445~~	~~.184~~	~~1~~
	23.69	M	12308	5.101	
	23.88	M	2690	1.115	
	24.76		2926	1.213	
M	~~24.95~~	~~M~~	~~4325~~	~~1.792~~	
	25.78		8336	3.455	
	25.97	M	4594	1.904	
	26.78		4446	1.842	
	26.96	M	7893	3.271	
	27.82		10816	4.482	
	28.04	M	3388	1.404	
	29.04		3647	1.511	
	29.30	M	13680	5.669	
	30.50		21013	8.709	
	32.27		3063	1.269	
	32.69	M	7965	3.301	
	34.45		10323	4.278	
	39.02		19720	9.176	
	40.53	M	30659	12.71	
	42.61		9704	4.021	
	46.89		20344	8.431	



DI 1
Sediment (in water)
Frac 1
20 ppm

RT	TYPE	AREA	AREA %
12.71		407	.050 17
13.27		1341	.165 3
14 80		836	.103
15.24		559	.068 9
16 28		5600	.699 3
S ~~17.13~~		~~5000~~	~~.617 3~~
17.69		5468	.674
18.14	M	39739	4.898
S ~~18.69~~	~~M~~	~~[illegible]~~	~~.285~~
18.88	M	6405	789 5
Mi 19.02	M	15993	1.971
20.29		12316	1.518
20.79	M	1182	.145 8
Mi ~~21.49~~		~~75172~~	~~9.266~~
22.32		959	.118 2
22.64	M	30969	3.817
Mi ~~23.37~~	~~M~~	~~1297~~	~~.159 9~~
23.74	M	153320	18.9
24.44	M	1772	.218 4
24 79	M	27359	3.372
25.32	M	6481	.798 9
25.81	M	101219	12.48
26.79	M	28916	3.564
27.83	M	103076	12.71
28.40	M	327	.040 31
29.03		9736	1.2
29.26	M	7784	.959 5
30.48		65167	8.033
31.34	M	695	.035 67
32.24		5340	.658 2
32.98	M	23439	2.889
34.40		28332	3.492
36.30		4107	506 2
0 ~~39.18~~		~~[illegible]~~	~~[illegible]~~
0 ~~40.44~~		~~[illegible]~~	~~[illegible]~~
0 ~~42.59~~		~~7700~~	~~.950 1~~

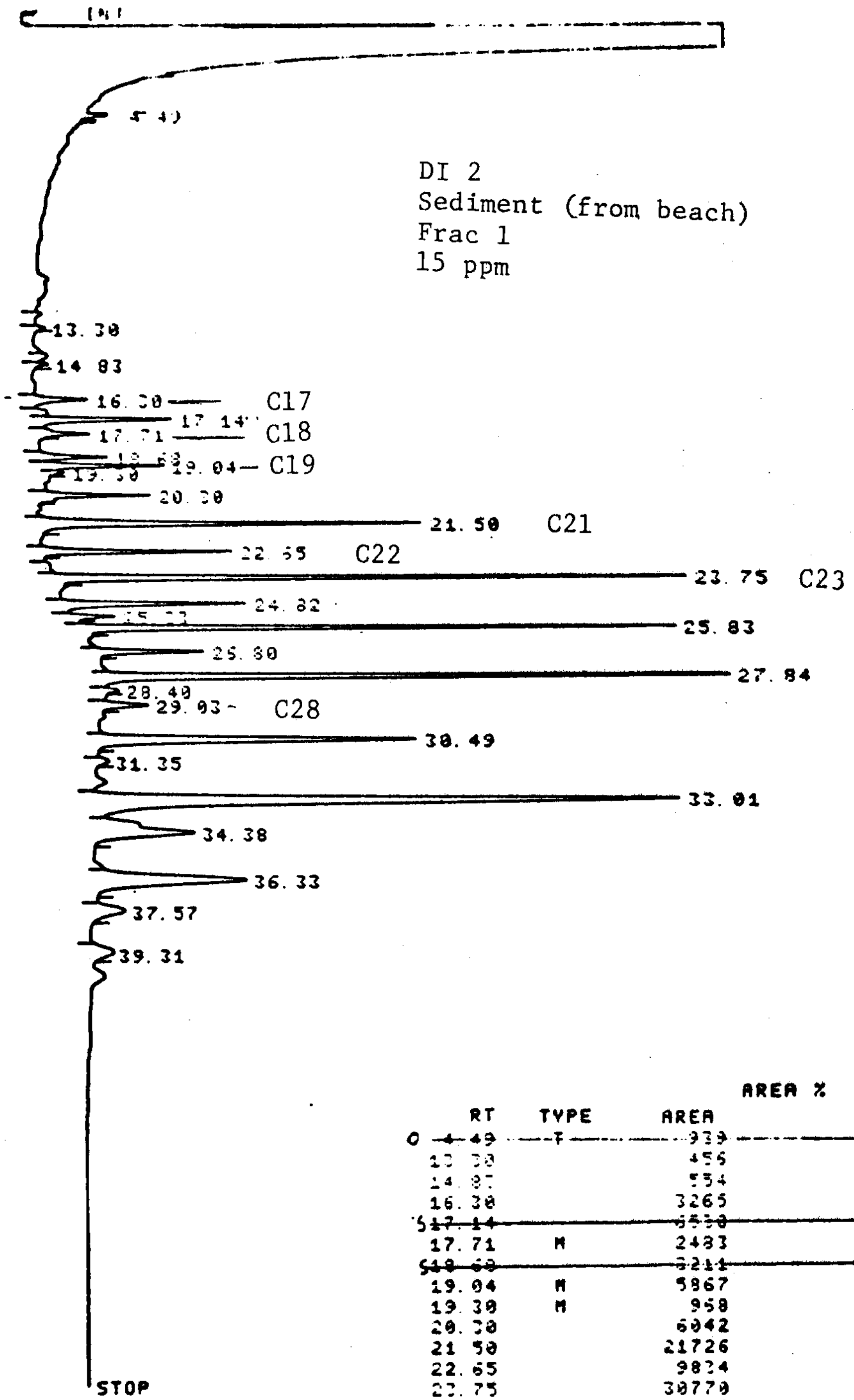


DI 1
Sediment (in water)
Frac 2
2.7 ppm

AREA %

	RT	TYPE	AREA	
O	~~8.34~~		~~5372~~	~~.791 5~~
S	~~17.18~~		~~2031~~	~~.299 2~~
	18.23		1712	.252 2
>	~~18.72~~		~~1059~~	~~.156~~
	20.44		1275	.187 8
M	~~21.44~~		~~850~~	~~.125 2~~
	22.53		734	.108 1
	22.80	M	1990	.293 2
	23.67		5182	.763 5
	24.15	M	469	.069 1
	24.73		1501	.221 1
	24.97	M	1181	.174
	25.76		4378	.645
	25.93	M	2521	.371 4
	26.76		1378	.203
	26.93	M	2076	.305 9
	27.80		1720	.253 4
	29.01		968	.142 6
	29.33		1863	.274 5
	30.39		12569	1.852
	32.15		2906	.428 1
	32.71	M	1624	.239 3
	34.22		45003	6.63
	36.26		2049	.301 9
O	~~[illegible]~~		~~[illegible]~~	~~[illegible]~~
	~~[illegible]~~		~~[illegible]~~	~~[illegible]~~
	~~[illegible]~~	~~M~~	~~[illegible]~~	~~[illegible]~~

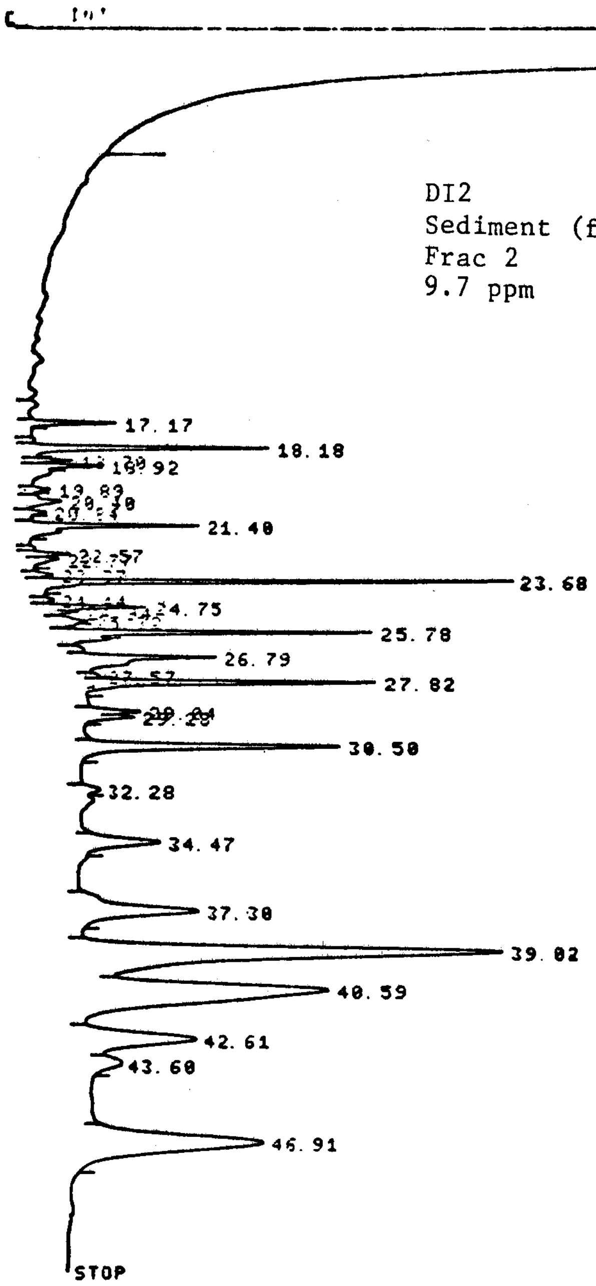
[illegible] REJECT [illegible]



DI 2
Sediment (from beach)
Frac 1
15 ppm

```
                              AREA %
     RT    TYPE       AREA
~~O  4.49     T          939                        .291 3~~
    13.30                456                        .141 7
    14.83                554                        .172 1
    16.30               3265                       1.014
~~5 17.14               6530                       2.031~~
    17.71    M          2483                        .771 5
~~5 18.68               3211                        .997 7~~
    19.04    M          5867                       1.823
    19.30    M           958                        .309 8
    20.30               6042                       1.877
    21.50              21726                       6.751
    22.65               9834                       3.056
    23.75              30770                       9.561
    24.82              10220                       3.175
    25.33    M          1951                        .606 3
    25.83              27709                       8.611
    26.80               5787                       1.798
    27.84              37702                      11.71
    28.40    M           709                        .220 3
    29.03               3043                        .945 5
    30.49              25877                       8.04
    31.35               1042                        .323 8
    33.01              66034                      20.52
    34.38    M         18005                       5.594
    36.33              23401                       7.271
~~O 37.57~~
~~O 39.31~~

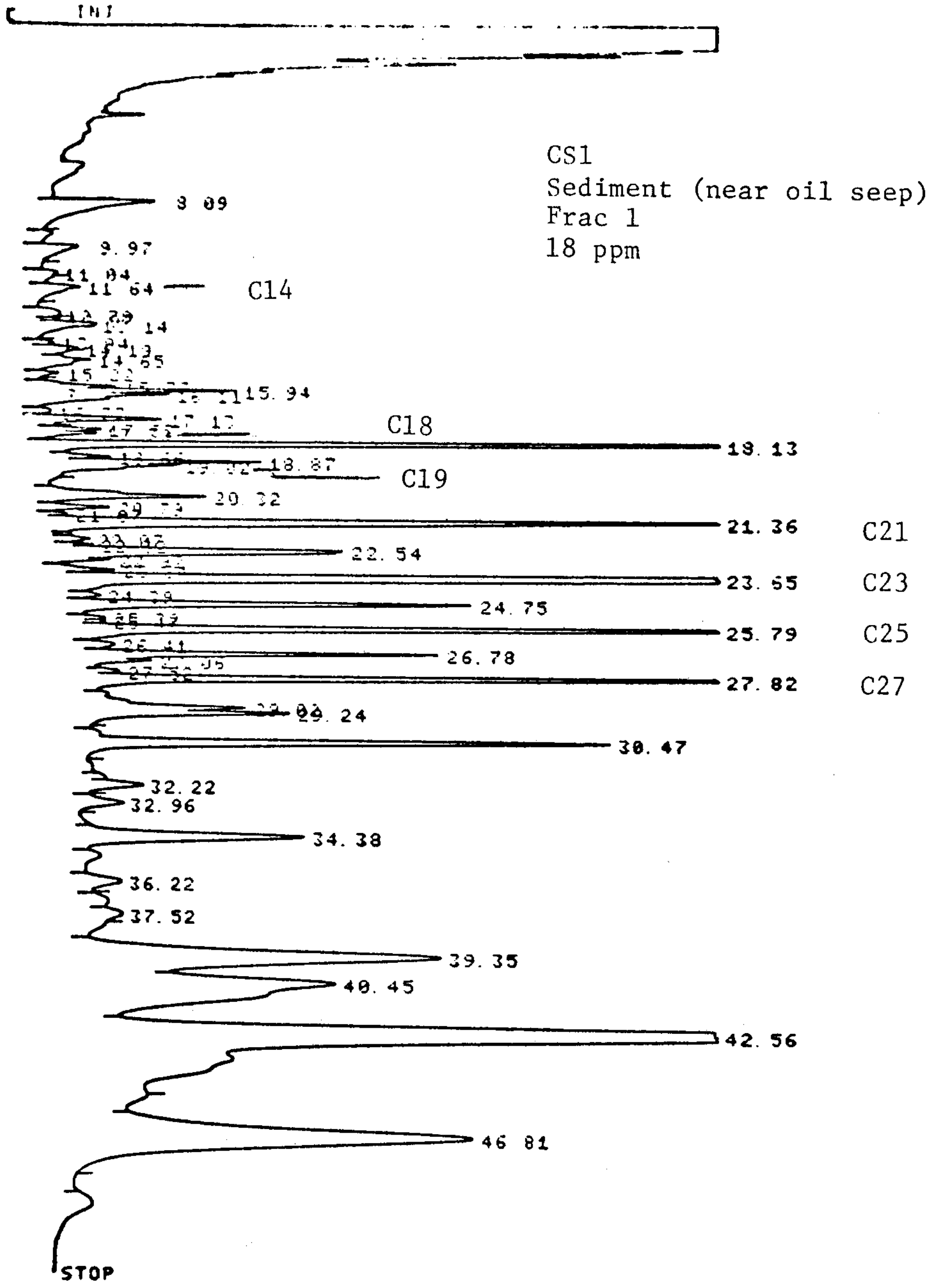
HP 3390A
DLY 4                  STOP 75                REJECT   100
```



DI2
Sediment (from beach)
Frac 2
9.7 ppm

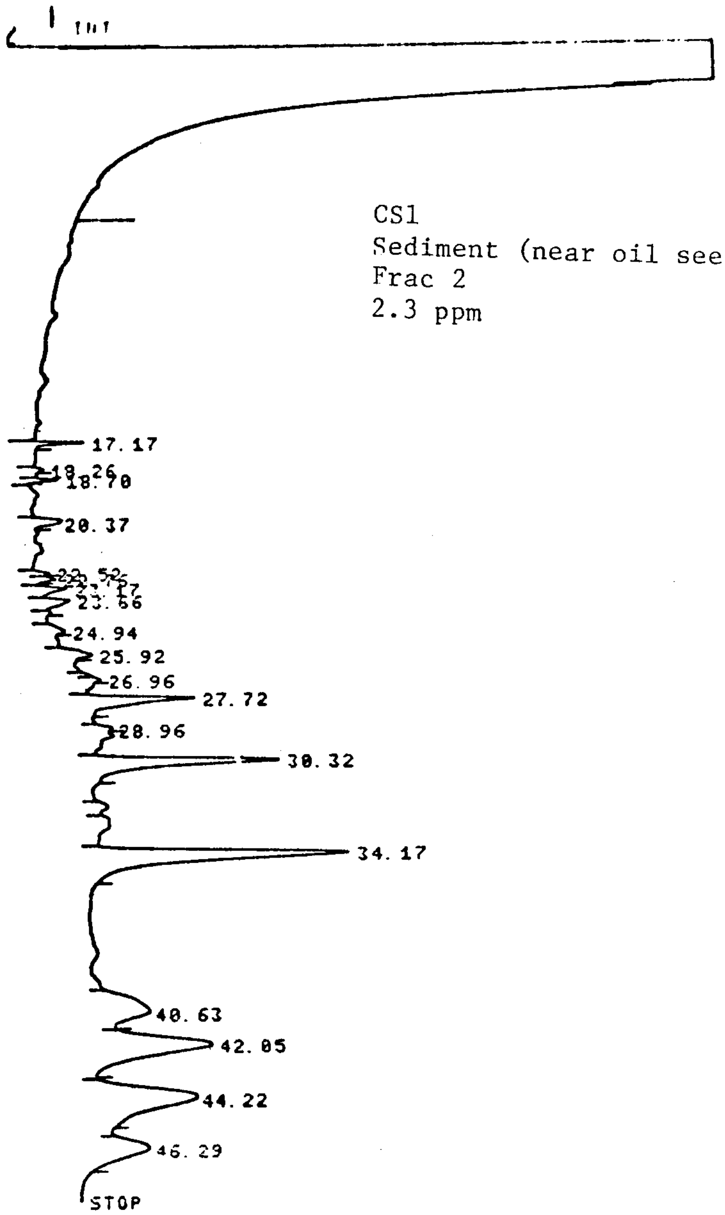
AREA %

	RT	TYPE	AREA	
S	~~17 17~~		~~[illegible]~~	~~[illegible] 4~~
	18 18		12211	3.039
S	~~19 70~~		~~[illegible]~~	~~[illegible] 9~~
	19 92	M	2748	.684
	19 89		808	201 1
	20 40		2553	.635 4
M	~~20 54~~	~~M~~	~~[illegible]~~	~~[illegible]~~
M	~~21 40~~		~~[illegible]~~	~~[illegible]~~
	22 57		1779	.442 3
	22 77	M	1727	.429 8
	23 37		964	.239 9
	23 68	M	23486	5.846
	24 44		450	.112
	24 75	M	4639	1.154
Ms	~~24 94~~	~~M~~	~~[illegible]~~	~~[illegible] 7~~
	25 32	M	971	.241 7
	25 78		12596	3.135
	26 79		9871	2.457
Ms	~~27 57~~		~~[illegible]~~	~~[illegible]~~
	27 82		16150	4.02
	29 04		3551	.883 8
	29 28	M	3545	[illegible]
	30 50		22573	[illegible]
	32 28		1306	.325 1
	34 47		10775	[illegible]
0	37 30		21902	5.451
0	39 02		83967	[illegible]
0	40 59	M	69706	[illegible]
0	42 61	M	27467	[illegible]
0	43 60	M	6348	[illegible]
	46 91		[illegible]	



CS1
Sediment (near oil seep)
Frac 1
18 ppm

RT	TYPE	AREA	
0 3.09		13519	1.15
0 9.97		4195	.356 1
0 11.04		557	.047 4
11.64		3620	.308 1
12.70		1246	.106
12.97		313	.026 64
13.14	M	4829	.410 9
13.94		710	.060 42
14.13	M	4043	.344
14.65	M	5839	.496 9
15.22	M	1012	.086 12
15.77		4155	.353 5
15.94	M	9198	.782 7
16.11	M	10978	.934 2
16.77	M	825	.070 21
5 ~~17.13~~	~~M~~	~~6665~~	~~.567 2~~
17.53		2156	.183 5
17.70	M	2758	.234 7
18.13	M	56744	4.829
5 ~~18.66~~	~~M~~	~~3731~~	~~.317 5~~
18.87	M	9932	.845 2
19.02	M	9067	.771 6
20.32		13133	1.118
20.73	M	2883	.245 3
21.07	M	483	.041 1
21.36	M	55063	4.686
22.07		1084	.092 25
22.32	M	371	.032 63
22.54	M	26999	2.298
22.92	M	2428	.206 5
23.34	M	3018	.256 8
23.65	M	140833	11.98
24.39	M	2828	.24
24.75	M	29963	2.55
25.32	M	2216	.188 5
25.47	M	1736	.147 7
25.79	M	61424	5.227
26.41	M	3594	.305 8
26.78	M	20818	1.772
27.06	M	5591	.475 8
27.52	M	3047	.259 3
27.82	M	52586	4.475
29.02	M	16379	1.394
29.24	M	16217	1.38
30.47		43197	3.676
32.22		3842	.326 9
32.96		4444	.378 2
34.38		28513	2.425
36.22		4153	.354 3
~~37.52~~		~~2042~~	~~.173 8~~
~~39.35~~		~~77519~~	~~6.597~~
~~40.45~~	~~M~~	~~75149~~	~~6.395~~
~~42.56~~	~~M~~	~~144149~~	~~12.27~~
~~46.81~~		~~105739~~	~~8.998~~



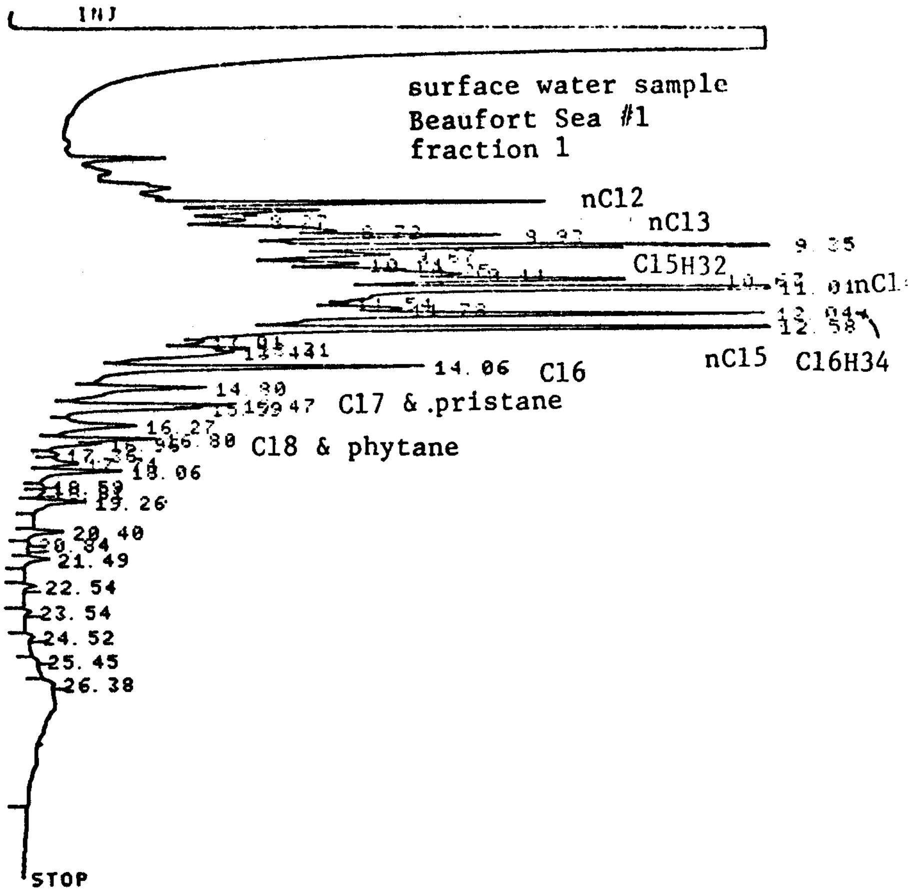
CS1
Sediment (near oil seep)
Frac 2
2.3 ppm

```
                                   AREA %
       RT    TYPE       AREA
5  17.17                2529                 1.389
   18.26                 527                  .289  4
>  18.70                1220                  .670  1
   20.37                2695                 1.48
   22.52                 163                  .064  00
   22.76                 785                  .431  1
   23.17                2113                 1.161
   23.66     M          3120                 1.714
m  24.94                1272                  .698  5
   25.92                2145                 1.178
   26.96                 534                  .293  3
   27.72               11712                 6.433
   28.96                 595                  .326  8
   30.32               21977                12.07
   34.17               41891                23.01
0  40.63               14786                 8.121
,  42.05               29863                16.41
0  44.22               31263                17.17
0  46.29               12849                 7.074


HP 3390A
LEV   3           STOP 75          REJECT   100
MV/M  .30         ATTN    4
```

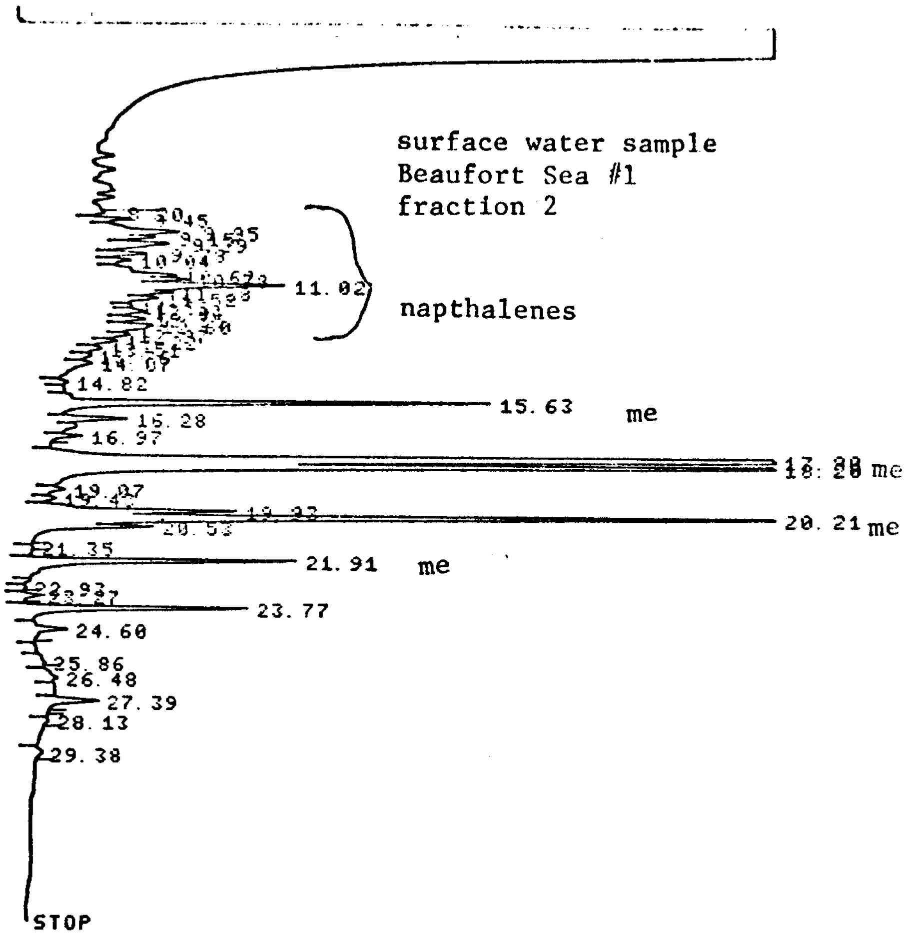
IX. APPENDIX II

ANNOTATED GAS CHROMATOGRAMS OF SURFACE WATER (SELECTED)



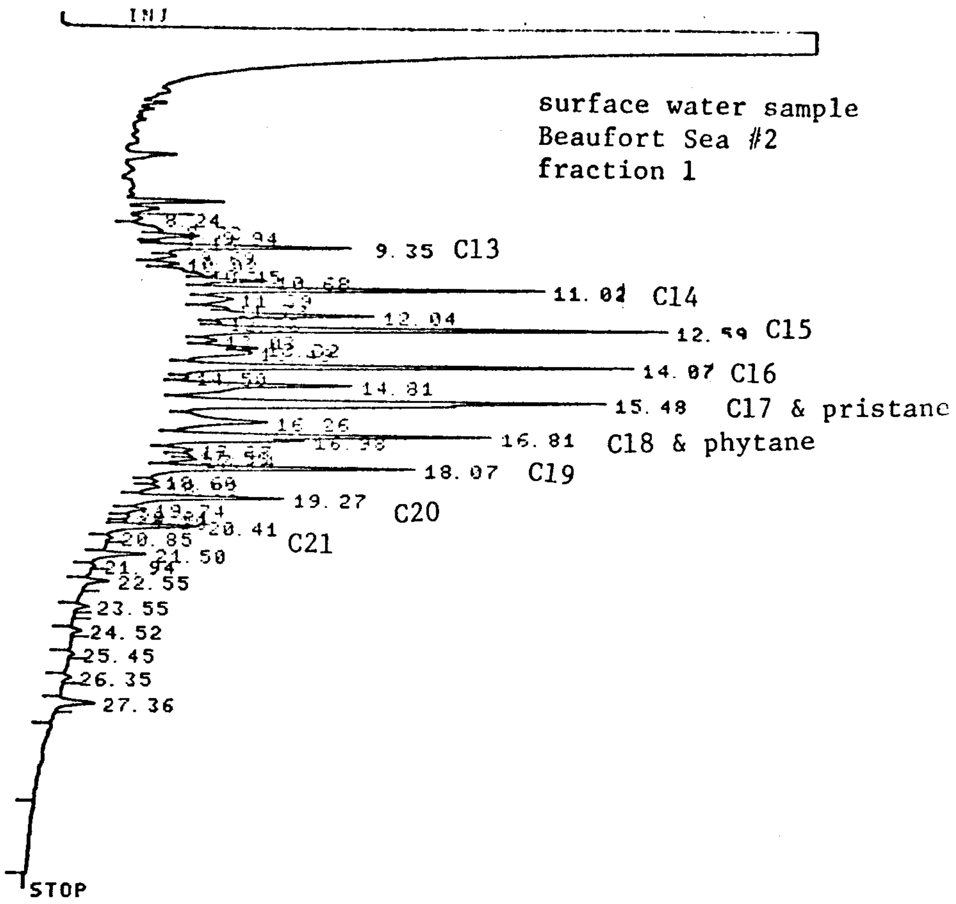
```
                          AREA %
  RT      TYPE      AREA
  8.27     TM      16942              2.458
  8.72     TM      28294              4.105
  8.93     TM      29727              4.313
  9.35     TM      61223              8.883
  9.67     TM      30230              4.386
 10.01     TM      22989              3.336
 10.25     TM      17145              2.488
 10.44     TM      30784              4.467
 10.67     TM      44182              6.411
 11.01     TM     104822             15.21
 11.54     TM      12606              1.829
 11.78     TM      26179              3.799
 12.04     TM      62458              9.058
 12.58     TM      64434              9.349
 13.01     TM      10587              1.536
 13.31     TM      11977              1.738
 13.44     TM      18879              2.739
 14.06     TM      29525              4.284
 14.80     TM      14581              2.116
 15.47     TM       9889              1.435
 15.59     TM       7743              1.123
 16.27     TM       9605              1.394
 16.80     TM       5752               .834 6
 16.96     TM       2791               .403 5
 17.36     TM        959               .139 3
 17.74     TM       2760               .400 5
 18.05     TM       4219               .612 2
 18.59     TM        101               .014 65
 18.81     T         195               .028 29
 19 26     T        2713               .394 4
 20.40     T        1670               .242 3
 20.84     TM        129               .018 72
 21.49              1206               .175
 22.54               605               .087 78
 23 54               348               .052 4
 24 52               369               .053 54
 25.45               151               .021 91
 26.38               364               .052 82

HP 3380A     699
SLP   5              STOP 45            REJECT   100
MV.M  .10            ATTN      4
```

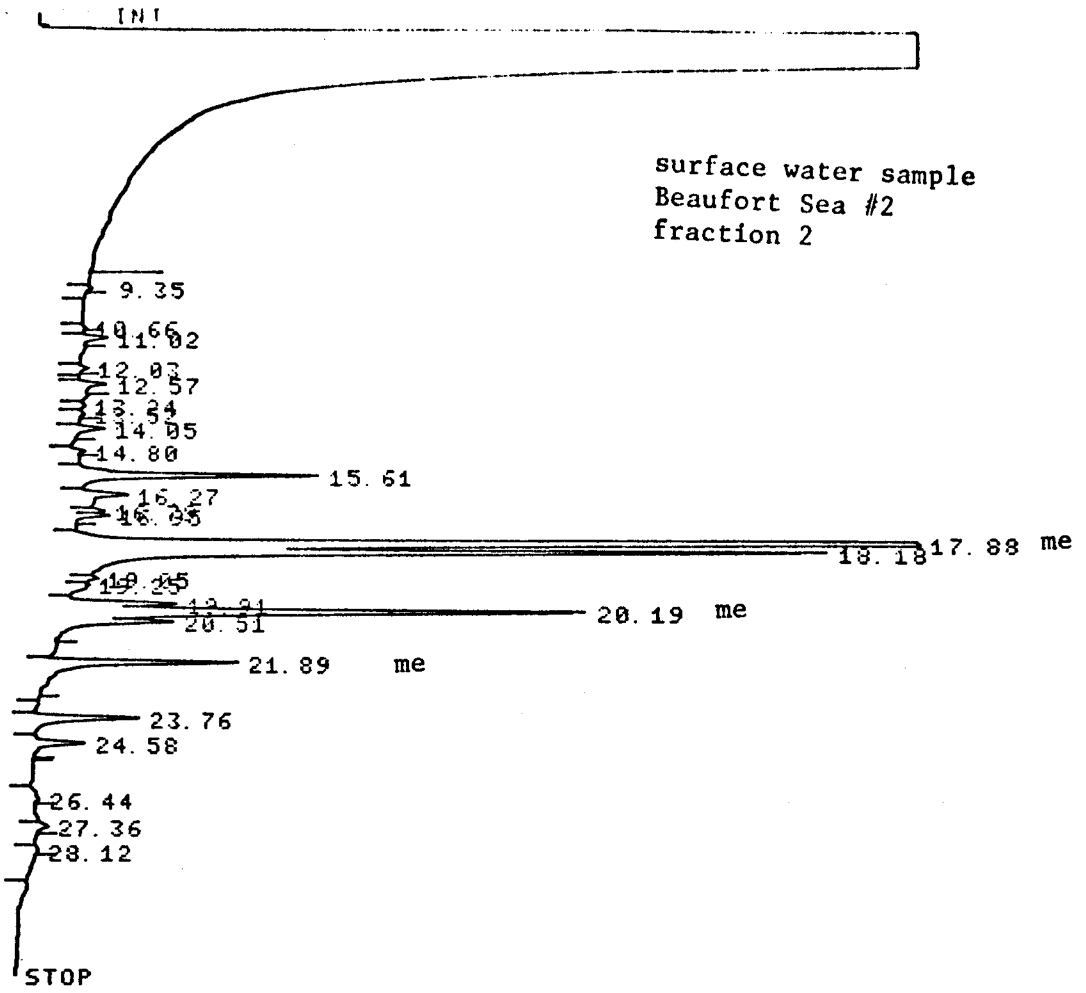


```
                                AREA %
    RT     TYPE       AREA
   8.20     TM         962                 .235 8
   8.45     TM        2374                 .581 9
   8.95     TM        9181                2.25
   9.15     TM        3822                 .936 8
   9.39     TM        7515                1.842
   9.78     TM        4377                1.073
  10.04     TM        3648                 .894 2
  10.62     TM       10146                2.487
  10.78     TM        6168                1.512
  11.02     TM       15822                3.878
  11.28     TM        5465                1.34
  11.52     TM        6874                1.685
  11.83     TM        3972                 .973 6
  12.04     TM        6334                1.553
  12.35     TM        5566                1.364
  12.60     TM        9157                2.244
  12.97     TM        4609                1.13
  13.22     TM        3620                 .887 3
  13.51     TM        2987                 .732 1
  13.76     TM        2252                 .552
  14.07     TM        3511                 .860 6
  14.82     TM         289                 .070 84
  15.63     T        20763                5.091
  16.28     TM        2959                 .725
  16.97     T          932                 .229 4
  17.90     T       103768               25.43
  18.20     TM       56635               13.88
  19.07     TM        1701                 .416 9
  19.43     TM        1125                 .275 7
  19.93     TM       11977                2.936
  20.21     TM       45716               11.21
  20.53     TM        7203                1.766
  21.91     T        15369                3.767
  22.93     T          115                 .029 13
  23.27     T          795                 .195 1
  23.77     T        12765                3.129
  24.60     TM        2697                 .661 1
  25.86     T          352                 .086 28
  26.48     T          605                 .148 3
  27.39     T         2995                 .734 1
  28.13                256                 .062 75
  29.38                594                 .145 6

HP 3380A
```



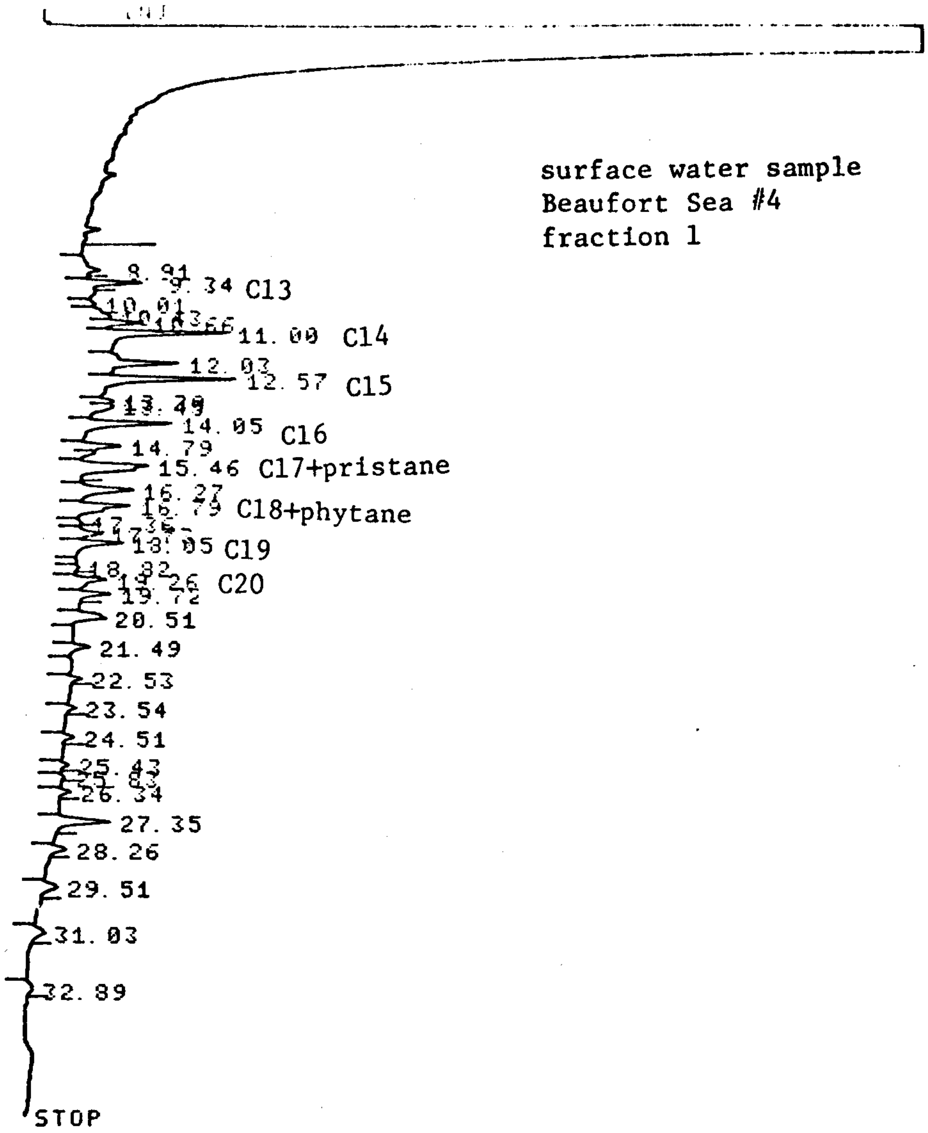
RT	TYPE	AREA	AREA %
8.24	TM	475	.176 7
8.73	TM	1972	.733 4
8.94	TM	3233	1.202
9.15	TM	464	.172 6
9.35	TM	9529	3.544
9.69	TM	1463	.544 1
10.02	TM	781	.290 5
10.45	TM	460	.171 1
10.68	T	2837	1.055
11.02	TM	15240	5.668
11.39	TM	3093	1.15
11.78	TM	1835	.682 5
12.04	TM	11276	4.194
12.33	TM	1652	.614 4
12.59	TM	24494	9.11
13.03	TM	2379	.884 8
13.32	TM	4780	1.778
13.49	TM	7234	2.69
14.07	TM	24289	9.033
14 59	TM	1387	.515 8
14.81	TM	15325	5.7
15.48	TM	35240	13.11
16.26	TM	14966	5.566
16.81	TM	17262	6 42
16.98	TM	8183	3.045
17.37	TM	3688	1.372
17.59	TM	2757	1.025
17.74	TM	3976	1.479
18.07	TM	16919	6.292
18.60	TM	2134	.793 7
18 83	TM	2827	1.051
19.27	TM	10205	3.795
19.74	TM	1880	.699 2
20.01	TM	984	.366
20.20	TM	598	.222 4
20 41	TM	4797	1.784
20 85	TM	262	.097 44
21.50	T	2297	.854 [illegible]
21 94	TM	[illegible]	.07[illegible]
22 55	T	1206	.448 5
23.55	T	628	.233 6
24 52		5[illegible]0	.215 [illegible]
[illegible]		[illegible]	.1[illegible]
[illegible]		[illegible]	1[illegible]1
27 36		2364	.879 2



surface water sample
Beaufort Sea #2
fraction 2

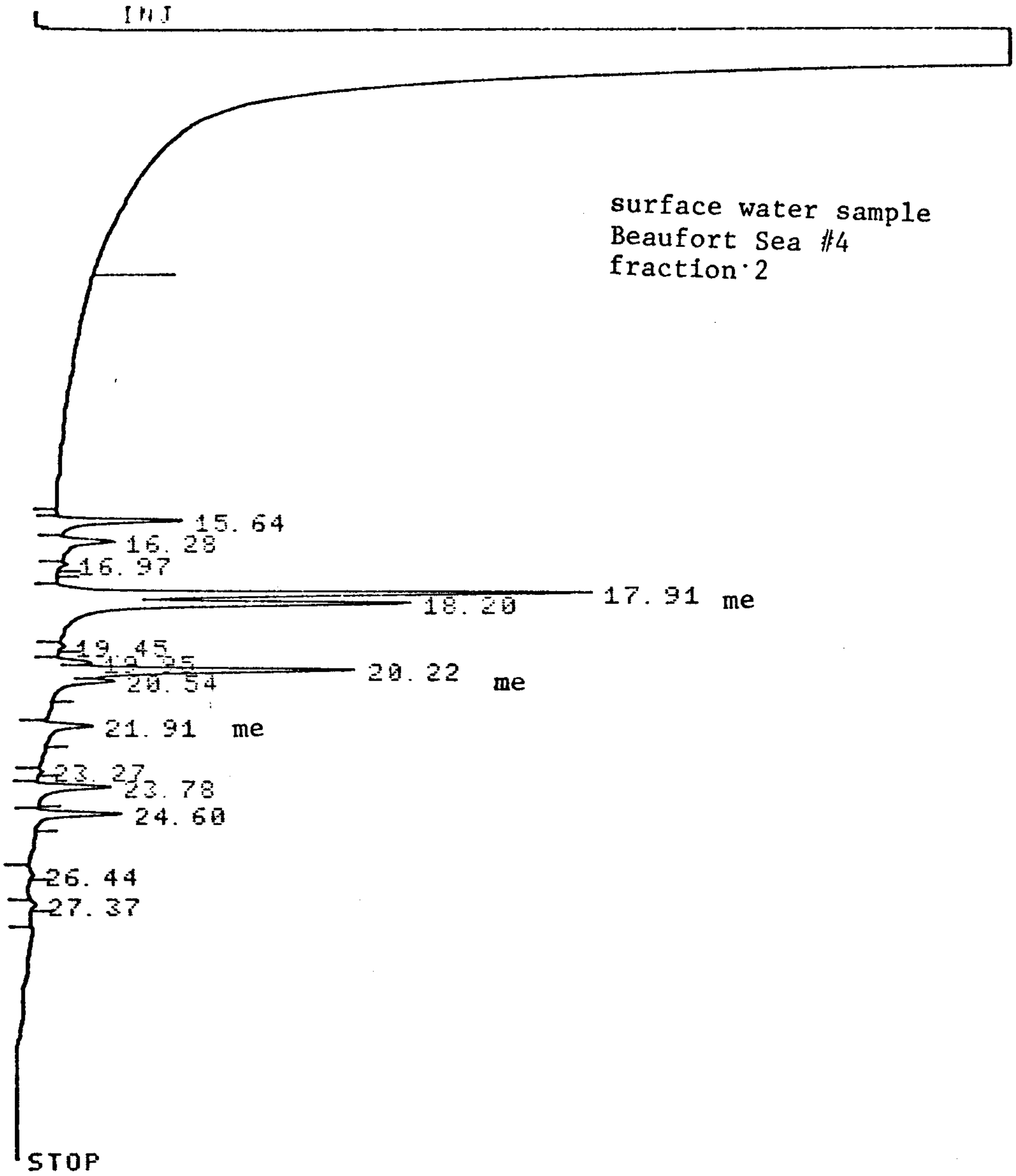
```
                          AREA %
    RT    TYPE      AREA
  9.35               193              .098 09
 10.66               105              .053 37
 11.02               955              .485 4
 12.03               359              .182 5
 12.57               898              .456 4
 13.24               175              .088 94
 13.52     M         215              .109 3
 14.05              1263              .641 9
 14.80               349              .176 9
 15.61             11653 -           5.923
 16.27     M        3767             1.915
 16.79     M        1225              .622 6
 16.95     M        1433              .728 3
 17.88             69834-           35.49
 18.18     M       40628-           20.65
 19.05     M        1733              .880 8
 19.25     M        2153             1.094
 19.91     M        5267 -           2.677
 20.19     M       23177 -          14.32
 20.51     M        6611 -           3.36
 21.89             10495 -           5.334
 23.76              5505 -           2.798
 24.58     T        2522-            1.282
 26.44               623              .316 6
 27.36               444              .225 7
 28.12               173              .087 93


HP 3380A
DLY  8.            STOP 45            PEJECT   100
MV/M  .10          ATTN .    4
```



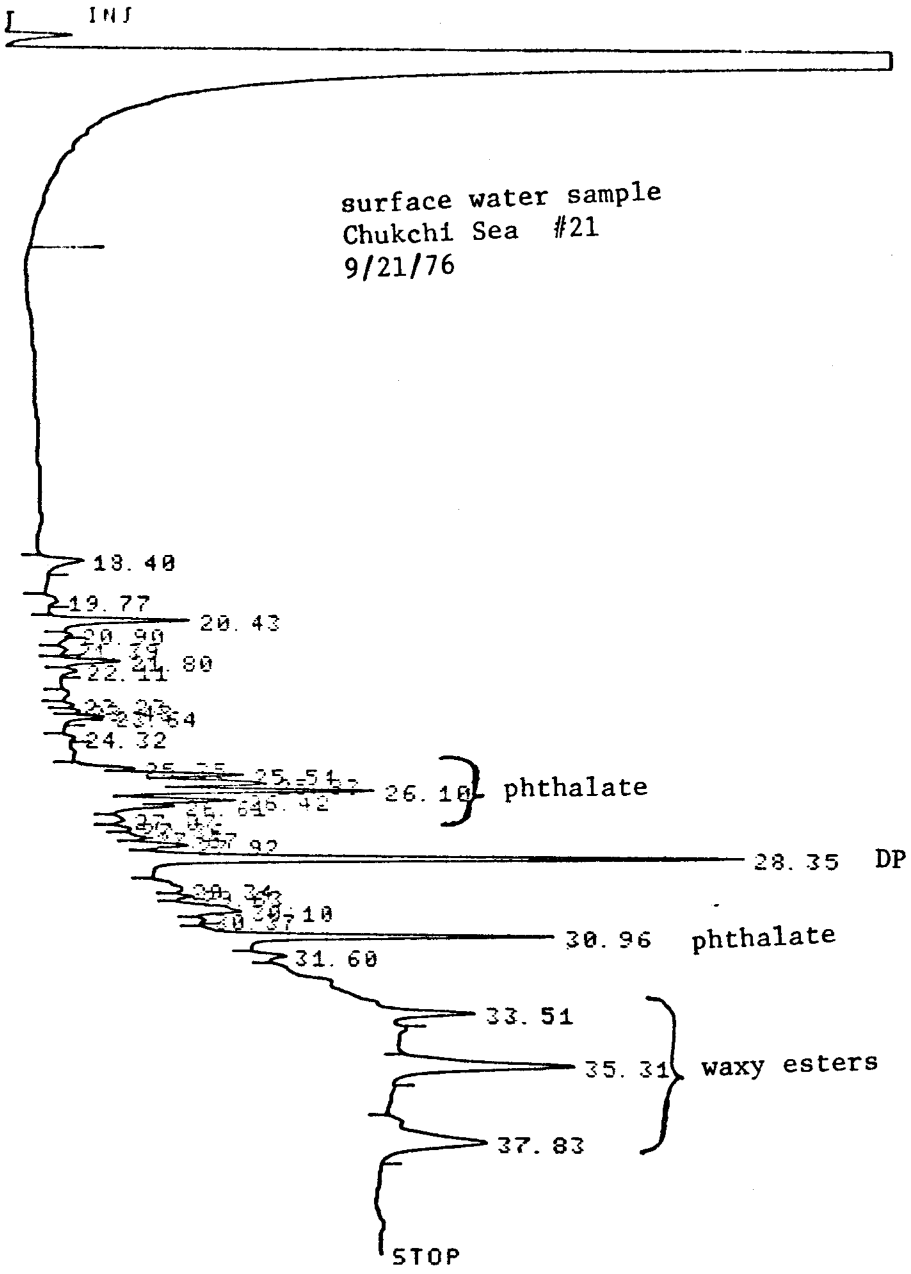
surface water sample
Beaufort Sea #4
fraction 1

```
                          AREA %
  RT     TYPE      AREA
 8.91               908          1.215
 9.34              1830          2.448
10.01               288           .385 3
10.43     M        1616          2.162
10.66     M        3086          4.128
11.00     M        9956         13.32
12.03     M        8479         11.34
12.57     M        9670         12.94
13.30     M        1454          1.945
13.45     M        2444          3.269
14.05     M        4561          6.101
14.79     M        1105          1.478
15.46              4850          6.488
16.27              3270          4.374
16.79     M        3130          4.187
17.35     M         116           .155 2
17.73              1105          1.478
18.05     M        2041          2.73
18.82               137           .183 3
19.26              1580          2.114
19.72     M        1397          1.869
20.51              1897          2.538
21.49               817          1.093
22.53               457           .611 3
23.54               382           .511
24.51               498           .666 2
25.43               339           .453 5
25.83               191           .255 5
26.34               541           .723 7
27.35              3015          4.033
28.26               826          1.105
29.51              1056          1.413
31.03              1045          1.398
```



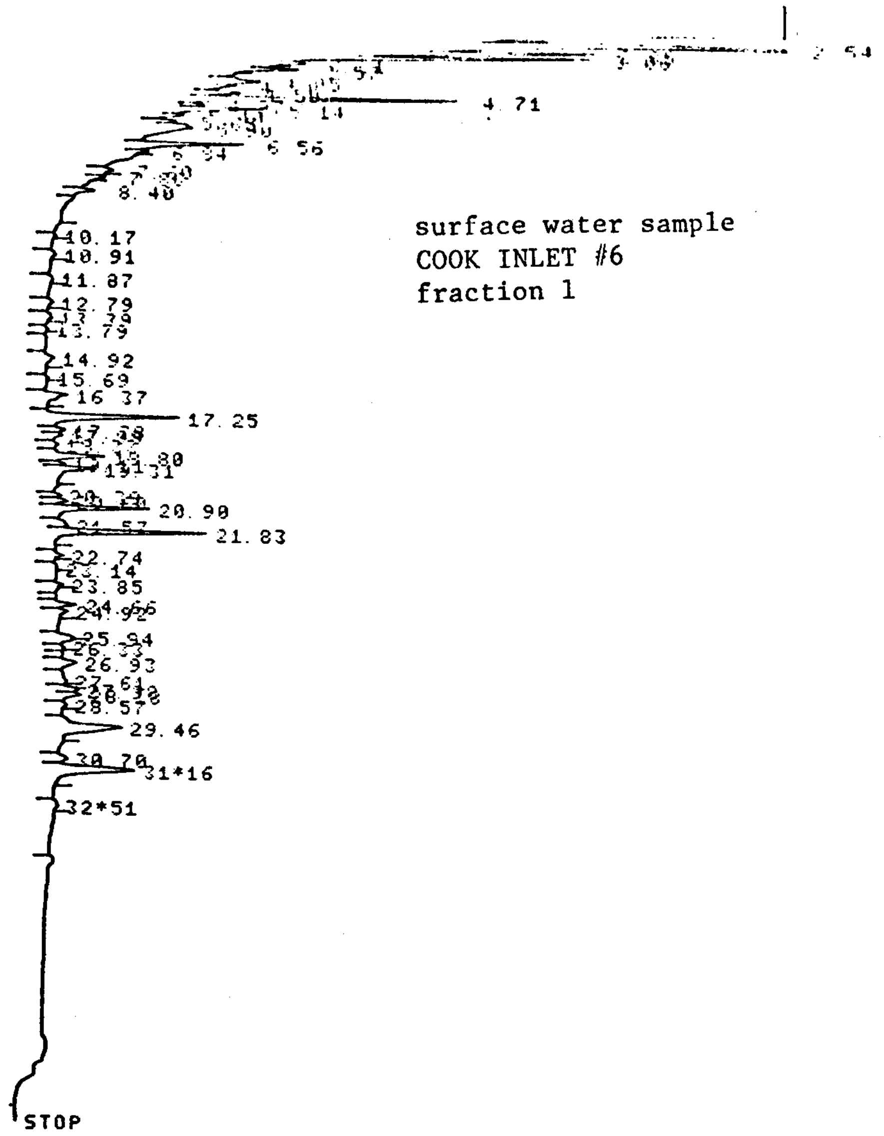
surface water sample
Beaufort Sea #4
fraction·2

RT	TYPE	AREA	AREA %
15.64		5978	7.572
16.28	T	2950	3.73[illegible]
16.97	TM	386	.488 9
17.91		21527	27.27
18.20	M	18769	23.77
19.45	T	255	.323
19.95	T	1261	1.597
20.22	M	14138	17.91
20.54	M	3076	3.896
21.91		2458	3.114
23.27		[illegible]	[illegible] 8
23.78		[illegible]	4.462
24.60		3530	4.471
26.44		368	.466 1
27.37		557	.705 5



surface water sample
Chukchi Sea #21
9/21/76

RT	TYPE	AREA	AREA %	
18.40		1444	1.784	
19.77		420	.518 9	
~~20.43~~		~~3258~~	~~4.025~~	S.
20.90	M	170	.21	
21.39		181	.223 6	
~~21.80~~		~~1299~~	~~1.605~~	S
22.11	M	416	.513 9	
~~23.23~~		~~195~~	~~.242 1~~	S
23.43	M	333	.411 4	
23.64	M	891	1.101	
24.32		155	.191 5	
25.35		1084	1.339	
25.54	M	3526	4.356	
25.83	M	6155	7.604	
26.10	M	6814	8.418	
26.42	M	3220	3.978	
26.61	M	1685	2.082	
27.07	M	440	.543 6	
27.36	M	294	.363 2	
27.67	M	625	.772 1	
27.92	M	1519	1.877	
28.35	M	14923	18.45	
29.34	M	833	1.103	
29.62	M	381	.470 7	
30.10	M	2041	2.521	
30.37	M	207	.255 7	
30.96		7605	9.395	

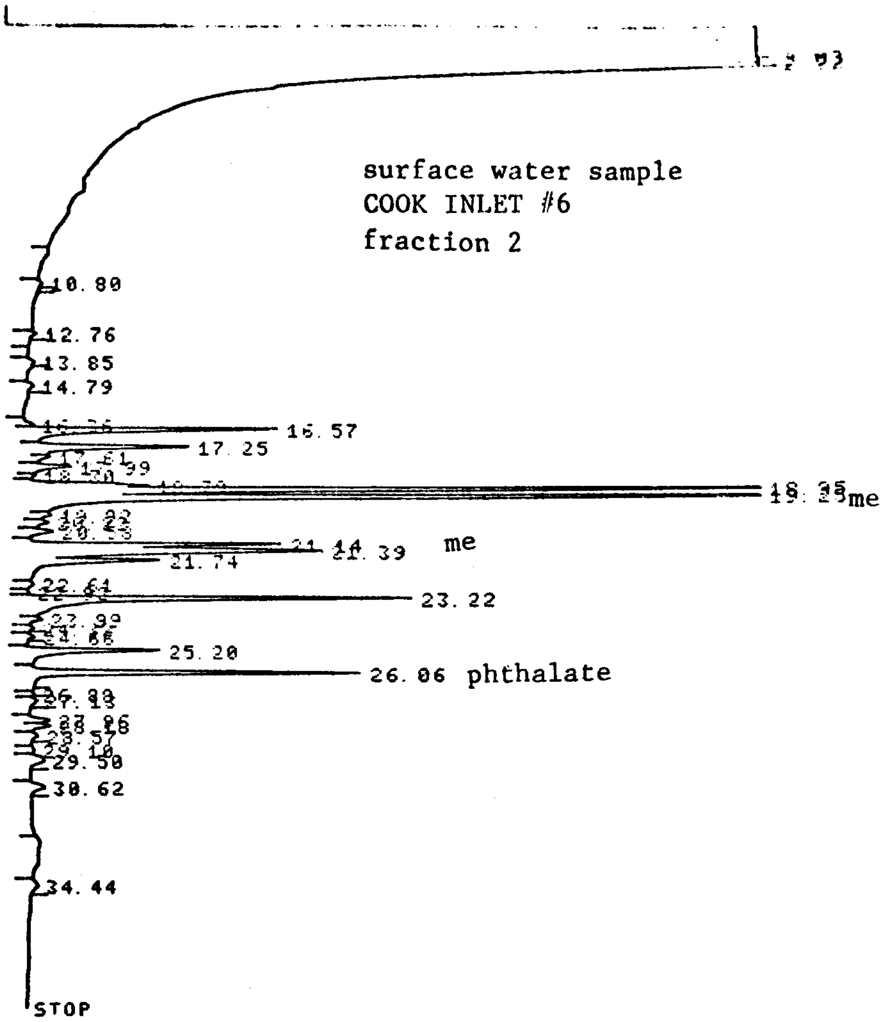


surface water sample
COOK INLET #6
fraction 1

AREA %

RT	TYPE	AREA	AREA %	
~~2.54~~	~~T~~	~~26526~~	~~21.29~~	
2.85	TM	8486	6.811	
3.06	TM	8125	6.521	
3.31	TM	596	.478 3	
3.57	T	1249	1.002	
4.05	T	2368	1.901	
4.21	TM	1107	.888 5	
4.50	TM	1848	1.483	
4.71	TM	10378	8.329	
4.97	TM	877	.703 9	B
5.14	TM	4165	3.343	
5.40	TM	860	.690 2	
5.65	TM	704	.565	
5.90	TM	4225	3.391	
6.56	TM	4378	3.514	
6.84	TM	467	.374 8	
7.60	T	414	.332 3	
7.86	T	215	.172 6	
~~8.40~~	~~T~~	[illegible]	[illegible]	
10.17		[illegible]	.109 2	
~~10.91~~		~~425~~	~~.341 1~~	B
11.87		324	.26	
~~12.79~~		~~382~~	~~.306 6~~	B
13.29		449	.360 4	
~~13.79~~		[illegible]	[illegible]	B
~~14.92~~		[illegible]	[illegible]	B
15.69		148	.118 8	
~~16.37~~		~~1649~~	~~1.32~~	
~~17.25~~		~~7960~~	~~6.389~~	S
17.78	M	922	.740 8	
17.98	M	740	.593 [illegible]	
[illegible]	M	412	[illegible]	
[illegible]	~~M~~	[illegible]	[illegible]	S
~~19.11~~	~~M~~	~~471~~	~~.378~~	S
19.21	M	2490	1.998	
[illegible]		[illegible]	[illegible]	D

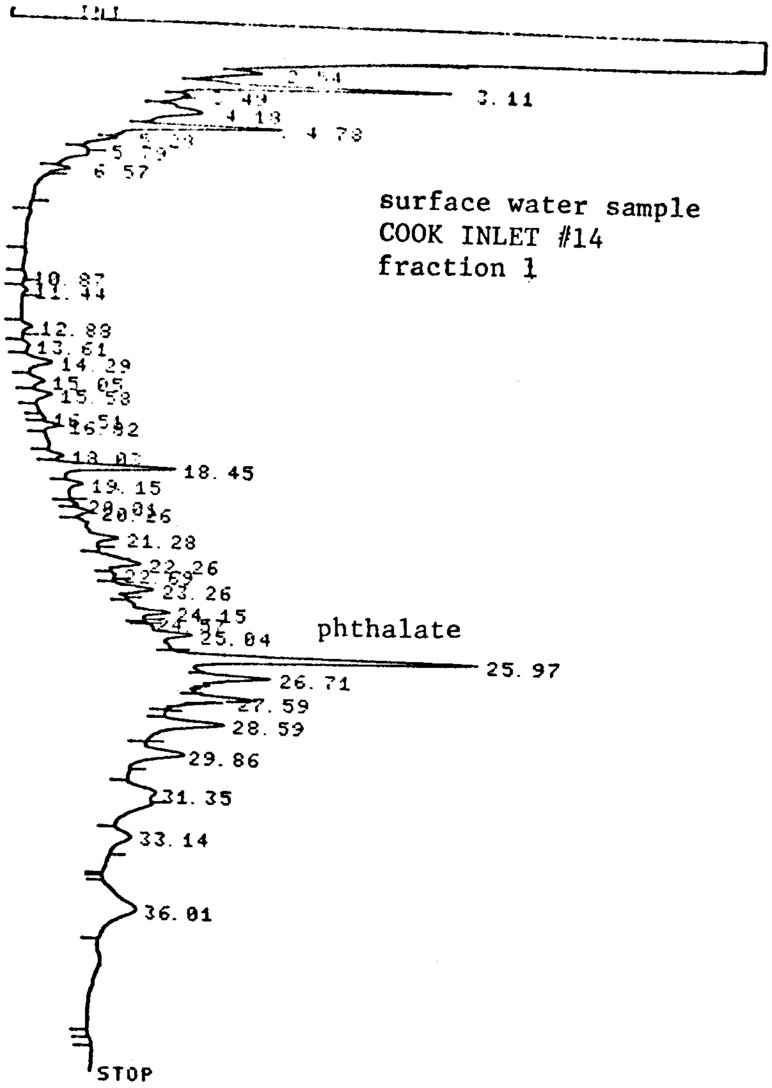
706



surface water sample
COOK INLET #6
fraction 2

RT	TYPE	AREA	AREA %
~~2.03~~	~~T~~	~~2764~~	~~1.147~~ B
~~2.22~~	~~TM~~	~~5738~~	~~2.381~~ B
10.80	T	255	.105 8
~~12.76~~		~~289~~	~~.119 9~~ B
13.85		295	.122 4
14.79		488	.202 5
16.36		591	.245 2
16.57	M	13858	5.751
~~17.25~~	~~M~~	~~10370~~	~~4.303~~ S
17.61	M	2182	.905 5
17.99	M	3015	1.251
18.30	M	619	.256 9
~~18.79~~	~~M~~	~~7071~~	~~2.934~~ S
18.95	M	39678	16.47
19.25	M	51225	21.26
19.92	M	1902	.789 3
20.22	M	1838	.762 7
~~20.50~~	~~M~~	~~1926~~	~~.799 2~~ S
21.14	M	11964	4.965
21.39	M	21772	9.035
21.74	M	9152	3.798
~~22.61~~	~~M~~	~~446~~	~~.185 1~~ B
23.22	M	21809	9.05
23.99	M	836	.346 9
24.32	M	268	.111 2
24.66		336	.139 4
25.20		7736	3.21
26.06	M	15533	6.446
27.13		343	.142 3
27.96		1175	.487 6
~~28.19~~	~~M~~	~~1224~~	~~.507 9~~ B
28.57	M	529	.219 5
29.10		304	.126 2
~~29.50~~	~~M~~	~~1468~~	~~.609 2~~ B
30.62		1136	.471 4
34.44		846	.351 1

```
HP 3380A     707
DLY  2            STOP 45         REJECT   100
MV/M   10         ATTN      4
```



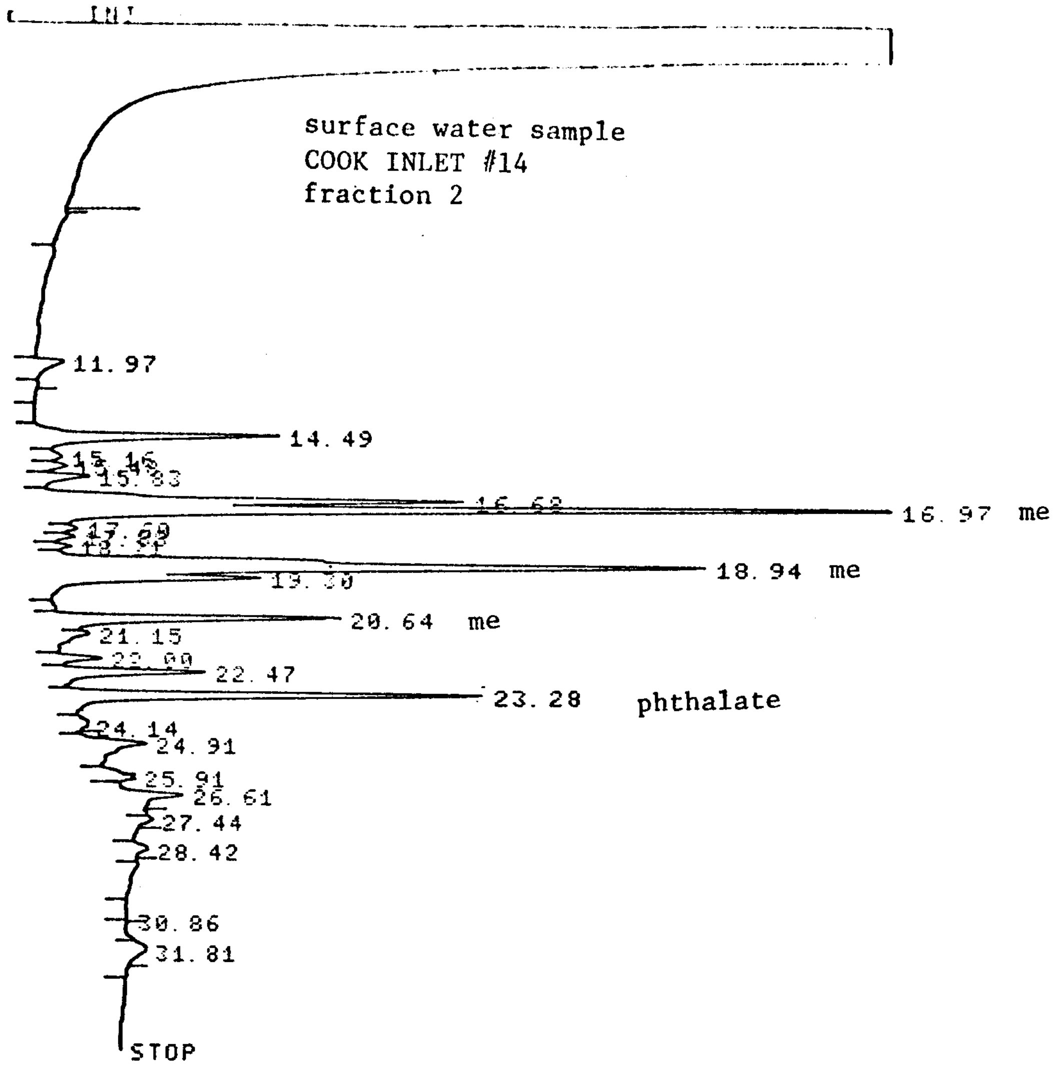
surface water sample
COOK INLET #14
fraction 1

phthalate

RT	TYPE	AREA	AREA %	
2.54	T	2326	1.578	
3.11	TM	13236	8.98	
3.49	TM	331	.224 6	
4.18	T	8299	5.631	
4.78	TM	10895	7.392	
5.28	TM	1170	.793 8	
6.57	T	808	.548 2	
10.87		318	.215 8	
11.44		367	.249	
12.88		762	.517	
13.61		469	.318 2	
~~14.29~~	~~M~~	~~2469~~	~~1.675~~	B
~~15.05~~	~~M~~	~~1214~~	~~.823 7~~	S
15.58	M	1513	1.027	
16.51		287	.194 7	
~~16.82~~	~~M~~	~~1038~~	~~.704 3~~	S
18.03		777	.527 2	
~~18.45~~	~~M~~	~~8388~~	~~5.691~~	B
~~19.15~~	~~M~~	~~1584~~	~~1.075~~	B
20.01		238	.161 5	
20.26	M	1170	.793 8	
21.28	M	2773	1.881	
22.26		3900	2.646	
22.69	M	523	.354 8	
23.26		2970	2.015	
24.15		2002	1.358	
~~25.04~~		~~2047~~	~~1.392~~	B
~~25.97~~		~~23062~~	~~15.65~~	B
~~26.71~~	~~M~~	~~13186~~	~~8.947~~	B
27.59	M	10394	7.052	
~~28.59~~		~~6531~~	~~4.431~~	B
29.86		5622	3.814	
31.35		1542	1.046	
33.14		2959	2.008	
36.01		11417	7.746	

708

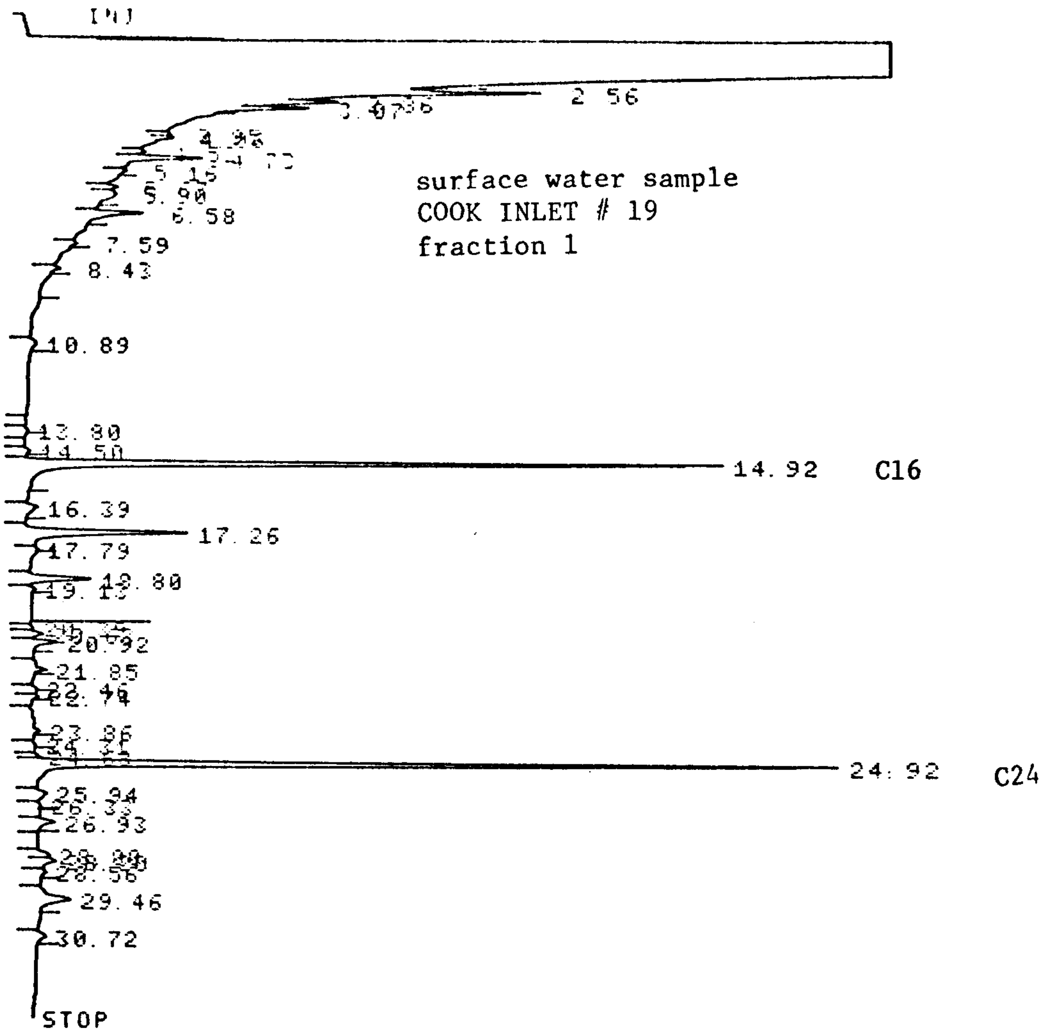
```
HP 3380A
DLY   2              STOP 45          REJECT    100
MV/M    10           ATTN      4
```



surface water sample
COOK INLET #14
fraction 2

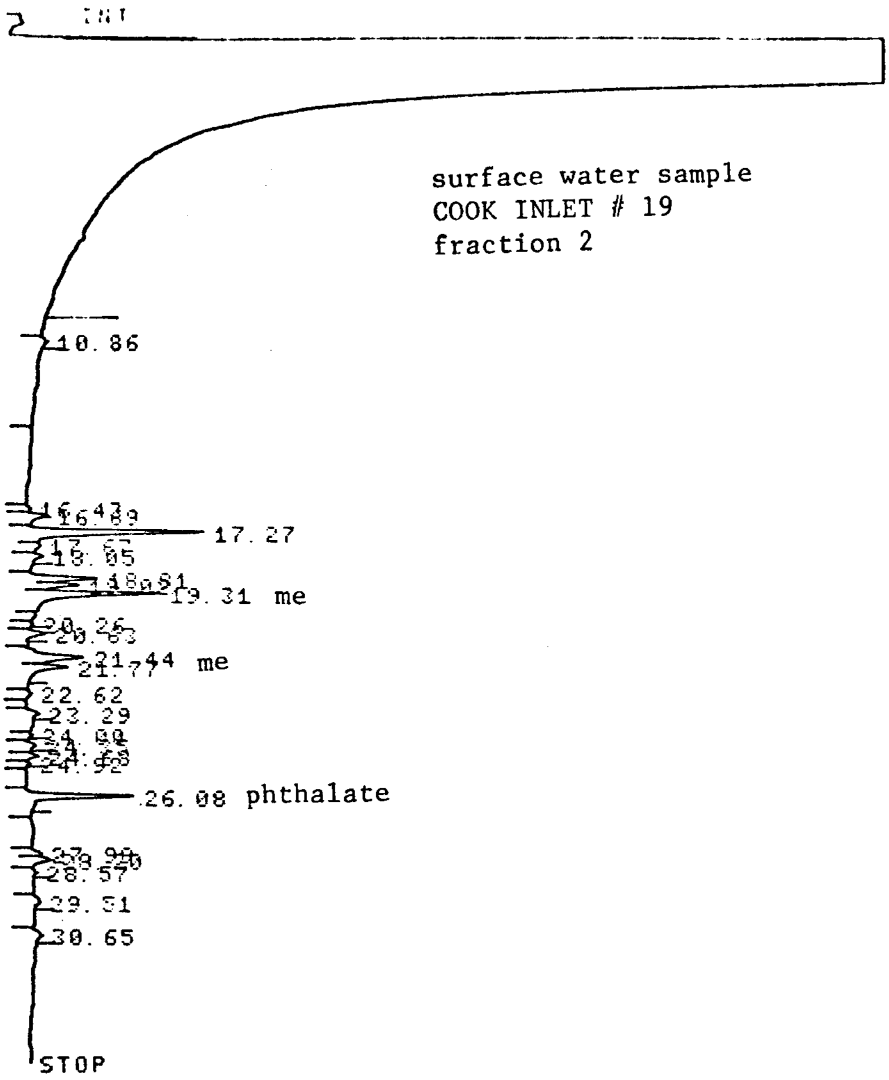
```
                               AREA %
   RT    TYPE      AREA
 11.97             2687             1.049
 14.49            18169             7.095
 15.16    T         792              .309 3
 15.48    TM       1015              .396 4
 15.83    TM       2232              .871 6
 16.68    M.      26380            10.3
 16.97    M       53482            20.88
 17.60    M        2096              .818 5
 17.88    M        1623              .633 8
 18.21    M        1253              .489 3
 18.94    M       58537            22.86
 19.30    M       13657             5.333
 20.64            16998             6.638
 21.15    M        3211             1.254
 22.00    M        2238              .873 9
 22.47    M        8901             3.476
 23.28    M       25074             9.791
 24.14    M        1246              .486 6
 24.91             5978             2.334
 25.91    M        2570             1.004
 26.61    M        4520             1.765
 27.44              427              .166 7
 28.42              994              .388 2
 31.81             2003              .782 2


HP 3380A
DLY   2.           STOP .45         REJECT    100
MV/M   .10         ATTN      4
```



surface water sample
COOK INLET # 19
fraction 1

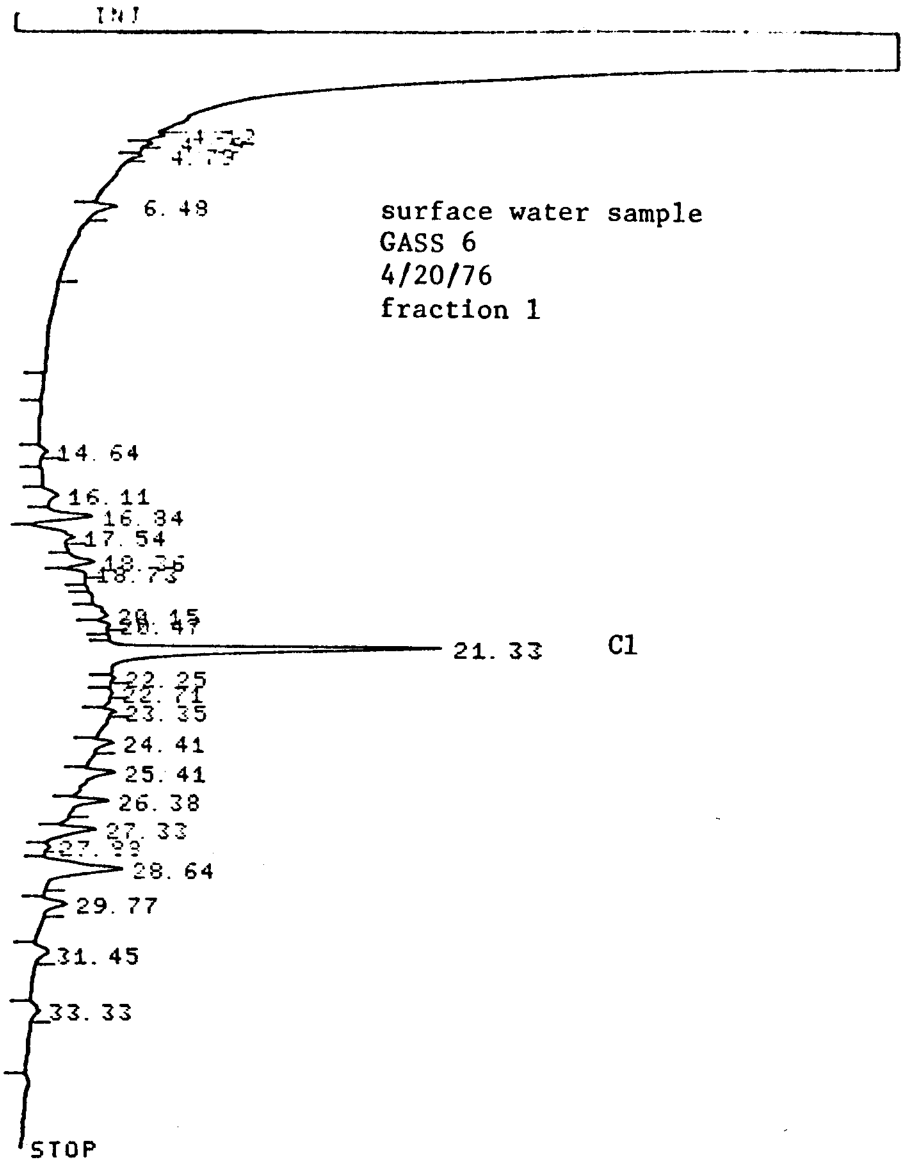
```
                        AREA %
   RT     TYPE      AREA
~~ 2.56    T         5370                    5.663~~ B
~~ 2.86    TM        1492                    1.573~~ B
~~ 3.07    TM        1569                    1.653~~ B
   3.95    T          204                     .215 1
~~ 4.06    TM         809                     .853~~ 1B
~~ 4.52    TM         293                     .309~~ B
~~ 4.73    TM        2560                    2.7~~ B
   5.16    TM         204                     .215 1
   5.67    T          415                     .437 6
~~ 5.90    TM        1209                    1.275~~ B
~~ 6.50    T         2169                    2.286~~ B
~~ 7.59    T          201                     .212~~ B
~~ 8.43    T          255                     .268~~ 9B
  10.89               511                     .538 9
~~13.80               112                     .118~~ 1 B
  14.50               166                     .175 1
  14.92             26598                   28.05
~~16.39               721                     .760~~ 3 B
~~17.26              7694                    8.113~~ S
~~17.79    M          174                     .183~~ 5 B
~~18.00              2731                    2.88~~ S
~~19.13    M          175                     .184~~ 5 B
~~20.39               104                     .109~~ 7 B
~~20.63    M          486                     .512~~ 5 S
  20.92    M         1086                    1.145
~~21.85               762                     .803~~ 5 B
~~22.74               115                     .121~~ 3 B
~~23.86               496                     .523~~ B
  24.68               204                     .215 1
  24.92    M   710  29783                   31.41
~~25.94    T          563                     .593~~ 7 B
~~26.33    TM         123                     .129~~ 7 B
~~26.93               741                     .781~~ 4 B
~~28.00               473                     .498~~ 8 B
~~28.20    M          971                    1.024~~ B
```



surface water sample
COOK INLET # 19
fraction 2

RT	TYPE	AREA	AREA %	
~~10.86~~		~~395~~	~~1.033~~	B
16.43		160	.418 6	
16.69	M	1004	2.627	
~~17.27~~	~~M~~	~~8485~~	~~22.2~~	S
17.67	M	753	1.97	
~~18.05~~	~~M~~	~~565~~	~~1.470~~	B
~~18.81~~		~~2825~~	~~7.391~~	S
19.02	M	2081	5.445	
19.31	M	6094	15.94	
20.26		101	.264 3	
~~20.63~~		~~791~~	~~2.07~~	S
21.44		3763	9.846	
21.77	M	2395	6.266	
~~22.62~~		~~218~~	~~.570 4~~	B
23.29		413	1.081	
~~24.00~~		~~144~~	~~.376 8~~	B
24.35		287	.750 9	
~~24.60~~		~~346~~	~~.905 3~~	B
24.92	M	119	.311 4	
26.08		4655	12.18	
27.99		392	1.026	
~~28.20~~	~~M~~	~~929~~	~~2.431~~	B
~~28.57~~	~~M~~	~~244~~	~~.638 4~~	B
~~29.51~~		~~502~~	~~1.313~~	B
~~30.65~~		~~559~~	~~1.463~~	B

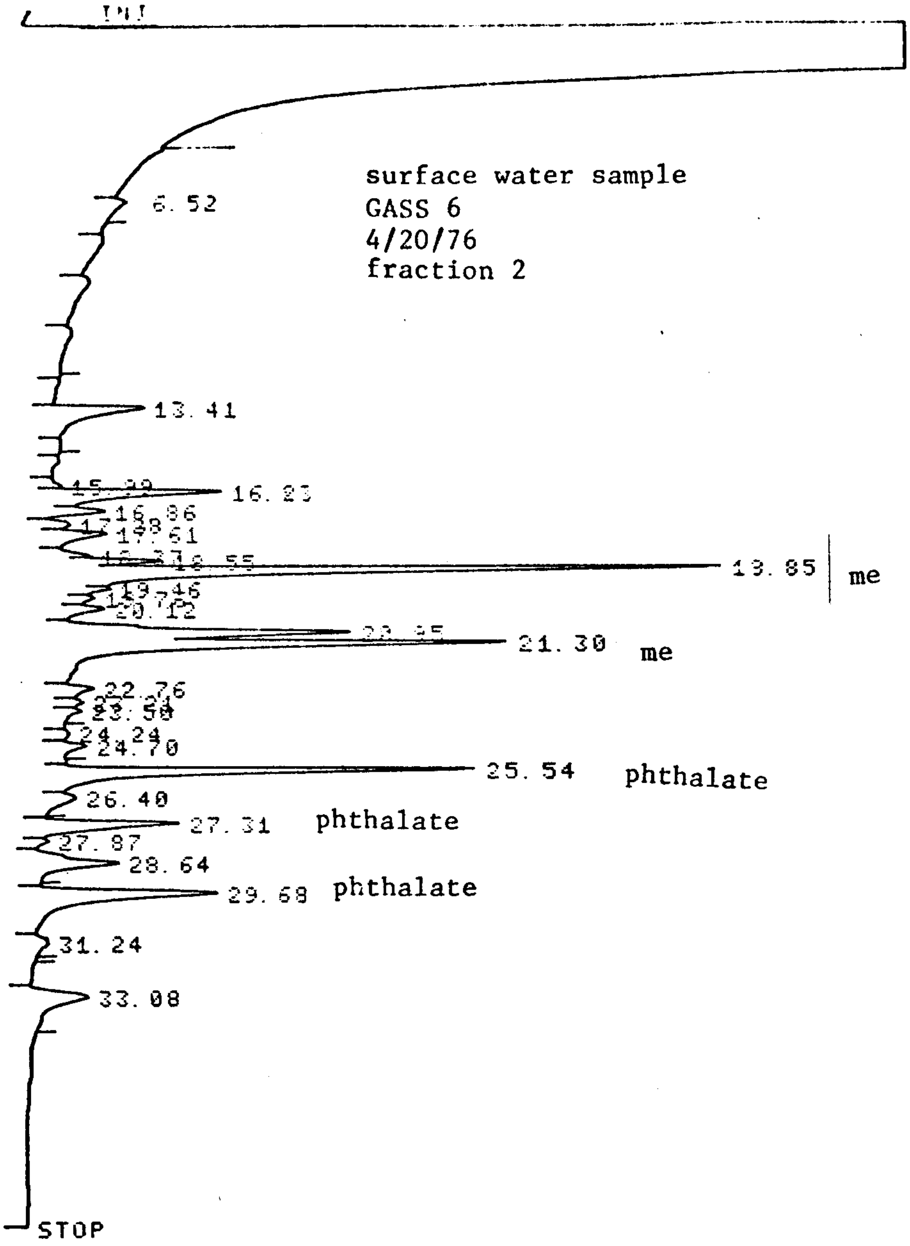
```
HP 3380A
DLY  2.            STOP 45          REJECT   100
MV/M  .10          ATTN     4
```



surface water sample
GASS 6
4/20/76
fraction 1

RT	TYPE	AREA	AREA %		
4.12	T	312	.557	3	
4.39	TM	201	.359		
4.79	T	267	.476	9	
6.48	T	1387	2.478		
14.64		518	.925	3	
16.11		2059	3.678		
~~16.84~~	~~M~~	~~4761~~	~~8.504~~		S
17.54	M	1995	3.564		
~~18.36~~		~~1677~~	~~2.996~~		S
18.73	M	523	.934	2	
~~20.15~~		~~877~~	~~1.567~~		S
20.47	M	347	.619	8	
21.33		20579	36.76		
22.25	M	256	.457	3	
22.71		218	.389	4	
23.35		388	.693	1	
24.41		1033	1.845		
25.41		2394	4.276		
26.38	M	1907	3.406		
27.33		2241	4.003		
27.88	T	205	.366	2	
28.64		7860	14.04		
29.77		1631	2.913		
31.45		1384	2.472		
33.33		963	1.72		

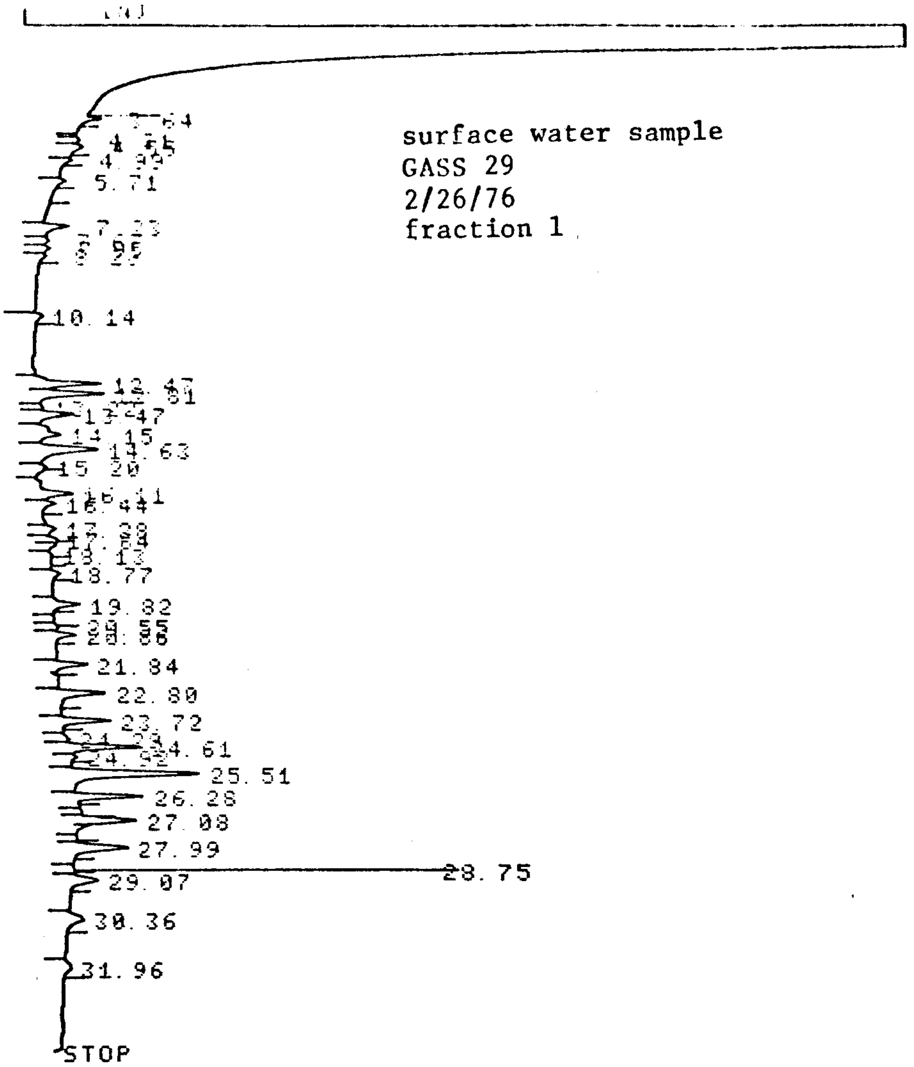
```
HP 3380A
DLY  4.            STOP 45 .          REJECT    100
```



surface water sample
GASS 6
4/20/76
fraction 2

AREA %

RT	TYPE	AREA			
6.52	T	1183	.585	2	
13.41		9828	4.861		
15.99		147	.072	71	
~~16.23~~	~~M~~	~~7113~~	~~3.510~~		β
~~16.86~~	~~T~~	~~2311~~	~~1.143~~		δ
17.28	TM	1195	.591	1	
17.61	TM	3765	1.862		
~~18.37~~	~~TM~~	~~789~~	~~.390~~	~~3~~	δ
18.55	M	4072	2.014		
18.85	M	42959	21.25		
19.46	T	280	.138	5	
19.76	TM	422	.208	7	
20.12	TM	1526	.754	8	
20.95	TM	23101	11.43		
21.30	M	33314	16.48		
22.76	M	2086	1.032		
23.21	M	1205	.596	5	
23.50	M	1057	.522	8	
24.24		267	.132	1	
24.70	M	1277	.631	6	
25.54		15619	7.726		
26.40	T	1521	.752	3	
27.31	T	10351	5.12		
27.87	TM	516	.255	2	
28.64	TM	8048	3.981		
29.68	T	18466	9.134		
31.24	TM	[illegible]	.674	2	

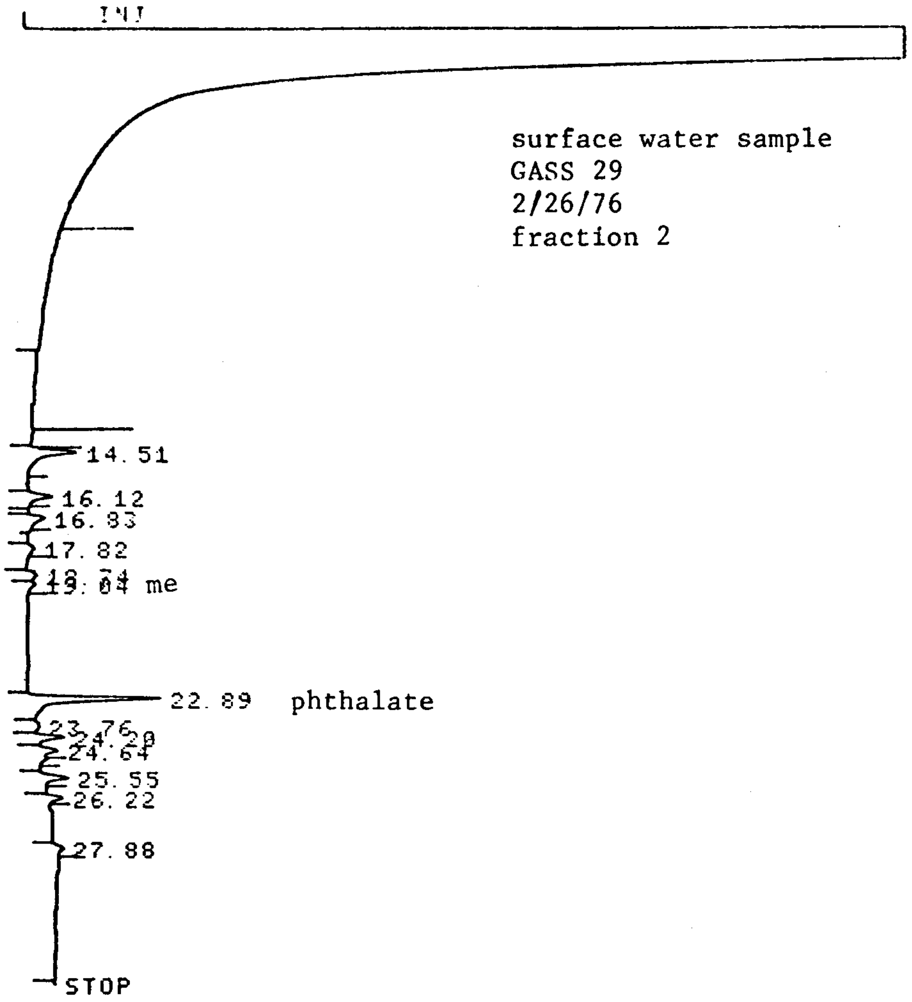


surface water sample
GASS 29
2/26/76
fraction 1

AREA %

RT	TYPE	AREA		
~~3.64~~	~~T~~	~~602~~	~~1.067~~	B
4.55	TM	437	.774 8	
4.99	T	174	.308 5	
5.71	T	368	.652 4	
~~7.23~~		~~1206~~	~~2.138~~	B
~~7.67~~	~~M~~	~~506~~	~~.897 1~~	B
7.95	M	493	.874 1	
8.20	M	360	.638 3	
~~10.14~~		~~877~~	~~1.555~~	B
~~12.47~~		~~3092~~	~~5.482~~	B
~~12.81~~	~~M~~	~~3285~~	~~5.824~~	B
13.22	M	253	.448 6	
~~13.47~~	~~M~~	~~1750~~	~~3.103~~	B
~~14.15~~	~~M~~	~~1649~~	~~2.924~~	B
~~14.63~~	~~M~~	~~3507~~	~~6.218~~	S
15.20	M	169	.299 6	
~~16.11~~		~~2087~~	~~3.7~~	S
16.44	M	850	1.507	
~~17.28~~		~~297~~	~~.526 6~~	S
17.64	M	125	.221 6	
18.13		108	.191 5	
18.77		413	.732 2	
19.82		1322	2.344	
20.55		115	.203 9	
20.86		874	1.55	
21.84		1665	2.952	
~~22.80~~		~~2389~~	~~4.236~~	B
23.72		2107'	3.736	
24.29		240	.425 5	
~~24.61~~	~~M~~	~~3362~~	~~5.961~~	B
~~24.92~~	~~M~~	~~344~~	~~.609 9~~	B
~~25.51~~		~~7607~~	~~13.49~~	B
26.28	M	714 2833	5.023	
~~27.08~~		~~2607~~	~~4.622~~	B
~~27.99~~		~~2891~~	~~5.126~~	B
28.75		[illegible]	[illegible]	

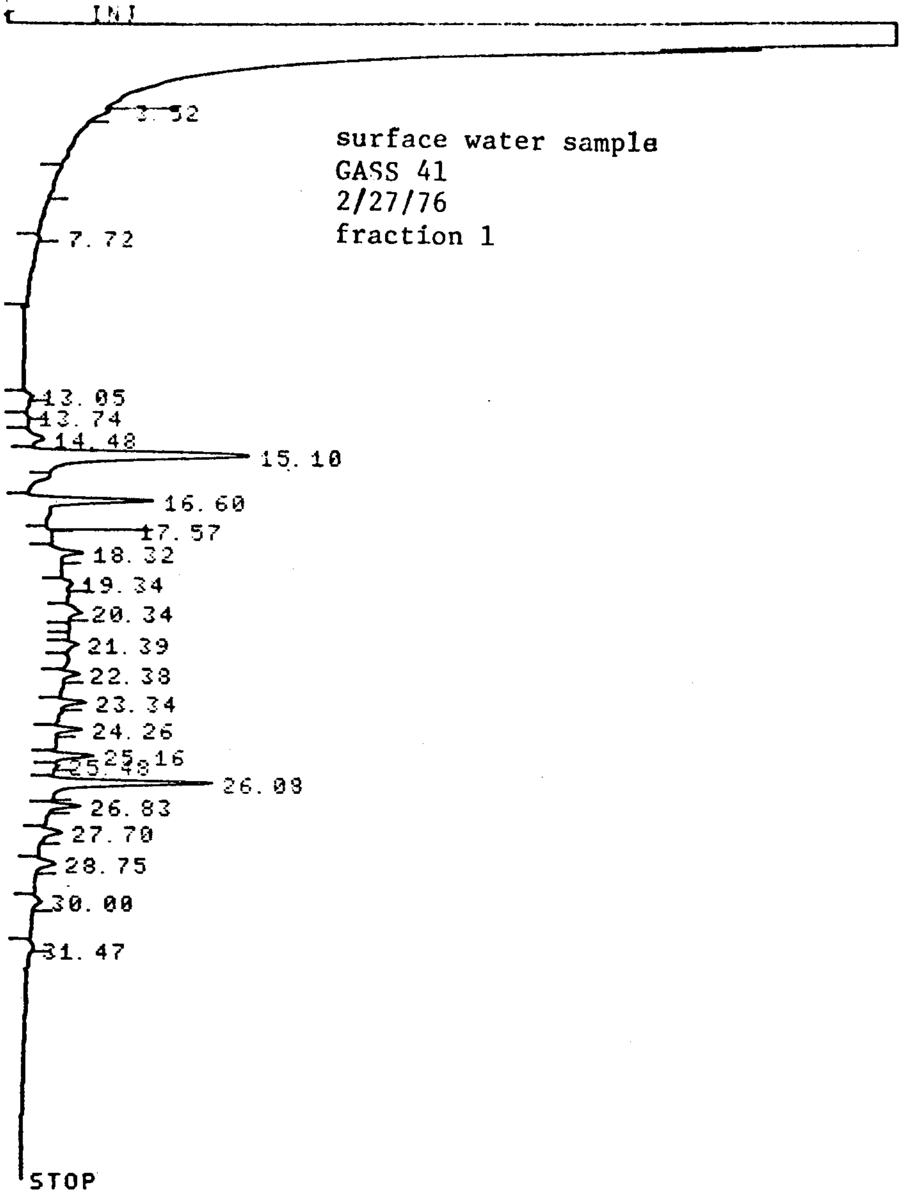
```
HP 3380A
DLY  2              STOP 45          REJECT   100
MV/M    10          ATTN      4
```



surface water sample
GASS 29
2/26/76
fraction 2

```
                          AREA %
   RT    TYPE       AREA
~~14.51                3294                16.45~~ S
~~16.12                1157                 5.777~~ S
~~16.83                 930                 4.644~~ S
~~17.82                 443                 2.212~~ S
 18.74                  696                 3.475
 19.04     M            619                 3.091
 22.89                 8281                41.35
~~23.76    T            346                 1.728~~ B
 24.20     TM          1197                 5.977
~~24.64    TM           759                 3.79~~ B
~~25.55                1198                 5.982~~ B
~~26.22                 660                 3.296~~ B
 27.88                  446                 2.227

HP 3380A
```



surface water sample
GASS 41
2/27/76
fraction 1

```
                         AREA %
   RT    TYPE      AREA
  3.52    T         387                 .788 9
  7.72              144                 .293 5
 13.05              249                 .507 6
 13.74              120                 .244 6
 14.48              939                1.914
~~15.10    M       17543               35.76~~  S
~~16.60             7428               15.14~~  S
 17.57    M         411                 .837 8
~~18.32             1393                2.839~~  S
~~19.34              432                 .880 6~~ B
 20.34             1099                2.24
 21.39              490                 .998 8
 22.38              757                1.543
 23.34             1113                2.269
 24.26             1165                2.375
~~25.16             1895                3.863~~  B
 25.48    M         211                 .430 1
~~26.08             8611               17.55~~  B
~~26.83             1258                2.564~~  B
~~27.70             1204                2.454~~  B
 28.75             1187                2.42
 30.00              659                1.343
 31.47              363                 .739 9
```

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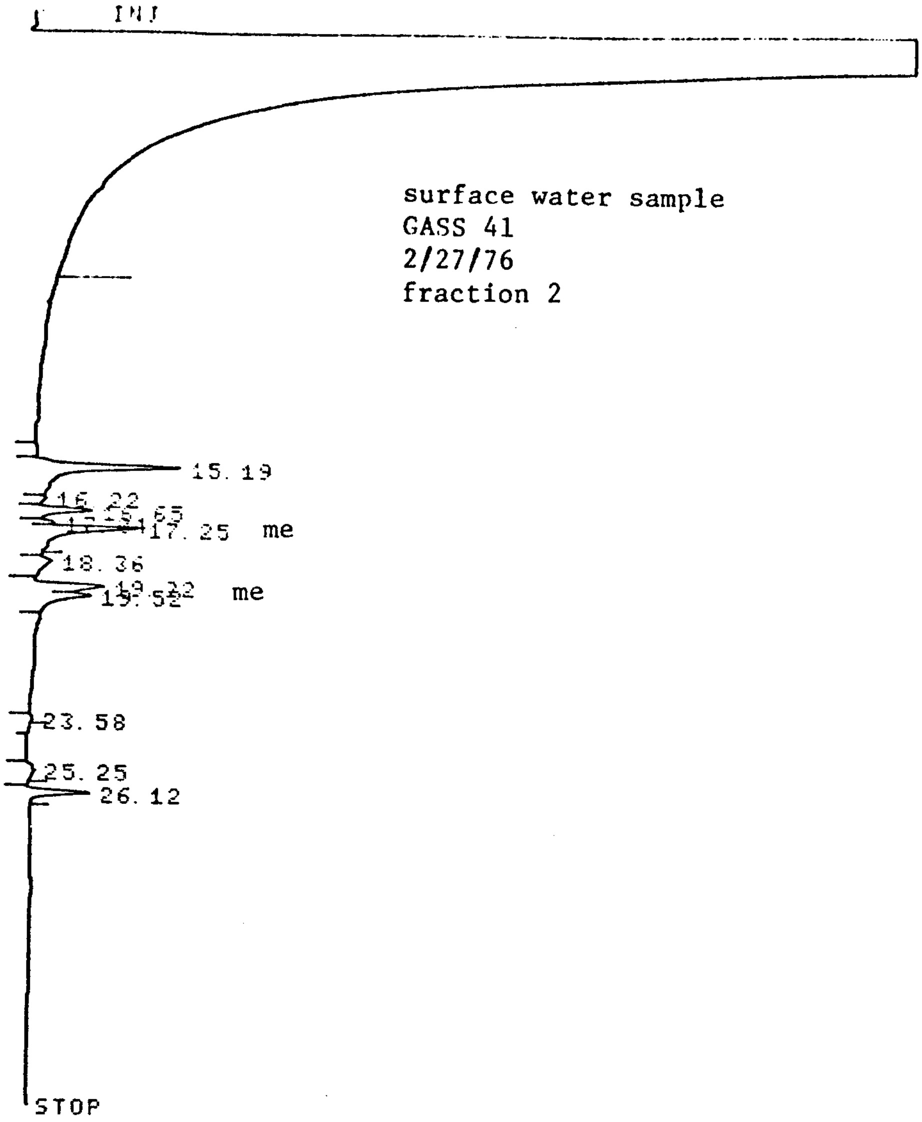
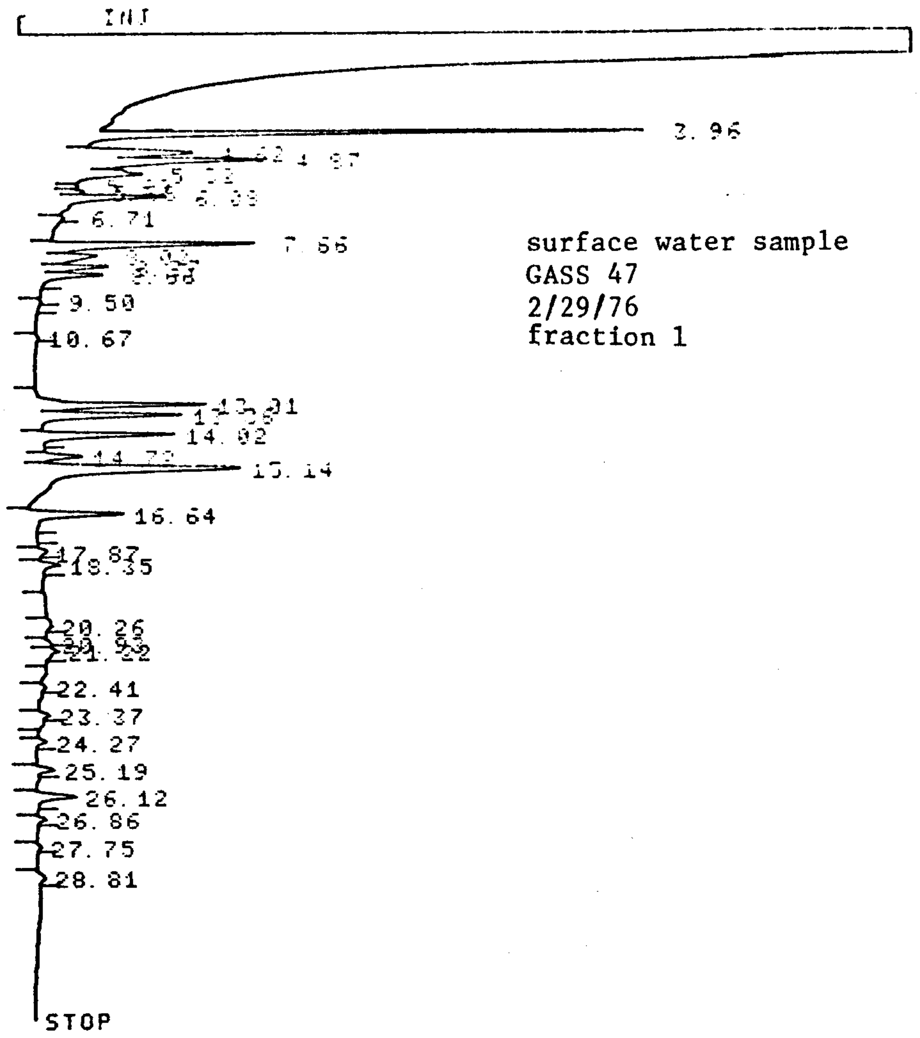
```
HP-3380A
DLY  2.            STOP 45            REJECT    10
MV/M   10          ATTN      4
```



surface water sample
GASS 41
2/27/76
fraction 2

RT	TYPE	AREA	AREA %
~~15.19~~		~~11284~~	~~31.5~~ S
16.22	T	178	496 9
~~16.65~~	~~TM~~	~~2460~~	~~6.867~~ S
17.04	TM	559	1.56
17.25	M	6783	18.93
~~18.36~~		~~1497~~	~~4.179~~ S
19.22	M	4820	13.46
19.52	M	4037	11.27
23.58		215	.600 2
~~25.25~~		~~857~~	~~2.392~~ B
~~26.12~~		~~3133~~	~~8.746~~ B

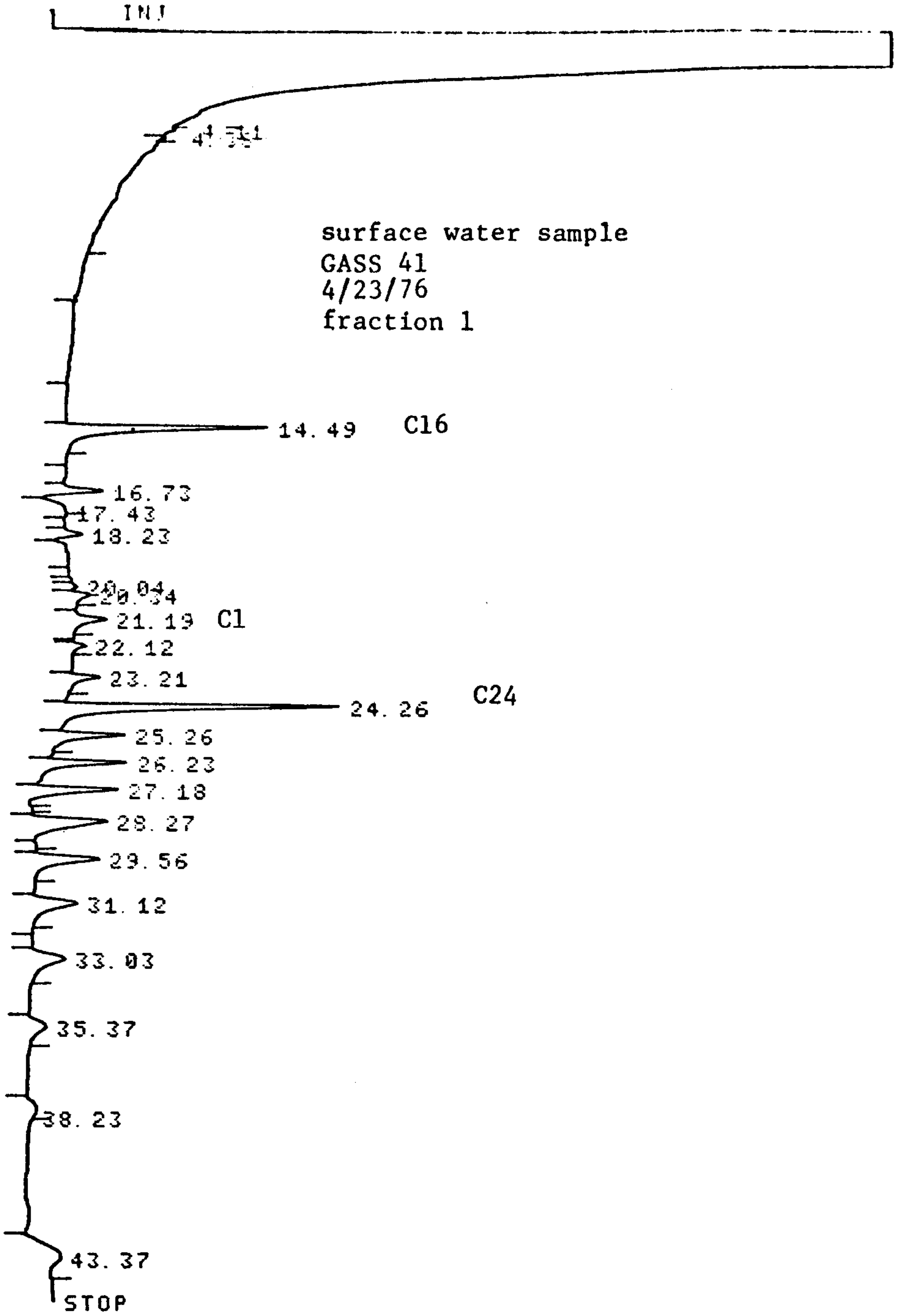
```
HP 3380A
DLY  2.           STOP 45          REJECT     10
MV/M    10        ATTN      4
```



surface water sample
GASS 47
2/29/76
fraction 1

AREA %

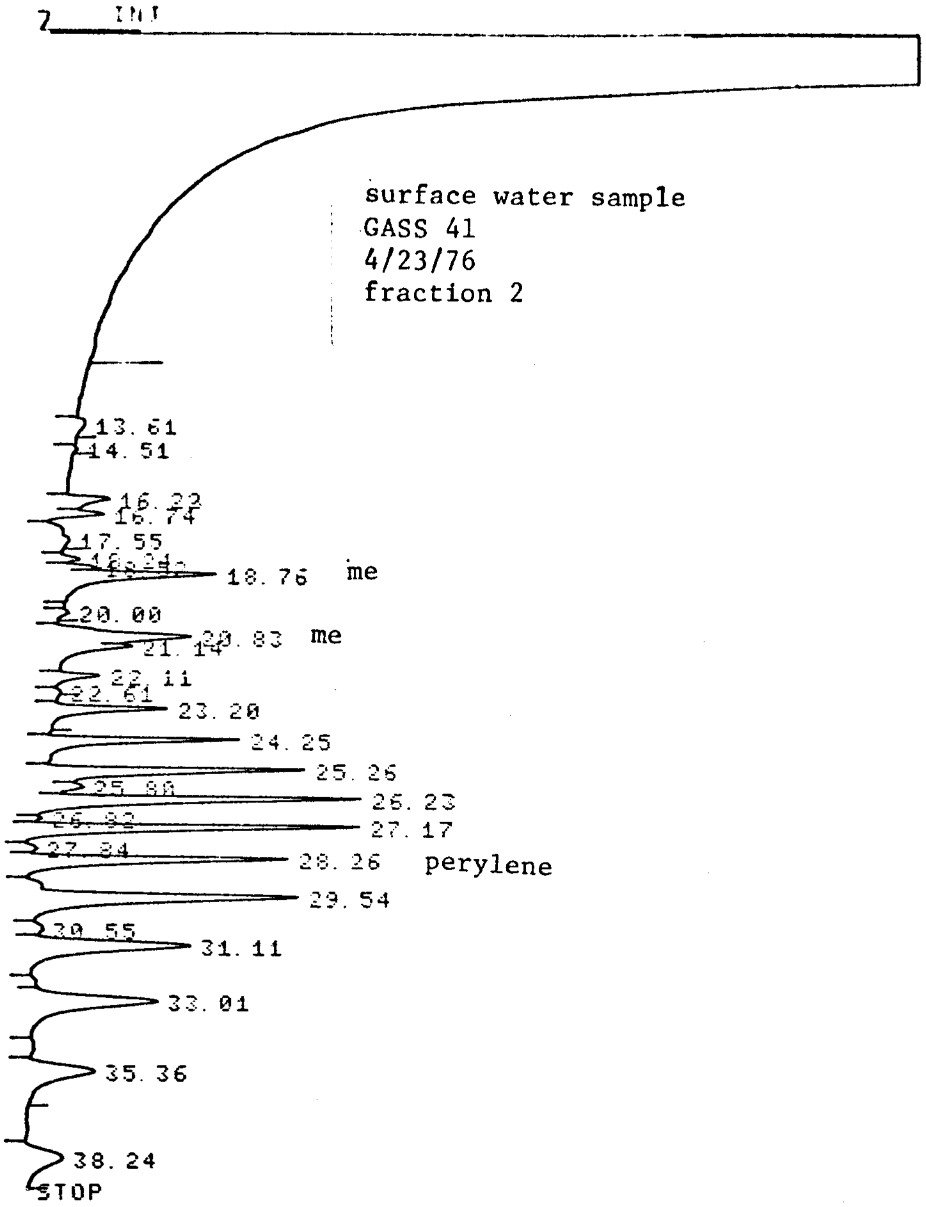
RT	TYPE	AREA		
3.96	T	19415	17.02	
4.62	TM	6757	5.922	
4.87	TM	9934	8.706	
5.32	TM	4637	4.064	
5.69	TM	284	.248	9
5.88	TM	599	.525	
6.08	TM	4791	4.199	
6.71	TM	182	.159	5
~~7.66~~	~~T~~	~~9214~~	~~8.075~~	B
8.02	TM	3128	2.741	
~~8.37~~	~~TM~~	~~2947~~	~~2.583~~	B
8.66	TM	2958	2.592	
9.50	T	107	.093	78
10.67		143	.125	3
~~13.01~~		~~8566~~	~~7.509~~	B
~~13.36~~	~~M~~	~~7164~~	~~6.279~~	B
~~14.02~~	~~M~~	~~5714~~	~~5.008~~	B
~~14.72~~		~~1902~~	~~1.667~~	B
~~15.14~~	~~M~~	~~12677~~	~~11.11~~	S
~~16.64~~	~~T~~	~~5051~~	~~4.427~~	
17.87		443	.388	3
~~18.35~~		~~882~~	~~.773~~	S
20.26		516	.452	2
20.93		54	.047	33
21.22		564	.494	3
22.41		262	.229	6
23.37		366	.320	8
24.27		459	.402	3
~~25.19~~		~~905~~	~~.793~~	2 S
~~26.12~~		~~2214~~	~~1.94~~	S
~~26.86~~		~~413~~	~~.362~~	B
~~27.75~~		~~295~~	~~.259~~	5 B
~~28.81~~		~~554~~	~~.485~~	5 B



surface water sample
GASS 41
4/23/76
fraction 1

AREA %

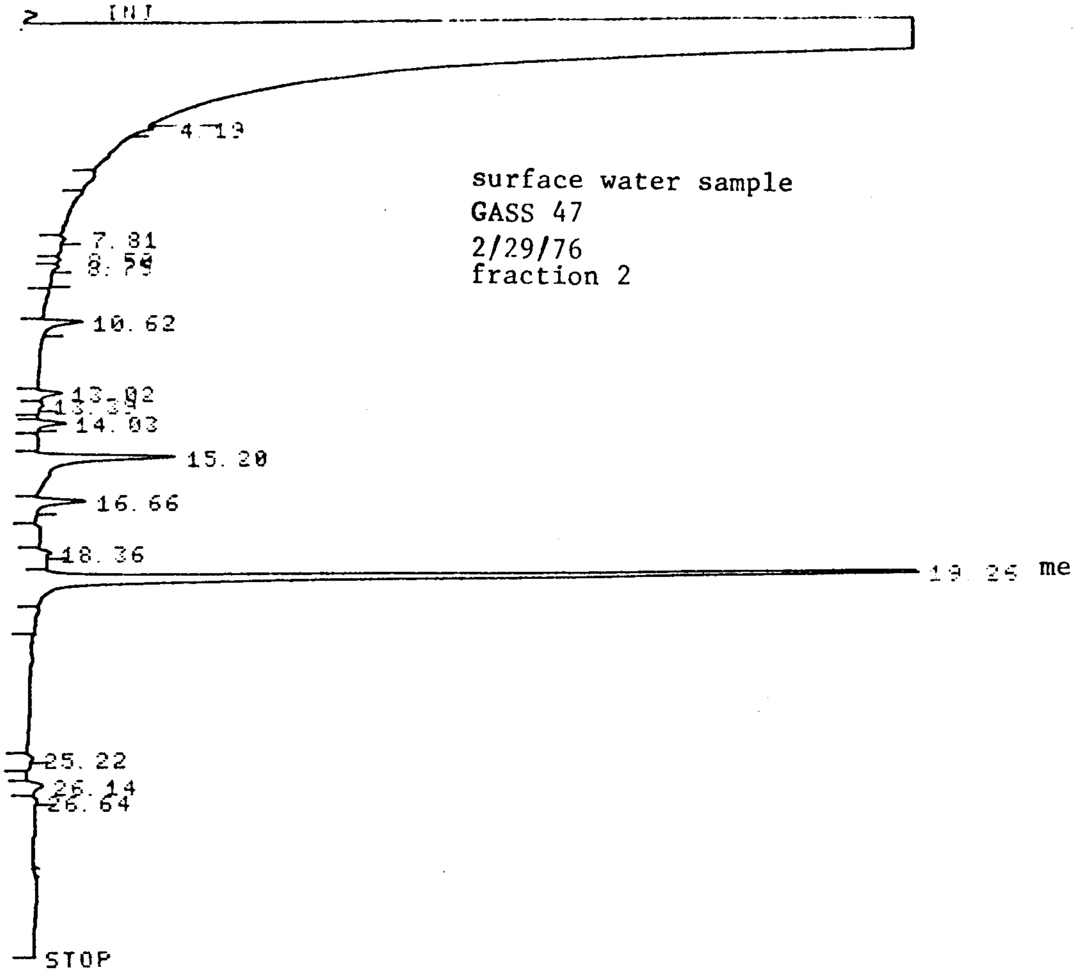
RT	TYPE	AREA		
4.11	T	226	.259	7
4.38	TM	143	.164	3
14.49		12846	14.76	
~~16.73~~		~~3260~~	~~3.746~~	S
17.43	M	1118	1.285	
~~18.23~~		~~1452~~	~~1.669~~	S
~~20.04~~		~~179~~	~~.205~~	~~7~~ S
20.34	M	1059	1.217	
21.19		2227	2.559	
22.12		578	.664	2
23 21		1900	2.183	
24.26		17068	19.61	
25.26	T	3987	4.582	
26.23	T	4798	5.514	
27.18	TM	5386	6.19	
28.27		7111	8.172	
29.56		5696	6.534	
31.12		4993	5.738	
33 03		4358	5.008	
35.37		2478	2.948	
38.23		1187 —	1.364	
4[illegible]		4977 —	5 7[illegible]	



surface water sample
GASS 41
4/23/76
fraction 2

AREA %

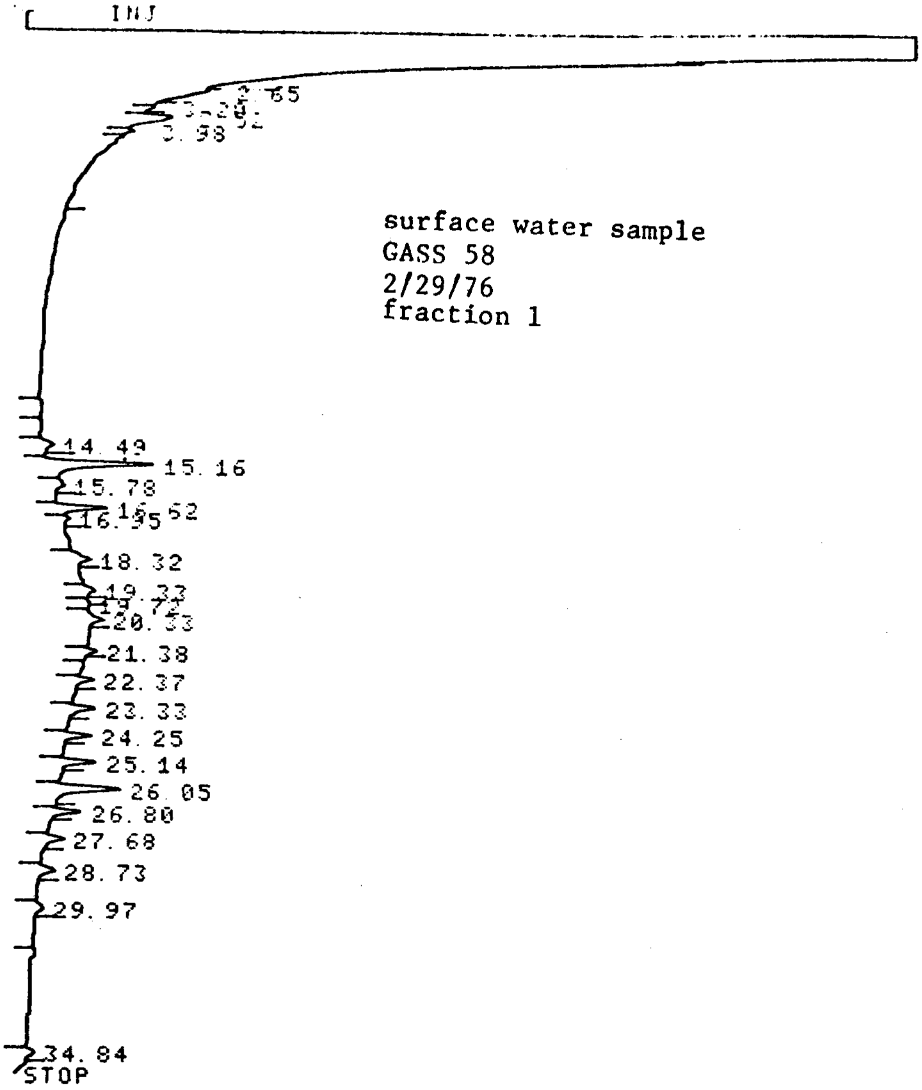
RT	TYPE	AREA		
13.61		1023	.467	2
14.51		194	.088	6
~~16.22~~		~~3705~~	~~1.692~~	B
~~16.74~~	~~M~~	~~3200~~	~~1.461~~	S
17.55	M	2202	1.006	
~~18.24~~		~~921~~	~~.420~~	~~6~~ S
18.52	M	1639	.748	5
18.76	M	14140	6.458	
~~20.00~~	~~T~~	~~427~~	~~.195~~	S
20.83		12280	5.608	
21.14	M	5798	2.648	
22.11	M	2427	1.108	
22.61	M	148	.067	59
23.20		6552	2.992	
24.25		10908	4.982	
25.26	M	17281	7.892	
25.80	T	864	.394	6
26.23	M	17933	8.19	
26.82	M	205	.093	62
27.17	M	19567	8.936	
27.84	M	673.	.307	4
28.26	M	18795	8.584	
29.54	M	26303	12.01	
30.55	M	1531	.699	2
31.11	M	17574	8.026	
33.01		15781	7.207	
35.36		9932	4.536	
38.24		6962	3.18	



surface water sample
GASS 47
2/29/76
fraction 2

```
                    AREA %
   RT    TYPE      AREA
  4.19    T         357                   .523
~~ 7.81    T         212                   .310~~  6 — B
~~ 8.50    T         205                   .301~~  8 — B
~~ 8.75    TM        264                   .386~~  7 — B
~~10.62             2011                  2.946~~    — B
~~13.02             1147                  1.68~~     — B
~~13.39    M         410                   .600~~  6 — B
~~14.03             1123                  1.645~~    — B
~~15.20            10369                 15.19~~     — S
~~16.66    T        2524                  3.698~~    — S
~~18.36              319                   .467~~  3 — S
 19.26             48086                 70.44
~~25.22              261                   .382~~  4 — B
~~26.14              745                  1.091~~    — B
 26.64    M         228                   .334

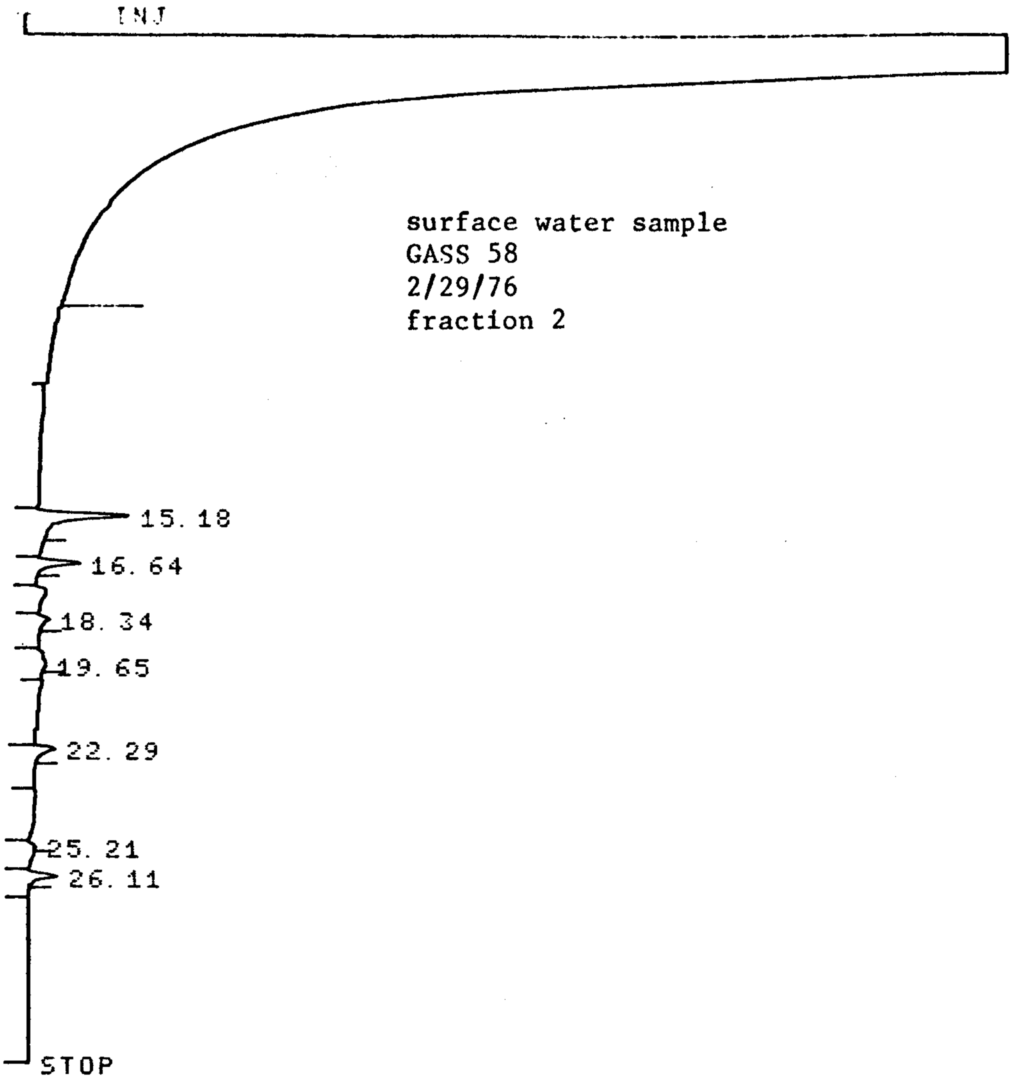
HP 3380A
DLY  2.           STOP 45           REJECT     10
MV/M  .10         ATTN      4
```



surface water sample
GASS 58
2/29/76
fraction 1

RT	TYPE	AREA	AREA %	
~~2.65~~	~~T~~	~~468~~	~~1.557~~	B
~~3.20~~	~~T~~	~~113~~	~~.376~~	B
~~3.52~~	~~T~~	~~2068~~	~~6.88~~	B
3.98	TM	232	.771	9
~~14.49~~		~~742~~	~~2.469~~	B
~~15.16~~		~~6427~~	~~21.38~~	S
15.78	M	953	3.171	
~~16.62~~		~~2370~~	~~7.885~~	S
16.95	M	476	1.584	
~~18.32~~		~~943~~	~~3.137~~	S
19.33		538	1.79	
19.72		119	.395	9
20.33		905	3.011	
21.38		530	1.763	
22.37		765	2.545	
23.33		1327	4.415	
24.25		1162	3.866	
~~25.14~~		~~1582~~	~~5.264~~	S
~~26.05~~		~~3821~~	~~12.71~~	S
~~26.80~~		~~1211~~	~~4.029~~	B
~~27.68~~		~~1097~~	~~3.65~~	B
~~28.73~~		~~1033~~	~~3.437~~	B
29.97		639	2.126	
34.84		535	1.78	

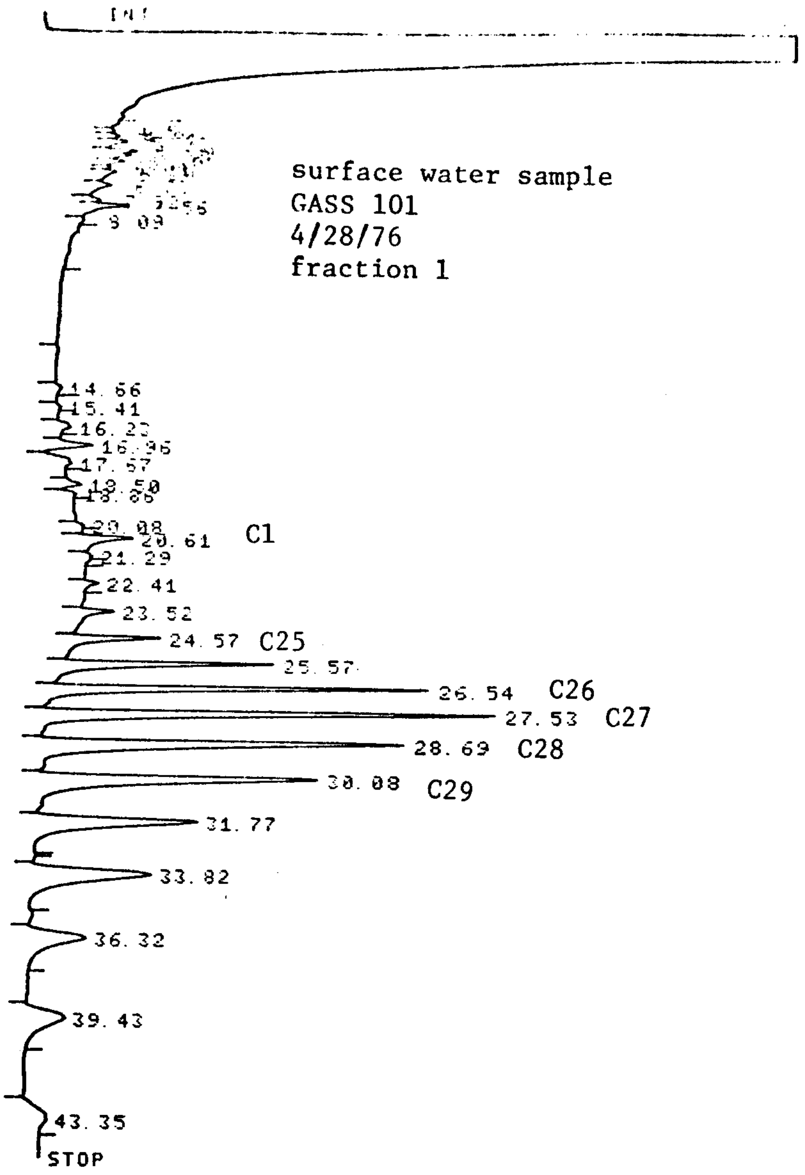
```
HP 3380A
DLY   2               STOP 45            REJECT     10
MV/M    10            ATTN      4
```



surface water sample
GASS 58
2/29/76
fraction 2

```
                              AREA %
    RT     TYPE        AREA
~~15.18                 5422.              45.83~~ S
~~16.64                 2002               16.92~~ S
~~18.34                  600                5.072~~ S
 19.65                   840                7.101
 22.29                  1285               10.86
 25.21                   207                1.75
 26.11                  1474               12.46

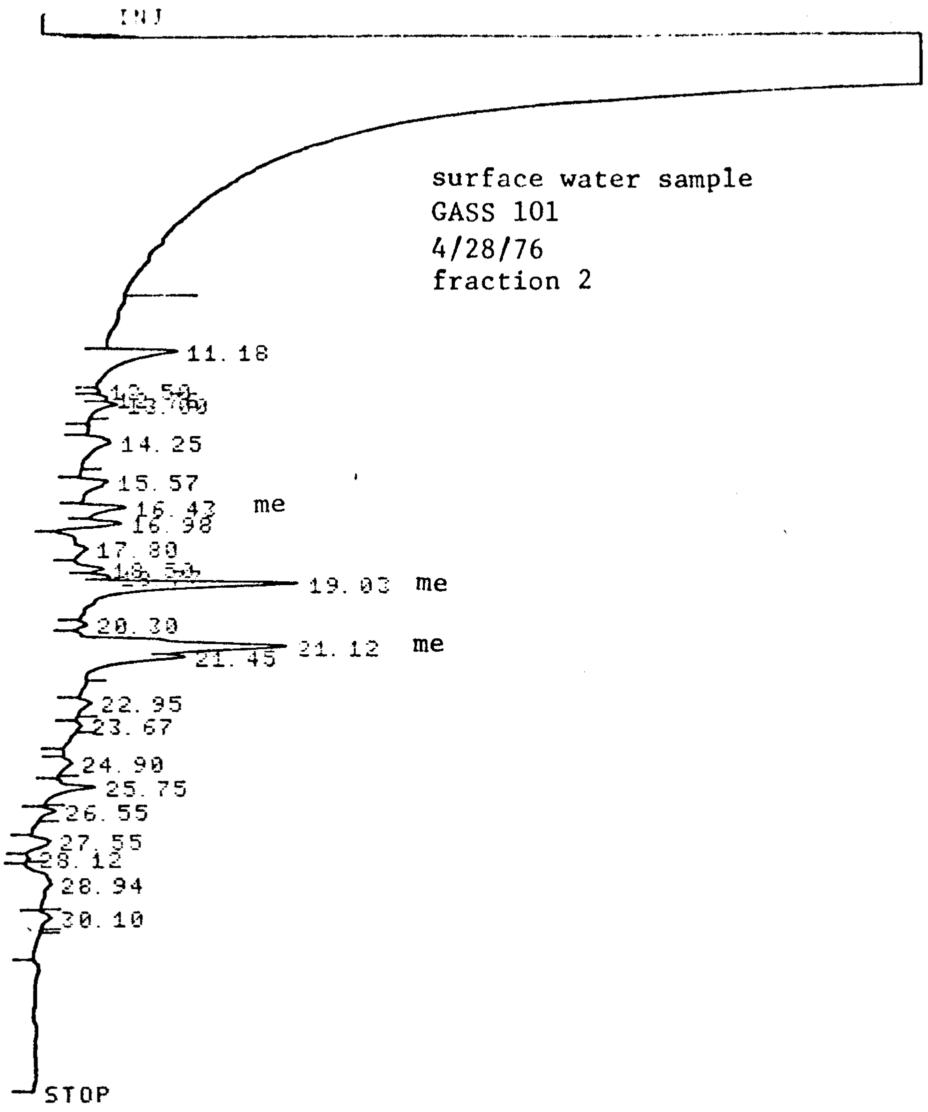
HP 3380A
DLY  2.          STOP 45          REJECT     10
MV/M   10        ATTN      4
```



surface water sample
GASS 101
4/28/76
fraction 1

AREA % ·

RT	TYPE	AREA		
4.58	T	150	.061 58	
4.81	TM	529	.217 2	
5.03	TM	1177	.483 2	
5.39	TM	1471	.603 9	
5.55	TM	1452	.596 1	
5.80	TM	1289	.529 2	
6.01	TM	538	.220 9	
6.20	TM	1726	.708 6	
6.73	TM	1561	.640 8	
7.32	TM	725	.297 6	
7.56	TM	3030	1.244	
8.09	TM	251	.103	
14.66		484	.198 7	
15.41		234	.096 06	
16.23		1153	.473 3	
~~16.96~~		~~3209~~	~~1.314~~	S
17.67	M	1902	.780 8	
~~18.50~~		~~1222~~	~~.502 1~~	S
18.86	M	558	.229 1	
~~20.08~~		~~146~~	~~.059 94~~	S
20.61		4799	1.97	
21.29	T	208	.085 39	
22.41		786	.322 7	
23.52		3306	1.357	
24.57	M	7134	2.929	
25.57	M	154[illegible]	6.326	
26.54	M	24[illegible]45	9.934	
27.53	M	32710	13.43	
28.69	M	35069	14.4	
30.08	M	31524	12.93	
31.77	T	21266	8.73	
33.82		19307	7.926	
36.32		112[illegible]0	4.6[illegible]1	
39.43		96[illegible]	[illegible]	

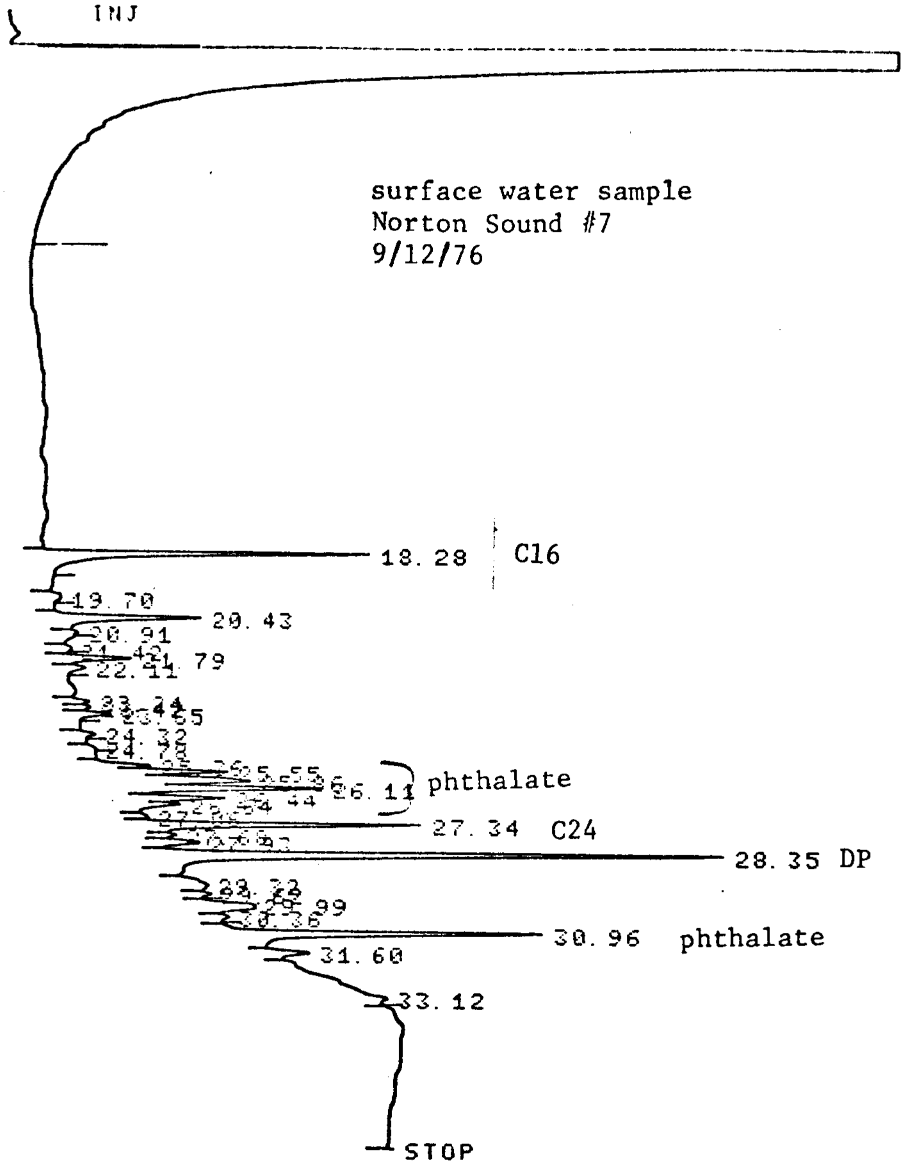


surface water sample
GASS 101
4/28/76
fraction 2

AREA %

RT	TYPE	AREA	AREA %	
11.18	T	7494	7.371	
12.50	TM	192	.188	9
12.76	TM	749	.736	7
13.00	TM	1654	1.627	
~~14.25~~	~~T~~	~~2914~~	~~2.866~~	B
15.57	T	4099	4.032	
16.43	TM	5325	5.238	
~~16.98~~	~~TM~~	~~4462~~	~~4.389~~	S
17.80	TM	4498	4.424	
~~18.50~~	~~TM~~	~~3160~~	~~3.108~~	S
18.77	TM	2446	2.406	
19.03	TM	21377	21.03	
20.30	TM	718	.706	2
21.12	TM	21409	21.06	
21.45	TM	8304	8.168	
22.95	T	1015	.998	4
23.67	T	311	.305	9
24.90	T	804	.790	8
25.75	T	2985	2.936	
26.55	T	732	.72	
27.55	T	1964	1.932	
~~28.12~~	~~TM~~	~~143~~	~~.140 7~~	B
~~28.94~~	~~T~~	~~4034~~	~~3.968~~	B
30.10	T	875	.860	7

HP 3380A
DLY 4 STOP 45 REJECT 100
MV/M 10 ATTN 4



surface water sample
Norton Sound #7
9/12/76

RT	TYPE	AREA	AREA %		
18.28		7953	12.25		
19.70		330	.508	3	
~~20.43~~		~~3431~~	~~5.285~~		S
20.91	M	134	.206	4	
21.42		167	.257	2	
~~21.79~~		~~1373~~	~~2.115~~		S
22.11	M	446	.687		
23.24		295	.454	4	
23.42	M	330	.508	3	
~~23.65~~	~~M~~	~~737~~	~~1.135~~		S
24.32		223	.343	5	
25.36		916	1.411		
25.55	M	2638	4.063		
25.86	M	4529	6.976		
26.11	M	4936	7.603		
26.44	M	2342	3.609		
26.64	M	1260	1.941		
27.06	M	272	.419		
27.34	M	5995	9.234		
27.68	M	553	.851	8	
27.93	M	1085	1.671		
28.35	M	13223	20.37		
29.32	M	806	1.242		
29.62	M	249	.383	5	
29.99		1835	2.827		
30.36	M	284	.437	5	
30.96		6888	10.61		
31.60	M	865	1.332		
33.12	M	824	1.269		

OCS COORDINATION OFFICE

University of Alaska

ENVIRONMENTAL DATA SUBMISSION SCHEDULE

DATE: March 31, 1977

CONTRACT NUMBER: 03-5-022-56 T/O NUMBER: 5 R.U. NUMBER: 275/276/294

PRINCIPAL INVESTIGATOR: Dr. D. G. Shaw

Submission dates are estimated only and will be updated, if necessary, each quarter. Data batches refer to data as identified in the data management plan.

Cruise/Field Operation	Collection Dates		Estimated Submission Dates[1]		
	From	To	Batch 1	2	3
Silas Bent Leg I #811	8/31/75	9/14/75	None	submitted	submitted
Discoverer Leg III #810	9/12/75	10/3/75	None	None	submitted
Discoverer Leg IV #812	10/3/75	10/16/75	(a)	None	submitted
Surveyor #814	10/28/75	11/17/75	None	submitted	None
North Pacific	4/25/75	8/7/75	submitted	None	None
Contract 03-5-022-34	Last	Year	submitted	submitted	submitted
Moana Wave MW 001	2/21/76	3/5/76	None	(a)	(a)
Miller Freeman	5/17/76	6/4/76	(a)	None	None
Glacier	8/18/76	9/3/76	None	(a)	None
Discoverer	9/10/76	9/24/76	None	(a)	(a)
Moana Wave	10/7/76	10/16/76	None	(a)	(a)
Acona	6/25/76	7/2/76	(a)	(a)	(a)

Note: [1] Data Management plan has been approved and made contractual.

(a) These data are contained in this Annual Report, which constitutes a data submission.

ANNUAL REPORT

Research Unit 413

TRACE METAL CONTENT OF BOTTOM SEDIMENT IN NORTHERN BERING SEA

Principal Investigator: Hans Nelson

U. S. Geological Survey

Menlo Park, California 94025

TRACE METAL CONTENT OF BOTTOM SEDIMENT IN NORTHERN BERING SEA - ANNUAL REPORT

1977 - Hans Nelson

Parts I, II, III, IV, and V.

We hope to complete baseline maps of selected groups of trace elements as outlined in the work statement. At present all analyses have been completed and all data resides on data files in computer storage. We are in the process of integrating all old and new bulk data sets into one master set with latitude and longitude locations and environmental information. When data files are complete, a table of all data will be listed out and Fisher K statistics will be run. On the basis of statistical results, elements will be plotted onto maps contoured into the third dimension by computer graphics. Our bulk data maps should be completed by June.

Enclosed is an example of a computer listing of elements Fisher K statistics that have been completed on part of the bulk set. Also enclosed is an example of a completed report on mercury for the Kuskokwim region. Others will follow as computer processing and maps are completed.

DATE 2/20/77

NO. BERING SEA, RAW DATA

SAMPLE	LATITUDE	LONGITUD	FE %-S	MG %-S	CA %-S	TI %-S	MN PPM-S	B PPM-S	BA PPM-S	CU PPM-S
69AMC100	63.6533	162.4850	5.0000	1.0000	2.0000	0.5000	1500.0000	100.0000	1000.0000	20.0000
69AMC101	64.1617	164.1267	3.0000	0.7000	2.0000	0.5000	700.0000	100.0000	1000.0000	10.0000
69AMC105	64.1767	166.5617	2.0000	0.7000	2.0000	0.5000	500.0000	100.0000	700.0000	10.0000
69AMC107	63.9667	167.3133	1.5000	0.3000	1.0000	0.3000	300.0000	100.0000	700.0000	7.0000
69AMC114	62.5233	165.9917	3.0000	0.7000	3.0000	0.5000	700.0000	70.0000	1000.0000	15.0000
69AMC116	63.7083	165.3283	5.0000	1.0000	3.0000	0.5000	700.0000	100.0000	1000.0000	15.0000
69AMC118	63.7600	166.0117	3.0000	0.7000	2.0000	0.5000	500.0000	70.0000	1000.0000	15.0000
69AMC120	63.6583	164.6167	3.0000	0.7000	3.0000	0.5000	500.0000	70.0000	1000.0000	15.0000
69AMC121	63.5917	163.9833	5.0000	1.0000	3.0000	0.7000	1500.0000	100.0000	1000.0000	20.0000
69AMC122	64.3750	165.7467	2.0000	0.7000	0.7000	0.5000	500.0000	100.0000	700.0000	15.0000
69AMC155	63.8667	165.7389	1.5000	0.5000	1.5000	0.3000	300.0000	100.0000	700.0000	7.0000
69AMC200	64.4300	165.4211	2.0000	0.7000	1.5000	0.5000	700.0000	100.0000	300.0000	7.0000
69AMC204	63.7767	170.0250	1.5000	0.3000	1.5000	0.3000	200.0000	100.0000	1000.0000	7.0000
69AMC206	63.6733	170.0000	3.0000	1.0000	2.0000	0.7000	500.0000	150.0000	700.0000	10.0000
69AMC207	63.7283	169.9033	2.0000	0.5000	1.0000	0.5000	300.0000	150.0000	700.0000	7.0000
69AMC208	63.7100	169.6100	2.0000	0.5000	2.0000	0.5000	300.0000	100.0000	1000.0000	10.0000
69AMC209	63.8900	169.4967	1.5000	0.3000	1.0000	0.3000	300.0000	100.0000	700.0000	7.0000
69AMC215	63.9000	170.8083	2.0000	0.5000	2.0000	0.5000	300.0000	70.0000	1000.0000	10.0000
69AMC216	64.0150	170.8250	1.5000	0.3000	1.5000	0.3000	200.0000	70.0000	1000.0000	7.0000
69AMC220	63.8550	171.9900	1.5000	0.3000	1.5000	0.3000	200.0000	70.0000	1000.0000	7.0000
69AMC221	63.8600	172.3000	2.0000	0.5000	1.5000	0.5000	300.0000	70.0000	1000.0000	7.0000
69AMC222	63.9467	172.5167	2.0000	0.7000	5.0000	0.5000	300.0000	150.0000	1000.0000	10.0000
69AMC223	64.0150	172.4183	1.5000	0.5000	3.0000	0.3000	300.0000	150.0000	1000.0000	7.0000
69AMC224	63.9717	172.2133	3.0000	0.7000	3.0000	0.7000	500.0000	100.0000	1000.0000	10.0000
69AMC227	64.1367	171.7883	3.0000	0.5000	3.0000	0.5000	300.0000	100.0000	1500.0000	7.0000
69AMC229	64.1350	171.2186	1.5000	0.2000	0.7000	0.2000	200.0000	100.0000	1000.0000	5.0000
69AMC230	64.2167	170.8686	1.0000	0.3000	1.5000	0.2000	150.0000	100.0000	1000.0000	7.0000
69AMC232	64.2583	170.3000	2.0000	0.5000	3.0000	0.7000	500.0000	100.0000	1000.0000	15.0000
69AMC235	64.4583	169.6617	1.0000	0.3000	0.5000	0.1500	150.0000	70.0000	700.0000	5.0000
69AMC237	65.0750	169.2450	1.5000	0.5000	0.7000	0.3000	300.0000	150.0000	500.0000	7.0000
69AMC245	65.1667	167.8867	1.5000	0.3000	0.7000	0.2000	300.0000	100.0000	700.0000	7.0000
69AMC247	65.2317	167.6583	1.5000	0.5000	1.0000	0.3000	500.0000	70.0000	700.0000	7.0000
69AMC250	65.1233	167.5000	0.7000	0.3000	0.7000	0.1500	200.0000	70.0000	500.0000	2.0000
69AMC251	65.1050	167.6200	0.7000	0.3000	0.7000	0.1500	150.0000	70.0000	500.0000	3.0000
69AMC252	65.0850	167.7233	1.5000	0.3000	0.7000	0.3000	300.0000	100.0000	700.0000	7.0000
69AMC253	65.0900	167.7833	1.5000	0.2000	0.5000	0.2000	300.0000	100.0000	500.0000	7.0000
69AMC255	64.9500	168.2500	1.0000	0.3000	0.5000	0.3000	300.0000	100.0000	500.0000	5.0000
70AMC7B	63.2917	172.3000	2.0000	0.5000	1.5000	0.3000	200.0000	100.0000	1000.0000	7.0000
70AMC11B	63.3083	170.9317	2.0000	0.5000	3.0000	0.3000	500.0000	70.0000	700.0000	7.0000
70AMC13B	63.1367	170.4667	2.0000	0.5000	2.0000	0.3000	500.0000	100.0000	700.0000	7.0000
70AMC14B	62.3133	170.6133	2.0000	0.7000	2.0000	0.5000	500.0000	100.0000	700.0000	10.0000
70AMC15B	62.9617	170.4567	2.0000	0.7000	3.0000	0.5000	300.0000	100.0000	1000.0000	10.0000

```
D0010  FISHER-K STATISTICS  -  U S G S STATPAC (07/15/76)                                                   DATE   2/20/77

                                                        NO. BERING SEA DATA, LOGS

       THE FOLLOWING STATISTICS ARE COMPUTED FOR THE UNQUALIFIED VALUES ONLY
 NO COLUMN             K1             SQRT(K2)             K2                K3                G1                K4                G2
                      MEAN          STD DEVIATION       VARIANCE                            SKEWNESS                          KURTOSIS
 28 LOG FE-S     0.3690048E+00     0.2085793E+00     0.4350531E-01     0.6572922E-02     0.7243445E+00     0.3089283E-02     0.1632200E+01
 29 LOG MG-S    -0.9919621E-01     0.2905827E+00     0.8443832E-01     0.2072453E-01     0.8446472E+00     0.1553157E-01     0.2178393E+01
 30 LOG CA-S     0.2379829E+00     0.3056527E+00     0.9342329E-01    -0.6307262E-02    -0.2206809E+00     0.4665647E-02     0.5345662E+00
 31 LOG TI-S    -0.3565886E+00     0.2029614E+00     0.4119334E-01    -0.3454819E-02    -0.4132233E+00    -0.1964540E-03    -0.1157729E+00
 32 LOG MN-S     0.2619236E+01     0.2568426E+00     0.6596811E-01     0.1976614E-01     0.1166597E+01     0.1236097E-01     0.2640432E+01
 33 LOG B -S     0.1915096E+01     0.2353227E+00     0.5537679E-01    -0.2817250E-01    -0.2161691E+01     0.2757179E-01     0.6991030E+01
 34 LOG BA-S     0.2748425E+01     0.2149210E+00     0.4619105E-01    -0.1312902E-01    -0.1322500E+01     0.3597101E-02     0.1665920E+01
 35 LOG CO-S     0.1095679E+01     0.2511416E+00     0.6307212E-01     0.1171839E-01     0.7397957E+00     0.5930168E-02     0.1470712E+01
 36 LOG CR-S     0.1673397E+01     0.2555532E+00     0.6530085E-01     0.2022569E-02     0.1207622E+00     0.5457699E-02     0.1276019E+01
 37 LOG CU-S     0.1139414E+01     0.3234581E+00     0.1046251E+00     0.3836935E-01     0.1133765E+01     0.4102874E-01     0.3746143E+01
 38 LOG LA-S     0.1626045E+01     0.1932798E+00     0.3735707E-01    -0.4719782E-02    -0.6536762E+00     0.9129592E-04     0.6541927E-01
 39 LOG NB-S     0.1065376E+01     0.1562176E+00     0.2441331E-01    -0.1145439E-03    -0.3002830E-01    -0.2592082E-03    -0.4349061E+00
 40 LOG NI-S     0.1358413E+01     0.2976256E+00     0.8858102E-01     0.4130028E-01     0.1566542E+01     0.5580362E-01     0.7111825E+01
 41 LOG PB-S     0.1270873E+01     0.2184778E+00     0.4773253E-01     0.2539816E-01     0.2483403E+01     0.3087130E-01     0.1354958E+02
 42 LOG SC-S     0.1121192E+01     0.1676785E+00     0.2811609E-01    -0.2981379E-02    -0.6323895E+00    -0.4390492E-03    -0.5553967E+00
 43 LOG SR-S     0.2342643E+01     0.2422416E+00     0.5868098E-01    -0.5097478E-02    -0.3585992E+00     0.3618954E-02     0.1059677E+01
 44 LOG V -S     0.1971839E+01     0.1829628E+00     0.3347539E-01    -0.1349269E-02    -0.2203009E+00    -0.5775681E-03    -0.5171936E+00
 45 LOG Y -S     0.1420664E+01     0.1779924E+00     0.3168130E-01     0.2172247E-02     0.3852164E+00     0.7453485E-04     0.7425975E-01
 46 LOG ZN-S     0.1853725E+01     0.2183067E+00     0.4765783E-01     0.6959606E-02     0.6689340E+00     0.9974430E-02     0.4391567E+01
 47 LOG ZR-S     0.2194491E+01     0.1935298E+00     0.3745380E-01     0.8943454E-02     0.1233847E+01     0.1041127E-01     0.7421844E+01
 49 LOG AL-S     0.7764083E+00     0.1402043E+00     0.1965724E-01    -0.6504372E-02    -0.2350051E+01     0.3996273E-02     0.1034213E+02
 49 LOG NA-S     0.2797549E+00     0.2294492E+00     0.5264693E-01    -0.3369262E-01    -0.2789188E+01     0.3421100E-01     0.1234297E+02
 50 LOG K -S     0.1976100E+00     0.2187779E+00     0.4786378E-01    -0.2008479E-01    -0.1918036E+01     0.1750445E-01     0.7640723E+01
 51 LOG GA-S     0.1168191E+01     0.1728703E+00     0.2988414E-01    -0.8768677E-02    -0.1697356E+01     0.3341304E-02     0.3741402E+01
 52 LOG YB-S     0.5521682E+00     0.1801947E+00     0.3247014E-01    -0.2924755E-02    -0.4998771E+00    -0.6330381E-04    -0.7901264E-01
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ANTILOGS

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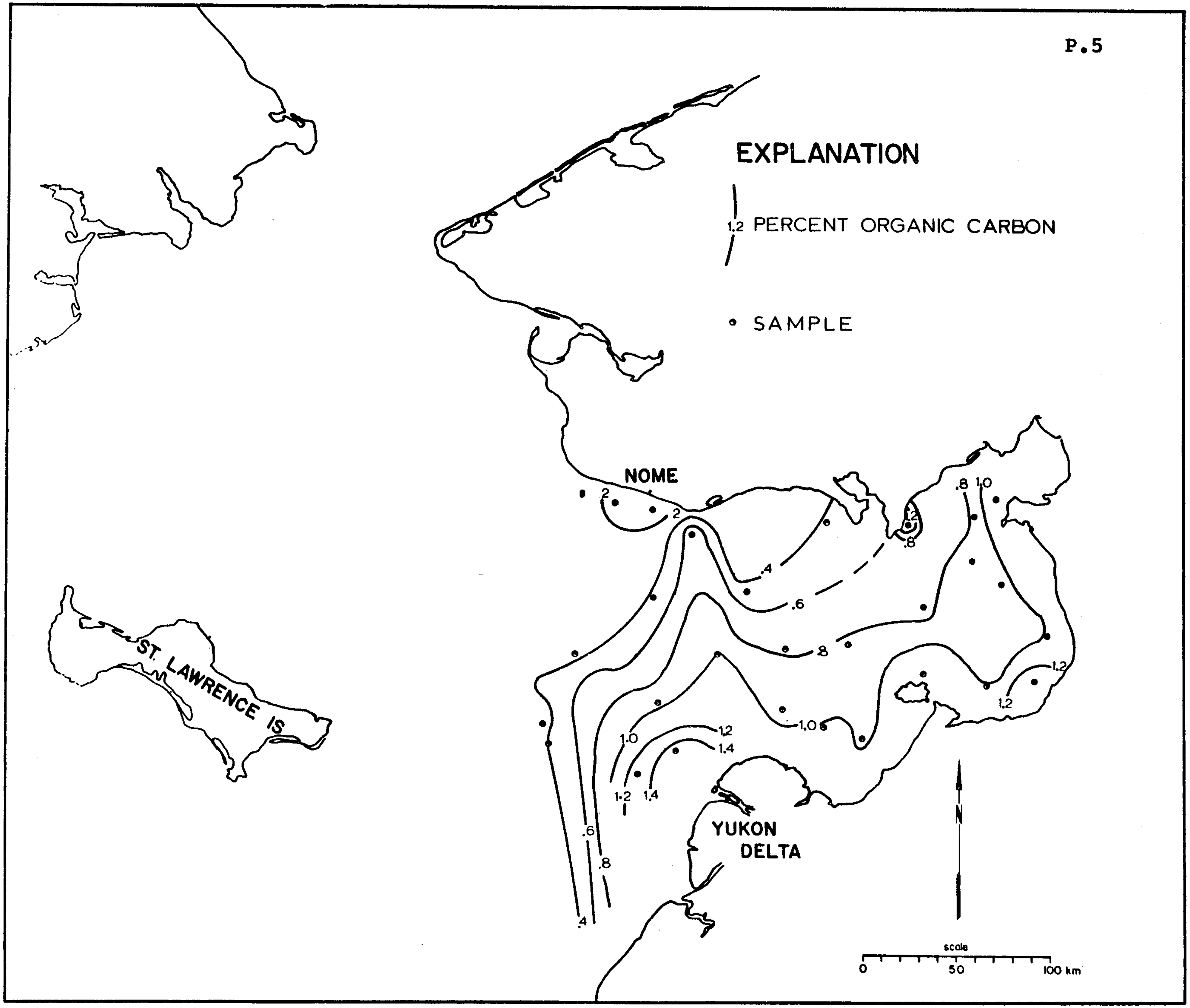
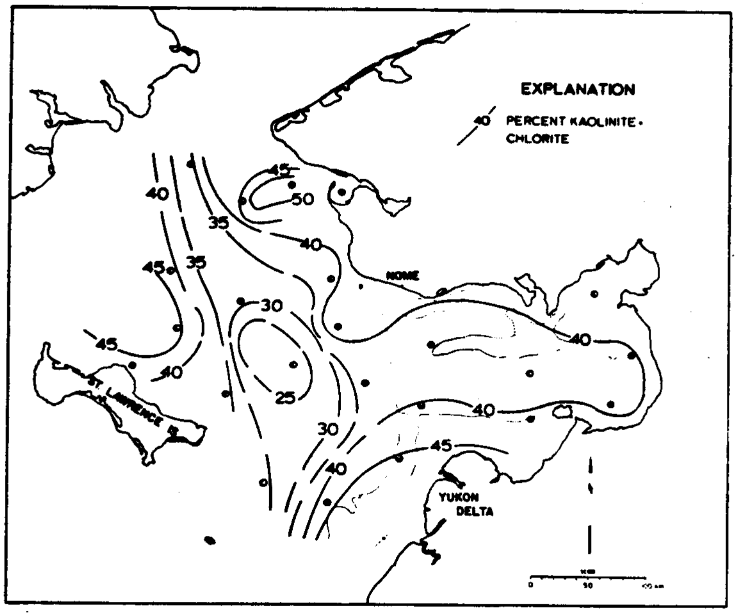
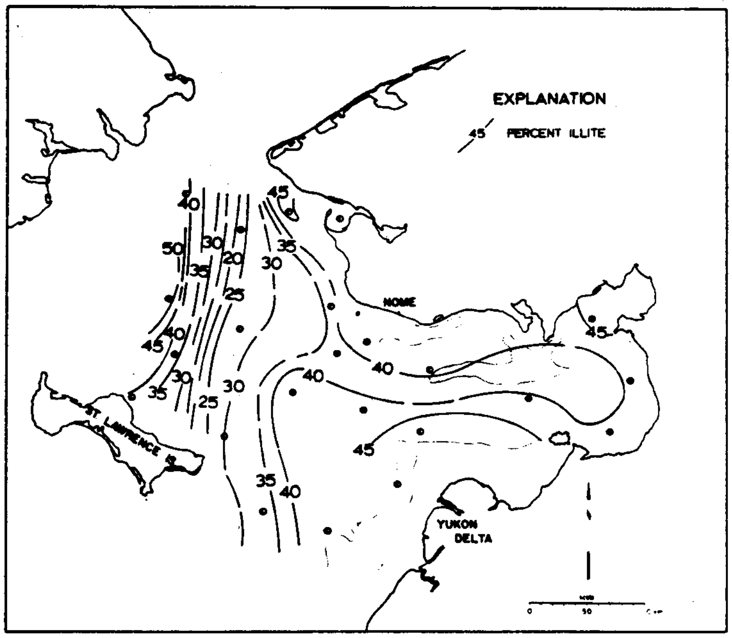
 NO COLUMN               GEOM MEAN        GEOM DEV
 28 LOG FE-S     0.2338863D+01     0.1616513D+01
 29 LOG MG-S     0.7957997D+00     0.1952463D+01
 30 LOG CA-S     0.1729746D+01     0.2021400D+01
 31 LOG TI-S     0.4399582D+00     0.1595737D+01
 32 LOG MN-S     0.4161163D+03     0.1805519D+01
 33 LOG B -S     0.8224276D+02     0.1719186D+01
 34 LOG BA-S     0.5603057D+03     0.1640292D+01
 35 LOG CO-S     0.1246162D+02     0.1782960D+01
 35 LOG CR-S     0.4714077D+02     0.1802403D+01
 37 LOG CU-S     0.1376524D+02     0.2105993D+01
 38 LOG LA-S     0.4227122D+02     0.1560557D+01
 39 LOG NB-S     0.1162454D+02     0.1433005D+01
 40 LOG NI-S     0.2335664D+02     0.1981384D+01
 41 LOG PB-S     0.1865840D+02     0.1653790D+01
 42 LOG SC-S     0.1322499D+02     0.1471223D+01
 43 LOG SR-S     0.2201114D+03     0.1746794D+01
 44 LOG V -S     0.9372142D+02     0.1523922D+01
 45 LOG Y -S     0.2670937D+02     0.1506581D+01
 46 LOG ZN-S     0.7130415D+02     0.1553129D+01
 47 LOG ZR-S     0.1566916D+03     0.1561435D+01
 48 LOG AL-S     0.5975069D+01     0.1381634D+01
 49 LOG NA-S     0.1904366D+01     0.1696091D+01
 50 LOG K -S     0.1576195D+01     0.1654924D+01
 51 LOG GA-S     0.1477059D+02     0.1489916D+01
```

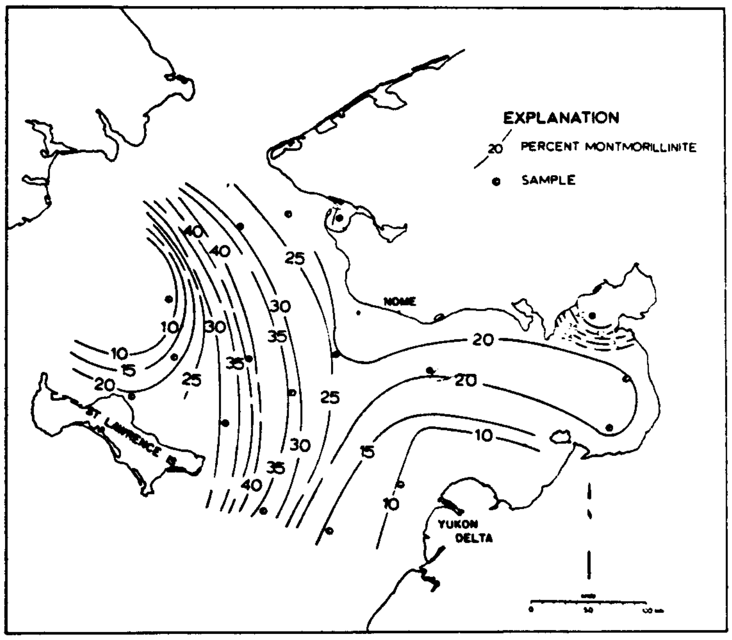
Element	S4-76 St. G. Basin		S4-76 Misc. Surf. Sediments		Northern Bering Sea (N = 221)		Northern Bering Sea (TT & S spls)	
	Geom. Mean	Geom. Dev.	Geom. Mean	Geom. Dev.	Geom. Mean	Geom. Dev.	Geom. Mean	Geom. Dev.
Al (%)					6.0	1.38	6.8	1.23
Ca (%)			3.6	1.29	1.7	2.02	2.2	1.53
Mg ($)	1.1	1.24	1.7	1.35	0.80	1.95	0.84	1.31
Fe (%)			4.1	1.36	2.3	1.62	2.4	1.40
K (%)			2.4	1.23	1.6	1.65	1.7	1.22
Na (%)	2.5	1.17	2.9	1.34	1.9	1.70	2.4	1.26
Ti (%)			0.36	1.34	0.44	1.60	0.55	1.31
B (ppm)	35	1.42	40	1.49	82	1.71	85	1.68
Ba (ppm)	580	1.24	710	1.24	560	1.64	590	1.23
Co (ppm)	11	1.37	10	1.38	12	1.78	12	1.30
Cr (ppm)	50	1.57	72	1.46	47	1.80	53	1.48
Cu (ppm)	30	1.92	22	1.80	13	2.10	15	1.52
Ga (ppm)	17	1.22	16	1.17	15	1.56	17	1.21
Mn (ppm)			470	1.25	420	1.81	380	1.52
Ni (ppm)	20	1.51	30	1.56	23	1.98	21	1.31
Sc (ppm)	15	1.29	14	1.25	13	1.47	17	1.23
Sr (ppm)	350	1.39	420	1.28	220	1.75	259	1.38
V (ppm)	130	1.42	110	1.42	94	1.52	116	1.23
Y (ppm)	24	1.32	25	1.25	27	1.51	25	1.38
Yb (ppm)	2.8	1.28	2.8	1.15	3.6	1.51	4.5	1.29
Zn (ppm)	80	1.32			71	1.65	68	1.27
Zr (ppm)	91	1.29	110	1.52	160	1.56	160	1.45


P.5

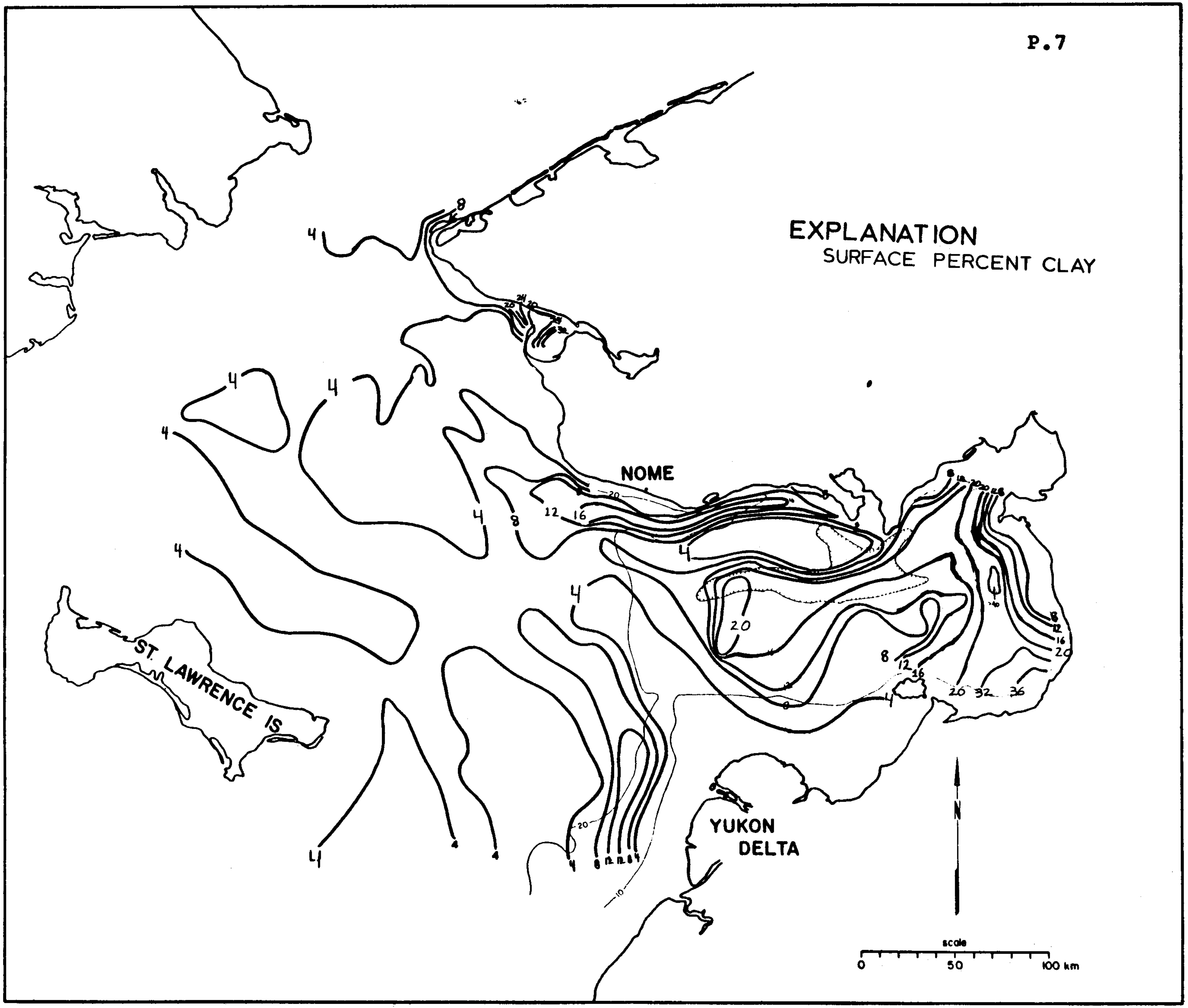
EXPLANATION
1.2 PERCENT ORGANIC CARBON
SAMPLE
NOME
ST. LAWRENCE IS
YUKON DELTA
2
2
.4
.6
.8
1.0
1.2
1.4
.8
1.0
1.2
1.2
1.0
1.2
1.4
1.2
1.4
.6
.8
.4
.8
N
scale
0
50
100 km


EXPLANATION
40 PERCENT KAOLINITE + CHLORITE
40
45
50
35
40
45
35
30
45
40
25
30
40
45
40
NOME
ST LAWRENCE IS
YUKON DELTA
0 50 100 km


EXPLANATION
45 PERCENT ILLITE
40
45
50
30
20
35
30
35
25
45
40
30
35
25
30
40
40
45
45
35
40
NOME
ST LAWRENCE IS
YUKON DELTA
0 50 100 km


EXPLANATION
20 PERCENT MONTMORILLINITE
SAMPLE
40
40
25
30
10
30
35
10
15
35
20
25
25
20
20
10
15
30
35
40
10
NOME
ST LAWRENCE IS
YUKON DELTA
0 50 100 km

P.7


EXPLANATION
SURFACE PERCENT CLAY
NOME
ST. LAWRENCE IS.
YUKON DELTA
N
scale
0
50
100 km
4
8
12
16
20
24
28
32
36

MERCURY DISPERSAL FROM LODE SOURCES IN THE KUSKOKWIM RIVER DRAINAGE, ALASKA

Hans Nelson, Bradley R. Larsen,
Everett A. Jenne and D. H. Sorg
U. S. Geological Survey
Menlo Park, California 94025

ABSTRACT

The Kuskokwim River is not industrially polluted, but has anomalous Hg content from cinnabar particles in bottom sediments near natural mineralized sources; Hg content is rapidly diluted downstream by physical mixing with other sediments. Mercury anomalies extend the greatest distance downstream in the tributaries, finest size-fraction of bottom sediment, river bank deposits, suspended sediment, and water; the latter two contribute the most Hg to the marine environment.

Recent studies of Hg dispersal in rivers have concentrated on systems that are polluted by industrial development and population centers (1). To provide a natural baseline for evaluating dispersal in polluted systems, this study focuses on Hg dispersal from natural mineralized sources in the Kuskokwim River drainage, a remote region isolated from population centers and industrial development. The numerous cinnabar lode sources (Fig. 1) (2) provide an excellent opportunity to compare Hg dispersal processes downstream from lode deposits that are either eroding naturally or more rapidly by mining.

Several earlier studies describe Hg distribution in mineralized areas (3). However, sampling intervals have not been closely spaced through complete stream sediment systems; Hg partitioning and dispersal pathways in water, suspended sediment, and by size fraction of bottom sediment have not all been traced throughout the same freshwater system to marine waters; and sample size has not been adequate to provide statistically significant results for bottom sediments containing Hg mainly in discrete mineral particles of cinnabar (HgS).

Previous study (4) in the Bering Sea region has shown that Hg dispersing in sediments from mineralized shoreline areas of the coast is transported mainly as the heavy mineral cinnabar (HgS) (sp. gr. 8.1). The relatively soft cinnabar is most concentrated in the heavy mineral fraction of the finest grain size of any sediment type and accumulates in heavy mineral fractions of beach areas with strong wave action. Offshore, the cinnabar mineral concentrations are rapidly diluted by physically mixing with sediment from nonmineralized areas. To ascertain if physical dilution is the dominant dispersal process in natural rivers, we have examined dispersal distance (distance required for Hg content to return to background values) in filtered water, suspended sediment, bulk sediment, and size fractions of heavy mineral concentrates downstream from mineralized areas over 840 km of the Kuskokwim River system.

Natural and mining-induced erosion has provided the dominant supply of Hg to the river because retorting of ores was done on only a modest scale up to 1972, when it was discontinued. A total of about 40,000 flasks (35 kg/flask) of Hg has been mined in this area in the past 50 years compared to 60,500 flasks of Hg mined at the world's largest mine in Almaden, Spain in the single year of 1972 (5). Because the Kuskokwim region remains relatively poorly prospected and exploited, the size of its deposits may be greater than these mining rates indicate (6).

Water and suspended-sediment samples were processed (7) from 32 stations and bulk bottom sediment was collected from 299 stations; sampling intervals for bottom sediments were 3-5 kilometers, except in tributaries and coastal areas where intervals were greater (Fig. 1). Bulk samples were collected with a drag dredge from a boat or by hand where possible. A small split of the original bulk sediment was analyzed for Hg content, but most of the 1-to 3-kg sample was hand panned to a heavy-mineral concentrate containing cinnabar particles. The concentrate was separated into >0.25 mm, 0.25-0.062 mm, and <0.062 mm size fractions. The larger two fractions were ground to -0.1 mm with hand mortar and pestal prior to analysis of Hg and associated elements of As, Ca, Fe and Mn (8).

Pan concentration and grinding eliminated particle sparsity effects in Hg values (9) (fractional gram subsamples do not always yield representative subsamples because the Hg present is concentrated in relatively few large cinnabar particles near mineralized sources). Concentration averaged 17 :1 (parts of bulk sediment: parts of heavy mineral concentrate) for the entire set of bottom samples, thus removing approximately 95% of each sample (light-weight minerals) from analysis. Concentration averaged less for bulk sand (10:1) showing, as expected, that they contain a higher content of heavy minerals than do gravel or mud. Average elimination of 90% of each sand sample by panning suggests that the slight differences in pan concentration for different sediment types had little effect on downstream trends of Hg values.

The content of Hg in filtered water and suspended sediment appears to be elevated throughout the entire middle and lower Kuskokwim drainage (water = 0.34 ± .13 ug/ℓ; suspended sediment = 3.9 ± .52 mg/kg) (Fig.2A) compared to background values in other similar, but unmineralized graywacke and volcanic terranes (water = 0.085 to 0.19 ug/ℓ, suspended sediment = 0.1 to 1 mg/kg) (10). The mean content of Hg remains the same in filtered water throughout the Kuskokwim system (Fig. 2); however, in suspended sediments mean value is significantly elevated in the tributaries where numerous sources exist (Figs. 1 & 2A) and then varies erratically to become much less in the upper and lower river and slightly elevated in the middle river and bay areas. The high Hg values in the middle river and bay areas cannot be attributed to specific mineralized sources or to varying organic carbon content in the suspended sediments.

The highest individual Hg anomalies in suspended sediment and filtered water occur near the largest mineralized sources of tributary streams; however, values decline rapidly downstream. The Hg anomalies in source areas for both water and suspended sediment usually are significantly lower than the bed sediment anomalies, and water values are much lower than any sediment values at a given source. This dispersal pattern of anomalies probably results because (a) most of the mercury appears to be entering the river system as particulate cinnabar in bottom sediment and (b) the diluting effect of water discharge always is greater than sediment discharge in any river, and similarly, the bottom sediment load of this river is estimated to be only about 10% of the annual suspended sediment load (11).

Throughout the Hg source areas in tributaries and the upper river (Fig. 1), local background levels of Hg (0.1 mg/kg) in bulk sand and silt bottom sediment are slightly higher than are normal background values (0.01 to 0.06 mg/kg) for similar sediment from nonpolluted and nonmineralized areas elsewhere around the Bering

Sea (4) (Fig. 2A). Local background values return to normal (0.06 mg/kg Hg) in bulk sediment of the lower Kuskokwim River and Bay. This suggests that cinnabar-bearing sediment eroded from the upstream sources (Fig. 1) has not enriched the Hg content sufficiently above normal background to be detectable in these downstream bulk bottom sediments.

The rate of dilution by mixing of nonmineralized sediment with mineralized sediment is less in tributaries than in the main river. As a result, the highest mean and individual sample Hg values in whole pan concentrates (including all size fractions) occur in those taken from channels, levees, and banks of tributaries (Fig. 1) (Table 1, E and F). Anomalous Hg values in concentrate samples also continue downstream for the greatest distance in tributaries (Figs. 1 & 2A). The distance required for the Hg content in pan concentrates to return to normal concentrate value of <1 mg/kg (table 1) is 10 to 25 km even below the largest river sources (Fig. 1, see Red Devil), whereas it ranges from 32 to 72 km in tributaries (Fig. 1). Nevertheless, the initial dilution of Hg values away from a source is extremely rapid, decreasing from a high of 500-1000 mg/kg to less than 5 mg/kg within a few kilometers downstream from either tributary or river sources.

Data from pan concentrates show that the Hg content in bottom sediment partitions physically by size, which affects the Hg dilution rate and dispersal distance (4) (Fig. 2). When comparing either individual samples or averaging samples from the entire river, Hg values in the finest fraction (<0.062 mm) are much higher than in the coarse fraction (>0.25 mm) of bed sediment concentrates, and the dispersal distance of the finer sizes is greater (Fig. 2A). Cinnabar in the finest (<0.062 mm) size fraction contributes the main part of the Hg content, even in Hg-rich gravelly deposits that are characteristic of the tributary and upper river source areas (Fig. 2A; table 1C).

Partitioning and dispersal of Hg suggest that dilution from physical mixing and not chemical mobilization is the main cause of downstream decrease in sediment Hg content. This relation seems true whether the Hg source is a natural cinnabar deposit, or a gold deposit where Hg amalgamation was used to refine ores. Every Hg anomaly in bottom sediment correlates with some nearby placer or lode cinnabar source, associated mineral deposit (i.e. stibnite (Sb_2S_3) - livingstonite (HgS-$2Sb_2S_3$), and/or amalgamation site (Fig. 11 (2, 4) rather than any parameter of chemical mobilization (12). The highest positive correlation coefficients with Hg values in bottom sediments are found for elements Cu, Sb, (not shown in Figure 2B) and As (.53, .51, .49 respectively); minerals bearing these elements are commonly associated with the cinnabar deposits of the Kuskokwim region (6). These elements show similar downstream physical dilution patterns except that Hg values decrease more rapidly as would be expected for its denser source minerals (sp. gr. = 8.1) compared to those of Cu, As, and Sb (sp. gr = ca. 4 to 6) (Fig. 2B). In contrast, the correlation of Hg with Fe and Mn is much less positive (.26 and .26 respectively) (Fig. 2B), which further suggests that Hg is not being rapidly mobilized into the water phase in source areas and then absorbed by oxides of Fe and Mn, as has been suggested for polluted rivers (12).

Increased Hg values in bulk bottom sediments from the tributaries and upper Kuskokwim River show no relation to organic content (Fig. 2C). However, in the lower river and bay, the fluvial, tide flat, and delta sediments that contain the finest grain size (13, 14) and the highest organic carbon content ($\geq$ 1.0%) do show slightly higher mean content of Hg (.11 mg/kg) than those sediments (.04 Hg) from nonmineralized locations containing less clay and/or organic matter ($\leq$.5% C). This mean value of .11 mg/kg Hg is quite close to the normal range of 0.01 to 0.1 mg/kg for bulk sediment with high organic content (4);

relatively high Hg values ($\leq$ 1.5 mg/kg) in individual samples containing maximum organic carbon content (20%) are many orders of magnitude less in Hg content than upstream sediments associated with lode sources (Fig. 1). These data and the fact that clay and organic debris are absent in concentrate samples emphasize that physical mixing of cinnabar-rich sediment with bed sediments containing low Hg concentrations clearly controls the dispersal process in mineralized regions. This contrasts with chemical mobilization and incorporation of Hg with clay, organic debris, or ferric hydroxide grain coatings in polluted fluvial systems (Fig. 2) (1) (12).

Levee and bank depositional sites consistently have the greatest Hg values throughout the river system (Table 1E) and show the most positive correlation of high Hg content with depositional environment. In the upper river the geometric mean is about twice as high for levee and bank deposits as that for the coarser adjacent channel sediments and 10 times greater than that for nonmineralized sediments away from Hg sources (Table 1E) (4). The levee deposits typically are finer grained (sand and sandy silt) than the gravelly sand of the upper channel (13) and consequently, are a depocenter for fine-grained cinnabar, which is most abundant (Fig. 2A). Probably the fine-grained cinnabar is preferentially carried to overbank deposition sites during spring flooding whereas coarser particles remain in channel deposits.

Increased distance of Hg dispersal due to retorting of Hg ore and possible correlative effects of chemical mobilization of Hg could not be verified for either river or tributary sources because the largest natural sources were also the sites where retorting had taken place. However, greater dispersal distance in bottom sediments can be attributed to increased erosion from physical disturbance at mining sites. On the main river, Egnaty Creek and Kolmokof mine are both small deposits (Fig. 1) (6), but dispersal distance is nearly two times greater for the mined deposit (Kolmokof) (Fig. 1) than the naturally eroding source. Dispersal distance from the Cinnabar Creek mine also is nearly double that of a recently discovered naturally eroding deposit of small size on Chineekluk Creek (Fig. 1) (6).

In summary, even in this moderate sized river (discharge ca. 44.6 km^3/year) (11, 15), physical mixing is very effective in diluting Hg values a short distance downstream from each source so that Hg in bottom sediment returns to normal by the time the sediments reach the lower river (Fig. 2); in comparison, effective downstream dilution in polluted European rivers is not achieved until estuaries are reached (16). Overbank and channel deposits close to lode Hg sources are important depositional sinks that remove Hg from dispersing bed load sediment. Unlike nonmineralized or polluted river systems elsewhere (1, 10), tidal flats and carbonaceous delta swamps are not so important Hg sinks on a per unit weight basis as are river levees and banks in the Kuskokwim drainage.

Cinnabar-rich sediment disperses the greatest distance in the finest size fraction (<0.062 mm); it extends further downstream in tributaries than in the main river where relatively more sediment and water from unmineralized terrane are available for dilution. Mining activity appears artificially to increase dispersal distance of cinnabar rich sediment because Hg is found greater distances downstream from mining sites than from similar-sized Hg deposits that are eroding naturally (Fig. 1).

On the basis of average Hg content measured in our study and discharge estimates (11, 15) at the river mouth, it is calculated that a total of 16,700 kg of Hg per year enters the marine environment from the Kuskokwim River. Of this total Hg content, 80% (13,400 kg) is transported by the water, 19% (3,130 kg) within suspended sediments and 1% (160 kg) within bed load sediment.

Table 1. --Mercury concentrations in water (ug/ℓ), suspended sediment (mg/kg) and both bulk and pan concentrates of bottom sediment (mg/kg) of different depositional environments and texture classes in the Kuskokwim River system. (Note: All data based on pan concentrate samples of bottom sediments except where noted; bulk indicates whole samples with no preconcentration; however, the >0.175 mm fraction was removed from Group I samples prior to analysis. All values manually rounded to one or two significant figures, dependent upon the reliability of the original analyses and according to computer parameter calculations.)

Sample Type	No. of Samples	Geometric mean	Range of 1st geometric dev	Minimum value	Maximum value
A. All Bulk Samples					
Water	11	0.34	0.13 - .9	<0.01	1.4
Suspended Sediment	22	3.9	0.52 - 30	<0.04	520
Bottom Sediment					
(Group I)	143	0.060	0.011- 0.33	0.01	370
(Group II)	156	0.18	0.038- 0.83	0.02	10
B. Bottom Sediments (All textures and depositional environments)					
All	275	0.35	0.056- 2.1	0.024	1700
Kuskokwim River plus all tributaries	208	0.49	0.074- 3.3	0.69	1700
Kuskokwim Bay plus local streams	40	0.12	0.043- .32	0.025	1.8
C. Texture (All depositional environments)					
Gravelly Deposits	51.0	0.64	0.062- 6.6	0.029	1700
Sandy Deposits	167.0	0.31	0.059- 1.7	0.024	51
Silty Deposits	36.0	0.24	0.059- 0.94	0.025	9.2
Clayey Deposits (Bulk)					

Table 1 (cont)

Sample Type	No. of Samples	Geometric mean	Range of 1st geometric dev.	Minimum value	Maximum value
D. Sand Bars and Islands (All textures)					
Kuskokwim River	28	0.26	0.066 - 0.99	0.024	3.1
E. Levees and Banks (All textures)					
All	113	0.57	0.94 - 3.4	0.049	750
Tributaries	16	2.1	0.29 -15.0	0.14	160
Upper Kuskokwim River	46	1.1	0.18 - 6.8	0.13	750
Middle Kuskokwim River	27	0.22	0.073 - 0.66	0.054	5.1
Lower Kuskokwim River	24	0.20	0.068 - 0.58	0.049	2.6
F. Channel (All textures)					
All	56	0.50	0.059 - 4.3	0.040	1700
Tributary	3	570	180 - 1800	170	1700
Upper Kuskokwim River	33	0.57	0.18 1.8	0.096	11
Middle Kuskokwim River	15	0.14	0.044 - 0.44	0.040	3.8
Lower Kuskokwim River	5	0.053	0.043 - 0.066	0.404	0.070
G. Kuskokwim Bay Depositional Environments (All textures)					
West beach	3	0.04	0.02 - 0.08	0.03	0.062
Northeast beach	16	0.13	0.059 - 0.26	0.029	0.89
West Tidal Flats	6	0.10	0.03 - 0.33	0.025	0.53
Northeast Tidal Flats	5	0.14	0.04 - 0.45	0.10	1.8
All Tidal Flats (bulk)	10	0.035	0.018 - 0.070	0.01	0.09
All Delta (bulk)	11	0.13	0.059 - 0.29	0.01	0.46

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7. Water samples were collected in acid washed polyethylene bottles, forced through 0.1mm cellulose acetate membrane filters with N_2 and preserved by freezing as soon as possible on the day collected as were filters with suspended sediment. Hg loss during thawing was prevented, and any Hg loss to the sample container during filtration and freezing was recovered, by addition of $KMnO_4$ (P. Avotins and E. A. Jenne, Jour. of Environ. Qual., 4, 515, 1975); digestion was at 80^{0} following transfer to Pyrex bottles and addition of $K_2S_2O_8$. Analysis of Hg was made by cold vapor atomic absorption using a $KMnO_4$-H_2SO_4 trap to eliminate both positive and negative interferences (S. H. Omang. Anal. Chim, Acta. 53, 415, 1971).

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14. Fine-grained suspended sediment, delta deposits, and tidal flats of this fluvial system are dominated by silts in this as well as other Arctic to sub-Arctic drainages (12). Clay content rarely exceeds 25%.

15. Calculations are based on Lisityn's (11) estimates of yearly water, suspended sediment, and bottom sediment discharge which appear to be verified by data from U. S. Geol. Sur. Water Supply Papers, Alaska, 1959, 1964, 1965, 1966, 1967 and from USGS, 1970, 1971 and 1972, Quality of Surface Waters of the United States, 1964, parts 12-16: U.S. Geol. Survey Water-Supply Papers 1959, 428 p., 1966, 492 p. and 2016, 431 p.

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17. We gratefully acknowledge assistance of (a) J. W. Ball and J. M. Burchard, (b) K. W. Leong, and (c) USGS Field Services Branch for analyses of (a) water and suspended sediment, (b) bulk sediment, and (c) pan concentrate samples respectively. Alaska Fish and Game Department assisted with field support and D. R. Kerr compiled data for Figures and Tables.

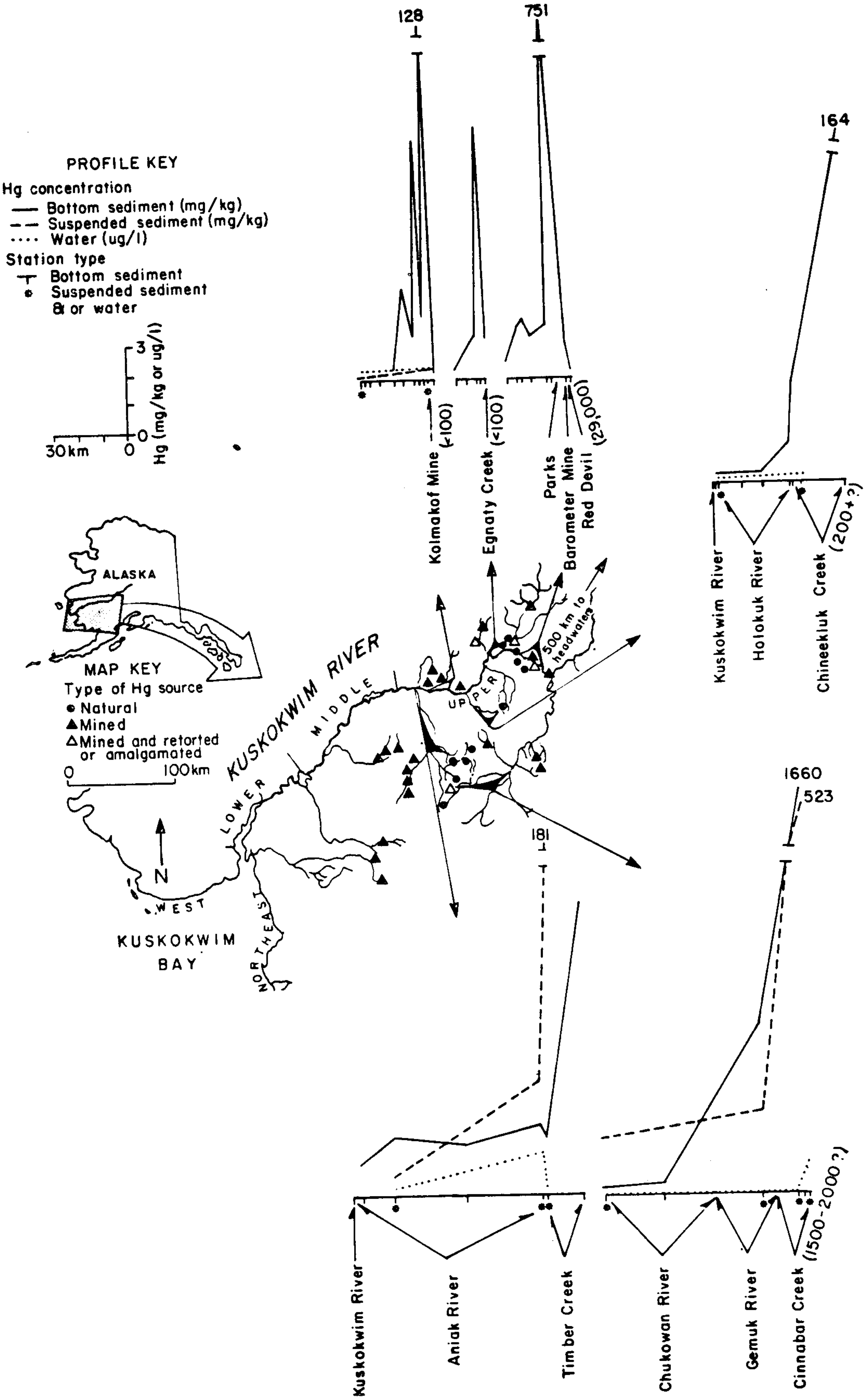
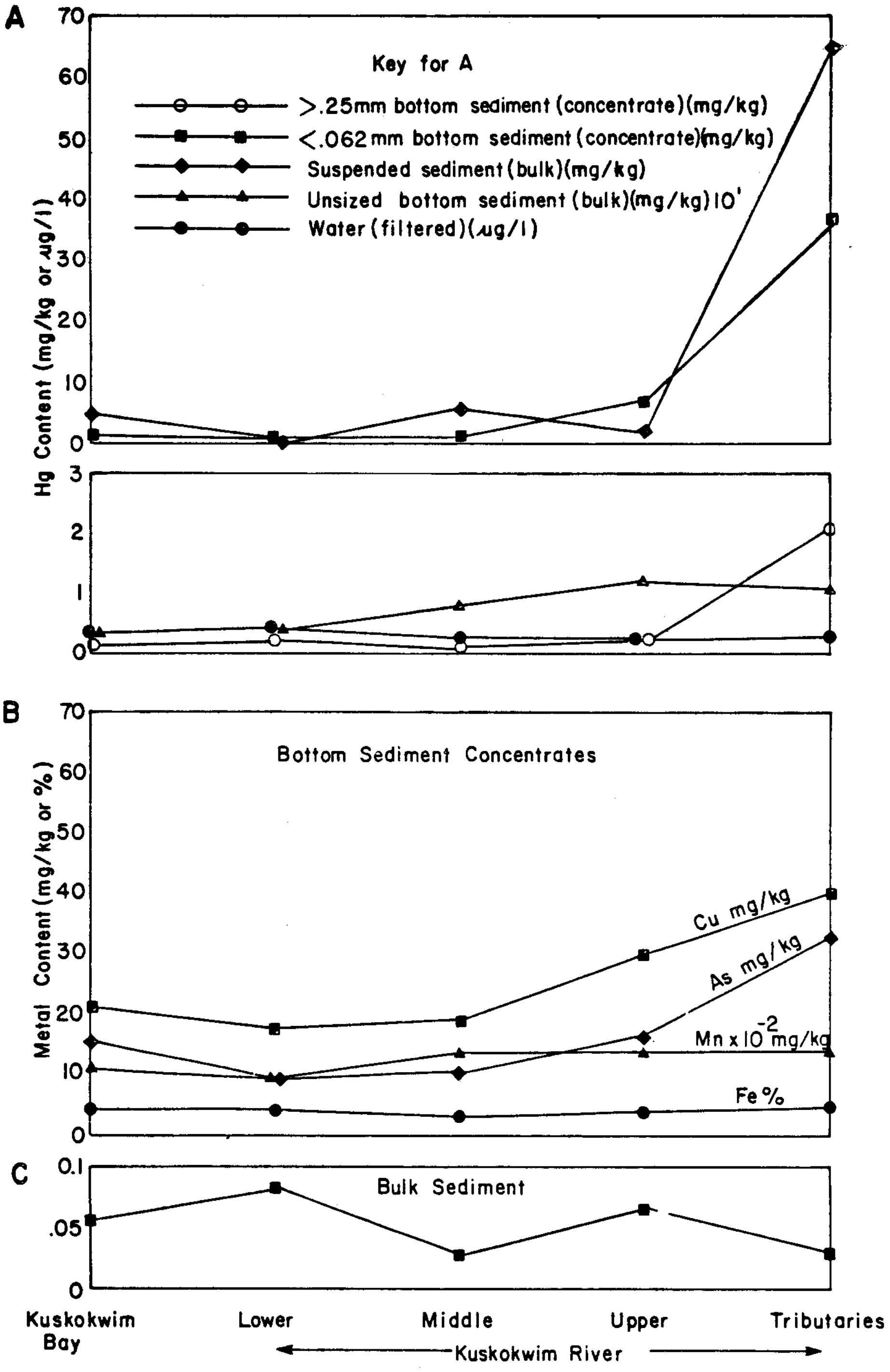


Figure 1 -- Location and type of Hg source in the middle and lower Kuskokwim drainage (2) and selected profiles of downstream dispersal of Hg based on pan concentrate samples. Total number of 76-pound flasks mined is given in parentheses at the largest sources (6). Records are not available for other minor sources, but probably less than 100 flasks have been produced at each.



Type			Number of Samples		
Bottom sediment	31	45	58	82	23
Suspended sediment	1	3	3	4	13
Water	1	3	3	4	14
Carbon (organic)	4	7	4	3	4

Figure 2 -- Average (geometric mean except for unsized bottom bulk sediment where median values are given) content of mercury, and associate elements in bulk suspended and bottom sediments, coarse and fine size fractions of pan concentrates, and water for tributary, upper, middle and lower Kuskokwim River and Bay. (Number of samples is as noted at base of figure except that <0.062 mm size fraction of middle and upper Kuskokwim River have only 16 samples each.)

Annual Report

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to

U.S. Department of Commerce
National Oceanic and Atmospheric Administration

Characterization of Organic Matter in Sediments from Gulf of Alaska, Bering and Beaufort Seas

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I. SUMMARY

During the past contract year sample collections have been made in the Beaufort Sea, using the Coast Guard Vessel GLACIER and the East Bering Sea, Norton Sound and Cook Inlet, using the U.S. Geological Survey vessel, the SEA SOUNDER. Approximately 100 sediment samples have been collected for analysis of (1) hydrocarbon gases, (2) total carbon, nitrogen and sulfur contents, and (3) high molecular weight hydrocarbon content. Analyses of all three components are presently under way.

The paraffin fraction of the high molecular weight hydrocarbons have been identified from samples from the Eastern Gulf of Alaska and the Eastern Bering Sea. In general it has been shown that:

1. The concentrations of total hydrocarbons in surface sediments from both areas, with the exception of one sample near Pribilof Canyon, is low compared to recent marine sediments from other environments.

2. The hydrocarbons in the sediments appear to be derived from a mixture of terrigenous and marine sources. In the Bering Sea, a terrigenous source predominates, while in the Gulf of Alaska, contribution from marine and terrigenous sources is approximately equal.

3. A series of n-alkanes and unresolved hydrocarbons in the n-C_{21} to n-C_{23} molecular weight range occurs in some samples from the Bering Sea and many of the sediments of the Gulf of Alaska. The source of these hydrocarbons may be either from petroleum or from unidentified marine organisms.

4. Sediments near the head of Pribilof Canyon appear to contain petroleum derived hydrocarbons. This is in contrast to most other samples of the Bering Sea which have no indications of petroleum addition. Several of the Gulf of Alaska sediments analyzed seem to indicate some petroleum contribution.

II. INTRODUCTION

A. General Nature and Scope of Study

Determine baseline concentrations and distributions of petroleum hydrocarbons in surface sediments of E. Bering Sea and W. Gulf of Alaska.

B. Specific Objective

A variety of criteria are necessary to characterize the concentration and distribution of hydrocarbons in surface sediments. In this report we give the results of gravimetric and gas chromatographic analysis of the hydrocarbons in surface sediments of E. Bering Sea and W. Gulf of Alaska.

C. Relevance to Problems of Petroleum Development

Various investigations have indicated that one of the fates of petroleum released into the marine environment is deposition with sediments. Once deposited, it is unknown whether the petroleum is buried intact, decomposed as a result of microbial weathering, or slowly dissolved out by the overlying water column. To understand these processes, it is necessary to determine the ambient concentrations and distributions of petroleum hydrocarbons in the sediments prior to exploration and development. Moreover, since petroleum hydrocarbons will be affected by the same processes as those which affect recent biogenic hydrocarbons, any information regarding the distribution and preservation of recent biogenic hydrocarbons is relevant to the fate of petroleum hydrocarbons in the marine environment.

Areas containing high contents of hydrocarbons could be the same areas that would potentially accumulate petroleum hydrocarbons in the event of a spill or chronic discharge. Gas chromatographic analysis, which defines the distribution pattern of hydrocarbons, may identify areas where labile components are preserved and could be accessible to benthic communities of organisms.

III. CURRENT STATE OF KNOWLEDGE

This is the first study of the distribution and concentration of hydrocarbons in surface sediments from these areas. The distribution of organic carbon in the S. Eastern Bering Sea has been described by Sharma (1974).

IV. STUDY AREA

The locations of the samples analyzed in this report are illustrated in Figure 1 and listed in Table 1. The stations are located on hydrographic sampling grids established by the University of Alaska (Burell, 1976). Sample locations were in part controlled by the fact that sediment samples could not be collected at all hydrographic stations occupied. Nevertheless, the samples analyzed are probably representative of those occurring in the Southeastern Bering Sea and Western Gulf of Alaska in terms of geographic distribution, water depth, and sources.

V. METHODS

Surface sediments were collected with $\sim 0.1\ m^3$ steel Van Veem grab samplers during summer 1975 cruises of the NOAA ship DISCOVERER, Legs III and IV. During sample collection care was taken to minimize hydrocarbon contamination of the sediment as much as possible. Except for the grab sampler, which had a hinge that could not be cleaned, all materials that contacted the sediment were cleaned and rinsed with organic solvents. Sediment samples were placed in pre-cleaned glass jars and frozen until analysis.

The methods of extraction and analysis of the hydrocarbons have been described in detail in a previous report (Annual Report, March 31, 1976, PO #F01770) and are essentially those recommended by BLM for hydrocarbon analysis. Briefly, the frozen sediments were placed in pre-cleaned cellulose extraction thimbles, washed with distilled H_2O to remove salts, and then freeze-dried for 48 hours. The freeze-dried sediments were then Soxhlet extracted for 100 hours using a toluene:methanol (3:7) azeotropic mixture, with one solvent change after 24 hours. The total extract was saponified under reflux for 4 hours, using 60 ml of a 1:1:1 mixture of 0.5 N KOH in water:methanol: toluene. The non-saponifiable fraction was chromatographed on a column of 1:2 alumina over silica gel, and successively eluted with 2 column volumes each of hexane, benzene, and methanol.

The saponification procedure does not completely remove methyl esters, which elute in the benzene fraction and interfere with the benzene fraction hydrocarbons during gas chromatographic analysis. Hence esters were removed from the benzene fraction using $AgNO_3$-impregnated silica gel thin-layer chromatography (TLC) plates and eluted with hexane:CH_2Cl_2 (9:1).

Gas chromatographic analysis of the hexane fraction was conducted using a Hewlett Packard Model 5830 A instrument, which is equipped with a linear temperature programmer, flame ionization detector, and electronic integrator. A glass support coated open tubular (SCOT) column, 50 m x 0.5 mm I.D., coated with OV-101 (SGE Scientific, Inc.) was used in the gas chromatograph without any modification of the injector and detector systems.

The column was temperature-programmed from 100°C to 275°C at 2°/min and held isothermal for 60 min. with a flow rate of 4 ml/min. of He.

The concentrations of the resolved hydrocarbons in the gas chromatograms were calculated using response factors (μgm/count) derived from injections of standards over a range of concentrations. Compounds were identified by comparison of retention times of known standards and by coinjection.

VI. RESULTS

Sample locations, water depths, and carbon, nitrogen, and sulfur analysis of the sediments as reported previously (Shaw, 1976) are included in Table 1.

Gravimetric analysis of the non-saponifiable extractable material and liquid-solid chromatography fractions are given in Tables 2 and 3. The total hydrocarbons is the sum of the hexane and benzene fractions. Hexane fractions less than equivalent weight of 1 μgm/gm dry sediment could not be accurately weighed using the Mettler balance and are listed as not determined in Tables 2 and 3.

The gravimetric data for the benzene fractions listed in Tables 2 and 3 are given as weight of the hydrocarbons which have been separated from non-hydrocarbons by silica gel-$AgNO_3$ thin-layer chromatography (TLC). The difference in the weight of the benzene fraction before and after this TLC procedure is listed in Table 4. The material removed by the TLC procedure consists of fatty acid methyl esters that were incompletely removed during saponification and subsequently eluted in the benzene fraction.

The results of the gas chromatographic analysis of the hexane fractions of sediments from the E. Bering Sea and W. Gulf of Alaska are listed in Tables 5 and 6 and illustrated graphically in Figures 2 through 5. As shown in Tables 5 and 6, individual n-alkane contents as low as 1 ngm/gm dry sediment could be detected. The original gas chromatogram of the hexane fractions of each sample has been reproduced and is included in Appendix I.

Odd-even and isoprenoid n-alkane ratios derived from gas chromatographic analysis of the hexane fractions of Bering Sea samples and Gulf of Alaska samples are listed in Tables 7 and 8. Total hydrocarbon/organic carbon and *n*-alkane/organic carbon ratios of surface sediments from E. Bering Sea (EBBS) and W. Gulf of Alaska samples are listed in Tables 9 and 10.

VII. DISCUSSION

A. Gravimetric Analysis

The gravimetric data describe the distribution and concentration of the hydrocarbons according to general analytical classifications. Anomalously high levels of total hydrocarbons, for example as indicated by the total hydrocarbon/organic carbon ratio, may indicate addition to the sediment of petroleum hydrocarbons.

In the E. Bering Sea the total hydrocarbons range from 2 to 22 μgm/gm dry sediment, with the exception of EBBS 35 which has a value of 241 μgm/gm dry sediment. This range of values is low compared to unpolluted recent marine sediments from other environments, which have concentrations between 30 and 100 μgm/gm and 10 to 100 times lower than values of total hydrocarbons in sediments contaminated by petroleum (Blumer and Sass, 1972; Palacas *et al.*, 1976; Kaplan *et al.*, 1976). EBBS 35 is anomalous because of its high content of total hydrocarbons, and may therefore have been exposed to petroleum hydrocarbons according to this criterion.

In general, the range in concentrations of hydrocarbons in the sediment samples can be explained by variations in sediment grain size and organic carbon content. Sharma (1974) has shown that the sediments in the Southeastern Bering Sea become progressively finer grained and contain higher organic carbon in moving west across the shelf, from nearshore to the edge of the shelf. The samples analyzed in this report follow the same trend, with low concentrations of total hydrocarbons and organic carbon in coarse grained sediments close to shore, and higher concentrations in finer grained sediments near the shelf edge.

In the sediment samples from the W. Gulf of Alaska, the concentration of total hydrocarbon ranges from less than 1 to 27 μgm/gm dry sediment. As in the Bering Sea samples, these values are low in comparison to other unpolluted coastal sediments. Similarly, the range in concentrations may be explained by variations in grain size and organic carbon, with higher concentrations in fine grained sediments of the basins and troughs sampled.

The total hydrocarbons represent less than 10% of the non-saponifiable extractable material in sediments from both the Bering Sea and Gulf of Alaska. The composition of the other organic material, which is in the methanol fraction or remains on the silica gel column, is not known.

B. Gas Chromatographic Analysis

Gas chromatographic analysis of the hexane fraction of the sediment extracts is a sensitive indicator of the sources of the hydrocarbons, especially those derived from petroleum. This is because petroleum hydrocarbons and recent biogenic hydrocarbons provide a number of characteristic differences when their hexane eluates are analyzed by gas chromatographic methods (National Academy of Sciences, 1975; Blumer and Sass, 1972). These include the presence of the homologous series of isoprenoids in approximately equal abundance, an odd/even ratio ~ 1, presence of an unresolved complex misture of hydrocarbons, or anomalously high values of resolved n-alkane/organic carbon ratios. In some cases these criteria may give equivocal results, and more detailed analysis, for example by gas chromatography/mass spectrometry, may be necessary to accurately determine the composition of the hydrocarbons.

Although the concentration and distribution of hydrocarbons in each sample is characteristically different, several general conclusions are indicated by the data in Tables 5 and 6. The range in total n-alkanes resolved by gas chromatography is from 60 to 2900 ngm/gm dry sediment in samples from both the Bering Sea and Gulf of Alaska and reflects the variability in sediment grain size and organic carbon content. The total n-alkanes/organic carbon ratios are less than 0.0011 for all samples (Tables 9 and 10). Much higher ratios would be expected if unweathered petroleum were introduced into the sediments (Palacas et al., 1976).

The distribution patterns of n-alkanes in the Bering Sea samples as indicated in Figures 2 and 3 are generally similar, in that the predominant n-alkanes are n-C_{27} and n-C_{29}. Low contents of pristane, phytane, and unidentified branched or unsaturated compounds are generally present. In the Gulf of Alaska samples the n-alkane distribution, as illustrated in Figures 4 and 5, are more variable, with predominant n-alkanes occurring at either n-C_{22} or n-C_{29}, or a mixture of both. Pristane, phytane and other as yet unidentified unsaturated hydrocarbons are present in varying amounts. Examples of gas chromatograms of hexane fractions representative of surface sediments from the E. Bering Sea are illustrated in Figure 6. The samples are characterized by a distribution of n-alkanes in the range n-C_{16} to n-C_{33}; the predominant n-alkanes are at n-C_{27} and n-C_{29} and the pattern displays an odd carbon predominance in the n-alkane range n-C_{23} to n-C_{33}.

Gas chromatographic criteria, such as the odd/even ratio greater >3, pristane/phytane ratios > 3, and the lack of an unresolved complex mixture of hydrocarbons characteristic of weathered petroleum, indicate that the source of these hydrocarbons is from recent biogenic organic material. The predominant hydrocarbons in higher plants are C_{25}-C_{33} n-alkanes (Calidcott and Eglinton, 1973; Eglinton and Hamilton, 1963) and thus the predominant source of hydrocarbons in the hexane fraction is from terrigenous organic material. Smaller amounts of hydrocarbons derived from marine organisms, such as pristane and unidentified unsaturated and branched hydrocarbons (Blumer et al., 1971; Clark and Blumer, 1967) are also indicated in the chromatograms.

It is surprising that EBBS 17, located in an area of high biological productivity (Probes, 1972) contains only small amounts of hydrocarbons derived from marine organisms. This may indicate rapid recycling and oxidation of organic material within the water column or at the sediment water interface at this station.

Figure 7 illustrates examples of gas chromatograms from hexane eluates of samples containing the upper range of hydrocarbon content derived from marine organisms in Bering Sea sediments. The hexane fraction of EBBS 41 shows a number of unidentified components in addition to the odd n-alkanes derived from terrigenous plants. These components are probably branched alkanes and alkenes found in many marine organisms (Youngblood and Blumer, 1973; Blumer et al., 1973).

Similarly, the chromatogram of EBBS 65 indicates the predominant odd n-alkenes n-C_{25}-n-C_{33} derived from terrigenous plants. In addition, a complex series of peaks eluting near n-C_{21}, both resolved and unresolved, is present. These hydrocarbons have been tentatively identified as C_{25}, C_{21} and C_{19} polyolefins based on comparison of retention times with other samples analyzed by gas chromatography-mass spectrometry (Kaplan et al., 1976) and are probably derived from a number of marine organisms. The presence of these relatively labile hydrocarbons in the sediments of this sample may indicate better preservation of organic material being deposited in these environments.

The chromatogram of the hexane fraction of EBBS 12 is different from most samples analyzed in that the predominant alkanes are n-C_{22} and n-C_{23}, there is only slight predominance of odd alkanes (odd/even ratio = 1.76) and an unresolved complex misture of hydrocarbons maximizing near C_{23}. These criteria may be indicative of petroleum contamination of the sediments, although gravimetric data, such as the total hydrocarbon/organic carbon and _n_-alkane/organic carbon ratios for these samples are not anomalous. Moreover, such hydrocarbon distributions have been identified in sediments from other environments and these have been attributed to unidentified marine or brackish water organisms (Palacas _et al._, 1972; Johnson and Calder, 1973).

Figure 8 illustrates gas chromatograms of hexane fractions of two samples near Pribalof Canyon and St. George Basin, one of which is indicative of contamination by petroleum hydrocarbons. The chromatogram of EBBS 35 shows a large unresolved complex mixture in the elution range 200° to 280°C, with a maximum at 280°C, and no resolved hydrocarbons. This type of hydrocarbon distribution is indicative of weathered petroleum, and is very similar to samples from Coal Oil Pt., California, an area of known petroleum seepage (Kaplan _et al._, 1976). The gravimetric data also indicate anomalously high levels of hydrocarbons for this sample, with a total hydrocarbon/organic carbon ratio of 0.059 (Table 9). The source of these petroleum hydrocarbons may be from submarine seeps, although none has been reported in the Bering Sea. However, Marlow and others (1977) have identified faults in the area which could allow leakage of petroleum from underlying reservoir rocks.

The chromatogram of the hexane fraction of EBBS 37 illustrated in Figure 8 indicates a mixture of _n_-alkanes predominantly derived from plant waxes. In contrast to the hydrocarbon distribution pattern of EBBS 35, that derived for EBBS 37 is much simpler, though the samples are located near each other. The chromatograms in Figure 9 illustrate the distribution pattern of hydrocarbons representative of samples from the Gulf of Alaska.

The chromatogram of the hexane fraction of GASS 133 is characterized by a bimodal distribution of n-alkanes between n-C_{15} and n-C_{33}, with maxima at n-C_{23} and n-C_{27}, with a small unresolved complex mixture near n-C_{22}. There is a slight odd carbon predominance in n-alkanes above n-C_{23}, indicating contribution from terrigenous plants although the overall odd/even ratio is only 2.02. The source of hydrocarbons in the C_{22} range is unknown, and could be derived from unidentified marine organisms as discussed above. The chromatogram of the hexane fraction of GASS 119 is also characterized by this maximum in n-alkanes at n-C_{21}-n-C_{23}, an unresolved complex mixture of hydrocarbons (hump) is also present in this range. In addition, higher molecular weight hydrocarbons to C_{33} are also abundant. Pristane, phytane, and the tentatively identified polyolefinic hydrocarbon eluting near n-C_{21} are also present. As in GASS 133, the source of hydrocarbons in the hexane fraction of this sample appears to be derived from a mixture of approximately equal amounts of terrigenous and marine sources.

The chromatogram of the hexane fraction of GASS 103 illustrates the predominance of the marine source of hydrocarbons in the sample. The chromatogram is characterized by abundant pristane, a smooth distribution of n-alkanes with maxima at n-C_{22}, and minor amounts of the C_{25} to C_{31} odd n-alkanes derived from terrigenous plants. Pristane has been found in many marine organisms, and is abundant in some fishes (Blumer et al., 1971). The non-selective distribution of n-alkanes maximizing near n-C_{22} and the corresponding unresolved complex mixture in the same boiling range found in many samples from the Gulf of Alaska sediments (e.g., GASS 101-105 and some Bering Sea sediments (EBBS 12, EBBS 59)) could be indicative of a petroleum source. However, other petroleum components, such as the homologous series of isoprenoids and the unresolved complex mixture in the entire boiling range 200° to 280°C, are conspicuously absent. The gravimetric data, such as the total hydrocarbons/organic carbon and _n_-alkane/organic carbon ratios, are not anomalously high, nor are the pristane/phytane, pristane/C_{17}, phytane/C_{18} ratios characteristically indicative of petroleum contamination. Although the data may rule out the possibility of dominant petroleum contribution to the sediments, in the _n_-C_{22} range, their source cannot yet be determined with the criteria available at this time.

IX. Conclusions

Gravimetric and gas chromatographic analysis of hexane fractions extracted from surface sediments from E. Bering Sea and W. Gulf of Alaska has been completed. The data indicate:

1. The concentration of total hydrocarbons in surface sediments from both areas, with the exception of one sample near Pribilof Canyon, is low compared to recent marine sediments from other environments.

2. The hydrocarbons in the sediments appear to be derived from a mixture of terrigenous and marine sources. In the Bering Sea, a terrigenous source predominates, while in the Gulf of Alaska, contribution from marine and terrigenous sources is approximately equal.

3. A series of _n_-alkanes and unresolved hydrocarbons in the _n_-C_{21} to _n_-C_{23} molecular weight range occurs in some samples from the Bering Sea and many of the sediments of the Gulf of Alaska. The source of these hydrocarbons may be either from petroleum or from unidentified marine organisms.

4. Sediments near the head of Pribilof Canyon appear to contain petroleum derived hydrocarbons. This is in contrast to most other samples of the Bering Sea which have no indications of petroleum addition. Several of the Gulf of Alaska sediments analyzed seem to indicate some petroleum contribution.

X. SUMMARY OF FOURTH QUARTER OPERATIONS

1. Characterization of the benzene fractions of the samples from Bering Sea and Gulf of Alaska analyzed in this report is ongoing. The samples have been separated by thin-layer chromatography and gas chromatography of these samples will be completed as soon as possible.

2. We have investigated more efficient analytical procedures that will prevent interference of fatty acid methyl esters in the benzene fractions. At the same time we have been investigating various aspects of the analytical procedure such as the freeze drying step, which could be a source of contamination during sample analysis.

3. Elemental (carbon, nitrogen, sulfur) analysis of samples collected during the period July-October 1976 in Gulf of Alaska, N. Bering Sea, and Beaufort Sea is in progress.

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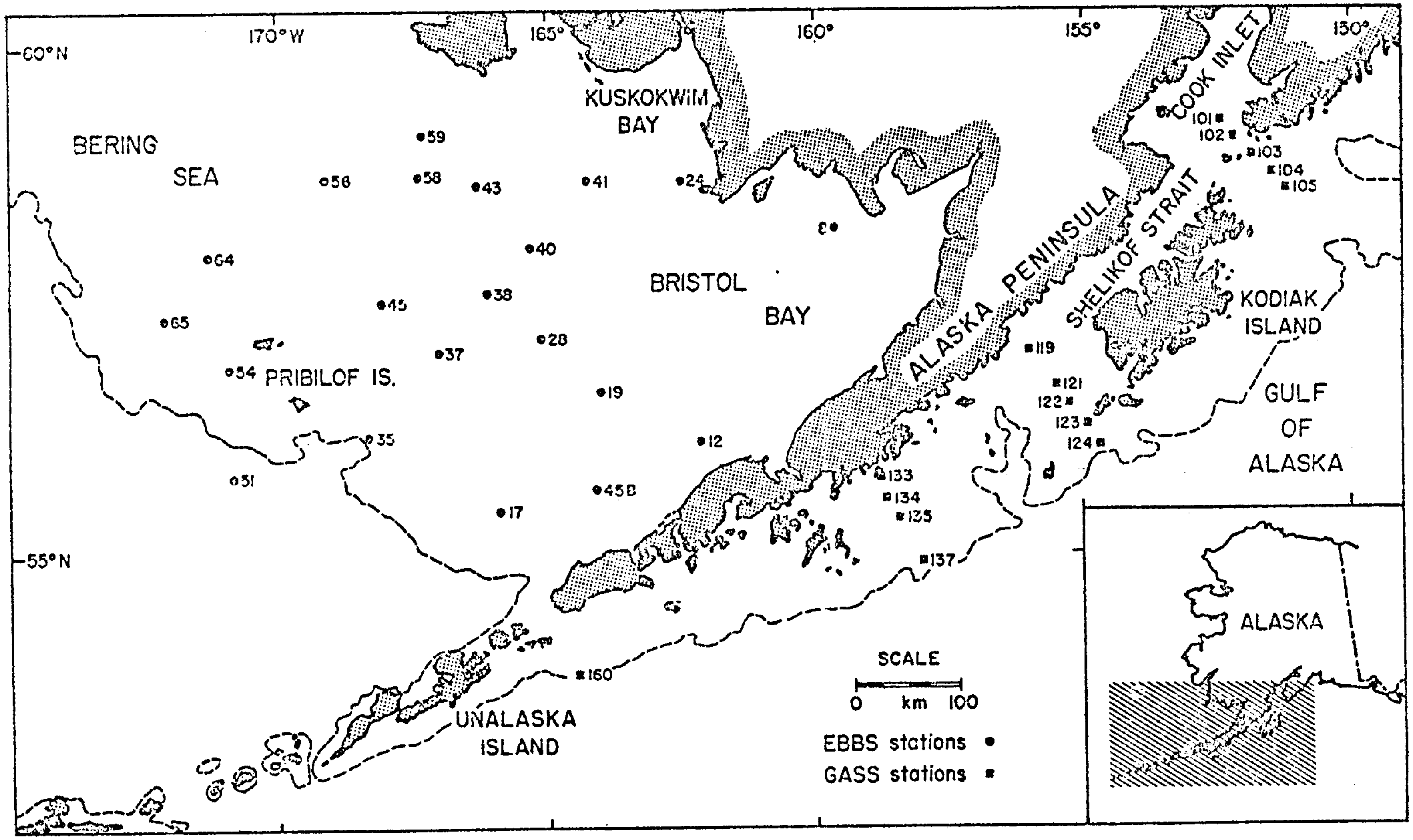

Figure 1. Locations of E. Bering Sea (EBBS) and W. Gulf of Alaska (GASS) stations occupied during legs III and IV of DISCOVER, September, 1975.

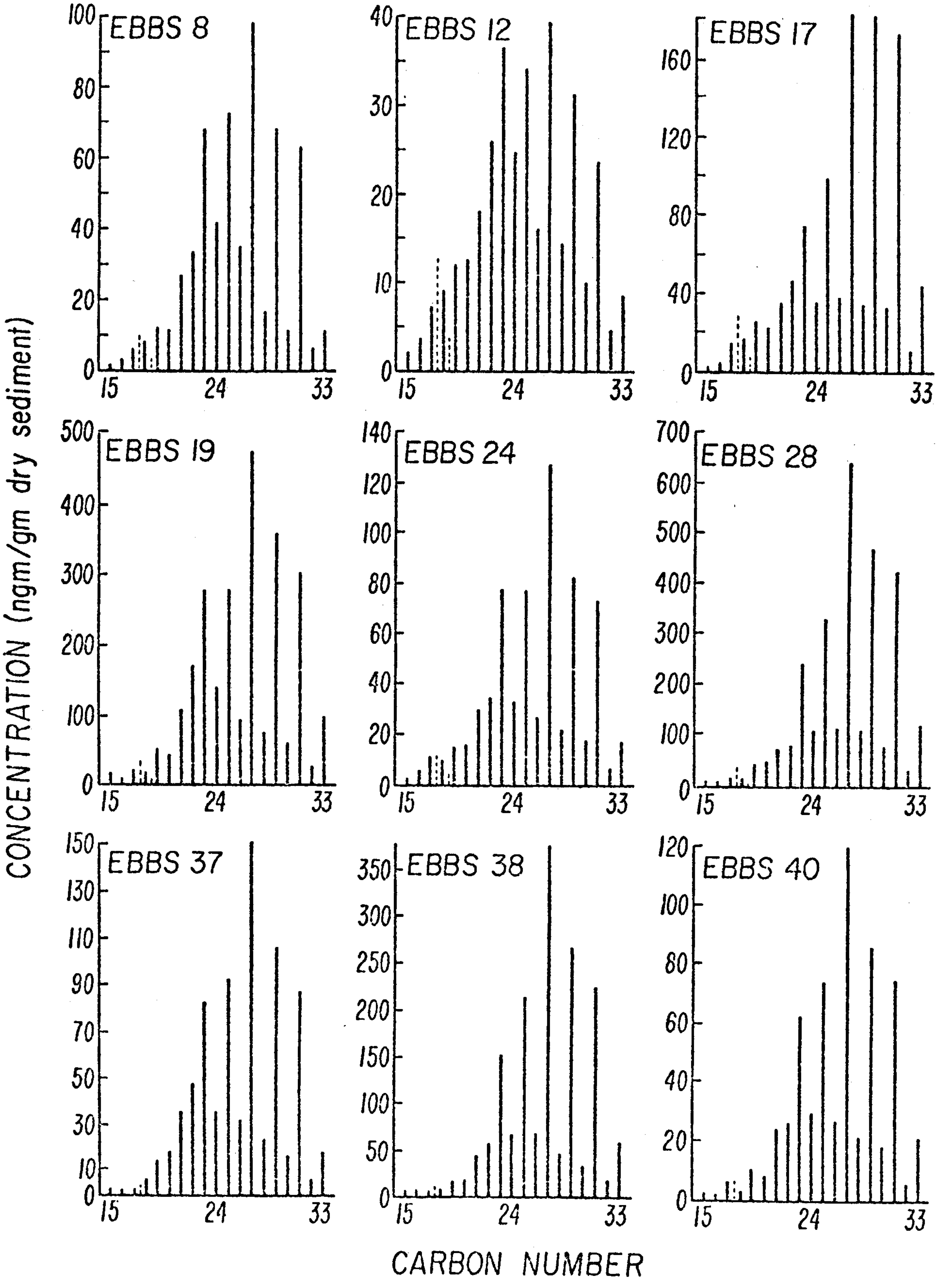

Figure 2. Distribution of n-alkanes and C_{19} and C_{20} isoprenoids in E. Bering Sea (EBBS) surface sediments.

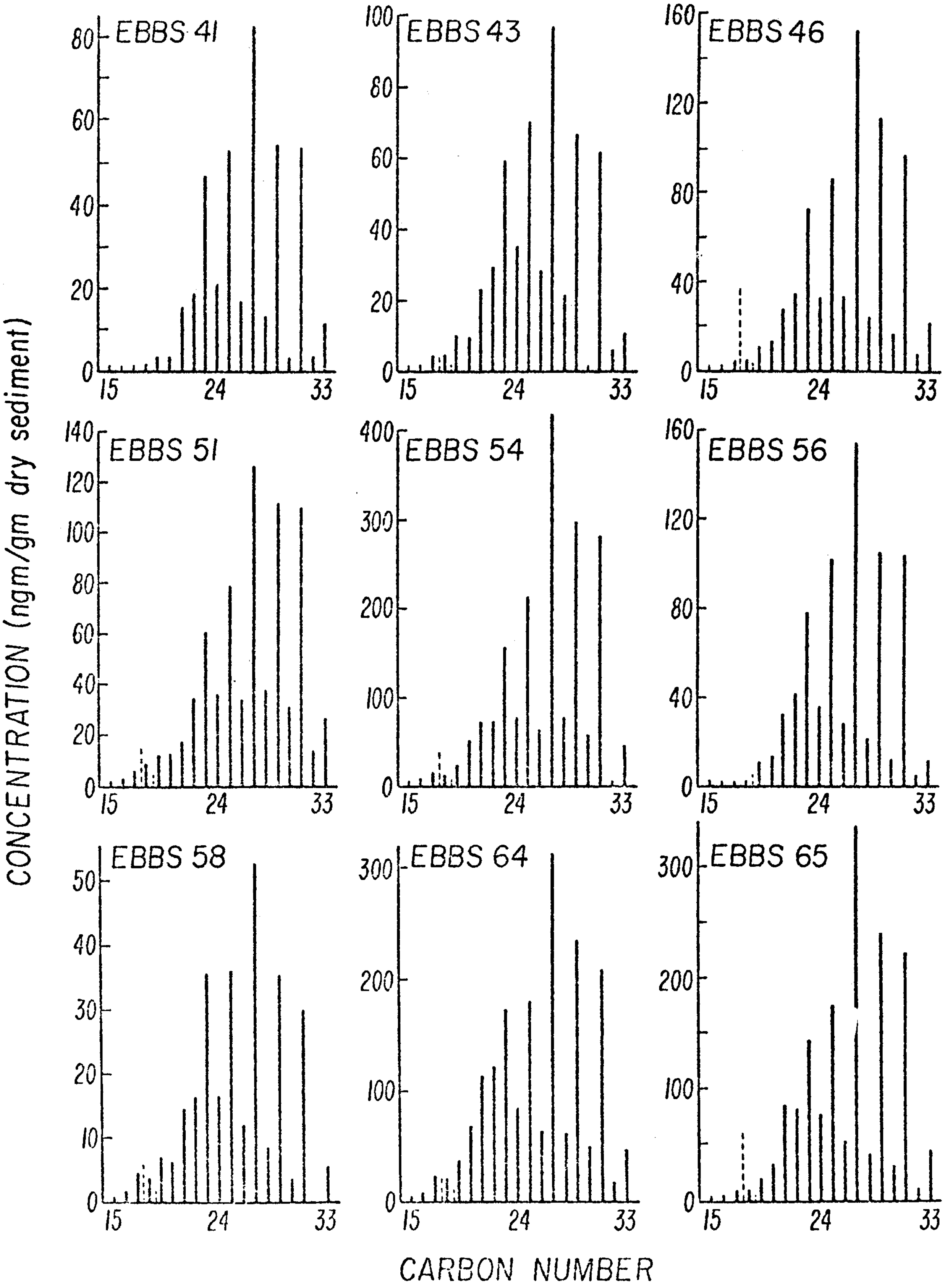

Figure 3. Distribution of n-alkanes and C_{19} and C_{20} isoprenoids in E. Bering Sea (EBBS) surface sediments.

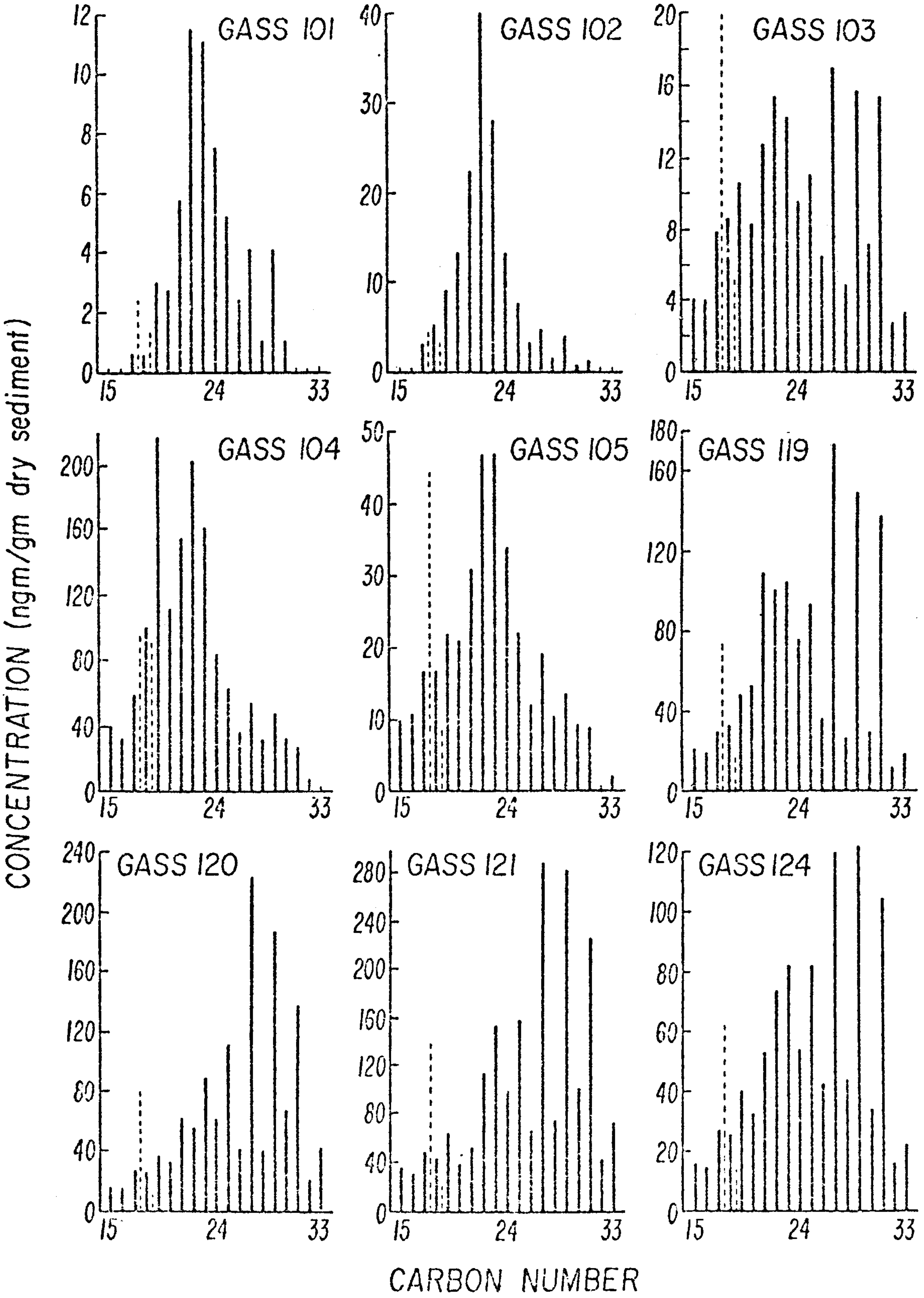

Figure 4. Distribution of n-alkanes and C_{19} and C_{20} isoprenoids in W. Gulf of Alaska (GASS) surface sediments.

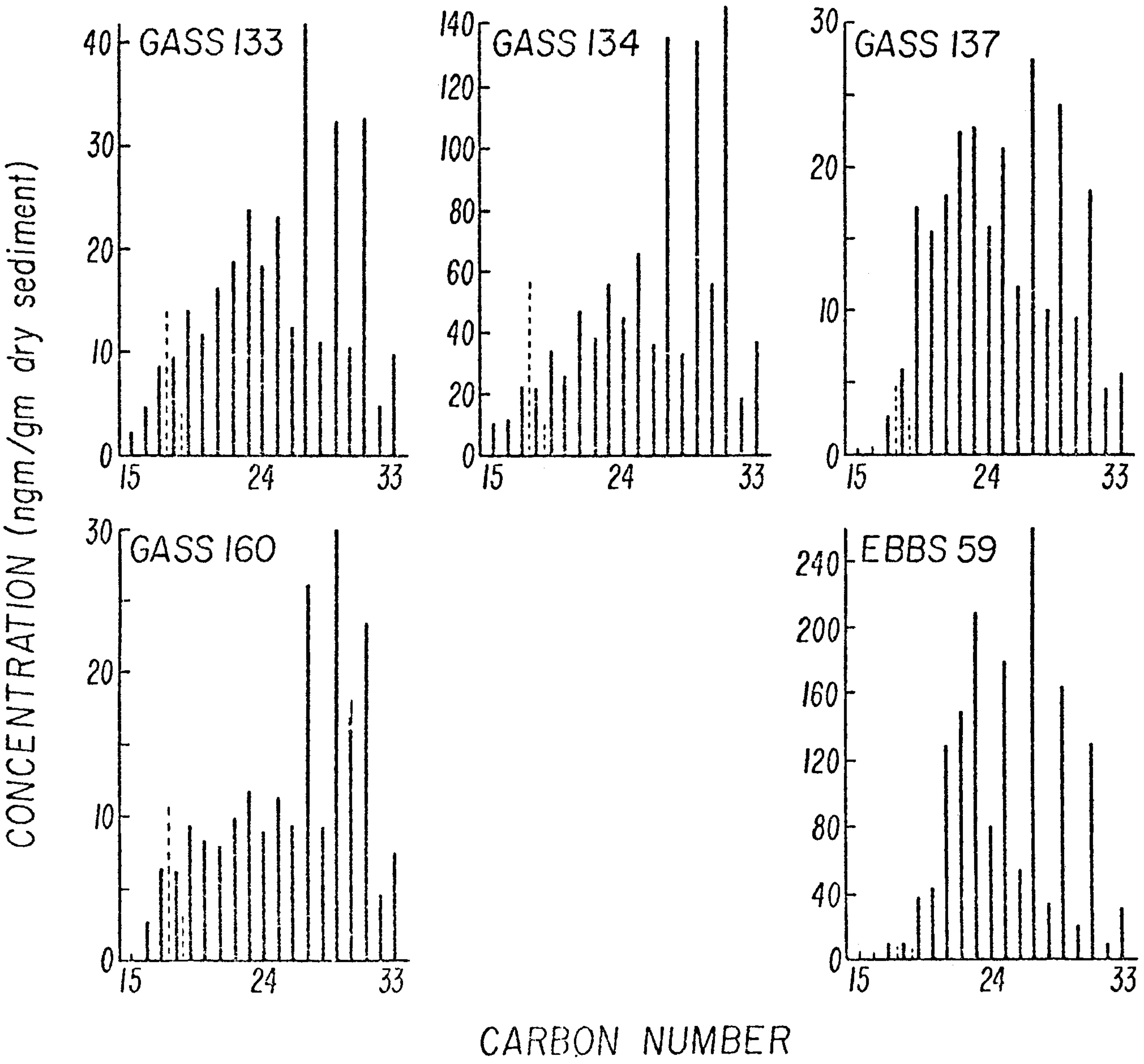

Figure 5. Distribution of n-alkanes and C_{19} and C_{20} isoprenoids in W. Gulf of Alaska (GASS) surface sediments.

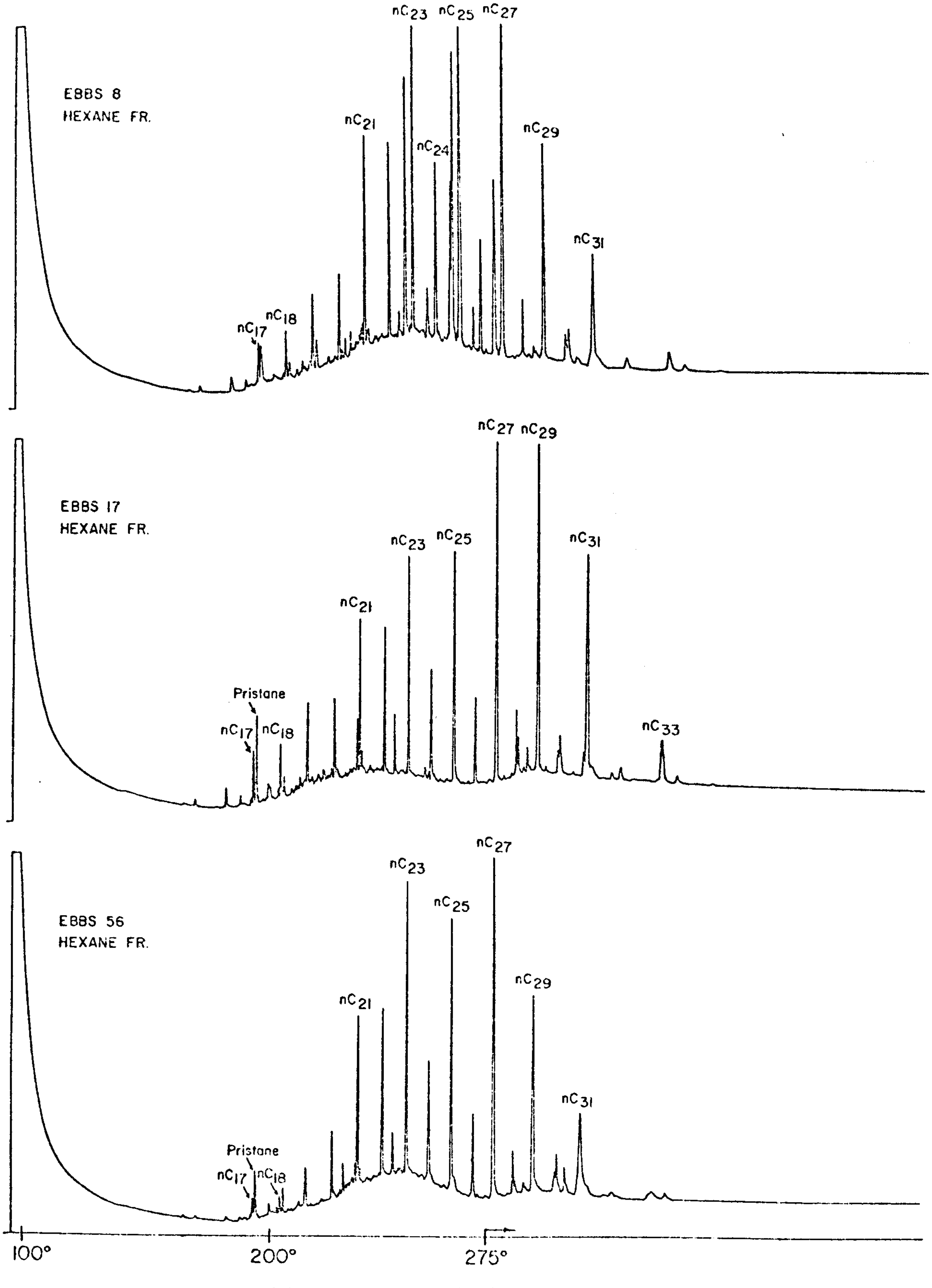

Figure 6. Gas chromatograms of hexane fractions extracted from surface sediments of E. Bering Sea.

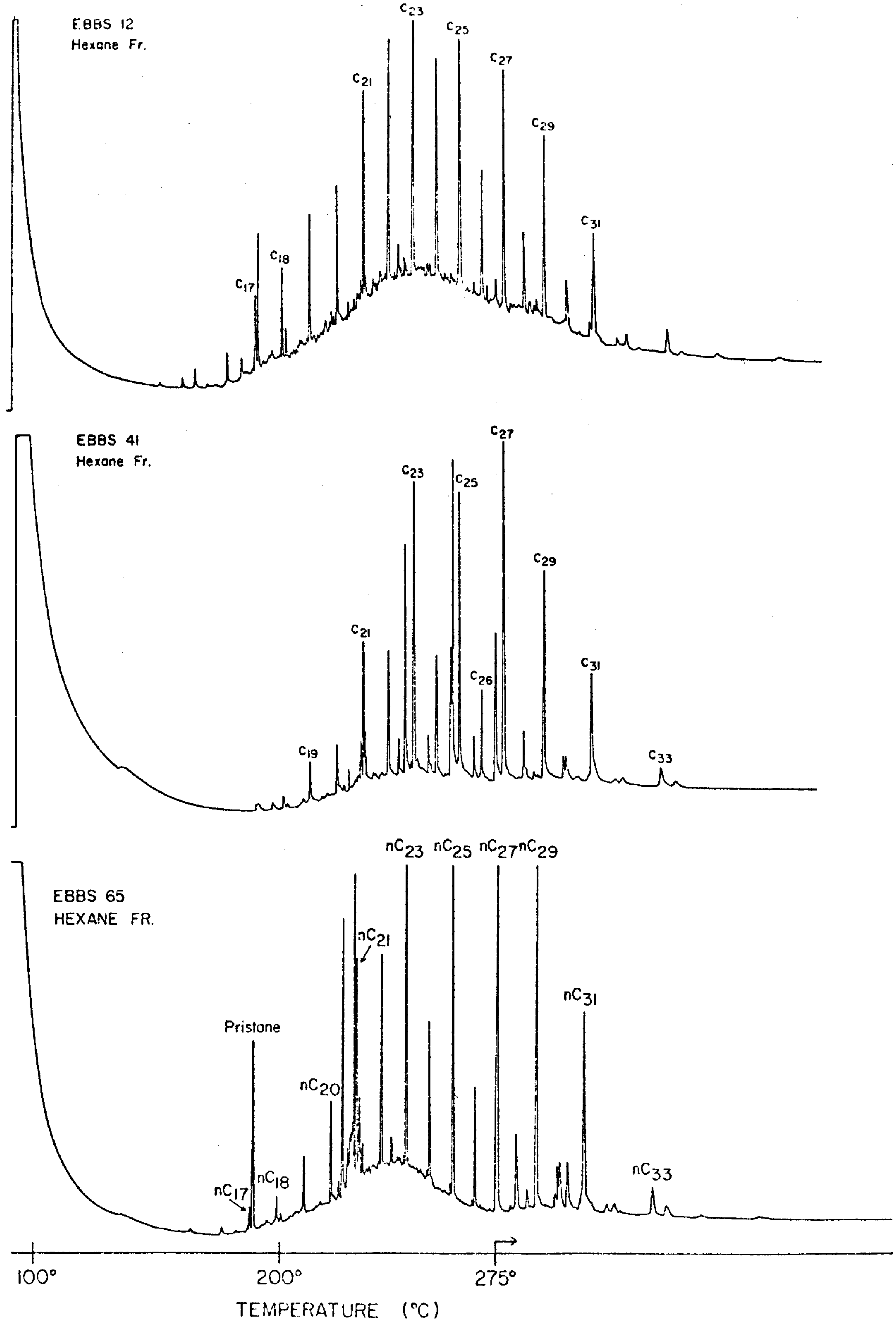

Figure 7. Gas chromatograms of hexane fractions extracted from surface sediments of E. Bering Sea.

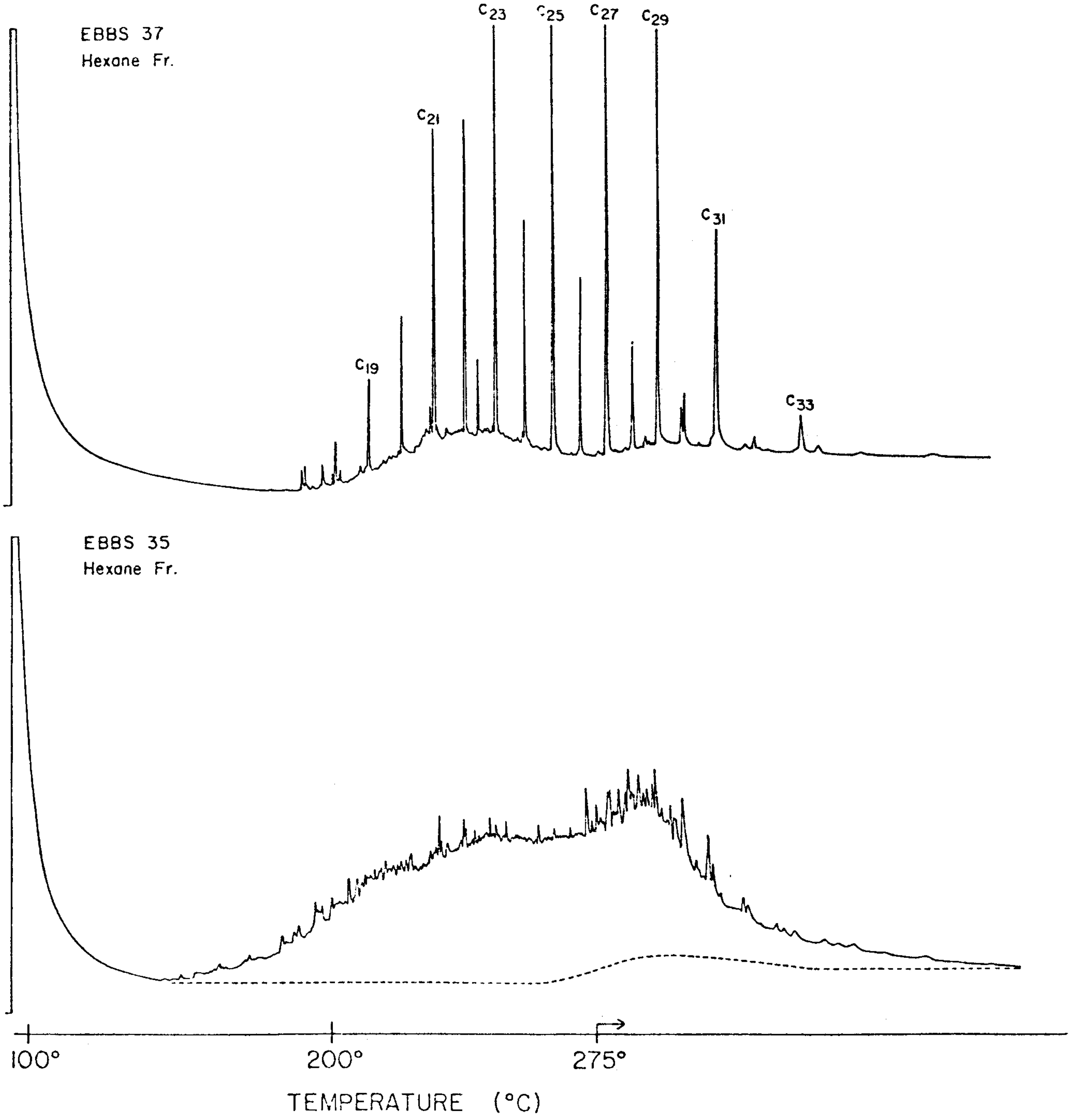

Figure 8. Gas chromatograms of hexane fractions extracted from surface sediments of E. Bering Sea.

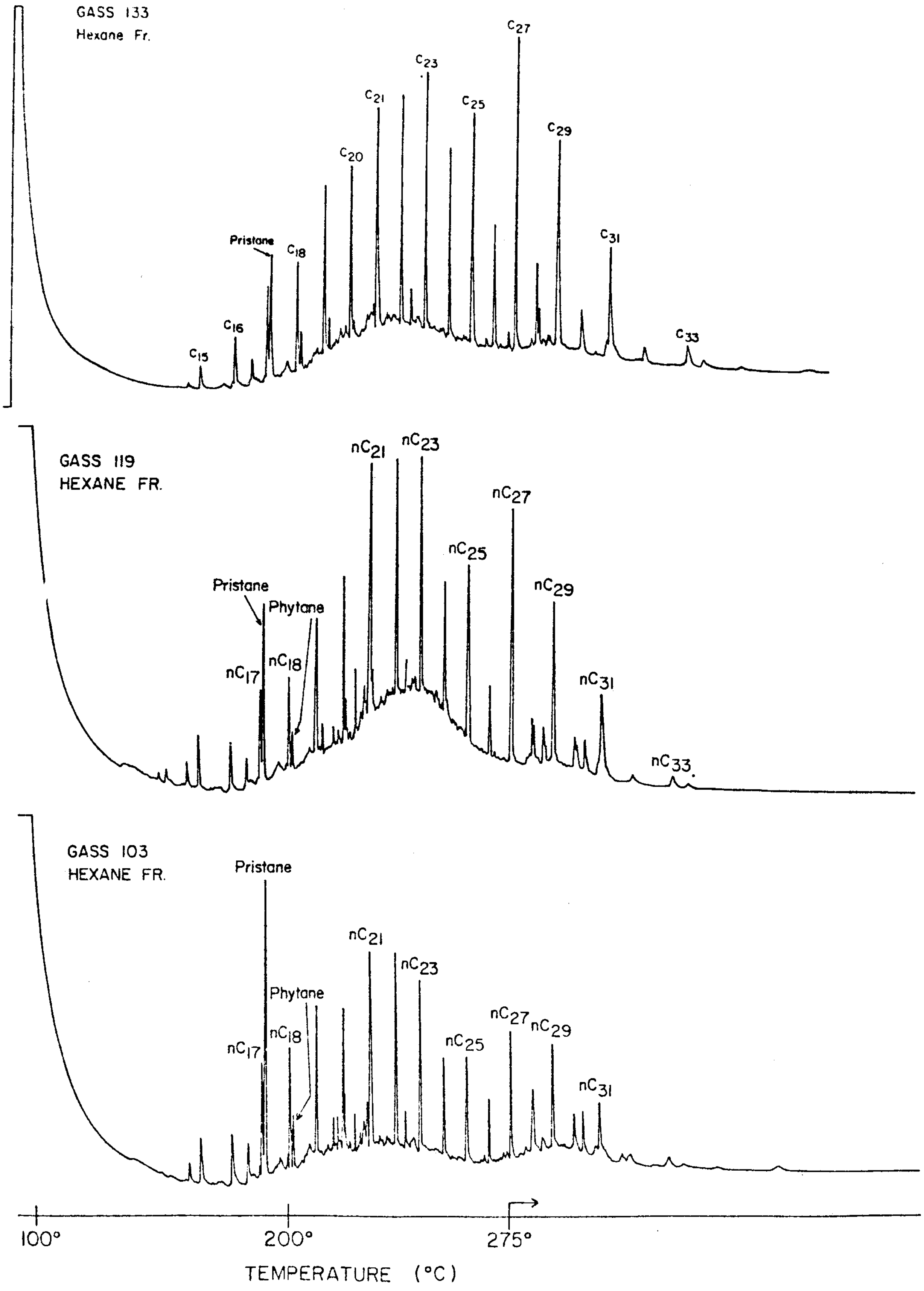

Figure 9. Gas chromatograms of hexane fractions extracted from surface sediments of W. Gulf of Alaska.

TABLE 1. ELEMENTAL ANALYSIS

Station	Latitude	Longitude	Water Depth (m)	Carbon (%) Total	Carbon (%) Organic	Carbon (%) $CaCO_3$	Nitrogen (%)	Sulfur (%)
<u>EASTERN BERING SEA</u>								
EBBS 8	58°17.9'N	159°31.6'W	26	0.27	0.23	0.33	0.026	0.051
EBBS 12	56°09.5'	162°09.5'	84	0.45	0.14	2.58	0.018	0.019
EBBS 17	55°26.4'	165°49.1'	119	0.92	0.76	1.33	0.089	0.090
EBBS 19	56°40.5'	163°56.6'	75	0.76	0.39	3.25	0.064	0.066
EBBS 24	58°46.4'	162°29.4'	47	0.37	0.33	0.33	0.032	0.057
EBBS 28	57°10.4'	165°04.4'	70	0.76	0.59	1.33	0.140	0.079
EBBS 35	56°12.4'	168°20.4'	160	0.54	0.41	1.08	0.038	0.014
EBBS 37	57°05.3'	167°00.6'	75	0.53	0.41	1.00	0.045	0.051
EBBS 38	57°40.1'	166°05.8'	66	0.84	0.66	1.50	0.074	0.045
EBBS 40	58°07.3'	165°15.6'	46	0.31	0.32	0.00	0.033	0.044
EBBS 41	58°46.9'	164°14.2'	36	0.61	0.37	2.00	0.008	0.027
EBBS 43	58°42.5'	166°16.0'	37	0.49	0.30	1.58	0.029	0.038
EBBS 46	57°34.5'	168°04.5'	70	0.95	0.42	4.40	0.043	0.045
EBBS 54	56°56.4'	170°54.8'	105	1.01	0.68	2.75	0.104	0.096
EBBS 56	58°06.5'	169°05.4'	71	0.61	0.47	1.67	0.083	0.099
EBBS 58	58°43.5'	167°21.0'	44	0.61	0.31	2.50	0.033	0.054
EBBS 59	59°11.9'	167°17.1'	38	0.53	0.27	2.17	0.029	.058
EBBS 64	58°01.5'	171°17.0'	90	1.07	0.77	2.50	0.094	0.127
EBBS 65	57°24.9'	172°04.6'	109	1.08	0.67	3.42	0.074	0.077
PMEL 45B	55°39.8'	164°04.1'	95	1.22	0.76	3.83	0.035	0.042
<u>WESTERN GULF OF ALASKA</u>								
GASS101	59°18.6'N	152°18.6'W	170	0.53	0.18	2.92	0.009	0.010
GASS102	59°10.1'	152°04.4'	101	2.44	0.18	18.83	0.019	0.016
GASS103	59°00.6'	151°48.2'	96	5.41	0.53	40.65	0.092	0.043
GASS104	58°50.0'	151°26.4'	100	2.65	0.39	18.83	0.046	0.020
GASS105	58°40.1'	151°07.3'	160	1.37	0.76	5.08	0.058	0.037
GASS119	57°06.0'	156°00.6'	250	1.25	0.74	4.25	0.083	0.063
GASS120	56°55.0'	155°44.1'	294	1.51	1.08	3.58	0.132	0.075
GASS121	56°43.6'	155°28.0'	238	1.81	1.13	5.66	0.150	0.010
GASS122	56°31.1'	155°11.9'	42	5.02	0.18	40.32	0.023	0.042
GASS123	56°19.1	154°55.1'	12	1.69	0.78	7.58	0.083	0.066
CASS124	56°07.0'	154°39.0'	107	1.41	0.92	4.08	0.105	0.071
GASS133	55°44.8'	158°49.3'	68	0.83	0.35	4.00	0.029	0.037
GASS134	55°33.6'	158°40.0'	152	1.59	1.09	4.17	0.101	0.150
GASS135	55°20.0'	158°25.4'	145	0.97	0.42	4.58	0.052	0.039
GASS137	54°55.0'	157°58.5'	102	2.15	0.34	15.08	0.019	0.020
GASS160	53°44.2'	164°26.3'	195	0.60	0.31	2.42	0.030	0.169

Table 2. Gravimetric analysis of hydrocarbons extracted from Eastern Bering Sea (EBBS) stations.

Station	Fraction (μgm/gm dry sediment) Nonsaponifiable	Hexane	Benzene	Methanol	Total Hydrocarbons*
8	89.5	5.7	2.8	90.3	8.5
12	43.9	3.4	1.4	32.9	4.8
17	217.7	13.0	5.2	180.0	18.2
19	412.4	7.4	4.5	173.5	11.9
24	132.4	6.1	5.4	116.4	11.5
28	1894.4	8.7	4.1	1097.2	12.8
35	839.4	180.1	60.8	233.3	240.9
37	137.2	5.8	4.0	56.9	9.8
38	289.5	4.9	10.6	166.8	15.5
40	111.9	1.9	2.6	77.2	4.5
41	103.4	1.4	0.5	96.4	1.9
43	119.5	2.4	2.7	90.0	5.1
46	176.4	4.3	7.5	96.1	11.8
51	88.8	2.8	0.6	81.9	3.4
54	177.3	7.4	9.9	147.5	17.3
56	382.1	10.6	8.5	263.7	19.1
58	218.3	3.8	2.8	118.5	6.6
59	194.2	6.4	6.2	100.3	12.6
64	274.0	12.3	9.8	237.3	22.1
65	214.9	6.9	9.6	136.3	16.5
PMEL 45B	179.5	3.9	4.9	74.5	8.8

*Total hydrocarbons = sum of hexane and benzene fractions.

n.d. = not determined

Table 3. Gravimetric analysis of hydrocarbons extracted from Western Gulf of Alaska (GASS) stations.

Station	Fraction (μgm/gm dry sediment) Nonsaponifiable	Hexane	Benzene	Methanol	Total Hydrocarbons*
101	34.0	n.d.	0.4	n.d.	n.d.
102	75.0	2.2	0.9	37.5	3.1
103	242.0	3.2	4.0	98.2	7.2
104	110.0	17.8	5.6	40.9	23.4
105	166.7	3.8	6.7	10.6	10.5
119	188.4	14.3	5.8	176.8	20.1
120	382.2	12.5	6.5	279.9	19.0
121	270.1	13.2	13.5	193.7	26.7
122	36.6	n.d.	0.6	18.3	n.d.
124	201.6	11.9	6.4	124.1	18.3
133	90.7	2.0	1.3	71.5	3.3
134	549.7	4.2	15.3	393.0	19.5
137	72.8	1.7	1.6	63.1	3.3
160	107.6	1.5	0.5	99.2	2.0

*Total hydrocarbons = sum hexane and benzene fractions.

n.d. = not determined

Table 4. Gravimetric analysis of benzene fraction of extracts from surface sediments from Eastern Bering Sea (EBBS) and Gulf of Alaska (GASS) before LCand after separation of fatty acid methyl esters from hydrocarbons by silica gel $AgNO_3$-thin layer chromatography (TLC).

Concentration (μgm/gm dry sediment)

EBBS Stations	LC*	$AgNO_3$-TLC	GASS Stations	LC*	$AgNO_3$-TLC
8	6.5	2.8	101	n.d.	0.4
12	1.7	1.4	102	2.9	0.9
17	9.1	5.2	103	6.4	4.0
19	13.2	4.5	104	5.3	5.6
24	7.6	5.4	105B	12.9	6.7
28	6.8	4.1	119	7.8	5.8
35	89.3	60.8	120	13.5	6.5
37	4.4	4.0	121	29.6	13.5
38	14.7	10.6	122	n.d.	0.6
40	3.7	2.6	124	19.2	6.4
41	0.7	0.5	133	2.0	1.3
43	3.3	2.7	134	21.1	15.3
46	8.6	7.5	137	1.7	1.6
51	1.4	0.6	160	1.5	0.5
54	12.4	9.9			
56	9.6	8.5			
58	9.8	2.8			
59	12.0	6.2			
64	15.7	9.8			
65	17.3	9.6			
45B	5.4	4.9			

*Concentration of benzene fraction of non-saponifiable extract separated by column chromatography

n.d. = not determined

Table 5. Gas chromatographic analysis of hexane fraction of hydrocarbons extracted from Eastern Bering Sea (EBBS) surface sediments.

n-alkane* concentration (ngm/gm dry sediment)

Station	16	17	Pr	18	Ph	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	Δ21**	Total n-Alkanes
8	2.3	6.0	8.9	7.4	3.3	11.6	10.9	26.0	32.7	67.9	31.0	71.9	23.0	95.6	16.3	67.9	10.9	62.1	5.6	11.0	n.d.	561.6
12	3.4	7.0	12.6	8.9	3.8	12.1	12.3	18.0	26.0	36.8	24.8	34.5	16.2	39.3	14.5	31.5	9.8	23.3	4.3	8.3	n.d.	330.6
17	5.5	14.9	26.9	16.5	6.8	25.8	22.8	35.0	45.9	74.1	36.5	98.6	39.2	184.1	34.2	184.3	33.9	175.0	11.0	46.2	20.9	1086.5
19	9.6	19.7	31.4	17.4	5.4	53.6	39.5	105.1	164.1	273.6	136.8	275.0	89.6	475.0	76.7	358.8	57.3	300.7	25.7	94.6	35.7	2572.8
24	4.5	9.6	10.1	9.6	3.0	13.9	15.3	28.9	34.5	76.6	33.1	76.9	26.6	120.6	21.4	81.0	16.8	73.1	5.9	16.3	n.d.	664.5
28	6.3	16.3	35.2	13.0	3.4	39.3	46.3	69.4	81.1	240.0	104.2	339.3	109.7	640.9	103.1	469.3	79.7	425.0	32.3	117.9	72.0	2932.8
35	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
37	n.d.	2.2	3.1	4.9	1.8	11.3	15.9	34.0	46.0	81.5	35.3	90.3	30.5	149.5	22.0	105.3	16.0	86.8	6.0	18.8	n.d.	756.0
38	n.d.	4.2	9.2	5.8	1.8	12.5	13.6	40.0	55.8	150.1	65.8	215.3	65.0	372.6	48.7	263.9	34.0	220.7	14.1	57.2	10.5	1639.3
40	2.3	5.7	6.1	5.4	1.7	9.2	8.6	24.6	25.7	62.0	29.0	73.0	25.0	119.7	21.0	85.7	18.0	74.0	5.7	20.6	n.d.	614.0
41	n.d.	n.d.	n.d.	1.7	0.7	4.8	5.5	15.9	18.4	45.7	20.9	53.9	16.9	83.6	13.5	56.9	5.9	55.8	3.2	10.7	13.9	413.3
43	1.5.	4.3	4.2	3.9	1.8	8.3	8.3	22.6	28.1	58.1	34.2	69.4	27.4	95.8	20.4	65.7	1.5	61.8	4.8	10.2	32.2	524.3
46	n.d.	3.5	36.2	5.0	2.0	12.4	10.6	26.9	33.5	71.0	31.5	86.8	31.9	152.4	23.2	112.5	18.2	96.5	7.4	20.9	2.6	740.1
51	2.7	6.5	13.8	8.2	4.0	22.5	17.3	31.4	34.5	61.2	35.7	78.8	35.2	126.2	38.6	112.9	31.6	100.9	13.4	26.0	53.7	773.1
54	5.5	12.0	36.7	11.5	4.2	9.2	51.5	70.7	69.0	156.0	74.7	214.2	66.5	412.5	74.0	295.3	56.0	282.3	18.0	46.7	39.8	2101.0
56	n.d.	3.5	11.7	1.5	4.0	6.3	13.5	32.4	41.5	78.4	36.3	91.4	28.5	155.7	20.0	107.2	11.6	104.4	4.1	11.8	14.0	751.0
58	1.0	38.	4.8	3.1	1.0	37.7	5.7	14.4	16.5	34.9	15.8	35.3	11.5	51.8	7.9	34.8	3.2	29.5	n.d.	4.7	8.8	280.2
59	2.6	9.6	8.0	9.9	4.6	32.3	44.3	128.5	148.1	210.1	81.2	179.0	53.9	258.6	34.1	166.3	19.9	128.2	8.6	30.5	50.1	1551.1
64	5.5	21.3	20.3	20.2	9.0	19.7	66.9	111.9	119.2	170.1	81.5	179.6	61.5	310.2	58.9	233.9	46.8	207.9	15.4	42.5	121.0	1785.4
65	2.7	8.3	64.4	10.9	3.9	29.8	30.9	84.2	81.6	143.1	73.8	173.5	54.1	334.5	39.7	241.1	30.4	218.7	11.7	44.0	239.0	1602.5
45B	4.3	10.5	18.5	10.1	4.9	4.9	30.3	50.5	95.5	106.3	60.9	66.7	23.7	86.3	18.8	77.1	15.0	71.3	5.0	18.0	15.4	780.1

*n-alkane chain length indicated by 15, 16, 17, etc.

**Δ21 includes hydrocarbons except C_{21} with a "Kovat" index between 2050 and 2110.

n.d. = not detected

n.r. = not resolved

Table 6. Gas chromatographic analysis of hexane fraction of hydrocarbons extracted from Western Gulf of Alaska (GASS) surface sediments.

n-Alkane* Concentration (ngm/gm dry sediment)

Station	16	17	Pr	18	Ph	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	Δ21**	Total n-Alkanes
101	n.d.	0.6	2.4	0.5	1.3	3.0	2.7	5.8	11.5	11.1	7.5	5.2	2.4	4.1	1.0	4.0	1.0	n.d.	n.d.	n.d.	2.5	60.3
102	n.d.	2.8	4.1	5.3	3.0	9.0	13.3	22.2	39.5	28.2	13.4	7.6	2.9	4.7	1.4	3.6	0.7	0.9	n.d.	n.d.	n.d.	155.5
103	4.0	7.8	22.1	8.3	4.4	10.5	8.1	12.7	15.5	14.1	9.5	11.0	6.5	17.0	4.8	15.7	7.1	15.3	2.8	2.97	14.0	173.6
104	33.0	60.7	9.56	100.0	91.7	218.5	111.7	166.7	207.7	161.4	84.6	61.9	35.2	54.9	31.4	47.0	31.9	27.5	7.2	n.d.	n.d.	1482.4
105	10.5	16.6	44.4	16.8	8.1	22.2	20.6	30.1	47.0	47.1	33.7	21.7	11.5	18.9	10.2	13.4	9.1	8.8	n.d.	1.7	17.3	339.9
119	19.0	29.5	73.7	33.3	16.2	48.2	52.7	109.3	98.7	104.8	75.8	92.9	36.1	172.9	26.2	147.5	28.5	137.1	10.8	18.6	151.2	852.8
120	14.2	27.4	79.4	26.0	11.6	37.6	30.6	60.5	56.2	88.7	60.6	109.0	43.4	222.3	41.1	186.8	66.8	135.3	22.2	42.2	63.1	1271.1
121	29.3	48.5	138.5	43.3	22.9	66.5	40.4	54.7	117.4	153.2	99.2	160.0	67.2	288.0	66.6	281.9	103.1	222.2	40.7	70.4	188.7	1999.7
124	14.8	26.1	61.8	25.7	13.7	40.0	32.0	52.7	73.2	81.9	53.8	81.4	42.2	119.7	44.3	122.8	34.5	104.6	17.6	22.1	44.82	1005.8
133	4.5	8.6	13.6	9.1	3.8	13.5	11.8	16.2	18.6	23.4	17.9	23.2	12.5	41.9	11.2	32.6	10.5	32.7	4.8	9.6	11.5	304.4
134	11.8	23.6	57.3	21.2	9.3	33.8	24.9	46.1	38.1	56.3	44.7	65.9	37.7	136.0	31.4	135.1	55.4	148.4	18.4	37.1	230.3	965.9
137	n.d.	2.6	4.6	6.0	2.5	17.3	15.6	18.2	22.6	22.9	15.7	21.3	11.6	27.6	10.0	24.5	9.5	18.5	4.5	5.6	18.1	275.5
160	2.6	6.1	10.5	5.9	2.7	9.1	8.3	7.9	9.8	11.4	8.7	11.3	9.2	25.7	9.1	29.7	8.1	23.5	4.5	7.4	14.5	197.7

*n-alkane chain length indicated by 15, 16, 17, etc.

**Δ21 includes hydrocarbons except C_{21} with a "Kovat" index between 2050 and 2110.

n.d. = not detected

Table 7. Odd-even and n-alkane/isoprenoid ratios of hexane fraction extracted from surface sediments from Eastern Bering Sea (EBBS) stations.

Station	Pristane/C_{17}	Phytane/C_{18}	Pristane/Phytane	Odd/Even
8	1.48	0.44	2.70	2.99
12	1.79	0.43	3.32	1.76
17	1.81	0.41	3.97	3.43
19	1.59	0.31	5.81	3.17
24	1.05	0.31	3.39	2.96
28	2.16	0.26	10.2	4.09
35	n.r.	n.r.	n.r.	n.r.
37	1.45	0.36	1.76	3.28
38	2.21	0.30	5.18	4.41
40	0.93	0.32	3.37	3.41
41	n.d.	0.41	n.d.	3.80
43	0.97	0.48	2.26	3.08
46	10.3	0.41	17.9	3.59
51	2.14	0.49	3.49	2.56
54	3.06	0.36	8.8	2.57
56	3.34	2.71	2.93	3.78
58	1.26	0.32	4.8	3.33
59	0.83	0.46	1.74	2.85
64	0.96	0.44	2.27	2.75
65	7.74	0.36	16.43	3.77
PMEL45B	1.76	0.49	3.78	1.96

n.d. = not determined

n.r. = not resolved

Table 8. Odd-even and n-alkane/isoprenoid ratios of hexane fraction extracted from surface sediments from Gulf of Alaska (GASS) stations.

Station	Pristane/C_{17}	Phytane/C_{18}	Pristane/Phytane	Odd/Even
101	3.73	2.83	1.81	1.28
102	1.48	0.57	1.38	1.03
103	2.82	0.53	5.00	1.61
104	1.58	0.92	1.04	1.31
105	2.67	0.48	5.48	1.13
119	2.49	0.49	4.56	1.24
120	2.89	0.44	6.86	2.52
121	2.86	0.53	6.04	2.23
124	2.37	0.53	4.52	1.97
133	1.58	0.42	3.54	2.02
134	2.42	0.44	6.17	2.41
137	1.76	0.42	1.86	1.68
160	1.73	0.46	3.94	2.00

Table 9. Total hydrocarbon/organic carbon and n-alkane/organic carbon ratios of surface sediments from E. Bering Sea (EBBS) samples.

Station	Organic Carbon (%)	Total Hydrocarbons (μgm/gm)	Total n-alkanes (μgm/gm)	HC/OC ($\times 10^{-4}$)	Alk/OC ($\times 10^{-4}$)
8	.23	8.5	.562	36.9	2.4
12	.14	4.8	.331	34.3	2.3
17	.76	18.2	1.087	23.9	1.4
19	.39	11.9	2.573	30.5	6.6
24	.33	11.5	.665	34.8	2.0
28	.59	12.8	2.933	21.7	5.0
35	.41	240.9	n.r.	587.6	n.r.
37	.41	9.8	.756	23.9	1.8
38	.66	15.5	1.639	23.5	2.5
40	.32	4.5	.614	14.1	1.9
41	.37	1.9	.413	5.1	1.1
43	.30	5.1	.524	17.0	1.8
46	.42	11.8	.740	28.1	1.8
51	n.d.	3.4	.773	25.4	n.d.
54	.68	17.3	2.101	25.4	3.1
56	.47	19.1	.751	40.6	1.6
58	.31	6.6	.280	21.3	0.9
59	.27	12.6	1.551	46.7	5.7
64	.77	22.1	1.785	28.7	2.3
65	.67	16.5	1.603	24.6	2.3
45B	.76	8.8	.781	11.6	1.0
Range				5-46.7	0.9-6.6

n.d. = not determined

n.r. = not resolved

Table 10. Total hydrocarbon/organic carbon and n-alkane/organic carbon ratios of surface sediments from W. Gulf of Alaska (GASS) samples.

Station	Organic Carbon (%)	Total Hydrocarbons (μgm/gm)	Total n-alkanes (μgm/gm)	HC/OC ($\times 10^{-4}$)	Alk/OC ($\times 10^{-4}$)
101	.18	n.d.	.060		0.3
102	.18	3.1	1.56	17.2	8.7
103	.53	7.2	.174	13.6	0.3
104	.39	23.4	1.482	60.0	3.8
105	.76	10.5	.340	13.8	0.5
119	.74	20.1	.853	1.15	1.2
121	.13	26.7	1.271	23.6	1.1
122	.18	n.d.	2.000	-	11.1
124	.92	18.3	1.006	19.9	1.1
133	.35	3.3	.304	9.4	0.9
134	1.09	19.5	.966	17.9	0.9
137	.34	3.3	.278	9.7	0.8
160	.31	2.0	.198	6.4	0.6
Range				1-60	.3-11

n.d. = not determined

Appendix I

Gas Chromatograms of Hexane Fractions Extracted from Surface Sediments of E. Bering Sea and Gulf of Alaska

Annual Report

April 1, 1976 to March 31, 1977

to

U.S. Department of Commerce
National Oceanic and Atmospheric Adminsitration

Characterization of Organic Matter in Sediments
from Gulf of Alaska, Bering and Beaufort Seas

Contract No. 03-6-022-35250, R.U. No. 480

(Formerly funded under University of Alaska Contract F-01770

OCSEAP Research Unit 480)

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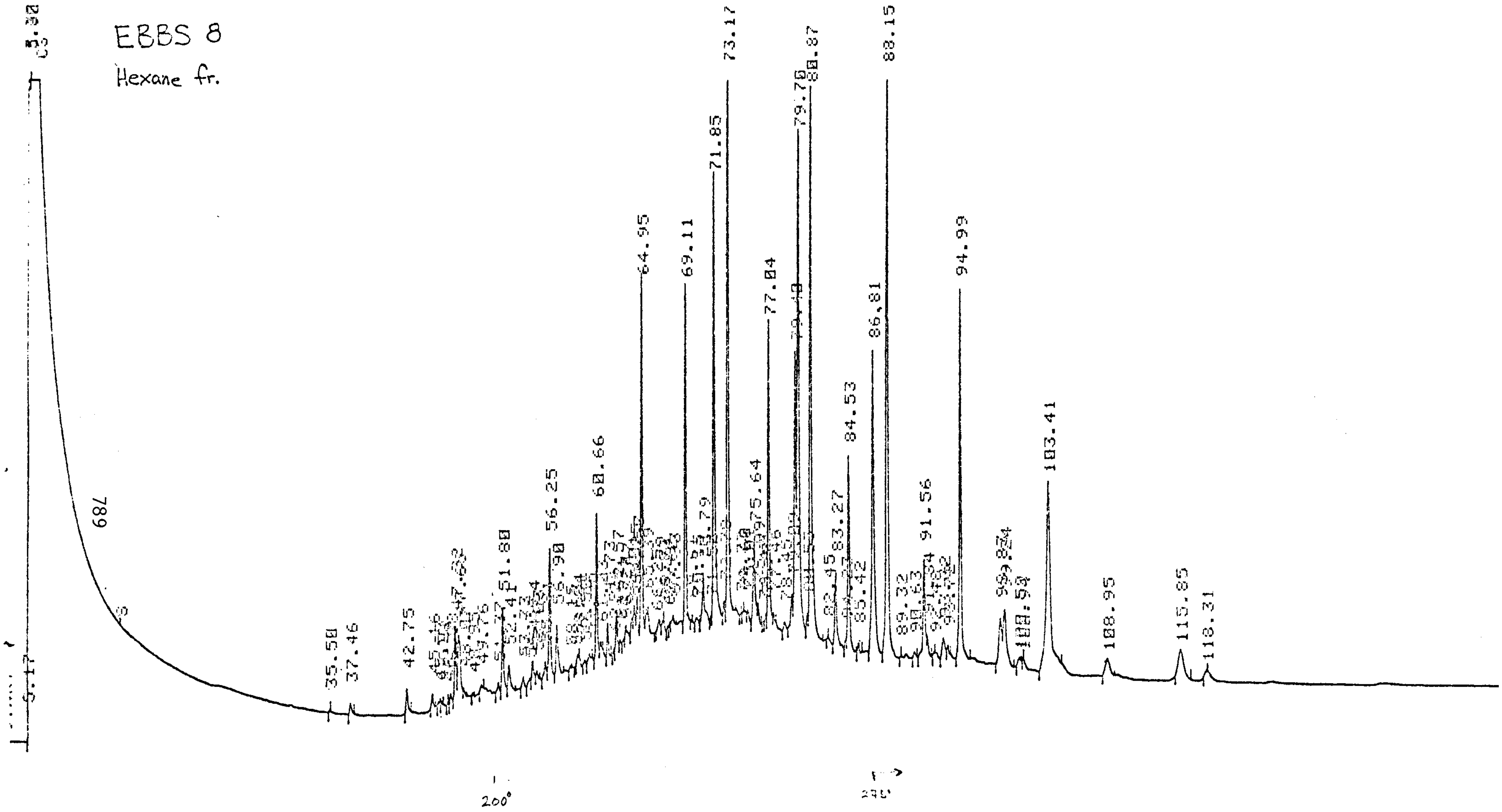
April 29, 1977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Hexane fr.
3.30
789
5.17
35.50
37.46
42.75
47.62
51.80
56.25
55.90
60.66
64.95
69.11
71.85
73.17
75.64
77.04
79.70
80.87
79.40
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84.53
85.42
86.81
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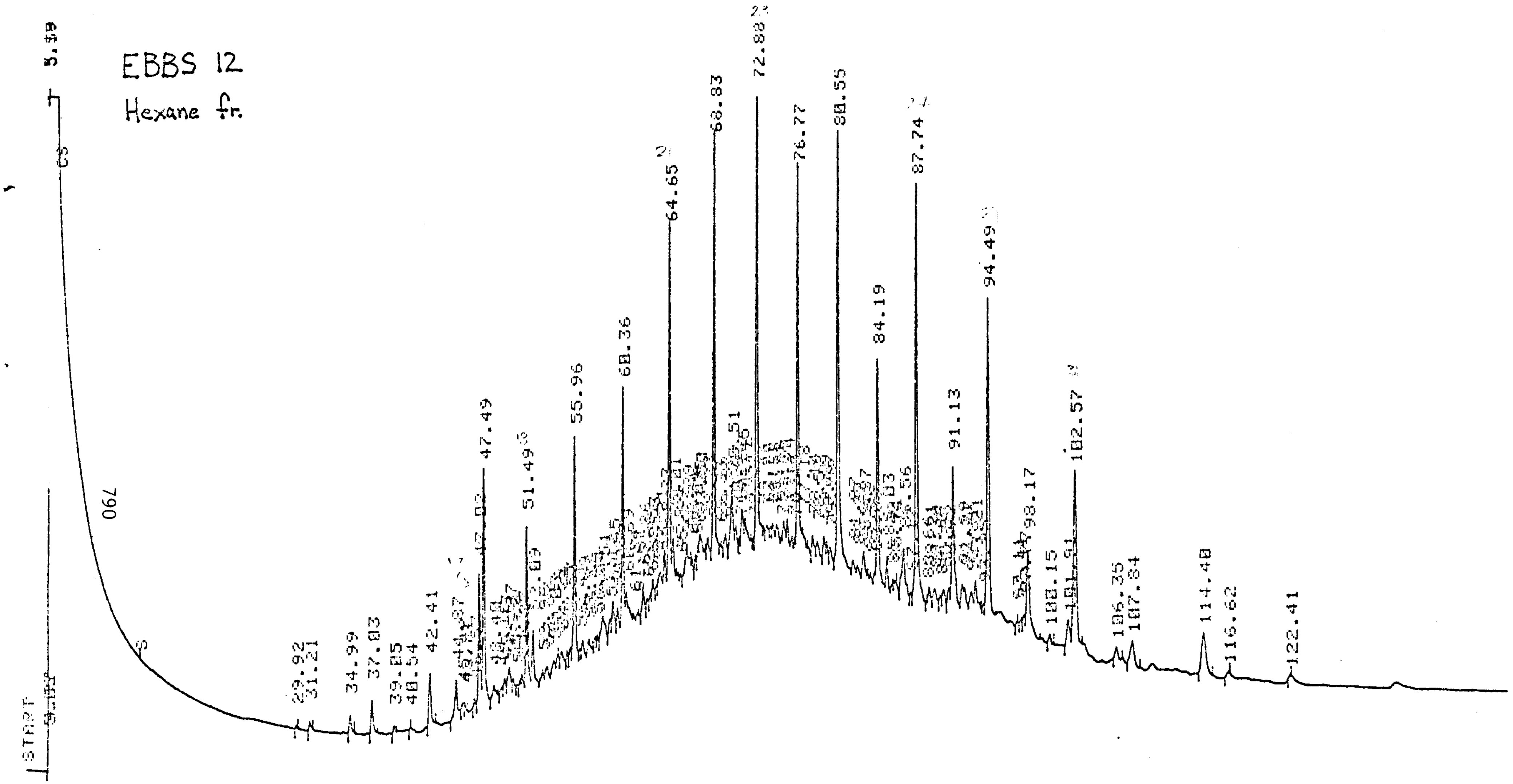
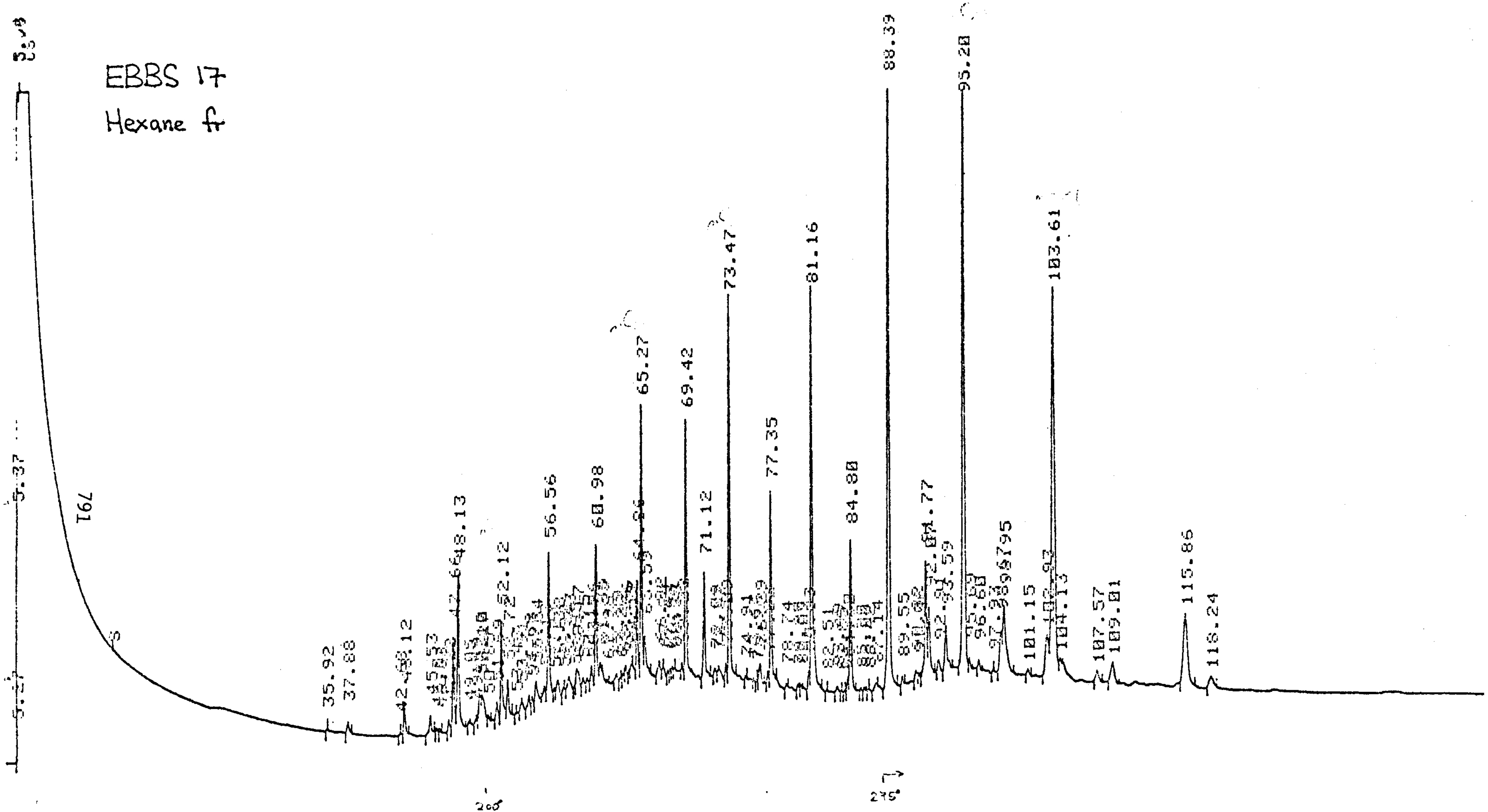


EBBS 12
Hexane fr.

111

EBBS 17
Hexane fr



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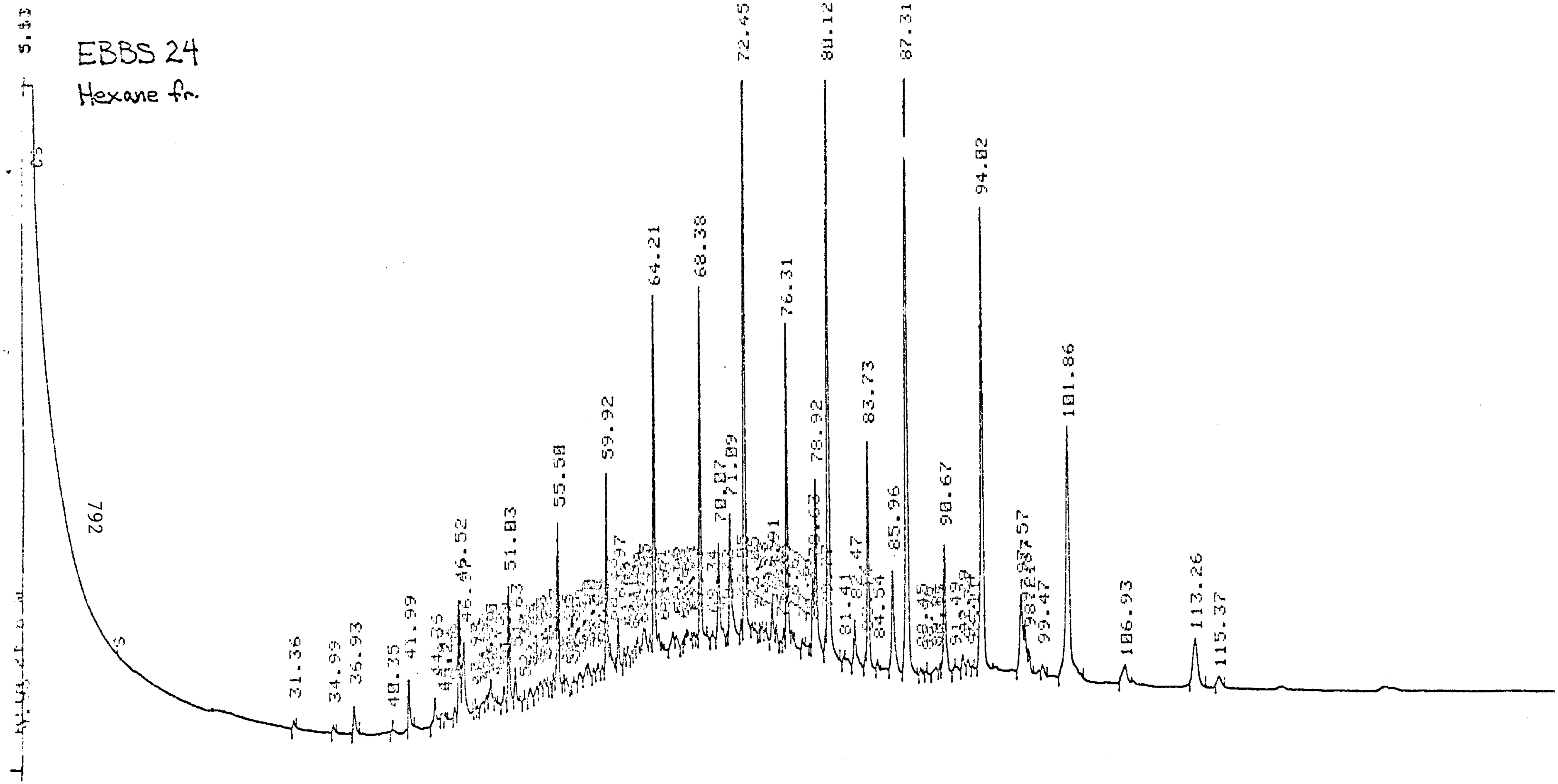
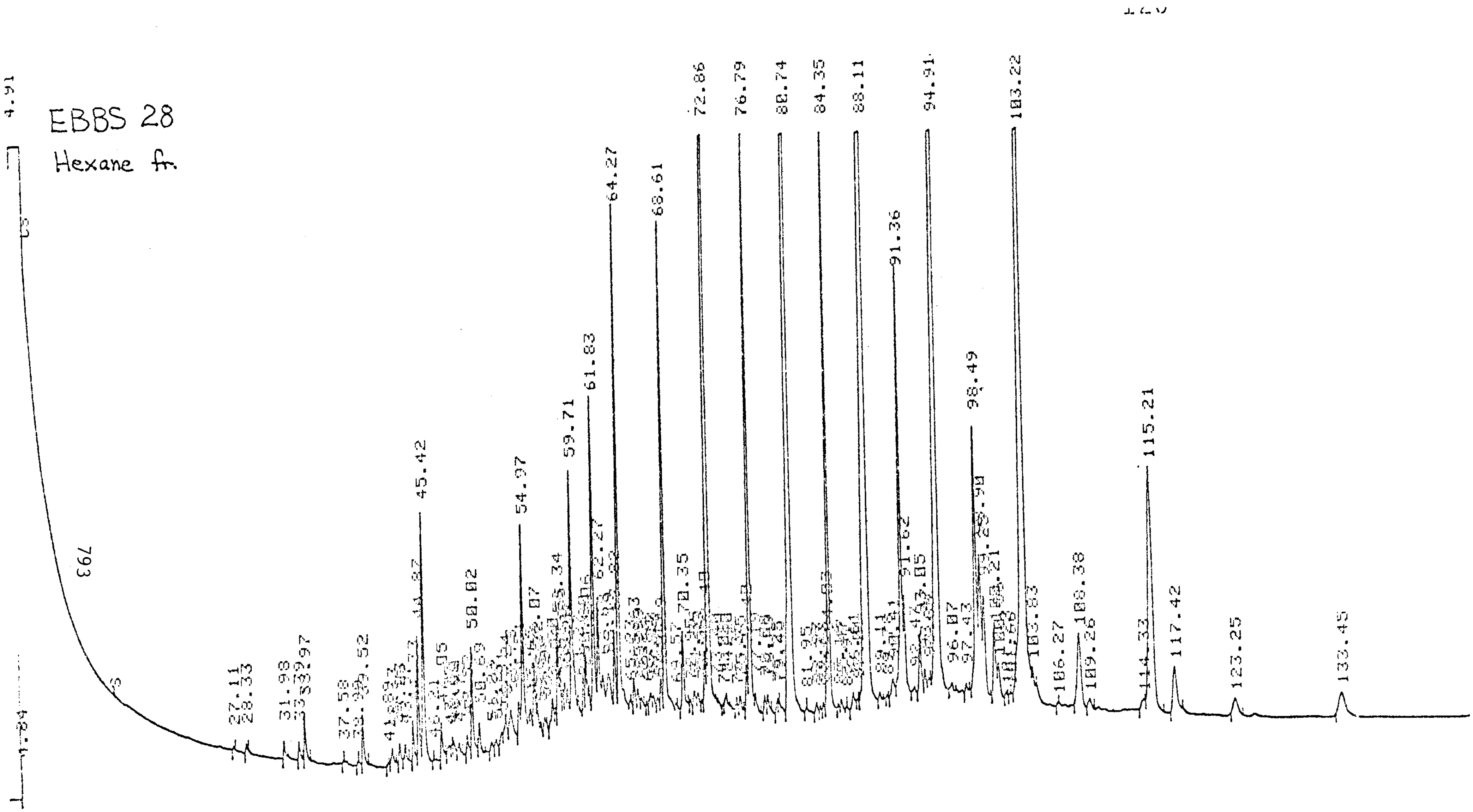
Hexane fr.

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Hexane fr.
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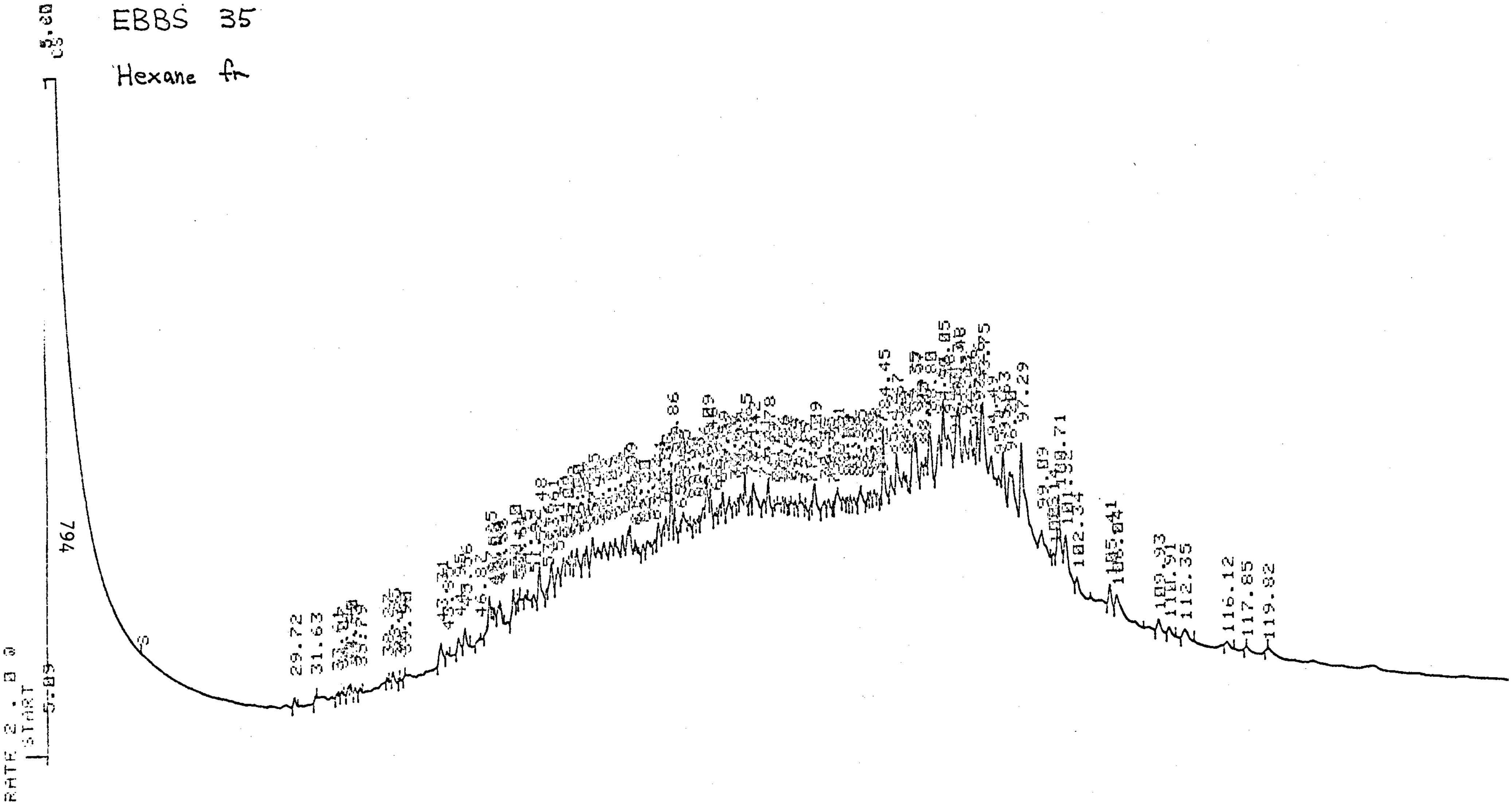
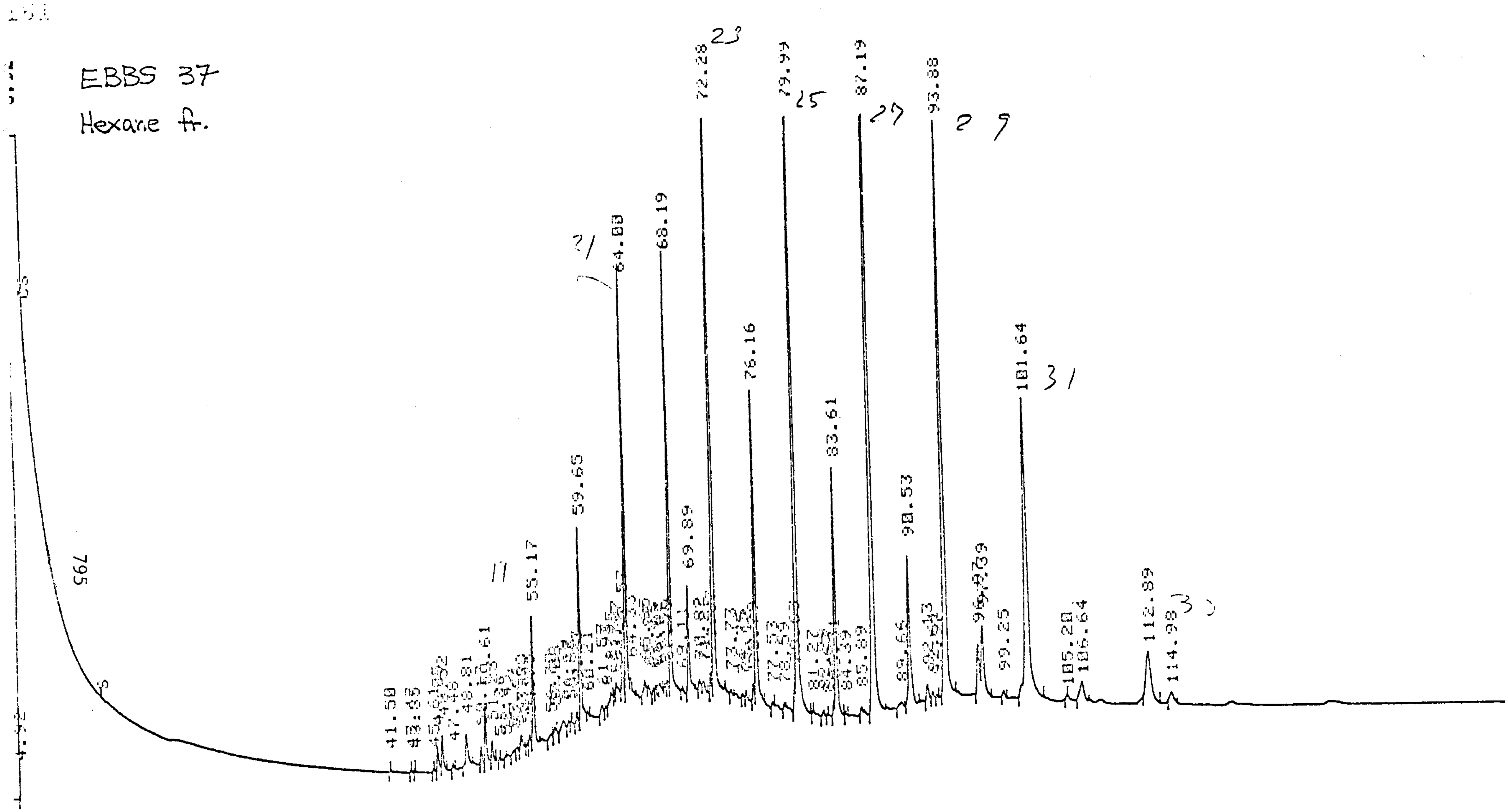
1.84
793
27.11
28.33
31.98
33.97
37.58
39.52
45.42
50.82
54.97
59.71
61.83
62.27
64.27
68.61
70.35
72.86
76.79
80.74
84.35
88.11
91.36
91.62
93.05
94.91
96.87
97.43
98.49
103.22
103.83
106.27
108.38
109.26
114.33
115.21
117.42
123.25
133.45

EBBS 35

Hexane fr

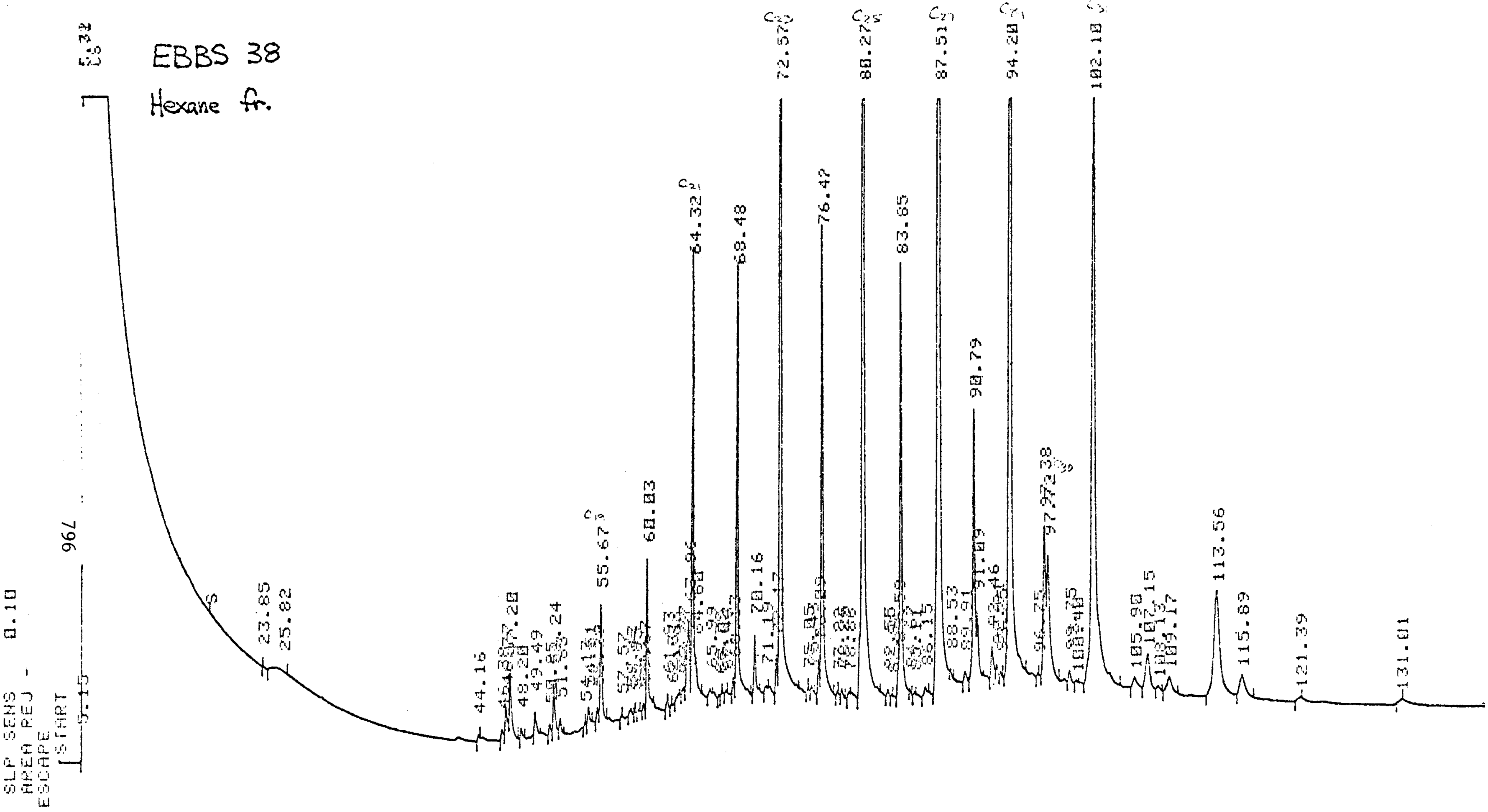




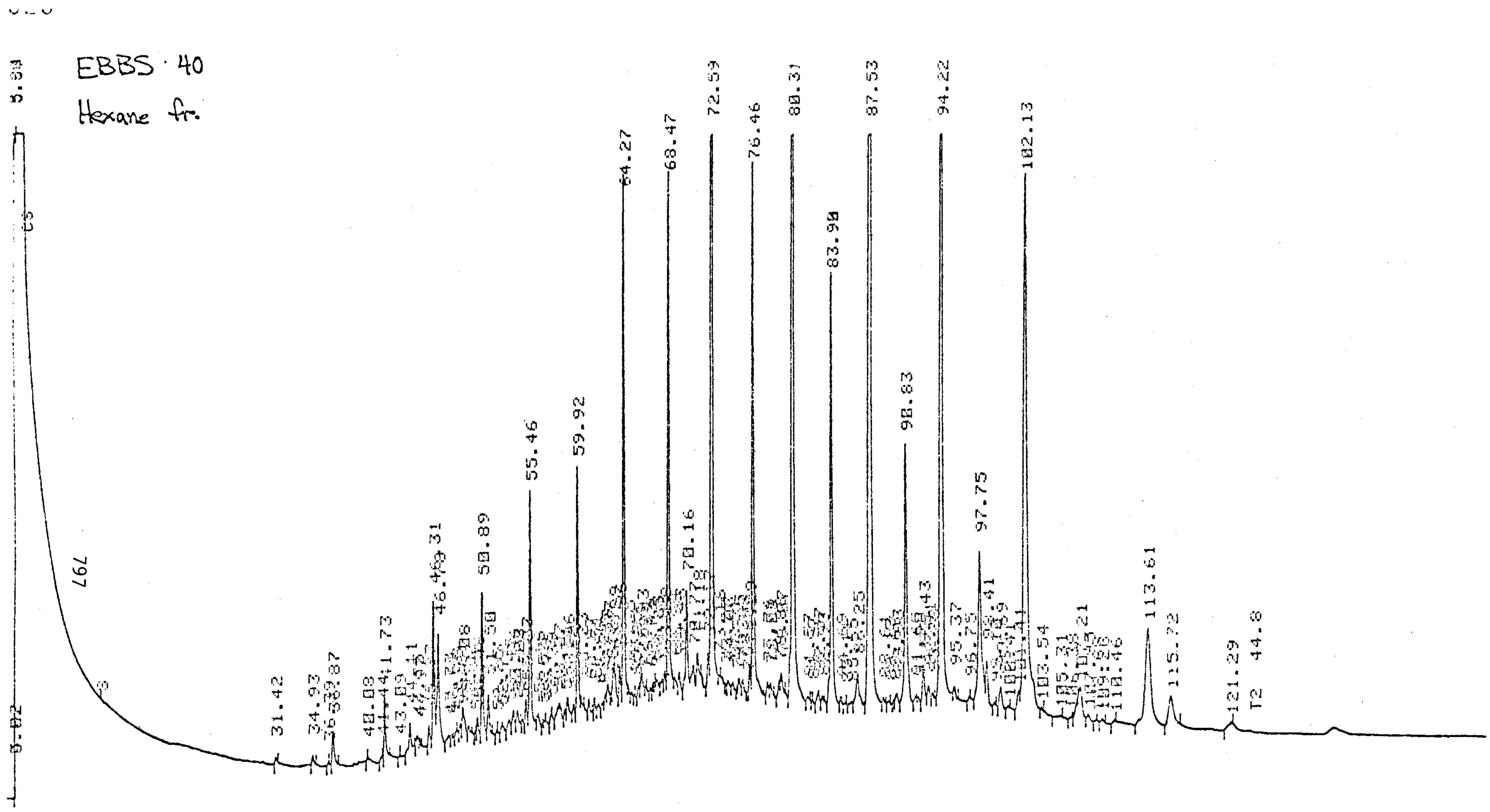
EBBS 37

Hexane fr.

EBBS 38
Hexane fr.

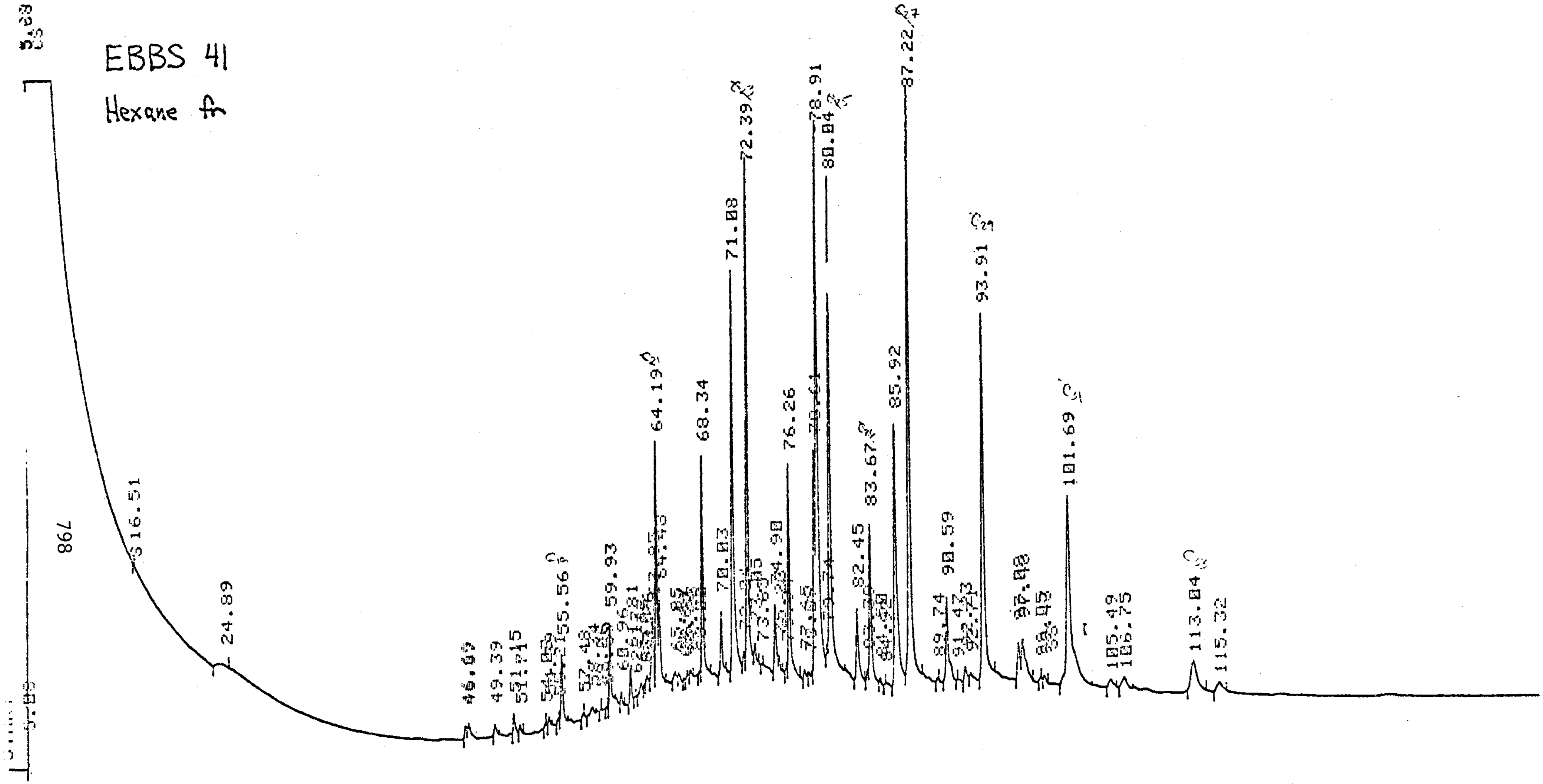


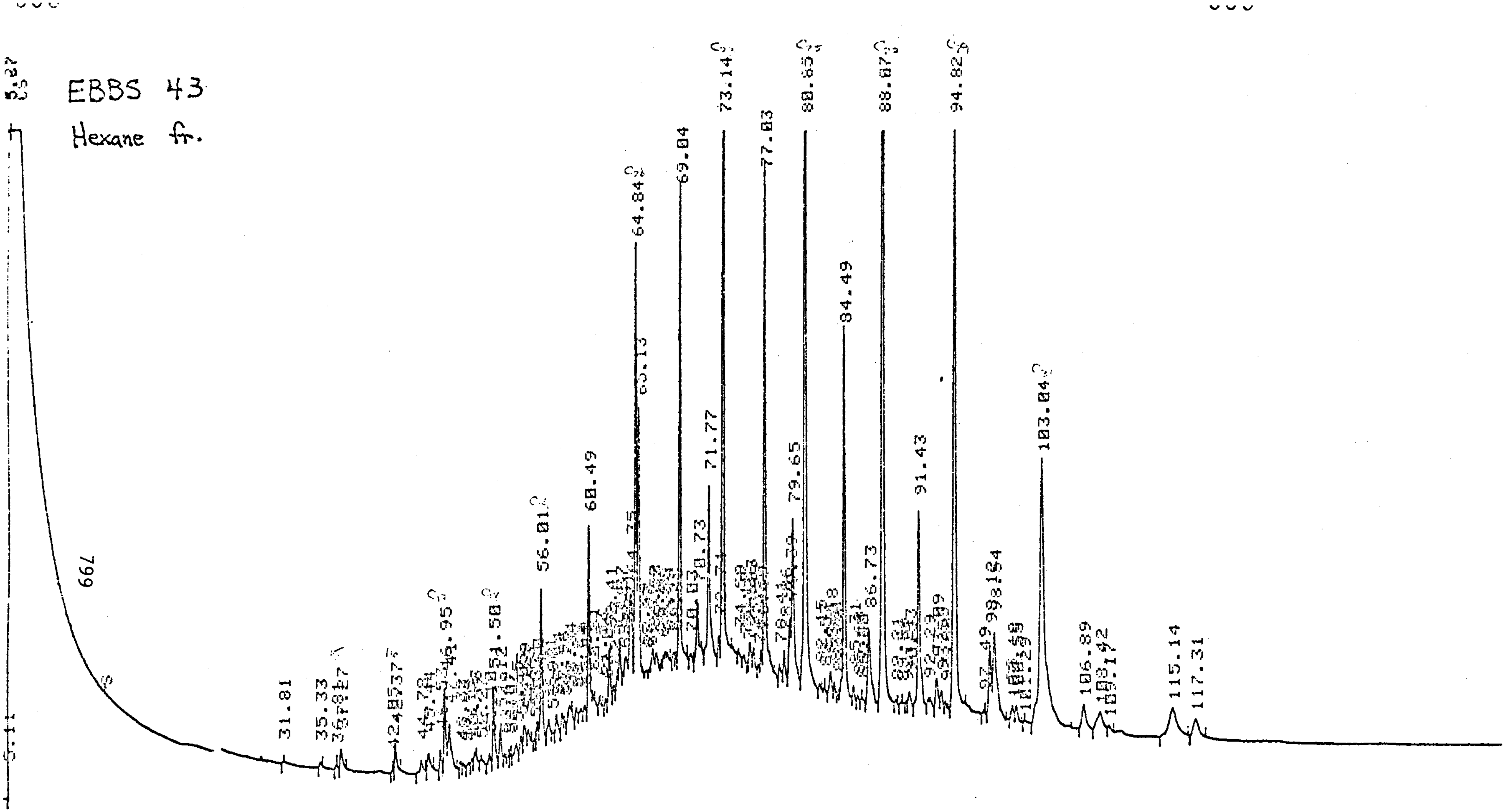
EBBS · 40
Hexane fr.



EBBS 41

Hexane fr




EBBS 43
Hexane fr.
3.27
31.81
35.33
42.85
44.78
48.95
51.50
56.01
60.49
64.84
65.13
69.04
70.73
71.77
73.14
77.03
79.65
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97.49
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108.42
115.14
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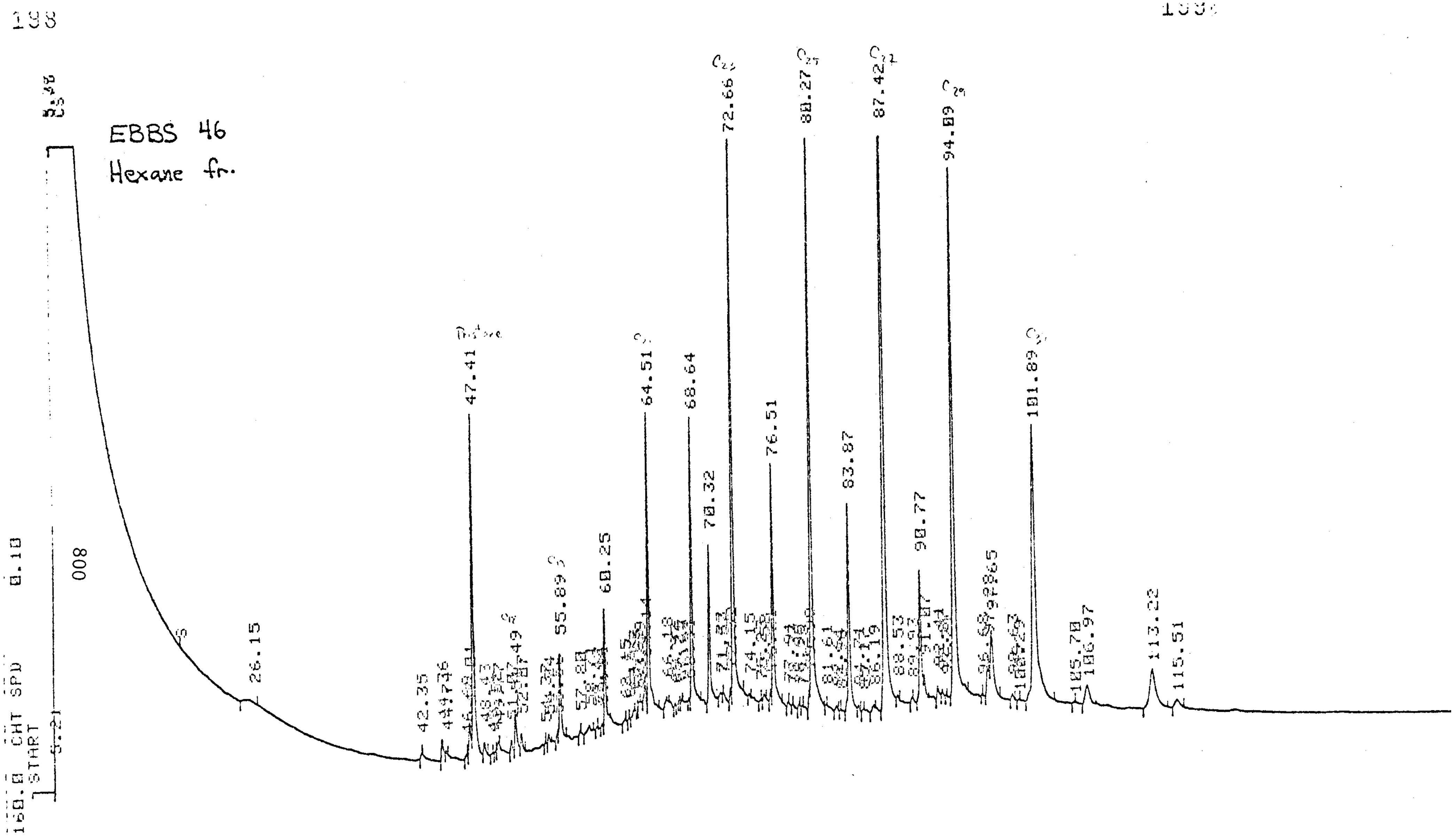
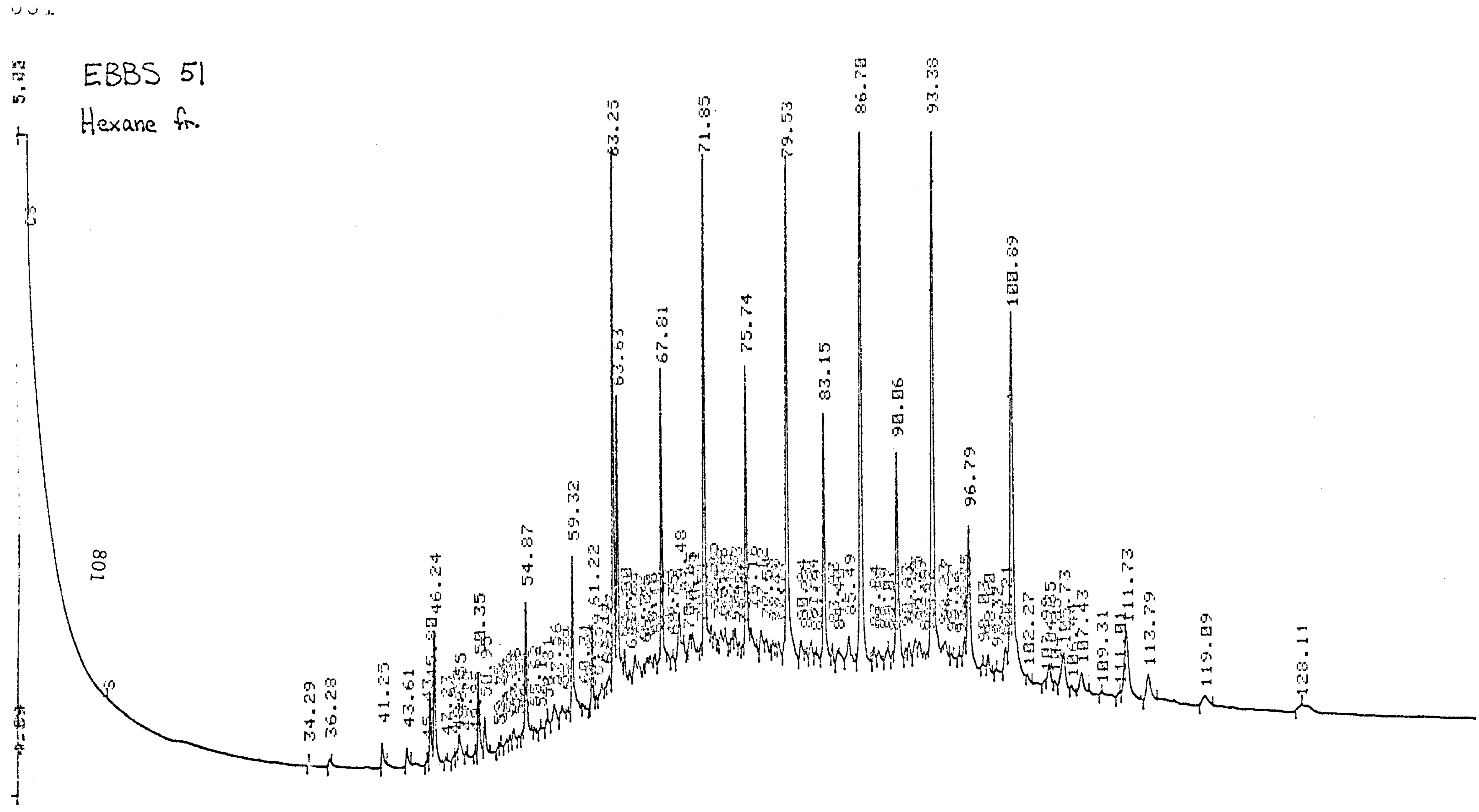
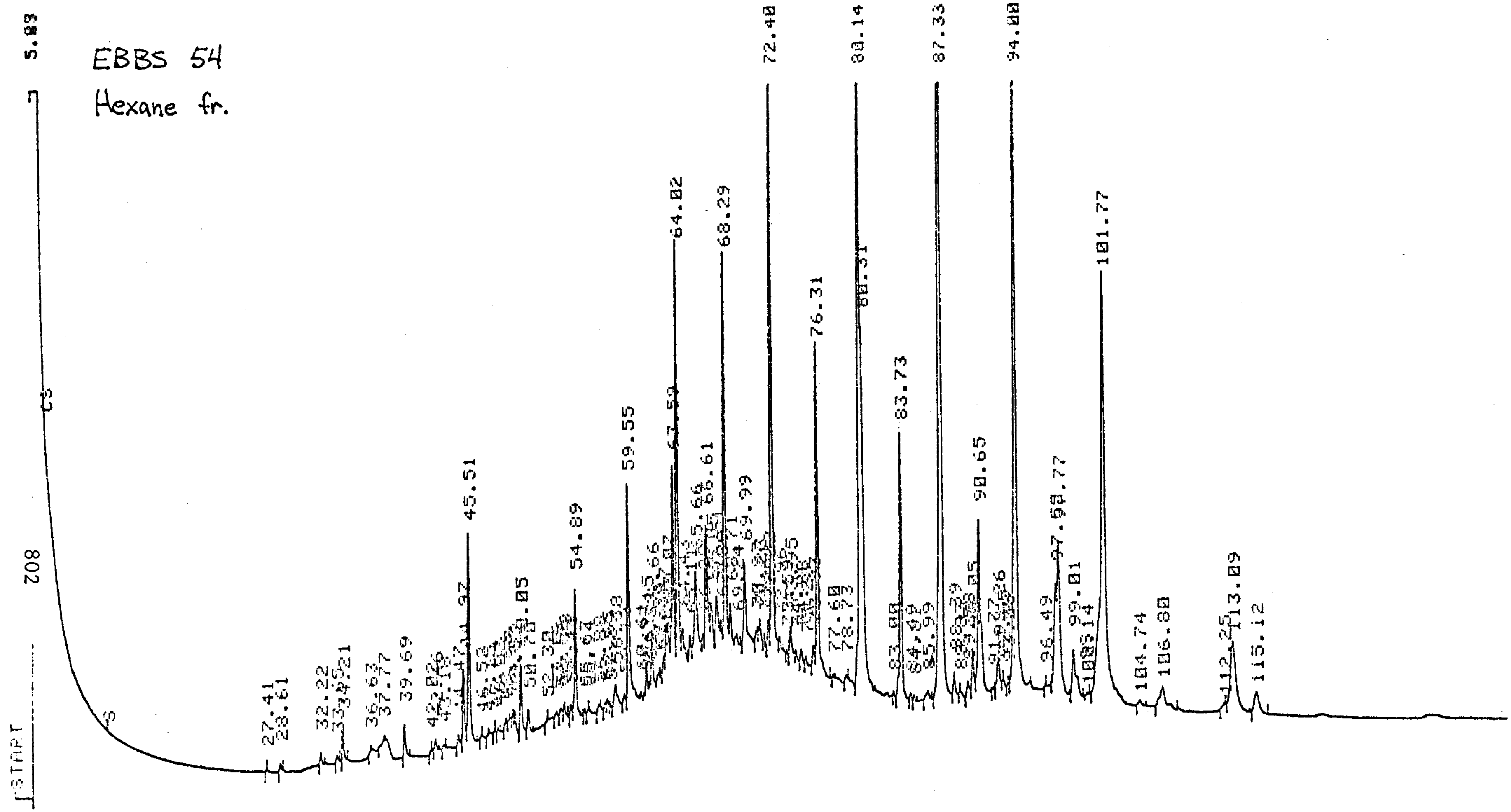

EBBS 46
Hexane fr.

EBBS 51

Hexane fr.

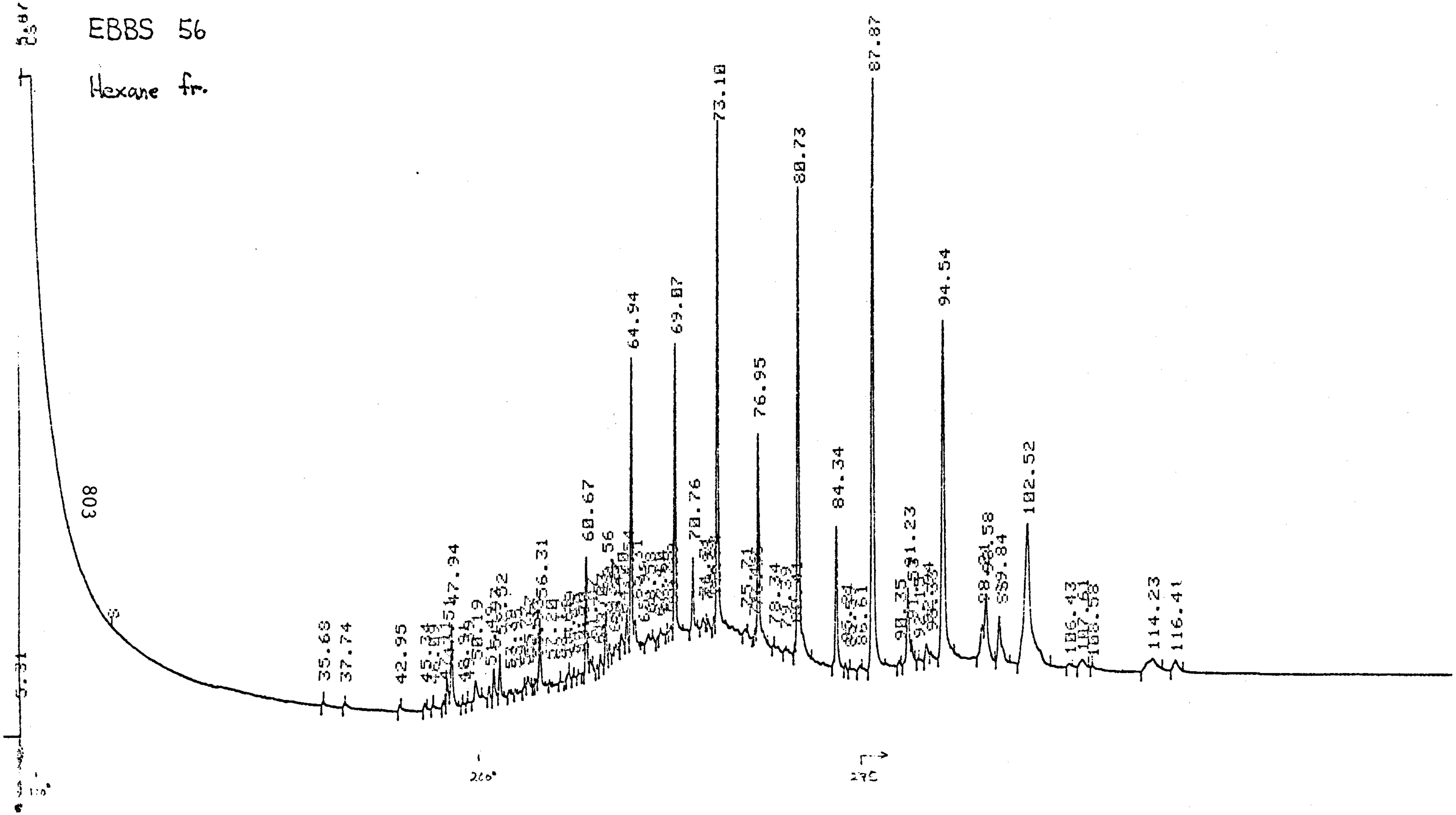




EBBS 54
Hexane fr.

EBBS 56

Hexane fr.



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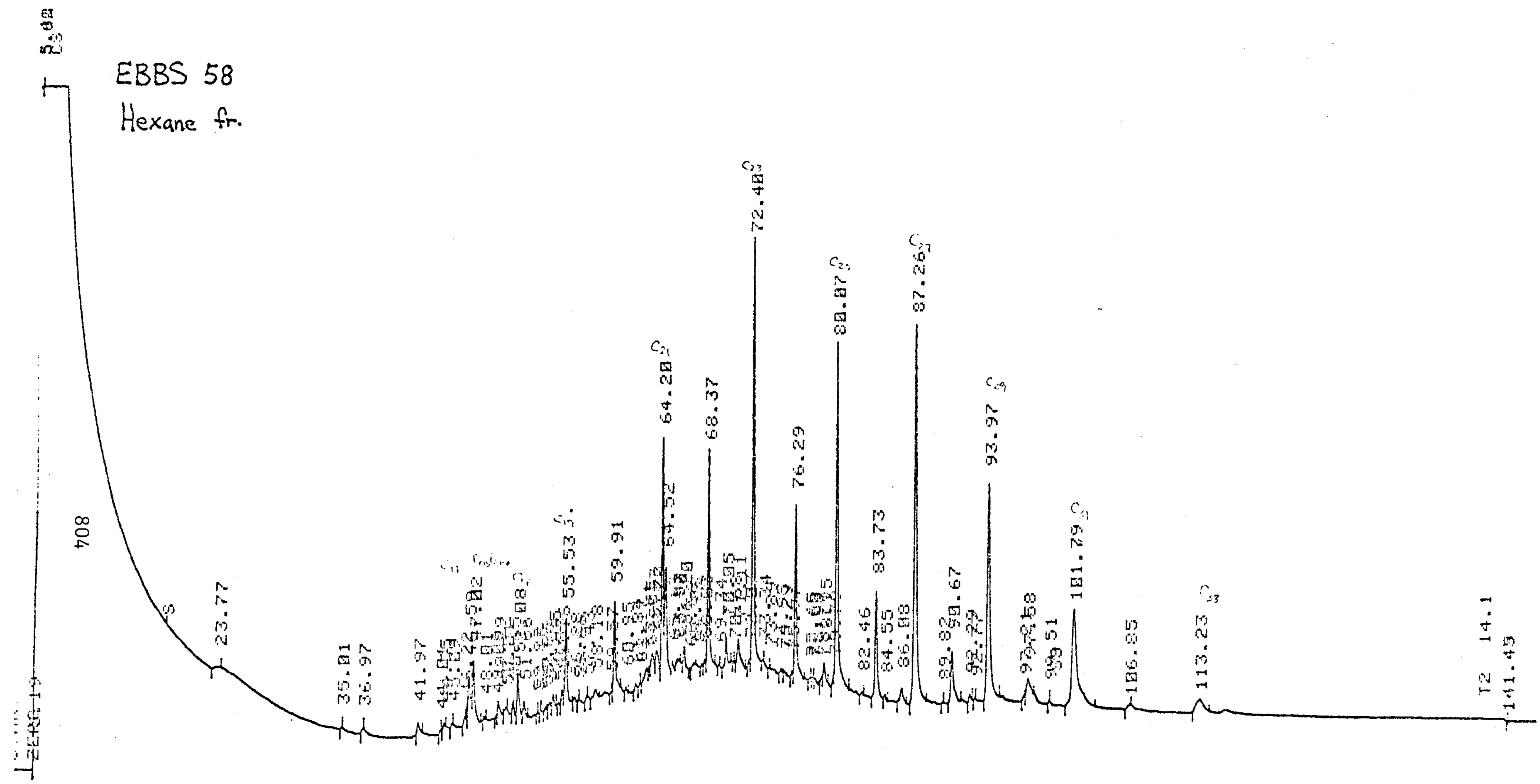

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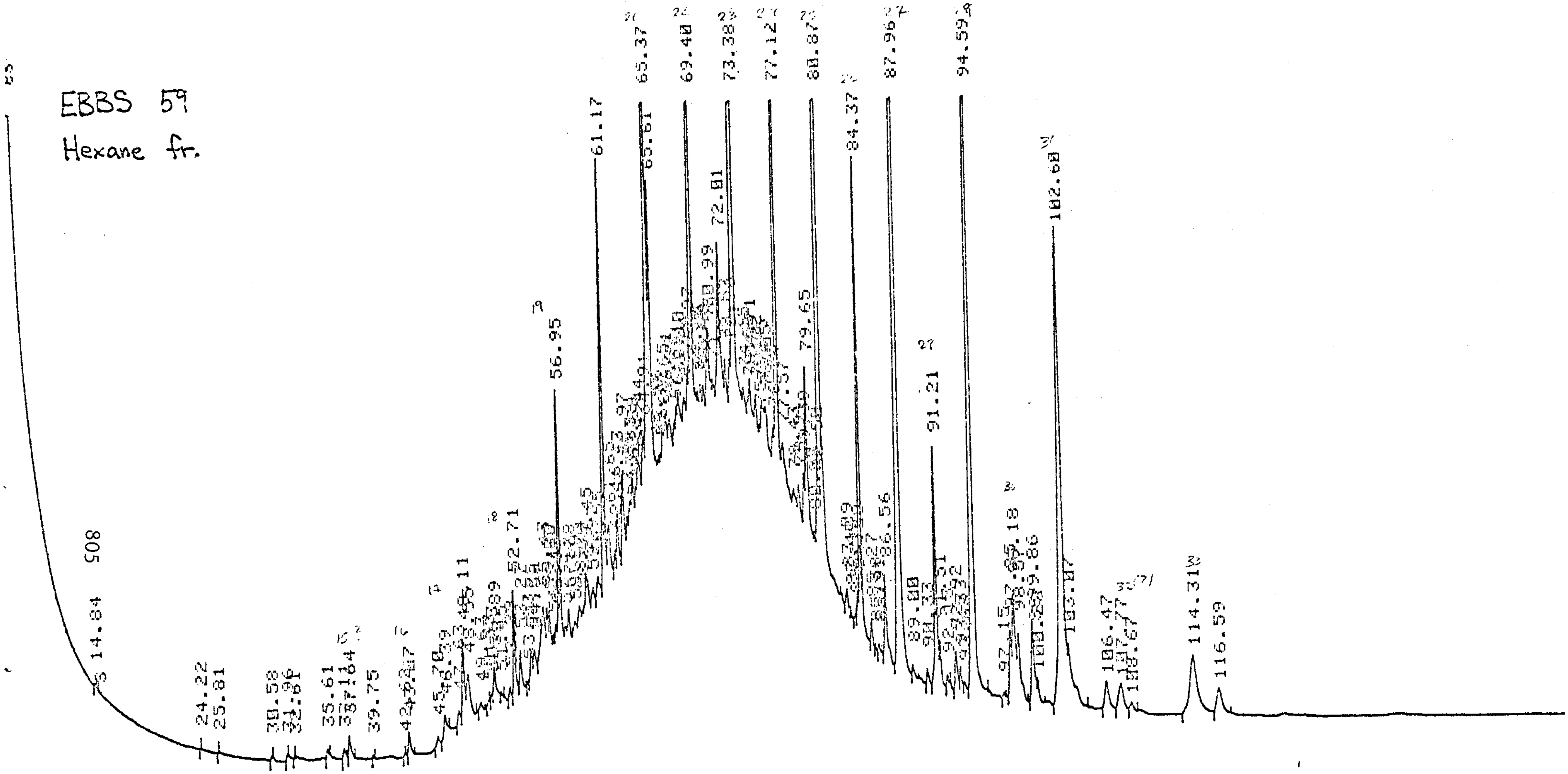

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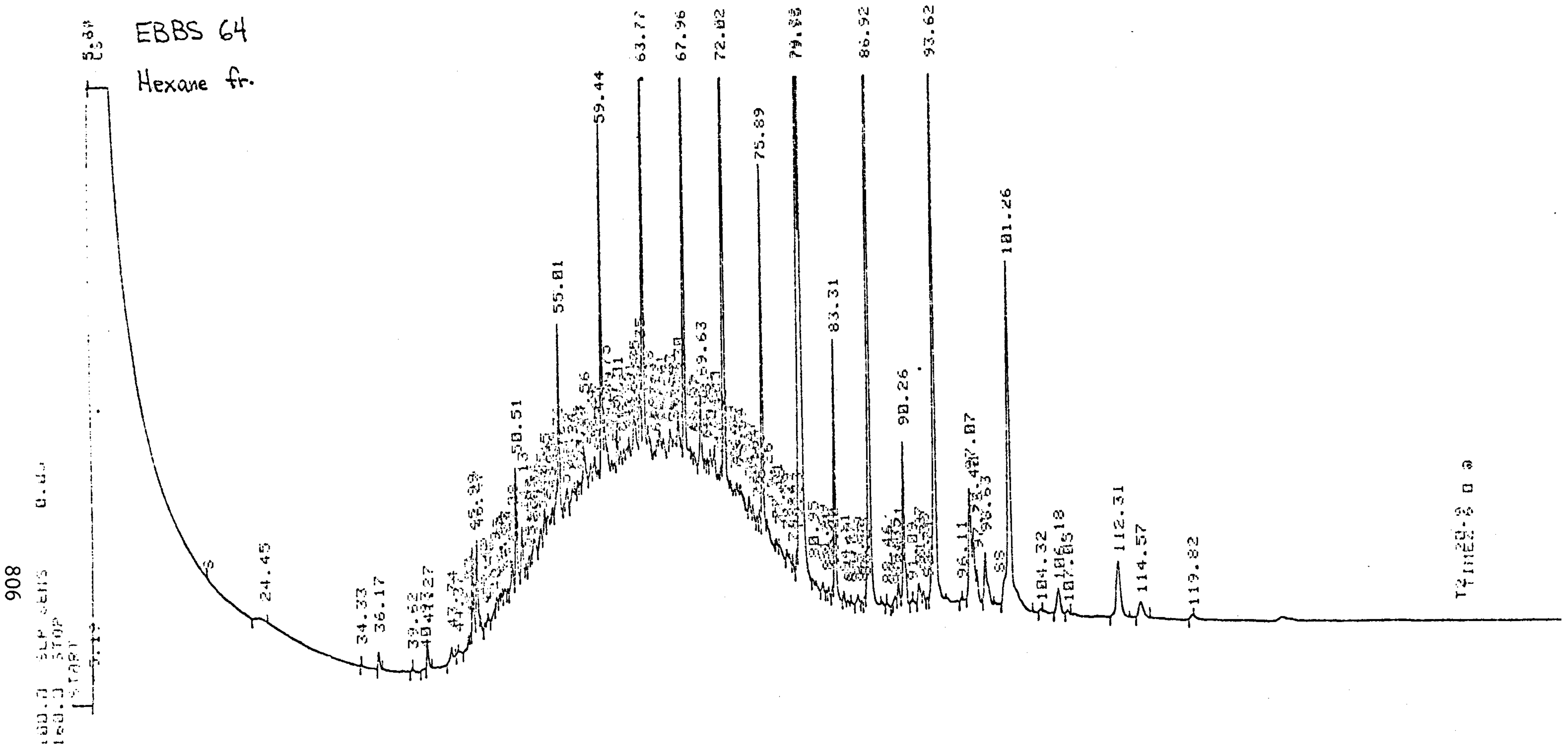
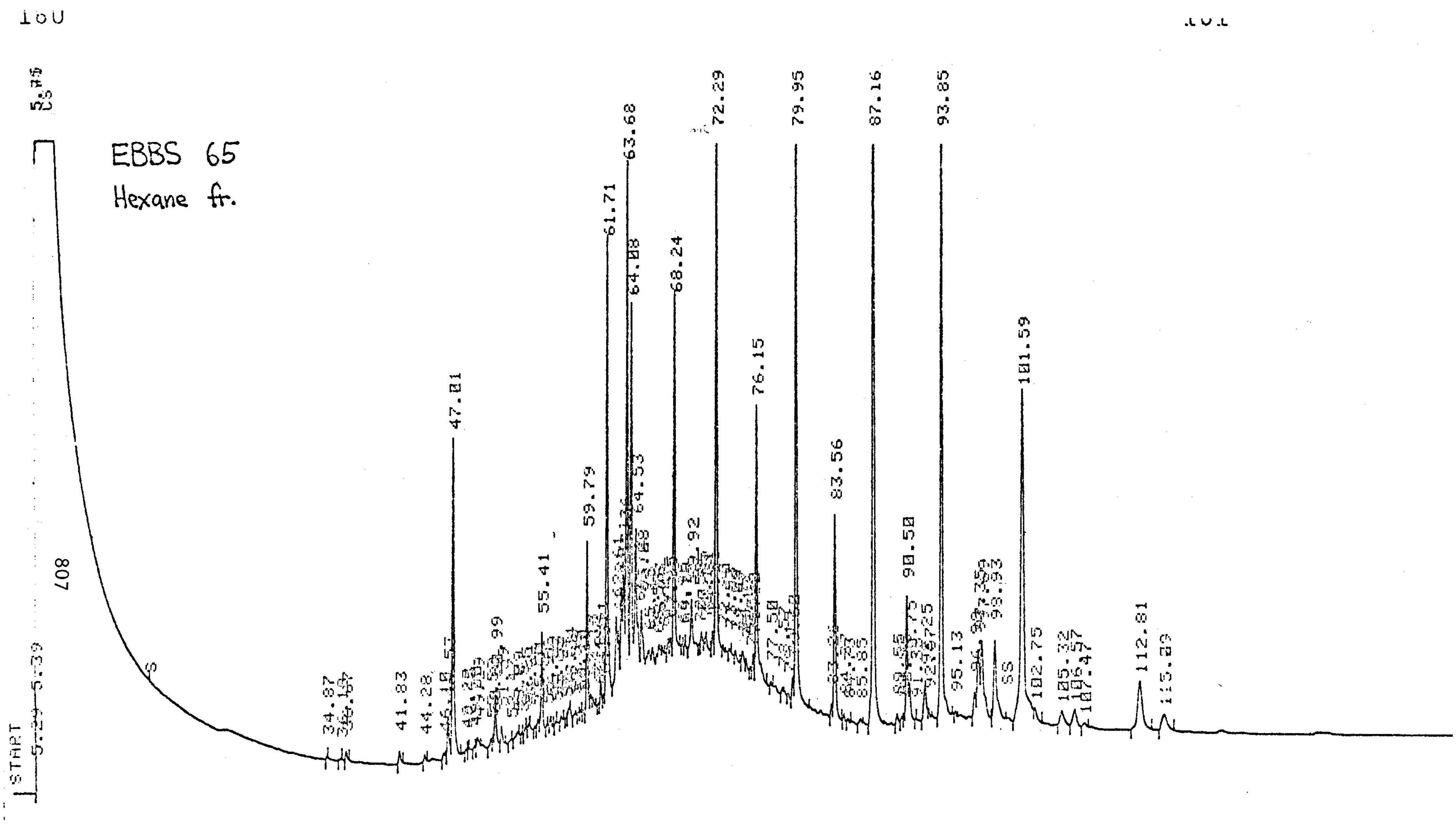
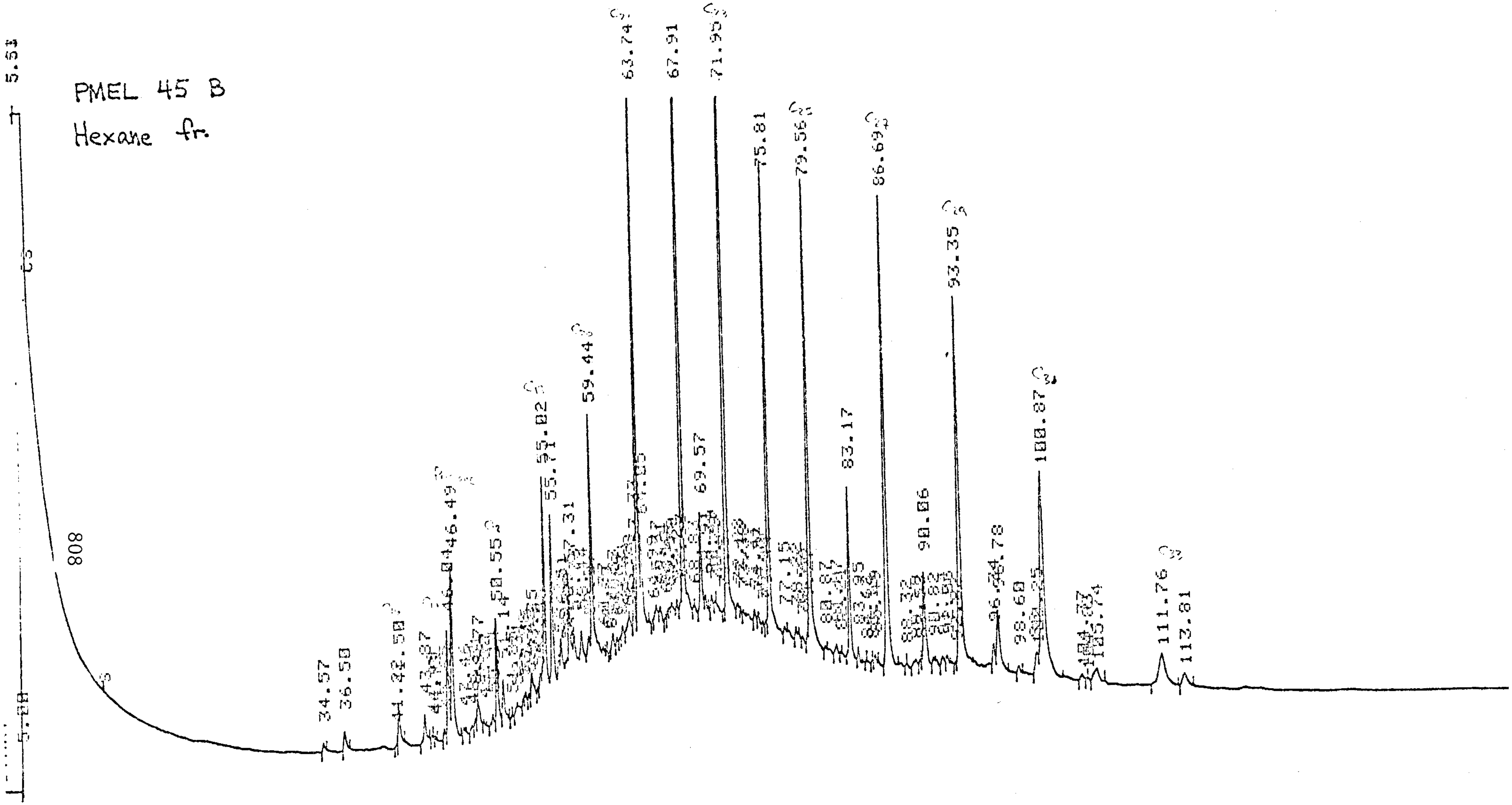
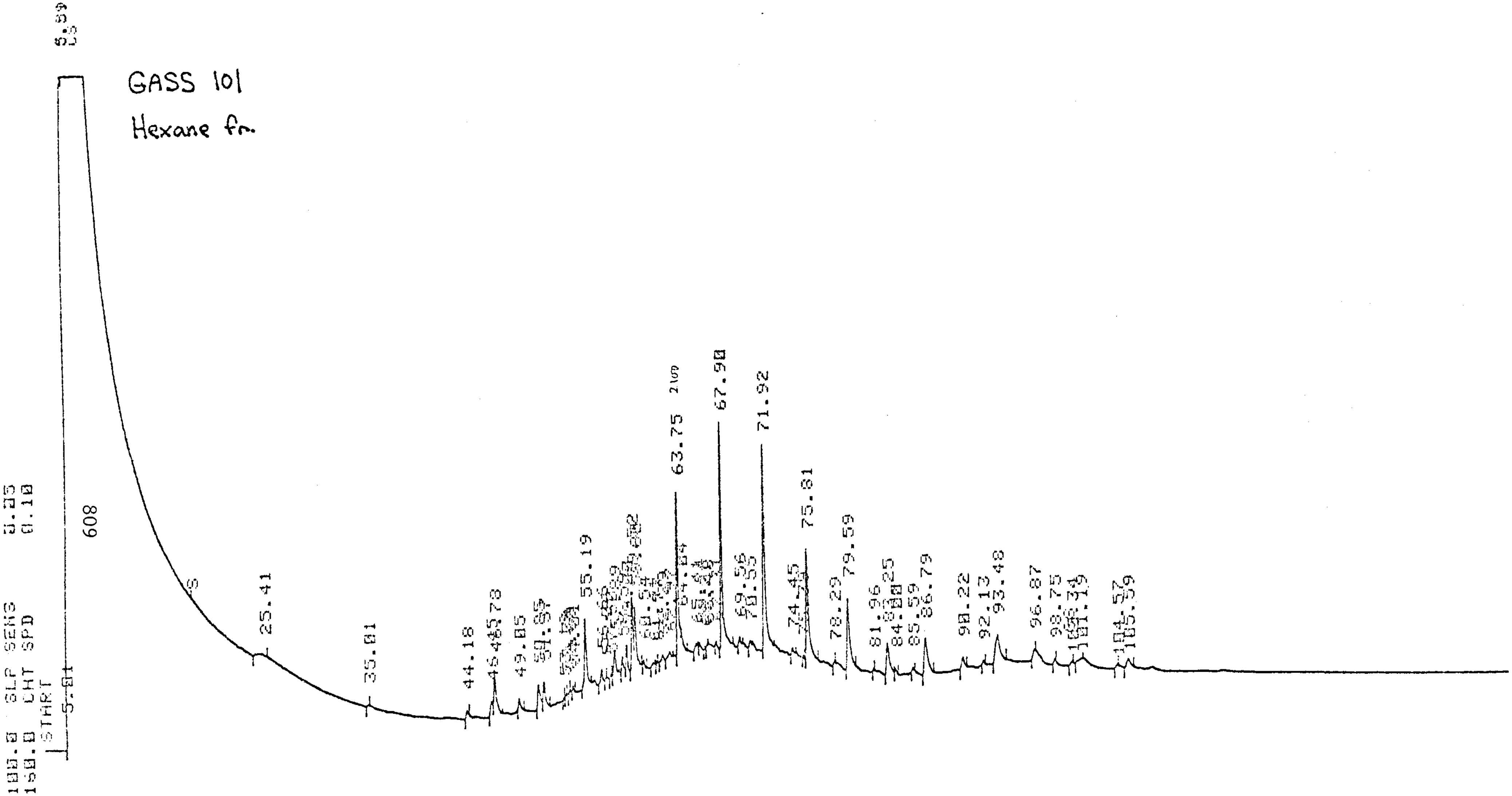



EBBS 65
Hexane fr.

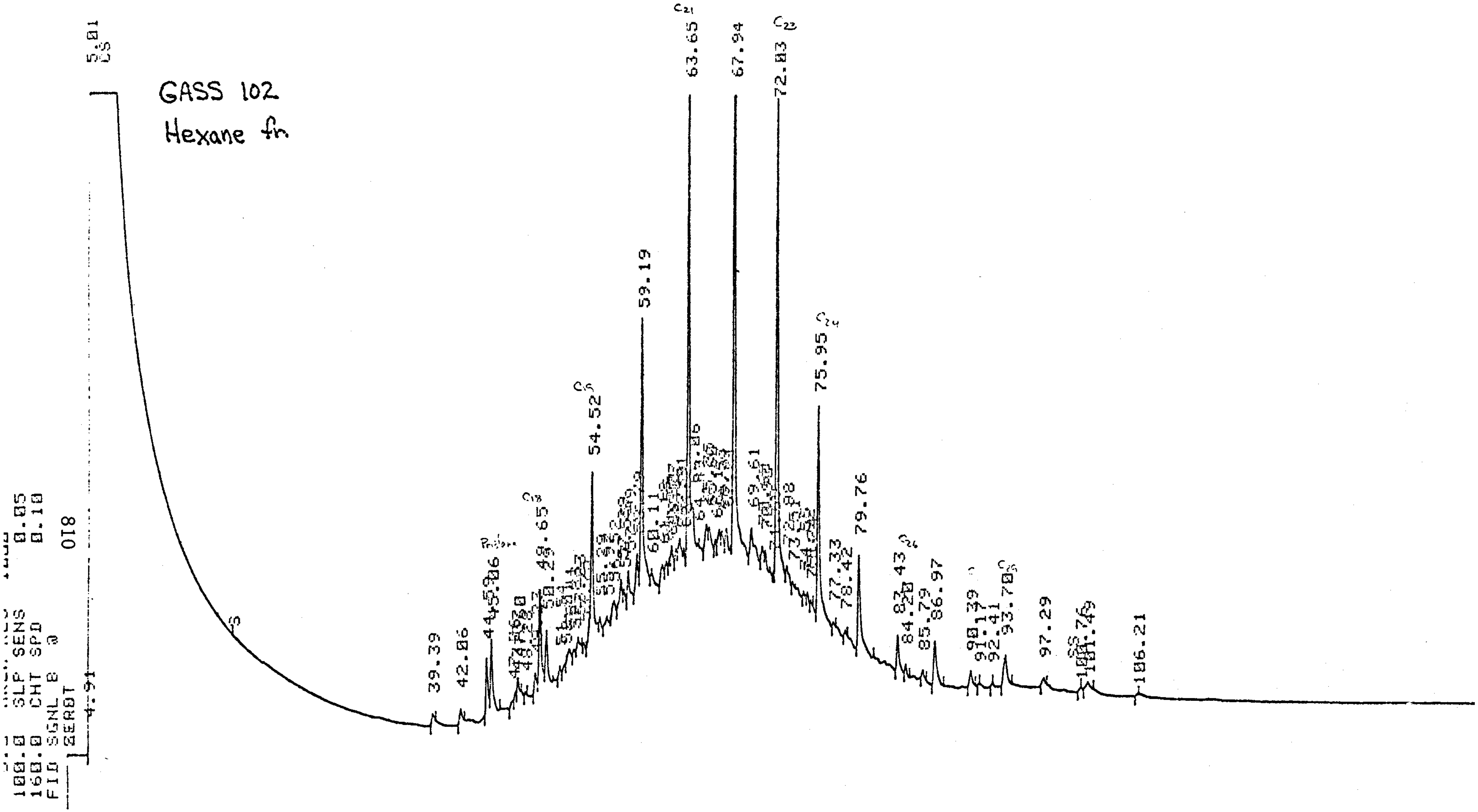
081

PMEL 45 B
Hexane fr.





GASS 101
Hexane fr.



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GASS 103
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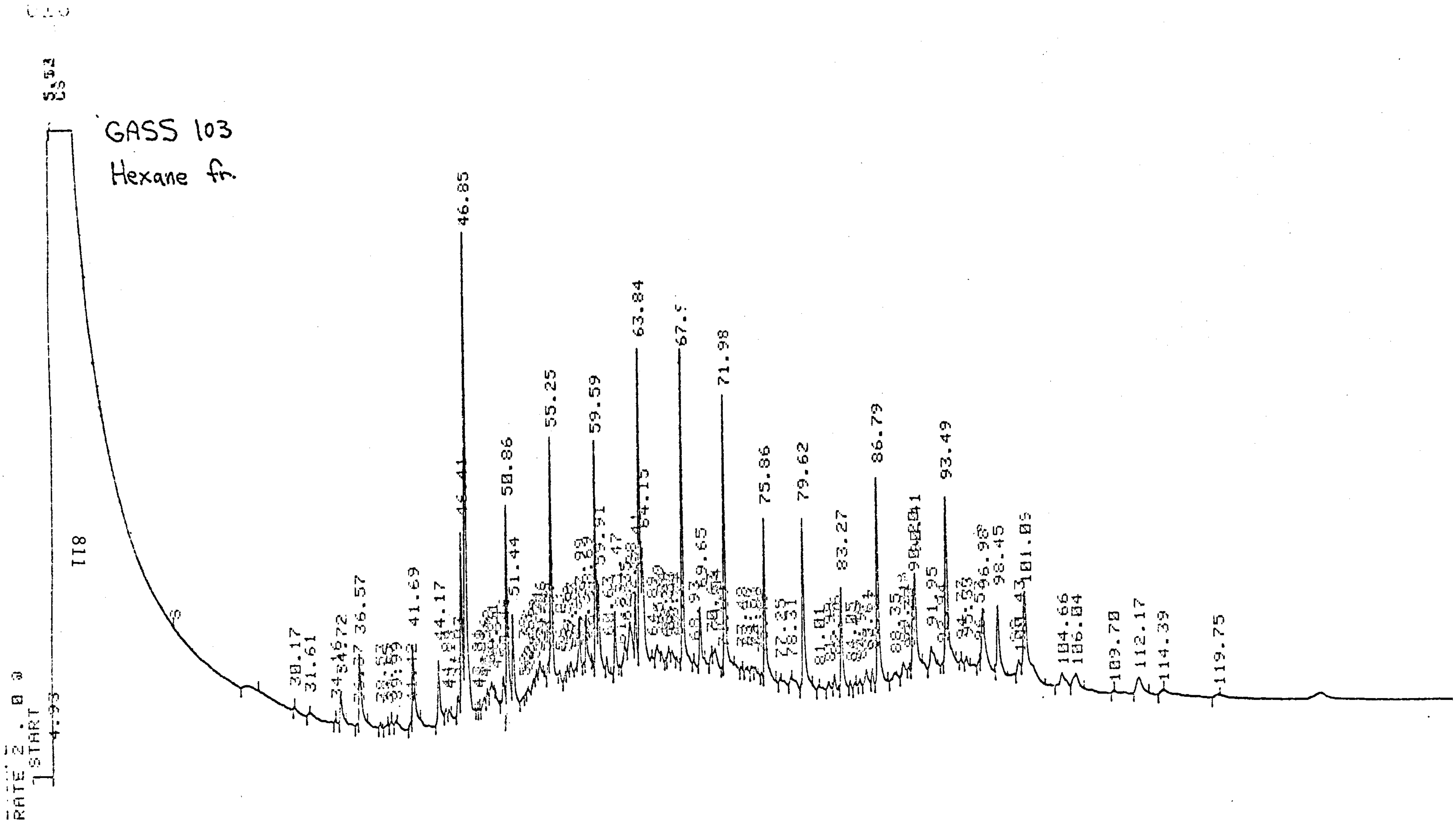

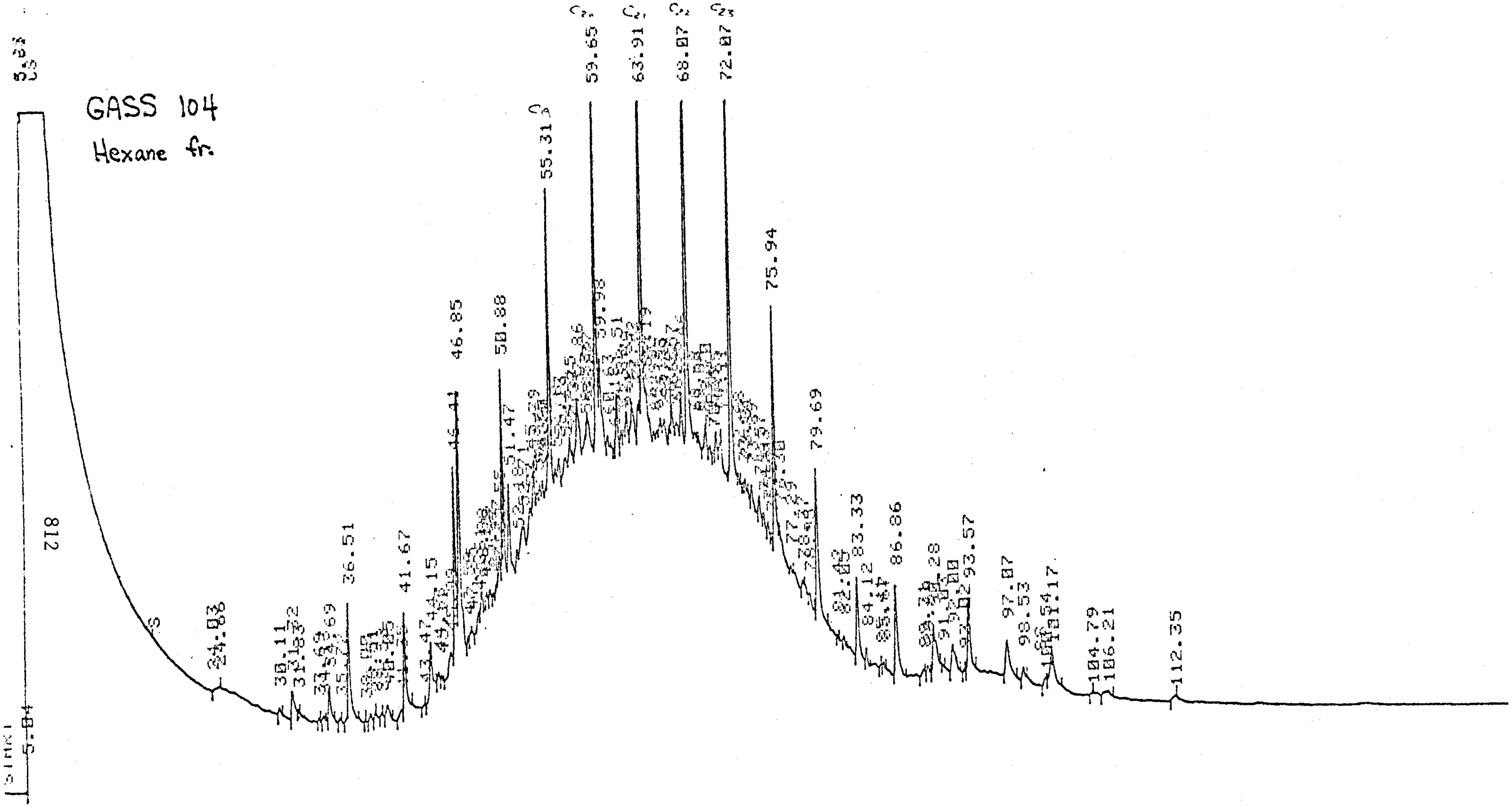

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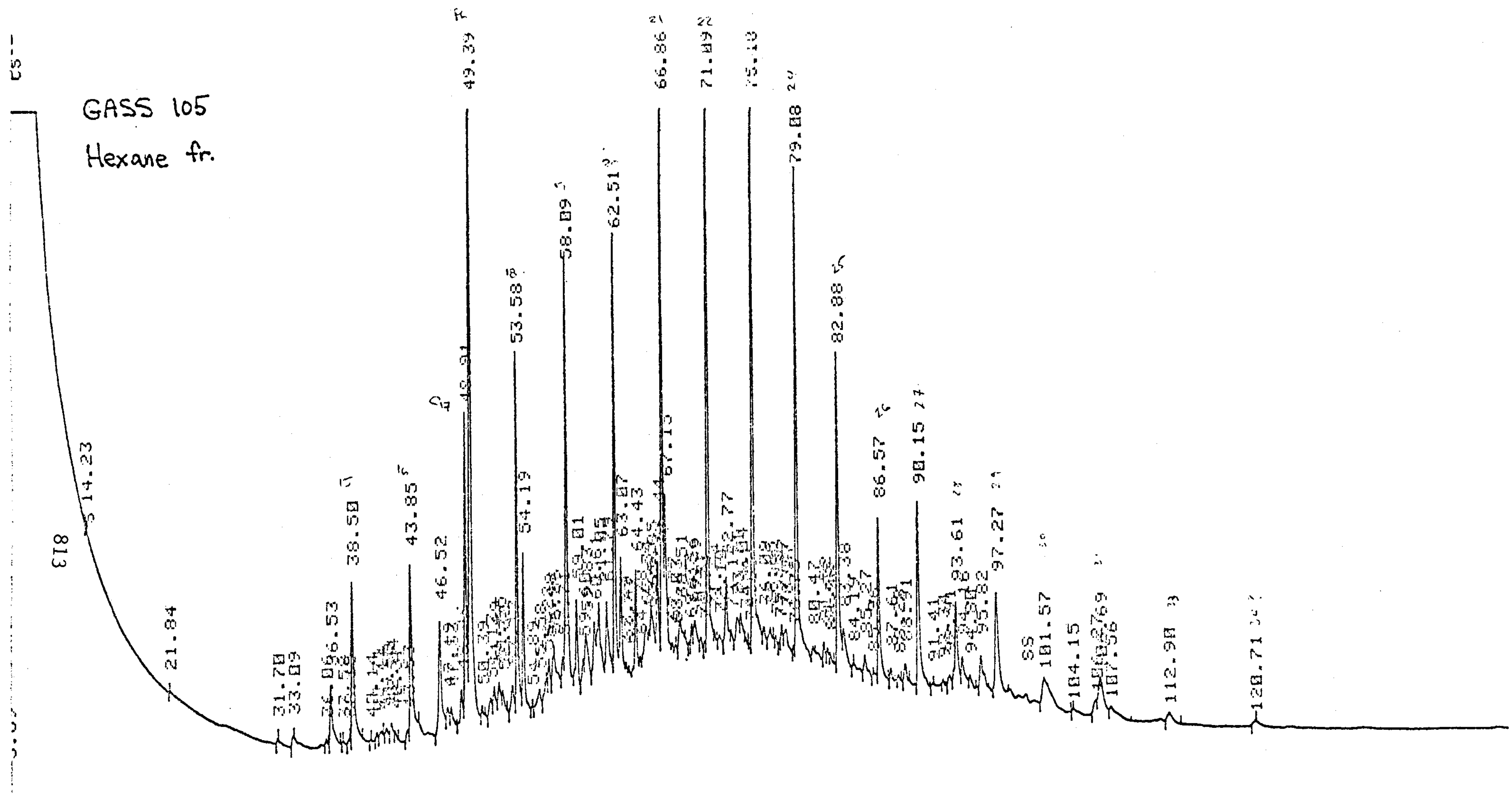

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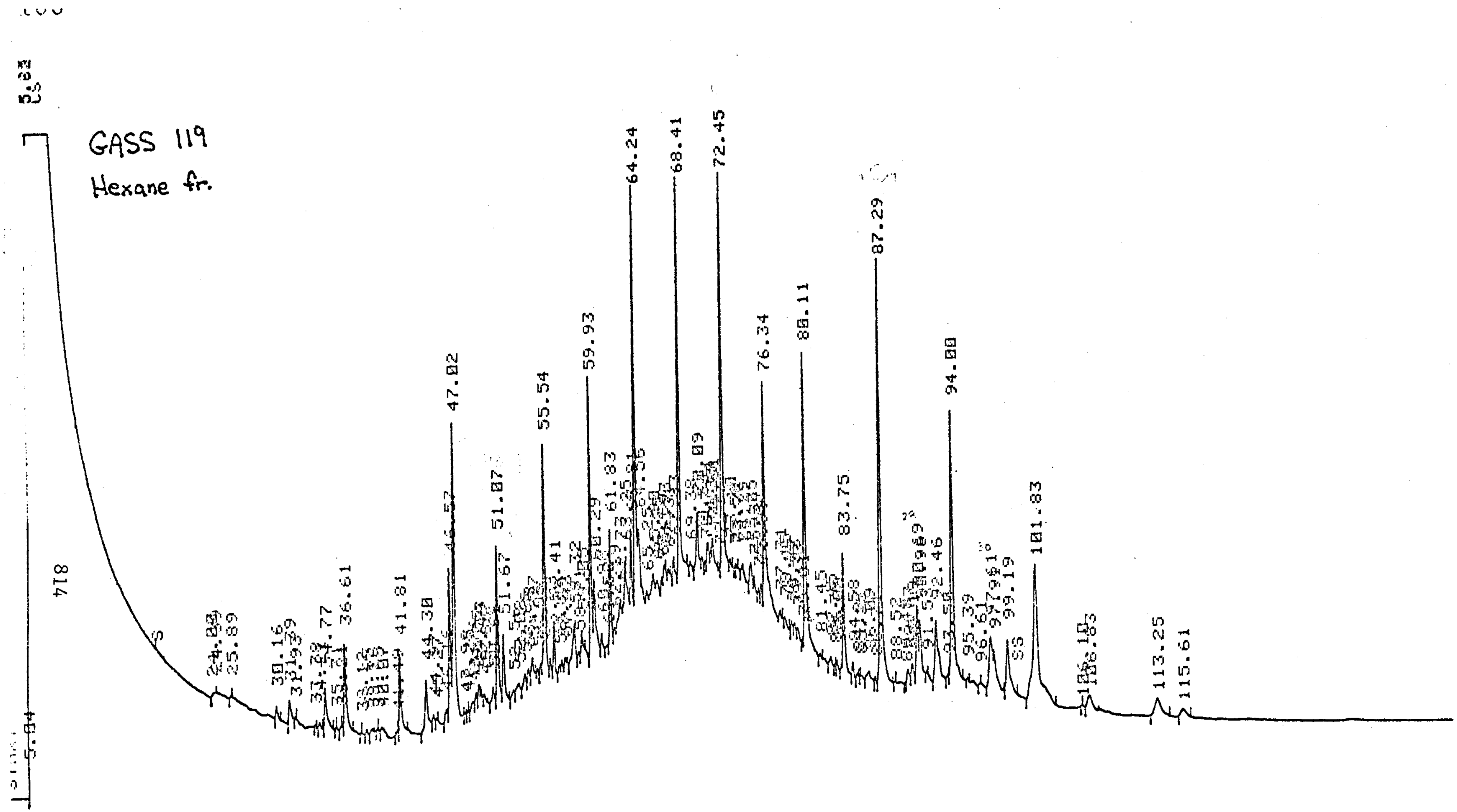

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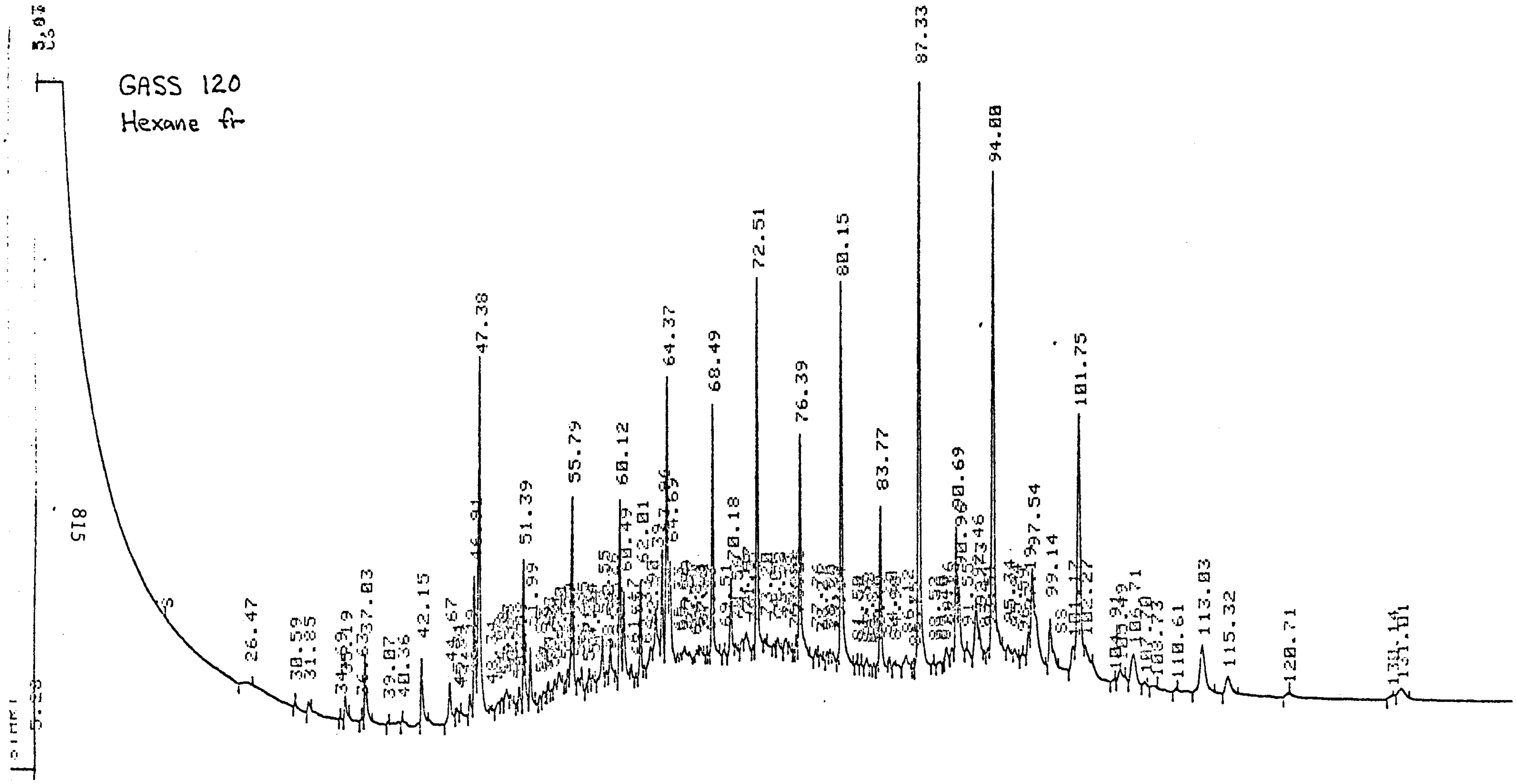

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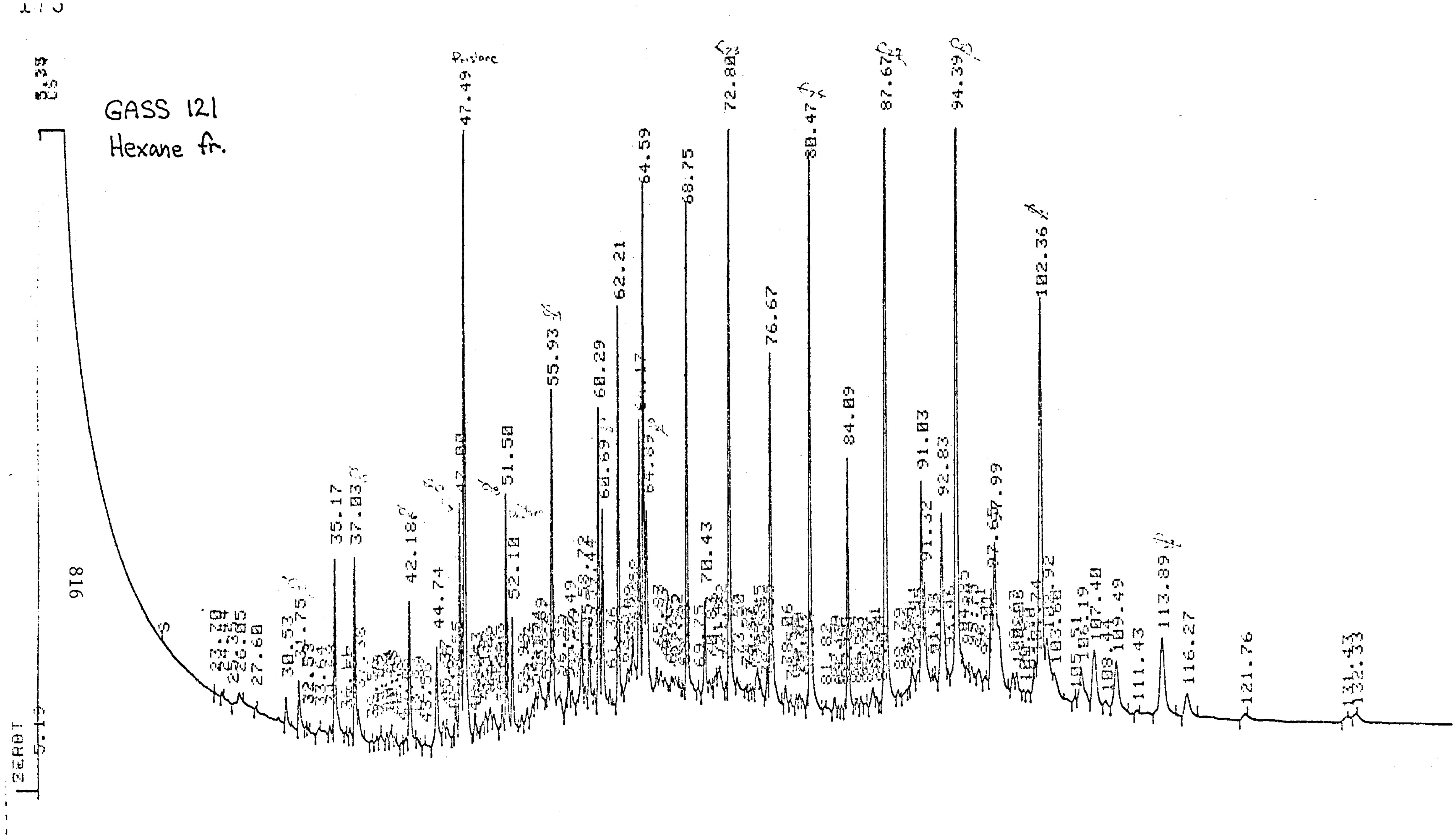
Hexane fr



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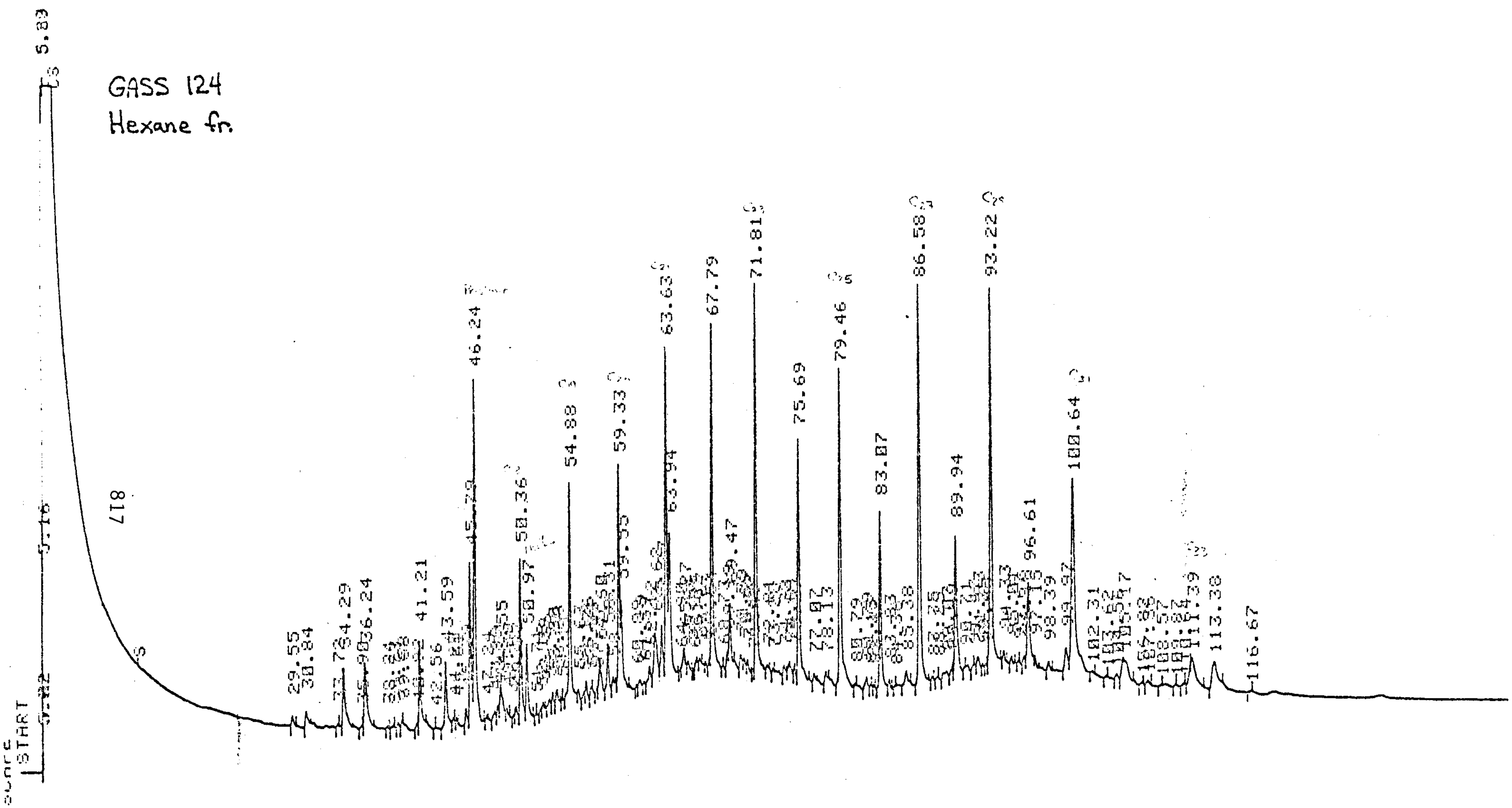
Hexane fr.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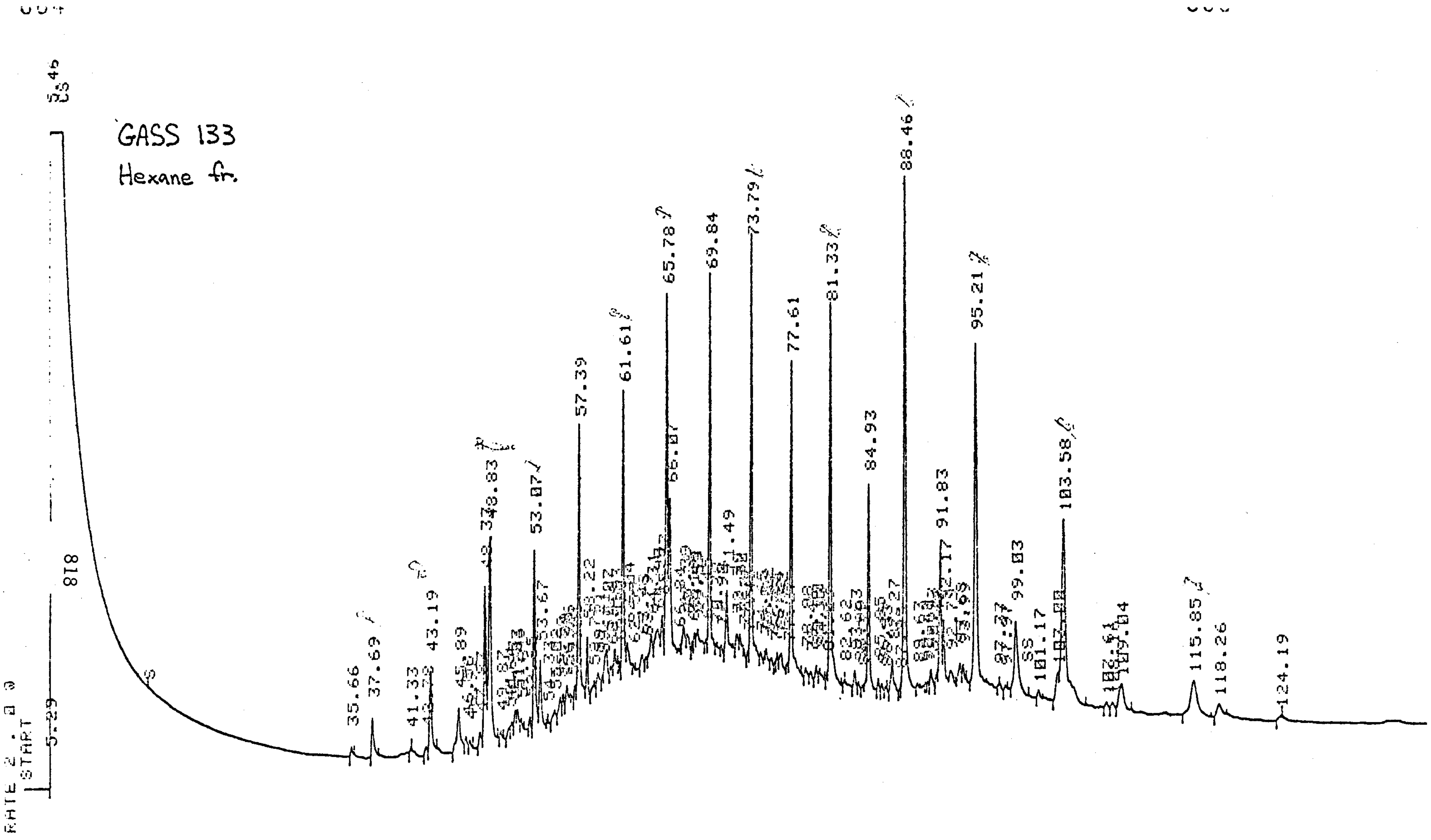
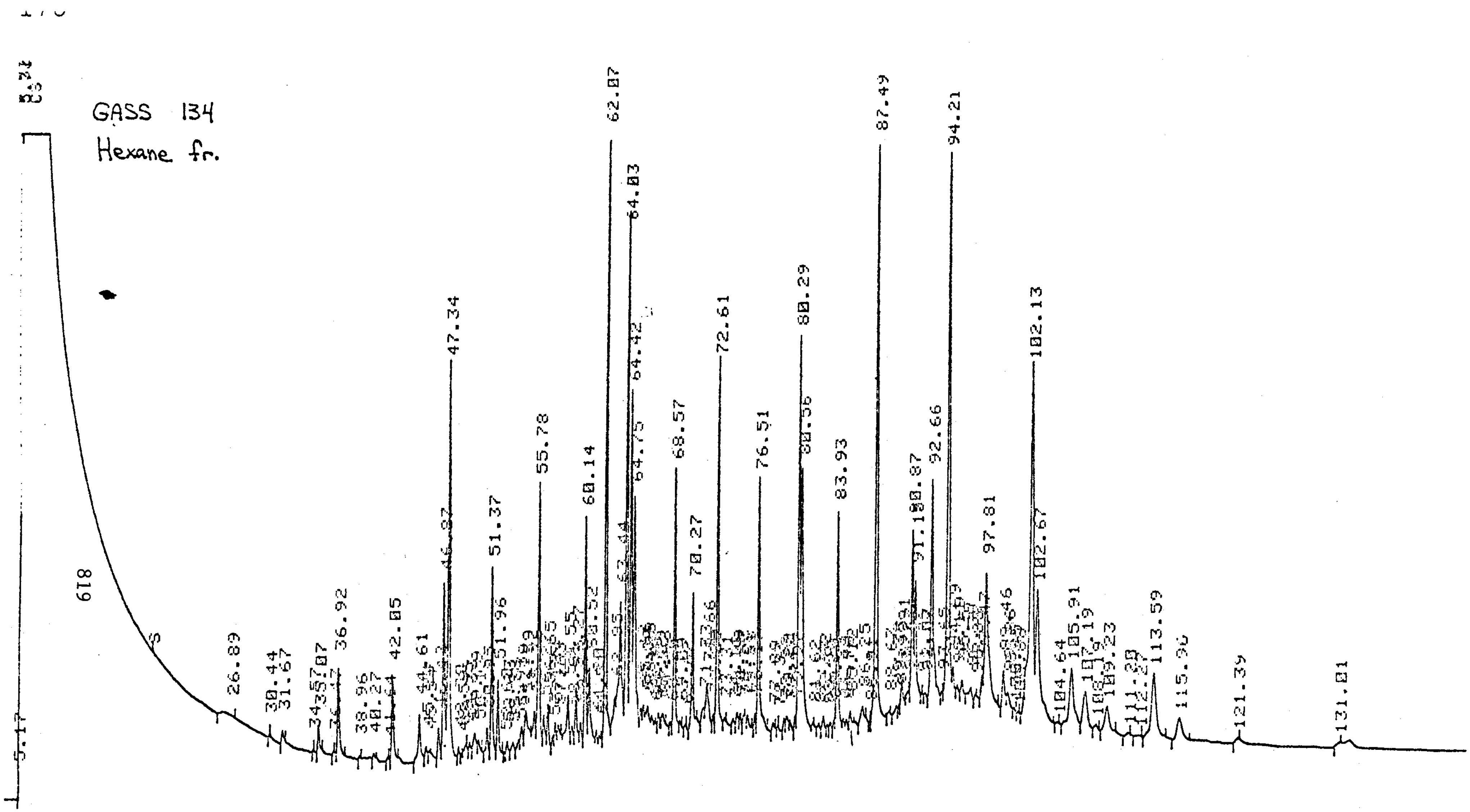
Hexane fr.

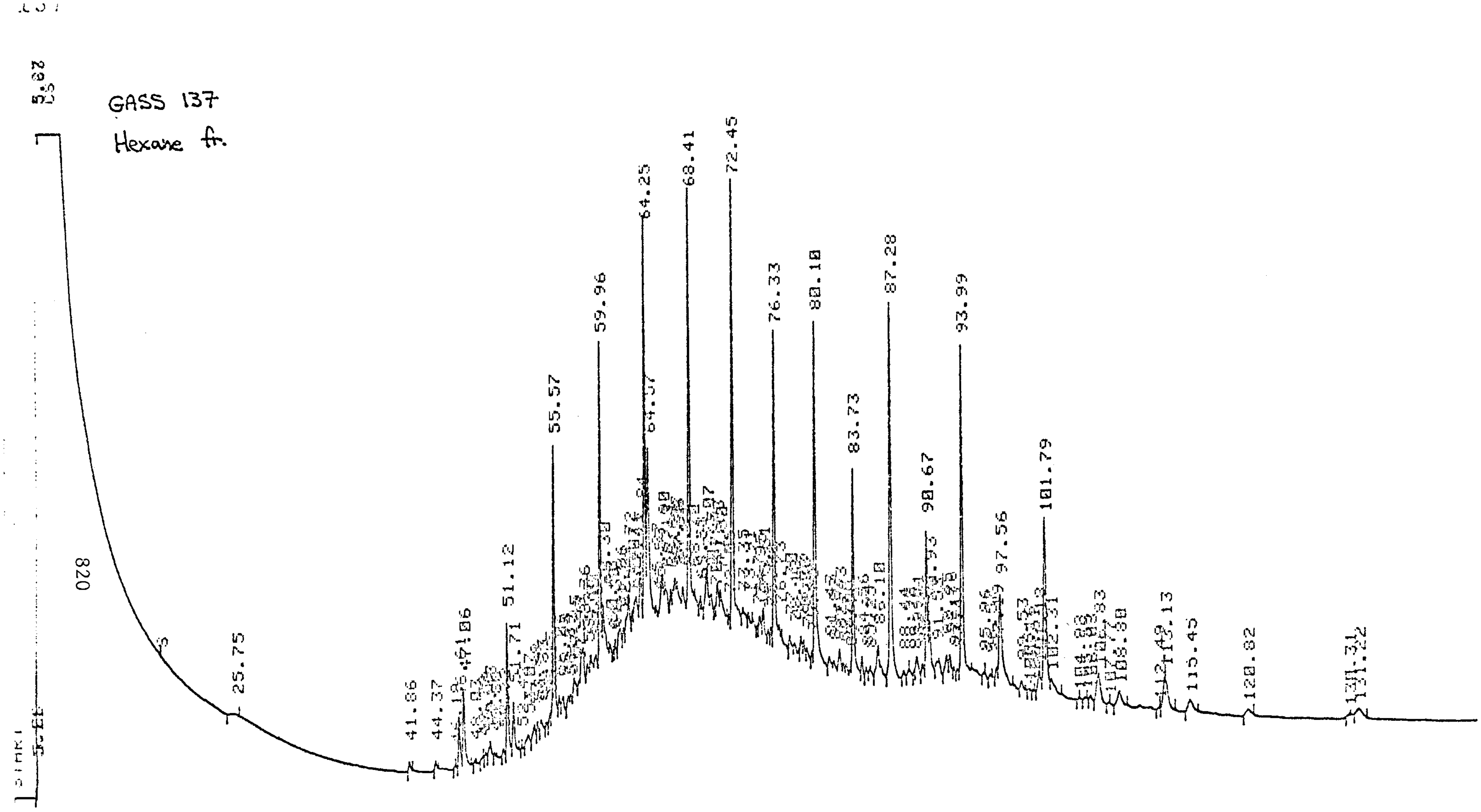
GASS 133
Hexane fr.



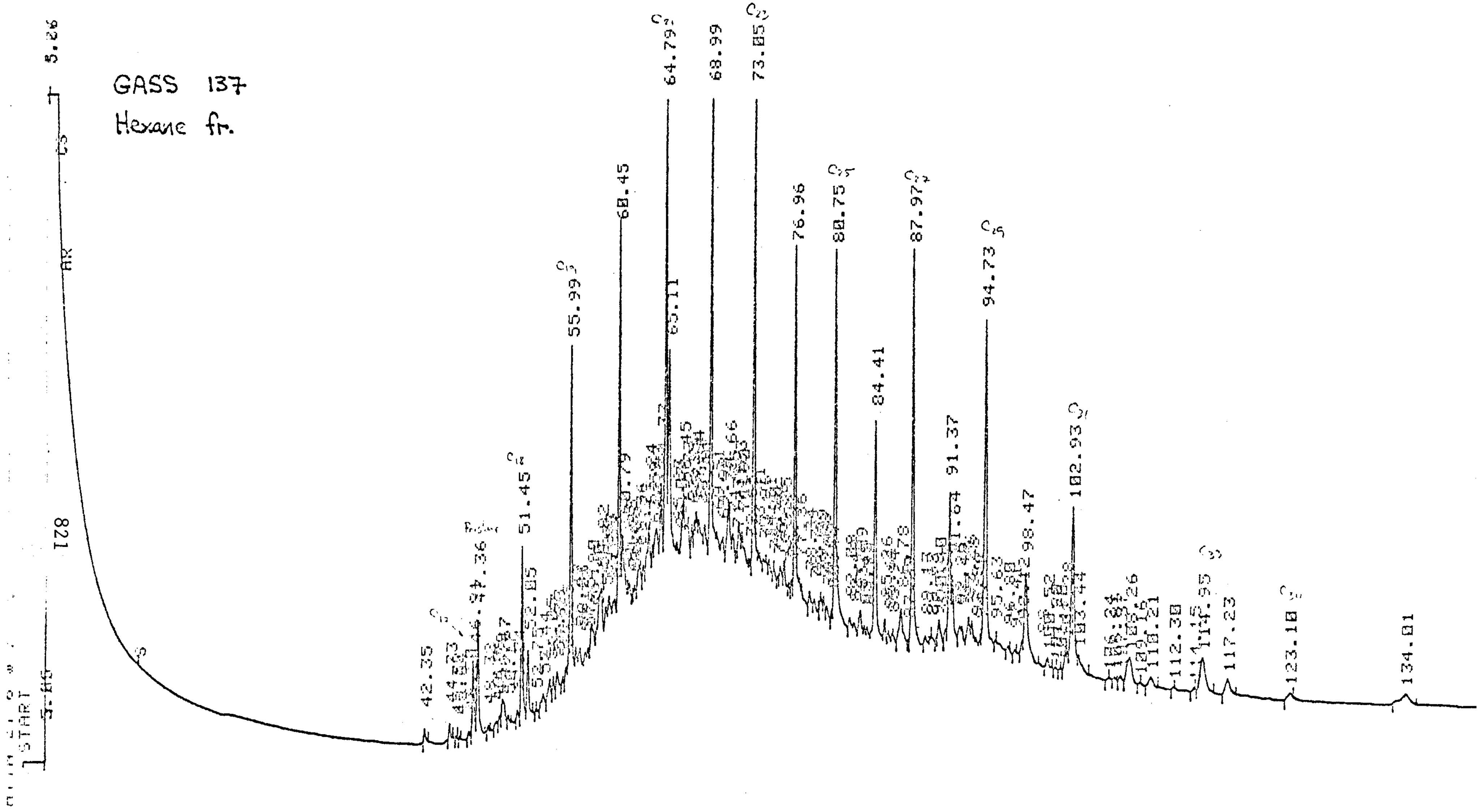


GASS 134
Hexane fr.

618

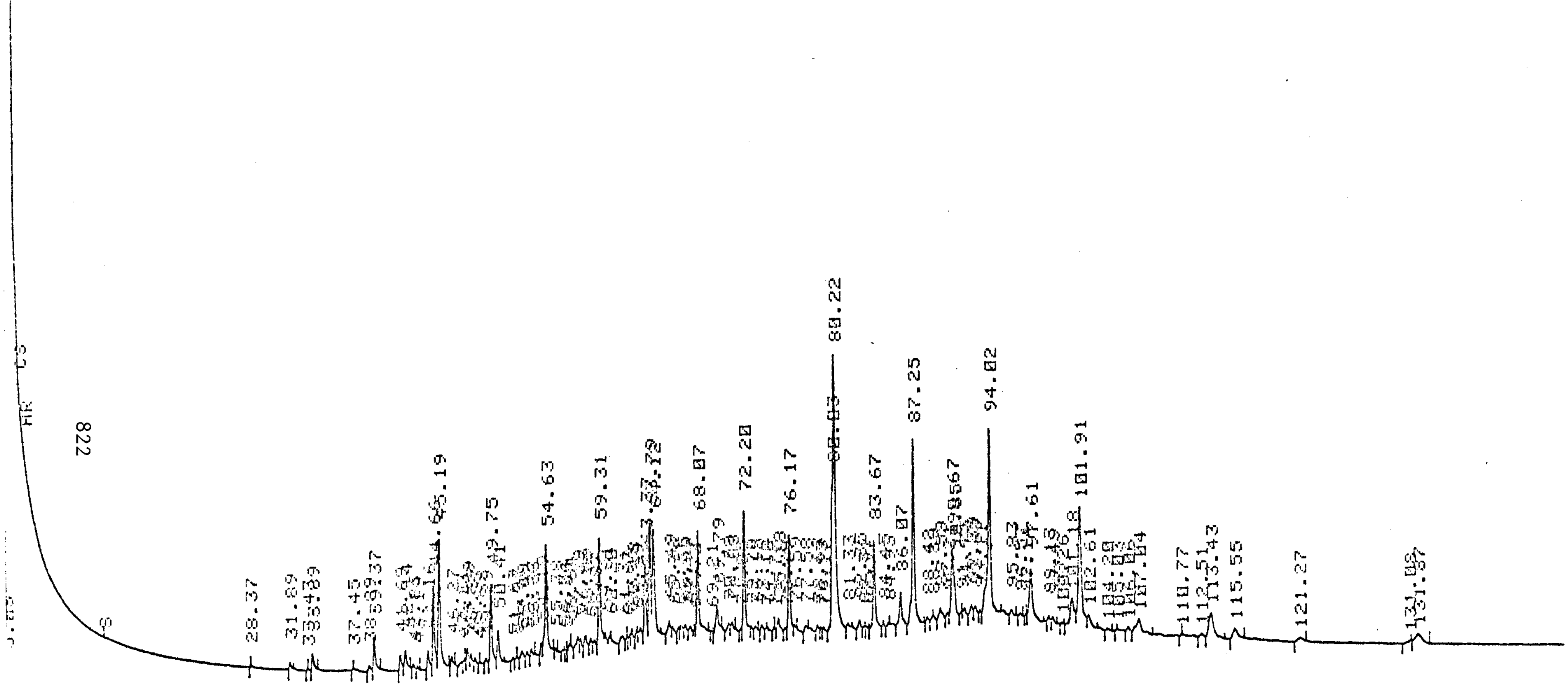


GASS 137
Hexane fr.


GASS 137
Hexane fr.
5.26
START
AR
42.35
Pristane
47.36
C18
51.45
C19
55.99
60.45
C21
64.79
65.11
68.99
C23
73.05
76.96
C25
80.75
84.41
C27
87.97
91.37
C29
94.73
98.47
C31
102.93
C33
114.95
117.23
C35
123.10
134.01

033

GASS 160
Hexane fr.



Not submitted in time for publication in last set of Quarterly Reports.

QUARTERLY REPORT

TO

UNIVERSITY OF ALASKA

Period from April 1 to September 30, 1976

from

Institute of Geophysics and Planetary Physics
University of California
Los Angeles, California 90024

for

"Characterization of Organic Matter in Sediments from Gulf of Alaska, Bering and Beaufort Seas"

Subcontract No. F-01770, P.O.# F01770

Research Unit 480

Introduction

Work completed during the period April 1 to September 30, 1976, included sample collection in Cook Inlet, Kodiak Shelf, Northern Bering Sea and Beaufort Sea, in addition to continuation of hydrocarbon analysis of samples collected during summer 1975 in Eastern Bering Sea and Gulf of Alaska. Analysis of fulvic acids, humic acids and kerogens from the Gulf of Alaska and Eastern Bering Sea are included as an Appendix to this report. Extraction and column chromatography on all samples collected during 1975 has been completed; gas chromatography and interpretations of results are being conducted at this time.

Sample Collection: July through October, 1976

During the 1976 summer season, 96 surface sediments were collected from Cook Inlet, Kodiak Shelf, Northern Bering Sea and Beaufort Sea for analysis of high molecular weight hydrocarbons (HMW-HC), low molecular weight hydrocarbons (LMW-HC) and carbon, nitrogen and sulfur. Sampling in the Cook Inlet, Norton Sound and Kodiak Shelf was conducted during U.S. Geological Survey cruise Sea 2-76WG, Sea 3-76-WG, Sea 5-76-BS of the R/V SEA SOUNDER. Sampling in the Beaufort Sea took place during a NOAA/OCSEP sponsored cruise of the USCGS GLACIER. Sample collection and subsampling methods and details of each cruise are described below.

Method of Collection

In the characterization and determination of baseline concentrations of hydrocarbons in recent sediments, it is critical that the surface layer be quantitatively collected because changes in the distribution of hydrocarbons in sediments as a result of petroleum development will initially be detected in the surface layer. Furthermore, it is essential that the samples are not contaminated with hydrocarbons during the collection procedure, for example, from paint or grease on the sample collection device.

With these requirements in mind, a modified aluminum Van Veem grab sampler, constructed of non-contaminating materials and capable of quantitatively collecting the sediment surface was purchased by UCLA, in order to collect samples during the 1976 summer sample collection period.

Details of the sampler are described in Callahan *et al*. (1976) and Soutar (in press). The main features of this sampler are (1) the incorporation of a frame which orients the grab normal to the sediment surface, a completely vented top which not only prevents blowing away of the fine surface layer but allows easy access to the sample after recovery, (2) the use of aluminum, stainless steel and teflon in construction, which precludes any contamination from hydrocarbons or trace metals, and (3) penetration into sand and gravel sediments.

The volume of sediment recovered is usually sufficiently large so that replicate HMW-HC and LMW-HC samples can be collected. Moreover, there was sufficient sediment for other investigators to collect samples for trace metals Pb-210, foraminiferal, microbiological or textural analyses.

In addition to this improved sampling device, a procedure for subsampling that is accurate, reproducible and non-contaminating was used. This procedure has been developed for use in the BLM Southern California Baseline Analysis Program, and involves the use of a template and scoop which allow sampling from 0-2 to 2-4 cm depths on the undisturbed surface layer of sediment recovered in the grab sampler.

When the grab sampler was brought on deck, a plastic bag was placed beneath the weight stand to prevent water from the hydrowire or weights from dripping into the sample. The top-loading doors were opened, and any supernatant water was siphoned off. Pre-cleaned templates for HMW-HC samples and stainless steel core tubes for LMW-HC subsamples were pushed into the sediments. HMW-HC subsamples were taken with a stainless steel scoop by sliding the scoop along the top of the template. Thus, accurate, repetitive samples of 0-2 and 2-4 cm depths could be taken. If it appeared that the surface layer had been disturbed during the sample collection, the template was not used and bulk or surface and subsurface samples were collected with a stainless steel spoon. Samples for C, N, S analysis (ES) were routinely collected with a stainless steel spoon. LMW-HC samples were removed in the core tubes and extruded into 600 ml tin cans and sealed as quickly as possible in the shipboard laboratory. These core tubes were used to minimize sample disruption and possible degassing of sediment.

Upon recovery, the sample was inspected and graded on a subjective scale of 1 (poor) to 5 (excellent). For example, an excellent sample had an essentially flat surface, the supernatant water was clear, and fine particulate material was present. In some cases, intact polychaete tubes protruded from the surface or mollusks, anthropods, etc. were recovered, indicating little disturbance at the sediment-water interface of the recovered sample.

On the other hand, a poor sample would be one in which extensive erosion and loss of the surface 1 cm of sediment had occurred as a result of drainage of the supernatant water through partially-closed grab sampler jaws.

Because of the difficulty in transporting the sampling device, the frame-supported Van Veem grab sampler could not be used in the USCGS GLACIER-Beaufort Sea cruise and remained onboard the R/V SEA SOUNDER. Instead, a large volume (0.9 m^3) aluminum Van Veem grab sampler having teflon hinges and top-opening doors was used. Although sample quality (in terms of recovery of the surface sediment layer) was much less than the frame-supported Van Veem grab sampler, this sampler was much better for hydrocarbon sampling than the more commonly-used Van Veem grab samplers or Shipek-type samplers that may contaminate the sample with paint or grease and are difficult to subsample.

Using this aluminum Van Veem grab sampler, supernatant water was drained off and the sample quality was rated when the sample was brought on deck. Subsamples for HMW-HC analyses, LMW-HC analyses and C, N, S (ES) analyses were collected with a pre-cleaned, stainless steel spoon and placed in the respective glass jars, tin cans or polyethylene vials. HMW-HC samples were scraped from the surface (~0-2 cm) and subsurface (~2-4 cm) of the sediment in the grab sampler (these depths are approximate, since no template could be used).

All samples were immediately frozen after collection until analyses were accomplished in the laboratory at UCLA.

1976 Sample Collection Cruises

Table 1 lists the station locations; water depths, quality of samples recovered and types of samples collected. During summer 1976, replicate samples for HMW-HC (HC or HA) and LMW-HC (GH or GA) analyses were collected at stations where sufficient samples of good quality were available.

Cruise Sea 2-76-WG of R/V SEA SOUNDER in Lower Cook Inlet departed Seaward on June 18 and arrived Homer, Alaska on July 1. Sediment samples for hydrocarbon analysis were collected at 24 stations which are shown in Fig. 1.

Cruise Sea-3-76-WG of the R/V SEA SOUNDER on Kodiak Shelf consisted of two legs. The first departing Homer on July 3 and arriving Kodiak on July 14, and the second leg departing Kodiak on July 17 and arriving at Kodiak on July 30. During this cruise, sediment samples for hydrocarbon analysis were collected at 36 stations, which are shown in Fig. 1.

Leg 1 of cruise Sea 5-76 of the R/V SEA SOUNDER in the Norton Sound, Northern Bering Sea, departed Dutch Harbor on September 17 and arrived in Nome, Alaska on September 30. Leg 2 of Cruise Sea 5-76 departed Nome on October 3 and arrived on October 14. During this time, sediment samples for hydrocarbon analysis were collected with the Soutar Van Veem grab sampler at 24 stations, which are shown in Fig. 2.

The NOAA/OSCEP sponsored cruise of the USCGS GLACIER in the Beaufort Sea (G-B-76) began off Prudhoe Bay on August 22 and terminated September 4 at Point Barrow. Sediment samples for hydrocarbon analysis were collected at 12 stations which are shown in Fig. 3. Ice conditions prevented the collection of a more complete set of samples.

References

Callahan, R. and A. Soutar (1976) Proceedings Oceans 76 Conference, Washington, D.C., August 1976.

Soutar, A. (1976) Collection of Benthic Sediments for Chemical Analysis, Report to Bureau of Land Management, Southern California Benthic and Water Column Baseline Research, Vol. III, Rept. 1.1, Science Applications, Inc., La Jolla.

Table 1. Station locations, depths, and rating, and type of sample collected during summer 1976 cruises in Cook Inlet, Kodiak Shelf, Northern Bering Sea and Beaufort Sea.

Station	Lat (N)	Lon (W)	Depth (m)	Rating[1]	Samples[2]				
					HC[3]	HA[3]	GH	GA	ES
Sea-2-76 WG - Cook Inlet									
8	59°11.38'	153°44.10'	36	2	0-2, 2-4	0-2, 2-4	1	1	1
14	59°30.6'	152°46.6'	61	4	0-2, 2-4	0-2, 2-4	1	1	1
15	59°31.8'	152°54.0'	45	4	0-2, 2-4	0-2, 2-4	1	1	1
16	59°23.2'	153°06.0'	48	4	0-2, 2-4	0-2, 2-4	1	1	1
17	59°20.7'	152°53.5'	74	4	0-2, 2-4	0-2, 2-4	1	1	1
18	59°11.90'	152°43.00'	122	3	0-2, 2-4	0-2, 2-4	1	1	1
19	58°56.25'	152°23.36'	75	4	0-2, 2-4	0-2, 2-4	1	1	1
23	58°55.70'	152°34.30'	170	2	0-2, 2-4	0-2, 2-4	1	1	1
24	58°58.49'	152°31.11'	147	4	0-2, 2-4	0-2, 2-4	1	1	1
26	59°08.1'	152°22.1'	119	4	0-2, 2-4	0-2, 2-4	1	1	1
27	59°26.30'	152°20.70'	74	3	0-2, 2-4	0-2, 2-4	1	1	1
28	59°21.35'	152°25.90'	78	2	0-2, 2-4	0-2, 2-4	1	1	1
29	59°14.98'	152°28.15'	89	3	0-2, 2-4	0-2, 2-4	1	1	1
30	59°16.65'	152°21.70'	91	3	0-2, 2-4	0-2, 2-4	1	1	1
33	59°26.35'	152°12.44'	50	4	0-2, 2-4	0-2, 2-4	1	1	1
34	59°36.5'	151°52.0'	28	3	0-2, 2-4	0-2, 2-4	1	1	1
37	59°45.9'	152°13.8'	56	1	bk	bk	-	-	1
39	59°40.75'	151°57.15'	35	1	bk	bk	-	-	1
41	59°36.25'	151°56.00'	30	3	0-2, 2-4	0-2, 2-4	1	1	1
42	59°36.20'	151°45.6'	30	2	0-2, 2-4	0-2, 2-4	1	1	1
43	59°36.63'	151°22.07'	52	4	0-2, 2-4	0-2, 2-4	1	1	1
44	59°36.25'	152°29.90'	65	4	bk	bk	1	1	1
48	60°00.0'	152°24.6'	45	2	0-2, 2-4	0-2, 2-4	1	1	1
Sea-3-76 WG - Kodiak Shelf									
52	58°24.42'	151°13.80'	52	4	0-2, 2-4	0-2, 2-4	1	1	1
53	58°12.70'	150°39.94'	86	1	bk	-	-	-	-
54	58°07.36'	150°30.26'	175	2	bk	bk	1	1	1
55	58°01.86'	150°21.64'	184	3	0-2, 2-4	0-2, 2-4	1	1	1
56	57°55.22'	150°12.77'	190	2	bk	bk	1	1	1
57	57°50.94'	150°03.74'	194	3	0-2, 2-4	0-2, 2-4	1	1	1

Station	Lat (N)	Lon (W)	Depth (m)	Rating[1]	Samples[2]				
					HC[3]	HA[3]	GH	GA	ES
58	57°46.99'	149°55.44'	232	3	bk	bk	1	1	1
59	57°46.60'	149°29.66'	495	2	bk	bk	1	1	1
60	57°45.96'	149°37.41'	444	4	0-2, 2-4	0-2, 2-4	1	1	1
67	57°59.70'	151°06.40'	82	2	bk	bk	1	1	1
68	57°28.10'	151°28.7'	154	3	0-2, 2-4	0-2, 2-4	1	1	1
69	57°23.25'	151°10.95'	80	1	bk	bk	1	1	1
70	57°24.08'	150°52.25'	96	2	surf	surf	1	-	1
71	57°19.99'	150°59.03'	95	2	0-2, 2-4	-	-	-	1
72	57°24.2'	151°05.1'	92	2	surf,subsurf	-	-	-	1
75	57°45.80'	151°08.05'	70	3	surf,subsurf	surf	-	-	1
79	58°13.23'	151°38.07'		2	bk	-	-	-	1
80	58°01.50'	151°21.90'	81	4	0-2, 2-4	bk	1	1	1
81	58°05.21'	151°14.55'	143	4	0-2, 2-4	0-2, 2-4	1	1	1
82	58°03.60'	151°15.90'		2.5	bk	bk	-	-	1
85	57°44.0'	151.45.00'	55	4	bk	bk	-	-	1
86	57°41.48'	151°34.70'	61	2.5	bk	bk	-	-	1
87	57°36.50'	151°47.65'	132	4	0-2, 2-4	0-2, 2-4	1	1	1
88	57°31.2'	151°38.0'	167	3	0-2, 2-4	0-2, 2-4	1	1	1
89	57°20.5'	152°44.5'	70	1	bk	bk	-	-	1
90	57°25.10'	151°51.90'	67	2	bk	bk	-	-	1
91	57°19.29'	152°04.82'	73	1	bk	bk	-	-	1
92	56°56.5'	152°33.0'	167	2.5	0-2, 2-4	0-2, 2-4	1	1	1
93	56°53.45'	152°40.90'	128	5	0-2, 2-4	0-2, 2-4	1	1	1
94	56°48.15'	152°52.60'	63	1	bk	bk	-	-	1
95	56°48.10'	153°21.35'	170	3	bk	bk	-	-	1
96	56°41.40'	153°05.90'	146	0	bk	bk	1	1	1
97	56°40.10'	153°10.02'	147	4	0-2, 2-4	0-2, 2-4	1	1	1
98	56°38.00'	153°16.00'	145	3	bk	bk	1	1	1
115	56°57.02'	152°06.28'	80	1	bk	bk	-	-	1
127	57°11.24'	151°29.59'	71	1	bk	bk	-	-	1
128	58°31.47'	149°21.90'	121	5	0-2, 2-4	0-2, 2-4	1	1	1

Station	Lat (N)	Lon (W)	Depth (m)	Rating[1]	Samples[2]				
					HC[3]	HA[3]	GH	GA	ES
129	58°35.85'	149°14.91'	95	1	bk	bk	-	-	1
130	58°42.35'	149°03.38'	149	2	0-2, 2-4	0-2, 2-4	1	1	1
131	58°44.99'	148°58.18'	214	3	0-2, 2-4	0-2, 2-4	-	-	1
132	58°49.24'	148°54.71'	236	2	bk	bk	-	-	1
138	58°22.27'	150°24.07'	61	5	0-4	0-4	-	-	1
<u>Sea-5-76</u> - Northern Bering Sea									
47	64°25'	165°29.90'	15	3	0-2, 2-4	0-2, 2-4	1	1	1
49	63°27.77'	163°52.57'	10	3	0-2, 2-4	0-2, 2-4	1	1	1
70	65°6,13'	167°40.40'	31	4	0-2, 2-4	0-2, 2-4	1	1	1
88	65°46.01'	168°05.51'	9	1	bk	-	-	-	-
104	64°57.85'	167°04.84'	14	1	bk	-	-	-	-
105	64°49.00'	166°44.00'	15	2	0-2, 2-4	0-2, 2-4	1	1	1
121	63°52.99'	163°01.34'	20	0	surf	subsurf	1	1	1
125	64°00.12'	162°24.60'	18	3	0-2, 2-4	0-2, 2-4	1	1	1
131	64°23.60'	161°49.27'	17	4	0-2, 2-4	0-2, 2-4	1	1	1
137	63°40.89'	161°13.29'	14	3	0-2, 2-4	0-2, 2-4	1	1	1
147	63°47.00'	163°41.50'	17	2	0-2, 2-4	0-2, 2-4	1	1	1
152	64°05.00'	164°26.50'	22	2	0-2, 2-4	0-2, 2-4	1	1	1
154	63°45.08'	164°37.43'	18	2	0-2, 2-4	0-2, 2-4	1	1	1
156	63°28.39	165°19.28'	17	3	0-2, 2-4	0-2, 2-4	1	1	1
157	63°18.11'	165°03.26'	8	1	surf	surf	1	1	1
160	62°54.50'	165°08.15'	10	1	surf	surf	1	1	1
162	63°02.80'	165°53.99'	21	3	0-2, 2-4	0-2, 2-4	1	1	1
166	63°14.62'	167°02.21'	26	1	surf,subsurf	-	1	1	1
168	63°26.25'	166°29.64'	28	1	surf, subsurf	-	1	1	1
169	63°34.79	166°05.53'	27	1	surf, subsurf	-	1	1	1
170	63°41.72'	165°45.81'	25	2	surf, subsurf	-	1	1	1
172	64°00.10'	165°29.25'	20	1	surf, subsurf	-	1	1	1
174	64°21.15'	165°00.40'	36	2	surf, subsurf	-	1	1	1
176	64°03.01'	166°59.59'		4	surf	-	-	-	-

Station	Lat (N)	Lon (W)	Depth (m)	Rating[1]	Samples[2]				
					HC[3]	HA[3]	GH	GA	ES
G-B-76 - Beaufort Sea									
1(R)	70°32'	147°33'	27	3	surf,subsurf	-	1	-	1
2(11)	70°39'	147°37'	26	2	surf, subsurf	surf,subsurf	1	1	1
3	70°47'	148°02'	25	3	surf,subsurf	surf,subsurf	1	1	1
4	70°57'	149°33'	25	3	surf,subsurf	surf,subsurf	1	1	1
5	71°08'	151°19'	23	2	surf,subsurf	surf,subsurf	1	1	1
6	71°43'	151°47'	1750	3	surf	subsurf	1	1	1
7	71°22'	152°20'	60	3	surf,subsurf	surf,subsurf	1	1	1
8	71°19'	152°32'	50	2	surf,subsurf	surf,subsurf	1	1	1
9	71°08'	152°57'	22	3	surf,subsurf	surf,subsurf	1	1	1
10	71°23'	154°21'	29	3	surf	subsurf	1	1	1
11	71°36'	155°32'	197	2	bk	-	-	-	1

[1] Quality of sample recovery based on a subjective scale of 5 (excellent) to 1 (poor).

[2] Subsamples collected from grab sample: HC and HA refer to replicate high molecular weight hydrocarbon samples, GH and GA refer to replicate low molecular weight hydrocarbon samples, and ES refers to samples collected for carbon (total, organic), nitrogen, and sulfur.

[3] Depth of subsample from grab sample: 0-2 cm, 2-4 cm, surface, subsurface, or bulk.

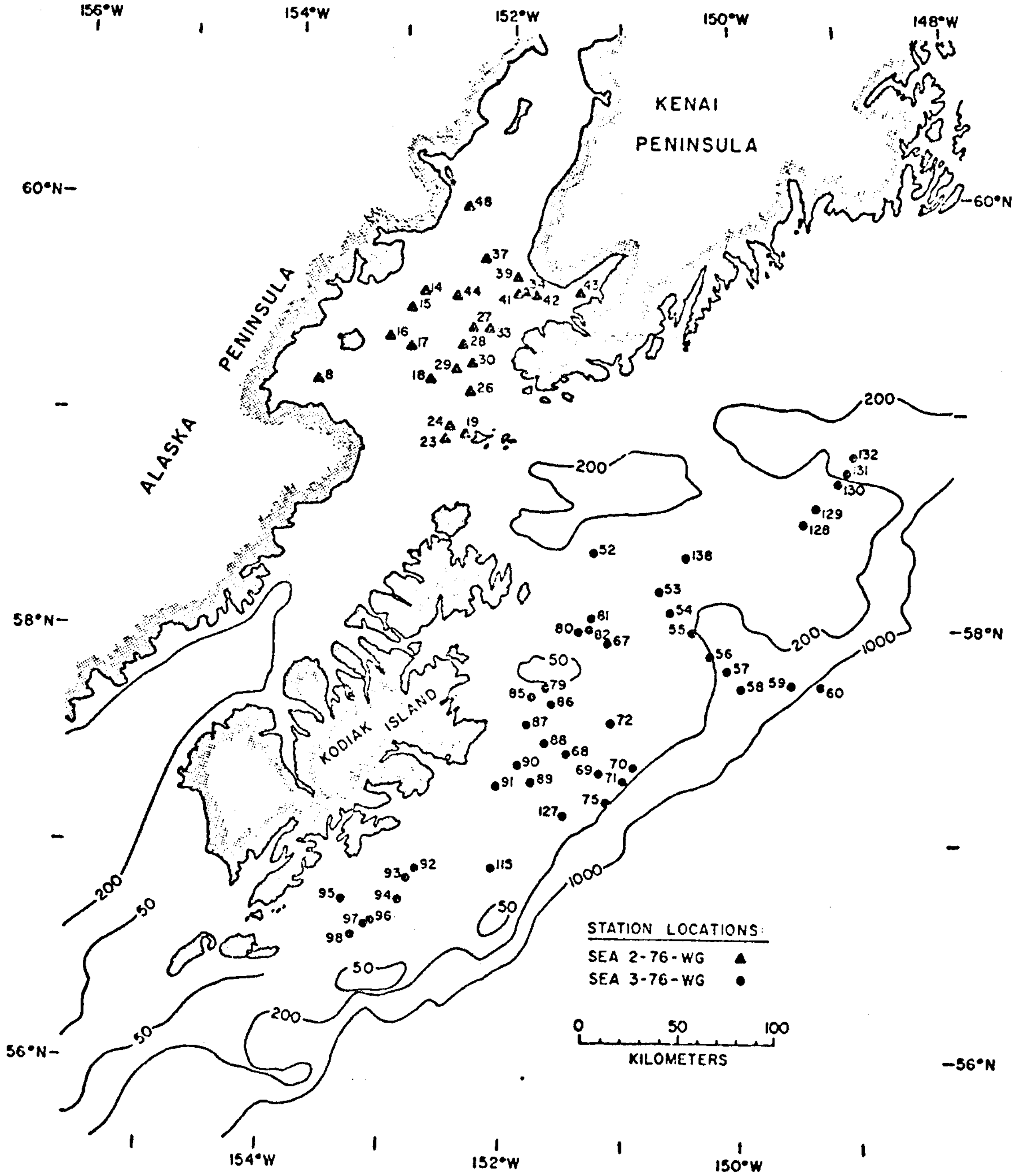


Figure 1. Thirty-six stations for collection of samples for hydrocarbon analysis.

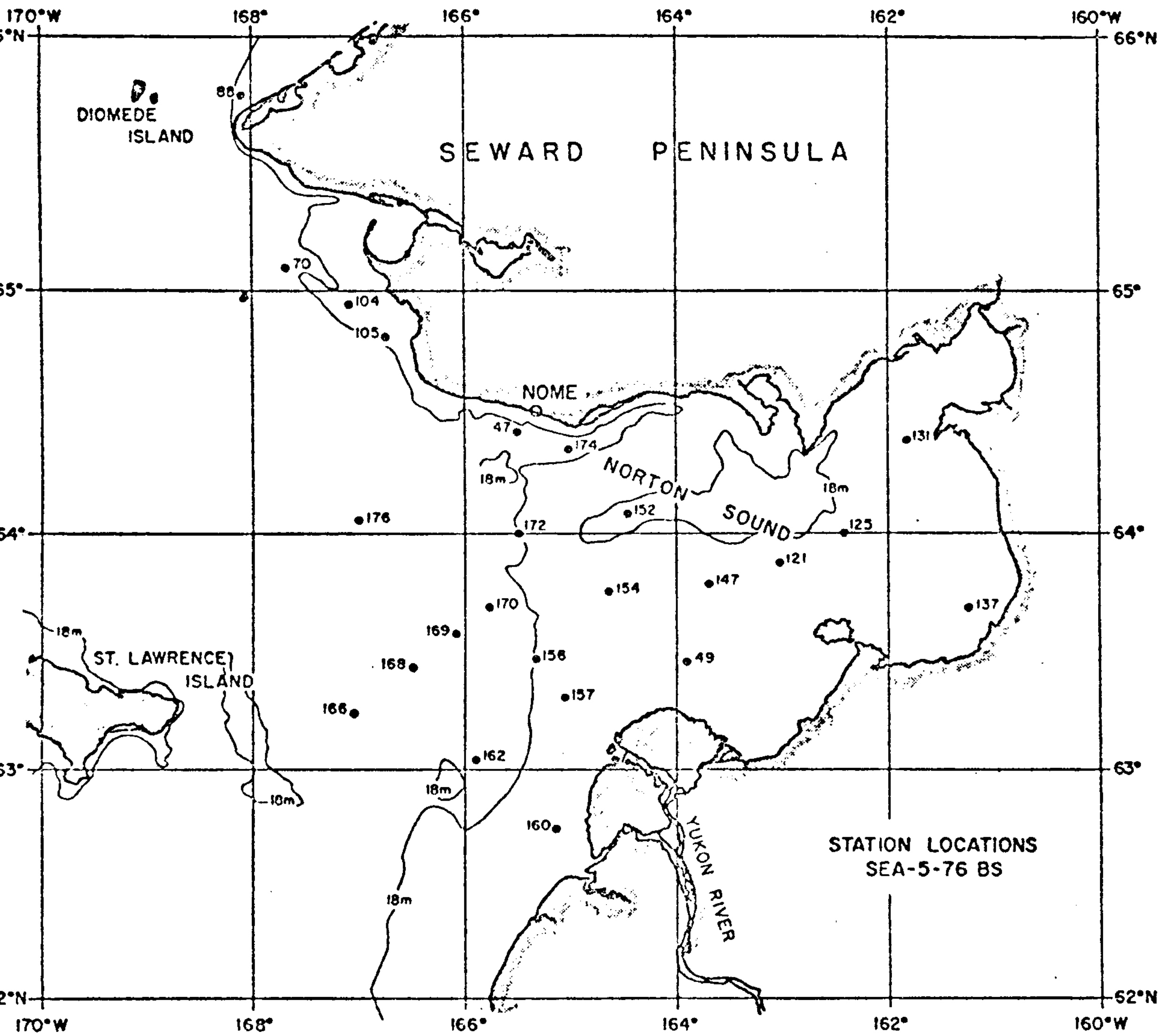


Figure 2. Grab sampler stations (24).

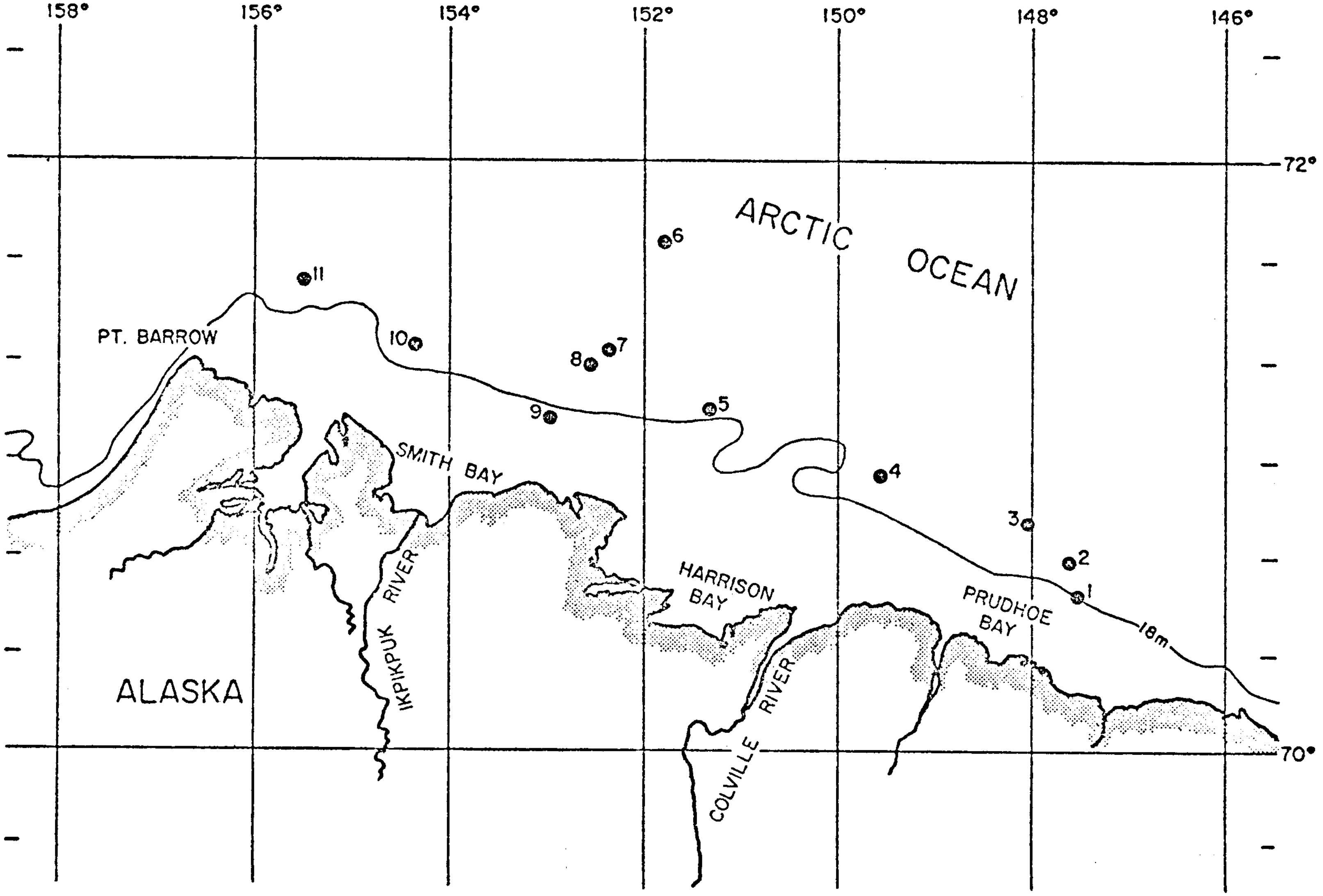


Figure 3. Twelve stations where sediment samples were collected.

Appendix I

FULVIC ACIDS, HUMIC ACIDS, AND KEROGENS FROM SEDIMENTS OF THE GULF OF ALASKA AND EASTERN BERING SEA

Supplement to Quarterly Report

April 1 to September 30, 1976

"Characterization of Organic Matter in Sediments
from Gulf of Alaska, Bering and Beaufort Seas"

Subcontract No. F-01770, P.O. #F01770

By:

K.E. Peters
I.R. Kaplan

FULVIC ACIDS, HUMIC ACIDS, AND KEROGENS FROM SEDIMENTS OF THE GULF OF ALASKA AND EASTERN BERING SEA

by

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ABSTRACT

Surface samples of sediment from the Gulf of Alaska and the eastern Bering Sea were analyzed by the Leco carbon technique for carbon as fulvic acid, humic acid, and kerogen. Preliminary data indicate a crude correlation between fulvic acid/humic acid ratios and proximity to shore which may be attributed to: (1) differing degrees of diagenesis, and/or (2) mixing of marine and terrestrial humic substances. Carbon isotope data support the contention that the relative proportions of marine and terrestrial organic matter influence the FA/HA ratio.

INTRODUCTION

Most of the organic matter provided to a basin of deposition is oxidized in the water column or surficial sediments to carbon dioxide and water. The remaining non-living organic matter consists predominantly of materials resistant to microbial degradation: fulvic acids, humic acids, and kerogen. Fulvic and humic acids are known collectively as "humic substances". Each of these fractions is operationally defined by the extraction procedure in Figure 1.

The objective of this work was to assess the organic content as fulvic acid (FA), humic acid (HA), and kerogen (K) in sediments of the Gulf of Alaska and eastern Bering Sea. Coupled with further data on other fractions of the organic matter in these sediments a better understanding of the distribution and processes affecting organic detritus in these areas may be reached.

METHOD

Sampling was conducted as described by Kaplan (1976). Samples ranging from 18 to 30 grams of sediment were extracted for FA, HA, and K by the procedures shown in Fig. 1. Localities of collection are shown in Figs. 2 and 3.

The extraction procedure utilized as little harsh chemical treatment as possible. This facilitated less alteration of organics and more quantitative recoveries. The resulting products contained varying amounts of resistant minerals and salts. Subsequent Leco carbon (model 572-100) analysis gave data on the FA, HA, and K residues as grams of carbon in the product per gram of acidified sample.

Selected freeze-dried samples were combusted under oxygen at 1000°C for 15 minutes on a carbon isotope preparation vacuum line described by Kaplan _et al_. (1970). Purified carbon dioxide product was trapped with liquid nitrogen and sealed into glass tubes for isotope ratio analysis using a Nuclide 660 Dual Collecting Isotope Ratio Mass Spectrometer.

RESULTS

The following observations were made (Table 1):

(1) Relatively coarse-grained, well-sorted Alaska sediments (as described in Appendix 1, Kaplan (1976)) contain less FA and HA than the other samples examined (for example, GASS 101, GASS 102).

(2) As indicated by the (FA+HA)/K ratios, the amount of kerogen appears to be independent of the concentration of humic substances. Small quantities of FA and HA in the coarser-grained samples, for example, did not preclude relatively large quantities of K.

(3) FA/HA ratios range from 1.03 to 8.27 in the samples. The mean of all samples was FA/HA = 2.4 with a 1.5 standard deviation.

(4) FA/HA ratios are generally high near shore (particularly in protected areas) and decrease toward deeper-water localities (Figures 2 and 3).

(5) FA+HA+K for each sample represented an average of 82% of the TOC (total organic carbon) as determined by Kaplan (1976) on acidified samples. Some or all of the remaining organic content can be accounted as toluene:methanol or chloroform:methanol soluble and was studied by others (Kaplan, 1976).

(6) Carbon isotope data indicate a correlation between the FA/HA ratio and the $\delta^{13}C_{PDB}$ of FA, HA, and K for selected samples.

DISCUSSION

Modification of the FA/HA ratio may be a result of the depositional environment and degree of diagenesis (for example, turbidity, depth of water column, depth of sediment burial, and redox conditions) or source mixing (for example, marine versus terrestrial components).

Early schemes of soil organic matter diagenesis considered FA to be a degradation product of HA but more recent carbon isotope data indicate that FA is a low molecular weight precursor in the process of polymerization of degraded organic material to HA (Nissenbaum and Schallinger, 1974). Nissenbaum and Kaplan (1972) have proposed a scheme for the evolution of organic matter in marine sediments: degraded cellular material → water-soluble complex of amino acids and carbohydrates → FA → HA → K. Huc and Durand (1973) extracted FA, HA, and K from recent argillaceous sediments of various origins using a similar technique to that employed here. In comparison to our data their FA/HA ratios expressed in grams C as FA/grams carbon as HA varied from 0.11 to 2.30. They observed a decrease in FA/HA with depth (cores 1.5 to 15 m deep) attendant with diagenesis. Surface samples yielded higher FA/HA ratios within the observed range of data comparable with our data. Since all of the Alaska samples were surface sediment we might assume an equal level of sediment diagenesis for each. Surface sediments in areas with slow sediment deposition however, (as might be expected in localities far from shore) may be much older than those in areas of rapid deposition. Consequently, the levels of early diagenesis for different samples may vary.

Stuermer and Harvey (1976, in press) have shown that in Sargasso Sea surface water the FA/HA ratio is higher (32.33) than in deep water (3.54). They suggest that the transformation of marine FA to HA occurs over time since the deep water contains organic matter which is older than surface water organic matter (Williams et al., 1969). These authors attribute their relatively low FA/HA ratios in coastal surface water (5.67) compared to the Sargasso Sea as a result of the shorter water column in which (1) recycling of humic substances by fluxes from bottom sediments results in further conversion of FA to HA, or (2) bacterial and mineral-catalyzed conversion of FA to HA on the more abundant particulate matter can occur.

Depositional control on the quantities of FA and HA is clear for some of the coarser-grained, better-sorted samples where FA and HA are absent or present in minute amounts (for example, GASS 101, GASS 102 at the mouth of the Cook Inlet, and GASS 122, Table 1 and Figure 2). Either the humic substances were not deposited (possibly due to a lack of fine particulate matter with which the humics might associate) or were winnowed out by currents along with clays after deposition. In any case, K often remains in substantial quantity.

Several processes may explain the lack of correlation between the amount of K in Alaska samples and the concentration of humic substances (as indicated by (FA+HA)/K ratios in Table 1). If we assume K to be an end product in the scheme of early organic diagenesis, differing degrees of diagenesis for surface samples might contribute to the variability of this ratio. A more important contribution may be the apparent winnowing of humic substances from well-sorted samples. Finally, not all of the K in a sample need be derived from the in situ humic substances. Sackett et al. (1974), for example, show that up to 90% of the K in sediments of the Ross Sea is allochthonous.

Van Krevelen (1961) discusses the mechanisms of humification as the alteration of terrestrial (lignin and/or cellulose) and marine (protein and carbohydrate) source materials. According to Welte (1974) marine organic matter is composed dominantly of various proteins, carbohydrates, and lipids, while terrestrial organic matter is made up of lignins, cellulose, and skleroproteins. It is tempting to speculate that there may be fundamental differences between marine and terrestrial humic substances which might be reflected in FA/HA ratios of paralic sediments; i.e., the innate ratios of FA/HA for marine and terrestrial material may differ for equivalent levels of diagenesis. Marine humic acids, for example, appear to be more paraffinic in nature while terrestrial humic acids may consist of a greater aromatic component (W.L. Orr, Mobil R&D, pers. comm.). Hedges and Parker (1976) noted a progressive decrease in lignin content from nearshore to deep-water sediments. This may parallel a decrease in terrestrial HA.

Terrestrial sedimentary organic detritus has $\delta^{13}C_{PDB}$ values of around -25‰ whereas marine muds contain material averaging -20‰ (Degens, 1969). Systematic variations of carbon isotope values as a result of mixing of organic matter from river to open marine sediments are observed (Sackett and Thompson, 1963; Schultz and Calder, 1976; Hedges and Parker, 1976). The carbon isotope data in Table 2 and Figure 4 support the contention that the relative quantities of marine and terrestrial components influence the FA/HA ratio of the sedimentary organic matter. High values of FA/HA correspond with typically terrestrial carbon isotope ratios while lower FA/HA values correspond with carbon isotope ratios typical of marine organic matter. The "lighter" (enriched in ^{12}C) isotope values of FA and HA relative to their corresponding kerogen supports the scheme proposed by Nissenbaum and Kaplan (1972) where K is a product of the diagenesis of humic substances.

CONCLUSIONS

There appears to be a crude correlation in surface samples of Alaskan marine sediments between the FA/HA ratio and proximity to protected environments near shore. One may attribute this correlation to (1) differing degrees of diagenesis of the humic substances as a result of depositional controls in the water/sediment column, and/or (2) mixing of marine and terrestrial humic substances, each with their characteristic FA/HA ratio. Carbon isotope data support the contention that the relative proportions of marine and terrestrial organic matter influence the FA/HA ratio.

ACKNOWLEDGMENTS

Special thanks is due Dr. Daniel Stuermer and Mark Sandstrom for helpful discussion, Patty Elkins and Michael Coltun for running most of the Leco carbon analyses, and Dave Winter for mass spectrometry. This research was supported by NOAA grant no. 03-6-022-35250 from the University of Alaska to UCLA.

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Table 1. Leco Carbon Analysis of Alaska Samples

Sample	Weight	$\frac{\text{FA (gm C)}}{\text{SAMPLE (gm)}}$	$\frac{\text{HA (gm C)}}{\text{SAMPLE (gm)}}$	$\frac{\text{K (gm C)}}{\text{SAMPLE (gm)}}$	FA/HA (±20%)	$\frac{\text{FA+HA}}{\text{K}}$	FA+HA+K	$\%\frac{\text{FA+HA+K}}{\text{TOC}}$	TOC†
PWS 13	19.33	7.90×10^{-4}	1.55×10^{-4}	3.31×10^{-3}	5.09	0.285	4.26×10^{-3}	60	0.71
GASS 01	19.10	2.49×10^{-3}	6.72×10^{-4}	4.72×10^{-3}	3.70	0.670	7.88×10^{-3}	113	0.77
41	20.76	3.00×10^{-4}	1.67×10^{-4}	3.65×10^{-3}	1.80	0.128	4.12×10^{-3}	49	0.84
43	30.00	6.85×10^{-4}	3.27×10^{-4}	3.39×10^{-3}*	2.09**	0.298	4.40×10^{-3}	67	0.66
50	18.15	9.13×10^{-4}	1.10×10^{-4}	5.03×10^{-3}	8.27	0.203	6.05×10^{-3}	78	0.78
51	19.31	4.76×10^{-4}	2.45×10^{-4}	5.64×10^{-3}	1.94	0.128	6.36×10^{-3}	87	0.73
52	30.00	5.90×10^{-4}	3.56×10^{-4}	4.85×10^{-3}*	1.66**	0.195	5.80×10^{-3}	72	0.81
54	22.38	2.99×10^{-4}	∿6.53×10^{-5}	9.91×10^{-3}	∿4.58	∿0.037	1.03×10^{-2}	201	0.51
55	30.00	1.57×10^{-3}	6.40×10^{-4}	3.18×10^{-3}*	2.45**	0.695	5.39×10^{-3}	67	0.92
101††	20.58	∿4.76×10^{-5}	--	1.58×10^{-3}	--	∿0.030	∿1.63×10^{-3}	90	0.18
102††	21.68	3.01×10^{-4}	--	1.09×10^{-3}	--	∿0.275	∿1.39×10^{-3}	77	0.18
103	20.93	8.91×10^{-4}	4.55×10^{-4}	3.13×10^{-3}	1.96	0.430	4.48×10^{-3}	85	0.53
105	21.28	1.27×10^{-3}	9.01×10^{-4}	4.70×10^{-3}	1.41	0.462	6.87×10^{-3}	90	0.76
119	20.88	1.15×10^{-3}	8.48×10^{-4}	3.98×10^{-3}	1.36	0.502	5.99×10^{-3}	81	0.74
120	19.81	2.28×10^{-3}	1.88×10^{-3}	9.51×10^{-3}	1.21	0.44	1.37×10^{-2}	127	1.08
121	20.46	2.04×10^{-3}	1.82×10^{-3}	5.84×10^{-3}	1.12	0.661	9.70×10^{-3}	86	1.13
122††	21.01	∿6.29×10^{-5}	∿2.88×10^{-5}	6.27×10^{-4}	∿2.18	∿0.146	7.19×10^{-4}	40	0.18
124	20.85	1.60×10^{-3}	1.23×10^{-3}	4.75×10^{-3}	1.30	0.596	7.58×10^{-3}	82	0.92
133	23.57	5.48×10^{-4}	1.76×10^{-4}	6.81×10^{-4}	3.11	1.06	1.40×10^{-3}	40	0.35
134	20.02	3.52×10^{-3}	1.99×10^{-3}	6.78×10^{-3}	1.77	0.81	1.23×10^{-2}	113	1.09
137	21.19	3.06×10^{-4}	1.44×10^{-4}	2.13×10^{-3}	2.13	0.211	2.58×10^{-3}	76	0.34
160	20.92	5.63×10^{-4}	2.77×10^{-4}	1.02×10^{-3}	2.03	0.823	1.86×10^{-3}	60	0.31
EBBS 17	19.90	2.17×10^{-3}	1.40×10^{-3}	3.37×10^{-3}	1.55	1.06	6.94×10^{-3}	91	0.76
19	20.90	1.83×10^{-3}	7.07×10^{-4}	2.19×10^{-3}	2.59	1.16	4.73×10^{-3}	121	0.39
35	20.12	6.67×10^{-4}	5.47×10^{-4}	1.75×10^{-3}	1.22	0.694	2.96×10^{-3}	72	0.41
37	21.15	8.00×10^{-4}	3.61×10^{-4}	1.27×10^{-3}	2.22	0.945	2.47×10^{-3}	60	0.41
40	20.26	3.30×10^{-4}	1.08×10^{-4}	1.60×10^{-3}	3.06	0.27	2.04×10^{-3}	64	0.32
41	20.17	1.83×10^{-4}	∿5.33×10^{-5}	1.46×10^{-3}	∿3.44	0.16	1.70×10^{-3}	46	0.37
43	20.21	--	∿6.10×10^{-5}	2.38×10^{-3}	--	--	∿2.44×10^{-3}	81	0.30
46	19.78	5.12×10^{-4}	4.00×10^{-4}	1.33×10^{-3}	1.28	0.686	2.24×10^{-3}	53	0.42
51	20.07	5.54×10^{-4}	5.36×10^{-4}	1.81×10^{-3}	1.03	0.60	2.90×10^{-3}	-	--
59	20.02	4.97×10^{-4}	2.48×10^{-4}	2.01×10^{-3}	2.00	0.37	2.76×10^{-3}	102	0.27
PMEL 45B	22.00	9.15×10^{-4}	5.75×10^{-4}	5.54×10^{-3}	1.59	0.269	7.03×10^{-3}	92	0.76

* = residue treated with HCl-HF prior to Leco carbon analysis.

** = less reliable FA and HA data due to sample transfer losses.

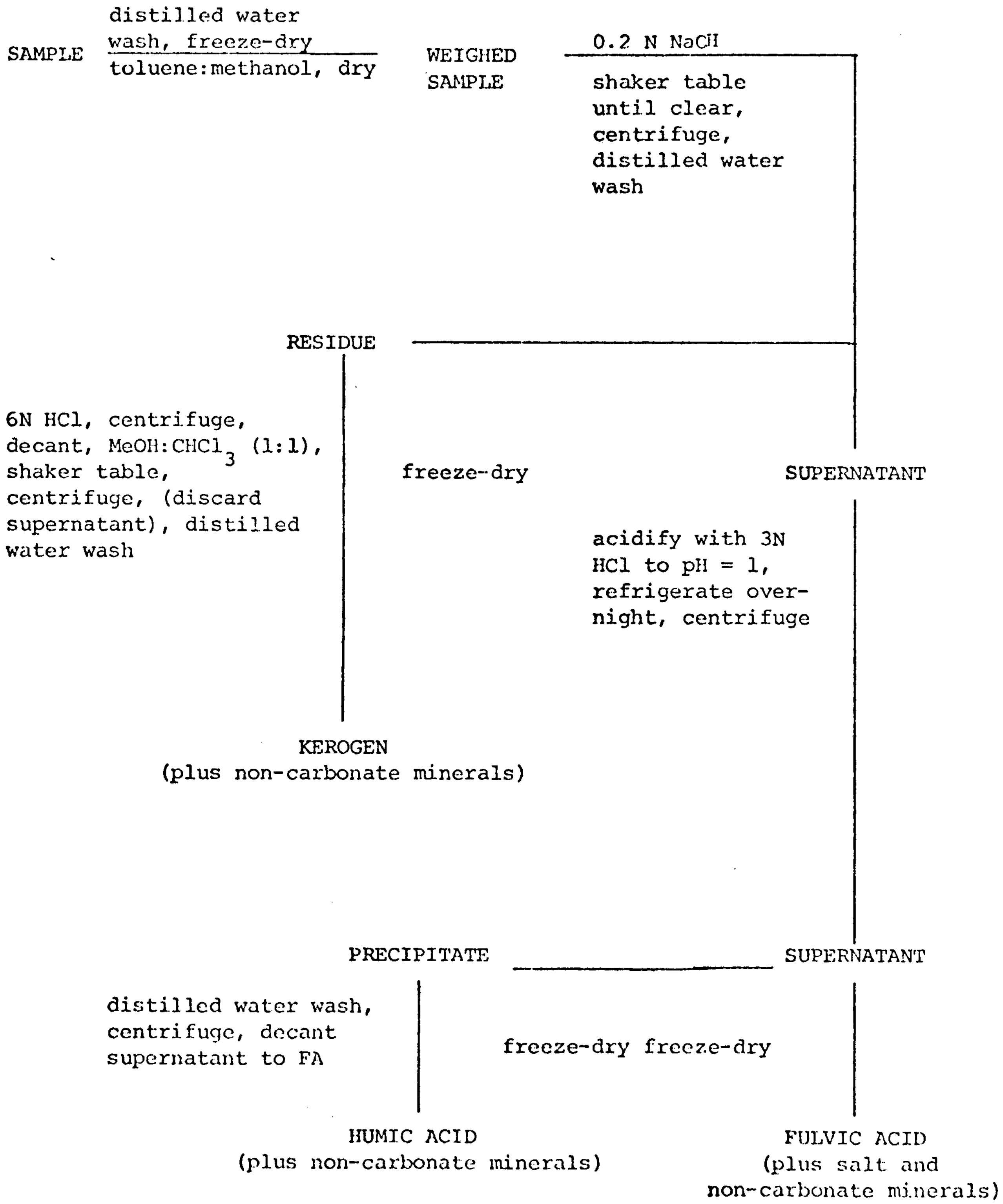
† = % total organic carbon as determined in Kaplan (1976).

†† = coarser-grained, better-sorted samples (for textural descriptions of untreated samples, see Appendix 1, Kaplan, 1976).

Table 2. $\delta^{13}C_{PDB}$ Isotope Data Summary

Sample	FA/HA	$\delta^{13}C$ FA	$\delta^{13}C$ HA	$\delta^{13}C$ K	$\delta^{13}C$ TOM	$\frac{FA+HA}{K}$
GASS 50	8.27	-24.58	-23.58	-25.92	-24.05	.203
PWS	5.09	-21.43	-22.47	-28.43	--	.285
GASS 01	3.70	-19.88	-22.12	-24.39	--	.070
GASS 137	2.03	-22.62	-22.02	-24.29	--	.211
GASS 119	1.36	-21.24	-20.98	-23.02	-21.50	.502
EBBS 35	1.22	-20.65	-20.21	-23.31	-21.11	.694

Figure 1. Extraction Procedure



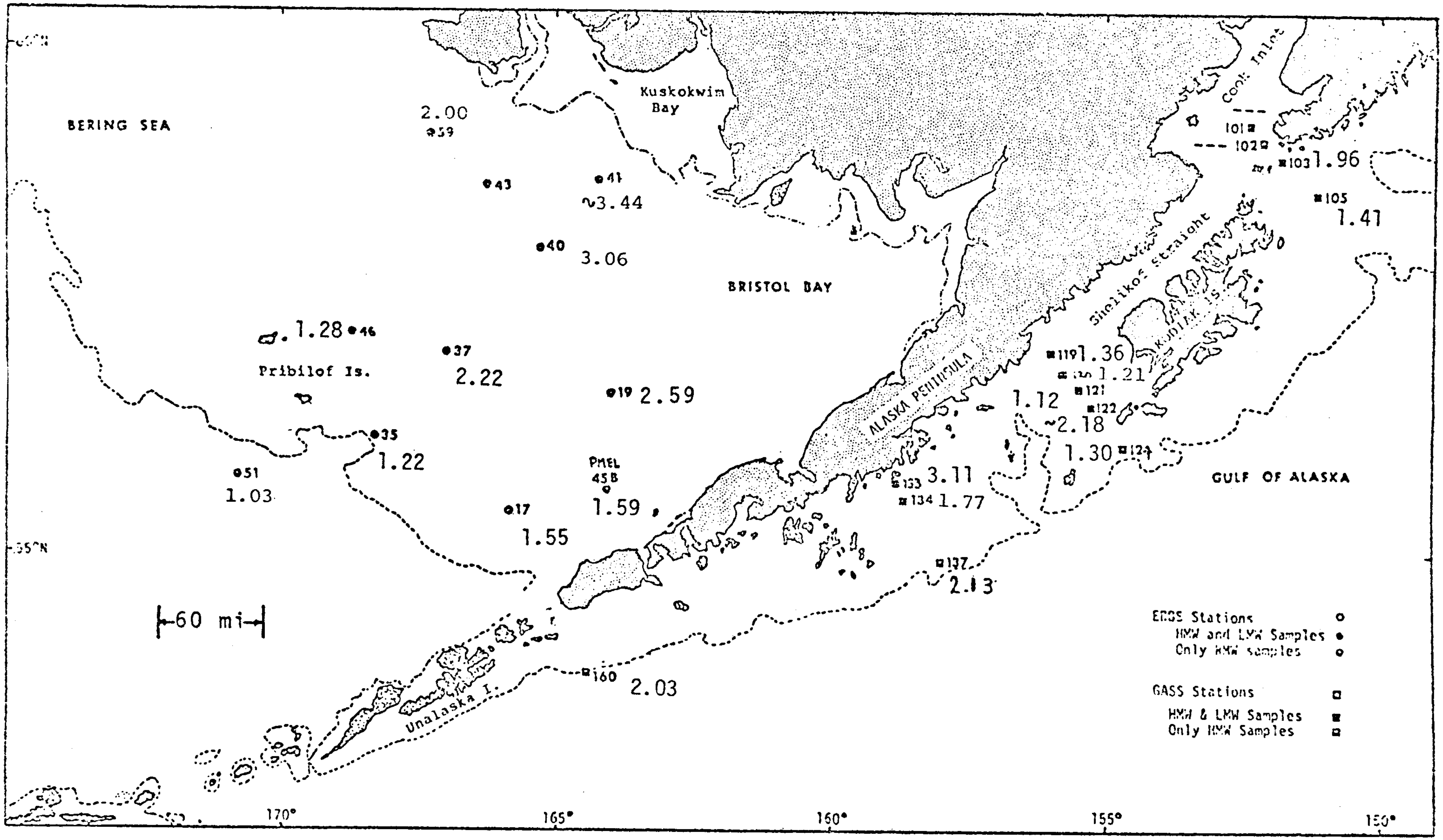


FIGURE 2. Eastern Bering Sea and Western Gulf of Alaska, FA/HA Ratios

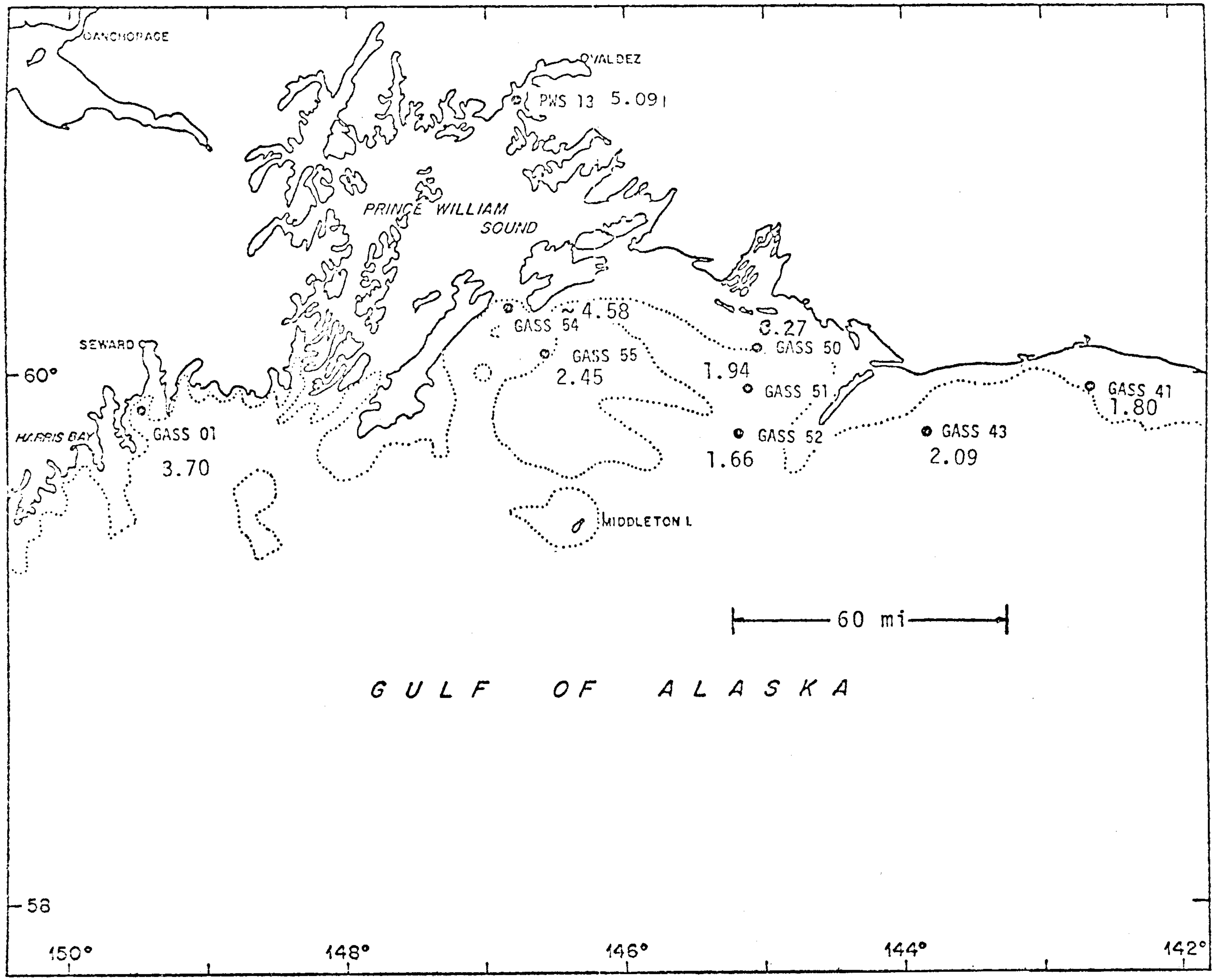


FIGURE 3. Eastern Gulf of Alaska, FA/HA Ratios

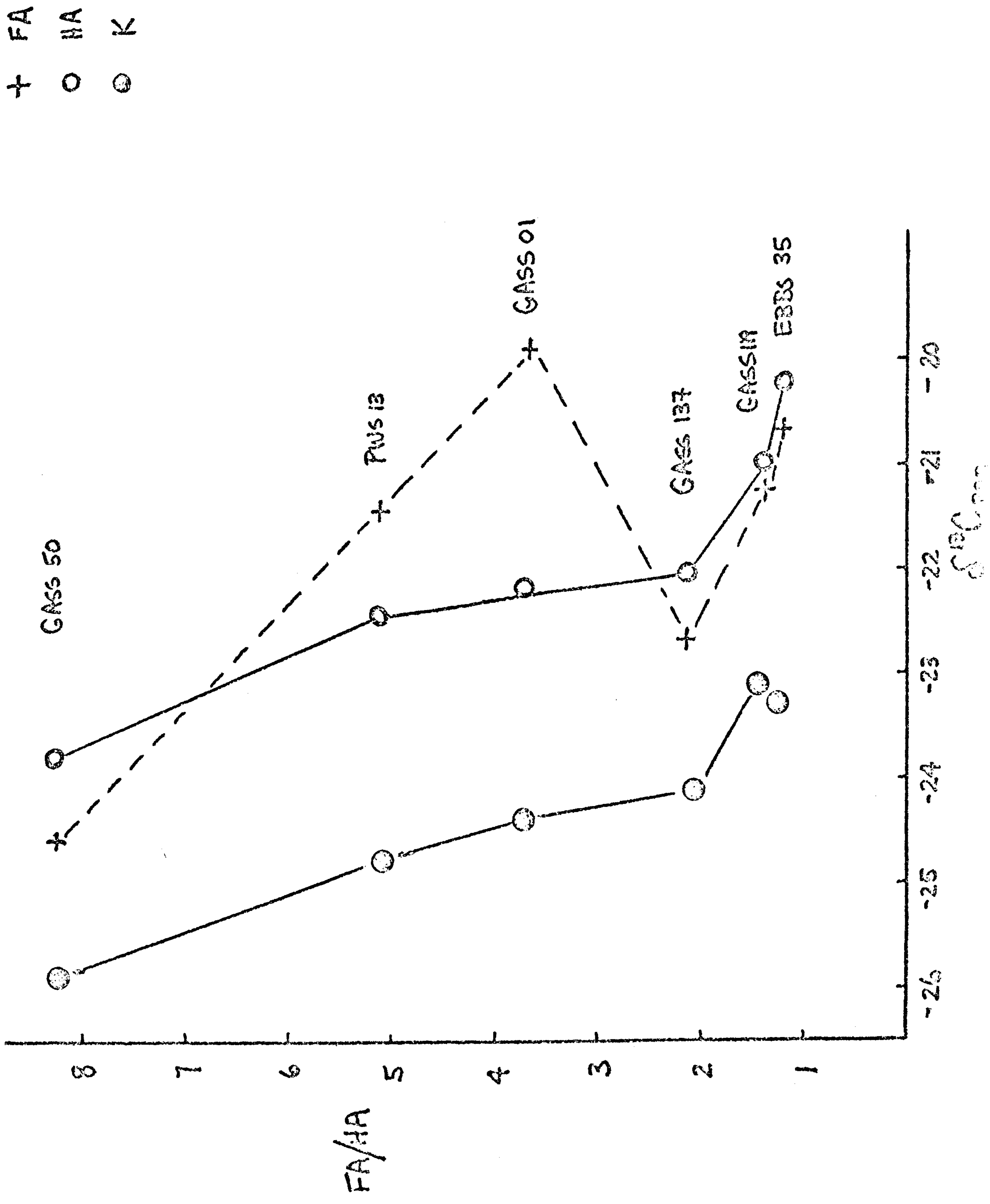


Figure 4. Isotope plot for sediment organic fractions.

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