Ved CRD1
for Kodiak

Outer Continental Shelf Environmental Assessment Program

Final Reports of Principal Investigators

Volume 33

July 1985

U.S. DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
National Ocean Service
Office of Oceanography and Marine Assessment
Ocean Assessments Division
Alaska Office

U.S. DEPARTMENT OF THE INTERIOR
Minerals Management Service

"Outer Continental Shelf Environmental Assessment Program Final Reports of Principal Investigators" ("OCSEAP Final Reports") continues the series entitled "Environmental Assessment of the Alaskan Continental Shelf Final Reports of Principal Investigators."

It is suggested that sections of this publication be cited as follows:

Kaplan, I. R., and M. I. Venkatesan. 1981. Characterization of organic matter in sediments from Gulf of Alaska, Bering Sea, and Beaufort Sea. U.S. Dep. Commer., NOAA, OCSEAP Final Rep. 33(1985): 101-191.

OCSEAP Final Reports are published by the U.S. Department of Commerce, National Oceanic and Atmospheric Administration, National Ocean Service, Office of Oceanography and Marine Assessment, Ocean Assessments Division, Alaska Office, Anchorage, and printed by the General Services Administration Printers in Juneau, Alaska.

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Anchorage, AK 99513

OUTER CONTINENTAL SHELF
ENVIRONMENTAL ASSESSMENT PROGRAM

FINAL REPORTS OF PRINCIPAL INVESTIGATORS

VOLUME 33

JULY 1985

U.S. DEPARTMENT OF COMMERCE
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
NATIONAL OCEAN SERVICE
OFFICE OF OCEANOGRAPHY AND MARINE ASSESSMENT
OCEAN ASSESSMENTS DIVISION
ALASKA OFFICE

ANCHORAGE, ALASKA

The facts, conclusions, and issues appearing in these reports are based on research results of the Outer Continental Shelf Environmental Assessment Program (OCSEAP), which is managed by the National Oceanic and Atmospheric Administration, U.S. Department of Commerce, and primarily funded by the Minerals Management Service, U.S. Department of the Interior, through interagency agreement.

Outer Continental Shelf Environmental Assessment Program

Final Reports of Principal Investigators

VOLUME 33 JULY 1985

CONTENTS

DISTRIBUTION AND DYNAMICS OF HEAVY METALS IN ALASKAN SHELF ENVIRONMENTS SUBJECT TO OIL DEVELOPMENT

by

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Final Report
Outer Continental Shelf Environmental Assessment Program
Research Unit 162

September 1979

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I. TASK OBJECTIVES

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

II. FIELD AND LABORATORY ACTIVITIES

A. Field Work

No field work performed during the preceding quarter.

B. Scientific Parties

N/A

C. Field Collection Methods

N/A

D. Laboratory Analysis Program

This report contains data on the heavy metal contents of lower Cook Inlet macrobenthos. The procedure used for this work is as follows:

∿ 0.5 g biota tissue dry-ashed for 24-48 hours in plasma furnace using operating conditions given in previous reports. Residue dissolved in 3 ml concentrated Ultrex HNO_3 and 1 ml 30% Ultrex H_2O_2. Heated gently in water bath till cessation of reaction. Diluted to 25 ml with triple distilled water and analysed spectrophotometrically.

III. RESULTS

A. Beaufort Sea

Work on this sub-contract was completed during the preceding quarter and a final report is included in the following section.

B. Lower Cook Inlet

We have now completed work on determining baseline concentrations of heavy metals in Cook Inlet biota. Some intertidal data has been given previously. This past year we have worked on obtaining precise and accurate data for certain metals in key macrobenthic species; notably tanner crab and shrimp. Because of the failure to obtain suitable samples via the relevant biology programs, the values given here relate exclusively to samples collected especially for this project by our own personnel. Data for crab and shrimp respectively are given in Tables I and II and for sole and king crab in Tables III and IV. Accuracy and precision data for this batch of data are given in Table V.

C. NEGOA Specific Study Sites

We have completed work on the assigned task of devising and testing extraction techniques for removing reproducible fractions of heavy metals from sediment. Details of the procedures used have been given in previous

TABLE I

LOWER COOK INLET
OSS *SURVEYOR* MARCH 1978

Heavy metal contents of tanner crab muscle tissue
(µg/g dry wt)

Duplicate data

Station No.	Trawl No.	Sex	Cd	Ni	Zn	Cu
56a3	-	?	.5	<.5	100	28.0
			.5	<.5	105	29.4
62aC2	9	M	.24	<.5	109	30.7
			.24	<.5	113	31.0
56a4		?	.11	<.5	89	68.9
			.11	<.5	92	72.1
62aC12	11	M	.12	<.5	111	30.0
			.12	<.5	111	29.1
62a14c		M	.11	<.5	119	20.2
			.12	<.5	119	21.9
62a13e	13	F	.08	<.5	94	21.5
			.09	<.5	98	22.5
23a		F	-	<.5	122	27.5
			.12	<.5	121	30.0
8b		F	.14	<.5	115	40.8
			.13	<.5	118	40.8
62aC5		F	.19	<.5	94	58.6
			.16	<.5	101	53.9
62aC13	11	M	.14	.16	131	13.2
			.24	.19	-	-
62aC4	9	M	.04	.13	128	25.5
			.19	.13	113	26.2
18a		M	nab	.19	122	37.2
			nab	.14	115	34.2
62a	13	M	.06	.13	112	26.5
			.05	.14	103	22.0
56a2		?	nab	.13	117	24.2
			nab	.11	119	25.3
62aC11	11	M	.12	<.5	116	40.6
			-	-	-	-

TABLE I

CONTINUED

Station No.	Trawl No.	Sex	Cd	Ni	Zn	Cu
62a13A	13	?	.09	<.5	118	25.9
			.08	<.5	116	31.4
62a13d	13	M	–	–	–	–
			.07	<.5	124	6.7
62aC3	9	M	.11	<.5	119	6.8
			.11	<.5	122	5.5
8		M	.07	<.5	119	9.2
			.08	<.5	119	9.9
62a14A	14	F	.26	.16	98	33.7
			.25	.13	108	29.5
62a13F	13	F	.81	.17	157	34.7
			–	–	–	–
5		F	.45	.11	107	58.2
			.29	.09	110	53.2
62a14d	14	M	.17	.09	112	19.6
			.14	nab	108	17.2
62aC6	10	M	.17	.09	112	19.6
			.14	nab	108	17.2
62aC10	11	?	.16	<.5	118	26.8
			.16	<.5	120	26.0
62a	13	?	.18	<.5	111	41.0
			.16	<.5	106	39.5
E2		M	.16	<.5	119	24.4
			.17	<.5	124	24.9
G2aC10	11		.17	<.5	123	35.9
			.17	<.5	123	33.8
56a1		?	.07	<.5	129	65.0
			.06	<.5	150	53.8

TABLE II

LOWER COOK INLET
OSS *SURVEYOR* MARCH 1978

Heavy metal contents of shrimp (μg/g dry wt)

Duplicate determinations

Station No.	Trawl No.	Species	Organ	Cd	Ni	Zn	Cu
62a	7	Crangon	Muscle	.14	.29	49.7	16.6
				.14	.19	49.2	18.8
62a	10	Humpy	Muscle	nab	.25	44.5	10.6
				nab	nab	45.6	10.3
37		Crangon	Muscle	.18	nab	49.5	36.2
				.16	nab	49.6	38.4
E3		Sand	Muscle	.62	.43	59.1	28.7
				.40	.27	56.6	25.9
62a		Pink	Muscle	nab	nab	47.3	13.9
				nab	.14	43.9	13.0
62a		Pandalid	Muscle	.53	.14	53.3	30.5
				–	.19	51.1	26.4
56al		Pandalid	Muscle	.16	<.5	39.1	13.2
				.23	<.5	68.8	33.6
56ab		Humpy	Muscle	.34	<.5	42.5	17.5
				–	–	–	–
E4		Humpy	Muscle	.11	<.5	40.0	8.7
				.09	<.5	39.5	8.9
38al		Coon Stripe	Muscle	–	<.5	44.4	14.9
				–	<.5	43.2	13.4
62al		Humpy	Eggs	.08	.57	92.5	5.9
				–	–	–	–
56		Pandalid	Eggs	.22	.78	95.0	6.6
				.17	.63	96.0	5.7
56ab		Humpy	Eyes	.16	4.4	63.7	87.4
				–	–	–	–
371		Coon stripe	Eyes	nab	3.5	79.8	119.2
				–	–	–	–
56		Pandalid	Eyes	.73	.77	71.0	119.9
				.47	.65	70.6	121.5

TABLE II

CONTINUED

Station No.	Trawl No.	Species	Organ	Cd	Ni	Zn	Cu
62a		Pandalid	Eggs	1.13	.83	98.5	28.6
				–	–	–	–
62a		Pandalid	Eyes	.66	3.0	69.1	96.0
				–	–	–	–
371		Coon stripe	Muscle	.10	.24	64.4	22.4
				.11	.40	61.7	24.3
56ab		Humpy	Muscle	.35	.88	47.2	16.0
				–	–	–	–

TABLE III

LOWER COOK INLET
OSS *SURVEYOR* MARCH 1978

Heavy metal contents of sole muscle tissue

Duplicate data (μg/g dry wt)

Station No.	Species	Cd	Ni	Zn	Cu
186	Yellow-fin	<.05	<.10	22.8	<5.0
		<.05	<.10	78.8	<5.0
25	Flat head	<.05	<.10	43.1	<5.0
		<.05	<.10	20.5	<5.0
38	Flat head	<.05	<.10	41.0	<5.0
		<.05	<.10	40.4	<5.0
45a	Flat head	<.05	<.10	37.1	<5.0
		<.05	<.10	26.4	<5.0

TABLE IV

LOWER COOK INLET
OSS *SURVEYOR* MARCH 1978

Heavy metal contents of king crab muscle tissue

Duplicate data (μg/g dry wt)

Station No.	Cd	Ni	Zn	Cu
18 (Kodiak)	-	-	189	96.6
	-	-	188	86.2
T3A	.14	.11	188	66.0
	.18	.09	210	72.9

TABLE V

LOWER COOK INLET

Heavy metal analysis of biota

Precision and accuracy data

NBS Orchard lead standard

Replicate	Zn	Cd	Cu	Ni
1	26.68	0.11	13.3	1.6
2	27.49	0.15	12.2	1.3
3	24.88	0.19	13.0	1.3
4	25.56	0.12	13.3	1.4
5	26.18	0.13	13.5	1.2
6	23.61	0.12	12.2	1.5
7	24.76	0.12	13.1	1.5
8	26.71	0.15	13.1	1.6
9	25.38	0.11	12.1	1.2
10	26.10	0.14	13.6	1.4
11	26.17	0.12	12.2	1.3
12	26.70	0.10	13.3	1.6
Mean	25.8 ± 1.0	0.13 ± 0.02	12.8 ± 0.6	1.41 ± 0.15
NBS Certified Value	25 ± 3	0.11 ± 0.01	12 ± 1	1.3 ± 0.2

reports. The method is very time consuming but appears to yield excellently reproducible numbers. The significance of the fractions this isolated is, as with all such methods, open to interpretation. Table VI lists revised — i.e. rerun — data for the peroxide extraction, and Table VII the corresponding acid extraction numbers for a core from Resurrection Bay expressly taken and treated for this purpose. The acid extractable fraction profiles are shown in Figures 1-5.

The primary objective of this work — determinations of the effects of anthropogenic impingements on the distribution and transport of heavy metals — has required, as explained previously, very detailed knowledge of the near benthic boundary physical transports. One component of this work therefore has been to look in detail at available current meter records for the specific study sites. In Appendix I are given spring-early winter time series unfiltered records for near bottom density, salinity and temperature recently obtained. Evidence from these data is presently being incorporated in a detailed analysis of chemical fluxes at the bottom of fjord basins.

IV. DISCUSSION

This program has consisted of a variety of projects ranging from single-cruise baseline reconnaissance studies to detailed work in specific study sites. For the former, tabulations of heavy metal and, sometimes, ancillary geochemical data have been given in the various reports as acquired. In most cases these data have been collected in isolation and no further scientific evaluation is possible.

TABLE VI

NEGOA SPECIFIC STUDY SITE: RESURRECTION BAY
R/V *ACONA* 267 OCTOBER 1978

H_2O_2 extract of sediments (revised procedure)
Mean of triplicate determinations (µg/g)

Core depth (cm)	Cd	Cu	Ni	Zn	Mn	Fe
0-10	2.02±.05	1.66 ±.06	5.39 ±.91	<1.3	18.48 ±2.7	71.6 ±9.2
10-20	2.19±.58	1.26 ±.08	5.51 ±.59	<1.3	10.99 ± .33	48.8 ±26.7
20-30	1.22±.27	1.02 ±.18	3.96 ±.36	<1.3	6.05 ± .34	69.8 ±20.8
30-40	1.19±.10	1.64 ±.78	4.00 ±.87	<1.3	7.06 ±1.39	51.7 ± 6.7
40-50	0.86±.18	0.92 ±.13	3.78 ±1.47	<1.3	4.91 ± .30	10.7 ± 4.3
50-60	0.73±.04	0.92 ±.11	4.49 ± .51	<1.3	3.23 ± .56	6.15 ± 0.07
60-85	0.78±.14	0.96 ±.03	4.96 ± .40	<1.3	3.85 ± .52	27.4 ±15.8

TABLE VII

NEGOA SPECIFIC STUDY SITE: RESURRECTION BAY
R/V *ACONA* 267 OCTOBER 1978

HCl extract of sediments

Mean of triplicate determinations (μg/g dry weight)

Core depth (cm)	Cd	Cu	Ni	Zn	Mn	Fe (x 10^{-3})
0-10	1.54 ±.04	52.8 ±1.4	22.4 ±1.3	60.1 ±3.6	330 ± 5	13.4 ±.32
10-20	1.42 ±.17	74.9 ± .53	26.5 ± .8	65.0 ±6.8	279 ±10	13.8 ±.71
20-30	1.50 ±.13	74.8 ±1.4	28.1 ± .25	69.6 ±1.1	273 ± 3	13.4 ±.32
30-40	1.44 ±.06	74.7 ±2.5	27.2 ± .6	68.7 ±1.6	268 ±10	13.8 ±.50
40-50	1.65 ±.05	72.4 ±2.0	28.3 ±1.1	69.6 ±2.4	266 ± 6	14.4 ±.26
50-60	1.67 ±.01	72.6 ±1.3	28.7 ± .35	69.4 ±1.9	275 ±13	14.4 ±.71
60-85	1.61 ±.08	71.3 ±4.6	28.9 ±1.2	71.6 ±3.7	268 ±18	13.5 ±1.0

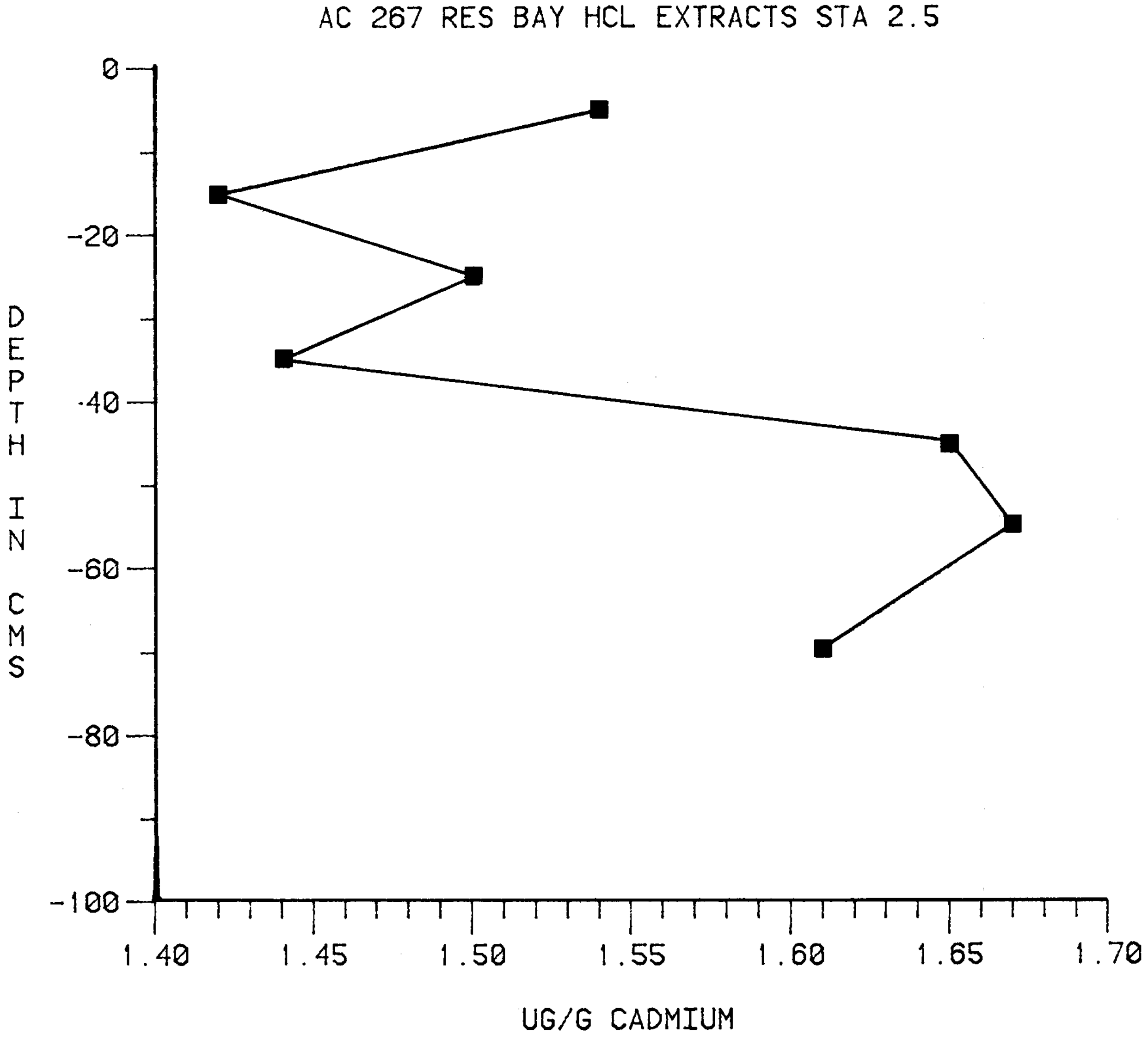

AC 267 RES BAY HCL EXTRACTS STA 2.5
0
-20
-40
-60
-80
-100
DEPTH IN CMS
1.40
1.45
1.50
1.55
1.60
1.65
1.70
UG/G CADMIUM

Figure 1.

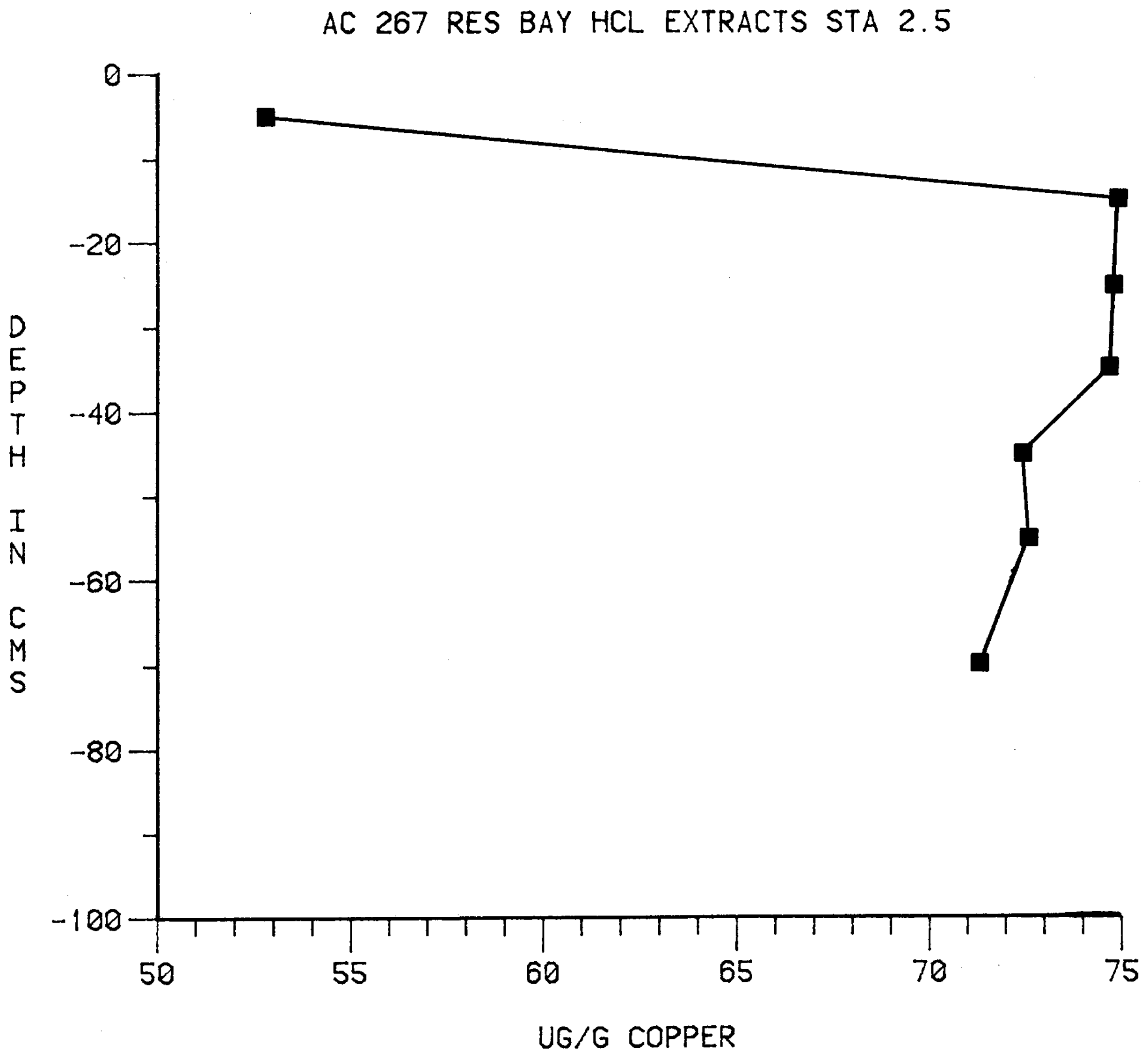

AC 267 RES BAY HCL EXTRACTS STA 2.5
0
-20
-40
-60
-80
-100
DEPTH IN CMS
50
55
60
65
70
75
UG/G COPPER

Figure 2.

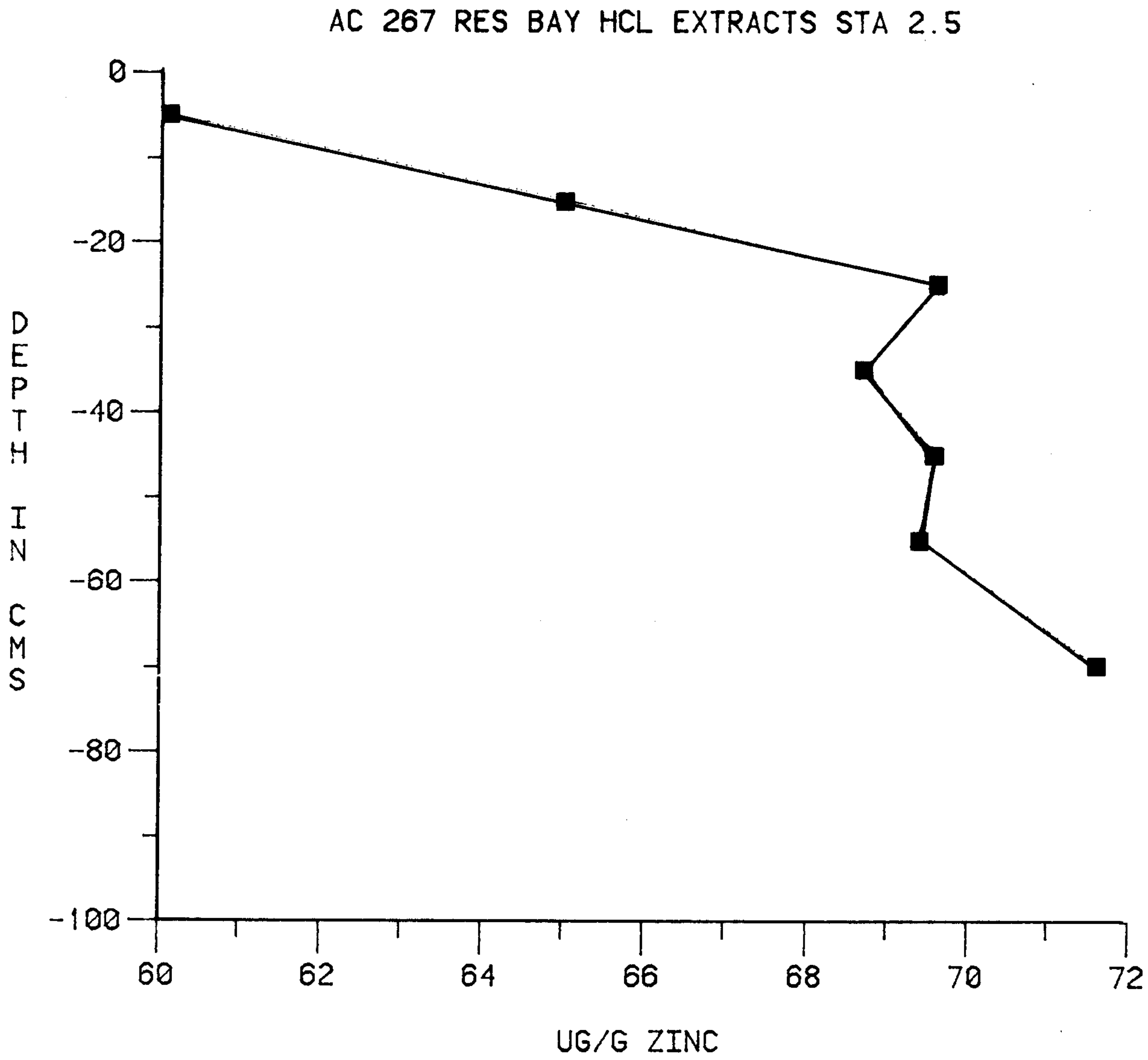

AC 267 RES BAY HCL EXTRACTS STA 2.5
0
-20
-40
-60
-80
-100
DEPTH IN CMS
60
62
64
66
68
70
72
UG/G ZINC

Figure 3.

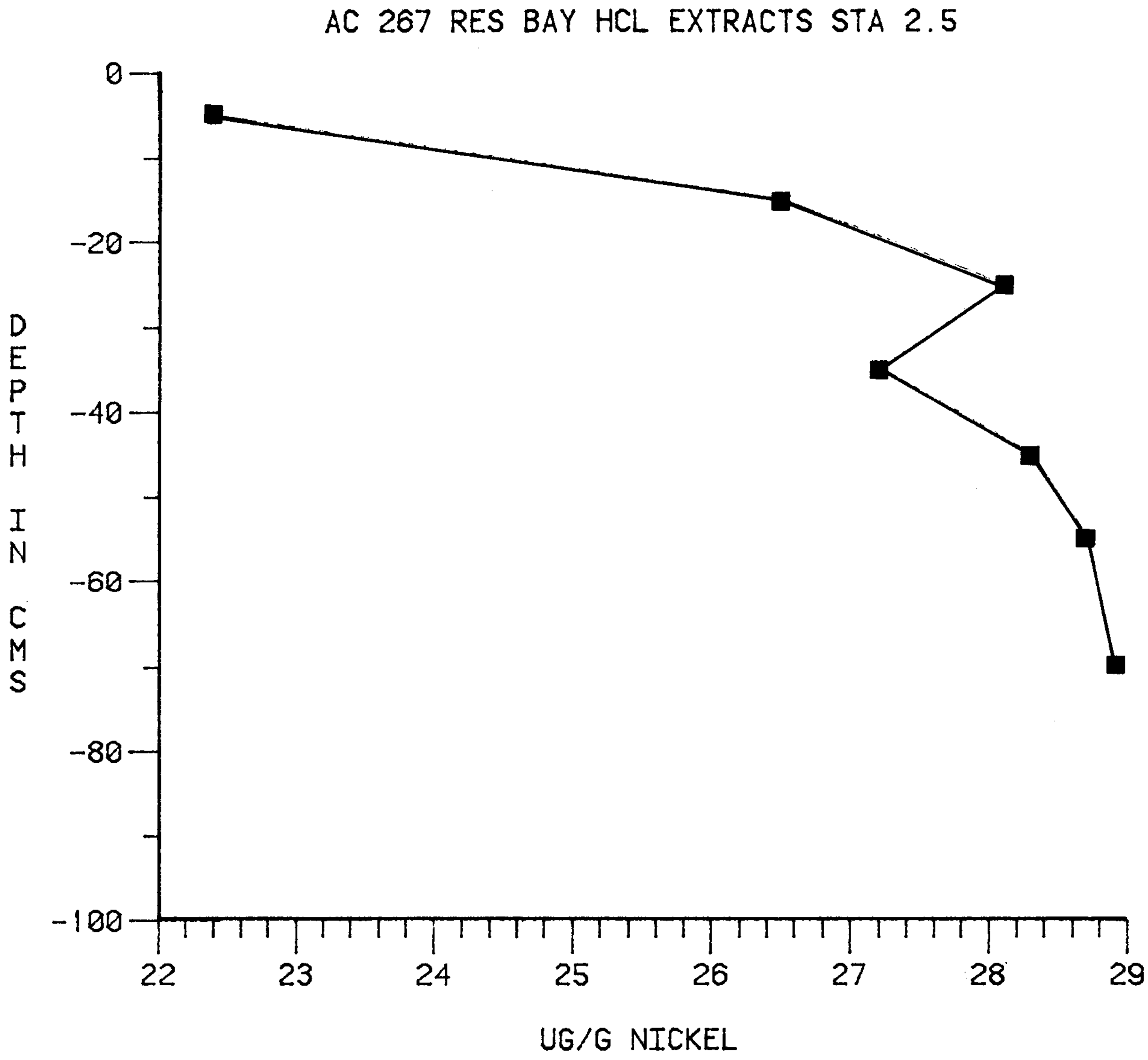

AC 267 RES BAY HCL EXTRACTS STA 2.5
0
-20
-40
-60
-80
-100
DEPTH IN CMS
22
23
24
25
26
27
28
29
UG/G NICKEL

Figure 4.

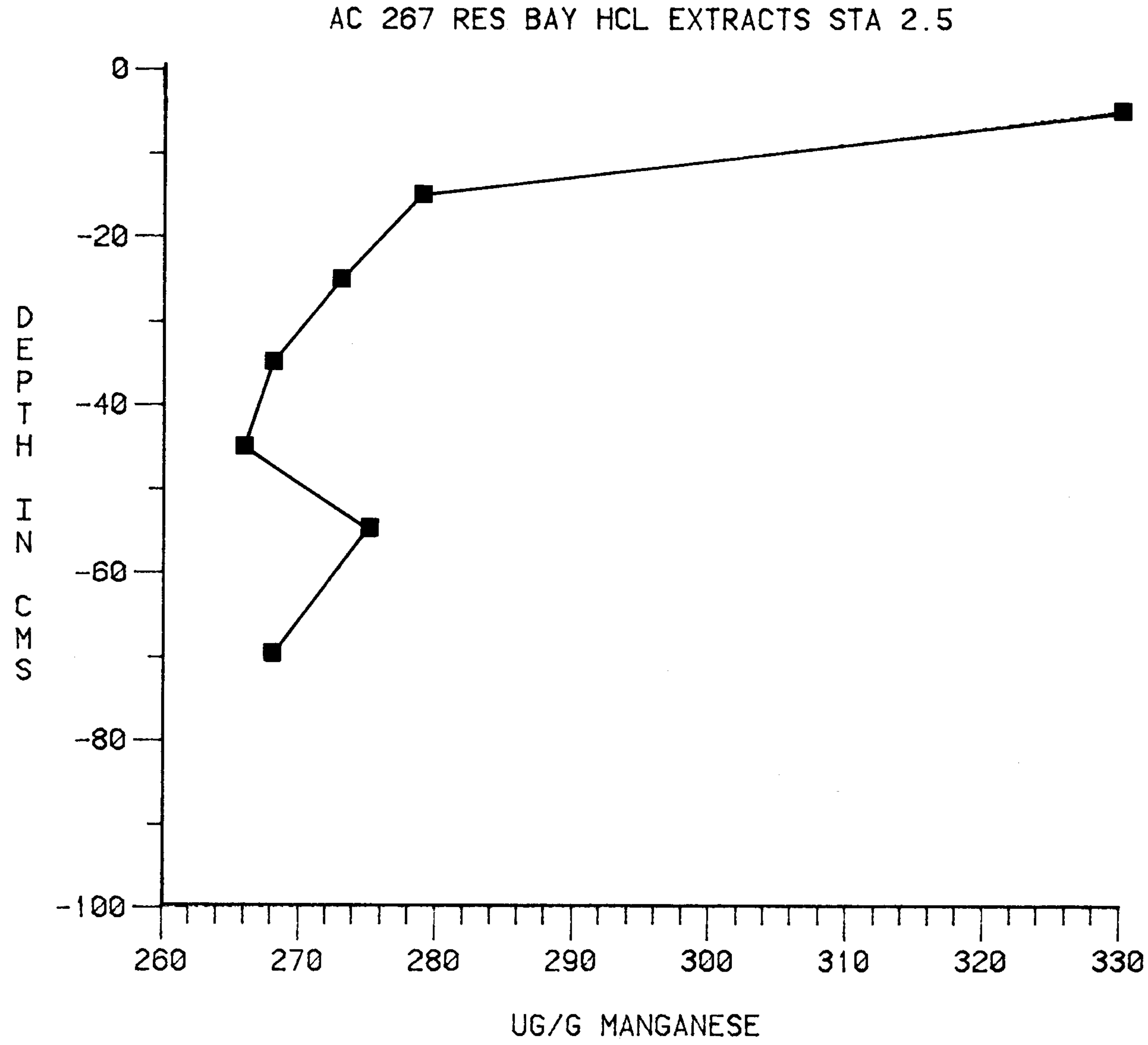

AC 267 RES BAY HCL EXTRACTS STA 2.5
0
-20
-40
-60
-80
-100
DEPTH IN CMS
260
270
280
290
300
310
320
330
UG/G MANGANESE

Figure 5.

Work performed in designated specific study sites has been designed to look at processes relevant to anthropogenic impingement on heavy metal cycling in coastal areas, and in these cases long term studies are required. The OCS program has given valuable aid to this type of problem but work will, of necessity, have to continue under other sponsorship. The major contribution of the Alaskan OCS program (with regard to heavy metal cycling and pollution) has been the major fillip given to work in the arctic and sub-arctic environment. The major weakness, as repeatedly pointed out, has been the emphasis on open shelf areas where physical and chemical conditions are such that measurable localized industrial impingement is exceedingly unlikely, rather than on coastal zones and estuaries. The latter regions are particularly prone and sensitive to chemical pollution.

The following summarizes the status of work on this project (initially by geographical region):

A. Beaufort Sea

Early offshore sampling was attempted from the U.S.C.G.C. *Glacier*. It proved to be virtually impossible to obtain either water or sediment samples suitable for trace metal analysis from this vessel under the prevailing cruise conditions. Some isolated data have been given in previous reports.

Nearshore (lagoonal) work was subsequently performed under subcontract to Dr. H. V. Weiss, whose final report is given here as Appendix II. This work was operated in conjunction with geological studies of the lagoons and is continuing separately from this project.

B. Bering Sea

Biota samples have been collected from a variety of cruises and localities by personnel not associated with this project. In most cases little or no ancillary oceanographic data pertaining to these samples was obtained. A large number of baseline heavy metal contents of a variety of bottom and benthic species has been given in previous reports, but for reasons given it is not possible to make any definitive oceanographic pronouncements from these numbers.

The major exception here is the work accomplished on heavy metal contents of seal species in the Bering Sea. Although it was not found to be possible to meet the original objectives of this specific subproject, collection and storage of samples was performed under our supervision and the results represent a reasonably coherent whole. Initial results were presented orally at the 1978 Alaska Science Conference. The following manuscript has been submitted for inclusion in the Bering Sea Symposium Volume:

> D. C. Burrell. Some heavy metal contents of Bering Sea seals.

Water and sediment samples were collected by us on one cruise only in the S. Bering Sea in 1975. Because of the limitations imposed on sampling it was not possible to collect water samples using currently acceptable techniques. Some samples were tested and discarded; some analyses were reported in early reports. These should be regarded as order of magnitude ranges only. In the summer of 1977 we expended considerable efforts on setting up a superior sampling procedure to obtain soluble heavy metal numbers from the (central) Bering Sea, taking advantage of the joint U.S.-Soviet expedition on the U.S.S.R. hydromet vessel *Volna*.

Good copper and lead numbers were obtained and these data are given as environmental background information data in the above referenced paper on seals.

Sediment samples suitable for heavy metal analysis were collected from two cruises in the S. Bering Sea and in Norton Sound in the summers of 1975 and 1976 respectively. Because of the nature of the sampling device required to obtain uncontaminated samples, it was not possible to obtain detailed coverage of the S. Bering Sea. These data, together with additional biological and sedimentological information and suspended sediment heavy metal distributions, will be presented in:

> D. C. Burrell, K. Tommos, A. S. Naidu and C. M. Hoskins. Some geochemical characteristics of Bering Sea sediment. Bering Sea Symposium Volume.

Work on the clay mineralogy of the surficial Bering Sea sediments was performed under sub-contract by Dr. A. S. Naidu, who has presented his results in several papers (e.g. see abstracts in 1978 Annual Report).

Sedimentological analysis has been carried out in detail and will be given in Ms. K. Tommos M.S. thesis with a summary in the above referenced paper.

C. Chukchi Sea

Size analysis and heavy metal contents of sediment extracts have been given previously for core samples collected on the single *Discoverer* cruise in the summer of 1976. Sampling density was limited, as in other areas, by the recovery ability of the noncontaminating corer. Water samples collected were later discarded as being unacceptable for trace metal analysis.

D. N.W. Gulf of Alaska

Heavy metal baseline data for samples collected on one and a partial cruise in 1975 given previously.

E. Lower Cook Inlet

The biota analyses given in this present report completes the program in this area.

F. NEGOA: Shelf

Summary of baseline data was given in 1978 Annual Report.

G. NEGOA: Yakutat Bay Specific Study Site

An initial report on work in this fjord was given in the 1978 Annual Report. Since then further work has been done on cycling of key heavy metals within the outer basin. Fragments of this work have been given in subsequent reports and a coherent summary of the chemistry obtained to date will appear in the M.S. thesis of T. Owens (see below).

Additional hydrographic data was collected on a non-OCS sponsored cruise in April of this year and the initial data on this was given in the June 1979 Quarterly Report. Additional cruise time is scheduled for later this year after which time the original hydrographic interpretation will be updated.

H. NEGOA: Resurrection Bay Specific Study Site

A very large body of data collected on a series of cruises starting in November 1977 has been given as obtained in the various reports. Some of this work is now beginning to appear in the open literature. Thus:

T. L. Owens, D. C. Burrell and H. V. Weiss. Reaction and flux of manganese within the oxic sediment and basin water of an Alaskan fjord. Proceedings of Fjord Oceanographic Workshop, in press.

An extended version of this paper will be submitted for journal publication next month. Full details of this work and of benthic cycling of other heavy metals will appear in T. L. Owens M.S. thesis which will be prepared early in 1980.

The central thesis regarding the potential effect of oil on the natural heavy metal regime is that such discharges change the biogeochemical environment at the benthic interface. The primary research objective at this stage has then been to understand considerably more about natural chemical cycles at this interface. In addition to the sediment-water column cycling referenced above, and the sediment-baseline studies cited below, we have also pursued work on the flux of nutrients across the interface and the related transport and consumption of oxygen near the sediments. Thus, the paper:

D. T. Heggie and D. C. Burrell. Sediment-seawater exchanges of nutrients and transition metals in an Alaskan fjord

is currently in press, and:

D. C. Burrell and D. T. Heggie. Seasonal and long-term circulation and chemical cycling in an Alaskan fjord

is to be presented at the Biennial Estuarine Conference. A pre-print of this paper is suffixed to this report as Appendix III.

Work in this important area is continuing and further reports and publications will appear in the future.

I. Aquaria Experiments on Food Chain Transfers

The final report on this sub-project was given in the 1979 Annual Report and a paper was given at the 1978 Alaska Science Conference. Since November 1978 primary sponsorship of this sub-project has been the Alaska Sea Grant Program. Work is continuing and further reports and publications will appear.

J. Survey of Se and Cr in the Shelf Environment

The Final Report of this sub-contract to Dr. T. Gosink is given in this report as Appendix IV.

K. Geochemistry and Flux of Particulate Sediment

The sub-project is an integral part of the work on the near-bottom flux of heavy metals. We are concerned here with the role of particulates in scavenging and transporting chemical species out of the water column of fjord basins, and one initial objective has been an attempt to derive and aluminosilicate-biogenic distribution model for these estuarine basins.

Six particulate sediment profiles, from Yakutat Bay (*Acona* cruises 240 and 246) and from Resurrection Bay (*Acona* cruises 254, 260 and 262) have been run through a reiterative linear bivariate least squares curve fitting program which forced the intercept to less than 10% (i.e., the approximate precision of the data) of the mean particulate load for each profile. The fitted curve was thus of the form:

$$PL = A + (B \times PAL) + (C \times POC)$$

and values generated for the constants A, B, and C are given below. This computed fractionation procedure assumes that the percent carbon content of the biogenic material and the percent Al content of the

MODEL COMPUTATION OF PARTICULATE SEDIMENT COMPOSITION

Cruise No.	Station Name	Constants (see text) A	B	C	R
240	Yak-7	20.85	12.61	2.41	0.999
246	Yak-7	-10.95	14.08	2.02	0.994
246	Yak-9	15.82	12.83	2.24	0.999
254	RES-2.5	0.21	10.91	2.08	0.999
260	RES-2.5	- 2.00	10.80	2.15	0.995
262	RES-2.5	38.14	10.79	1.97	0.984

aluminosilicates remains constant with depth: it also assumes that the bulk of the inorganic material contains aluminum. Considering the precision and accuracy of the separate analyses and the resulting uncertainties caused by forcing the linear fit, these assumptions are probably acceptable for an initial model. Given these assumptions, the constant A should be zero: in the non-ideal case it represents a summation of the analytical error and violation of the assumptions.

The constants B and C are reciprocals of the average fraction of aluminum content of the inorganic and of the fraction of carbon content of the biogenic material respectively. All XRD studies of the clay fraction of the coastal sediments in the vicinity of Resurrection Bay show a preponderance of chlorite and illite. However, the low range obtained for B ($\sim$ 5) would be consistent with low aluminum minerals. We are currently carrying out direct microscopic examination of the particulate material in Resurrection Bay. Meanwhile it seems possible that the discrete sampling misses a substantial fraction of sedimenting material. Direct sediment trap experiments will help clarify this problem, but at the present time, sedimentation rates determined via the interstitial sulfate reduction method have given values an order of magnitude greater than could be supported by the indicated particulate flux based on discrete load measurements and assumed mean size. The range determined for the constant C fits, to a remarkable degree, the values expected for a predominantly diatomaceous bloom.

There has been some recent criticism concerning possible error in determining suspended sediment loads where sub-samples are drawn from the sampling bottle after various unsystematic delays. This potential problem has been of concern to us also. Where some delay is unavoidable the Niskin bottles are inverted several times (without agitation) prior to draining the sample. We attempt, however, to always drain immediately on collection. Replicate 1-liter subsamples have been filtered on separate cruises with the following results:

SUSPENDED LOAD SAMPLING TESTS

Cruise	Station	Depth (m)	Delay (min)	Mean load (mg)	Standard deviation
272	RES 2.5	20	∿ 2	0.35	0.08
276	RES 2.5	30	∿ 2	0.32	0.05
276	RES 4	20	∿15	0.42	0.15

It is clear that where even only a relatively small delay between sampling and analysis is allowed significant error results. Various other sampling bottles have been considered but it is intended to continue using Go-Flo Niskin but to use various sizes so that the entire volume can be filtered.

As described in last year's proposal, we have constructed two sediment traps of the type designed by PMEL (Lawrence *et al.*, unpublished data). Two separate deployments have been made of one unit. The first trap was set in October (1978) and retrieved in December: at that time it was discovered that the timing mechanism had flooded and prevented closure. Although this voided quantitative data some material was retained for chemical analysis. This same trap was redeployed with a new timer unit in December for retrieval in April (1979) but the entire unit was lost because of severe corrosion of the attachment bolts. A second unit was set in Resurrection Bay on a current meter mooring in March of this year. When this instrument was recovered in May it was found that the trap had prematurely closed. It appears that similar problems have been encountered by PMEL in Alaskan waters: a success rate of 15 out of 22 deployed. Because this project does not have the resources for more than a few instruments, and in view of the long time intervals involved before problems are discovered, it appears that a simpler design is required.

In the course of the last year a laser particle counting instrument manufactured by Spectrex Corporation has been evaluated for sizing marine suspensions. This potentially elegant technique has been unsatisfactory for the following reasons:

i. Inability to calibrate with external standards

Standard solutions in optical quality quartz bottles are provided for calibration of the particle counter. Three of these standard solutions (0, 205, 635 particles/counts per ml) are used progressively to set the threshold settings on the particle counter; however, for the two separate high count bottles, agreement between the stated figure (637, 635) and the instrument has never been achieved (the manufacturers admit their inability to do the same).

The manufacturers further imply that the original counting of the standard solutions was simply performed on a similar instrument; i.e., there is no independent external check on the counting accuracy. This process of "internal" calibration becomes more doubtful when one calibrates the particle sizing attachment, a multichannel analyzer with digital display and paper printout.

Standard settings (threshold, gain) are adjusted until the particle count readings on both instruments agree to within 5% for particles greater than 3 μ. The standard settings, however, have originally been determined to provide size intervals of 5 μ in 16 different channels so that any change in the gain setting alters this size interval. The manufacturer cannot provide information as to size intervals obtained for different settings of the gain knob thus introducing considerable uncertainty into the size distribution data (e.g., is the interval 4 μ or 6 μ or 7 μ).

ii. No significant difference detected between different seawater samples, apparently primarily due to lack of sensitivity and high count rates

Although the lack of "absolute" calibration was suspected initially, it was hoped that relative size distributions could be used to distinguish different particle populations in different seawater samples. Analysis of the size distribution data has shown that the variation between samples is similar to the variation between duplicates; this is true for samples collected in two different localities over three seasons. Furthermore, when seawater samples were "spiked" with concentrations of standard size microspheres greatly in excess of expected natural populations, there was little or no difference in the resulting profiles and plots. It would thus appear that this light scattering technique is not sensitive enough to detect the differences expected in seawater particulate populations.

For the particle counter the manufacturer recommends that should counts exceed the display (999) the sample should be diluted in order to avoid multiple counting of the same particle. The average seawater sample usually exceeds the display 3 or 4 times, introducing another counting error.

Masking of particles by those closest to the laser source, while a problem in low density problem becomes a major constraint in normal seawater samples.

The above factors combined with the improbability of there being a representative particle population in the beam for the 20 seconds of the count renders the counting procedure somewhat doubtful. Dilution of the sample is not desirable since it drastically alters the particle populations (not a linear response), voids the obvious benefits of unmanipulated samples and dramatically increases the amount of time spent counting the samples.

III. Inordinate processing time to obtain usable data

To obtain usable data (even if of doubtful quality) an inordinately large amount of time is consumed in the initial counting, filtering of samples and counting of the filtrate to determine background, subtraction of both profiles, computer manipulation to plot different frequency curves and the final interpretation.

The data obtained, assuming validity, is not readily comparable to that of other researchers all of whom use Coulter Counter techniques which measure volume (independent of shape) rather than area (dependent on shape) measure by the Spectrex machine.

iv. Delicacy of the instrument for use at sea

The instrument has proved to be delicate for shipboard use, malfunction 3 out of 5 times.

The Spectrex laser particle counter is, therefore, unsuitable for our purpose and its use will be discontinued in the future.

APPENDIX I

ANALYSIS OF LATE SPRING — EARLY WINTER CURRENT METER RECORDS SET AT DEPTH IN THE RESURRECTION BAY BASIN

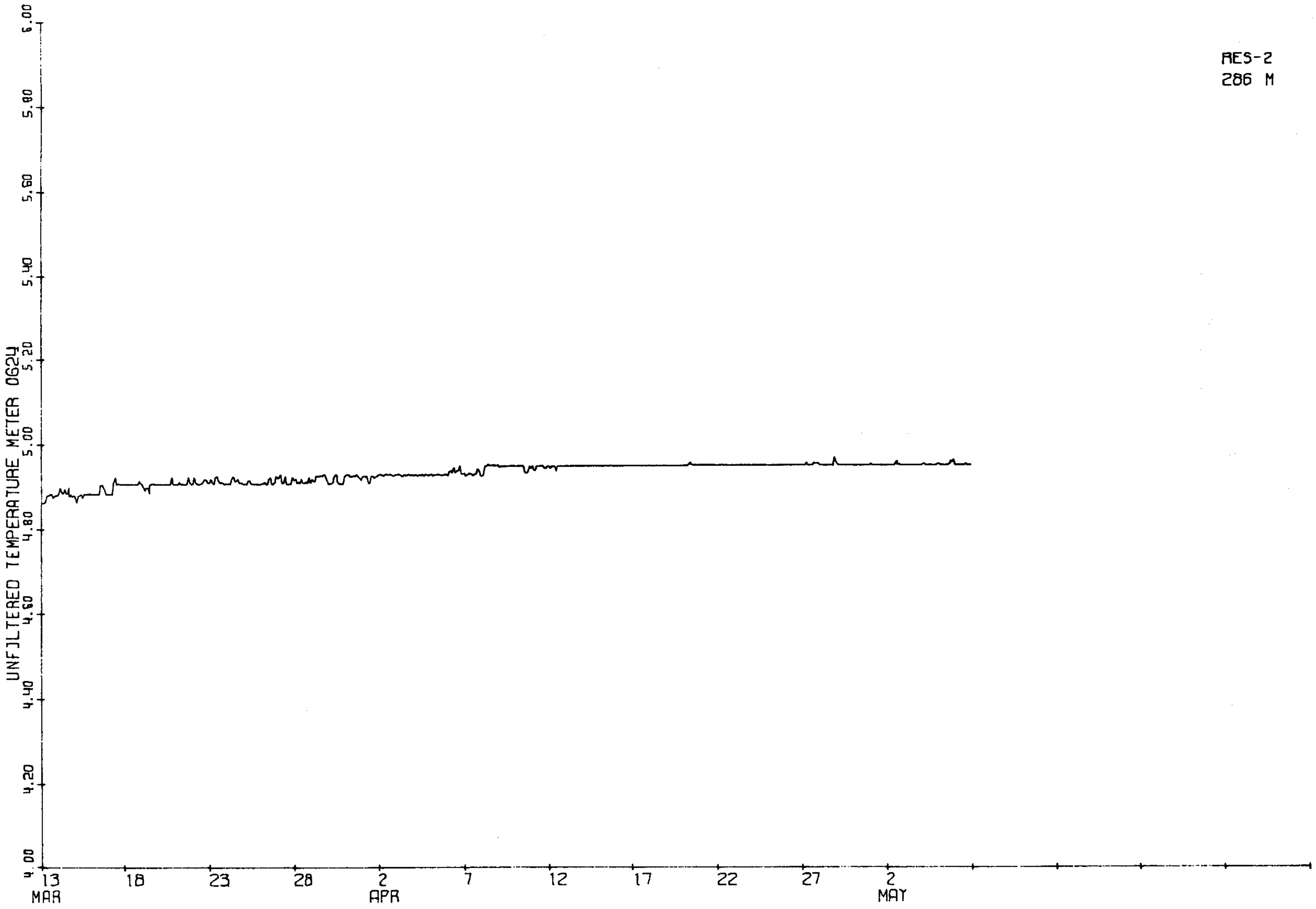

RES-2
286 M
UNFILTERED TEMPERATURE METER 0624
6.00
5.80
5.60
5.40
5.20
5.00
4.80
4.60
4.40
4.20
4.00
13
MAR
18
23
28
2
APR
7
12
17
22
27
2
MAY

Figure 1.

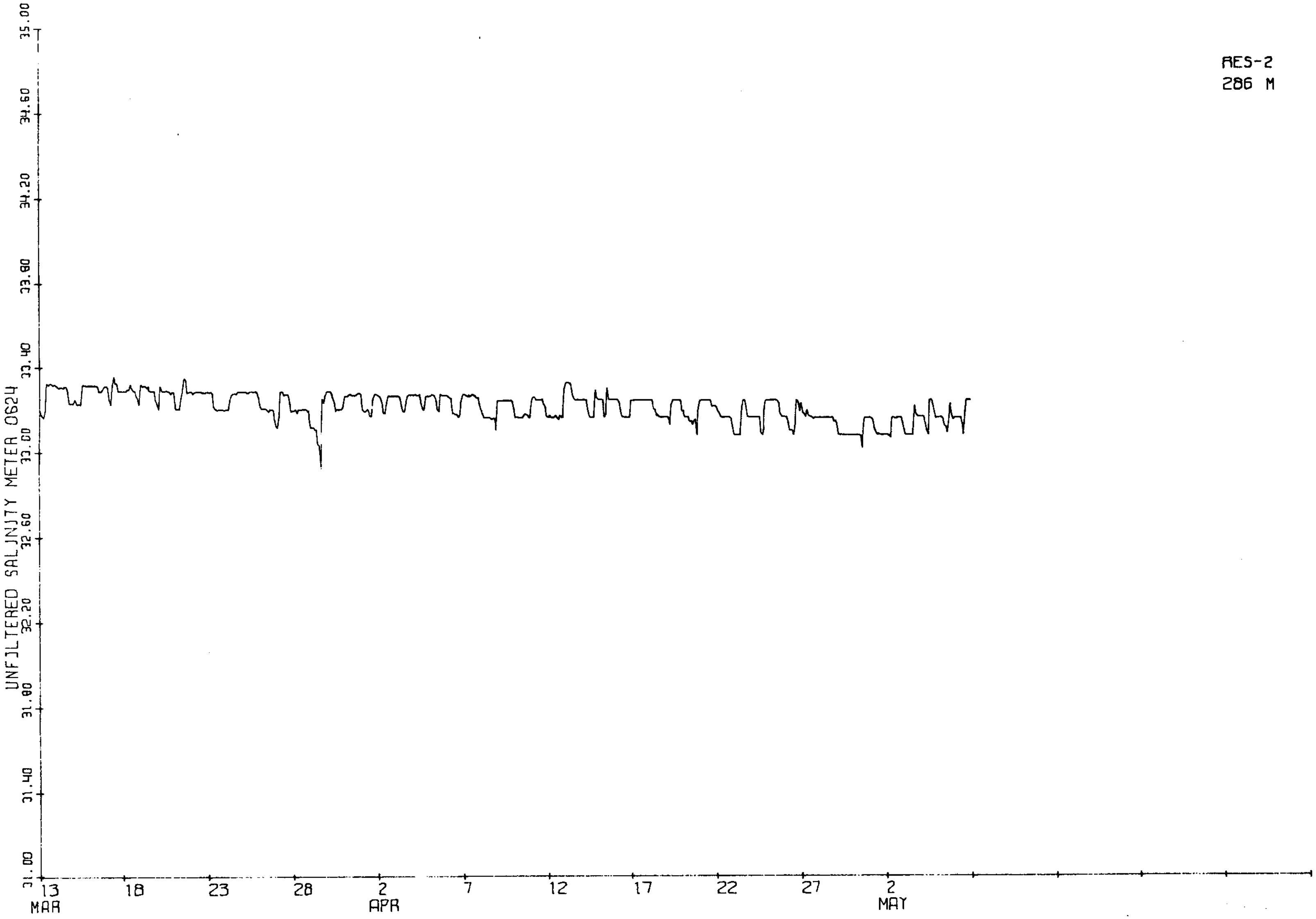

RES-2
286 M
UNFILTERED SALINITY METER 0624
35.00
34.60
34.20
33.80
33.40
33.00
32.60
32.20
31.80
31.40
31.00
13
MAR
18
23
28
2
APR
7
12
17
22
27
2
MAY

Figure 2.

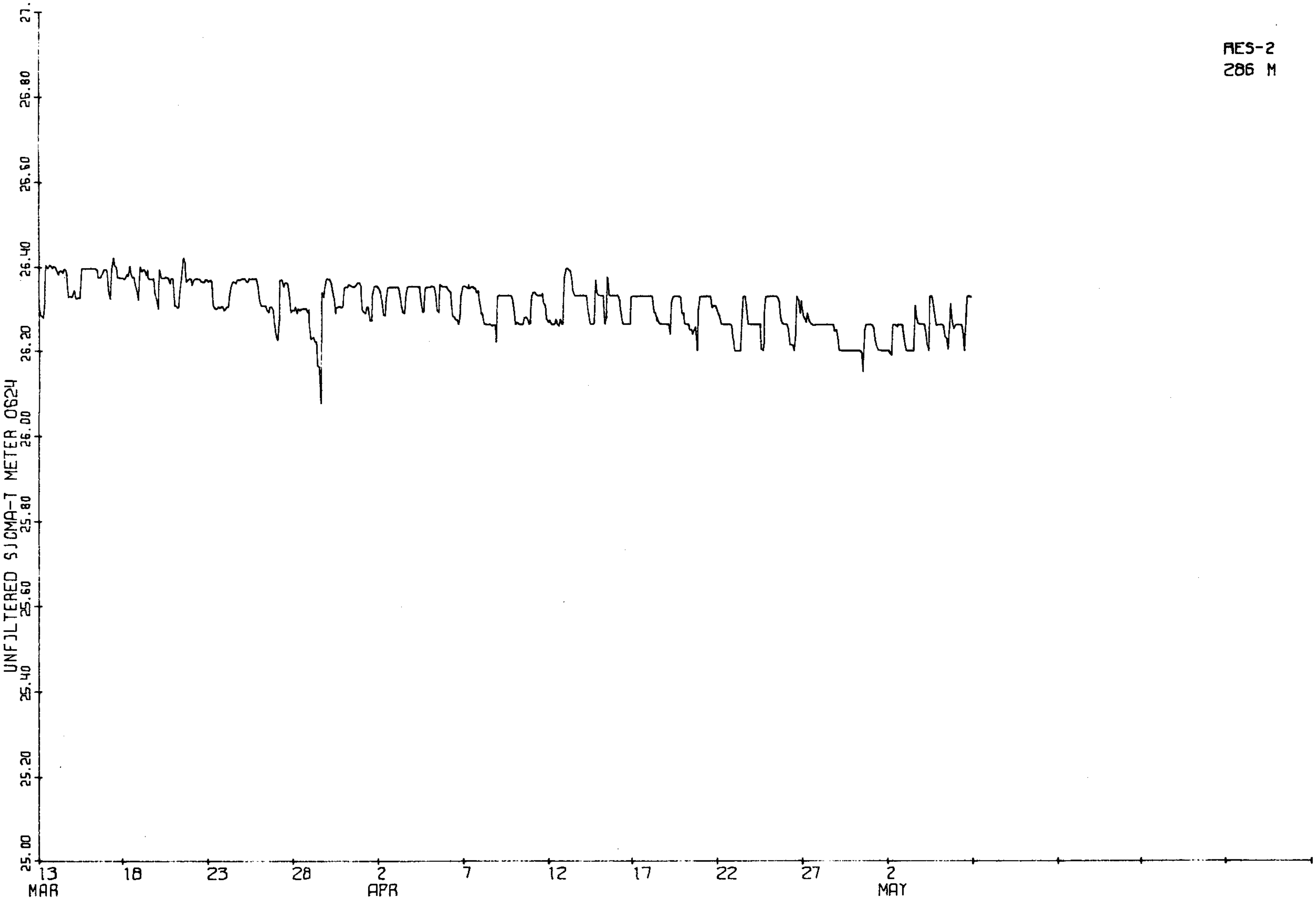
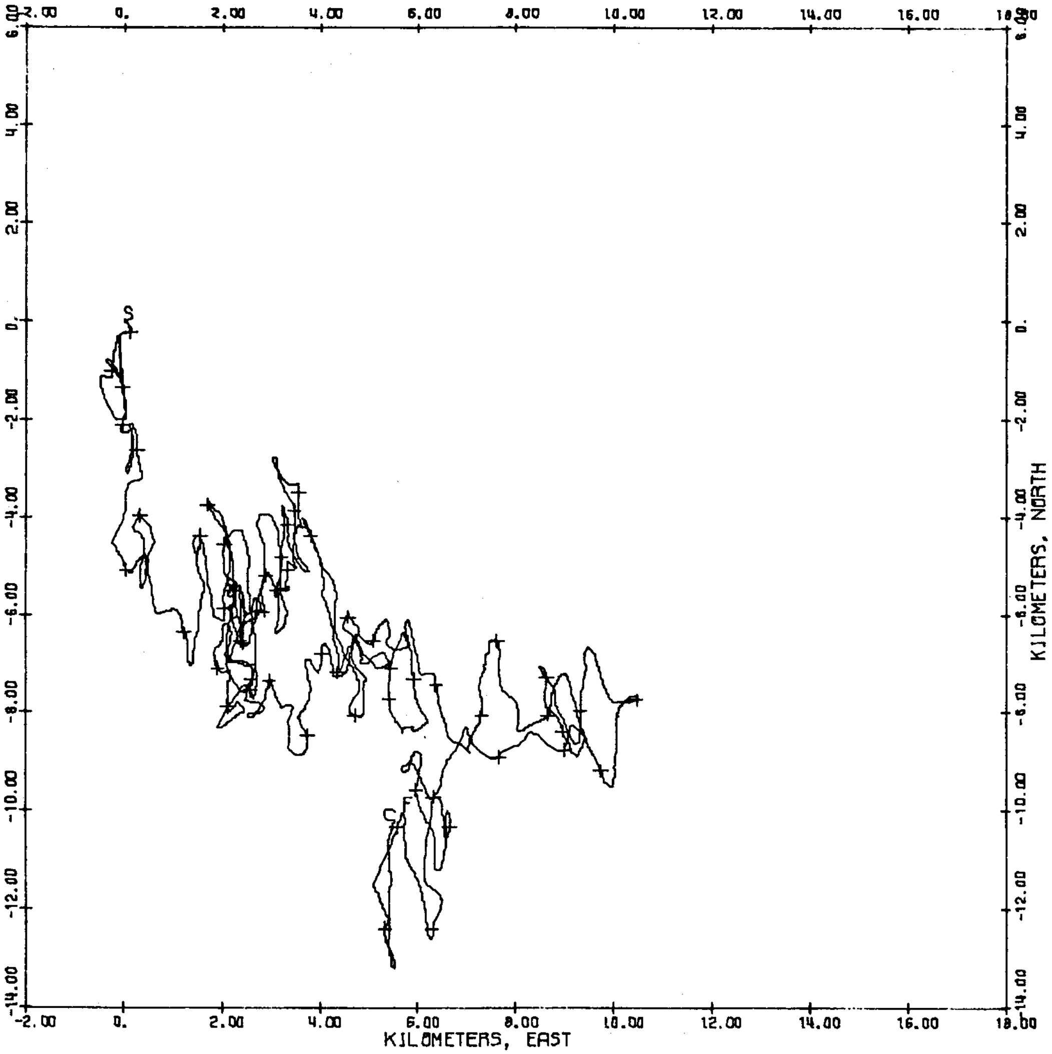

RES-2
286 M
UNFILTERED SIGMA-T METER 0624
27.00
26.80
26.60
26.40
26.20
26.00
25.80
25.60
25.40
25.20
25.00
13
MAR
18
23
28
2
APR
7
12
17
22
27
2
MAY

Figure 3.



RES-2
286 M
FIRST RECORD AT 2130 UT 13 MAR
1 DAYS BETWEEN TIC MARKS

Figure 4.

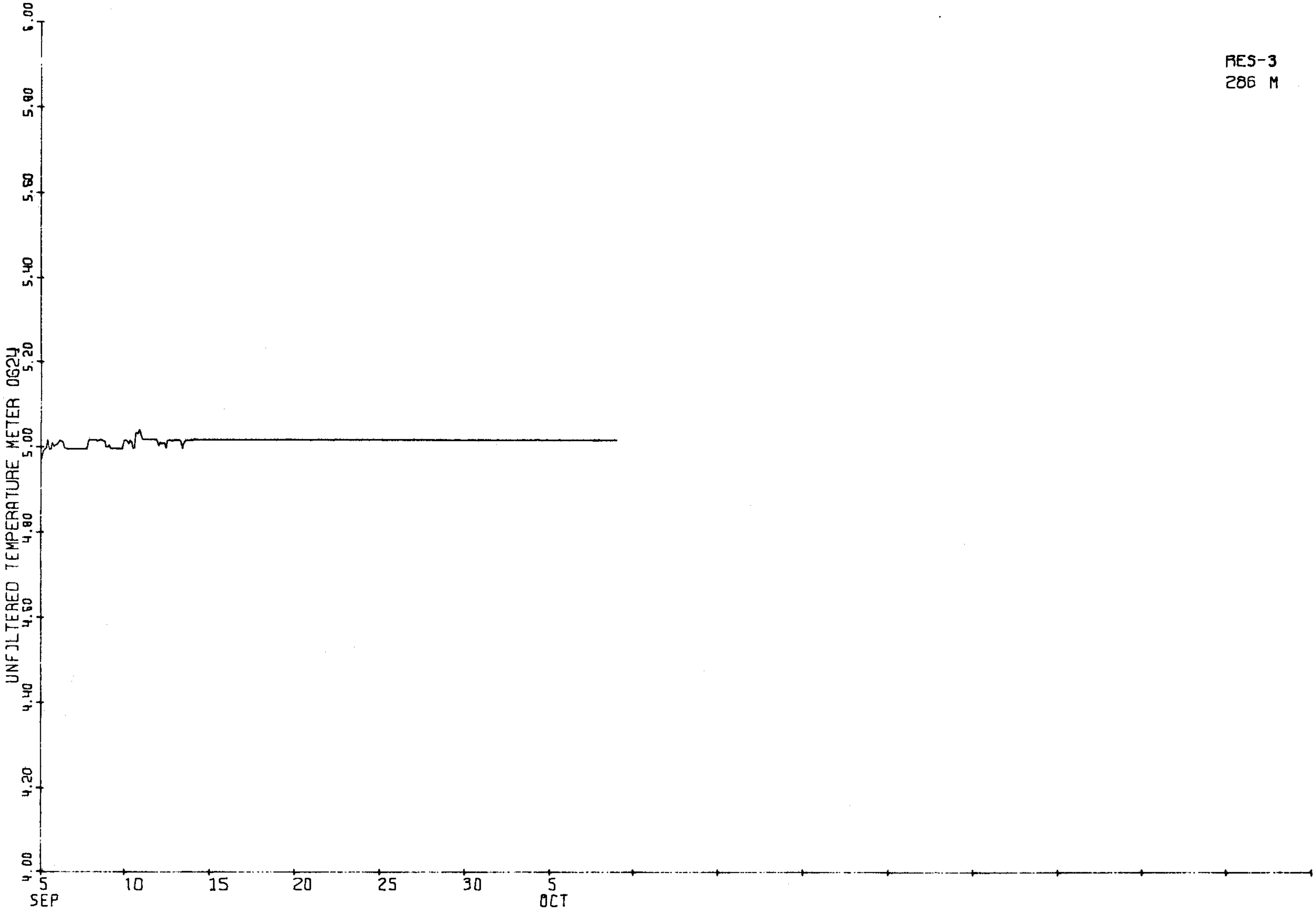

RES-3
286 M
UNFILTERED TEMPERATURE METER 0624
6.00
5.80
5.60
5.40
5.20
5.00
4.80
4.60
4.40
4.20
4.00
5
SEP
10
15
20
25
30
5
OCT

Figure 5.

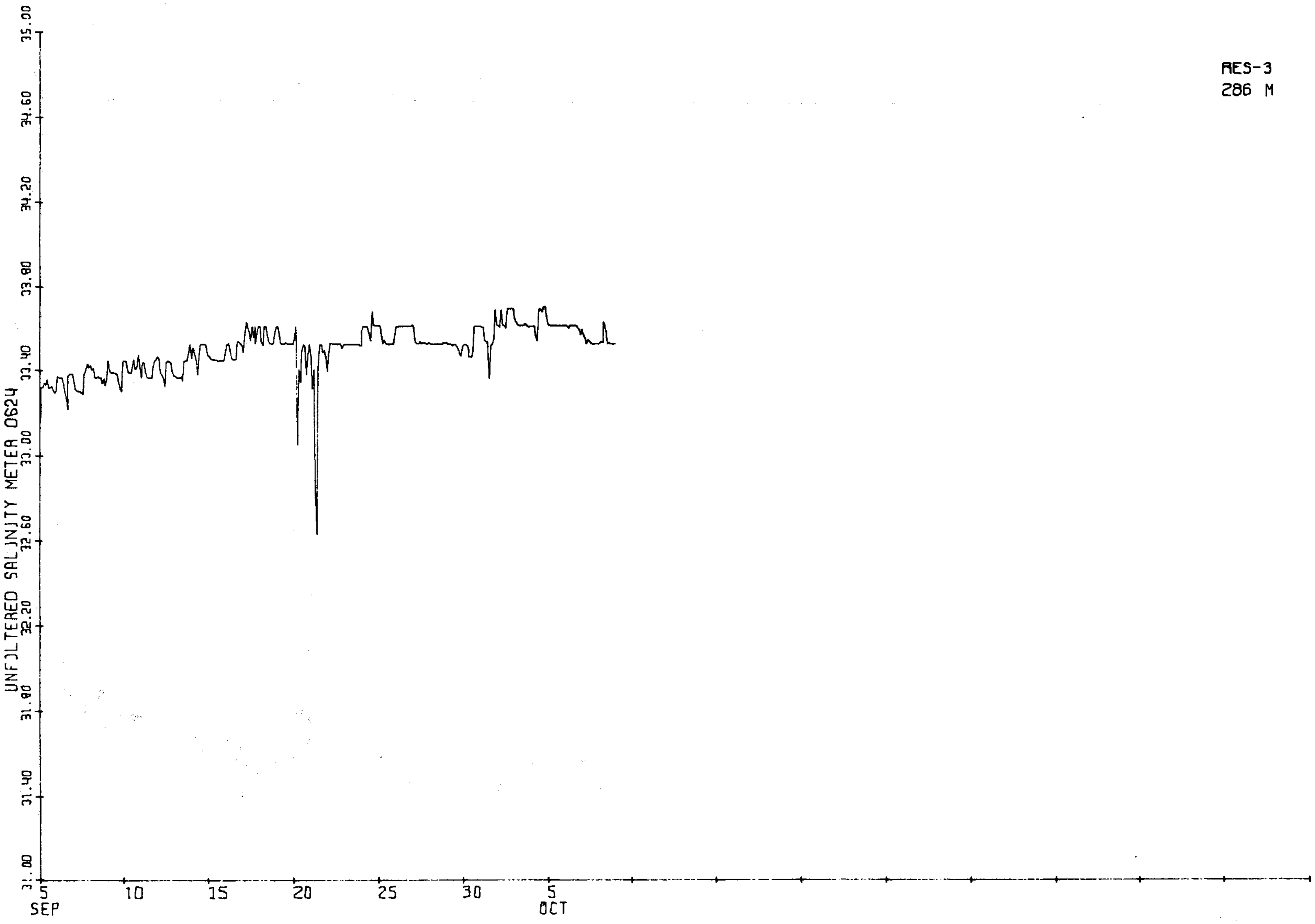

RES-3
286 M
UNFILTERED SALINITY METER 0624
35.00
34.60
34.20
33.80
33.40
33.00
32.60
32.20
31.80
31.40
31.00
5
SEP
10
15
20
25
30
5
OCT

Figure 6.

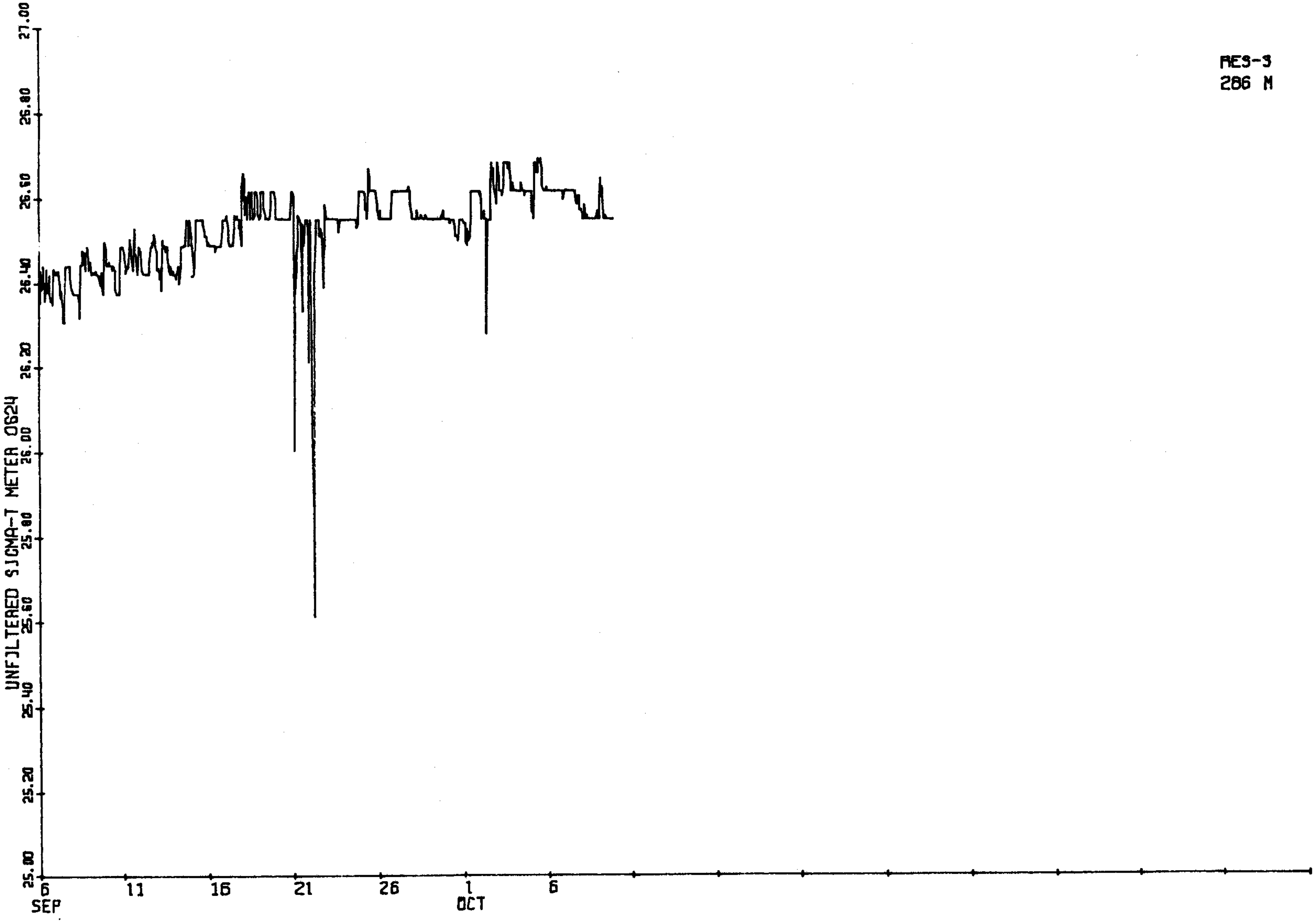

UNFILTERED SIGMA-T METER 0624
27.00
26.80
26.60
26.40
26.20
26.00
25.80
25.60
25.40
25.20
25.00
6
SEP
11
16
21
26
1
OCT
6
RES-3
286 M

Figure 7.

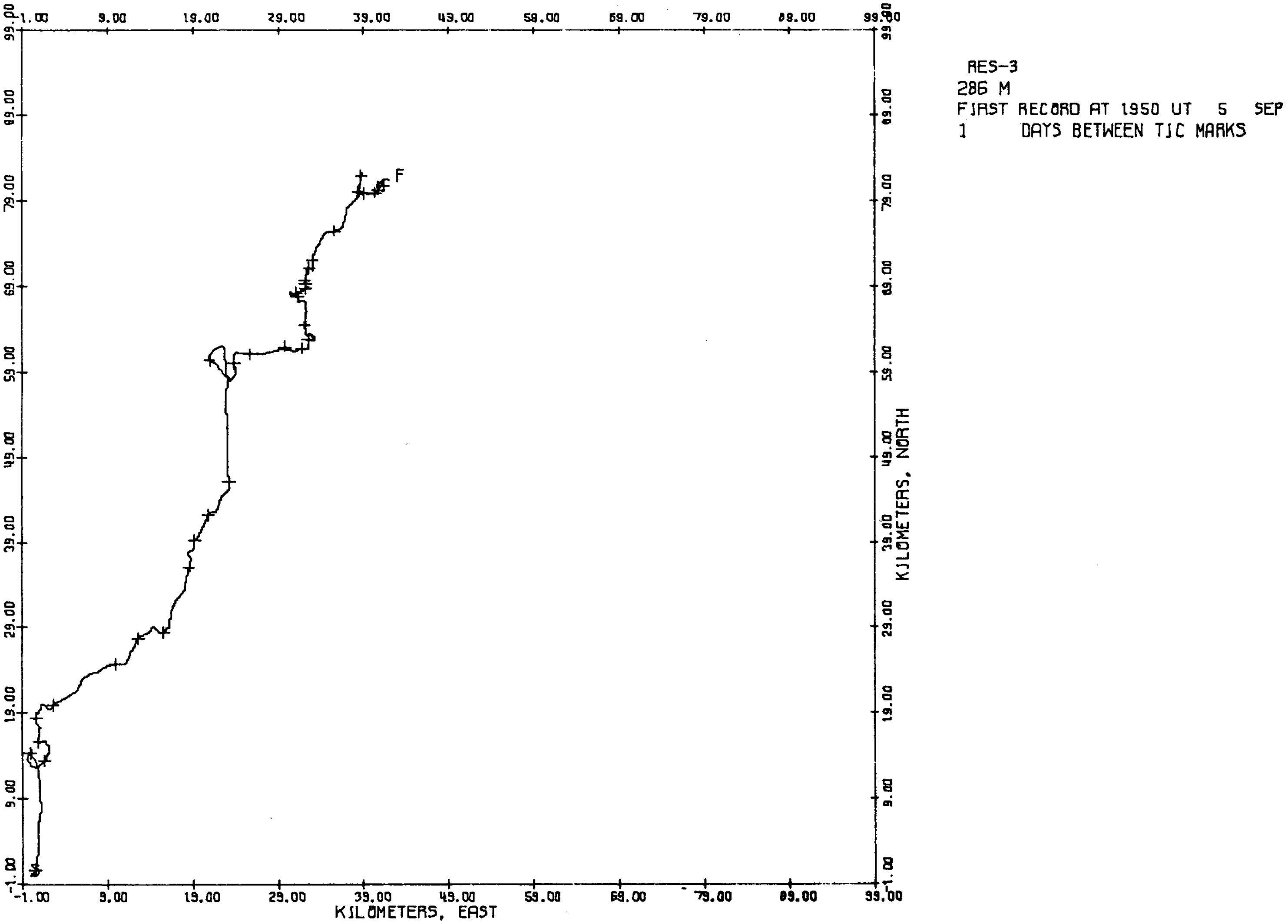

RES-3
286 M
FIRST RECORD AT 1950 UT 5 SEP
1 DAYS BETWEEN TIC MARKS
F
-1.00
9.00
19.00
29.00
39.00
49.00
59.00
69.00
79.00
89.00
99.00
KILOMETERS, EAST
KILOMETERS, NORTH

Figure 8.

APPENDIX II

THE IRON, MANGANESE, COPPER AND VANADIUM CONTENT OF WATERS IN THE ENVIRONS OF SIMPSON LAGOON

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San Diego

Simpson Lagoon abutting the northern coast of Alaska is a region potentially subject to impact by activities associated with oil exploration and production. A study was undertaken to quantify waters in this environment relative to a number of trace metals. The E_h and pH changes associated with decomposition of oil in sediment may result in the mobilization of compounds of manganese and iron, together with elements such as copper and vanadium which coprecipitate with them; thus, these elements were selected for study.

Since the lagoon waters are a composite of the Beaufort Sea and the Colville and Kuparuk Rivers, representative samples from these sources were analyzed. To understand qualitatively the relative contribution of the atmospheric and lithospheric components to this environment, the elemental composition of the snow in the surrounding area was compared with the results obtained for the river samples.

SAMPLE COLLECTIONS AND PREPARATION FOR ANALYSIS

Snows were collected 19 January 1978 from the surface of the Colville and Kuparuk Rivers. The collection sites were situated approximately 85 mi from the Arctic coast and in the delta region of the rivers. Samples were maintained in the frozen state until processed in the clean room at IMS, University of Alaska. Snows were transferred from the plastic bags in which they were originally collected to 4-l polyethylene containers. Melting was accelerated by immersion in a hot-water bath. When the bottle was essentially filled with the sample, it was acidified with 40-ml of high-purity nitric acid (J. T. Baker, Ultrex). (The two samples recovered from inland locations were grossly contaminated with particulate and were therefore discarded.)

River waters were procured on 2-3 August 1978 at five locations along each river (Figure 1). The site farthest upstream on the Colville River was at the point of entry of the Killik River. Water which entered from the Killik River was murky and confined to the eastern bank, while the mainstream water was clear. A sample of each was collected and designated C-1A and C-1B, respectively.

Surface water was obtained from 13 locations in Simpson Lagoon between 3-15 August 1978 (Figure 2).

On 18 August 1978, by hydrocast from aboard USCG *Northwind*, samples of Beaufort Sea water at depths of 3, 20, and 35 m were secured at station 70°56.5'N and 149°17'W (Figure 1).

The river, lagoon, and seawater samples were filtered through 0.4-mu Nuclepore filter membranes and stored in polyethylene bottles after acidification with high-purity nitric acid to a final concentration of 1% (v/v). Filtrations always occurred less than 12 h after the sample collection.

ANALYTICAL PROCEDURES

Atomic Absorption Spectrometry

A Perkin-Elmer Model 306 instrument equipped with a hot-graphite furnace and an automatic delivery accessory was used for atomic absorption measurements. For snow and river water, the material was introduced directly into the furnace to determine Cu, Mn, and Fe. The Fe content of lagoon and Beaufort seawater was measured after first diluting the samples with an equivalent volume of 2% nitric acid. All determinations were performed by the method of additions. The error in replicate analyses was approximately 5-10%.

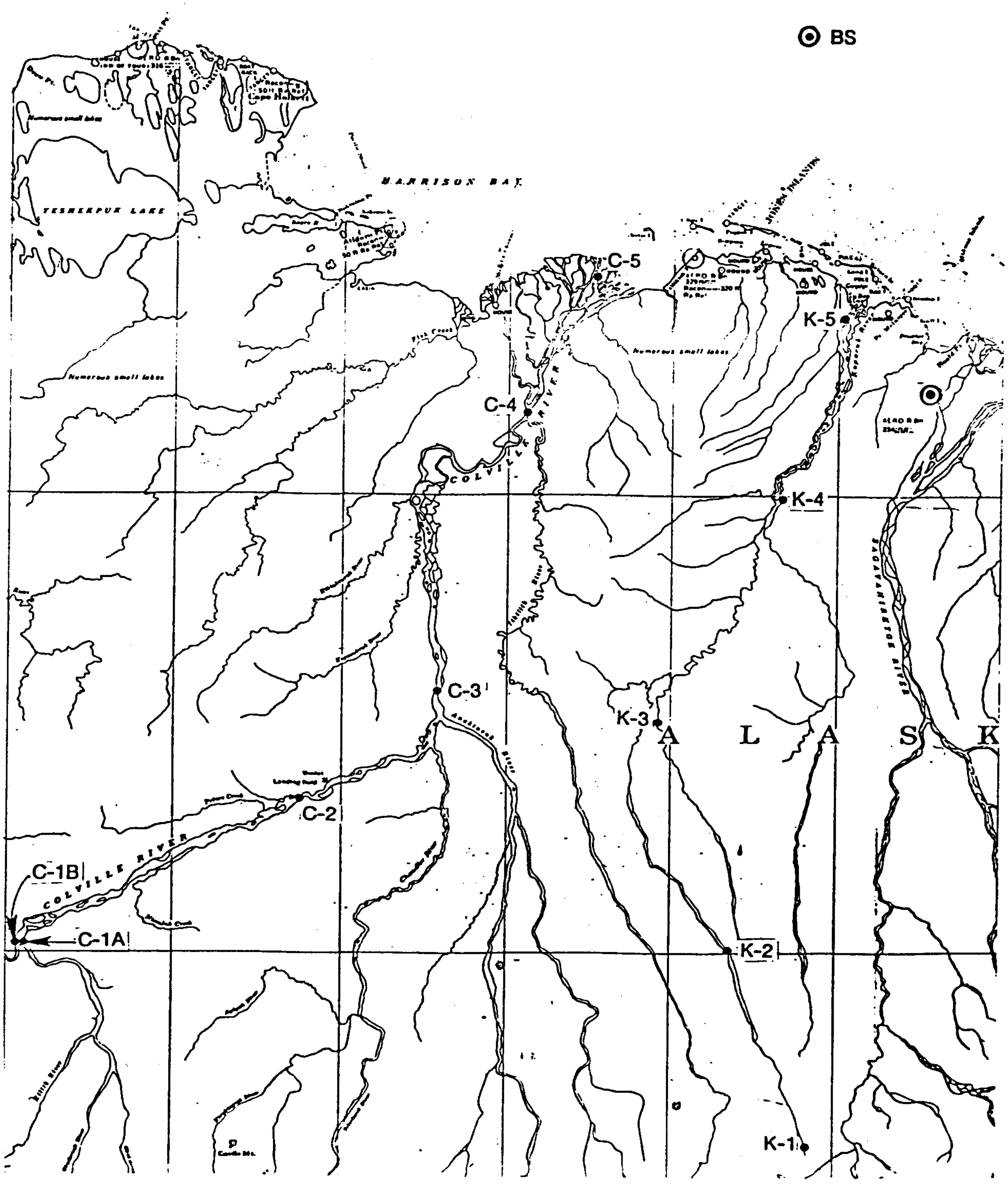
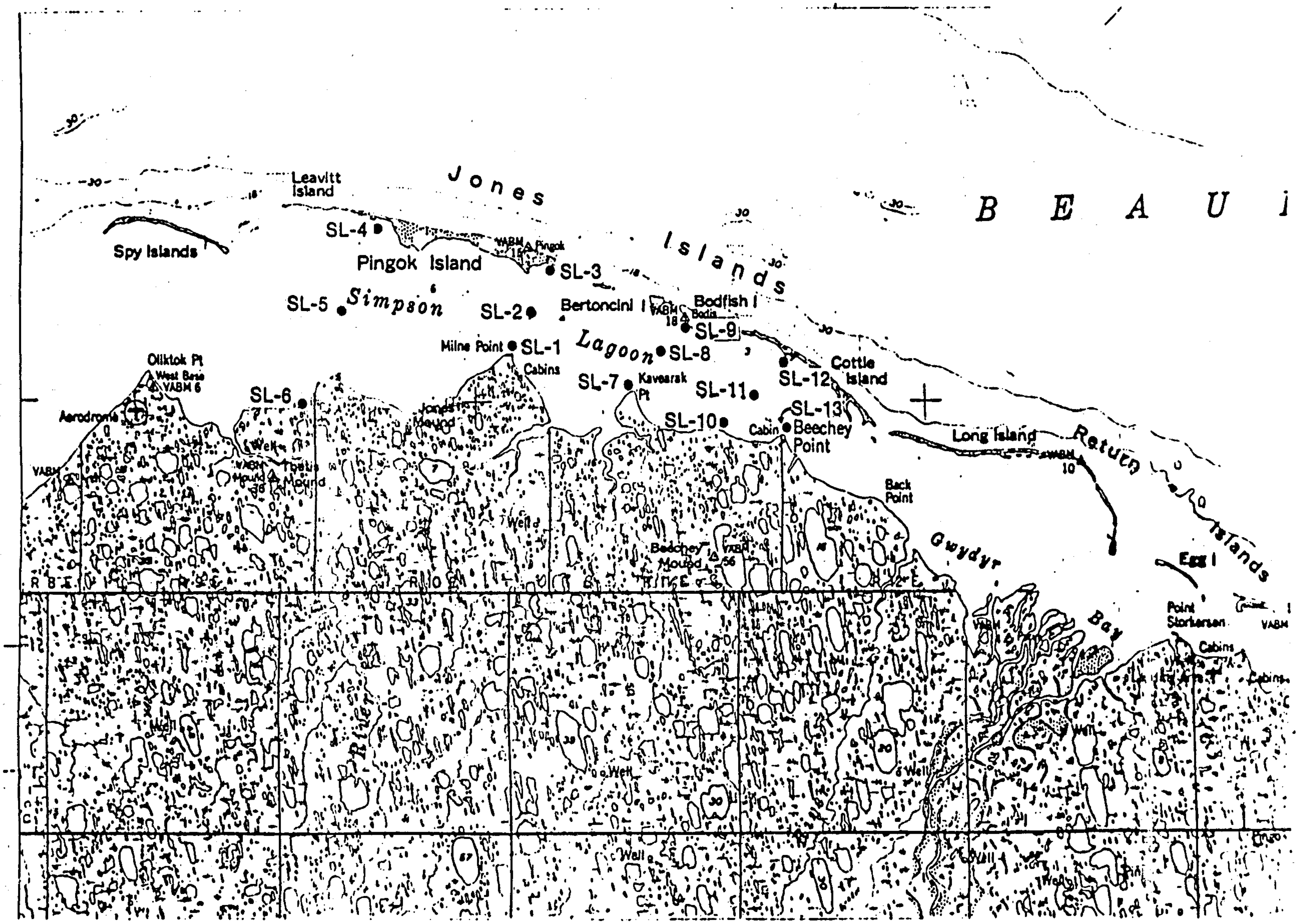

BS
HARRISON BAY
TESHEKPUK LAKE
Numerous small lakes
Numerous small lakes
Numerous small lakes
C-5
C-4
COLVILLE RIVER
C-3
C-2
COLVILLE RIVER
C-1B
C-1A
K-5
K-4
K-3
A L A S K
K-2
K-1

Figure 1.


B E A U
Jones Islands
Leavitt Island
Spy Islands
Pingok Island
VABM Pingok 15
SL-1
SL-2
SL-3
SL-4
SL-5
SL-6
SL-7
SL-8
SL-9
SL-10
SL-11
SL-12
SL-13
Simpson Lagoon
Bertoncini I
Bodfish I
Milne Point
Cabins
Kavearak Pt
Cottle Island
Cabin
Beechey Point
Oliktok Pt
West Base
VABM 6
Aerodrome
Jones Mound
Well
Thetis Mound
Beechey Mound
Long Island
Return Islands
Back Point
Gwydyr Bay
Egg I
Point Storkersen
Cabins
30
18
R 10 E

Neutron Activation Analysis

Neutron activation analysis was used to determine the concentration of vanadium in all aqueous media and the copper and manganese in the saline waters.

The methods employed were compared with those methods developed independently at another laboratory (1,2). The results of this intercalibration study indicated that the procedures described herein provide reliable measurements of the elements at natural levels in seawater.

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

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

Isolation of Copper and Manganese from Seawater. Aliquots of sample (250 ml) were transferred to containers and received 0.1 ml of a carrier-free ^{54}Mn. An oxine solution (2.5 ml) was stirred into the sample, and an ammonia solution was added until the pH of the solution attained a value of 7-8. Crystallization was encouraged by agitation with a rod. After the solution stood for 1 to 2 hs, the crystals were collected on a 0.4-mu Nuclepore filter membrane. The filter and adhering crystals were transferred to an irradiation vial and the gamma-ray activity of the solution was measured in a well-type NaI(Tl) detector and compared with a ^{54}Mn tracer standard.

Blanks. The copper and manganese content was determined, at least in duplicate, for oxine (250 mg), ethyl alcohol (2.5 ml) and ammonium hydroxide (2.5 ml). These reagents were used in these amounts in the preirradiation processing. These elements were also quantified in 2.5-ml aliquots of high-purity nitric acid (J. T. Baker, Ultrex).

A procedural blank was determined in quadruplicate on 250-ml aliquots of seawater filtrates freed of copper and manganese by previous cocrystallization with oxine. The filtrates were acidified with 1 ml of Ultrex nitric acid spiked with ^{54}Mn, and the elements were cocrystallized as described above.

Data show that following the initial acidification, 0.003 ± 0.001 and 0.022 ± 0.004 ug of Mn and Cu were added to the sample by way of oxine, ethyl alcohol, and ammonium hydroxide. If nitric acid of the quality analyzed had been used in the acidification process, an additional 0.003 ± 0.001 and 0.005 ± 0.001 of the respective elements would have been introduced.

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

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

Radiochemical Purification and Measurement. After irradiation the sample or blank was quantitatively transferred with 50 ml of 3 N HCl to a vessel that contained 1 and 2 ml of copper and manganese carriers, respectively. All blanks received a standard-quantity of ^{54}Mn and, except for the oxine blank, they also received 250 mg of oxine. H_2S gas was bubbled for 30 s through the solution, and the resultant CuS precipitate was collected by filtration. The CuS was dissolved in about 10 drops of freshly prepared aqua regia, evaporated to dryness, and then diluted to 30 ml with water. The solution was filtered through a sintered glass disc to separate insoluble matter. Then 10 ml of concentrated hydrochloric acid were added to the filtrate, and CuS was precipitated and separated. The filtrate from the initial copper separation was made ammoniacal, and the precipitated oxinate was collected and then dissolved in 50 ml of concentrated nitric acid. The solution was heated over a flame for several minutes to degrade the oxine, while hot solid potassium bromate was added to precipitate manganese dioxide. After cooling in an ice-bath, the precipitate was separated by filtration.

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

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

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

Carrier Yield Determinations. The filter membrane containing the precipitated copper and manganese was folded and inserted into 1.3-ml, snap-top, polyethylene vial to which 0.6 ml of distilled water was added. Standards (0.6 ml of carrier solution) placed in similar vials also received a blank filter membrane to reproduce volume and geometric conditions. Samples and standards were irradiated for precisely 60 s in a pneumatic tube facility with the reactor at full power. The 511-keV photopeak of ^{64}Cu and 847-keV photopeak of ^{56}Mn were measured in the manner described for the sample. After correction for decay from the end of the irradiation, comparison of the reirradiated samples with standards allowed calculation of the copper carrier yield.

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

Sensitivity. At the end of a 2-h irradiation period, 2.5×10^3 and 6.0×10^4 photopeak counts min^{-1} were accumulated per microgram of Cu and Mn. Thus, submicrogram amounts of these elements were quantifiable with an acceptable counting statistical error. Since the usual concentrations of Mn and Cu in seawater center around tenths of a part per billion (ppb) for Mn and ppb for Cu, even the modest irradiation schedule adopted provides for adequate sensitivity. In replicate analyses, the error for copper at the 0.3-μg level was 6%, while the error for manganese at the 0.16-μg level was 3% (1).

Vanadium. Vanadium and vanadium tracer were coprecipitated from seawater with ferric hydroxide upon the addition of ammonia. The hydroxide was isolated, bombarded with neutrons, and activated. ^{52}V was measured by gamma-ray, pulse-height analysis.

Chemicals and Tracer. Iron carrier solution was prepared by dissolving 99.999% pure iron powder in aqua regia and diluting with distilled water to a final concentration of 10 mg/ml. Vanadium-48 solution in the carrier free form was prepared as vanadium (IV) in 0.1 M hydrochloric acid. Vanadium standard (2 μg/ml) was made from a commercial 100-ppm standard prepared from ammonium metavandate. Other reagents used were of analytical reagent grade.

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

Isolation of Vanadium from Seawater. Iron carrier (1 mg/100 g of sample) was added to a weighed amount (100 g) of acidified seawater. A known ^{48}V activity, usually about 10^4 cpm, was also added. The pH was adjusted to about 7 with 8 M ammonia. The precipitate was coagulated by warming, collected on a sintered-glass disc of medium porosity, washed with water to remove residual salts, and dissolved in a small volume of 8 M nitric acid (4.13 ml). The recovery of ^{48}V in this solution was determined by comparison of its gamma-ray activity with that of a tracer standard (to provide information on the amount of sample solution transferred to the vial).

Blanks and Standards. Three blanks were prepared: 100 μl of the iron carrier solution in 8 M nitric acid, and 8 M ammonia. The standards were also made in 8 M nitric acid and contained 0.2 μg of vanadium. Blanks, standards, and samples all had the same volume, obtained by weighing the solution, the specific gravity of which was known.

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

Sensitivity. With the irradiation schedule used, about 1.5×10^4 counts/μg of vanadium are acquired in the photopeak area. Thus sub-microgram quantities of vanadium are quantifiable with a fitting counting statistical error. The standard deviation for samples at concentrations of a fraction of a ppb is approximately 5% (2).

RESULTS AND DISCUSSION

The concentration for vanadium, manganese, iron, and copper in the waters analyzed appears in Table 1.

Vanadium

The vanadium content of two snow samples was 0.08 ppb and agrees with the values reported for snows deposited in the environs of Barrow in 1972 (3).

The average concentration in the Kuparuk River was 0.07 ± 0.03 ppb, and for the Colville River it was 0.12 ± 0.03 ppb. Thus, the vanadium content of Kuparuk River water is accounted for by atmospheric input as reflected by snow composition, while in the Colville River an incremental quantity is accumulated through dissolution of terrestrial material. The variations in the concentration are attributable to error associated with measurement of solutions at concentrations in the range of parts per trillion.

In the lagoon the concentration was relatively constant (0.29 ± 0.03) and intermediate between the rivers and the Beaufort Sea. Except ppb

Table 1.

Concentration (μg/kg) of V, Mn, Cu, and Fe in Waters.

		Elements				
Source	Location*	V	Mn	Cu	Fe	
Snow	1	0.08	3.0	0.3	20.8	±0.7
	2	0.08	2.2	0.9	24.8	±0.5
Colville River	1A	0.07	5.2	1.0	42.7	
	1B	0.12	2.7	2.3	106.0	
	2	0.11	4.0	1.5	42.5	
	3	0.13	5.7	1.7	64.8	
	4	0.16	7.8	2.5	48.5	
	5	0.14	9.6	1.4	46.9	
Kuparuk River	1	0.09	1.3	1.2	4.0	
	2	0.04	1.2	0.8	20.0	
	3	0.05	6.3	0.9	8.3	
	4	0.10	2.3	0.8	(757)	
	5	0.09	2.3	1.2	8.7	
Simpson Lagoon	1	0.26	16.9	1.2	6.9	
	2	0.29	21.9	1.5	8.7	±0.3
	3	0.30	20.9	1.1	9.5	
	4	0.30	19.0	1.4	5.9	
	5	0.27	18.2	1.5	11.8	
	6	0.26	17.5	1.3	14.2	
	7	0.34	18.7	1.3	6.9	
	8	0.31	20.6	1.5	5.3	
	9	0.31	16.9	1.0	13.0	
	10	0.30	18.1	1.4	9.3	
	11	0.24	16.6	1.1	7.6	
	12	0.34	18.0	1.0	3.1	
	13	0.28	17.9	1.3	8.5	±0.2
Beaufort Sea	Depth (m)					
	BS 3	0.50	3.2	2.1	(111)	
	20	1.04	0.5	0.4	6.9	
	35	1.13	1.7	0.8	14.1	

*See figures 1 and 2 for locations.

for the surface water, the Beaufort Sea samples were a factor of three greater than those from the lagoon. Yet the concentrations are lower than have been observed in the waters of other locations. For example, in the Adriatic Sea (2) and in waters collected in a transect from 30°N to 12°S latitude in the Eastern Pacific Ocean (unpublished data) the concentrations closely center at about 1.7 ppb. Further in the waters off Yakutat, Alaska, a constant value of 1.4 ppb was obtained in a vertical profile up to depths of 170 m at each of two locations (4).

Copper

The average value of copper in snow was 0.6 ± 0.3 ppb. This analysis agrees with contemporary deposits (post-1945) at the Dye-3 and Camp Century sites in Greenland (5). The average determination was 1.0 ± 0.2 ppb and 1.7 ± 0.6 ppb for the Kuparuk and Colville Rivers, respectively. Thus in addition to the atmospheric component, terrigenous input contributed to the copper content of the rivers.

The surface sample in the Beaufort Sea contained 2.1 g/kg while underlying waters were close to the usual sea water values (< 1 ppb).

In the lagoon the quantity was fairly constant (1.3 ± 0.2 ppb) and not distinctly different from the rivers.

Iron

The assay of iron on the snow samples was 22.8 ± 2.0 ppb. By comparison with this result and excluding a single non-representative sample (774 ppb) the Kuparuk River was relatively depleted in this element (10.3 ± 6.8 ppb): on the other hand water from the Colville River was enriched (58.6 ± 24.6 ppb). With regard to sample location _1_ in the

Colville River, it may be noted that the iron in the muddy water entering from the Killik River was less concentrated than the segment derived from the upstream Colville River waters. Perhaps adsorption of dissolved iron by the greater suspended particulate load accounts for this difference.

In Simpson Lagoon the iron values ranged from 3.1-14.2 ppb. This wide variation is unexpected for these waters where wave and tidal action in the relatively shallow lagoon should induce homogeneity. Replicate analyses of samples indicate that this spread in concentration is not attributable to error in the analytical measurement. Perhaps the lapse in time of 4-8 hours between sample collection and subsequent filtration and acidification was responsible for the variations. That substantial fractions of soluble iron in seawater samples disappear and become associated with particulate matter even upon only brief enclosure in containers has been reported (6).

In the Beaufort Sea, the concentration in a surface sample was 111 ppb. Presumably this inordinately high value for seawater was the result of local contamination. The concentration at 20 and 30 m (6.9 and 14.1 ppb) approximated that of lagoon waters.

Manganese

The average manganese content in snow was 2.6 ± 0.4 ppb. This value approximates the upper level determined in snows collected from the area of Barrow in 1972 (3). A comparable concentration appeared in water from the Kuparuk River (2.7 ppb), while Colville River water samples contained about twice the quantity (5.8 ppb). In the Colville River samples, the concentration also appears to increase as the waters flow downstream.

A relatively uniform value of 18.5 ± 1.6 ppb was observed in the lagoon. Water from the Beaufort Sea ranged from 2.1 ppb at the surface to 0.4-0.8 ppb at greater depths. Since the lagoon water is an admixture of river and seawater, the source of the elevated manganese concentration resides within the lagoon. Clearly the introduction of manganese from the sediments either through mobilization from surface deposits or by upward diffusion of dissolved manganese in the pore water accounts for this circumstance.

CONCLUSIONS

The concentrations of vanadium, manganese, iron, and copper in snow, river, lagoon, and Beaufort Sea water in the environs of Simpson Lagoon were determined. These values will serve as a baseline by which comparisons can be made at some future date to determine the influence of activities associated with exploration and production of petroleum upon the concentration of these elements in this environment.

REFERENCES

1) Weiss, H. V., Kenis, P. R., Korkisch, J., and Steffan, I. Determinations of Copper and Manganese in Sea Water by Neutron Activation Analysis and Atomic Absorption Spectrometry. Analytical Chemica Acta 104 337-343 (1979).

2) Weiss, H. V., Guttman, Korkisch, J., and Steffan, I. Comparison of Methods for the Determination of Vanadium in Seawater. Talanta 24 509-511 (1977).

3) Weiss, H. V., Herron, M. M., and Langway, C. C., Jr. Natural Enrichment of Elements in Snow. Nature 274 352-353 (1978).

4) Burrell, D. C. Quarterly Report on Distribution and Dynamics of Heavy Metals in Alaskan Shelf Environments Subject to Oil Development. Dated 10/1/77-12/31/77.

5) Weiss, H. V., Bertine, K. K., Koide, M., and Goldberg, E. D. The Chemical Composition of a Greenland Glacier. Geochimica et Cosmochimica Acta 39 1-10 (1978).

6) Lewin, J., and Chen, C. Changes in the Concentration of Soluble and Particulate Iron in Seawater Enclosed in Containers. Limnology and Oceanography 18 580-596 (1973).

APPENDIX III

SEASONAL AND LONG TERM CIRCULATION AND CHEMICAL CYCLING IN AN ALASKAN FJORD

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ABSTRACT

Resurrection Bay — a single-silled fjord estuary on the northeast Gulf of Alaska coast — shows distinct seasonal hydrographic patterns related to meterological and oceanographic conditions on the adjacent continental shelf. Deep water renewal of the basin (observed over the period 1973-79) follows the appearance of a density maxima at sill depth during the summer. The deep basin appears to be largely advectively isolated through the winter. Oxygen consumption at depth within the inner fjord is highest in late summer — early winter, coincident with estimates of highest particulate organic flux into the basin and maximum nutrient regeneration. Near bottom dissolved oxygen contents increase in late winter. Minimum bottom water concentrations were higher during 1977-79 compared with 1972-75; the change coincides with decreased input of anthropogenic carbon.

INTRODUCTION

Fjords are glacially formed estuaries. Most, including the one described here, are relatively deep and contain one or more sub-surface sills which impede the free exchange of water at depth. It is this latter characteristic which has elicited the interest of estuarine chemists because of the potentiality for localized (and usually seasonal) anoxia within the water column. Although most usually a natural phenomenon, this behavior may be exacerbated, or the condition may be induced in an otherwise aerated fjord, by anthropogenic carbon loading.

Fjords also potentially offer advantages to geochemists studying the movement and reaction of soluble chemical and particulate phases within estuarines — the major reaction site for river influxed material — since the salinity gradient zone is usually underlain by an enclosed marine basin which also physically confines the products of sediment-seawater reactions.

Because of their morphology, water circulation within silled fjords may be considered as comprising two components: a surface estuarine circulation cell overlying marine basins — defined by the sills — within which the predominant circulation may be largely decoupled from that of the surface zone. This paper is concerned chiefly with transports within the sub-surface zone and specifically within the basin of a single-silled fjord.

RESURRECTION BAY

Resurrection Bay is a high latitude (60°N) estuary located on the Kenai Peninsula of southcentral Alaska (Figure 1). This fjord is approximately 30 km long and 6-8 km wide with a sill at 185 m depth protecting a basin of mean depth around 290 m. The inlet is orientated N-S and the outer reaches exchange freely with the adjacent northeast Gulf of Alaska shelf.

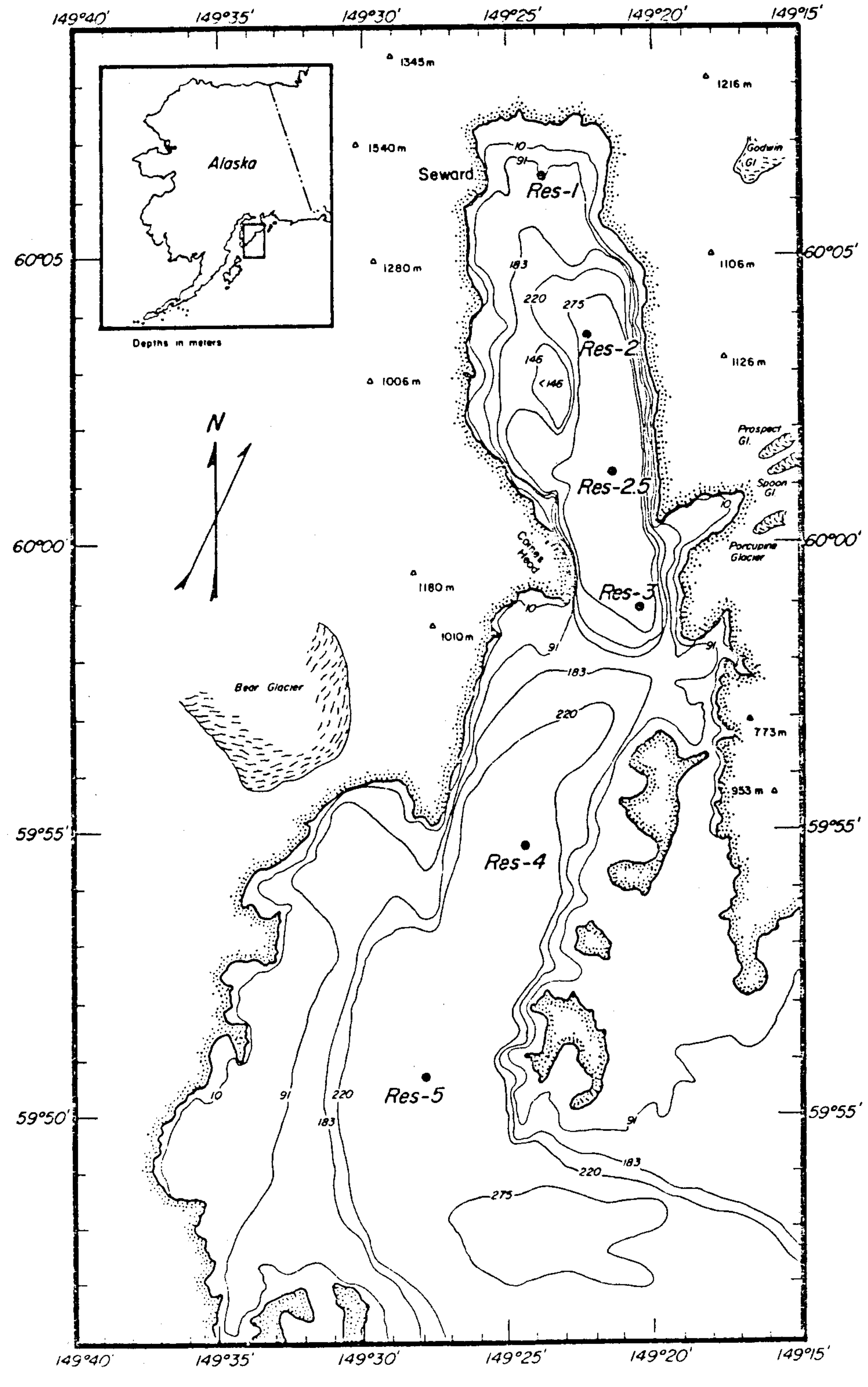


Figure 1. Resurrection Bay, southcentral Alaska, showing location of standard stations.

In a recent survey of Pacific fjords, Pickard and Stanton (1979) suggest freshwater inflow as the single most important factor affecting water properties. Precipitation is high along the entire fjord-coast of Alaska, but the principal freshwater inflow into this inlet — the Resurrection River at the head — constitutes only a few percent of the tidal prism (which in turn is only some 2% of the volume of the fjord) and appears not to be a major influence on the upper circulation. This freshwater inflow is markedly seasonal (Figure 2; more recent data are not available) with a maximum in late summer-fall (> 500 m^3 sec^{-1}) and around an order of magnitude less than this in mid-winter. Niebauer (1979), using numerical modeling techniques, considers the surface circulation to be dominated by the local wind regime; year-round current measurements have not been made. Local winter winds are predominantly northerly (down fjord) and southerly in the summer.

DEEP WATER CIRCULATION WITHIN N.W. PACIFIC FJORDS

The mechanics of fjord deep water circulation (i.e., that below the influence of forces driving the local surface currents) have been studied for a number of fjord-estuaries along the Pacific northwest coast. The various potential forces may be conveniently considered in terms of those originating within and outside the fjord. Ozretich (1975) has shown that local influences — wind, tides, freshwater runoff — in various combinations result in partial replacement of deep water within Lake Nitinat; Anderson and Devol (1973) consider seasonal deep water renewal within Saanich Inlet (both of these fjords are on the southern end of Vancouver Island) to be attributable to contiguous coastal upwelling. From Pickard's (1967) general survey of southeast Alaska fjords, and more recent data on northeast Gulf estuaries, Muench and Heggie (1978) suggest a pattern of increasing external control northwards into sub-arctic

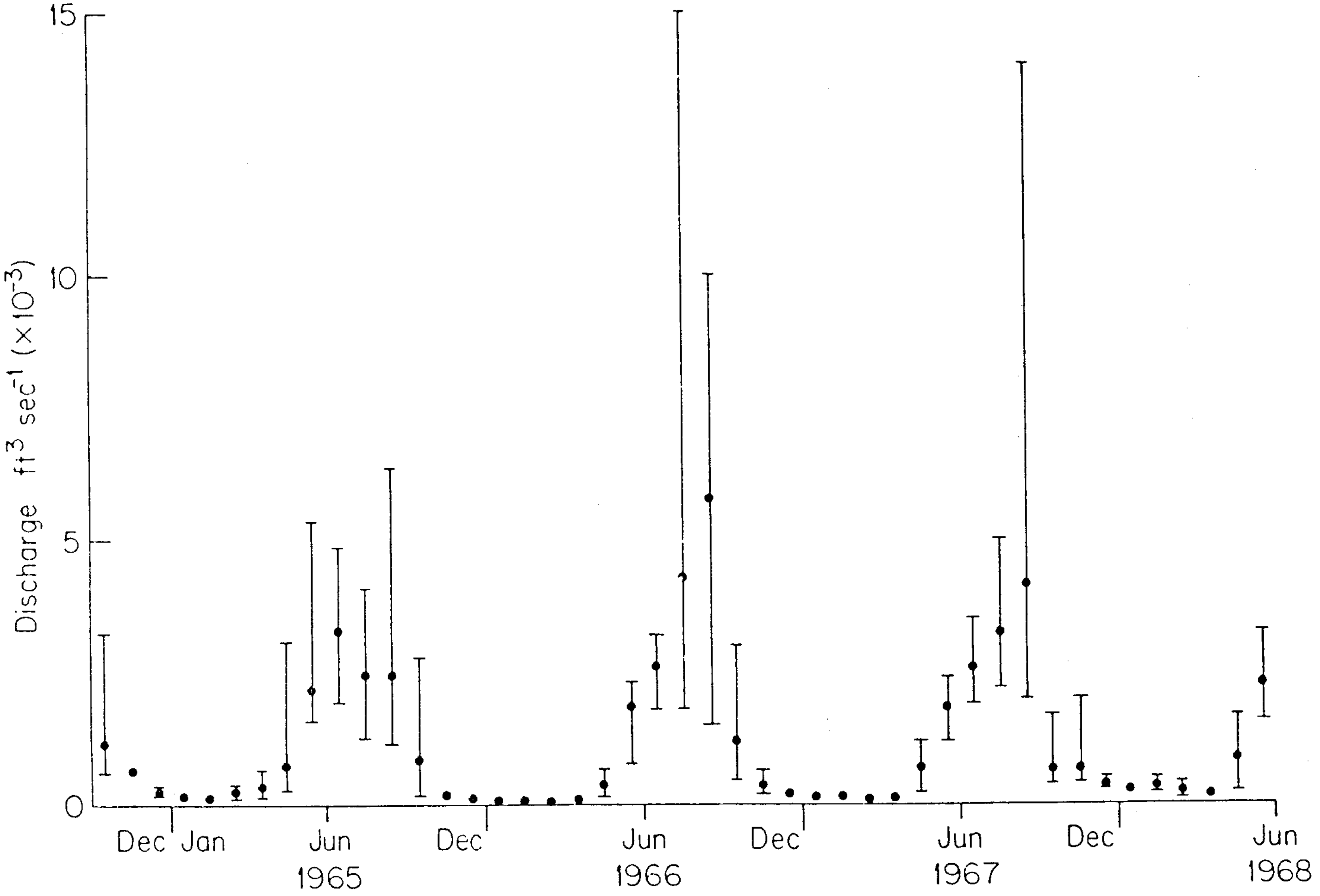


Figure 2. Seasonal discharge of Resurrection River 1965-68 (unpublished USGS data).

Alaska. In the absence of a strong seaward freshwater gradient, such as is the case in Resurrection Bay, density differences between the marine source water and the fjord basin water would be expected to be the critical factor influencing exchange of the latter.

SEASONAL PATTERNS ON THE N.E. GULF SHELF

In a multi-year study of the water characteristics of the northeastern shelf waters of the Gulf of Alaska, Royer (1975) has shown that persistent seasonal meteorological conditions result in a pattern of contrasting summer-winter surface water transport along the coast of southcentral Alaska. The locality of the dominant Aleutian low over the Gulf produces strong easterly winds and the resultant Ekman transport creates a strong (northern) coastal convergence. The winter low pressure system is replaced by the weaker (and more southerly) north Pacific high through the summer (approximately May-September) and relaxation of the intense winter downwelling permits run-up of more dense water ($\sigma_t > 26.0$) onto the shelf and hence into the outer reaches of those fjords — like Resurrection Bay — which have direct access to the shelf (Figure 3).

TRANSPORT WITHIN THE RESURRECTION BAY BASIN

Summer coastal waters in the vicinity of Resurrection Bay show minimum surface and maximum deep densities with a zone of minimum annual density variation located at around 150 m (Figure 3). Based largely on the few examples well studied to date, Muench and Heggie (1978) have postulated a practical classification of Alaskan fjords based on the depth relationship between this latter zone and the depth of the barrier sill. Thus relatively denser water isadvected over shallow sills to replace the enclosed basin water in the

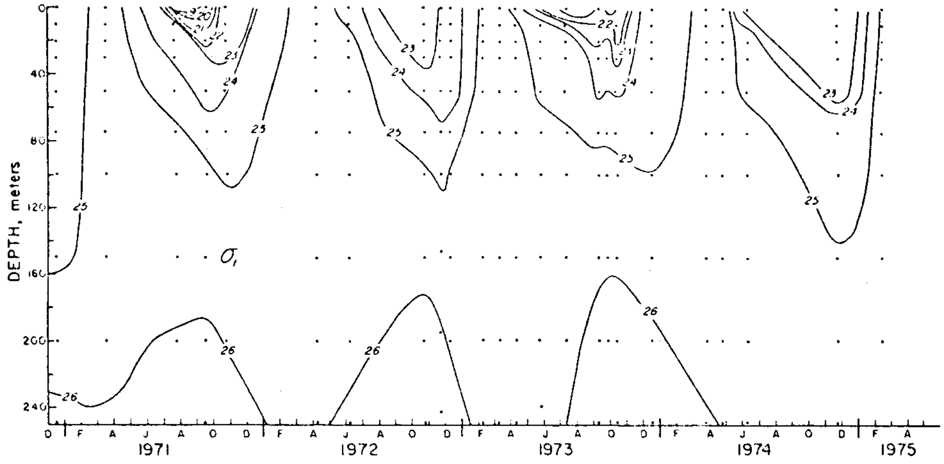


Figure 3. Seasonal density distribution at Station Res 5 (after Royer, 1975).

oceanographic winter (e.g. Aialik and Unakwik Inlets, Muench and Heggie, 1978; Yakutat Bay, Burrell, unpublished data). Resurrection Bay has a deep (approximately 185 m depth) sill and flushing of the basin by dense water upwelled into the outer reaches of the fjord occurs during the summer months. Seasonal observations over the period November 1972-July 1975 and again from November of 1977 through June 1979 show this to be the case. Renewal of the basin water may begin as early as April-May, but major influx and penetration to the bottom of the basin occurs during late summer-early fall when the density of the source water at sill height is at a maximum (Figure 4). Figure 5 illustrates longitudinal density distributions through the deep basin water replacement period of 1974.

We have computed (Heggie and Burrell, manuscript in preparation) volume transports, and hence the percent replacement of the basin, from 1972-79 temperature and salinity data using simple mass balances. Transport during the flushing event of 1973 was sufficient to replace the topographic basin volume 3-4 times over but the fractional replacement was approximately half this the following summer. Current meter records for a 35 day September-October 1973 period (Figure 6) show continuous inflow at 285 m and apparent bolus-type injections into the deep basin following a period of prevailing up-channel winds. With the reestablishment of winter shelf convergence conditions, the density of the sill-height source water outside the sill decreases. The more uniform and less marked rate of change at depth within the basin (Figure 7) suggests that property changes through the winter here are predominantly due to turbulent diffusion. Figure 4 illustrates the closer correspondence of seasonal patterns at sill height (200 m) within and outside the basin compared with that between the waters at 250 m at these same localities. Continuous salinity and temperature records obtained from current meters set for 55 days adjacent to the basin floor

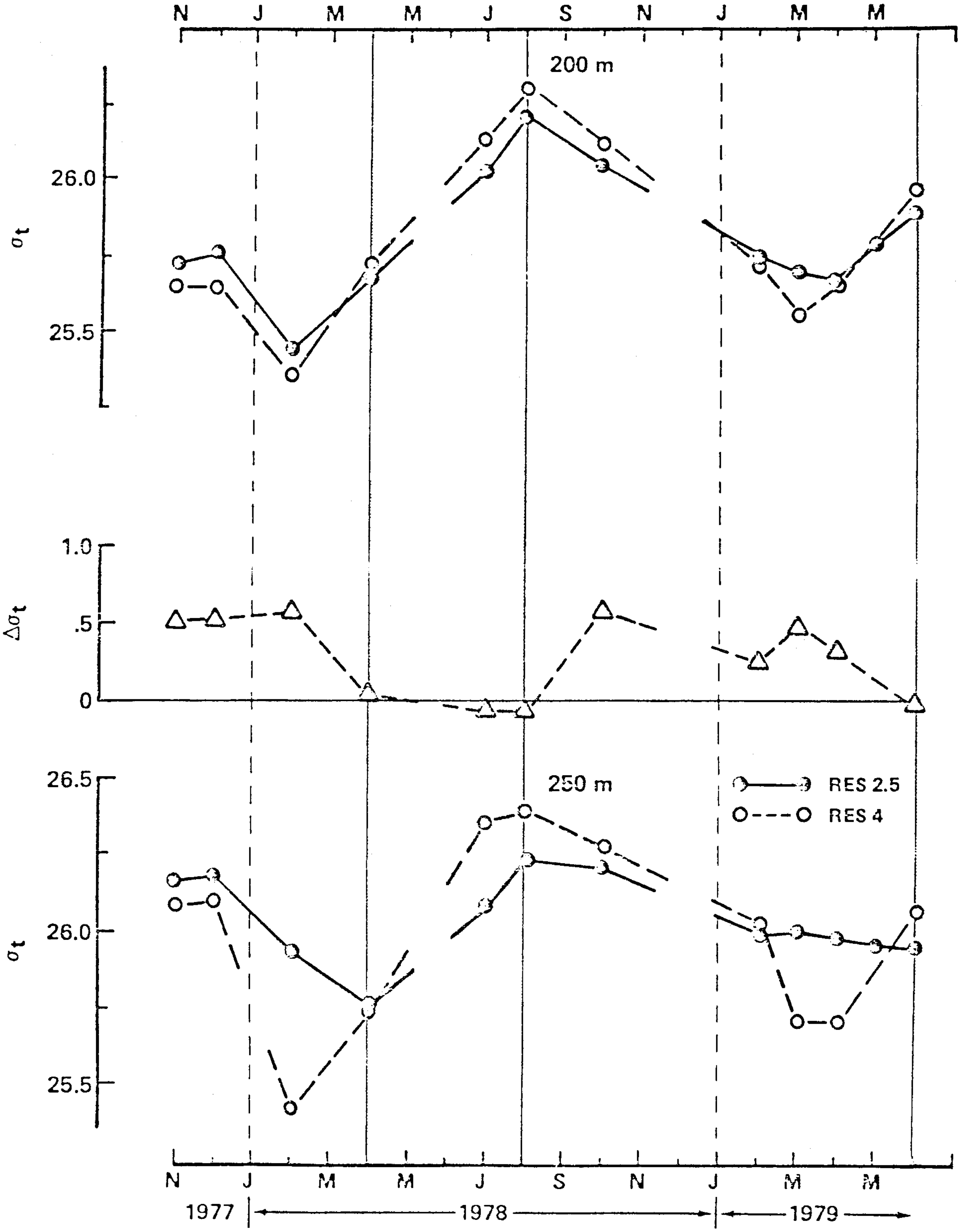


Figure 4. Density distribution at sill height (200 m) and depth (250 m) at Stations Res 4 and 2.5, November 1977-June 1979. The screened area in this and subsequent figures designates the primary annual basin flushing period (from $\Delta\sigma_t$: see text).

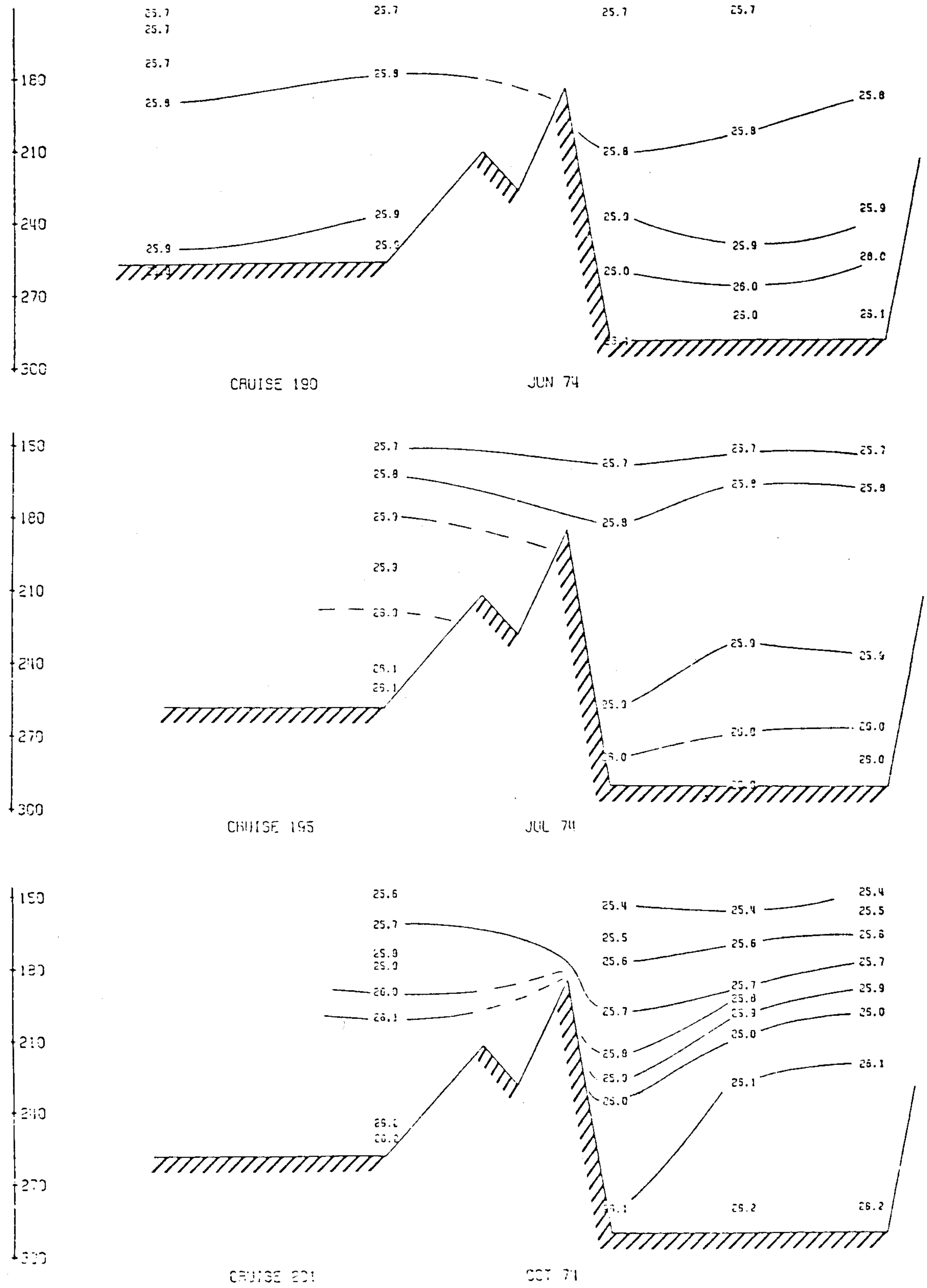


Figure 5. Longitudinal density profiles: summer-winter 1974.

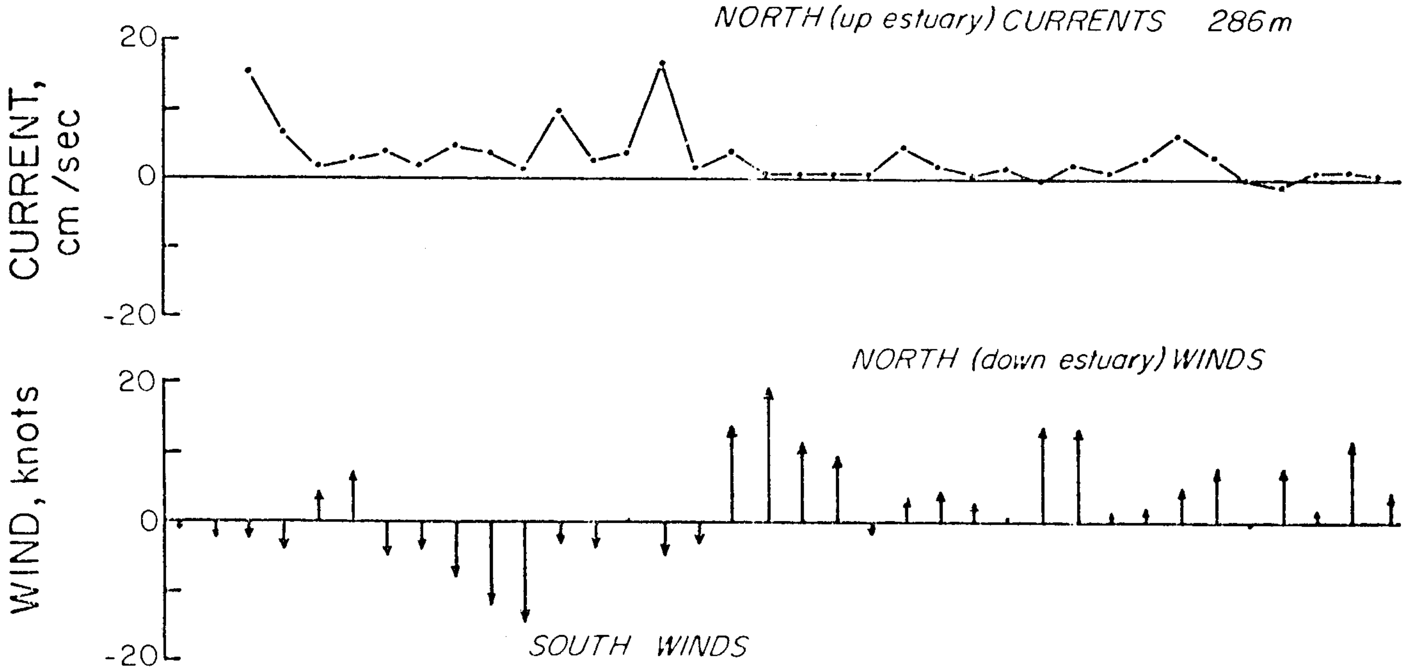


Figure 6. N-S current vectors at depth (286 m) in the basin during major water renewal period (September 5= October 9, 1973) and prevailing (N-S) winds.

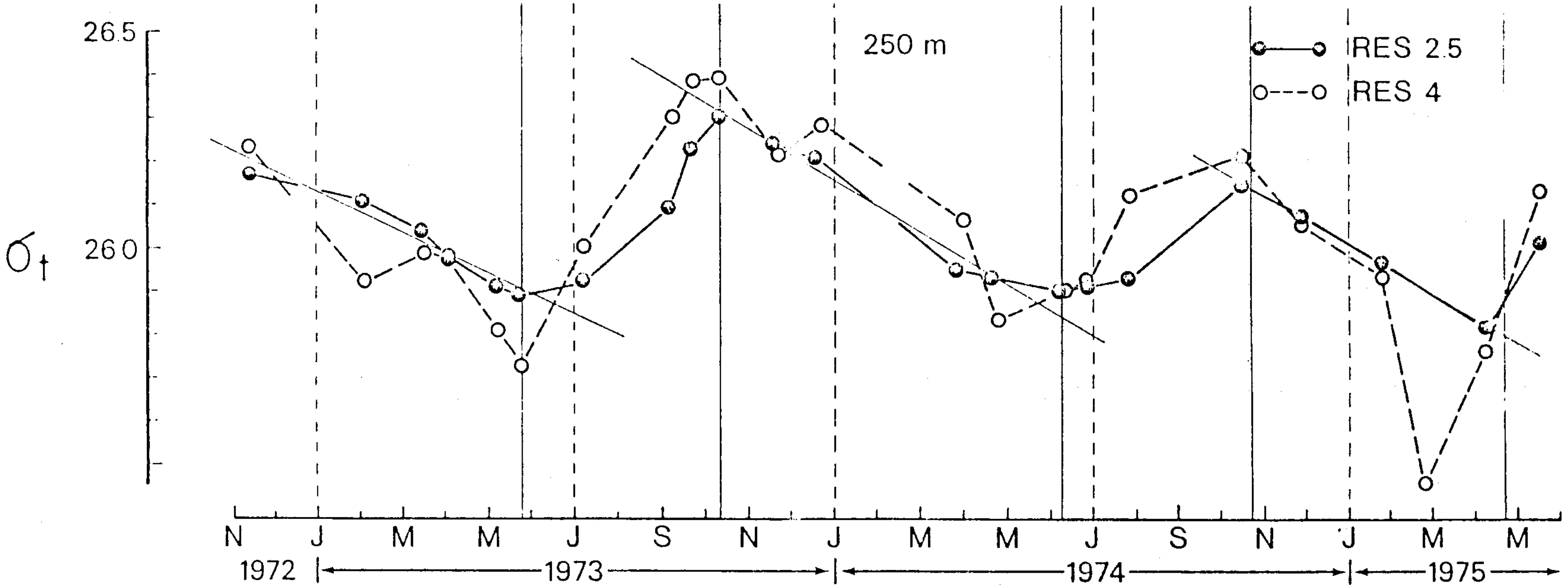


Figure 7. Density distribution at 250 m within and outside the sill, November 1972-May 1975.

in March-May (1973) show tidal influences and net southward drift of some 8 km over this period. But, unlike similar observations made in September-October, there is no evidence for replacement of resident basin water at this depth (285 m). Figure 8 schematically illustrates the postulated principal circulation patterns in this fjord during winter and summer as determined from March-May and September-October current meter records (1973; summarized in Heggie *et al.*, 1977) and using a simple model for volume continuity estimates of net transports. Aperiodic influxes of more dense water occur at shallower depths in the winter water column: the time series σ_t data given in Figure 9 demonstrate such an occurrence at 200 m in February-March of 1973. Conversely, the numerical model of Niebauer (1979) predicts penetration of less dense water into the basin under conditions simulating shelf downwelling and this has led him to postulate the possibility of near continuous renewal of bottom water. Although the effects of the intense winter coastal downwelling may impinge on the inner fjord, we believe that preservation of stratification across the sill depth contour, in contrast to the more homogeneous conditions present on the shelf, supports the contention that vertical transport changes from advection with diffusion above the sill to a predominantly diffusive mode within the basin through the winter season. In determining non-conservative basin distributions, uncertainties in the reaction terms are likely to be greater than those due to incorrect allocation of the mode of transport: we have previously applied non-advective equations to late winter distributions of manganese in this basin, for example; (Owens *et al.*, 1979). For representational simplicity basin water renewal is conveniently designated in the illustrations given in this report as that period when the density difference between 200 m source water and water at 250 m within the basin ($\Delta\ \sigma_t$ of Figure 4) approaches zero.

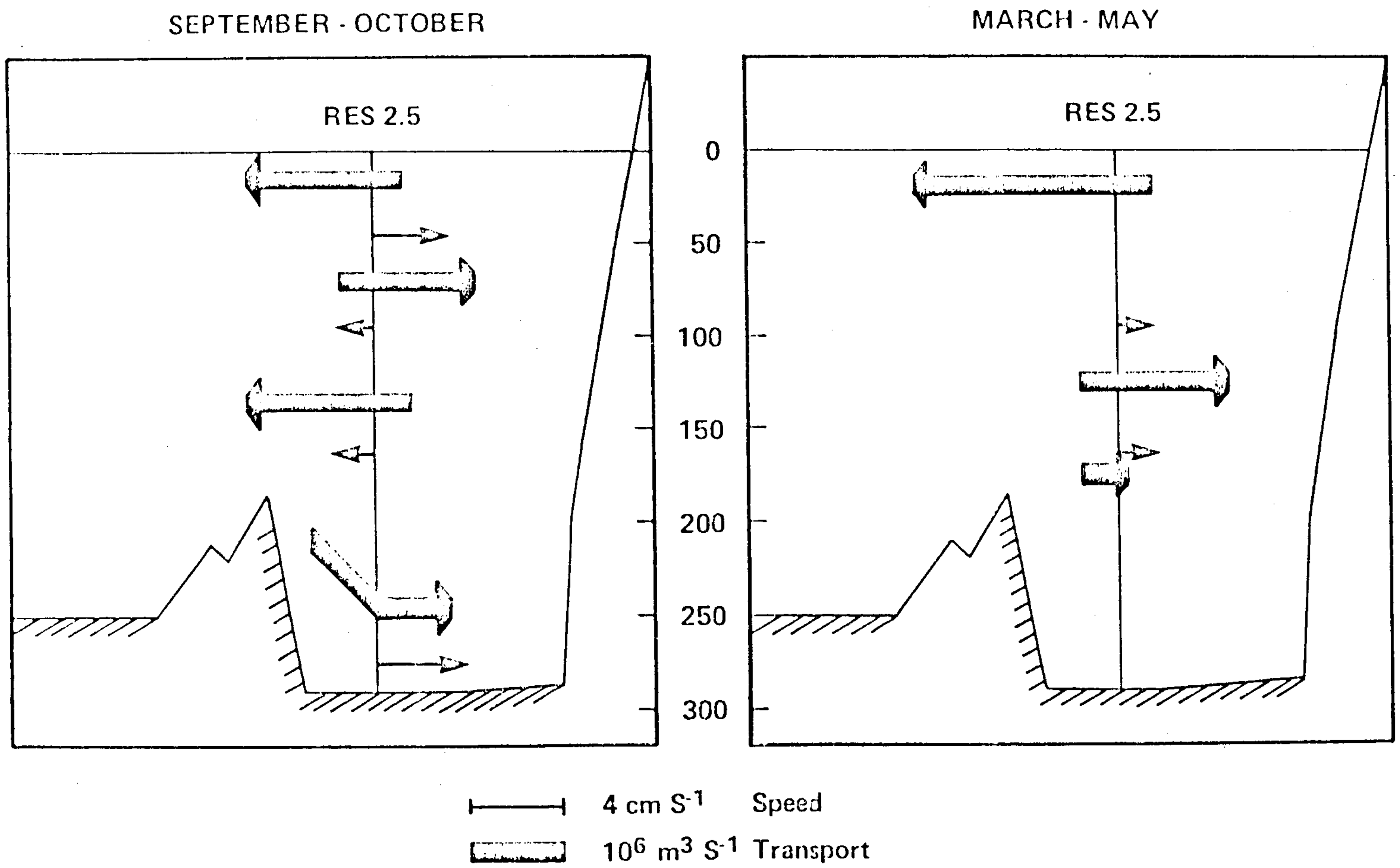


Figure 8. Schematic of proposed principal winter-summer (1973) circulation patterns in Resurrection Bay.

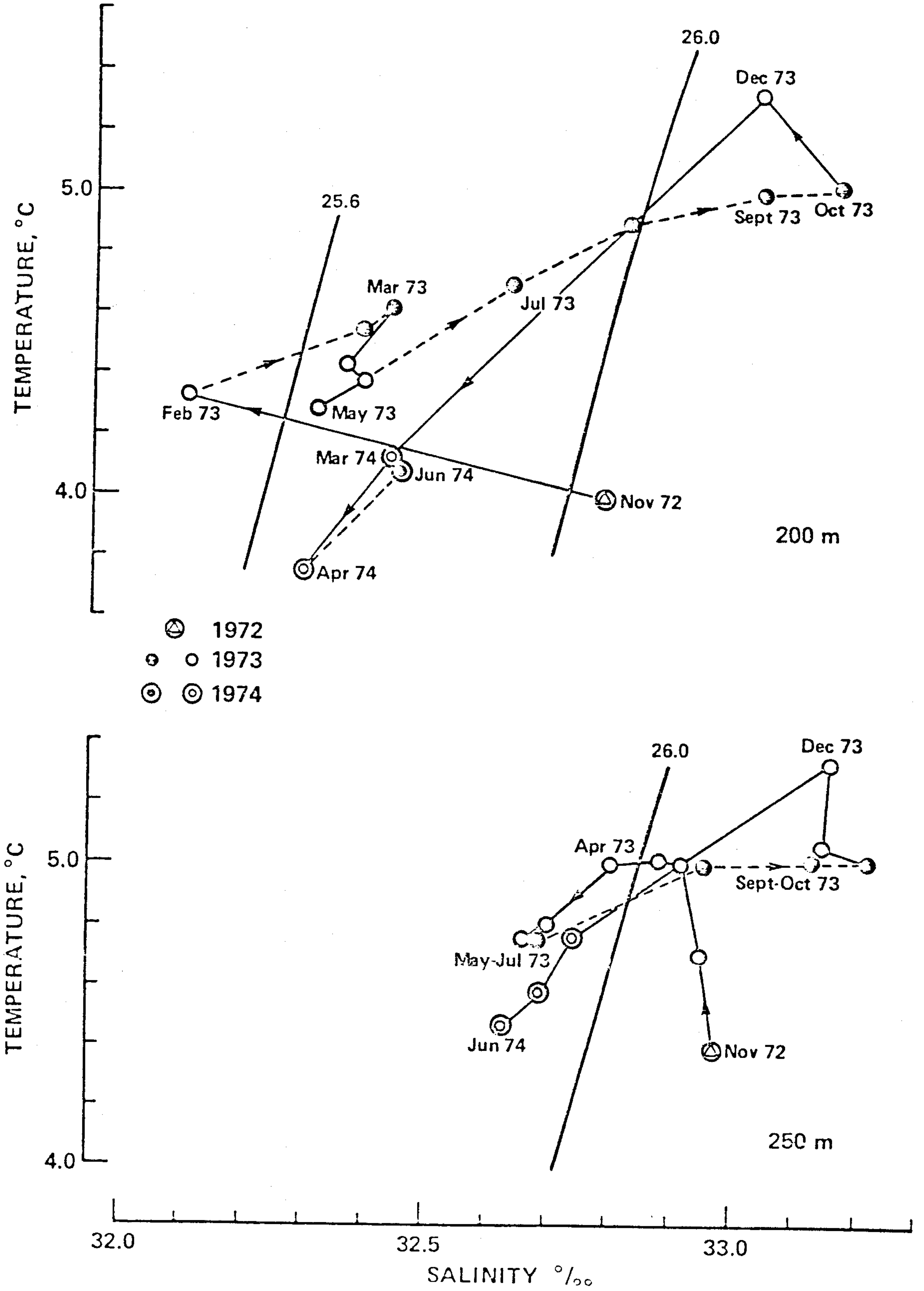


Figure 9. Time series σ_t at 200 and 250 m at Res 2.5, November 1972-June 1974. •--• shows periods of influx of denser water.

SEASONAL TEMPERATURES AND SALINITY

The time series vertical temperature distribution outside the sill (Station Res 4; Figure 10) reflects summer stratification and the tendency to winter uniformity throughout the column. Near surface temperatures for the 1977-79 observation period are somewhat higher than for 1972-75; this conforms with the trend to surface warming noted in recent years for the adjacent Gulf shelf. The surface water temperature maximum created in the summer penetrates downward into the basin and is eroded by vertical mixing and exchange to the cold arctic air during the winter. Figure 9 illustrates migration of this core at 250 m within the basin: impact on the density is minimal. In these sub-polar waters, density and salinity distributions covary and seasonal salinity patterns are similar to those given for σ_t in Figures 4 and 7. "Source water" salinity at sill height decreases through early-mid winter and there is an increasingly positive gradient over this period from close to the benthic boundary towards the sill. Diffusional loss of salt from the deep basin persists until the next spring-summer flushing cycle begins.

Rattray (1967) determined that the fjord basin salinity distribution was largely controlled by horizontal advection and vertical diffusion. In the absence of systematic horizontal gradients within the winter basin, Heggie (1977) computed eddy diffusion and conductivity coefficients using the salinity and temperature data collected at Station Res 2.5 over the period 1972-75. Year-round values of K_z at sill height thus determined ranged between 1.2 and 7.3 $cm^2 \ sec^{-1}$ (mean of 3.9 $cm^2 \ sec^{-1}$).

Figure 11 illustrates the seasonal (1977-78) T-S character of the Resurrection Bay basin waters. The range is from near vertical homogeneity at the time of advective replacement to near linearity towards the end of the winter isolation (e.g. July and April, respectively). The slope reversal is due to impact of the summer temperature spike.

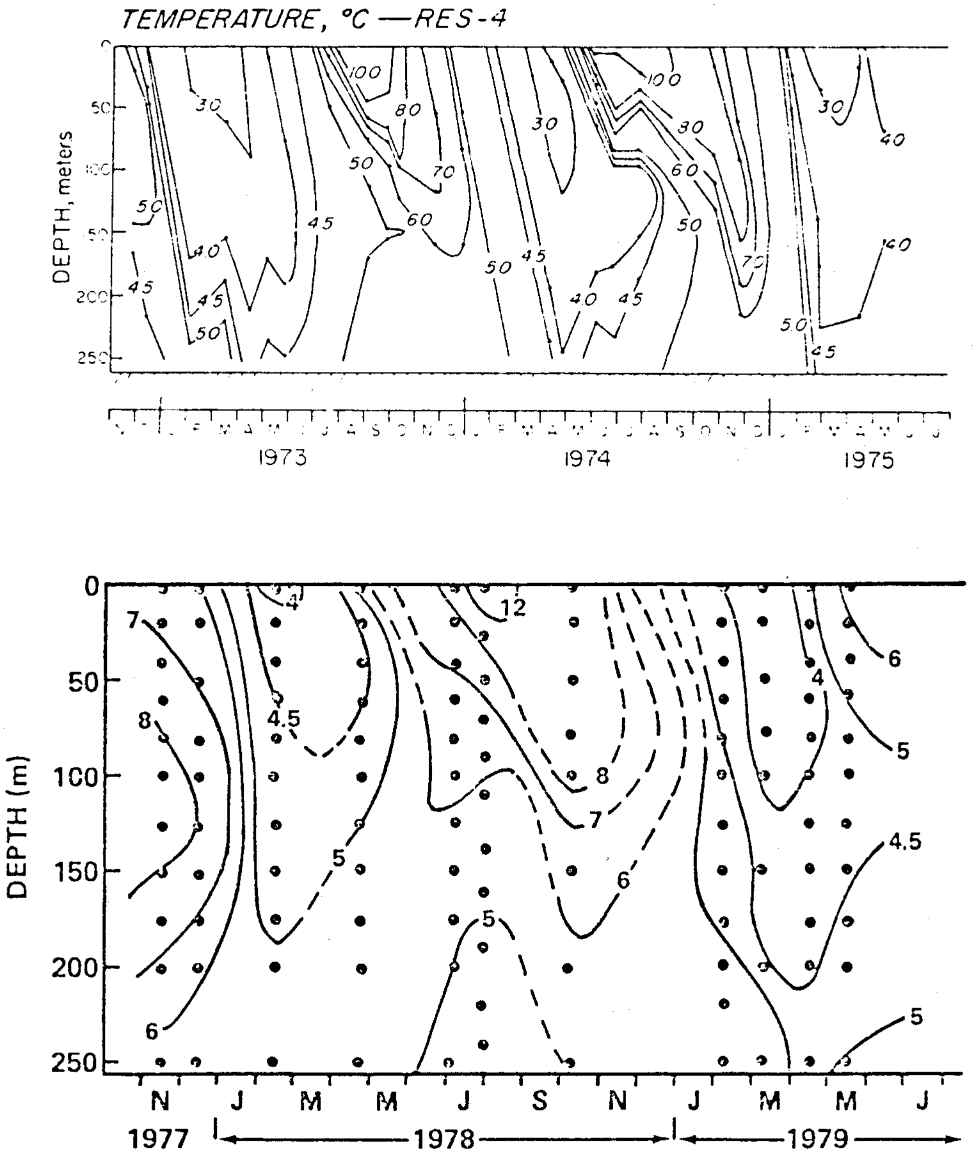


Figure 10. Temperature distribution outside the sill (Res 4) through the periods November 1972-May 1975 and November 1977-May 1979.

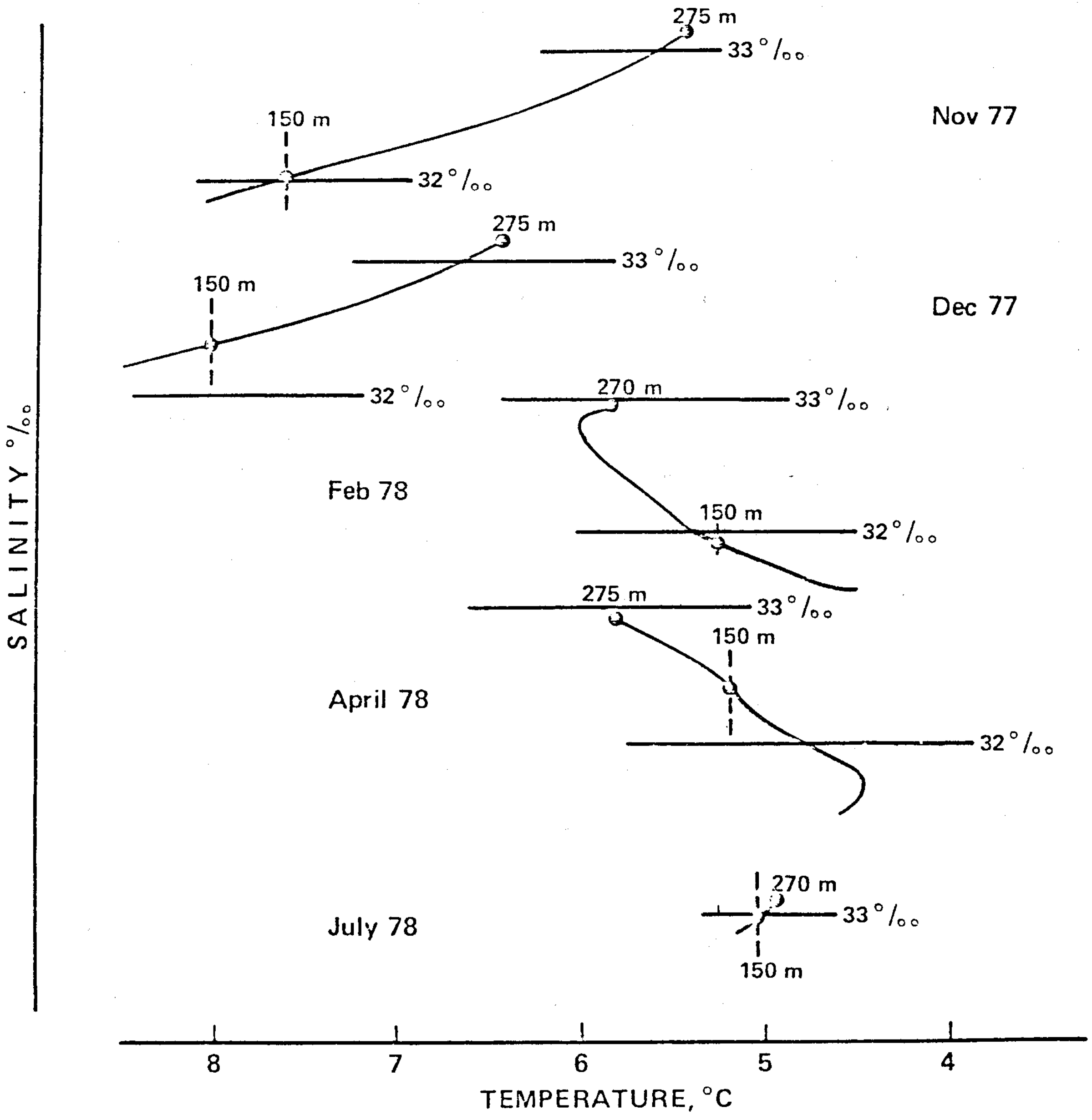


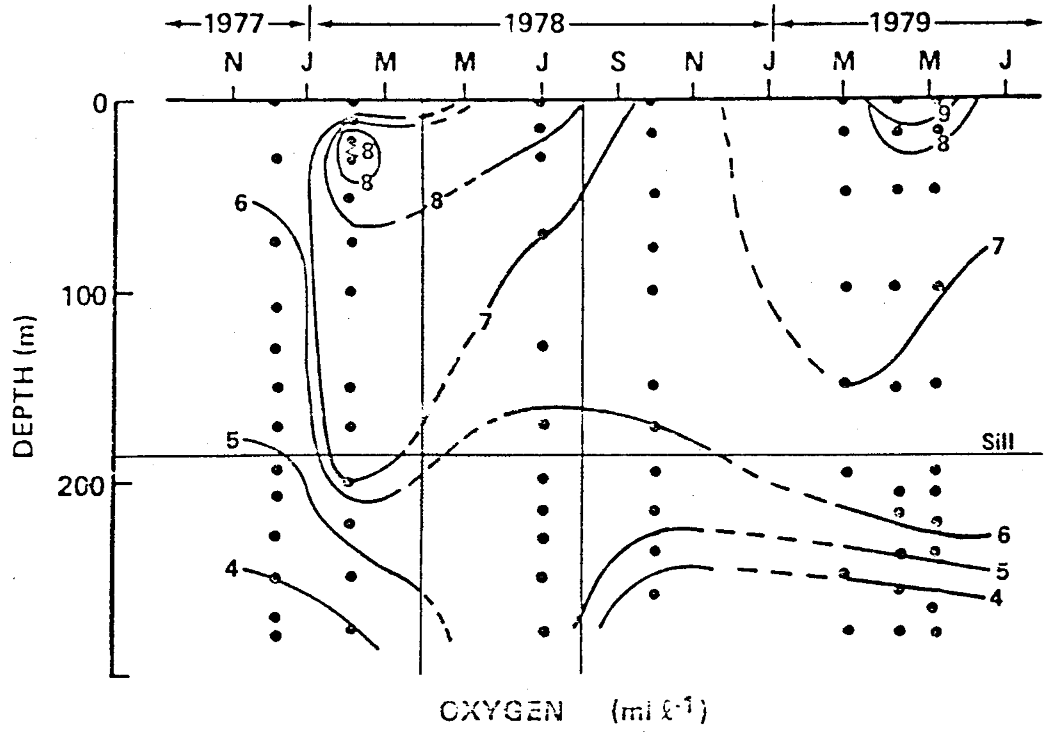
Figure 11. Seasonal T-S character of the basin winter (Res 2.5 below 150 m). November 1977-July 1978.

CONSUMPTION AND TRANSPORT OF OXYGEN

The behavior of dissolved oxygen is of concern in all inhabited coastal areas but, as noted, particularly so in fjords where free exchange of water close to the sediment boundary is inhibited. Many fjords — including the examples on Vancouver Island cited previously — are anoxic at depth either semi-permanently or intermittently. Water column anoxia has never been observed in any Alaskan fjord however. It is of interest to examine why this should be so and hence to project the effects of increasing anthropogenic impacts in the future.

The time series distribution of oxygen within the basin at Station Res 2.5 over the 1977-79 observation period is shown in Figures 12 and 13. Oxygen is near vertically homogeneous within the basin during the summer flushing cycle. Through the winter period of near advective isolation the dissolved oxygen content at sill height progressively increases; near the sediment interface concentrations initially decrease then steadily increase through mid-late winter. Figure 14 gives concentrations at the same station at 275 and 200 m for 1972-75. For this latter period near bottom oxygen decreases to < 1 ml ℓ^{-1} in the early winter and the oxygen depletion continues for longer, but the pattern is similar for the two observation periods and represents the seasonal behavior in this fjord basin.

Heggie and Burrell (unpublished manuscript) have computed a mean annual integrated oxygen consumption rate for water below sill depth in the basin over this April 1973-May 1975 period of 37 ml cm^{-2} yr^{-1}. Of this, from the surface sediment nitrate gradient, Heggie and Burrell (1979) estimated that oxygen is consumed in the sediment at around 0.5 ml cm^{-2} yr^{-1}. We do not presently know the total seasonal carbon flux into the basin but primary productivity measurements made in 1974-75 (Heggie *et al.*, 1977) may be projected at around 19 moles C $m^{-2}yr^{-1}$, up to 60% of which may be accounted for in the deep water by applying



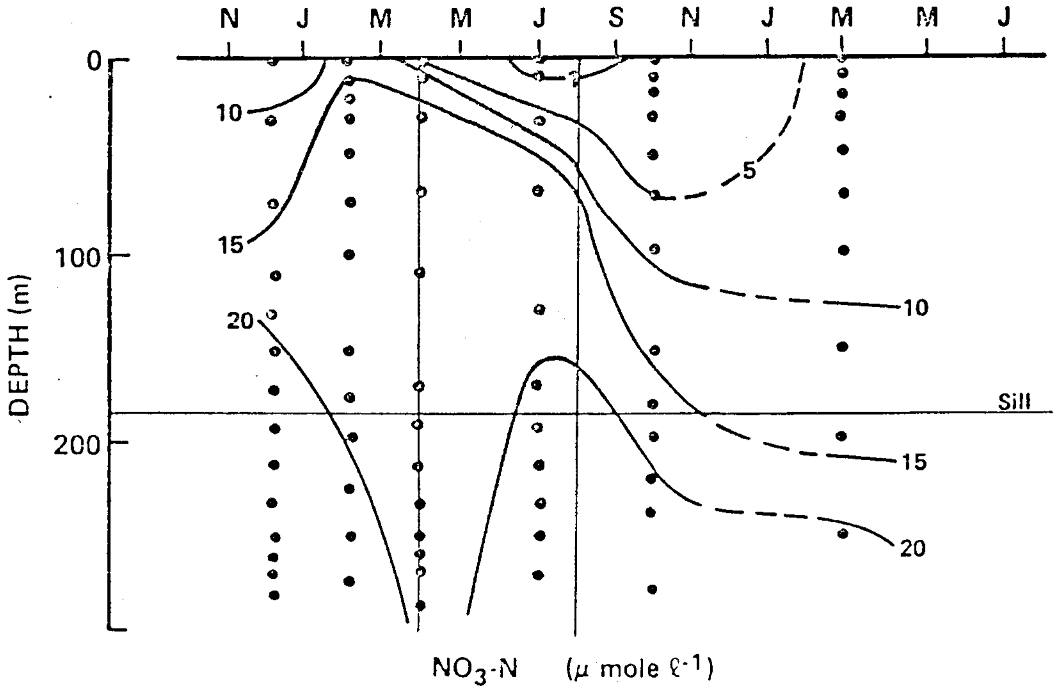


Figure 12. Distribution of dissolved oxygen (ml ℓ^{-1}) and nitrate (μM NO_3-N) at Res 2.5, 1977-79.

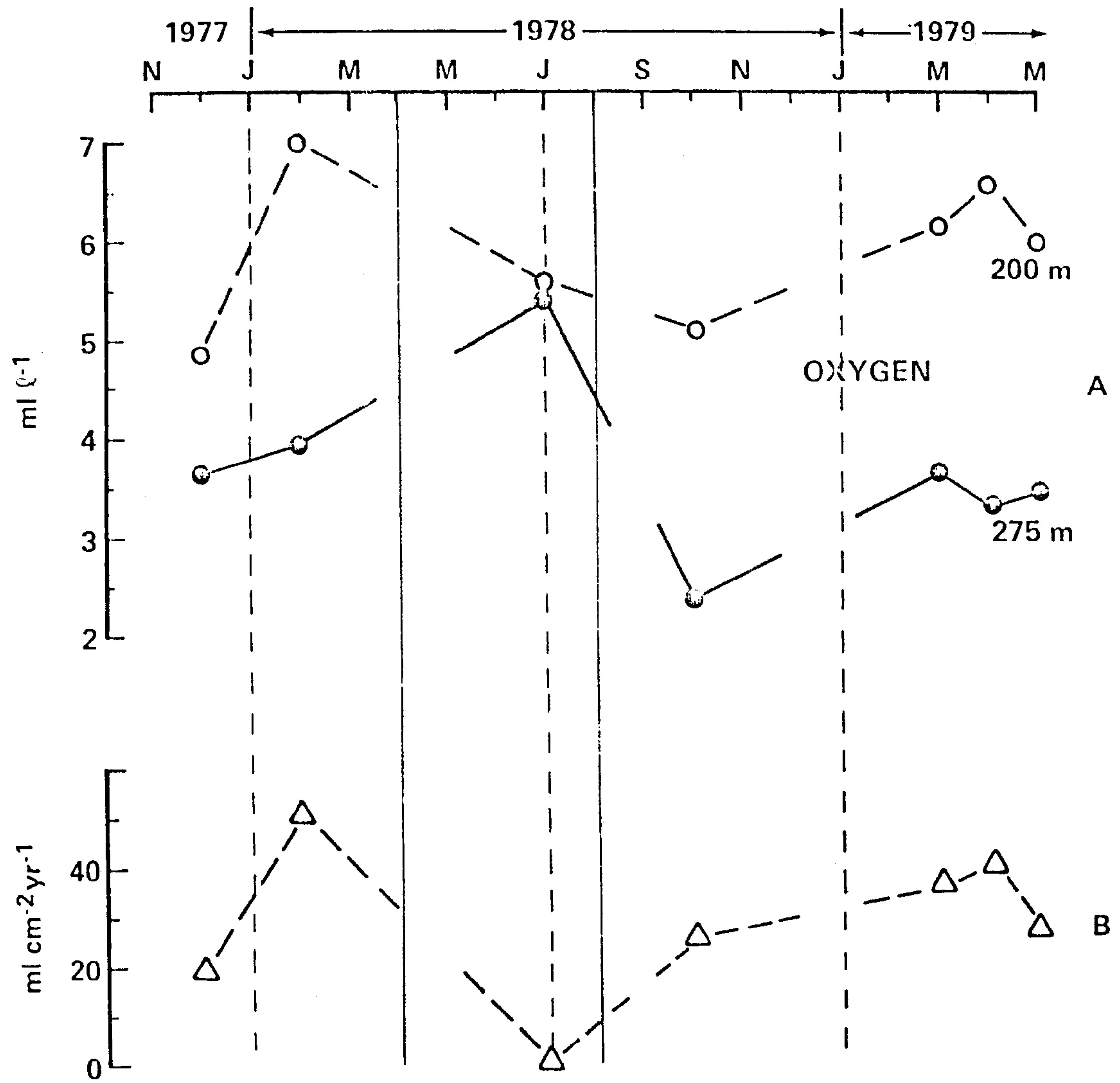


Figure 13. A. Dissolved oxygen concentrations (ml ℓ^{-1}) at 200 and 275 m at Res 2.5, November 1977-May 1979.
B. Oxygen flux based on linear gradient between 200 and 250 m and K_z of 3.5 cm^2 sec^{-1}.

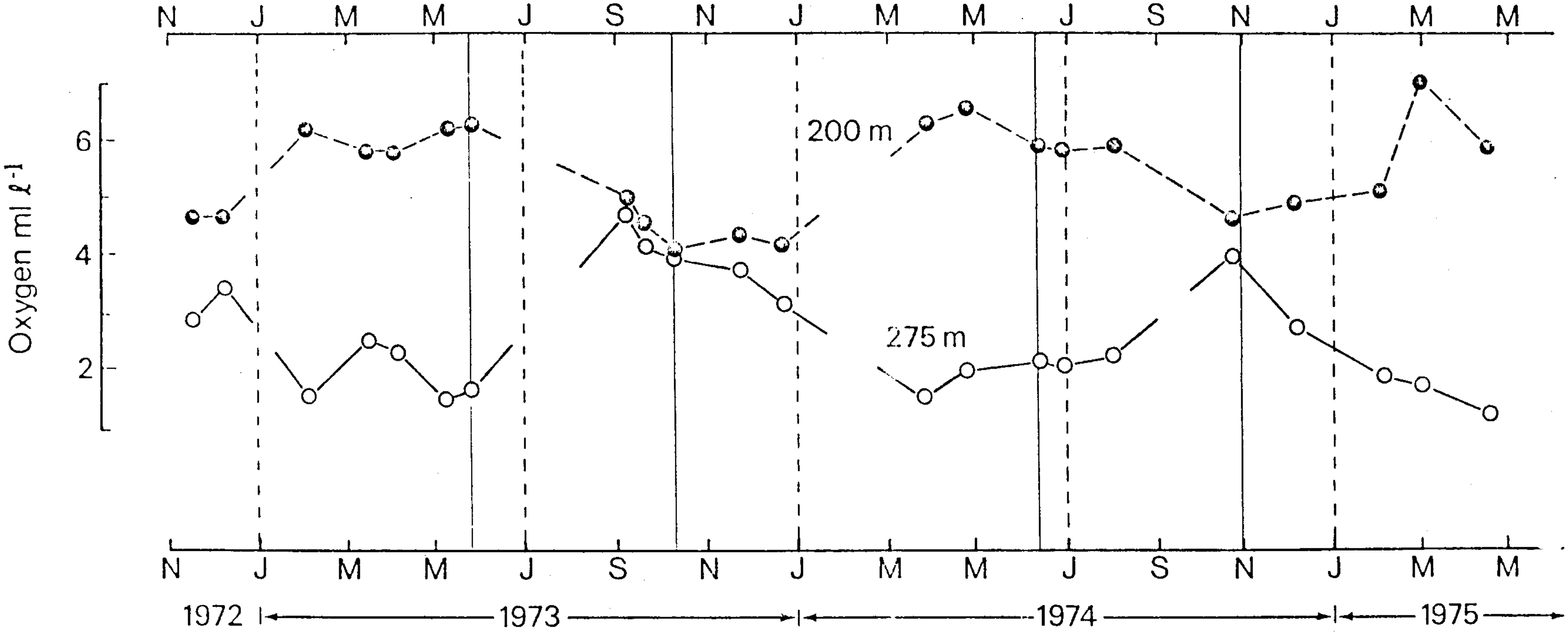


Figure 14. Dissolved oxygen concentrations (ml ℓ^{-1}) at 200 and 275 m at Res 2.5, November 1972-April 1975.

"Redfield stoichiometry" for the organic material. The distribution of carbon in the basin is highly seasonal, however. Discrete (0.4 μm filtered) particulate organic carbon contents below sill depth are at a maximum and minimum in early and late winter respectively. Applying a mean settling rate of 10^{-3} cm sec^{-1} (Owens *et al.*, 1979) yields corresponding downward fluxes at these seasons of 36 and 15 g C m^{-2} yr^{-1}. This range is some order of magnitude less than the computed mean annual surface productivity — an upper limit to the *in situ* biogenic carbon flux — but is not incompatible considering the class of particle likely to be collected by this technique. Larger biogenic debris would be expected to appear at the sediment surface predominantly during late summer-fall and to substantially increase the computed particulate flux.

Figure 15 shows time series (apparent) oxygen utilization over the period January 1973-January 1975 at 250 and 275 m within the basin. Oxidation of organic material in the column is highest during early winter and consumption decreases during the remainder of the winter period with the diminished carbon flux. Increasing basin oxygen concentrations through mid-late winter may be attributed to the combined effects of turbulent diffusional supply of oxygen from the progressively increasing sill height "reservoir" and decreased consumption.

It was noted above that basin oxygen consumption appears to have decreased in recent years. Figure 16 summarizes the time series distribution of dissolved oxygen at 275 m. During the observational hiatus between July 1975 and October 1977, fish processing waste from a cannery located at the head of Resurrection Bay ceased to be dumped into the basin. It seems likely that the bottom water oxygen concentrations — minimum values of ∿ 1.0 and ∿ 2.5 ml ℓ^{-1} for the earlier and later period respectively — reflect this.

Within the basin, nutrient concentrations initially increase at the beginning of the "isolation" period, then decrease through much of the remaining oceanographic winter period (Figure 17); the expected antithetical trends to

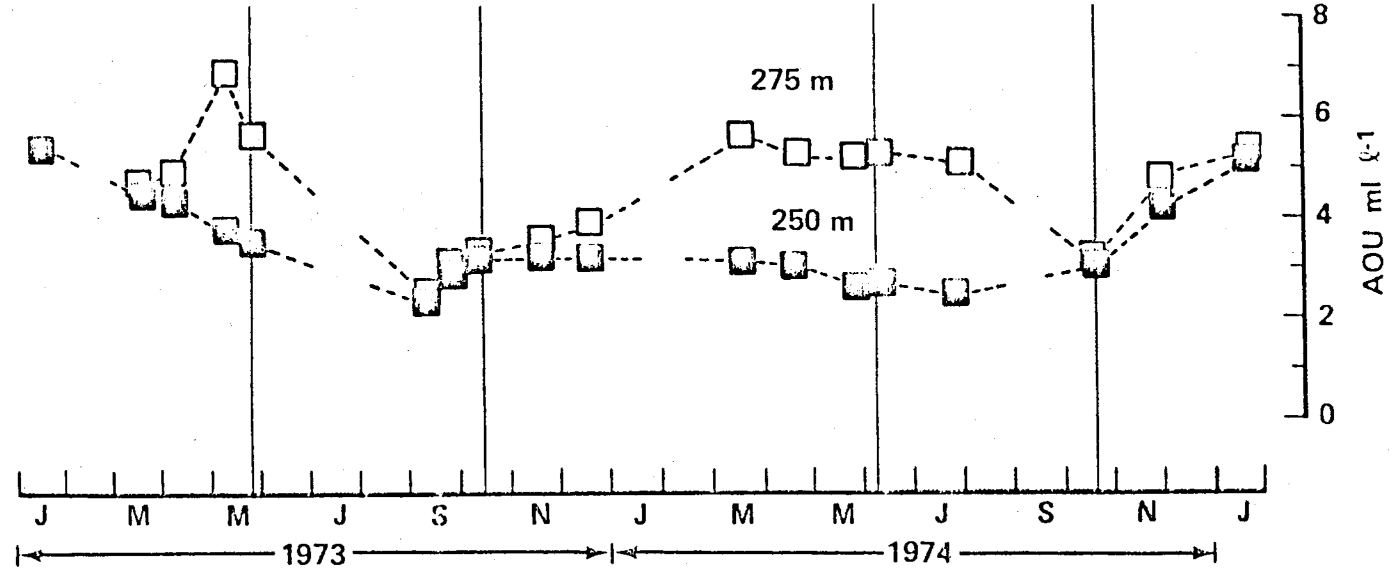


Figure 15. Time series (apparent) oxygen utilization at 250 and 275 m within the basin (Res 2.5), January 1973-January 1975.

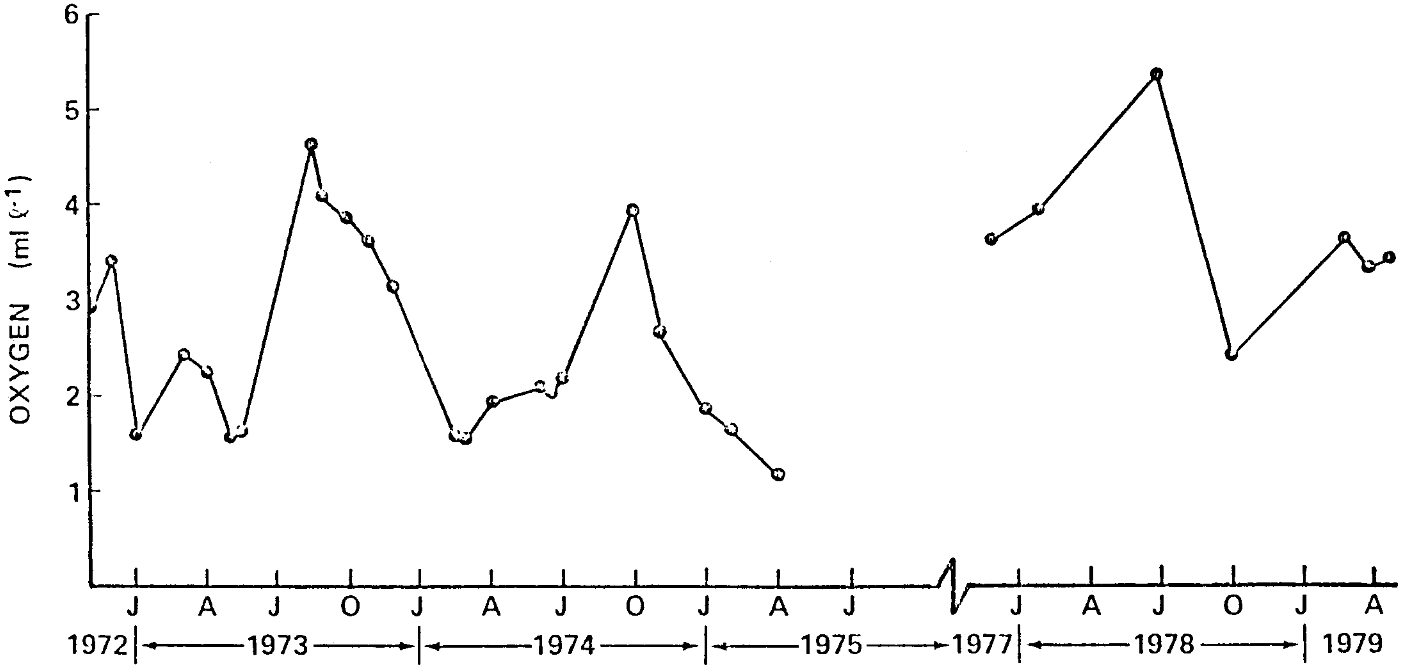


Figure 16. Seasonal dissolved oxygen contents (ml ℓ^{-1}) close to the basin floor (275 m at RES 2.5).

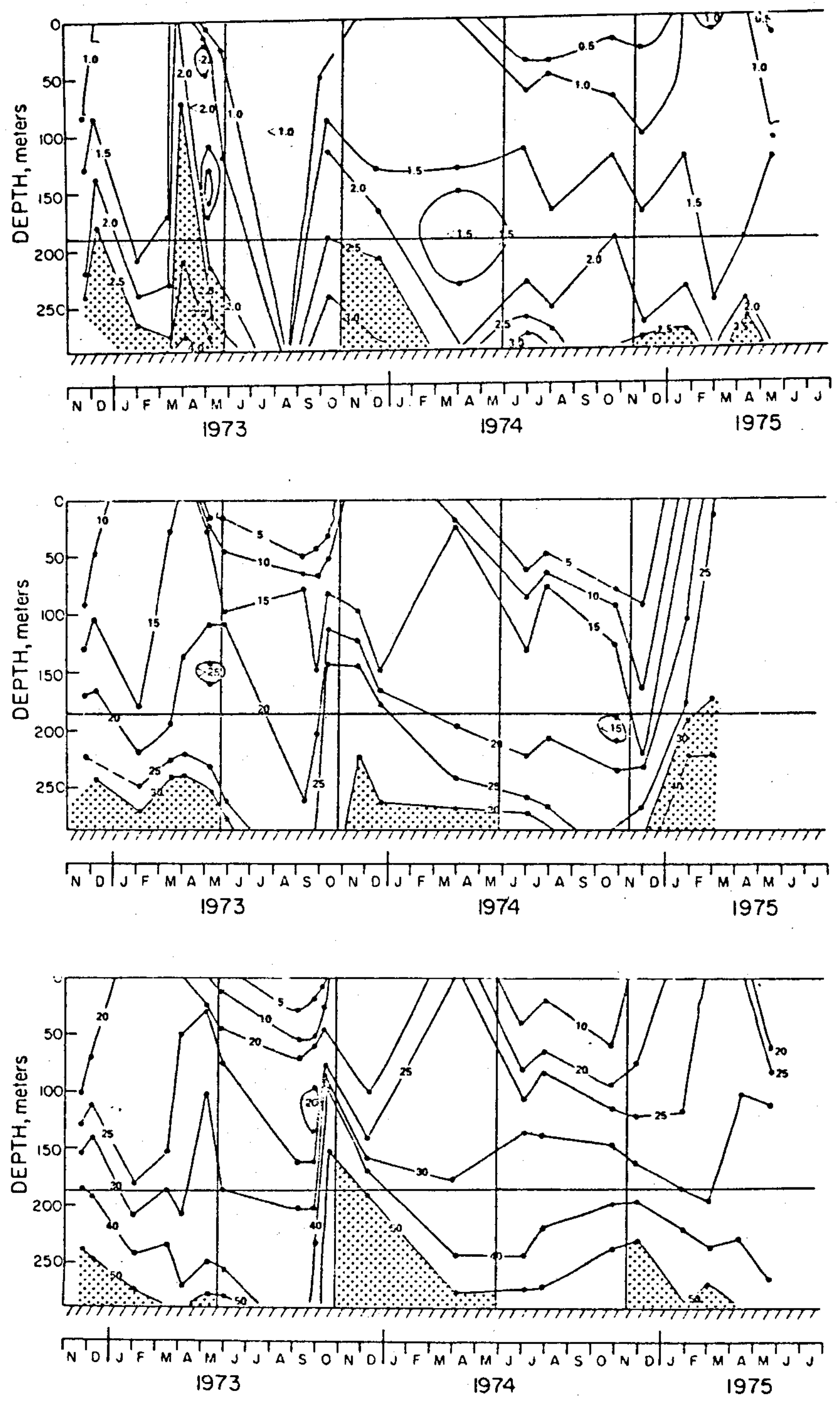


Figure 17. Seasonal distribution of (a) phosphate (b) nitrate (c) silicate at Res 2.5, November 1972-May 1975 after Heggie *et al.*(1977). Horizontal division marks sill depth.

that of oxygen. (Figure 12 also illustrates this behavior for NO_3-N through the more recent observation period.) Remineralization increases with depth in the basin (Figure 15). From estimates of the minimum flux (molecular diffusive) of nutrients across the sediment-seawater boundary in this fjord, Heggie and Burrell (1979) have postulated that this flux is less important than regeneration in the water column (or freshwater supply) in maintaining the geochemical mass balance.

SUMMARY

The sill depth of Resurrection Bay (at approximately 185 m) is such that complete flushing of the basin occurs in late summer-fall when dense water ($\sigma_t > 26.0$) is upwelled into the outer fjord. The deep basin is believed to be largely advectively isolated through the oceanographic winter. Diffusional loss of salt from the basin persists until the next spring-summer flushing cycle. A summer-formed temperature maximum migrates into the basin and dissipates throughout the winter: spring basin T-S plots are linear. This seasonal pattern is related to meteorological conditions over the adjacent Gulf of Alaska, and annual renewal has been observed every year in which observations have been made (1973-75 and 1977-79).

During the winter, dissolved oxygen in the basin above the sediment surface initially decreases, then increases until onset of the succeeding renewal period. The distribution of regenerated nutrients at depth, and preliminary carbon fluxes computed into the basin, demonstrate that the bulk of the organic matter produced in the surface waters impinges on the basin in late summer-fall and that oxygen consumption is progressively reduced through the remaining winter season. The near-bottom increase in winter oxygen utilization continued for longer, and dissolved oxygen was reduced to lower concentrations, over the 1973-74 period than was observed in 1977-78. This is believed due to reduced discharge of anthropogenic carbon into the basin between these periods. The mid-late winter increase in oxygen at depth in the basin is attributed to decreased consumption and to diffusional supply from the upper basin zone. Under these conditions, anoxic conditions are unlikely to occur in the basin water column.

ACKNOWLEDGEMENTS

Contribution No. XXX from the Institute of Marine Science. Major support has been from the Department of Energy (E(45-1)2229) and the BLM/NOAA OCS Program (03-5-022-50). Also in part by the National Science Foundation (G9 37963), the Alaska Sea Grant Program (04-6-155-44039) and the State of Alaska. We are grateful to Tom Owens and Susan Sugai for certain analytical and other technical assistance.

REFERENCES CITED

Anderson, J. J. and A. H. Devol. 1973. Deep water renewal in Saanich Inlet, an intermittently axonic basin. *Estuar. Coast. Mar. Sci.* 1:1-10.

Heggie, D. T. 1977. Copper in the sea: A physical-chemical study of reservoirs, fluxes and pathways in an Alaskan fjord. Unpublished Ph.D. thesis, Inst. Mar. Sci., University of Alaska, Fairbanks. 214 p.

Heggie, D. T., D. W. Boisseau and D. C. Burrell. 1977. Hydrography, nutrient chemistry and primary productivity of Resurrection Bay, Alaska, 1972-75. Report R77-2, Inst. Mar. Sci., University of Alaska, Fairbanks. 111 p.

Heggie, D. T. and D. C. Burrell. 1979. Sediment-seawater exhanges of nutrients and transition metals in an Alaskan fjord. Proceedings Fjord Oceanographic Workshop, Victoria, B.C., June 1979, in press.

Muench, R. B. and D. T. Heggie. 1978. Deep water exchange in Alaskan sub-arctic fjords, pp. 239-267. *In*: B. Kjerfve (ed.), Estuarine Transport Processes. University of S. Carolina Press, Columbia, S. Carolina.

Niebauer, H. J. 1979. A numerical model of circulation in a continental shelf — silled fjord coupled system. *Estuar. Coast. Mar. Sci.*, in press.

Owens, T. L., D. C. Burrell and H. V. Weiss. 1979. Reaction and flux of manganese within the oxic sediment and basin water of an Alaskan fjord. Proceedings Fjord Oceanographic Workshop, Victoria, B.C., June 1979, in press.

Ozretich, R. S. 1975. Mechanism for deep water renewal in Lake Nitinat, a permanently anoxic fjord. *Estuar. Coast. Mar. Sci.* 3:189-200.

Pickard, G. L. 1967. Some oceanographic characteristics of the larger inlets of southeast Alaska. *J. Fish. Res. Bd. Can.* 24:1475-1506.

Pickard, G. L. and B. R. Stanton. 1979. Pacific fjords: A review of their water characteristics. Report No. 34. Department Oceanography, University British Columbia, 66 p.

Rattray, M. 1967. Some aspects of the dynamics of circulation in fjords, pp. 52-62. *In*: C. H. Lauff (ed.), Estuaries. Assoc. Advance. Science Publ. No. 83, Washington, D.C.

Royer, T. C. 1975. Seasonal variations of waters in the northern Gulf of Alaska. *Deep-Sea Res*. 22:403-416.

APPENDIX IV

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

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General

The elemencs selenium and chromium fall into the category of being essential to biological systems and yet toxic to them if the concentrations exceed very low limits. While both elements are readily detectable in sediments and biological tissue, they are very dilute in seawater. Aside from radioactivity and gas chromatographic methods, selenium and chromium species would have to be preconcentrated from seawater before normal survey work by atomic absorption could be achieved. Proper storage procedures for selenium have nevery been published.

Selenium

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

The principle species of selenium in seawater is selenite with concentrations on the order of 50 to 500 ppb; most commonly at the low end of the range.

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

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

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

Chromium

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

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

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

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

GAS CHROMATOGRAPHIC ANALYSIS OF SELENIUM AND CHROMIUM

General

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

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

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

Selenium

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

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

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

Chromium

The analysis of chromium by gas chromatography is a relatively simple matter. The chelate compound is very stable and may be stored for an indefinite period of time with reasonable care. It is advantageous to accomplish the analysis at sea because the electron capture detector gas chromatographic set up for selenium is the same for chromium except for a temperature adjustment to the column.

The only interference is contamination by aluminum, but this can be eliminated by a base wash. Occasionally other interference due to polymers of the reagent (trifluoroacetylacetone) crops up.

Both the hexavalent and trivalent valent forms of chromium are detected simultaneously by this procedure.

SYNOPSIS OF RESULTS

Selenium

Water. The average open ocean concentration of seawater is about 100 ppb. We have observed in the study areas the concentration is usually below a detection limit of ∿0.05 ppb. When the values are higher it is usually for surface waters, and seemingly for those rich in biota.

Sediment. Only surface oxygenated sediments have been studied. Again in keeping with expectations, the majority of samples are below the detection limit of about 10 ppb. Most detectable quantities are between 15 and 30 ppb with a few highs up to 200 ppb.

Biota. Selenium in this material is highly variable from the normal average of a few tenths of a ppm to more than 10 ppm for specific organs. Gelatinous material in Beaufort Sea water was observed to contain the equivalent of 4 ppb of selenium per liter of seawater.

Chromium

Water. Most samples contained about 0.3 ppb of chromium. A fair number were near or below the detection limit of about 0.02 ppb. High values were < 2 ppb. Raw water values were slightly higher (factors of 1 to 4) with samples nearer coastal influence showing the highest values.

Sediments. Numerous surface sediment analyses have been reported in the range of 0.2 to 6 ppm. Most analyses are around 1-2 ppm. A few are below the 0.2 ppm level.

Biota. Samples have not as yet been recorded.

CONCLUSIONS

The only unusual character to these analyses are the water samples which are lower than average values for both selenium and chromium, particularly the former. Surface sediment and biological materials appear normal.

Chromium shows a completely normal clean environment picture, with the water on the low side of average. Coastal sediment has some influence on raising the water column values slightly.

Selenium also shows a clean environment. The water column is particularly devoid of selenium except surface waters when copious biological material is present.

CHARACTERIZATION OF ORGANIC MATTER IN SEDIMENTS FROM GULF OF ALASKA, BERING SEA, AND BEAUFORT SEA

by

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Final Report
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Research Unit 480

June 1981

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ACKNOWLEDGEMENTS

We gratefully acknowledge the following individuals for their contributions that made this report possible:

Research Scientists: Mark Sandstrom, who took an active interest in the initial stages of the project in sample collection and analysis; Shmuel Brenner, who helped to organize the project; Edward Ruth, who performed GC/MS analysis of the samples; and Jaime Bonilla, who participated in the laboratory sample preparations.

Technicians: David Meredith, Dana Blumfield, Dara Blumfield, Tom Fisher, Tim Maloney and Vicky Meyers.

Report Production: Lynne Newton

Graphics: Jean Sells and Lowell Weymouth

We would like to thank Dr. Walter E. Reed for his encouragement in the initial stages of this project, E. Ruth, D. Winter, D. Meredith and J. Haines (University of Louisville, Kentucky) and J.W. Wiggs (University of Alaska) for sample collection and the crews of the ships: DISCOVERER, USCGS GLACIER, SEA SOUNDER, SURVEYOR AND USCGS POLAR STAR for their cooperation in collecting the sediment samples.

SPECIAL NOTE

This is the final report of our investigations of the high molecular weight hydrocarbons in the Alaskan continental shelf. Most of the data presented here also have been presented in our earlier annual reports. Because of refinements and revisions in the analytical procedures, numbers presented in the text, tables and figures of this final report may differ from and supersede those in the earlier versions.

SUMMARY

The distribution and concentration of high molecular weight hydrocarbons in surficial sediments from the outer continental shelf of Alaska were determined as part of an environmental survey. Sediments were collected from the proposed lease areas of Beaufort Sea, southeastern Bering Sea, Norton Sound, Navarin Basin, Gulf of Alaska, Kodiak Shelf and Cook Inlet. The objectives of the investigation were: 1) to establish the baseline hydrocarbon levels of sediment samples in the areas, 2) to characterize the distribution and nature of these hydrocarbons, 3) to assess the possible source of the hydrocarbons in surface sediments, whether biogenic or anthropogenic, and 4) to understand the probable pathways of hydrocarbon transport in the area in case of an oil spill. The sediment samples were analyzed for total carbon, organic carbon, aliphatic and aromatic hydrocarbon contents. Capillary gas chromatography and gas chromatography-mass spectrometry techniques were utilized to study the hydrocarbon components. Our extensive investigations indicate that the sediment in the study areas is generally unpolluted with a very few exceptions. Beaufort Sea sediments have the highest hydrocarbon budget while Kodiak Shelf sediments have the lowest. The characteristics of the aliphatic hydrocarbons are typical of a mixture of marine autochthonous and terrestrial allochthonous components. Norton Sound and Cook Inlet sediments contain the highest and Kodiak Shelf, the lowest levels of terrigenous input while the other areas shown intermediate trend. The distribution of polycyclic aromatic hydrocarbons (PAH) is complex and shows a pyrolytic source in all the study areas. Bioaccumulation of PAH is probably prevalent in Gulf of Alaska and Kodiak Shelf areas.

Two stations, north of Kalgin Island, in lower Cook Inlet and one station in southeastern Bering Sea show typical weathered petroleum distribution of

n-alkanes and triterpenoids. The hydrocarbons distribution pattern in the sediments suggest that petroleum hydrocarbons released from any major spill, tank or pipeline blowout in upper Cook Inlet would be dispersed and redeposited eventually in Shelikof Strait and possibly in Gulf of Alaska, west of Kodiak Shelf. The distribution profile of especially n-alkanes and perylene in Navarin Basin would indicate that any petroleum contaminant from production activities in Norton Sound or southeastern Bering Sea could affect Navarin Basin equally or more than the other two areas.

Presence in large amounts of the relatively labile polyolefins in a few stations in southeastern Bering Sea and Gulf of Alaska, and, in all the stations in Kodiak Shelf and Navarin Basin implies relatively less oxidizing depositional environment. Such areas where sediments apparently accumulate and preserve labile lipids would be most affected by pollutants introduced into the marine environment.

The above-mentioned sensitive areas should therefore be the main target of any future environmental monitoring program whenever fossil fuel developments are carried out in the vicinity.

INTRODUCTION

General Nature and Scope of Study

This final report describes the progress made during the period July 1975 through December 1980 in a study of the abundance and dynamics of hydrocarbons in the surface sediments from the Alaskan continental shelf. A knowledge of the baseline levels of classes of hydrocarbons and specific hydrocarbon pollution indicators in the marine sediments is very important in order to assess any environmental impact by petroleum development on the outer continental shelf.

The first year cruise experience (1975-1976), emphasized the importance of proper sampling devices and the methods of collection. The objectives of the 1976-1977 studies were to develop a set of experimental conditions that would yield reproducible results in the trace analysis so that it could be used on a routine basis for several samples. After this goal was reached, the samples were analyzed and the hydrocarbons were quantitatively estimated in the sediments from different parts of the Alaskan area.

From 1977 to 1979, the emphasis was diverted to the Lower Cook Inlet area and several cruises were conducted to collect sediment samples in view of the oil development in Upper Cook Inlet.

The objectives of the 1979-1980 programs were to provide more information on the sediments from Norton Sound and Navarin Basin.

Specific Objectives

The objectives of this investigation were to achieve the following results:

1. To establish the baseline hydrocarbon levels in the sediments from the proposed lease areas in the Alaskan continental shelf by measuring aliphatic and aromatic hydrocarbons.

2. To characterize the distribution and nature of these hydrocarbons.

3. To assess the possible source of the hydrocarbons, in surface sediments; whether biogenic or anthropogenic.

4. To understand the probable pathways of hydrocarbon transport in the event of oil spill in the areas.

Relevance to Problems of Petroleum Development

Sediment samples were collected from proposed lease areas in the Alaskan Seas. Oil production and transport is well established in Beaufort Sea and it had started in upper Cook Inlet. Exploratory drilling has been performed on six out of 87 blocks leased in lower Cook Inlet from October, 1977. The second part of the sale in lower Cook Inlet, with Shelikof Strait, is scheduled for September, 1981 (Wright, 1980). Information on the present level of hydrocarbons in these areas is required to assess, in the future, any chronic pollution arising from offshore drilling for oil and gas, or any residual effect resulting from an accidental spill or blow-out. The baseline data should therefore be helpful in monitoring the cleanliness of the future Alaskan marine environment.

Current State of Knowledge

Studies on the Alaskan Seas are relatively scant to date. Hydrocarbons and their possible precursors were investigated in the few samples in Beaufort Sea by Peake *et al*. (1972). Aliphatic and aromatic hydrocarbons have been analyzed by Shaw *et al*. (1979) in Beaufort Sea nearshore sediments. Aromatic hydrocarbons in fish and sediment in Prince William Sound, northeast Gulf of Alaska, have also been reported (Chester *et al*., 1976). An extensive and informative study on hydrocarbons in sediments, water, organisms and fish in Beaufort Sea, along the Canadian border, was published by Wong *et al*. (1976).

Studies undertaken by our group on organic constituents of sediments from different parts of the Alaskan Seas are probably the most extensive investigations of hydrocarbons in this area as far as we know. Our data from analyses of sediments from the study area indicate that the Alaskan continental shelf is generally unpolluted except in a very few stations.

STUDY AREA AND CRUISES

We have analyzed samples from all regions of interest to NOAA/OCSEAP: the Beaufort Sea, the Bering Sea, the Gulf of Alaska, Kodiak Shelf, Norton Sound, Cook Inlet and Navarin Basin. The details of when, where and how samples were collected are specified in Table 1. Station locations are presented in Figures 1-8.

METHODS

Sediment samples were kept frozen from the time of collection until the beginning of anlaysis.

Elemental Analysis*

Elemental sulfur analysis was carried out on freeze-dried sediment samples. Twenty to forty milligrams of the powdered sample was combusted with the accelerator (Cu chips and Fe filings) in a LECO (Laboratory Equipment Corporation) induction furnace (Model No. 523). The resulting sulfur gases were titrated according to ASTM procedure E30-47, using a LECO (Model No. 517) titrator. The total sulfur content was corrected for sea salt sulfate content. Total carbon and organic carbon (that remaining after treatment with 3N HCl) were measured with a LECO acid-base semi-automatic carbon determinator or on a LECO No. 589-600 Low Carbon Analyzer.

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* The details of the procedures are given in the respective manuals of LECO, 3000 Lakeview Avenue, St. Joseph, Michigan 49085

Analysis of High Molecular Weight Hydrocarbons

Initially, a methodology recommended by BLM was followed to analyze the sediment samples from the eastern Bering Sea and Gulf of Alaska. These samples had to be cleaned by thin-layer chromatography to remove the methyl esters from aromatic compounds eluted by benzene (Kaplan *et al.*, 1977). This methodology was improved subsequently to avoid contamination from freeze drying and to obtain ester-free aromatic hydrocarbons. Freeze-drying was replaced by wet extraction with methanol. Based upon a suggestion by R. Bieri (Virginia Institute of Marine Science), only silica gel was used instead of the original silica gel--alumina column chromatography. The solvent mixture, hexane: benzene (3:2 V/V) was found to elute only the aromatic hydrocarbons, leaving behind the esters in the column. The following methodology incorporating these modifications was adopted for all the samples in our program except for the above-mentioned two areas.

A pre-cleaned cellulose thimble of known weight was filled to approximately 2/3 of its capacity with a thawed sediment sample and placed in a beaker-like funnel. The interstitial water was allowed to drain into an Erlenmeyer flask. The sediment was then washed with about 150 ml of organically clean double-distilled water to remove salts. The filtrate and the interstitial water was extracted three times with 25 ml of hexane and saved for later analysis (A).

The wet sample in the thimble was extracted in a Soxhlet extractor with 500 ml of methanol for 24 hours and then with 500 ml of toluene:methanol (3:7) for 76 hours. The methanol extract was concentrated to 100 ml, added to a separatory funnel with clean water and extracted with 100 ml of hexane three times (B). If an emulsion formed, saturated NaCl solution was added before extracting into hexane. The hexane fractions (A and B) were combined with the toluene: methanol extract and concentrated to about 5 ml.

Activated copper wire was dipped into the extract to test for sulfur. If a blackening of the wire was observed, the sulfur was removed by passing the extract through a column of activated fine copper granules (J.T. Baker). The eluate was concentrated to 5 ml and saponified by refluxing for four hours with 40 ml of 1N KOH in 1:1 water:methanol. A 5Å molecular sieve trap on top of the condenser prevented contamination from external sources. The mixture was then diluted with an equal volume of saturated sodium chloride solution. If no emulsion was observed, the mixture was extracted three or four times with hexane and concentrated with a rotary evaporator. If an emulsion did occur, the extract was centrifuged three times with hexane in a glass jar with a teflon-lined cap. The organic phases were combined and back-extracted with an equal volume of saturated sodium chloride solution. The aqueous solution was then re-extracted once with hexane and all the organic phases combined and concentrated to 2 ml. This non-saponifiable fraction was transferred to a 2 ml vial using a glass syringe and the solvent was removed on a sand bath at 40°C under a stream of nitrogen. A subsample of about 5 $\mu\ell$ was transferred onto the pan of a Mettler ME22 electrobalance and the residue after evaporation of the solvent was weighed. The weight was extrapolated to the total volume of the fraction.

Pre-cleaned silica gel was activated at 235°C for 16 hours and packed with hexane in a column with a length-to-i.d. ratio of 20. A weight ratio of 200 parts of silica gel to one part of the sample was used. Aliphatic hydrocarbons were eluted with ∿ 1 column volume of hexane, after the void volume was discarded. Alkenes containing less than four double bonds were also eluted by hexane. Aromatic hydrocarbons were eluted with ∿ two column volumes of 3:2 hexane:benzene mixture. Highly unsaturated alkenes and cycloalkenes eluted along with 2- to 7-ring aromatic hydrocarbons. The fractions were reduced to 100-150 $\mu\ell$ and weighed on the Mettler as before, prior to gas chromatography.

The amount of hexane extractable lipids (nonsaponifiable) determined the size of column used in column chromatography. The conditions of column operations as standardized in our laboratory are given in the following table:

Total mg Non-saponifiable lipid	Column Internal Diameter	Silica gel for column (g)	Height of silica column (cm)	Hexane (ml)		Hexane:Benzene 3:2 (ml)	
				Reject volume	Elution volume	Reject volume	Elution volume
0 - 12.5	0.7	~2.5	14	1.5	8	2	12
12.5- 35	1.0	~7	17.5	5.0	15	7	25
35 - 130	1.5	~ 26	30	20	50	25	100
130 - 230	1.9	~ 46	38	35	90	45	175
> 230:	Use percentage of sample adequate to run in the column with ID 1 cm or 1.5 cm						

Materials

1. Solvents

All solvents used were high purity grade solvents (Burdick and Jackson "distilled in glass" grade). The chemicals were of A.R. grade.

2. Water

Trace organics were removed from double-distilled water by passing it through a column of Chromosorb 102, which was prewashed with dichloromethane.

3. Soxhlet Thimbles

Single thickness cellulose (Whatman) thimbles were shaken three times overnight with toluene:methanol 3:7 in glass jars on a shaker table.

4. Glassware

All glassware was cleaned with detergent, dipped in chromic-sulfuric acid solution, and rinsed successively with distilled water and methanol and dried at 110°C. Before use, the glassware was rinsed with dichloromethane as well as the solvent to be used in extraction. Syringes were sonicated three times in dichloromethane and then rinsed once with the same solvent.

5. Silica Gel

Silica gel was first sonicated with dichloromethane-methanol and then with hexane prior to activation.

6. Sodium Chloride

NaCl was heated overnight at 500°C.

7. Potassium Hydroxide

KOH was fued at 500°C for two hours in a nickel crucible.

8. Copper Granules

Copper granules were cleaned successively with 6N HCl, acetone and hexane.

Samples collected in 1975 were analyzed by Hewlett-Packard Model No. 5830A gas chromatograph with FID detector. A glass SCOT column, 50m x 0.5 mm, coated with OV-101 (SGE Scientific, Inc.) was used. The aliphatic fractions and aromatic fractions of Cook Inlet sediment samples studied in 1977 were analyzed by modified Varian 1400 and 1520C gas chromatographs, respectively. They were equipped with a Grob injector and glass capillary columns (OV-101, J&W). The remainder of the samples in the program were analyzed by Hewlett-Packard Model No. 5840A gas chromatgraph equipped with 30m x 0.25 mm glass capillary column coated with OV-101 (J&W). Navarin Basin (1980) samples were analyzed in the same instrument, but with a fused silica capillary column (SP 2100, 25 m x 0.2 mm). Helium was used as a carrier gas. A detailed methodology concerning samples of a particular cruise is given in the annual reports (Kaplan et al., 1977, 1979, 1980; Brenner et al., 1978).

The integrated areas were fed into a PDP 11/10 computer and the concentrations of individual hydrocarbons on dry weight sediment basis were computed.

Gas chromatographic-mass spectrometric analyses (GC/MS) were carried out on a Finnigan model 4000 Quadrupole Mass Spectrometer directly interfaced with a Finnigan Model 9610 gas chromatograph. The GC was equipped with a glass capillary

(OV-101 J&W) for the analyses of aliphatic fractions. The aromatic fractions were analyzed using a SE 54 (J&W) glass capillary column. The GC/MS analyses of Navarin Basin samples were performed with a fused silica capillary column as described for gas chromatography. The mass spectrometric data were acquired and processed using a Finnigan Incos Model 2300 data system. About 25% of all the fractions separated by column chromatography (10-15% of the number of sediment samples studied in the program) were analyzed by GC/MS.

Data of all the samples were submitted on 044 format to the Data Center at Washington, D.C. Due to the complexity of distribution of numerous isomers, the identification of an aromatic component by GC/MS in one sediment sample cannot be extrapolated to a peak with the same Kovats index in another sample. It is not possible to run all the fractions (over 200) in GC/MS either. For the above reasons, concentrations of the aromatic hydrocarbon components were computed only for those samples run by GC/MS and reported on the coding sheets. The discussion on individual aromatic compounds is therefore restricted to GC/MS data only in this report.

RESULTS

Elemental analysis (total and organic carbon), complete gravimetric and gas chromatographic data have been submitted in earlier quarterly and annual reports for all the sediments analyzed in the program. We present here only a summary of selected organic geochemical data for each area studied in tables from 2 through 13. Data on polycyclic aromatic hydrocarbons presented in tables 11-13 refer to the resolved PAH compounds identified by GC/MS and quantitated by external standards. The total resolved PAH discussed in the text of this report refer to the sum of only those PAH compounds listed in the tables. Table 14 contains the comparative organic geochemical data from different areas in the Alaskan Shelf. Figures 1-8 show the station locations at different cruises. Gas chromatograms of hexane and hexane:benzene fractions of representative samples from various areas are presented in Figures 9 through 14. The relative distribution of extended di- and triterpenoids of sediments from a few stations are represented in figures 15-18 based upon the m/z 191 peak intensity from GC/MS analyses. Pertinent analytical results from sediments of different areas are summarized in Figure 19 for comparison. Appendix I shows the structures cited in the text. A detailed discussion on the organic geochemistry of Navarin Basin sediments is presented in this report since the samples were collected and analyzed after the submission of our last annual report in April, 1980.

Table 1. Areas of sediment sampling for heavy molecular weight hydrocarbon study from the Alaskan Shelf

Area	Date of Collection	Cruise	Sampler type	No. of samples analyzed
Southeastern Bering Sea	9/75	Discoverer	Steel Van Veen grab sampler	21
Gulf of Alaska	10/75			20
Beaufort Sea	8/76	USCGS Glacier	Aluminum Van Veen	11
Norton Sound	10/76	Sea Sounder	Modified Aluminum Van Veen sampler	18
	7/77			12[1]
	7/79	Discoverer		21
Kodiak Shelf	7/76	Sea Sounder	Van Veen sampler	15
Cook Inlet	6/76	Sea Sounder	Van Veen sampler	23
	11/77	Surveyor	Van Veen sampler	9[2]
	4/78	Discoverer	Van Veen sampler	18
	8/78	Discoverer	Van Veen sampler	17
	5/79	Discoverer, Miss Vicki Ann (Charter boat)	Van Veen Sampler Shipek grab sampler, mud snapping, sampling device	14
Navarin Basin	4/80	USCGS Polar Star	Modified Van Veen, small Van Veen	28[3]

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[1] Four samples were collected from vibracores and box cores by Dr. K. Kvenvolden's group, USGS, California.

[2] Collected by Ms. J.W. Wiggs of University of Alaska.

[3] Collected by J. Haines of the University of Louisville, KY.

Table 2. Gravimetric and gas chromatographic data of Beaufort Sea sediment samples (1976 cruise)

Station Number*	Aliphatic Fraction[a] (μg/g)	Aromatic Fraction[a] (μg/g)	n-Alkanes (μg/g)[a]	Org. C (%)	$\frac{HC}{OC}\times10^4$ [b]	$\frac{n\text{-Alkanes}}{OC}\times10^4$ [c]	Pr/Ph	$\frac{Odd}{Even}$ [d]
1	14.31	9.42	2.99	0.89	26.7	3.41	1.60	3.37
2	24.88	15.49	1.44	0.74	54.6	2.03	1.32	4.29
3	41.02	18.7	3.36	0.91	65.6	3.69	1.82	1.78
4	36.30	14.11	3.12	0.63	80.0	4.43	2.04	3.37
5	28.43	13.99	3.21	0.83	51.1	3.91	2.11	3.58
6	19.87	12.56	4.63	1.01	32.1	4.91	1.82	3.57
7	12.83	8.46	2.09	0.79	27.0	2.88	2.55	3.25
8	16.46	12.65	4.17	0.39	74.6	10.88	2.50	3.83
9	23.73	9.40	3.73	0.68	48.7	5.53	1.73	3.53
10	34.53	14.59	5.08	0.63	78.0	8.17	1.89	3.91
11	22.44	12.15	1.84	0.51	67.8	3.67	1.67	5.00

* All are surface samples except 11 which is a bulk sample. Elementary sulfur was detected only in Sample 11.

a = Based on extracted dry sediment.

b = HC = total hydrocarbons, sum of aliphatic and aromatic fractions in μg/g dry sediment; OC = organic carbon

c = n-alkanes resolved by gas chromatography

d = odd/even = summed from C_{15} to C_{34}.

Pr = Pristane; Ph = Phytane

Table 3. Gravimetric and gas chromatographic data of Southeastern Bering Sea Sediment Samples

Station Number*	Aliphatic fraction (μg/g)[a]	Aromatic fraction (μg/g)[a]	*n*-Alkanes (μg/g)[a]	Organic carbon (%)	$\frac{HC}{OC} \times 10^{4}$[b]	$\frac{n\text{-alkanes}}{OC} \times 10^{4}$[c]	$\frac{Pr}{Ph}$	$\frac{Odd}{Even}$[d]
8	5.7	2.8	0.56	0.23	36.9	2.4	2.70	2.99
12	3.4	1.4	0.33	0.14	34.3	2.3	3.32	1.76
17	13.0	5.2	1.09	0.76	23.9	1.4	3.97	3.43
19	7.4	4.5	2.57	0.39	30.5	6.6	5.81	3.17
24	6.1	5.4	0.66	0.33	34.8	2.0	3.39	2.96
28	8.7	4.1	2.93	0.59	21.7	5.0	10.20	4.09
35	180.1	60.8	n.r.	0.41	587.6	n.r.	n.r.	n.r.
37	5.8	4.0	0.76	0.41	23.9	1.8	1.76	3.28
38	4.9	10.6	1.64	0.66	23.5	2.5	5.18	4.41
40	1.9	2.6	0.61	0.32	14.1	1.9	3.37	3.41
41	1.4	0.5	0.41	0.37	5.1	1.1	n.d.	3.80
43	2.4	2.7	0.52	0.30	17.0	1.8	2.26	3.08
46	4.3	7.5	0.74	0.42	28.1	1.8	17.90	3.59
51	2.8	0.6	0.77	n.d.	25.4	n.d.	3.49	2.56
54	7.4	9.9	2.10	0.68	25.4	3.1	8.80	2.57
56	10.6	8.5	0.75	0.47	40.6	1.6	2.93	3.78
58	3.8	2.8	0.28	0.31	21.3	0.9	4.80	3.33
59	6.4	6.2	1.55	0.27	46.7	5.7	1.74	2.85
64	12.3	9.8	1.79	0.77	28.7	2.3	2.27	2.75
65	6.9	9.6	1.60	0.67	24.6	2.3	16.43	3.77
45B	3.9	4.9	0.78	0.76	11.6	1.0	3.78	1.96

* = Bulk samples of the upper 0-10 cm of surface sediment

n.r. = not resolved
n.d. = not determined

For explanation of the remainder of the symbols and abbreviations, see Table 2.

Table 4 . Gravimetric and gas chromatographic data of Norton Sound sediment samples

Station No.*	Aliphatic fraction (μg/g)[a]	Aromatic fraction (μg/g)[a]	*n*-alkanes (μg/g)[a]	Organic carbon (%)	$\frac{HC}{OC} \times 10^4$ [b]	$\frac{n\text{-alkanes} \times 10^4}{OC}$ [c]	$\frac{Pr}{Ph}$	$\frac{Odd}{Even}$ [d]
1976								
47	9.6	7.5	3.28	0.93	18.4	3.7	2.00**	5.38
49	24.8	4.1	5.69	1.12	25.8	5.1	1.50**	6.06
70	2.2	6.2	0.01	0.31	27.1	0.1	8.00	1.65
88B	3.9	5.7	0.69	0.53	18.2	1.3	2.14	4.11
105	1.8	0.9	0.07	0.93	2.9	0.1	n.d.	11.21
125	0.1	2.4	0.69	1.18	2.6	1.3	2.00	4.02
131	9.0	2.9	7.18	0.96	27.3	6.3	n.d.	2.80
137	17.8	4.5	8.69	n.d.	n.d.	n.d.	3.00**	4.07
147	6.8	2.3	2.24	0.33	27.5	6.8	1.80**	2.85
154	16.3	4.2	5.45	0.99	20.7	5.5	3.60**	5.69
156	7.1	5.5	5.06	1.30	9.7	3.9	2.67**	5.57
162	2.3	2.3	0.45	0.92	5.0	0.5	2.00**	4.75
166S	1.1	0.8	0.16	1.16	1.6	0.1	4.00**	5.16
168S	3.2	2.2	1.48	1.10	4.9	1.4	3.50**	5.26
169S	2.6	4.0	0.95	0.33	20.1	2.9	3.60	4.47
170S	4.4	2.2	2.57	0.52	12.8	4.9	n.d.	5.80
172S	10.9	3.8	2.89	0.87	16.9	3.3	n.d.	4.70
174S	3.9	2.0	1.79	0.82	7.2	2.2	6.00**	4.50
1977								
34	0.8	0.7	0.09	0.12	12.4	0.8	2.0**	4.55
35	2.2	1.1	0.57	0.59	5.7	0.9	7.0**	5.15
39S	0.6	0.2	0.09	0.38	2.3	0.2	2.5**	5.35
41S	2.5	0.8	0.23	0.44	7.5	0.5	4.0**	4.78
42S	4.4	1.9	0.83	0.32	19.9	2.6	5.5**	4.78
43	1.0	1.7	0.38	0.60	4.5	0.6	6.5**	4.22
44	2.1	0.9	0.25	0.52	5.7	0.5	6.0**	3.21
48S	5.8	5.0	1.60	4.23	2.6	0.4	5.0**	6.37
14¶	5.4	1.3	1.22	0.28	23.8	4.4	3.1**	5.26
17¶	5.5	2.7	1.75	0.24	18.9	2.0	1.3**	5.12
17†	14.1	2.2	2.18	0.86	26.3	6.4	3.0**	5.67
17§	3.2	0.9	0.95	0.50	8.0	1.9	4.0**	5.34

Table 4 . Gravimetric and gas chromatographic data of Norton Sound sediment samples (continued)

Station No.	Aliphatic fraction (μg/g)	Aromatic fraction (μg/g)	n-Alkanes (μg/g)	Organic carbon (%)	$\frac{HC}{OC} \times 10^4$	$\frac{\text{n-alkanes}}{OC}$	$\frac{Pr}{Ph}$	$\frac{Odd}{Even}$
1979								
1	4.7	3.3	3.54	0.72	11.1	4.9	0.75	3.37
1††	17.6	3.8	4.29	--	--	--	--	2.76
5	17.8	8.8	5.53	0.74	35.9	7.7	--	3.91
5§§	20.1	4.1	6.41	--	--	--	2.82	3.89
7	9.7	6.1	4.32	0.57	27.7	7.6	--	3.80
8	1.6	1.5	0.59	0.46	6.7	12.9	1.71	3.27
13	4.5	5.1	2.08	0.38	25.2	5.5	1.65	4.32
15	4.0	1.8	1.63	0.48	11.9	3.4	2.47	3.81
18	3.2	1.5	2.22	0.48	9.8	4.6	1.86	4.04
20	5.4	1.5	1.50	0.40	17.3	3.8	--	4.03
21	9.1	5.1	2.85	0.47	30.2	6.1	--	4.40
22	8.9	5.5	2.83	0.86	16.8	3.3	2.44	3.35
25	5.2	2.0	1.57	0.66	10.8	2.4	--	4.12
29A	2.8	1.0	1.38	0.41	9.3	3.4	1.50	4.33
29B	3.9	lost	1.34	0.54	--	2.5	--	3.56
33A	1.7	0.9	0.29	--	--	--	--	4.09
36	8.7	1.7	1.74	--	--	--	--	3.97
40	2.3	0.1	0.06	0.17	14.1	0.4	--	5.27
47A	1.4	1.1	0.44	--	--	--	--	4.29
49	2.5	3.0	0.61	--	--	--	8.88	4.18
50	1.7	1.9	0.25	0.28	12.9	0.9	--	3.87

Samples are 0-2 cm except B = bulk; S = surface; ¶ = 0-3 cm; † = vibracore, 0-3 cm; § = 160 cm vibracore, (USGS): †† = 15-25 cm; §§ = 82-90 cm; Samples 14-17 belong to a different program (USGS). ** Approximate values based upon peak heights. For explanation of remainder of symbols and abbreviations, see Table 2.

Table 5. Gravimetric and gas chromatographic data of Navarin Basin sediment samples (1980 cruise)

Station Number*	Aliphatic Fraction (µg/g)[a]	Aromatic Fraction (µg/g)[a]	n-Alkanes (µg/g)[a] µg/g	Organic C (%) mg/g	$\frac{HC}{OC} \times 10^4$ [b]	$\frac{n\text{-Alkanes}}{OC} \times 10^4$ [c]	$\frac{Odd}{Even}$ [d]
2	8.13	2.24	0.27	0.49 4.9	21.2	0.57	3.99
3	1.37	1.74	0.32	0.89	3.5	0.37	4.88
4	1.93	2.49	0.30	0.36	12.3	0.84	4.88
5	2.25	2.93	0.42	0.43	12.0	1.00	4.77
6	4.86	3.75	0.52	0.59	14.6	0.89	4.75
7	7.16	9.18	1.45	1.04	15.7	1.40	4.85
8	15.38	7.31	1.93	--	--	--	4.88
9	11.51	4.78	1.52	0.90	18.1	1.70	4.74
10	4.82	8.21	1.63	1.08	12.1	1.52	4.84
12	18.02	8.67	1.28	0.96	27.8	1.34	4.10
13	1.83	2.83	0.52	0.68	6.9	0.77	4.27
14	8.94	11.93	1.98	1.20	17.4	1.65	4.10
15	8.33	6.81	1.98	1.18	12.8	1.68	3.55
16	21.83	7.20	1.60	1.02	28.5	1.58	3.75
17	6.01	10.65	1.30	1.15	14.5	1.14	4.26
18	47.50	4.97	1.60	1.18	44.5	1.36	3.72
19	7.55	9.17	1.37	0.98	17.1	1.41	4.00
20	34.66	10.40	1.83	--	--	--	4.15
21	12.32	16.50	2.63	1.07	26.9	2.46	4.38
22	8.03	9.25	1.39	1.08	16.0	1.29	4.07
23	8.68	5.58	1.46	0.85	16.8	1.73	4.60
24	29.63	14.82	1.86	1.12	39.7	1.67	4.18
25	1.95	2.73	0.24	1.38	3.4	0.18	3.67
26	1.63	0.78	0.48	0.27	8.9	1.81	4.29
28	4.41	6.23	0.77	0.42	25.3	1.85	4.45
30	4.04	1.14	0.20	0.19	27.3	1.07	3.55
32	7.56	2.13	0.28	0.20	48.5	1.41	4.42
33	7.07	1.36	0.42	0.32	26.3	1.31	4.08

*Samples 2-10 are from 0-2 cm taken with modified Van Veen grab sampler; 12-33 are predominantly surface, but taken with a small Van Veen sampler.

For explanation of remainder of symbols and abbreviations, see Table 2.

Table 6. Aliphatic Hydrocarbon Concentrations (ng/g) in 1980 Navarin Basin Sediment Samples

Station†	$\underline{n}$-C$_{17}$	Pristane	$\underline{n}$-C$_{18}$	$\underline{n}$-C$_{19}$	$\underline{n}$-C$_{20}$	$\underline{n}$-C$_{21}$	$\underline{n}$-C$_{22}$	$\underline{n}$-C$_{23}$	$\underline{n}$-C$_{24}$	$\underline{n}$-C$_{25}$
2					2	9	8	24	11	35
3		1	1	2	2	22	8	25	12	38
4				1	2	15	8	23	11	34
5	1	2	1	3	4	36	12	32	16	45
6	2	4	2	4	5	35	14	41	20	59
7	4	6	4	8	11	116	36	111	53	167
8		3	2	9	12	145	48	150	70	222
9	4	11	3	7	10	104	40	124	58	180
10	3	9	3	10	11	76	43	133	61	194
12				6	9	37	34	110	49	156
13	1		2	4	5	10	15	45	21	64
14			3	9	15	55	54	168	75	238
15	4		5	13	19	51	63	191	86	268
16				9	13	31	46	142	61	195
17	2	1	3	7	11	16	39	121	56	172
18				9	14	32	51	160	66	209
19			2	7	10	39	37	113	52	161
20				7	12	51	47	153	66	221
21			3	11	16	53	71	220	104	324
22	3	4	3	6	9	36	35	109	51	161
23	4	4	4	11	12	79	39	120	58	180
24				9	12	47	44	144	66	222
25		3		3	4	19	13	36	15	41
26			1	2	4	17	17	52	23	69
28	2		2	5	7	25	23	70	30	98
30	2		2	2	3	8	8	21	9	25
32					2	9	10	30	12	39
33				3	4	14	13	41	17	54

† = Samples 2-10 are from 0-2 cm taken with the modified Van Veen grab sampler. 12-33 are predominantly surface but taken with a small Van Veen sampler. $\underline{n}$-C$_{15}$ was detected only in samples 9 and 23 at the level of 2 ng/g; $\underline{n}$-C$_{16}$ was detected only in samples 9, 23 and 30 at the level of 2 ng/g; Phytane was not detected in any of the samples.

Table 6. (Continued)

Station†	n-C_{26}	n-C_{27}	n-C_{28}	n-C_{29}	n-C_{30}	n-C_{31}	n-C_{32}	n-C_{33}	n-C_{34}	Total n-Alkanes
2	11	61	8	44	14	40	2	11		279
3	13	66	10	50	5	55	4	16	1	328
4	12	60	10	55	5	50	3	15		304
5	15	79	11	70	7	67	5	22		428
6	20	106	15	82	8	79	5	26		525
7	56	291	41	226	22	211	14	71		1454
8	75	393	57	311	33	290	18	92	4	1931
9	61	318	45	240	25	219	13	65	3	1528
10	64	343	48	272	27	246	14	76	4	1637
12	51	270	35	214	54	179	9	59		1282
13	21	107	17	90	9	79	5	25		524
14	79	410	59	330	75	292	17	92	4	1985
15	90	466	79	431	50	395	25	125	5	1984
16	63	330	44	260	77	232	17	70		1607
17	57	286	40	217	29	183	11	56	3	1308
18	66	329	42	240	74	214	10	71		1603
19	55	282	42	230	55	206	12	65	3	1377
20	76	382	53	299	72	275	15	93		1838
21	113	563	84	437	51	408	26	130	6	2635
22	55	286	42	239	58	216	13	67	3	1398
23	63	316	48	255	29	239				1467
24	77	389	56	315	68	287	21	93		1865
25	12	49	6	26	13	18		4		248
26	21	103	13	74	7	62	4	18	1	489
28	31	168	22	127	17	106	6	33	1	776
30	8	38	5	28	6	26		8		204
32	13	62	8	43	8	38		9		282
33	17	87	11	63	15	58	3	18		420

Table 7. Gravimetric and gas chromatographic data of Western Gulf of Alaska sediment samples (1975 cruise)

Station Number *	Aliphatic fraction (μg/g)[a]	Aromatic fraction (μg/g)[a]	n-Alkanes (μg/g)[a]	Organic C (%)	$\frac{HC}{OC} \times 10^4$ [b]	$\frac{\text{n-Alkanes}}{OC} \times 10^4$ [c]	$\frac{Pr}{Ph}$	$\frac{Odd}{Even}$ [d]
101	1.1	0.4	0.06	0.18	8.3	0.3	1.81	1.28
102	2.2	0.9	0.16	0.18	17.2	0.9	1.38	1.03
103	3.2	4.0	0.17	0.53	13.6	0.3	5.00	1.61
104	17.8	5.6	1.48	0.39	60.0	3.8	1.04	1.31
105	3.8	6.7	0.34	0.76	13.8	0.5	5.48	1.13
119	14.3	5.8	0.85	0.74	27.2	1.2	4.56	1.24
120	12.5	6.5	1.27	0.13	146.2	9.7	6.86	2.52
121	13.2	13.5	2.00	0.18	148.3	11.1	6.04	2.23
124	11.9	6.4	1.0	0.92	19.9	1.1	4.52	1.97
133	2.0	1.3	0.30	0.35	9.4	0.9	3.54	2.02
134	4.3	15.3	0.97	1.09	17.9	0.9	6.17	2.41
137	1.7	1.6	0.28	0.34	9.7	0.8	1.86	1.68
160	1.5	0.5	0.20	0.31	6.4	0.6	3.94	2.00

* All are bulk samples of the upper 0-10 cm of surface sediment.

For explanation of the remainder of the symbols and abbreviations, see Table 2.

Table 8. Gravimetric and gas chromatographic data of Eastern and Central Gulf of Alaska sediment samples (1975 cruise)

Station Number*	Aliphatic fraction (μg/g)[a]	Aromatic fraction (μg/g)[a]	n-Alkanes (μg/g)[a]	Organic C (%)	$\frac{HC}{OC} \times 10^4$[b]	$\frac{\text{n-Alkanes}}{OC} \times 10^4$[c]	$\frac{Odd}{Even}$[d]
41	7.07	14.84	6.59	0.84	26.1	7.84	1.2
43	18.71	11.23	2.21	0.66	45.4	3.34	1.2
50	29.77	10.59	6.80	0.78	51.7	8.71	1.2
51	26.11	11.19	5.01	0.73	51.1	6.87	1.9
52	15.52	5.77	5.95	0.81	26.3	7.35	1.3
54	20.55	13.41	8.39	0.51	66.6	16.45	1.1
107	12.27	6.63	4.42	0.92	20.5	4.81	1.2

* All are bulk samples of the upper 0-10 cm of surface sediment.

For explanation of the remainder of the symbols and abbreviations, see Table 2.

Table 9. Gravimetric and gas chromatographic data of Kodiak Shelf sediment samples (1976 cruise).

Station Number *	Aliphatic fraction (μg/g)[a]	Aromatic fraction (μg/g)[a]	n-Alkanes (μg/g)[a]	Organic C (%)	$\frac{HC}{OC} \times 10^4$ [b]	$\frac{\text{n-Alkanes}}{OC} \times 10^4$ [c]	$\frac{Pr}{Ph}$	$\frac{Odd}{Even}$ [d]
52	1.20	2.15	0.08	0.34	9.9	0.24	2.3	1.9
57	1.44	1.42	0.04	0.36	7.9	0.14	2.4	1.9
60	2.15	2.84	0.26	0.31	16.1	0.77	6.1	1.7
68	2.29	1.43	0.12	0.60	6.2	0.20	10.4	1.7
72	1.57	0.89	0.67	0.23	10.7	2.89	3.0**	3.8
75	2.06	0.36	0.03	0.33	7.3	0.08	12.2	0.8
80	0.51	0.47	0.01	0.35	2.8	0.03	6.2	2.1
80'	0.69	0.58	0.03	0.35	3.7	0.09	17.7	1.8
81	2.65	2.86	0.34	0.50	11.0	0.74	10.8	2.1
87	0.79	1.53	0.02	0.45	5.2	0.04	4.5**	2.6
92	5.13	6.64	0.84	1.17	10.1	0.71	6.4	1.3
93	1.87	2.27	0.27	1.01	4.1	0.27	2.8**	2.6
97	4.21	5.16	0.42	2.45	3.8	0.21	4.0	1.3
98	7.79	10.88	0.20	2.15	8.7	0.09	6.0	2.8
130	1.87	2.97	0.20	0.91	5.3	0.24	4.4	1.5

* Samples are 0-2 cm except 80', which is 2-4 cm; elemental sulfur detected only in sample 92.

** Approximate values based upon measured peak heights.

For explanation of remainder of symbols and abbreviations, see Table 2.

Table 10. Gravimetric and gas chromatographic data of Cook Inlet sediment samples

Station*	Depth (m)	Aliphatic Fraction (μg/g)	Aromatic Fraction (μg/g)	TALK Total n-Alkanes (μg/g)	CPI $\frac{\text{Odd}}{\text{Even}}$	$\frac{\text{Pr}}{\text{Ph}}$	$\frac{\text{n-Alk.}}{\text{Org.C}} \times 10^4$
Summer, 1976**							
14	61	0.44	0.48	0.02	1.5	2.4	2.2
18	122	0.66	0.99	0.09	2.4	11.0	1.0
41	30	0.82	0.81	0.14	4.1	3.9	1.2
42	30	1.81	3.27	0.55	2.7	4.8	2.0
43	52	16.10	23.81	3.66	2.9	6.0	11.0
48	45	4.54	2.49	1.26	3.2	4.2	8.7
Summer, 1977**†							
37'	33	8.15	6.62	2.10	4.3	10.1	22.6
40	82	2.58	2.58	0.58	3.4	5.0	3.9
227	88	7.69	16.78	1.68	3.1	4.6	5.9
227^R	88	7.79	9.60	1.61	3.9	4.7	7.3
Spring, 1978							
201	22	4.49	3.24	1.06	5.2	3.3	1.7
203	38	1.24	1.05	0.24	5.7	2.7	0.4
204	34	2.12	1.91	0.46	4.1	3.0	1.0
211	19	1.27	1.26	0.48	4.4	3.3	1.5
212	26	1.58	1.42	0.21	3.7	2.6	0.5
213	33	1.14	1.27	0.23	4.9	2.9	0.4
214	53	1.41	1.35	0.28	3.7	3.7	0.6
233	14	2.27	2.06	0.48	3.9	4.9	1.2
233^R	14	2.70	2.45	0.38	3.4	3.5	---
234	38	0.99	0.61	0.03	2.1	4.1	0.1
245	46	1.17	1.01	0.12	4.0	2.5	0.3
247	20	1.02	0.87	0.11	2.5	2.8	0.6
255	42	1.45	14.10	0.12	3.0	4.9	0.5
265	16	28.81	8.74	0.54	1.1	0.8	3.6
370	112	3.09	3.66	1.47	4.0	4.3	2.1
380	57	2.91	1.72	0.24	5.7	5.0	0.4
390	170	2.13	2.56	0.30	3.5	4.9	0.6
394	171	2.06	3.83	0.66	2.0	4.9	0.9
Summer, 1978							
204	33	1.42	1.48	0.26	4.8	1.1	0.4
205	138	1.14	1.06	0.14	2.4	3.0	0.3
206	90	0.88	1.86	0.10	3.3	6.7	0.3
212	24	2.14	1.54	0.36	4.6	3.2	0.6
215	78	0.48	0.63	0.06	2.7	2.0	0.1
217	71	0.44	0.42	0.03	2.3	12.7	0.1
234	39	1.94	0.96	0.31	1.2	0.8	1.0
378	92	1.26	2.61	0.17	3.5	5.2	----
384	176	2.00	3.66	0.26	1.5	6.7	0.4
388	214	5.81	9.97	0.35	1.9	10.1	0.3
390	165	1.97	1.89	0.33	3.7	5.4	0.6
398	---	0.17	2.48	0.08	1.5	8.9	0.2

Table 10 continued

				TAlk	CPI		
UC100	150	0.99	0.75	0.05	1.9	2.6	0.2
UC200	150	1.24	1.35	0.10	1.9	8.3	0.3
UC300	101	4.55	5.16	1.11	2.9	5.3	1.6
CB8	---	13.08	7.24	1.38	4.6	1.6	1.5
CB8^R	---	9.43	7.68	1.66	4.8	2.0	1.8
Spring, 1979							
11	190	2.01	1.34	0.22	4.3	6.5	0.7
12	28	1.36.	2.13	0.42	5.6	3.5	4.6
13	200	1.11	5.65	0.10	2.4	n.d.	0.4
16A§	---	1.52	0.66	0.36	7.4	2.0	---
16B§	---	3.51	4.19	0.46	5.9	n.d.	---
17	45	3.66	4.20	1.47	3.8	3.5	3.9
18	180	0.43	3.04	0.04	1.7	n.d.	0.1
19	30	0.53	1.08	0.22	4.9	n.d.	1.5
22	35	1.99	0.28	<.01	n.d.	n.d.	---
23	35	0.54	0.87	<.01	n.d.	n.d.	n.d.
25	10	0.96	0.73	0.20	4.2	2.5	0.7
27	20	0.80	0.27	0.01	1.2	0.9	0.2
30	56	0.92	1.01	0.09	3.2	5.3	---
31	106	0.48	0.48	0.01	0.9	n.d.	0.1
				.01-1.66	0.9-7.4		

---

* For brevity, latitude and longitude are not given. Exact locations can be obtained from M.I.V. All samples are 0-2 cm except wherever mentioned. NO elemental sulfur detected in any of these samples.

** Data of some samples from central Cook Inlet and Kachemak bay in these cruises omitted for brevity, but reported for samples collected from the same area in subsequent cruises.

R = replicate
† = 0-4 cm
§ = Bulk samples, collected by mud snapping sampling device
n.d. = not determined; too low to be calculated accurately
odd/even = summed from C_{15} to C_{33}

Table 11. Polycyclic Aromatic Hydrocarbons in Sediment Samples Analyzed by GC/MS (ng/g)

Area	Beaufort Sea (1976)		Gulf of Alaska (1975)	Kodiak Shelf (1976)		Navarin Basin (1980)	
Station Number	1	7	54	80	98	10	15
O-xylene (XYL)	13.0	--	--	--	--	T	T
Isopropylbenzene (IPB)	T	--	--	--	--	--	--
n-Propylbenzene (NPB)	T	--	--	--	--	--	--
Indan (IND)	T	--	--	--	--	--	T
1,2,3,4-Tetramethylbenzene (TMB)	T	--	--	--	--	--	T
Naphthalene (NPH)	2.0	T	T	--	1.5	T	T
2-Methylnaphthalene (2MN)	11.5	6.9	T	T	T	T	T
1-Methylnaphthalene (1MN)	7.9	5.7	T	T	T	T	T
Biphenyl (BPH)	3.2	2.4	T	T	T	T	T
2,6-Dimethylnaphthalene	--	9.0	T	0.3	3.3	T	T
Dimethylnaphthalenes (DMN)[1]	--	12.9	T	0.4	6.5	T	T
Trimethylnaphthalenes (TMN)	--	--	13.4	0.6[3]	6.0	T	T
Fluorene (FLU)	1.7	8.1[2]	T	T	6.1	T	T
Dibenzothiophene (DBT)	6.0	--	--	--	--	--	5.1
Phenanthrene (PHN)	32.9	31.3	34.9	2.2[3]	43.8	3.2	4.5
Anthracene (ANT)	T	T	T	--	T	T	T
Methylphenanthrenes (MPH)	78.0	86.6	110	1.7	37.2	10	11
Fluoranthene (FLA)	12.2	23.1	T	0.7	18.9	T	6.8
Pyrene (PYR)	16.5[4]	25.7[4]	8.6	0.3	15.1[4]	T	2.4
Benz[a]anthracene (BAA)	--	--	--	T	--	1.6	T
Chrysene (CHR)	21.2	28.6	18.6	0.5	40.4	T	T
Benz[e]pyrene (BEP)	T	T	1.0	T	T	T	T
Benz[a]pyrene (BAP)	T	T	--	--	T	T	T
Perylene (PER)	10.0	40.8	1.9	T	T	12.1	6.9
Simonellite (SIM)	See PYR	See PYR	--	--	See PYR	T	T
Cadalene (CAD)	--	14.4	4.0	T	--	T	T
Retene (RET)	29.1	62.1	26.1	0.5[3]	18.8[3]	2.2	4.8

T = trace

[1] = Excludes 2,6-dimethylnaphthalene when identified

[2] = Coelutes with dimethylnaphthalene

[3] = Coelutes with unknown compound

[4] = Coelutes with simonellite

Table 12. Polycyclic aromatic hydrocarbons in sediment samples analyzed by GC/MS (ng/g)

	Southeastern Bering Sea		Norton Sound (1976)		Norton Sound (1977)		Norton Sound (1979)
	Station 59	Station 64	Station 131	Station 166	Station 35	Station 43	Station 25
O-Xylene	--	--	--	T	T	--	0.2
Isopropylbenzene	--	--	--	--	--	--	--
n-Propylbenzene	--	--	--	T	T	--	--
Indan	--	--	--	--	--	--	--
1,2,3,4-Tetramethylbenzene	--	--	--	T	--	--	--
Naphthalene	T	T	T	T	T	--	T
2-Methylnaphthalene	T	T	T	T	T	T	T
1-Methylnaphthalene	T	T	T	T	T	T	T
Biphenyl	--	--	T	T	T	T	--
2,6-Dimethylnaphthalene	--	--	T	T	--	--	--
Dimethylnaphthalenes^1	--	--	T	T	--	--	0.1
Trimethylnaphthalenes	--	--	T	T	T	T	0.3
Fluorene	--	--	T	--	T	T	0.1
Dibenzothiophene	--	--	--	--	--	--	--
Phenanthrene	0.3	1.1	4.2^2	0.2	1.9^2	0.8^2	0.4
Anthracene	--	--	--	--	T	T	--
Methylphenanthrenes	0.5	1.3	0.6	T	--	0.2	0.8
Fluoranthene	--	3.0	T	0.1	0.5	T	T
Pyrene	1.4	5.0	2.2^3	0.1^3	0.2	T	0.2
Benz(a)anthracene	--	--	--	--	T	--	--
Chrysene	1.2	0.9	3.0^2	0.6	T	0.4	1.0
Benz(e)pyrene	--	T	T	T	--	--	T
Benz(a)pyrene	--	--	--	--	T	T	--
Perylene	T	T	9.8	T	T	1.3	9.4
Simonellite	--	--	--	See Pyrene	T	T	T
Cadalene	T	--	0.3	T	--	--	T
Retene	1.8	7.3	2.8^2	--	T	3.1^2	1.4

T = trace

[1] = Excludes 2,6-dimethylnaphthalene when identified

[2] = Coelutes with unknown compound

[3] = Coelutes with simonellite

Table 13. Polycyclic Aromatic Hydrocarbons in Sediments Analyzed by GC/MS (ng/g) in Cook Inlet

Station	203	233	234	265	UC300	388	398	CB8	17
Naphthalene (NAP)	T	T	T	0	T*	--	--	T	T
2-Methylnaphthalene (2MN)	T	T	0.7	0.3	T	T	--	--	2.2
1-Methylnaphthalene (1MN)	T	T	T	0.2	T	T	--	--	0.6
Biphenyl (BPH)	--	--	0.7	--	T	--	--	T	T
Dimethylnaphthalenes (DMN)	T	T	2.7	5.3	3.4	27.4	--	T	4.1
Trimethylnaphthalenes (TMN)	1.6	T	2.7	21.6	9.4	24.5	--	4.2	8.7
Fluorene (FLU)	1.8	0.7	T	--	3.0*	5.3	--	0.8	T
Dibenzothiophene (DBT)	--	--	--	T	--	--	--	--	--
Phenanthrene (PHN)	10.4	2.3	4.1	18.2	14.5	63.8	2.1	8.4	14.7
Anthracene (ANT)	--	--	--	--	--	--	--	T	--
Methylphenanthrenes (MPH)	11.9	6.0	9.7	T	55.4*	124.0*	5.4	23.3	16.4
Fluoranthene (FLA)	5.5	--	T	--	T	10.4	--	T	T
Pyrene (PYR)	3.9	1.2	T	31.2	3.0	5.7	0.6	7.2	4.6
Benz[a]anthracene (BAA)	--	--	T	--	T	T	--	T	T
Chrysene (CHR)§	3.1	1.9	1.3	22.9	T*	6.9	1.5	15.2	T
Benz[e]pyrene (BEP)	T	T	0.6	1.2	T	5.2	--	--	--
Benz[a]pyrene (BAP)	--	--	T	T	--	T	--	--	--
Perylene (PER)	3.9	3.1	1.9	23.1*	14.8	8.2	T	50.9	8.4
Simonellite (SIM)	4.9	3.9	1.2	See PYR	22.7	4.7*	1.1	266.3	--
Cadalene (CAD)	2.2	0.3	T	--	2.6	5.5	--	14.0	5.8
Retene (RET)	7.6	3.6	1.1	38.1	5.8	18.6*	--	54.7	17.4

T = trace
† = coelutes with simonellite
* = coelutes with unknown compound
§ = coelutes with triphenylene

Table 14. Comparative organic geochemical data from different areas in the Alaskan shelf

Area	% Org. C range	Total Hydrocarbons^1	Range in ng/g					
			Resolved n-Alkanes^2	Resolved PAH^{2,3}	n-Alkane Maxima	$\frac{\text{odd}}{\text{even}}$ Range	$\frac{\text{Pr}}{\text{Ph}}$ Range	UCM
Beaufort Sea	0.4 - 1.0	20,000-50,000	1,400-5,000	200-300	27 or 29	1.8-5.0	1.5-2.5	no
S.E. Bering Sea	0.1 - 0.8	1,900-22,000 (240,000)	300-2,900	3-20	27 or 29	1.8-4.0	2-18	no**
Norton Sound	0.1 - 1.3	1,900-29,000	10-5,400 (7,200; 8,700)	1-20	27	1.7-6.3 (11.0)	1-8	no
Navarin Basin	0.1 - 1.4	2,400-52,000	250-2,600	20-40	27	3.5-4.8	--*	no
Gulf of Alaska	0.1 - 1.1	1,500-26,000	60-2,000	100-200	22 and 27 or 29	1.0-2.5	1-7	yes**
Kodiak Shelf	0.2 - 1.2 (2.15;2.45)	900-18,000	10-800	6-100 (200)	27 or 29	0.8-2.8 (3.8)	2-18	no**
Cook Inlet	0.1 - 1.4	900-39,000	< 10-3,600	10-300	27 or 29	0.9-5.9 (7.4)	1-12	no**

1 = Total hydrocarbons = sum of aliphatic and aromatic fractions from column chromatography.

2 = gas chromatographic data

3 = sum of PAH identified by GC/MS and tabulated in tables 10-12. Inlet samples show UCM typical of weathered petroleum

* = Phytane below detection limits

** = Narrow UCM around C_{20}-C_{23} in all samples in Gulf of Alaska and in only a few samples in Kodiak Shelf and Cook Inlet. In Cook Inlet, two samples, and in southeastern Bering Sea, 1 sample, show UCM typical of weathered petroleum.

(Values beyond the general range characteristic of a given area are quoted in parentheses).

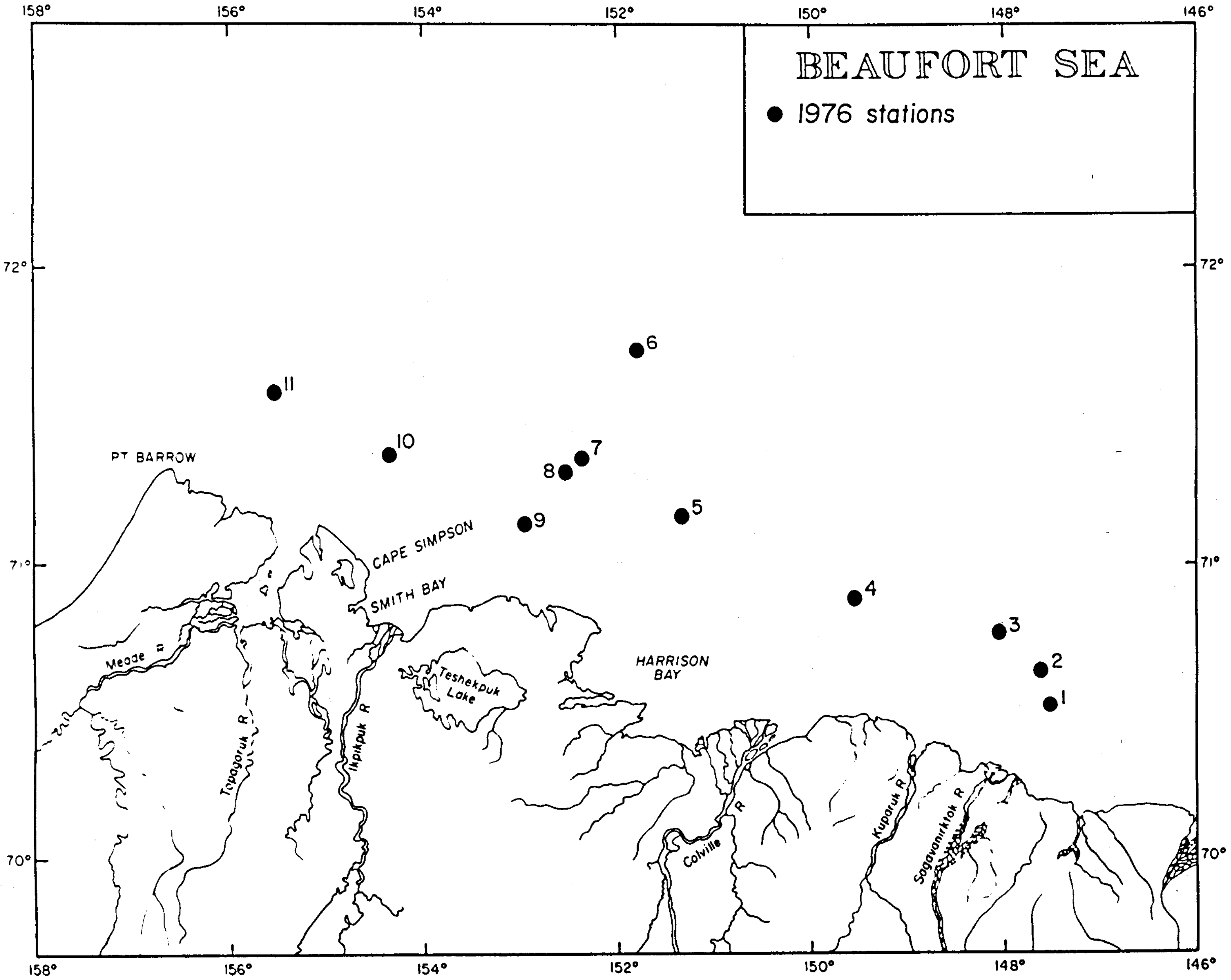


Figure 1: Sample locations in Beaufort Sea.

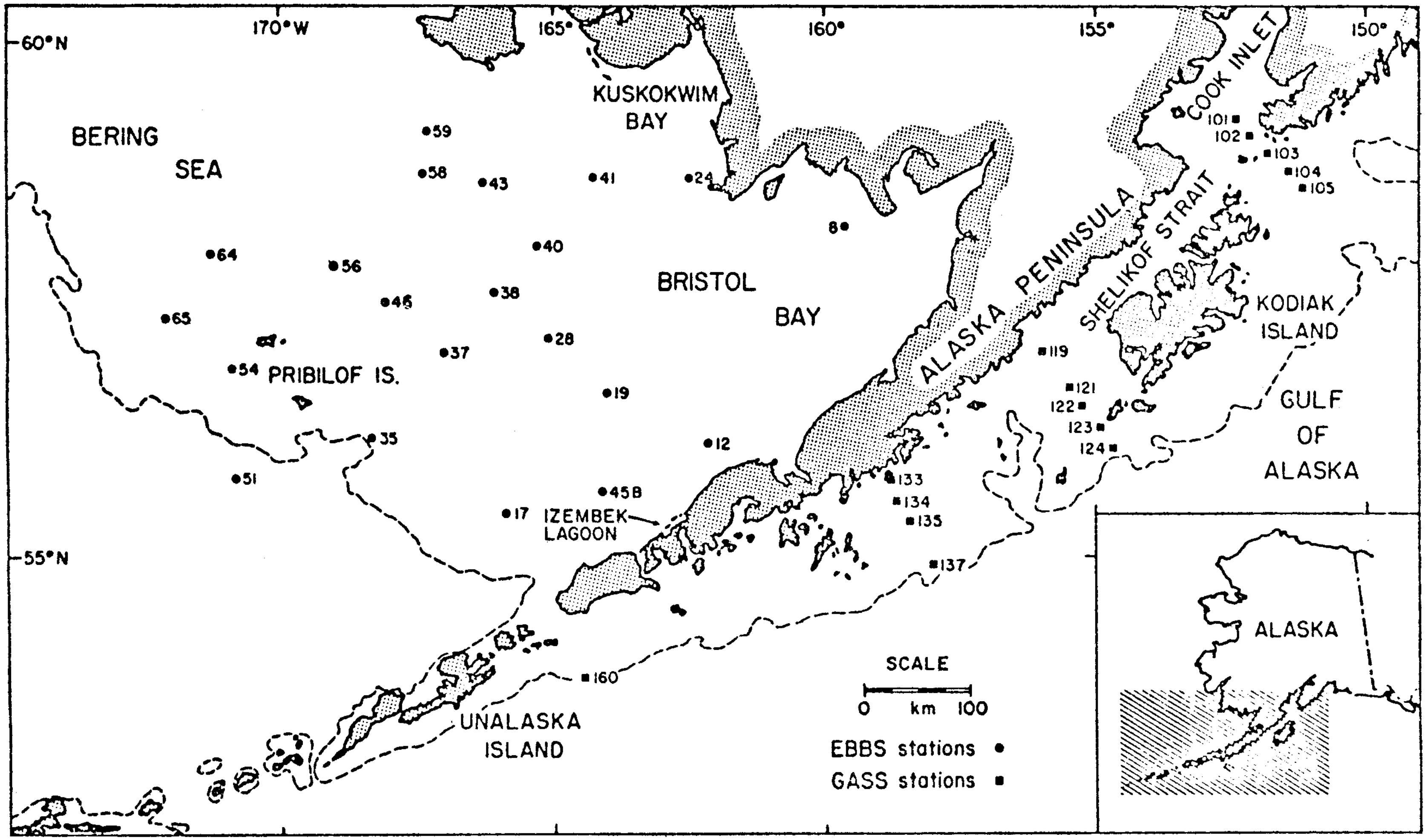


Figure 2: Sample locations in southeastern Bering Sea and western Gulf of Alaska.

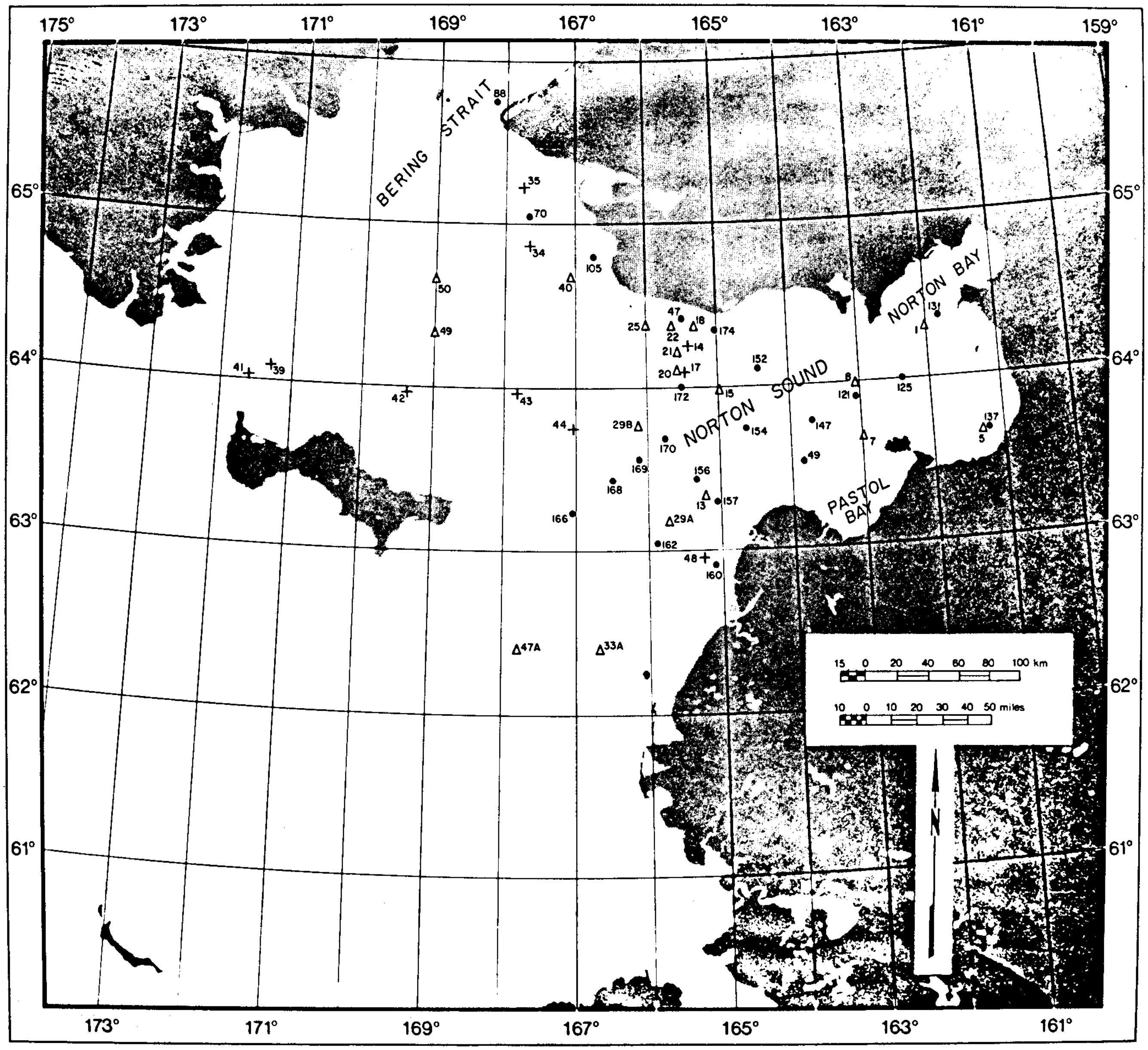


Figure 3: Sample locations in Norton Sound. ● 1976 samples; + 1977 sample; △ 1979 samples.

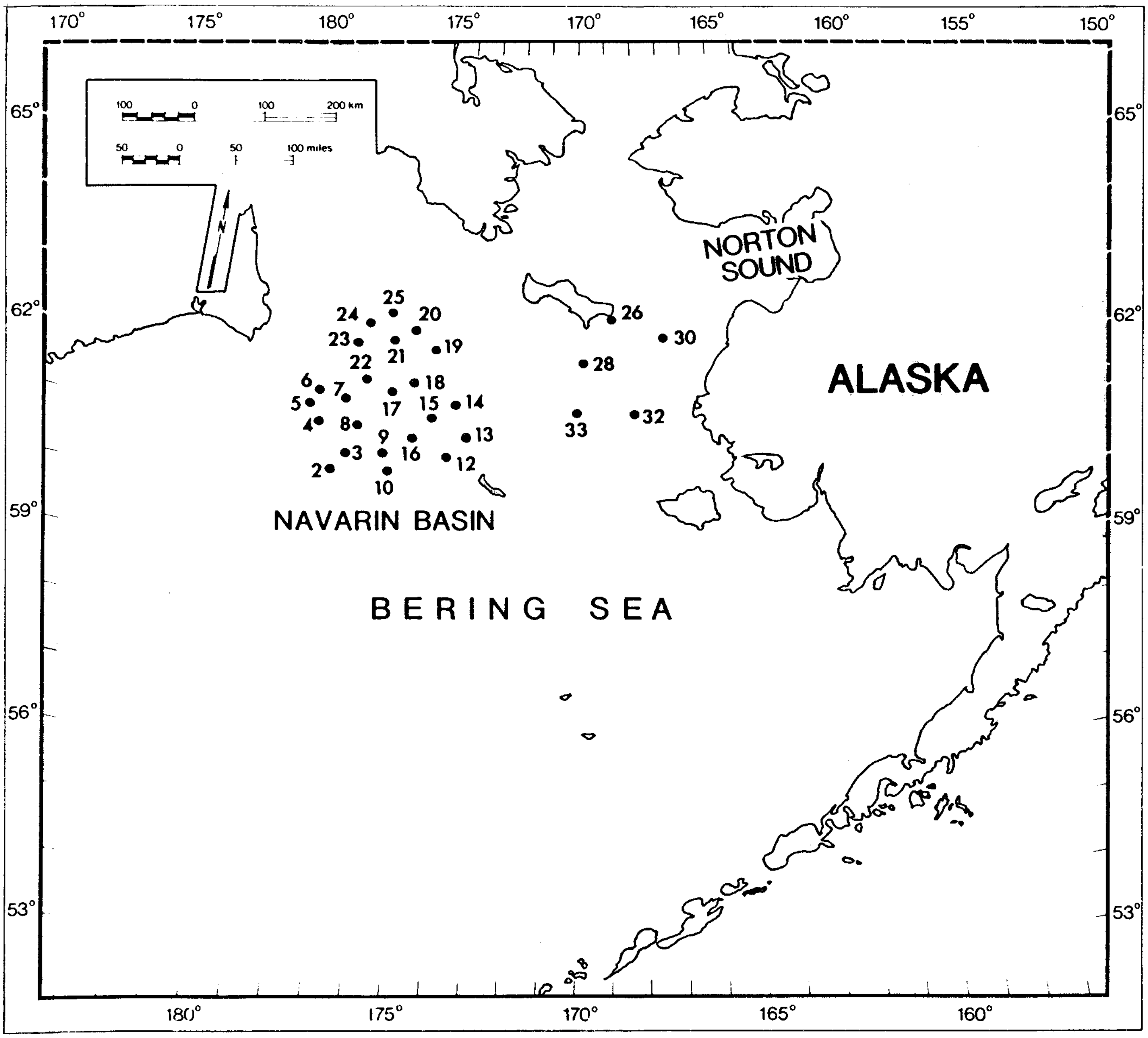


Figure 4: Sample locations in Navarin Basin.

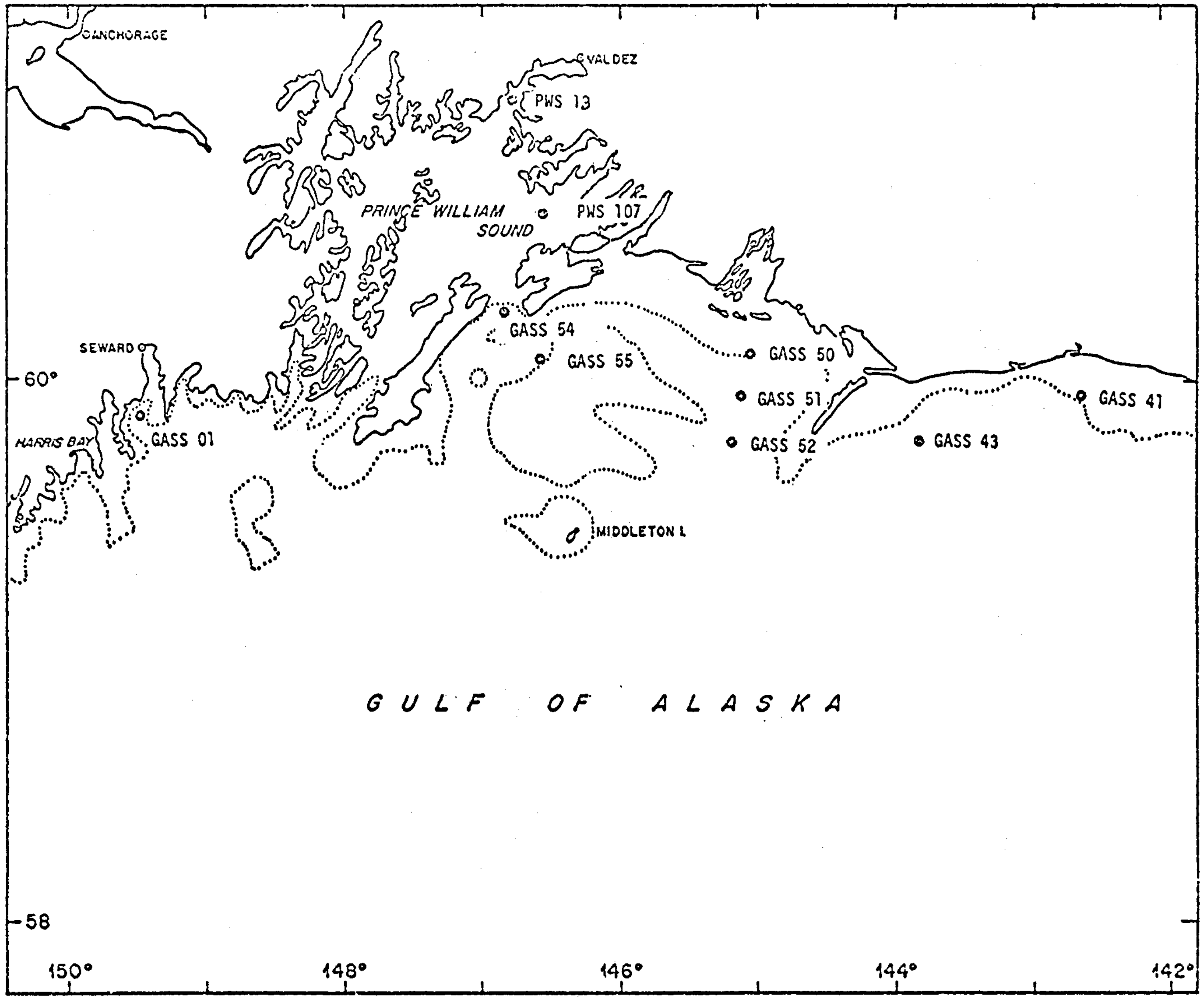


Figure 5: Sample locations in central and eastern Gulf of Alaska.

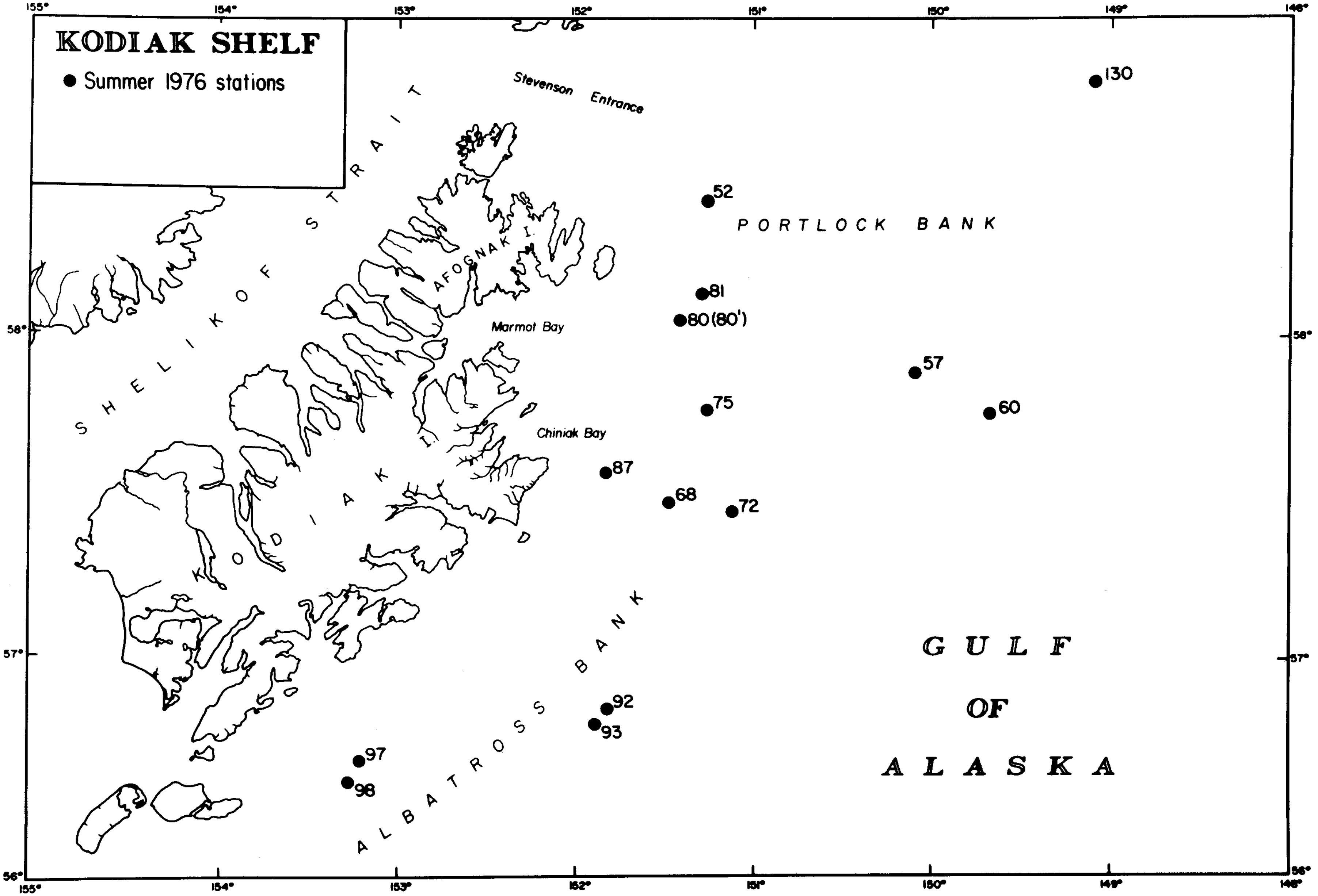


Figure 6: Sample locations in Kodiak Shelf.

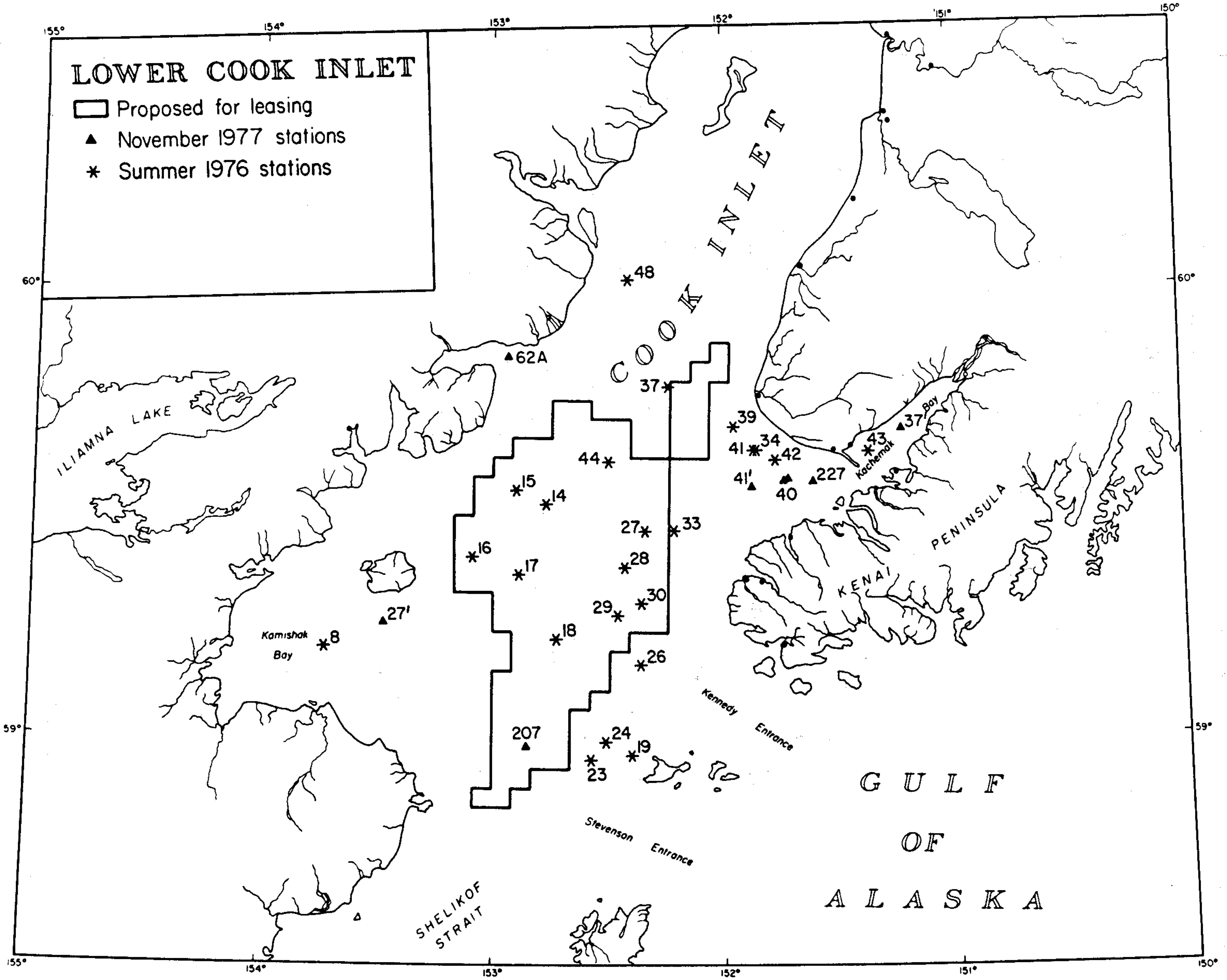


Figure 7: Sample locations in Cook Inlet; 1976 and 1977 cruises.

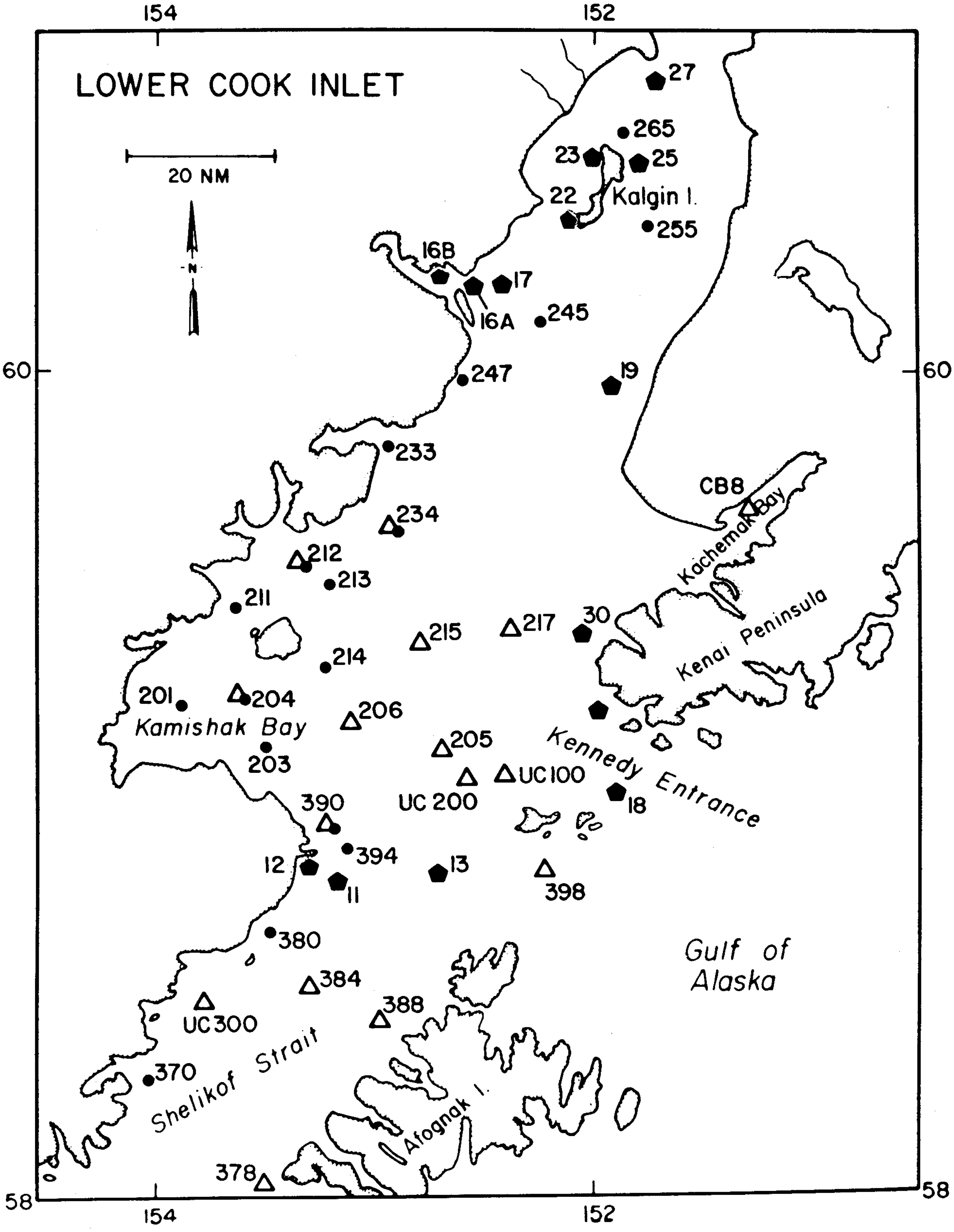


Figure 8: Sample locations in Cook Inlet. ● 1978 spring samples; △ 1978 summer samples; ⬟ 1979 spring samples.

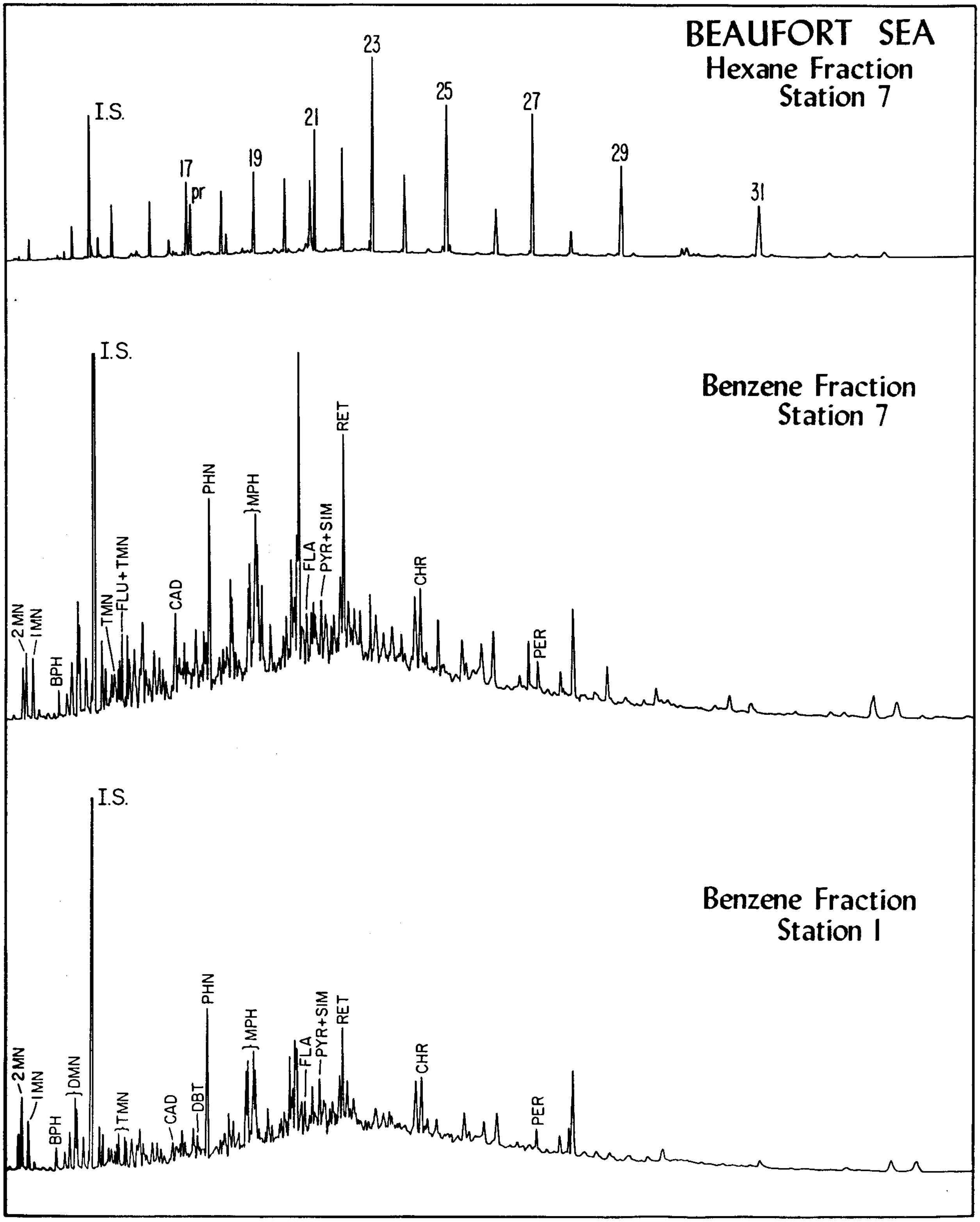


Figure 9: Gas chromatographic traces of hexane and benzene (hexane:benzene) fractions from Beaufort Sea sediments.

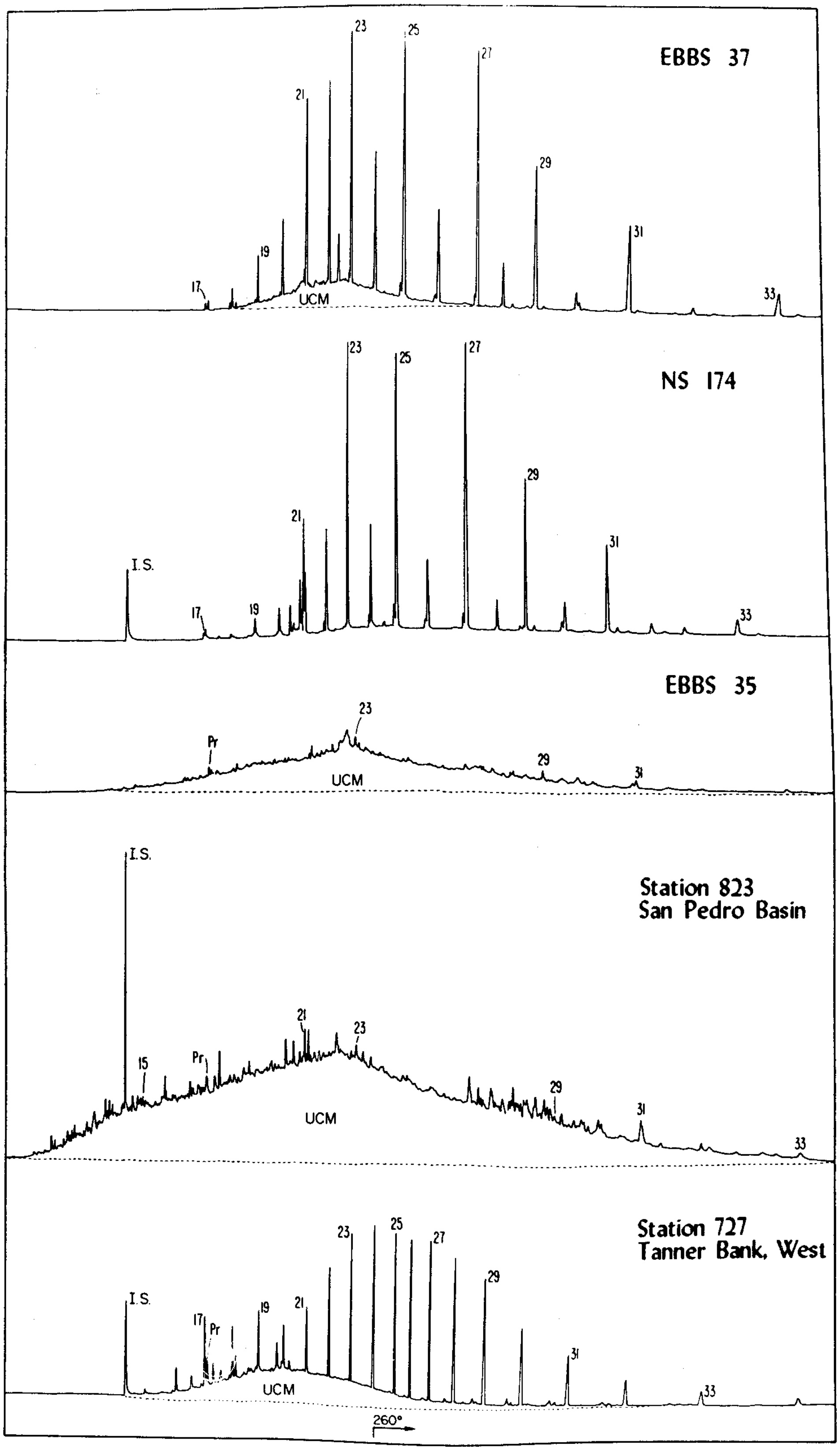


Figure 10: Gas chromatographic traces of hexane fractions from southeastern Bering Sea (EBBS), Norton Sound (NS) and Southern California Bight (San Pedro Basin and Tanner Bank) sediments.

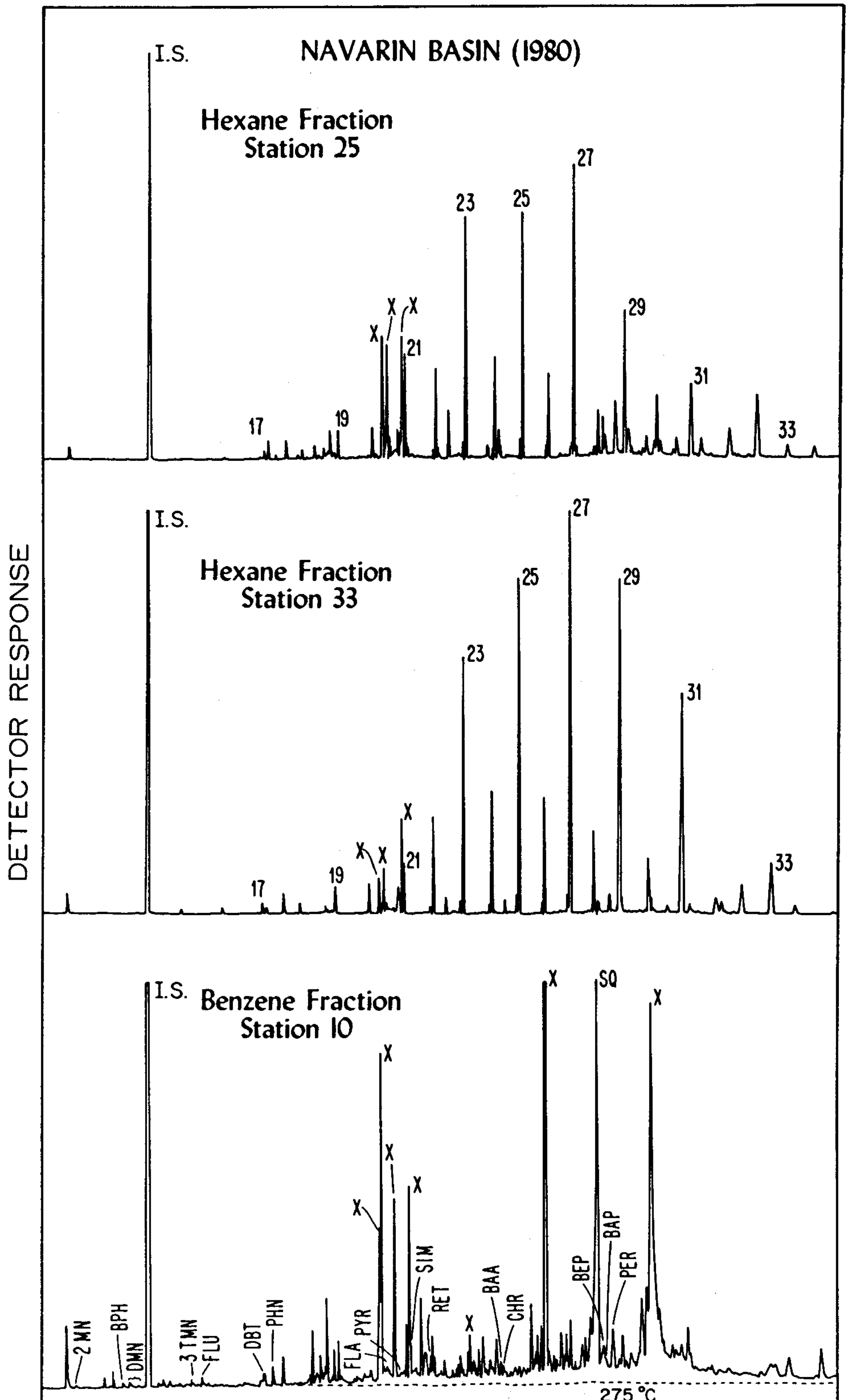


Figure 11: Gas chromatographic traces of hexane and benzene (hexane:benzene) fractions from Navarin Basin sediments.

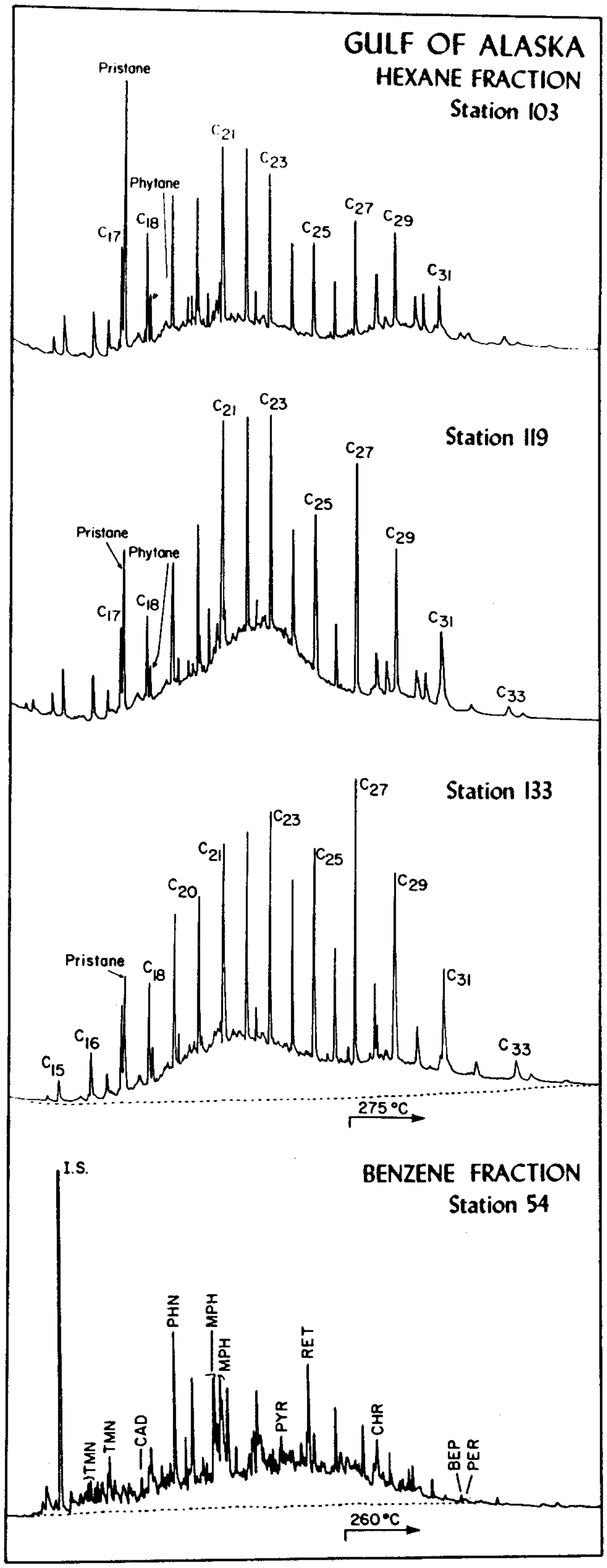


Figure 12: Gas chromatographic traces of hexane and benzene fractions from Gulf of Alaska sediments.

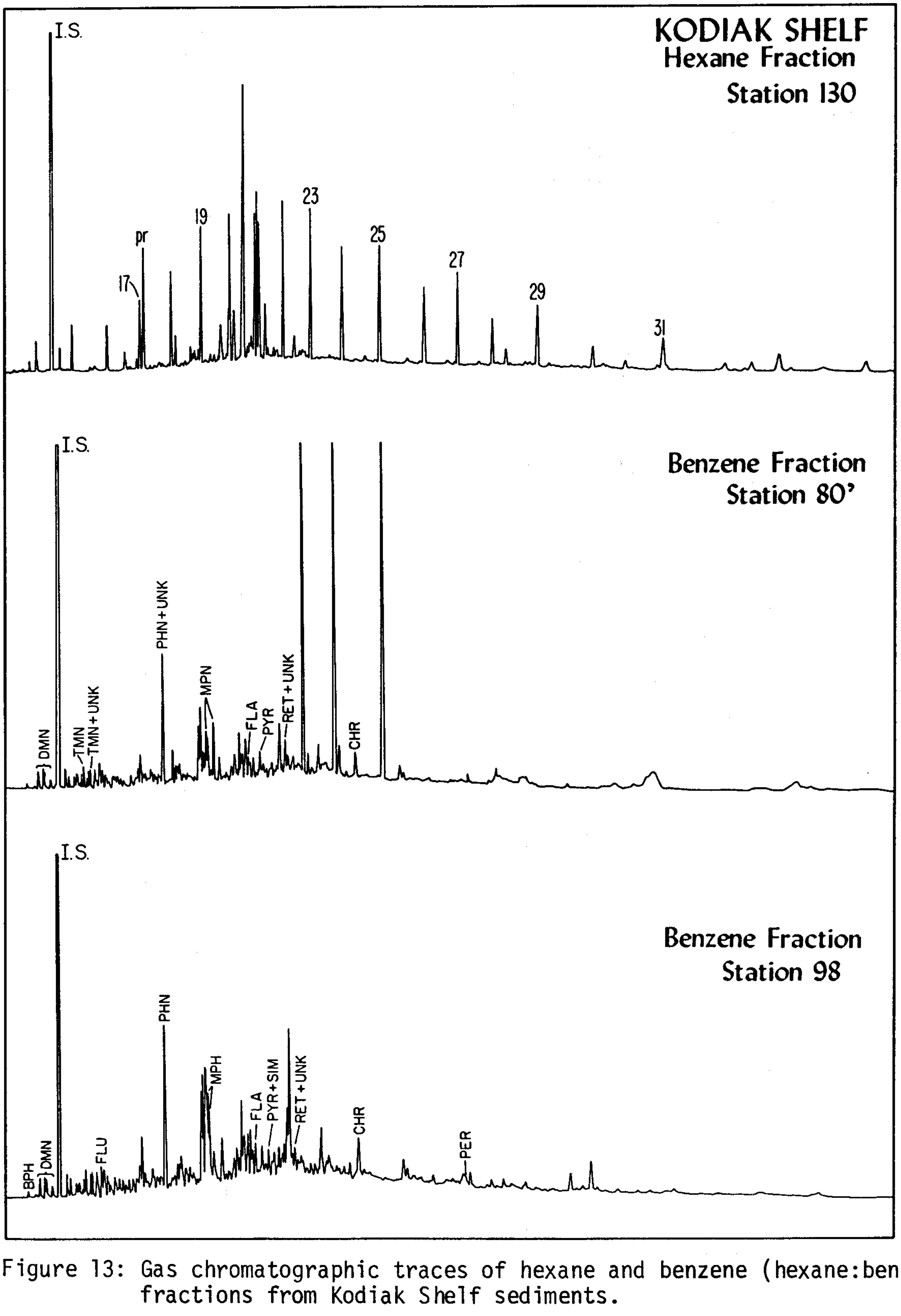


Figure 13: Gas chromatographic traces of hexane and benzene (hexane:benzene) fractions from Kodiak Shelf sediments.

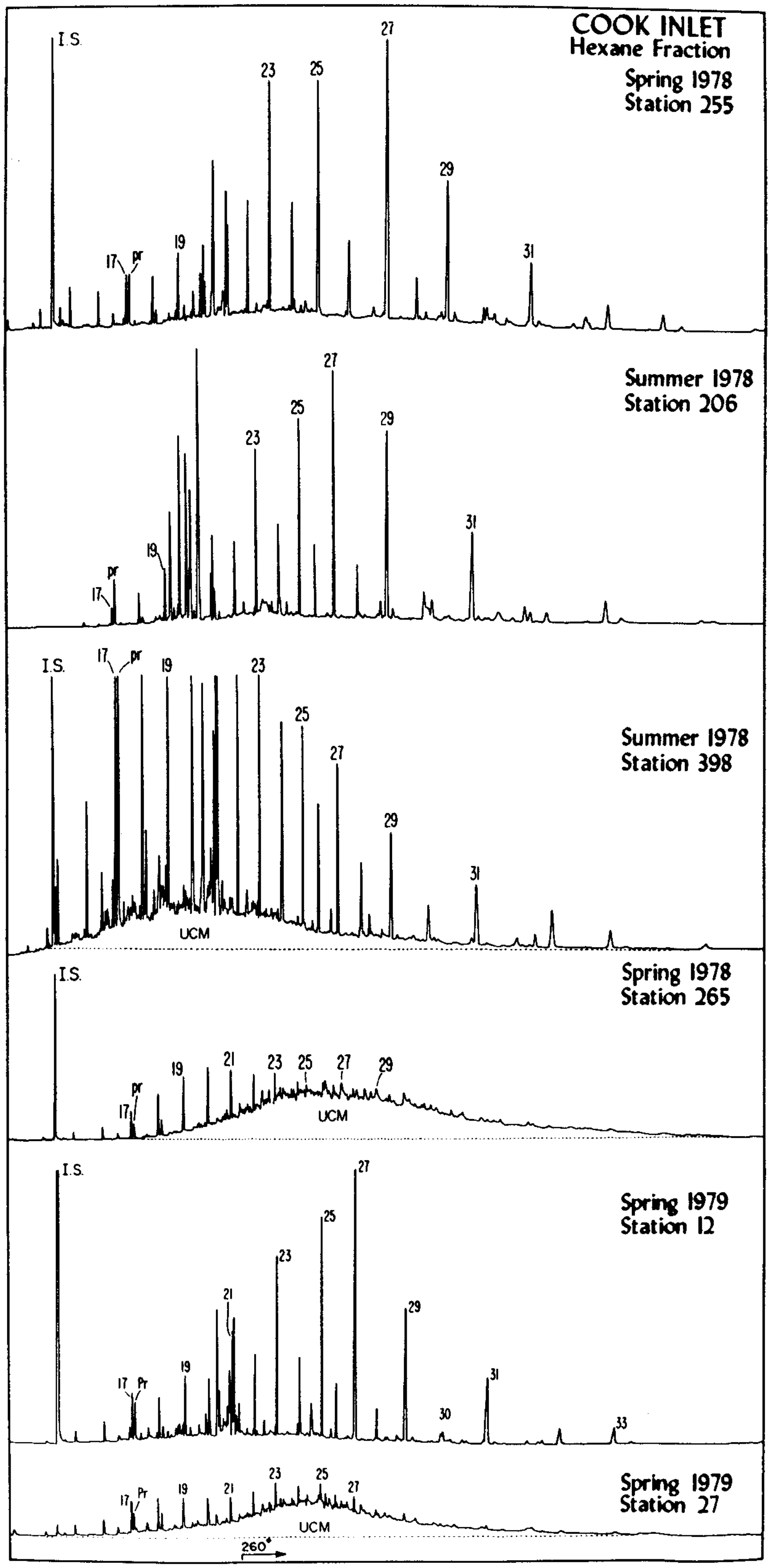


Figure 14: Gas chromatographic traces of hexane fractions from Cook Inlet sediments.

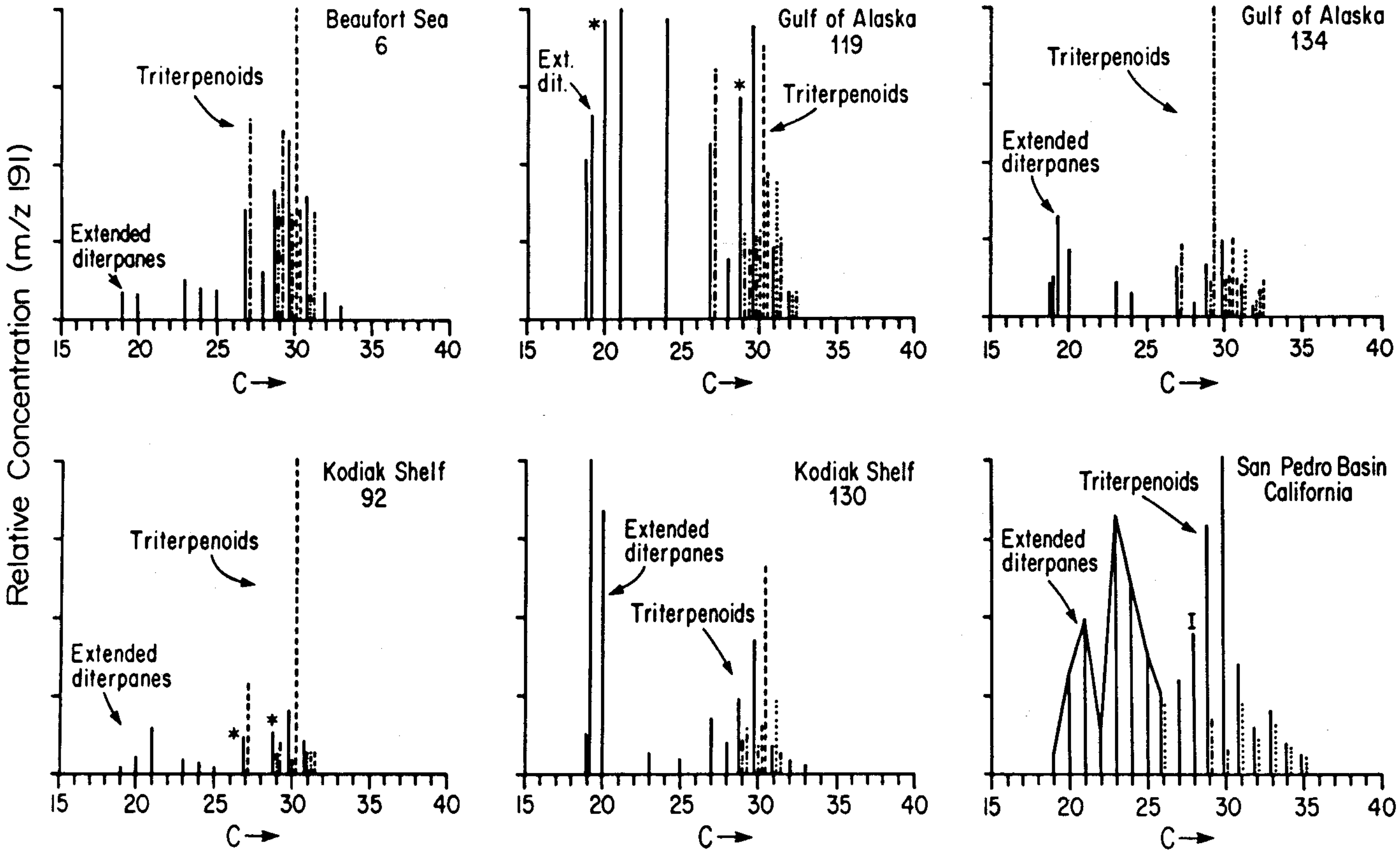


Figure 15: Relative distribution histograms of di- and triterpenoids based upon m/z 191 mass chromatograms. Beaufort Sea, Gulf of Alaska and Kodiak Shelf. 17α,21β (diasteromers at position 22 indicated by continuous and dotted lines ⋯⋯); —·—·— 17β,21β; —···— 17β,21α; ----mono-enes; ✱ coeluting with unknown.

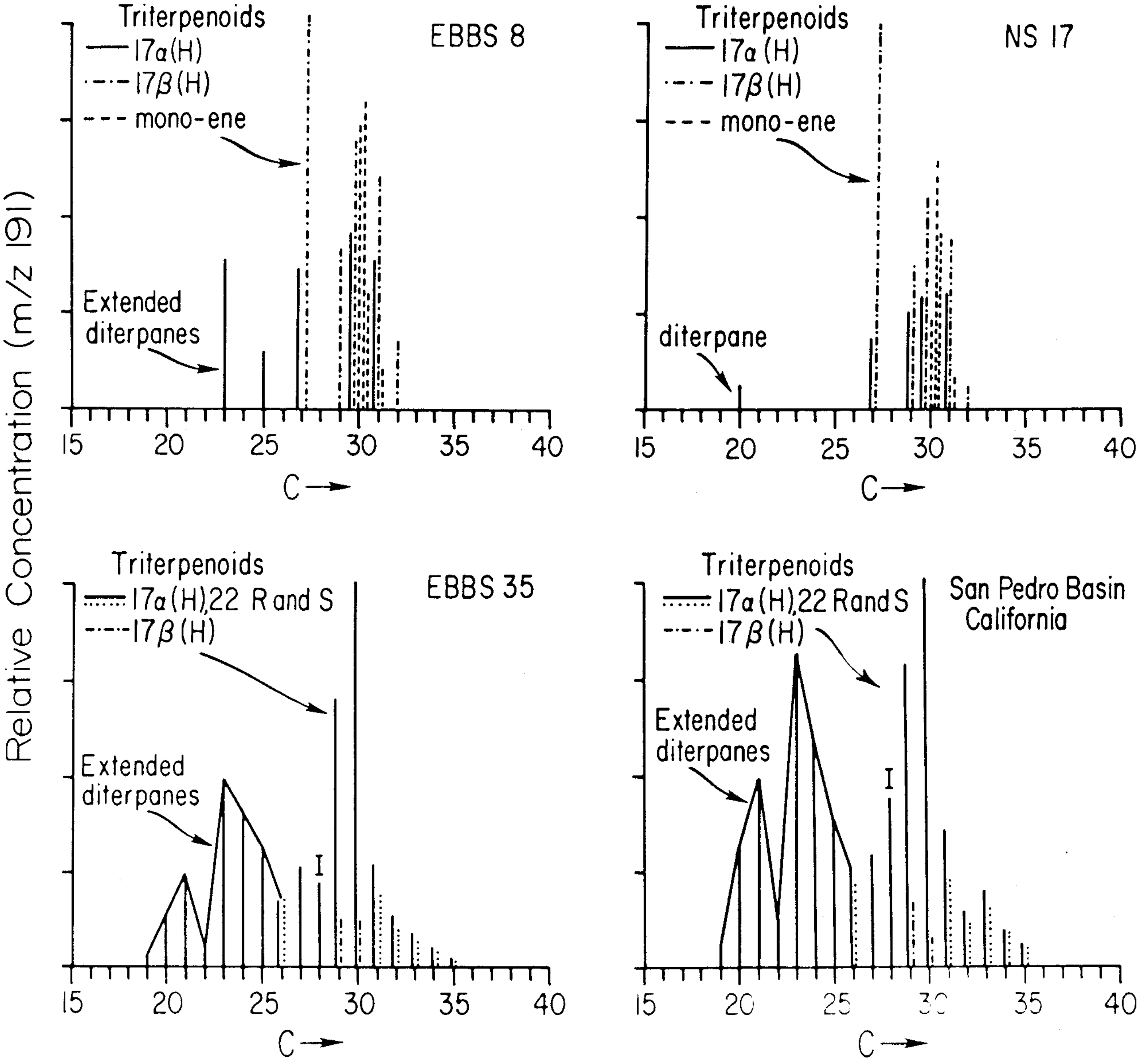


Figure 16. Relative distribution histograms of di- and triterpenoids based upon m/z 191 mass chromatograms. EBBS = southeastern Bering Sea, NS = Norton Sound. For explanation of symbols, refer to Fig. 15.

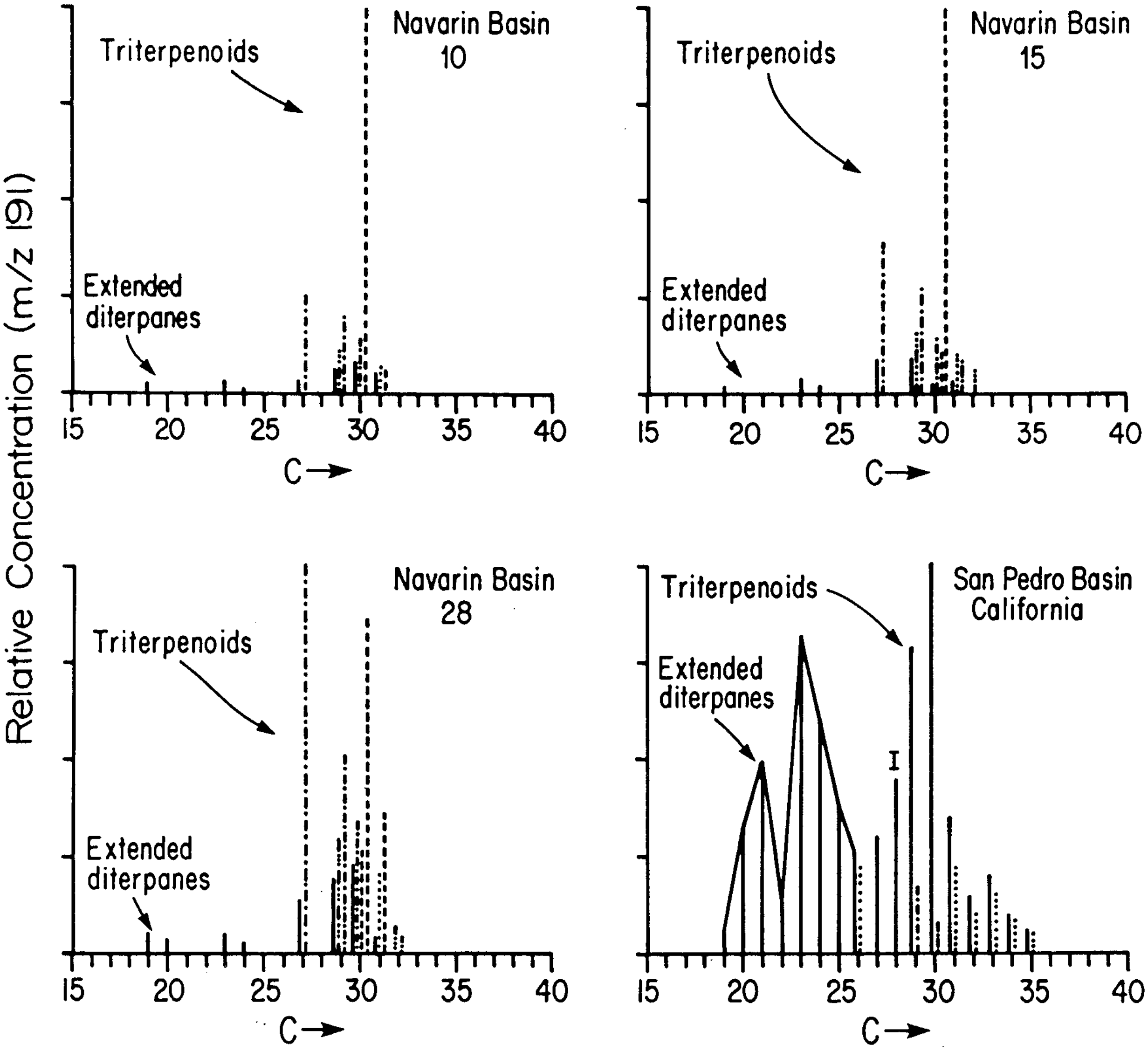


Figure 17: Relative distribution histograms of di- and triterpenoids based upon m/z 191 mass chromatograms. Navarin Basin. For explanation of symbols, refer to Fig. 15.

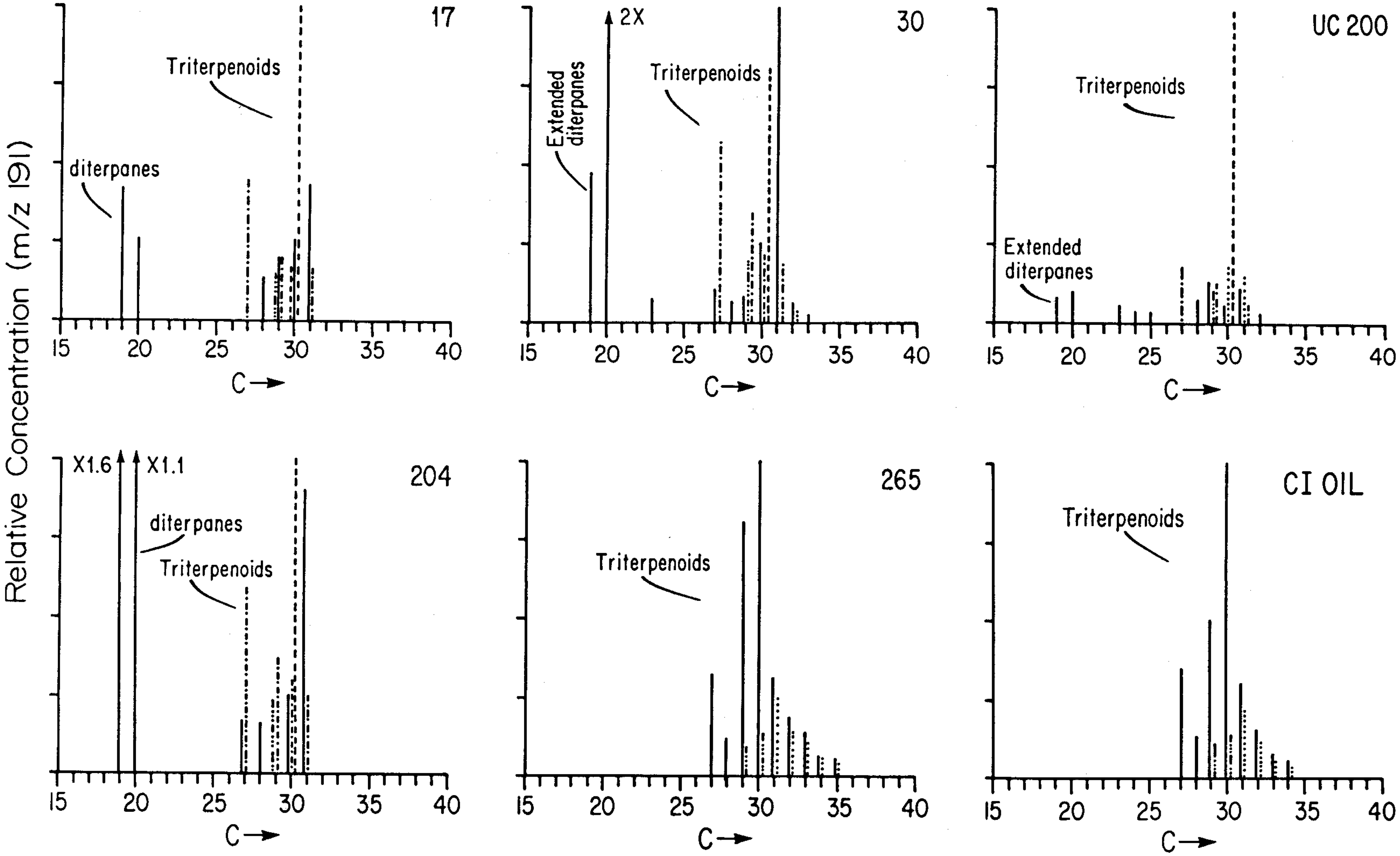


Figure 18: Relative distribution histograms of di- and triterpenoids based upon m/z 191 mass chromatograms. Lower Cook Inlet sediments and Cook Inlet oil. For explanation of symbols, refer to Fig. 15.

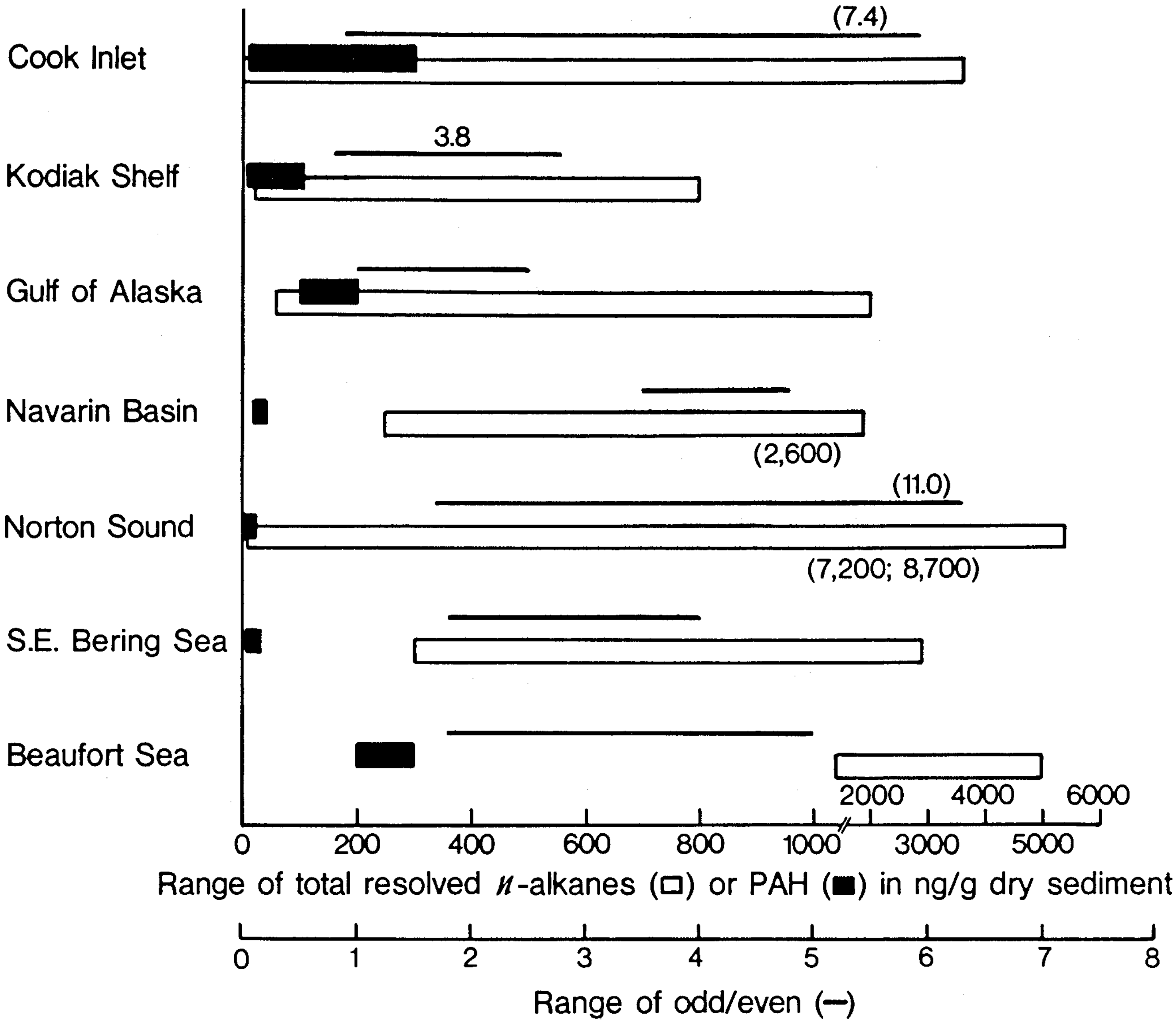


Figure 19: Selected organic geochemical data of sediments from different areas in the Alaskan outer continental shelf.

DISCUSSION

The vast latitudinal expanse of the Alaskan Shelf encompasses a variety of characteristic sedimentary and oceanographic regimes. Therefore, is was considered appropriate to discuss the organic geochemical data in the several regions of the Alaskan Shelf in terms of various geographic sections from north to south. The coastal region, including the shelf, is divided into the following areas: 1) Beaufort Sea, 2) Southeastern Bering Sea, 3) Norton Sound, 4) Navarin Basin, 5) Gulf of Alaska, 6) Kodiak Shelf and 7) Cook Inlet.

Beaufort Sea

Organic Carbon:

The organic carbon content ranges from 0.4 to 1.01 (Table 2) and is comparable to values reported for the continental shelf sediments (Naidu, 1978) from the Beaufort Sea collected in 1977. No clear trend in regional distribution is seen in the organic carbon contents. The values are typical of unpolluted geographical locations (Palacas et al., 1976).

Hydrocarbons:

The concentration ranges of total hydrocarbons and resolved n-alkanes, respectively, are 20,000-50,000 ng/g and 1,400-5,000 ng/g (Table 2) and these are less than the values reported for nearshore sediments (Shaw et al., 1978) and eastern Beaufort Sea sediments on the Canadian border (Wong et al., 1976). The n-alkanes maximize at C_{27} or C_{29} and there is no measurable unresolved complex mixture (Fig. 9). The odd-even carbon preference data (Table 2) also indicate substantial input of terrigenous detritus in these sediments (Eglinton and Hamilton, 1963; Kolattakudy, and Walton, 1973). This is not surprising in view of the number of rivers along the shores of the study area, such as the

Meade, Ikpikpuk and Colville Rivers. Stations from 1 to 4 in particular receive the terrigenous input from Colville River, since clay mineral assemblages in the Barter Island are thought to originate in the Colville River (Naidu, 1978).

A marine biogenic origin for some of the organic matter is also indicated by the presence of pristane and heptadecane, which are derived from marine plankton. Phytane is also present in detectable quantities and Pr/Ph is generally between 1.5 to 2.5 (Table 2). The presence of phytane and Pr/Ph ratios around 1.0 in marine sediments are often inferred as indicating petroleum pollution (Speers and Whitehead, 1969; Zafiriou et al., 1972). However, several unpolluted sediment samples from the estuarine environment of the English Channel were found to have Pr/Ph ratios of almost unity and this was attributed to bacteria (Tissier and Oudin 1973). Bacterial may therefore account for the presence of some phytane in Beaufort Sea sediments. In short, the absence of unresolved complex mixture signal and the distribution pattern of major alkanes in the Beaufort Sea sediments can be attributed to recent biogenic-rich source with little or no anthropogenic input.

Small amounts of alkenes from C_{15} to C_{23} with one or two degrees of unsaturation have been detected by GC/MS analyses. These olefins could be of biogenic origin.

Several steranes, diterpanes (Structure I in Appendix I) and triterpenoids such as adiantane, hopane (III, $R=C_3H_7$), 22,29,30trisnorhopane (II, R=H) and a C_{31} methyltriterpane have been detected in sample 6 (Fig. 15). These triterpenoids and their extended homologs have probably been derived from recent biogenic activity (Simoneit, 1977) and not from petroleum (Dastillung and Albrecht, 1976). The absence of one of the two diastereomers at position 22 of the extended triterpanes also suggests the absence of petroleum input (Dastillung and Albrecht, 1976). These diastereomers are commonly found as 1:1 mixture in petroleum polluted sediments as in Southern California Bight (Simoneit and Kaplan, 1980; Venkatesan _et al_., 1980a).

The concentration of the resolved polynuclear aromatic hydrocarbons (PAH) is 200-300 ng/g (Table 12) in the sediments, and is generally comparable to the data reported by Wong and co-workers (1976) for sediments collected to the east of the present study area.

In the two samples, 1 and 7, analyzed by GC/MS, relatively large amounts of naphthalene, phenanthrene, pyrene, chrysene, etc. and their mono- and di-substituted alkyl homologs have been identified and the relative abundance decreases rapidly with further alkyl substitution (Figure 9, Table 12). This type of PAH distribution was previously found to result from mixed input from pyrolytic sources and possibly fossil fuel (Youngblood and Blumer, 1975). Similar observation on the nearshore sediment from Maguire Islands close to our station 1 has been reported by Shaw _et al_. (1979). Boreal forest fires are reported to be an insignificant source of PAH for the area (Wong _et al_., 1976). Lower latitude natural fires cannot be an important source of sedimentary PAH at those latitudes and hence such remote forest fires are also unlikely source in the distant Beaufort Sea environment (Laflamme and Hites, 1978). Long-distance transport from anthropogenic sources through atmospheric fallout could be an important source of the pyrolytic PAH in Beaufort Sea sediments (Shaw _et al_., 1979; Laflamme and Hites, 1978; Lunde and Bjorseth, 1977; Rahn _et al_., 1977). The other potential source of fossil PAH may be coal outcrops on the Meade River and the oil seep area near Smith Bay. The longshore bottom currents flowing westward (Pelletier, 1975) could carry eroded source materials discharged by the MacKenzie River into the area studied. MacKenzie River flows through regions with known fossil fuel deposits such as the Athabasca tar sands and Norman well oil seepage area. It is quite possible that unidentified offshore or onshore oil seeps also exist near the area of investigation.

Perylene is present at the same level as other PAH in these surface sediments (Station 1-10 ng/g; Station 7-40 ng/g; Table 11). Lower values have been reported ($\leq$ 7 ng/g) for Southeastern Beaufort Sea surface sediments by Wong *et al*. (1976). Perylene content is not anomalously high in the region as found in Namibian Shelf (Wakeham *et al*., 1979) and the origin of perylene is uncertain. It could be from terrestrial (Bergmann *et al*., 1964) or marine (Wakeham *et al*., 1979) sources.

The presence of cadalene, retene and simonellite in these samples add support to the *n*-alkanes distribution for terrigenous input (Simoneit, 1977). Cadalene is thought to be derived from the diagenetic alteration of cadinene and other sesquiterpenes from higher plants. Simonellite (traces) and retene (the most abundant of the three) found in these sediments are the products of diagenesis of the diterpane, abietic acid occurring in higher plants, especially conifers. These compounds have been identified in the nearshore Beaufort Sea sediments (Shaw *et al*., 1978) and the abundance of retene was attributed to the peat material which has not undergone sufficient diagenetic alteration to provide a full suite of fossil PAH.

Southeastern Bering Sea

Organic Carbon:

The organic carbon values are low (Table 3) considering the relatively high biological productivity of this continental shelf region (Simoneit, 1975), apparently as a result of a combination of oxic conditions at the sediment surface and a high-energy depositional environment (Sharma, 1974). The organic carbon content increases with decreasing mean grain size of the sediment (Bordovskiy, 1965; Sharma, 1974). Sediments in this region are reported to become progressively finer-grained from nearshore to the edge of the shelf (Sharma, 1974). The total hydrocarbon content of these sediments follows the same trend, with low concentrations of total hydrocarbons in coarse-grained sediments close to shore and higher concentrations in fine-grained sediments near the shelf edge (Table 3).

Hydrocarbons:

A detailed discussion of the distribution and dynamics of hydrocarbons in the eastern Bering Sea Shelf can be found in Venkatesan et al. (1980b). Only a brief summary of the study will be presented here.

The alkanes in sediments of the study area generally show a bimodal distribution typical of a mixture of allochthonous and autochthonous sources (Fig. 10; Table 3). In short, the absence of unresolved complex mixture and the distribution pattern of n-alkanes in most of the stations studied can be attributed to recent biogenic sources characteristic of unpolluted environments.

The only exception is sample 35, as presented in Fig. 10, whose gas chromatogram is characterized by a broad UCM in the entire elution range, with no measurable, resolved hydrocarbons. This pattern is typical of weathered petroleum contamination and is similar to the sediments from Southern California nearshore basins (Venkatesan et al., 1980a). The source of these hydrocarbons may be natural submarine seepage, although none have been reported in the southern Bering Sea shelf. However, faults in this area (Marlow et al., 1976) could allow leakage of petroleum from underlying reservoir rocks. The extensive fishing operations around this area make an anthropogenic origin for these hydrodarbons possible; it seems unlikely, however, since the chromatogram from station 37 (Fig. 10) and other samples from this area of intensive fishing do not show evidence of such petroleum contribution.

The anomalously high pristane content in some of the stations could be from the Calanus copepods found in this area (Motoda and Minoda, 1974) which contain high concentrations of pristane (Blumer et al., 1964) relative to other zooplankton genera.

In most of the stations, the triterpenoids appear to be derived mainly from bacteria or algae (DeRosa et al., 1971; Cardoso et al., 1976), and consist of 17β(H)-hop-22(29)-ene (diploptene, IV in Appendix I), hop-17,(21)-ene (V), 17β(H)-22,29,30-trisnorphpane (II, R=H, 17β), and 17β(H)-hopane (III, R=C_3H_7) and the series of extended 17β(H)-hopanes ranging from C_{31} to C_{33}, with only minor amounts of the 17α(H)-hopanes (III). These sediments contain predominantly C_{27}, C_{30}, and C_{31} ββ triterpanes (Fig. 16). Several C_{30} triterpenes with a double bond in addition to diploptene have also been detected. Most of the C_{29} triterpanes found are not hopanes and their identity has not yet been determined. The extended hopanes (> C_{31}) are present as single C-22 diastereomers. The presence of predominantly 17β(H) stereomers and of the triterpenes which are present in living organisms indicates that these compounds are of recent biogenic origin. The presence of only small quantities of 17α(H) stereoisomers suggests that there is no input from petroleum components (Dastillung and Albrecht, 1976; Simoneit and Kaplan, 1980; Venkatesan et al., 1980a). As a comparison, an example of recent sediment from San Pedro Basin Southern California Bight is given in Fig. 16, where the triterpanes are predominantly the 17α(H) homologs, and the extended hopanes (III) are present as one: one mixtures of the C-22 diasteromers (Venkatesan et al., 1980a). There, the dominant homolog is 17α(H), 18α(H), 21β(H)-28,30-bisnorhopane ($C_{28}H_{48}$) which has been proposed to be a molecular marker of Southern California petroleum (Seifert et al., 1978; Simoneit and Kaplan, 1980). Stations from the Eastern Bering Sea contain no C_{28} triterpenoid.

The only exception is station EBBS 35 (Fig. 16), which shows a triterpenoidal distribution very similar to petroleum-contaminated Southern California sediments. This is consistent with the observed n-alkane distribution pattern of this station, typical of weathered petroleum. This sample consists predominantly of 17α(H) homologs and the extended hopanes are present as one:one mixtures of the C-22 diastereomers. The C_{28} bisnorhopane found in Southern California petroleum is also found in this sample, but is much less abundant than in Southern California Bight sediments (Venkatesan et al., 1980a).

The resolved PAH compounds are at the level of 3-20 ng/g in the area, much less than those found in Beaufort Sea sediments. Concentrations of selected PAH compounds are presented in Table 12. In general, the parent PAH compounds are more abundant than their alkyl homologs, indicating pyrolytic origin (Youngblood and Blumer, 1975) possibly derived from forest fires or long distance transport through atmospheric fallout (Lund and Bjorseth, 1977; Rahn et al., 1977).

The allochthonous lipids, the primary source of hydrocarbons in these surface sediments, are probably transported to the continental shelf by river discharge and erosion and redistribution of surface sediments. Correlation of the hydrocarbon distribution in the sediments of the eastern Bering Sea with the hydrocarbons extracted from eelgrass (Zostera marina) and sediments from within Izembek Lagoon indicates that the latter environment may not be a significant source of hydrocarbons in the outer shelf sediments. However, carbon isotopic analysis of humic and kerogenous substances from the lagoon and shelf sediments indicates that these biologically refractory organic materials may be transported to the shelf environment (Venkatesan et al., 1980b).

The presence of relatively small amounts of autochthonous hydrocarbons in the sediments, in spite of the high biological productivity of the region suggests rapid and efficient recycling of marine lipids within the water column or at the sediment-water interface. Presence of higher concentrations of relatively labile hydrocarbons derived from the autochthonous sources, identified in only a few stations on the Bering Sea shelf, may be important in an assessment of the fate and effects of petroleum products introduced into this marine environment. Any petroleum contamination and deposition in those environments may last a long time.

Norton Sound

Organic Carbon:

Total organic carbon content (Table 4) ranges from 0.12 to 1.3% and is similar to Beaufort Sea, southeastern Bering Sea and other uncontaminated marine sedimentary regimes. Sediments in the open ocean have a slightly lower carbon content in general than those nearshore. Apparently, the organic carbon content in this region, unlike that of the southeastern Bering Sea sediments, is generally related to the distance from the presumed terrigenous source, the Yukon River.

Hydrocarbons:

The distribution and dynamics of hydrocarbons in Norton Sound sediments can be found in Venkatesan *et al.* (1980b) in greater detail. Only a brief review of our study in this area will be reported here.

The *n*-alkanes in these sediments are of biogenic origin, consisting of a mixed input from marine and terrestrial environments as seen from the gas chromatograms (Fig. 10) and the data on odd/even ratios, etc. in Table 4. The terrigenous input is apparently diluted with marine contribution gradually from nearshore (Stations 1, 5, 7, 49, 131, 137) to the open ocean (33A and 47A; Fig. 3). Sediments from the Yukon prodelta are the richest in hydrocarbons. The northern part of Norton Sound seems to be impoverished in hydrocarbons, because there are no major rivers contributing to terrigenous silt.

Sediments from stations in Norton Sound, south of Nome (Stations 47, 172, 174, 14, 15, 16, 17, 18 and 22) suspected to be near petroleum gas seeps (Cline and Holmes, 1977) do not show *n*-alkane and triterpenoidal distributions characteristic of petroleum (Fig. 16 e.g., NS 17).

Polycyclic aromatic hydrocarbons in Norton Sound surficial sediments show pyrolytic origin (Table 12). A core analyzed from station 5 from surface down to 90 cm contains increasing amounts of phenanthrene, fluoranthene and benzo(e)-

pyrene, with depth. This trend emphasizes the importance of natural (forest) fires in the area, contributing to PAH in the preanthropogenic period. Perylene depth profile is not well defined, although it is the most abundant PAH in the core. However, a general decrease in the concentration of perylene is observed from nearshore to offshore sediments. This may lead us to conclude that perylene is derived from a terrigenous precursor although, in the absence of comparable data on depth profiles from a station in the open ocean (where terrestrial input is minimal), a marine precursor cannot be ruled out.

The di- and triterpenoids are of biogenic origin (Fig. 16). A detailed discussion of the triterpenoids in these sediments is presented by Kaplan _et al_ (1980) and Venkatesan _et al_. (1980b).

Navarin Basin

Sample Collection:

In the cruise of the USCGC POLAR STAR in May, 1980 (Table 1) sediment samples, 2-25, were collected from Navarin Basin and samples 26-33 from around St. Lawrence Island and Cape Romanzof (Fig. 4). Surface (0-2 cm) samples, 2-11, were collected with a modified Van Veen sampler after which the sampler was lost in the Bering Sea. The rest of the samples are bulk samples, retrieved from a small Van Veen sampler.

Organic Carbon:

Organic carbon content (Table 5) of the sediments falls within the range from 0.1 to 1.4%, comparable to values observed in any other part of the Alaskan Shelf and is typical of unpolluted marine sediments (Palacas _et al_., 1976). These values are much lower than those observed in areas which have highly reducing conditions, such as Saanich Inlet and the Black Sea (Nissenbaum _et al_., 1971; Degens, 1971). No clear trend in regional distribution within the area is seen for the organic carbon contents.

Hydrocarbons:

The contents of the various resolved hydrocarbons are presented in Table 6. The total resolved n-alkane content ranges from 0.25 to 2.6 μg/g and is comparable to that found in Southeastern Bering Sea (Venkatesan et al., 1980b). Considering the remoteness of the area, the n-alkane contents of the sediments in this region is high, thus probably indicating greater contribution from marine productivity.

Representative gas chromatograms are presented in Fig. 4. The gas chromatograms exhibit flat baselines and a maximum at n-C_{27}. The odd/even ratios are similar to those observed in Norton Sound falling within a narrow range from 3.5 to 4.8, indicative of substantial terrigenous influx. This is contrary to what is expected from the geography of the region where allochthonous input from rivers and lagoons should be minimal. This is also surprising in view of our observation in the Norton Sound region (Venkatesan et al., 1980b) where the terrigenous detritus appeared to be diluted by open ocean sedimentation. However, the data suggests that at least part of the terrigenous detritus is transported to this Basin from the Yukon River delta in Norton Sound. Probably smaller waves with shorter periods generated by northeasterly winds move southward in the direction of Navarin Basin (Larsen et al., 1980); or, sediment could possibly be transported from the southern Bering Sea where major wave trains originate and move northward into Navarin Basin and Norton Sound.

Pristane is present in a few samples and in very low amounts (1-11 ng/g). Phytane if present is below the detection limits, again indicating that the environment is "clean", free of petroleum hydrocarbons.

In short, the absence of unresolved complex mixture signals and the distribution pattern of major alkanes in the Navarin Basin sediments can be attributed entirely to recent biogenic input.

The sediments in this basin contain much larger amounts of olefins eluting around Kovats indices 2100, 2600, 2800 and 3000, than the n-alkanes and aromatic compounds compared to any other area in the Alaskan shelf. The most dominant olefins around 2100 may be the same alkenes found in other parts of the Alaskan Seas (Kaplan et al., 1979; 1980). The other olefins occurring in the gas chromatograms of the aromatic fractions are next in order of abundance (at least 80% of that eluting around Kovats index 2100). In most of the samples analyzed (23 out of 28) olefins at Kovats index ∿ 2600, ∿ 2800 and ∿ 3000 are the dominant compounds in the polynuclear aromatic hydrocarbons fraction. The distribution pattern of these three major olefins in the sediments from Navarin Basin is unique to this area in the entire Alaskan Shelf studied so far. A few sediments in other parts of Alaska contain moderate amounts of squalene, an olefin eluting around Kovats index 2800. The olefin eluting around KI 2600 is a C_{25} tetraene similar to the one reported by Barrick and Hedges (1981) from Puget Sound sediments. Yet as far as we know the olefin eluting around Kovats index 3030 has not been reported in the literature. This is a $C_{30}H_{50}$ compound which is prominent in all the samples. The mass spectra indicates that it is a fused bicyclic tetraene with the two fused rings at one end of the molecule. The identity of the compound needs to be confirmed by hydrogenation. This could be an intermediate product between squalene and a triterpenoid. The abundance of these polyolefins indicate input from phytoplankton or zooplankton.

Trace amounts of diterpanes ranging from C_{19} to C_{24} have been identified by GC/MS (Fig. 17). These are probably derived from resinous higher plants (Simoneit 1977). Diterpenes also occur in small amounts.

In most of the stations, the triterpenoids appear to be derived mainly from bacteria or algae (DeRosa et al., 1971; Cardoso et al., 1976) and consist of 17β(H)-hop-22(29)-ene (diploptene, IV) as the most predominant component (Fig. 17).

The other predominant homologs are the C_{27} triterpenoid, 17β(H)-22,29,30-trisnorhopane (II, R=H) and C_{30} and C_{31}, 17β(H),21β(H)-hopanes (II). The C_{29} moretane (17β(H),21α(H) and iso-hop-13(18)-ene are present in moderate amounts in most of the stations. The presence of minor quantities of 17α(H) stereomers and the presence or predominance of only one C-22 diastereomer (in hopanes $\geq C_{31}$) suggest the absence of input from petroleum components (Dastillung and Albrecht, 1976; Simoneit and Kaplan, 1980; Venkatesan et al., 1980a)

The resolved polycyclic aromatic hydrocarbons (PAH, 20-40 ng/g, Table 11) in sediments from this area are comparable to those found in Norton Sound and southeastern Bering Sea and an order of magnitude less than in Beaufort Sea sediments (Table 11). The presence of phenanthrene, methylphenanthrenes, pyrene and floroanthene indicates pyrolytic sources rather than input from crude oil shales (Coleman et al., 1973; Youngblood and Blumer, 1975).

Perylene is present in large amounts (6-12 ng/g) compared to other PAHs in the samples. It has to be noted, however, that in Norton Sound, samples of perylene content appeared to decrease progressively from nearshore to offshore sediments suggestive of a terrigenous precursor for perylene (Venkatesan et al., 1980b) in the area. The data in the Navarin Basin lends support to this argument. Note that substantial terrigenous influx has been indicated earlier by higher odd/even ratios in Navarin Basin.

Cadalene and simonellite occur only in traces whereas retene is found in measureable amounts (Table 11). These diterpenoids are molecular markers derived from terrigenous resinous plants again, suggesting the allochthonous input into the Basin.

By virtue of its location, Navarin Basin should be expected to be impoverished in terrestrial material. Yet our data do indicate substantial terrigenous hydrocarbons in the sediments. The hydrocarbon and n-alkane contents, and odd/even ratios are in the same range as observed for Norton Sound and southeastern

Bering Sea. This would suggest that the latter two areas contribute terrestrial matter to Navarin Basin by wave action and sediment transport. Consequently any oil spillage arising from future petroleum development in Norton Sound or southeastern Bering Sea would be expected to affect the benthic ecosystem in Navarin Basin as well. Hydrocarbon levels should therefore be monitored in Navarin Basin also in the event of exploration and drilling in the other two areas.

Gulf of Alaska

Organic Carbon:

The organic carbon content (Table 7 and 8) varies from 0.1 to 1.1% and is similar to that observed in southeastern Bering Sea and Norton Sound sediments. This low amount is characteristic of unpolluted environments. No clear trend of organic carbon content with grain size or distance from the shore is evident.

Hydrocarbons:

Total hydrocarbons and resolved n-alkanes are comparable to those found in southeastern Bering Sea (Tables 7 and 8). The alkanes range in length from n-C_{15} to n-C_{33}, and have a bimodal distribution with maxima at either n-C_{22} and/or n-C_{27} or C_{29}. An odd carbon predominance exists in the C_{25} to C_{33} region, while no such predominance exists in the C_{22} region. Therefore, the resultant odd/even ratio from C_{15} to C_{33} falls in the range 1 - 2.5 (Tables 7 and 8). Associated with the cluster of n-alkanes maximizing at n-C_{22} is a narrow unresolved complex mixture as illustrated in the chromatograms in Figure 12. The nonselective distribution of n-alkanes maximizing around n-C_{22} and the associated unresolved complex mixture could be derived from bacterial decomposition of algal material (Johnson and Calder, 1973; Cranwell, 1976) rather than from petroleum. The lack of petroleum residues in these sediments is consistent with the absence of oil-utilizing microorganisms in this area (Atlas, 1976). The alkanes from n-C_{25} to n-C_{33} with odd carbon preference are characteristic of terrigenous higher plants whose contribution is probably not enough to dilute the autochthonous contribution from microbial activity. In contrast to the predominance of allochthonous hydrocarbons in the southeastern Bering Sea, much wider range in the relative proportion of marine and terrestrial hydrocarbons is encountered in the Gulf of Alaska sediments. This is consistent with the textural distribution of sediments which varies considerably, regionally as well as locally, in the Gulf (Sharma, 1979), while a gradation in the sediment grain size is evident in the eastern Bering Sea from nearshore to offshore.

The di- and triterpenoids are of biogenic origin with the predominance of 17β(H),21β(H)-hopanes and also several di- and triterpenes (Figure 15). The 17α(H),21β(H)-hopane (C_{30}) is present at relatively higher levels in station 119 than encountered in other Alaskan areas. Yet, the lack of a homologous series of extended triterpanes and the absence of both the diasteromers at position 22 with 1:1 ratios would indicate the absence of petroleum in the sediments.

Resolved PAH compounds in this region is an order of magnitude greater than those found in Bering Sea or Norton Sound, but comparable to that in Beaufort Sea (Table 11). Since microbial activity appears to be dominant in this area, it is possible that by unknown mechanisms, the marine bacterial population could accumulate (Hase and Hites, 1976) or contribute to the PAH content, in addition to long distance atmospheric transport of pyrolytic PAH. Methylphenanthrenes and phenanthrene are the dominant PAH and pyrene is present in moderate amount whereas fluoranthene is found only in traces. Fluoranthene to pyrene ratio is much less than that found in other Alaskan areas or in the Recent sediments from other parts of the world (LaFlamme and Hites, 1978). This type of distribution leads us to conclude that pyrolytic PAH have less significant contribution to the area than probably bacterial synthesis or bioaccumulation of specific PAHs. However, a more detailed study is necessary before any meaningful conclusion is drawn regarding the sources of PAHs. Terrigenous input is indicated by the presence of retene, cadalene and simonellite as is evident from the *n*-alkane distribution.

The presence of relatively labile polyolefins in sediments, eluting around n-C_{21} may indicate relatively less oxidizing depositional environments as discussed previously on the southeastern Bering Sea sediments. The sediments at station 121 and 134 have high organic carbon (1.1%) and clay contents compared to other Gulf of Alaska and Southeastern Bering Sea sediments, suggesting a sedimentary regime favorable to the accumulation of organic material. Sediments which apparently accumulate and preserve labile lipids should be considered areas of continental shelf that would be most affected by petroleum introduced into the marine environment.

Kodiak Shelf:

Organic Carbon:

Organic carbon content (Table 9) is within the range 0.2 - 1.2% and comparable to values typical of unpolluted marine sediments and similar to those found in eastern Bering Sea and Gulf of Alaska. Stations 97 and 98 have the highest percent organic carbon (2.15; 2.45%, Table 9) and these stations contain sediments of clayey silts. Two other stations having organic carbon $\geq$ 1.0% (92 and 93%, Table 9) are in the region reported to contain clayey silty sand, while in the rest of the stations studied, mainly sandy gravel or gravelly sand prevail (Sharma, 1979). This would explain the low organic carbon content observed in most of the sediment samples.

Hydrocarbons:

The total resolved n-alkanes range from 20 to 800 ng/g (Table 9). Distinct trends in hydrocarbon distribution were not noticed, although the highest hydrocarbon levels and organic carbon contents were found at the southernmost stations, 92, 97 and 98. In general, excluding these three stations, Kodiak area sediments have the least lipid and n-alkane content of all the sites investigated. The resolved n-alkanes (10-420 ng/g) are less by an order of magnitude compared to those of Beaufort Sea sediments and about 2-5 times less than in any other Alaskan area studied.

A representative gas chromatogram is given in Figure 13. Most of them have a maximum at $\underline{n}$-C_{27}, except a few which maximize at $\underline{n}$-C_{29}. The odd/even ratios are generally between 0.8 and 2.8 and are conspicuously lower than in the other sites, indicating that terrigenous input is substantially reduced in this area (Table 9). Unlike the other regions which may receive allochthonous material from rivers and intertidal marshes, transport of allochthonous material to the area around Kodiak Shelf is expected to be minimal because of the steep rugged topography of the Alaskan Peninsula which borders the shelf on one side and the Pacific water and the Gulf of Alaska on the other side. This region lacks large rivers and barrier island marshes. However, allochtonous organic material may be transported to this area from Cook Inlet, although the major sediment transport is reported to be through Shelikof Strait into the western Gulf of Alaska (Sharma, 1979).

A very narrow unresolved complex mixture signal localized around $\underline{n}$-C_{21} to $\underline{n}$-C_{23} could be attributed to the bacterial decomposition (Johnson and Calder, 1973; Cranwell, 1976) of algal material rather than a petroleum source. It is more likely that sediments in the west and south, rather than east of Kodiak Shelf would be contaminated with petroleum where hydrocarbons from natural seeps in Cape Douglas or from the oil and gas production in upper Cook Inlet would be expected to be transported by surface currents and deposited.

The abundance of polyolefins in the sediments indicate input from phytoplankton or zooplankton and similar polyolefins have been detected in continental shelf sediments from the Gulf of Mexico (Gearing et al., 1976) and the Atlantic Coast (Farrington et al., 1977). Kodiak area is known for high biological productivity and is important for commercial and sport fisheries. It is therefore not surprising to see relatively more input of marine organic matter into sediments around this area.

Several diterpanes, diterpenes, triterpanes and their extended homologs characteristic of biogenic origin have been detected in the two samples (stations 92 and 130) analyzed by GC/MS, similar to the other areas studied. The two diastereomers (S and R) at position 22 of the C_{31} and C_{32} triterpanes have been detected in both the samples and the diastereomer eluting earlier is present only in trace amounts mixed with a C_{30} triterpene (Figure 15).

The concentrations of resolved aromatic hydrocarbons are in the range of 6-100 ng/g except in station 98 (200 ng/g) which has the highest aromatic content of all the stations in the area (table 11, Fig. 13). Station 80 represented in the figure shows typical distribution pattern of aromatic compounds in the area (not considering the three major peaks which will be discussed later). Samples 80 and 98 contain phenanthrene, methylphenanthrenes, naphthalene, fluoranthene, pyrene, chrysene and their methylated homologs (Table 11). Benzo(E)pyrene, pyrelene and coronene were detected in both the samples, whereas benzo(A)pyrene is present only in station 98. In station 80, the three major peaks are 2-butoxy-2-oxoethylbutylphthalate, bis(2-hexyl-ethyladipate) and dioctylphthalate, respectively, the sources for which are unknown. No other station in this area appears to contain these compounds, as evident from the gas chromatographic profiles. Procedure blank did not contain these compounds. The PAH content in Kodiak area sediments is comparable to that in Gulf of Alaska. Since the *n*-alkanes profile indicates substantial marine input, it is likely that marine bacteria contribute to the PAH budget in these sediments probably by bioaccumulation (Hase and Hites, 1976) in addition to pyrolytic input.

Traces of simonellite, cadalene and retene are present but are usually less abundant than those found in Norton Sound, southeastern Bering Sea, Gulf of Alaska or Navarin Basin. This indicates much less terrigenous input in this region.

Sediments in a few stations having high organic carbon and clay contents relative to other stations in this region imply a favorable sedimentary regime for the accumulation of organic material. This region where sediments apparently accumulate and preserve especially labile lipids such as alkenes derived from the autochthonous sources, may be important in the assessment of the fate and effects of petroleum into the marine environment. Any petroleum deposition in those environments may have a long residence time.

Cook Inlet

Organic Carbon:

The total organic carbon contents vary from 0.06 to 1.57% and are characteristic of unpolluted, relatively coarse marine sediments (Table 10). The Kachemak Bay and Shelikof Strait regions contain relatively fine-grained sediments and higher organic carbon content (> 1%) than the sandy gravel or gravel (Sharma, 1979) found in the northern and central regions of Cook Inlet, including Kamishak Bay. This might indicate enhanced hydrocarbon accumulation in the two former regions. The higher values observed in Kachemak Bay are also from the very high primary productivity persisting over several months in this area. Phytoplankton productivity and standig stocks of chlorophyll a, found to be highest in Kachemak Bay, decrease steadily to low values in the middle of the inlet (Larrance et al., 1977). Part of the organic matter that is produced in the Kachemak Bay region probably settles to the sea floor and gets buried within the sediments. However, the remaining fraction of the organic matter produced in Kachemak Bay may eventually be deposited in Shelikof Strait via the net water circulation to the north in the eastern shore and to the southwest along the western shore into Shelikof Strait (Muench et al., 1978; Hein et al., 1979). This would contribute to the higher organic carbon content in the Shelikof Strait area.

Hydrocarbons:

Replicate samples collected from a total of six stations on different cruises had similar gravimetric and gas chromatographic data (Table 10) within the limits of experimental error, indicating the homogeneity of samples retrieved and reliability of the experimental method employed. The analyses of samples from stations 204, 212, and 390 in both spring and summer (1978) also gave similar gravimetric and gas chromatographic results (Table 10), indicating that there might be no apparent seasonal variation in the hydrocarbon input to the sediments (Kaplan _et al._, 1979). These findings may be related to the study of Roubal and Atlas (1978) who observed no significant differences between counts of hydrocarbon utilizers in summer-fall and winter-spring samples from lower Cook Inlet despite the higher concentrations of suspended matter found in spring (Feely _et al._, 1978). Thus, the data for all the samples are discussed in this report emphasizing the geographical distribution of hydrocarbons in the sediments rather than the seasonal variation.

The lipid, total hydrocarbon, alkane, and resolved _n_-alkane contents follow the same trend as organic carbon. They are generally high in and around Kachemak Bay (stations 37', 43 and 227; Figures 7 and 8, Table 10) and low in the central and upper parts (except stations 27, 255 and 265) of lower Cook Inlet. Stations near Shelikof Strait are next to Kachemak Bay in the order of abundance of lipids and alkanes, whereas the western part (Kamishak Bay) is moderately enriched with lipids. A detailed discussion of the hydrocarbons distribution in the area can be found in the annual report by Kaplan _et al._ (1980).

The _n_-alkanes in sediments of the study area generally show a bimodal distribution of biogenic origin, typical of mixed marine and terrestrial hydrocarbons (Fig. 14). An odd-carbon predominance of _n_-alkanes characteristic of terrigenous plants is evident in most stations (Table 10), suggesting the influence of major rivers in the area. The _n_-fatty acids (unbound) present in these samples are also typical of a mixed marine and terrestrial input.

A few stations in Shelikof Strait and near Barren Islands (UC100, UC200, UC300, 378, 394 and 398; e.g., Fig. 14) show moderately large unresolved complex mixtures in the gas chromatograms of their aliphatic fractions. The GC/MS data (Fig. 18) of these samples rule out the presence of oil input. This type of distribution could be attributed to bacterial decomposition of algal material (Johnson and Calder, 1973; Cranwell 1976)

Exceptions are stations 265 and 27 north of Kalgin Island, which show distributions of n-alkanes and triterpenoids, characteristic of oil pollution (Fig. 14 and 18). The triterpenoidal distribution of sediments from Station 265 is similar to that in Cook Inlet oil (samples obtained from J. Payne, SAI, California) as illustrated in Fig. 18. In both the sediment and oil, the diterpanes occur as mixtures and therefore, are not represented in the histogram. Oil production activities in upper Cook Inlet may be the contaminating source in Station 27 and 265. However, the possibility of a local seep around Kalgin Island with similar triterpenoidal distribution cannot be ruled out.

The following are other data which corroborate our results on HMWHC from station 265: The source of anomalously high concentrations of ethane and propane observed in upper Cook Inlet has been attributed to chronic petroleum seeps and/or fossil fuel development in the area (Cline et al., 1979). The petroleum hydrocarbon pollution apparent at stations 265 and 266 (northeast of 265, sediment not collected for HMWHC analysis) has also been inferred from microbiological studies. The effect of crude oil on the uptake of glucose and glutamic acid in the water samples were minimal in the stations taken nearest to the existing drilling platforms north of Kalgin Island (stations 265 and 266), indicating that the populations in this area have been exposed to crude oil and thus are resistant to its acute effects (Griffiths and Morita, 1979).

A complex mixture of PAH compounds was identified by GC/MS in all the sediments (Table 13). The relative distribution of parent homologs and their alkylated derivatives is characteristic of pyrolytic (natural and/or anthropogenic) sources.

Perylene is found in the samples from trace amounts to 50 ng/g. Like any other aliphatic or aromatic compound, perylene is also found at higher concentrations in Kachemak Bay (CB9-51 ng/g) and Shelikof Strait (388, UC300) than in Kamishak Bay or the central part of Cook Inlet (203, 233, Table 13). Origin of perylene in these sediments is most probably terrestrial (Bergmann et al., 1964; Aizenshtat, 1973). GC/MS analysis of sediments from deep cores at different stations would give more information about the origin and precursors of perylene.

The Kalgin Island area is probably the most important commerical fishing region for salmon (Stern, 1976) and halibut. Our data indicate that the sediments from this region have been contaminated with petroleum possibly from the production activities in upper Cook Inlet. This could lead to detrimental effects on the ecosystem in this region. Oil released chronically at low levels may not be deleterious since the pollutants appear to get diluted and dispersed within a short distance from the source, owing to the dynamics of water circulation in the area. But any major spill, tank or pipeline blowout may release hydrocarbons in considerable amounts such that they would be dispersed and redeposited eventually in Shelikof Strait. In that event, marine life around Shelikof Strait will be the most affected. Indeed, studies of Feely et al., (1979) show that little sedimentation occurs in the central basin of lower Cook Inlet and that the embayments along the coasts of lower Cook Inlet and Shelikof Strait may be receiving most of the fine particulates discharged from the coastal rivers of upper Cook Inlet. Further, suspended particles from Cook Inlet have been shown to be efficient scavengers of crude oil (Feely et al., 1978). Thus, any modern sediment deposited in Shelikof Strait should reflect major changes in upper Cook Inlet or in Kachemak Bay. Future environmental monitoring studies should therefore be concentrated around Kalgin Island and Shelikof Strait.

CONCLUSIONS

Organic Carbon

The organic carbon content ranges generally from 0.1 to 1.4% in the sediments from Alaskan Continental Shelf (Table 14) and these values are typical of unpolluted marine sediments. Sediments in the open ocean have a slightly lower carbon content than those from nearshore e.g., in Norton Sound and Cook Inlet. In southeastern Bering Sea, however, the sediments are progressively finer-grained from nearshore to the edge of the shelf and the organic carbon content increases gradually from nearshore to the shelf edge. In short, the organic carbon content in the Alaskan sediment is related to the distance from the terrigenous source of detrital minerals.

Hydrocarbons

The alkanes in sediments of the Alaskan outer continental shelf generally show a bimodal distribution (Table 14) of biogenic origin, typical of a mixture of marine autochthonous and terrestrial allochthonous hydrocarbons with few abiotic and no detectable anthropogenic components. This is indicated by greater than unity of odd/even values and by the dominance of odd chain length _n_-alkanes of C_{23} to C_{31} carbon atoms. These _n_-alkanes are derived from higher plants (Maxwell, 1971) as a result of inputs from terrigenous detritus (Simoneit, 1977). Marine origin is indicated by the dominance of heptadecane and pristane in some samples (Sargent _et al_., 1976). Pristane particularly in the Bering Sea region could be contributed by _Calanus_ copepods (Motoda and Minoda, 1974). Phytane when present in moderate amounts can be thought to be produced biosynthetically (Maxwell _et al_., 1971) by bacteria (Tissot and Oudin, 1973), rather than from petroleum (Zafiriou _et al_., 1972). In short, the absence of unresolved complex mixture signal and the distribution patterns of major alkanes in the Alaskan Seas are characteristic of a pristine environment. A narrow unresolved complex mixture signal localized around n-C_{21} to n-C_{23} in all the Gulf of Alaska and a few of Kodiak Shelf and Cook Inlet sediment samples, has been observed. This could be attributed to the bacterial decomposition (Johnson and Calder, 1973; Cranwell, 1976) of algal material rather than a petroleum source.

The molecular markers such as diterpenoids, 17β(H),21β(H) and olefinic triterpenoids and extended 17β(H),21β(H)-hopanes also reflect biogenic origin of the lipids in most of the sediment samples.

Exceptions are stations 27 and 265, north of Kalgin Island, in lower Cook Inlet, which show a typical weathered petroleum distribution of n-alkanes. The triterpenoidal residue consists predominantly of 17α-hopanes and R and S diastereomers at position 22 in nearly 1:1 abundance which are characteristic of petroleum contamination. This material could probably be derived from petroleum production and transport in upper Cook Inlet.

The n-alkane and triterpenoidal distribution in Station 35 from southeastern Bering Sea also reflect a weathered petroleum input.

Some of the stations near Norton Sound, south of Nome, suspected to be near natural gas seeps do not show n-alkane and triterpenoidal distributions characteristic of petroleum.

A complex mixture of PAH compounds is identified by GC/MS in all the sediments. The relative distribution of parent homologs and their alkylated derivatives is characteristic of pyrolytic (natural and/or anthropogenic) sources. Station 1 in Beaufort Sea possibly shows fossil PaH input to some extent. Perylene 1,12 benzoperylene and coronene whose origin is still debatable have been detected in all sediment extracts. A gradual decrease in the concentration of perylene with distance from the presumed terrigenous source is noted in Norton Sound sediment samples. Also, in our extensive investigation of surface sediments from the entire Alaskan Seas, we found that Kodiak Shelf sediments contain only trace amounts of perylene, although other PAH compounds are relatively more abundant in these samples. Kodiak Shelf is noted for is high biological productivity where marine hydrocarbons predominate over terrestrial hydrocarbon components. Navarin Basin sediments which show substantial terrestrial input, also contain relatively higher perylene content (Table 11), although little terrigenous influx would be expected from its geographical location in the offshore area as discussed earlier. Thus, our data indicate that it is most likely the terrigenous precursor which contributes to the generation of perylene in Alaska, rather than a marine precursor as suggested by Wakeham *et al*. (1979) from their study of perylene in two Nambian Shelf sediment cores in the offshore area of southwest Africa, where terrestrial input is minimal. They found perylene content to increase with depth of the sediment core. We have analyzed a core from station 5 in Norton Sound (nearshore, where terrestrial input is considerable) from 0-2 cm to 90 cm at 5-10 cm intervals. Perylene is the most abundant PAH compound throughout the core (to be published). There are fluctuations in the perylene depth profile in this core and it is not clear whether there is a significant increase in its concentration as a function of depth. Fluctuations in the quantity of precursor input may be the reason for this type of depth concentration profile. However, we do not have data on the depth profile of perylene concentration from an offshore Alaskan area where terrestrial input is negligible. Therefore, marine precursor for perylene cannot be ruled out, either. Analyses of a sediment core from Kodiak Shelf (terrigenous source minimal) would be helpful in confirming whether perylene in Alaskan sediments is derived from a terrestrial or marine origin.

Distribution and Dynamics of Hydrocarbons in Different Areas of Alaskan Outer Continental Shelf: A Comparative Study and its Implications

High molecular weight hydrocarbon data of surface sediments from different regions of the Alaskan shelf indicate that the entire Alaskan area is uniformly "clean" free of petroleum contaminants except in a few isolated cases. Table 14 shows that the organic carbon content in these sediments is $\leq$ 1.5%, characteristic of pristine environment. Unresolved complex mixture is present in a very few samples and the total hydrocarbon contents in the sediments vary from 0.9 to 50 μg/g. These values are low; petroleum hydrocarbon levels of uncontaminated coastal sediments elsewhere are usually below 70μg/g (Clark and MacLeod 1977). However, there are differences in the hydrocarbon contents in the various areas of the Alaskan shelf. Beaufort Sea sediments have the highest hydrocarbon budget, whereas Kodiak Shelf sediments have the lowest. Resolved n-alkanes follow the same trend (Fig. 19), but PAH compounds do not exhibit the same pattern and the Gulf of Alaska and Kodiak Shelf sediments are rich in PAH biologically-produced, as well as those produced by pyrolytic combustion. Even though the PAH content in the above two areas is as high as that observed in Beaufort Sea sediments, the pyrolytic and biogenic imprint predominates in the former areas while a mixed pyrolytic and fossil PAH profile is reflected in the latter (Tables 11-13).

Terrigenous influx is indicated by the maxima at C_{27} or C_{29} in all the sediments (Table 14). The odd/even ratios in Fig. 19 illustrate that the terrestrial input varies from region to region in the Alaskan outer continental shelf. Of all the areas investigated, Norton Sound and Cook Inlet receive the maximum plant wax contribution whereas Gulf of Alaska and Kodiak Shelf, the least. Beaufort Sea, Navarin Basin and southeastern Bering Sea are second in the order of plant wax content. Allochthonous hydrocarbons are to be expected in Beaufort Sea, Cook Inlet, Norton Sound and Bering Sea from their geographical location. It is rather surprising to notice relatively higher terrigenous lipids in Navarin Basin. Terrestrial lipids are probably transported to this area from southeastern Bering Sea and/or Yukon Prodelta in Norton Sound. In short, Navarin Basin could be a sink for terrigenous lipids. This implies that any petroleum contaminant from production activities in Norton Sound or southeastern Bering Sea could affect Navarin Basin equally or more than the other two areas.

In the lower Cook Inlet area, the lipid, hydrocarbons and organic carbon contents are generally high in and around Kachemak Bay and stations in Shelikof Strait are next in the order of the abundance of organic matter. Central and upper parts of the inlet have the least. It appears that organic matter produced in Kachemak and Kamishak Bays may be deposited in the Shelikof Strait, an hypothesis which is consistent with the postulated net circulation pattern of the water and suspended matter (Muench et al., 1978; Feely et al., 1979). This observation suggests that petroleum hydrocarbons released in considerable amounts resulting from any major spill, tank or pipeline blow out in upper Cook Inlet would be dispersed and redeposited eventually in Shelikof Strait. Further, suspended particles from Cook Inlet are known to be efficient scavengers of crude oil (Feely et al., 1978). Future environmental monitoring studies should therefore be focussed on Kalgin Island (where petroleum hydrocarbons have been identified) and Shelikof Strait.

The major sediment transport from Cook Inlet is through Shelikof Strait into Western Gulf of Alaska (Sharma, 1975). Petroleum hydrocarbons could therefore be traced in the sediments of Gulf of Alaska in the event of major oil release from upper or lower Cook Inlet in the future. Eastern Kodiak Shelf would probably be less affected except in a few southernmost stations. Sediments in these stations have higher clay and organic carbon contents and imply favourable regime for the accumulation of organic material.

Relatively labile polyolefins are present in large amounts in a few stations in southeastern Bering Sea, Gulf of Alaska, in all the stations in Kodiak Shelf and Navarin Basin. This may indicate relatively less oxidizing depositional environment. Such areas of the continental shelf where sediments apparently accumulate and preserve labile lipids would be most affected by petroleum introduced into the marine environment.

Thus our organic geochemical study is able to point out areas of sedimentation which would be more affected by petroleum pollution. Future environmental monitoring studies should be focussed on these sensitive areas whenever exploration or oil drilling operations are carried out in the vicinity.

REFERENCES

Aizenshtat, Z. (1973). Perylene and its geochemical significance. *Geochim. Cosmochim. Acta 37*, 559-567.

Atlas, (1976). Annual Report to Outer Continental Shelf Environmental Assessment Program: In: OCSEAP, Vol. 9, 287-346.

Bergmann, E.D., R. Ikan and J. Kashman (1964). The occurrence of perylene in Huleh Peat. *Israel J. Chem. 2*, 171-172.

Blumer, M., M.M. Mullin and D.W. Thomas (1964). Pristane in the marine environment. *Helgolaender Wiss. Meeresuntersuch 10*, 187.

Bordovskiy (1965). Accumulation and transformation of organic substances in marine sediments. *Mar. Geol. 3*, 3-82.

Brenner, S., I.R. Kaplan, M.I. Venkatesan, J. Bonilla, E. Ruth, T. Fisher, T. Maloney, and D. Meredith (1978). RU #480 Annual Report to OCSEAP, U.S. Dept. of Commerce, NOAA, Characterization of Organic Matter in Sediments from Lower Cook Inlet, 20 pp. ✓

Cardoso, J., P.W. Brooks, G. Eglinton, R. Goodfellow, J.R. Maxwell and R.P. Philp (1976). In: *Environmental Biogeochemistry* (J.O. Nriagu, ed.), p. 149-174, Ann Arbor Science Publishers, Ann Arbor, Michigan, USA.

Chester, S.N., G.H. Gump, H.S. Hartz, W.E. May, S.M. Dyszel and D.P. Enagonio (1976). Trace Hydrocarbon Analysis: The NBS Prince William Sound/NE Gulf of Alaska Baseline Study, NBS Tech. Note 889, 66 pp.

Cline, J.D. and M.L. Holmes (1977). Submarine seepage of natural gas in Norton Sound, Alaska. *Science 198*, 1149-53.

Cline, J.D., C. Katz and A. Young (1979). Distribution and abundance of low molecular weight hydrocarbons and suspended hydrocarbons in Cook Inlet, Alaska. Annual Report to OCSEAP, *5*, 264-325.

Coleman, H.J., J.E. Doley, D.E. Hirsch, and C.J. Thompson (1973). Compositional studies of a high-boiling 370-535°C distillate from Prudhoe Bay, Alaska, crude oil. *Anal. Chem. 45*, 1724-1737.

Cranwell, P.A. (1976). Decomposition of aquatic biota and sediment formation: Organic compounds in detritus resulting from microbial attack on the alga, *Ceratium hirundinella*. *Freshwater Biol. 6*, 41-48.

Dastillung, M. and P. Albrecht (1976). Molecular test for oil pollution in surface sediments. *Mar. Pollut Bull. 7*, 13-15.

Degens, E.T. (1971). Sedimentological history of the Black Sea over the Last 25,000 years. In: *Geology and History of Turkey* (A.S. Campbell, ed.), Pet. Explor. Soc. of Libya.

DeRosa, M., A. Gambacorta, L. Minale and J.D. Bu'Lock (1971). Bacterial triterpenes. *Chem. Comm. 1971*, 619-620.

Eglinton, G. and R.J. Hamilton (1963). The distribution of alkanes. In: *Chemical Plant Taxonomy*, (T. Swain, ed.), Academic Press, N.Y., 187-196.

Farrington, J.W., N.M. Frew, P.M. Girchwend and B.W. Tripp (1977). Hydrocarbons in cores of northwestern Atlantic coastal and continental margin sediments. *Est. Coastal Mar. Science 5*, 793-808.

Feely, R.A., G.J. Massoth and M. Lamb (1978). Composition, transport and deposition of suspended matter in Lower Cook Inlet and Shelikof Strait, Alaska. Quarterly Report to OCSEAP; DOC/DOI; pp. 27.

Feely, R.A., J.D. Cline, G. Massoth, A.J. Paulson and M.F. Lamb (1979). Composition, transport and deposition of suspended matter in Lower Cook Inlet and Shelikof Strait, Alaska. Annual Report to OCSEAP DOI/DOI, *5*, 195-263.

Gearing, P., J.N. Gearing, T.F. Lytle and J.S. Lytle (1976). Hydrocarbons in 60 Northeast Gulf of Mexico shelf sediments: A preliminary survey. *Geochim. Cosmochim. Acta 40*, 1005-1017.

Griffiths, R.P. and R.Y. Morita (1979). Study of microbial activity and crude oil-microbial interactions in the waters and sediments of Cook Inlet and the Beaufort Sea. Annual Report to OCSEAP. DOC/DOI, *5*, pp. 63-142.

Hase, H. and R.A. Hites (1976). On the origin of polycyclic aromatic hydrocarbons in recent sediments: Biosynthesis by anaerobic bacteria. *Geochim. Cosmochim. Acta 40*, 1141-1143.

✓ Hein, J.R., A.H. Bouma, M.A. Hampton and C.R. Ross (1979). Clay mineralogy, fine-grained sediment dispersal, and inferred crurrent patterns, lower Cook Inlet and Kodiak Shelf, Alaska. *Sed. Geol. 24*, 291-306.

Johnson, R.W. and J.A. Calder (1973). Early diagenesis of fatty acids and hydrocarbons in a salt marsh environment. *Geochim. Comsochim. Acta 37*, 1943-1955.

✓ Kaplan, I.R., W.E. Reed, M.W. Sandstrom and M.I. Venkatesan (1977). RU #480, Annual report to OCSEAP, U.S. Dept. of Commerce, NOAA. Characterization of organic matter in sediments from Gulf of Alaska, Bering and Beaufort Seas; 16 pp.

✓ Kaplan, I.R., M.I. Venkatesan, S. Brenner, E. Ruth, J. Bonilla, and D. Meredith (1979). RU #480, Annual Report to OCSEAP, U.S. Dept. of Commerce, NOAA. Characterization of organic matter in sediments from Gulf of Alaska, Bering and Beaufort Seas; 22 pp.

✓ Kaplan, I.R., M.I. Venkatesan, E. Ruth and D. Meredith (1980). RU #480, Annual Report to OCSEAP, U.S. Dept. of Commerce, NOAA. Characterization of Organic Matter in Sediments from Cook Inlet and Norton Sound. In: *Environmental Assessment of the Alaskan Continental Shelf*, *5*, 597-659.

Kollatukudy, P.E. and T.J. Walton (1973). The Biochemistry of Plant Cuticular Lipids. In: *Progress in the Chemistry of Fats and Other Lipids*, (R.D. Holman, Ed.), Vol. XIII, Part 3, Pergamon, N.Y., 121-175.

Laflamme, R.E. and R.A. Hites (1978). The global distribution of polycyclic aromatic hydrocarbons in Recent sediments. *Geochim. Cosmochim. Acta 42*, 289-303.

Larrance, J.D., D.A. Tennant, A.J. Chester and P.A. Ruffio (1977). Phytoplankton and primary productivity in the northeast Gulf of Alaska. Annual Report to OCSEAP, DOC/DOI, 10, 1-136.

Larsen, M.C., C.H. Nelson and D.R. Thor (1980). Sedimentary processes and potential geologic hazards on the sea floor of the Northern Bering Sea. In: The Eastern Bering Sea Shelf: Oceanography and Resources (D.W. Hood and J.A. Calder, Eds.), Vol. 1; 247-261.

Lunde, G. and A. Bjorseth (1977). Polycyclic aromatic hydrocarbons in longrange transported aerosols. Nature 268; 518-519.

Marlow, M.S., H. McLean, T.L. Vallier, D.W. Scholl, J.V. Gardner and R. Powers (1976). Preliminary report on the regional geology, oil and gas potential and environmental hazards of the Bering Sea Shelf south of St. Lawrence Island, Alaska. U.S. Geol. Surv. Open File Report 76-785.

Maxwell, J.R., C.T. Pillinger and G. Eglinton (1971). Organic geochemistry. Quarterly Review 25; 571-628.

Motoda, S. and T. Minoda (1974). Plankton of the Bering Sea. In: Oceanography of the Bering Sea, (D.W. Hood and E.J. Kelly, Eds.), Univ. of Alaska, Fairbanks; 202-242.

✓ Muench, R.D., H.O. Mofjeld and R.L. Charnell (1978). J. Geophys. Res. 83; 5090-5098.

Naidu, A.S. (1978). Quarterly Report to OCSEAP, U.S. Dept. of Commerce, NOAA. Environmental Assessment of the Alaskan Continental Shelf, Sediment Characteristics, Stability and Origin of the Barrier Island-Lagoon Complex, North Arctic Alaska; pp. 703-717.

Nissenbaum, A., M.J. Baedecker and I.R. Kaplan (1971). Studies on dissolved organic matter from interstitial water of a reducing marine fjord. In: Advances in Organic Geochemistry (H.R.V. Gaertner and H. Wehner, Eds.), Pergamon Press, Oxford (1972); pp. 427-440.

Palacas, J.G., P.M. Gerrild, A.H. Love and A.A. Roberts (1976). Baseline concentrations of hydrocarbons in Barrier-Island quartz sand, Northeastern Gulf of Mexico. Geol. 4; 81-84.

Peake, E., M. Strosher, B.L. Baker, R. Gossen, R.G. McCrossan, C.J. Yorath and G.W. Hodgson (1972). The potential of Arctic sediments: Hydrocarbons and possible precursors in Beaufort Sea sediments. In: Proceedings of the International Geological Congress, 24th Session, Montreal, Section 5; 28-37.

Pelletier, B.P. (1975). Technical Report No. 25a to Beaufort Sea Project, Dept. of the Environment, Victoria, B.C. Sediment Dispersal in the Southern Beaufort Sea; pp. 80.

Rahn, K.A., R.D. Borys and G.E. Shaw (1977). The Asian source of Arctic haze bands. Nature 268; 713-715.

Sargent, J.R., R.F. Lee and J.C. Nerenzel (1976). Marine waxes. In: Chemistry and Biochemistry of Natural Waxes, (P.E. Kolattukudy, Ed.), Elsevier, New York; 49-91.

Seifert, W.K., J.M. Moldowan, G.W. Smith and E.V. Whitehead (1978). First proof of a C_{28}-pentacyclic triterpane in petroleum. Nature 271; 436-437.

Sharma, G.D. (1974). Contemporary sedimentary regimes of the Eastern Bering Sea. In: Oceanography of the Bering Sea, Occ. Publ. No. 2, (D.W. Hood and D.J. Kelley, Eds.), Inst. Mar. Sci. Univ. of Alaska, Fairbanks; 517-552.

Sharma, G.D. (1979). The Alaskan Shelf Hydrographic, Sedimentary and Geochemical Environment, Springer-Verlag, New York; pp. 498.

Shaw, D.G., D.J. McIntosh, and E.R. Smith (1979). Arene and alkane hydrocarbons in nearshore Beaufort Sea sediments. Est. Coastal Mar. Sci. 9; 435-449.

Simoneit, B.R.T. (1975). Sources of organic matter in oceanic sediments. Ph.D. Thesis, Univ. of Bristol, England; 300 pp.

Simoneit, B.R.T. (1977). The Black Sea: A sink for terrigenous lipids. Deep-Sea Res. 24; 813-830.

Simoneit, B.R.T. and I.R. Kaplan (1980). Triterpenoids as molecular indicators of paleoseepage in Recent sediments of the Southern California Bight. Mar. Environ. Res; 113-128.

Speers, G.C. and E.V. Whitehead (1969). Crude petroleum. In: Organic Geochemistry, (G. Eglinton and M.T.J. Murphy, Eds.), Springer-Verlag; 638-675.

Stern, L.J. (1976). Determination and description of the status of knowledge of the distribution, abundance and migrations of salmonids in the Gulf of Alaska and Bering Sea. Quarterly Report to OCSEAP 2; 586-748.

Tissier, M. and J.L. Oudin (1973). Characteristics of naturally-occurring and pollutant hydrocarbons in marine sediments, Prev. Cont. of Oil Spills Joint Conf. Proc, A.P.I. Publishers; 205-214.

Venkatesan, M.I., S. Brenner, E. Ruth, J. Bonilla and I.R. Kaplan (1980a). Hydrocarbons in age-dated sediment cores from two basins in the Southern California Bight. Geochim. Cosmochim. Acta 44; 789-802.

Venkatesan, M.I., M. Sandstrom, S. Brenner, E. Ruth, J. Bonilla, I.R. Kaplan and W.E. Reed (1980b). Organic geochemistry of surficial sediments from the Eastern Bering Sea Shelf: Oceanography and Resources. (D.W. Hood and J.A. Calder, Eds.), Vol. 1; 389-409.

Wakeham, S.G., C. Schaffner, W. Giger, J.J. Boon and J.W. DeLeeuw (1979). Perylene in sediments from the Nambian Shelf. Geochim. Cosmochim. Acta 43; 1141-1144.

Wong, C.S., W.J. Cretney, R.W. MacDonald and P. Christensen (1976). Technical Report No. 38 to Beaufort Sea Project, Dept. of the Environment, Victoria, B.C. Hydrocarbon levels in the marine environment of the Southern Beaufort Sea, 113 pp.

Youngblood, W.W. and M. Blumer (1975). Polycyclic aromatic hydrocarbons in the environment: Homologous series in soils and Recent marine sediments. Geochim. Cosmochim. Acta 39; 1303-1314.

Zafiriou, O., M. Blumer and J. Myers (1972). Woods Hole Oceanographic Institution Technical Report, WHO I-72-55. Correlation of oils and oil products by gas chromatography.

PUBLICATIONS AND PRESENTATIONS

Following is a list of publications and presentations that have resulted from the research unit so far:

Sandstrom, M., W.E. Reed and I.R. Kaplan (1977). Recycling of organic matter in recent sediments from the Southeastern Bering Sea and Western Gulf of Alaska. Abstract sent to the symposium on "Nature and Distribution of Organic Matter in Recent Continental Shelf Sediments". Geological Society of America, Seattle, Washington.

Kaplan, I.R. (1979). Organic geochemistry of surficial sediments from Eastern Bering Sea. Presented in the symposium on "The Bering Sea Shelf: Oceanography and Resources", OCSEAP, NOAA, Anchorage, Alaska.

Venkatesan, M.I., M. Sandstrom, S. Brenner, E. Ruth, J. Bonilla, I.R. Kaplan and W.E. Reed (1980). Organic geochemistry of surficial sediments from the Eastern Bering Sea. In: The Eastern Bering Sea Shelf: Oceanography and Resources, (D.W. Hood and J.A. Calder, Eds.), Vol. 1, OMPA/DOC, USA; 389-409.

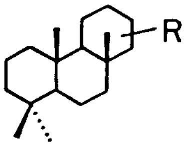
Atlas, R.M., M.I. Venkatesan, I.R. Kaplan, R.A. Feely, R.P. Griffiths and R.Y. Morita (1980). Distribution of hydrocarbons and microbial populations related to sedimentation processes in Cook Inlet and Norton Sound, Alaska. Submitted to Estuarine, Coastal and Shelf Science

Venkatesan, M.I., S. Brenner, E. Ruth, J. Bonilla and I.R. Kaplan (1980). Organic geochemistry of surficial sediments from lower Cook Inlet, Alaska. To be submitted to Chemical Geology.

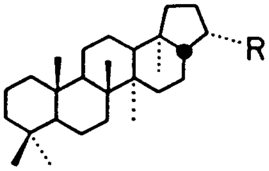
Venkatesan, M.I. et al. (1980). Distribution and dynamics of hydrocarbons in different areas of Alaskan outer continental shelf: A comparative study and its implications. In preparation.

APPENDIX I

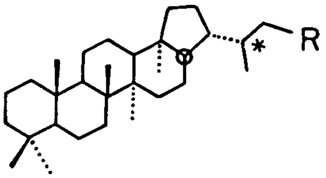
STRUCTURES CITED IN THE TEXT



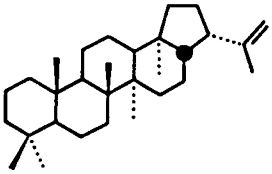
I. extended diterpanes, C_nH_{2n-4}
R=C_2H_5-$C_{12}H_{25}$



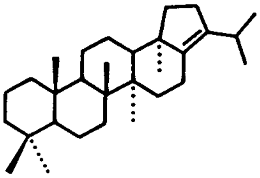
II. 17β (H),
21β(H)-hopanes, C_nH_{2n-8}
R=H,C_2H_5,C_3H_7



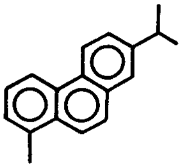
III. extended 17α (H),
21β (H)-hopanes, C_nH_{2n-8}
R=CH_3-C_5H_{11}



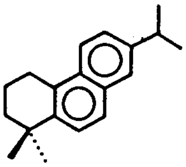
IV. diploptene, $C_{30}H_{50}$



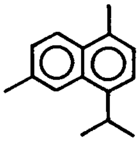
V. hop-17(21)-ene, $C_{30}H_{50}$



VI. retene, $C_{18}H_{18}$



VII. simonellite, $C_{19}H_{24}$



VIII. cadalene, $C_{15}H_{18}$

DISTRIBUTION OF TRACE ELEMENTS IN BOTTOM SEDIMENT OF THE NORTHERN BERING SEA

by

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Final Report
Outer Continental Shelf Environmental Assessment Program
Research Unit 413

July 1980

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I. SUMMARY

2-dimensional contour and 3-dimensional value-surface maps of semi-quantitative emission spectographic analyses for over 50 elements in surface sediment from 180 sampling stations are presented. For purposes of discussion, certain of these elements have been grouped into the following categories: petroleum indicators, heavy metals, potentially toxic elements, chemically sensitive elements, major elements, minor elements, and a group of elements of economic interest.

Of the petroleum indicator elements, Ni and V, Ni showed only average concentrations in sediment near a gas seep 35 km south of Nome, Alaska; V showed slightly lower values in samples taken recently from the gas-seep area and relatively high values in samples collected earlier from the same area. High amounts of V and Ni were found in sediment 40 km west of the south tip of St. Lawrence Island, suggesting that potential petroleum seeps should be searched for in this area. All other anomalous values for Ni and V seem to be related to specific sediment types or to nearby onshore sources.

The elements Zr, Sn, Cr, and Ce were categorized as heavy metals. Zr is found in high amounts in sediment surrounding the Yukon Delta and in Norton Sound. It is generally low in sediment in the region of the Chirikov Basin. Very high Zr concentrations are found off NE Cape of St. Lawrence Island as well as off the western and southern portions of St. Lawrence Island. These high amounts are probably derived from zircon containing quartz-monzanite plutons widely dispersed throughout the island. Sn was detected in only 23 samples. High concentrations were found off Cape Prince of Wales, in Anadyr Strait; and in the areas of King Island, Port Clarence, Bluff, Cape Rodney, and off the north central coast of St. Lawrence Island. It is possible that the high values in Anadyr Strait, Port Clarence and King Island are hydraulically concentrated. Values in other areas appear to be derived from immediate land sources. Cr is evenly distributed except for high concentrations close to Stuart Island, at locations south and north of St. Lawrence Island, and off Cape Prince of Wales. These high amounts appear to be closely related to the mafic rock types found on adjacent land areas. Cerium is found in few raw-bulk samples but where present it is associated with lanthanum and neodymium which suggests the presence of the heavy mineral monazite. The greatest concentrations of Zn, Cr and Ce were found in a sample taken from 30 km south of Cape Prince of Wales. Because this sample also contains the highest amounts of Ti, Mn, La, Sc, Y, Yb and Nd, it may indicate a significant placer area.

Of the potentially toxic elements, Sb, As, Cu, Pb and Zn, Sb was detected in only a few samples from the Bluff, NE Cape of St. Lawrence Island, and Stuart Island beaches. <u>As</u> was detected only in samples from Bluff beach where lode cinnabar deposits occur. High concentrations for Cu, Pb, and Zn occur together in the same areas off St. Lawrence Island, along the southern coast of the Seward Peninsula and in Norton Sound. These high values seem directly related to highly mineralized areas in concentrations adjacent to land areas. Cu and Zn also show the same trend as Zr, with high values off the Yukon Delta in Norton Sound and low values in the Chirikov Basin.

Value-surface maps for the chemically or environmentally sensitive elements Fe, Mn, Co and Ba all show high concentrations off the volcanogenic areas of north-central St. Lawrence Island and Stuart Island. They also exhibit high values off Yukon Delta and low values within Chirikov Basin. Ba is singled out in this group because of its use in drilling muds. It also exhibits high concentrations surrounding Yukon Delta, near Stuart Island and along the southern coast of the Seward Peninsula. Maximum values occur off the southern edge of St. Lawrence Island and in the middle of Anadyr Strait. The elevated Ba concentrations off the Yukon Delta probably originate in sediment from the Yukon River drainage as do higher concentrations of Zr, Cu, Zn, Fe, and Mn. The anomalies near Stuart Island and Seward Peninsula appear to be derived from specific land sources.

Of the major elements, the highest amounts of Ti, as with Fe and Mn discussed above, are in sediment found close to volcanic source rocks of Stuart Island and St. Lawrence Island, although the highest value of Ti is from a sample from 30 km south of Cape Prince of Wales. Sediment containing high concentrations of Ti, Fe and Mn is typically found in regions associated with mafic rock types. Ca and Mg also exhibit elevated values in these areas but are in greatest abundance in sediment south of Port Clarence and offshore from Cape Prince of Wales where paleozoic limestone formations are found. Value-surface maps for Na, K, and Al do not show strong trends. Concentrations of K are highest off NE Cape of St. Lawrence Island, and are probably related to the granitic bodies there. Al shows highest values in the Stuart Island area and eastern Norton Sound. Mn, Fe, Ti, and to a lesser degree Ca, Mg, Na, K, and Al all have high concentrations in the region of the Yukon Delta and in Norton Sound. The highest amount of P was in a sample from an enclosed basin northeast of St. Lawrence Island.

Of the minor elements, Sr has the highest correlation coefficients with K, Na, and Ba, but the highest Sr values as depicted by value-surface maps correlate with the highest Ca values. Concentrations of Sc correlate closest to concentrations of Ti, Fe, V, La, and Mn and Sc shows the same broad high anomaly surrounding the Yukon Delta and the low anomaly in the Chirikov Basin already mentioned for Ti, Fe, and Mn. Ga has high correlation coefficients with La, Sc and Ti and high amounts of Ga are found in Anadyr Strait and the eastern end of Norton Sound. Nb is concentrated east of Cape Darby and may be related to the high concentrations of Nb reported in stream sediments from Cape Darby peninsula. Nd correlates closely with Ce and La. Concentrations of Y follow the trend of high amounts in the Yukon Delta/Norton Sound area and lowest amounts in Chirikov Basin. Yb has the highest correlation coefficients with Mn, Zn, and Y and also is found in greater concentration in the area of the Yukon Holocene sediment distribution. Ag is found in 8 samples close to areas of St. Lawrence Island known to have silver mineralization, close to Stuart Island, the Yukon Delta, Cape Nome, and Bluff. The highest concentrations of Mo were found close to Stuart Island off Cape Prince of Wales in a sample containing a high amount of Sn, and in a Bluff beach sample.

Q-mode factor analysis showed that 4 factors were sufficient to explain 92% of the variance between samples. A map of loadings for the most significant factor (Factor III) covers an area that roughly corresponds to the area of Yukon Holocene sediment deposition and an area NW of St. Lawrence Island. Elements that are related to Factor III are La, Na, Ga, Ba, Sr, Sc, K, V and Al. A map of loadings for the next most significant factor (Factor I) corresponds approximately to the extent of relict sediment cover in Chirikov Basin. Elements related to Factor I are B, V, Yb, Ba and Al. These two factors (Factors I and II) seem to explain the trend exhibited by many of the elements of generally high concentrations in sediment surrounding the Yukon Delta and in the Norton Sound area and generally low concentrations in the Chirikov Basin. However, some of the elements that show this trend most conspicuously are not closely related to Factor III, but instead are better related to Factor II. Distribution of samples with high loadings for Factor II corresponds roughly to the highly mineralized areas along the southern Seward Peninsula. Elements related to Factor II are Y, Yb, Ti, Fe, Sc, Co, V and Mn. Plots of Factor IV loadings indicate this factor correlates somewhat with subaqueous glacial morain deposits. The one correlative element is Nb.

II. INTRODUCTION

A. General Nature and Scope of Study

This study has been undertaken to assess the major and trace element content of bulk bottom sediment in the northern Bering Sea. The values arrived at are useful as geochemical baseline data that can be compared with similar data from bottom sediment in the same region and elsewhere. The data are also useful for monitoring possible changes in chemistry of the bottom sediments that might result from future development in the region. Present anomalously high major and trace element concentrations are mapped and related to highly mineralized sources on land so that these high values will not be mistaken at some future time as sites of contamination caused by mineral resource development.

B. Specific Objectives

More specifically, this study considers 7 groups of elements of varying environmental significance and resource potential; we map their areal distribution in surface sediments and relate these to probable sediment source. The 7 groups of elements include: (1) V and Ni as possible petroleum indicators; (2) the heavy metals Sn, Zr, Ce, and Cr as possible indicators of placer deposits (Hg and Au are considered in separate studies, see Nelson et al., 1975; and Nelson and Hopkins, 1972); (3) the potentially toxic elements Pb, Cu, Zn, As, Sb, and Cd (Hg is considered elsewhere, see above); (4) Fe, Mn, Co, and Ba as elements which are sensitive to change in the chemistry of the sedimentary environment, with Ba as a particular indicator of petroleum drilling muds; (5) a suite of major and trace elements, and (6) a miscellaneous group of economic elements.

The data are both graphically and statistically displayed. Computer maps have been generated that display both contoured and 3-dimensional value-surfaces for each element. Geometric means and deviations as well as value ranges for each element are given in Tables I and II. Results of correlation analyses are found in Tables III and IV. Maps showing the generalized geology of the area, the sampling locations and onshore mineralizaton sites, and the significant offshore anomalies are depicted in Figs. 1, 2, and 3. A map of significant Q-mode factor loadings is found in Fig. 4.

III. CURRENT STATE OF KNOWLEDGE

The toxic element Hg, has been previously studied in the sediments of this area by Nelson, et al., 1975. Gold placer deposits in the nearshore areas of Nome-Bluff and in the offshore areas of Chirikov Basin have been extensively studied by Nelson and Hopkins, 1972. Reports by McManus, et al. (1977), Venkatarathnam (1971), and Sheth, (1971), discuss in detail the related topic of heavy mineral and sediment distribution, dispersal and provenance in the northern Bering Sea shelf region. Gardner et al., (1980), have completed a study similar to this one in the central and southern Bering Sea shelf regions.

IV. STUDY AREA

The bottom surface sediment samples analyzed for this study came from 180 sampling stations spread over Norton Basin (Fig. 2). The western part of the area, Chirikov Basin, is covered with what is thought to be relict medium-fine sand (Nelson and Hopkins, 1972). The region surrounding the Yukon Delta as well as much of Norton Sound, and several depressions in an eastern corridor extending up to the Bering Strait, is generally covered with more recent sediment grading from coarse silt to fine sand. The major source of Holocene sediment in this region is the Yukon River (Nelson and Creager, 1977). There

TABLE I

Geometric means, geometric deviations, central and expected value ranges, and maximum and minimum values for different element groups in the Northern Bering Sea.

Element Group	Element	Geometric Mean	Geometric Deviation	Central Range*	Expected range**	Minimum Values	Maximum Values
Petroleum Index Elements	Ni	22.7 ppm	2.01	11.3 - 45.6	5.6 - 91.6	7.0	1500.0
	V	87.3 ppm	1.51	57.8 - 131.8	38.3 - 198.9	30.0	200.0
Heavy Metal Element	Sn	too few values				N	100.0
	Zr	162.4 ppm	1.56	104.2 - 253.1	66.8 - 394.5	50.0	2000.0 G
	Cr	45.2 ppm	1.82	24.8 - 82.5	13.6 - 150.4	10.0	1000.0
	Ce	too few values				N	300.
Toxic Elements	Pb	20.5 ppm	1.66	12.3 - 34.0	7.4 - 56.5	N	500.0
	Cu	12.6 ppm	2.17	5.8 - 27.4	2.7 - 59.5	3.0	700.0
	Zn	72.8 ppm	1.70	42.8 - 124.0	25.1 - 211.0	N	1000.0
	As	too few values				N	3000.0 ppm
	Sb	too few values				N	1000.0 ppm
Chemically or Environmentally Sensitive Elements	Fe	2.29%	1.63	1.4 - 3.7	.86 - 6.1	.7	10.0 G
	Mn	462.5 ppm	1.88	245.7 - 870.6	130.5 - 1638.8	150.0	7000.0
	Co	11.6 ppm	1.80	6.4 - 20.9	3.6 - 37.7	5.0	100.0
	Ba	551.3 ppm	1.70	323.6 - 939.3	189.9 - 1600.3	100.0	1500.0
Major Elements	Al	5.6%	1.40	4.0 - 7.9	2.9 - 11.0	.7	10.0
	Na	1.7%	1.72	1.0 - 3.0	.6 - 5.2	.07	3.0
	K	1.5%	1.74	.9 - 2.7	.5 - 4.6	.1	5.0
	Ca	1.6%	2.06	.8 - 3.4	.4 - 7.0	.2	10.0 G
	Mg	.8%	2.08	.4 - 1.7	.2 - 3.5	.15	10.0 G
	Ti	.4%	1.59	.3 - .7	.2 - 1.1	.1	2.0
	P	too few values				N	.7%
Minor Elements	Sr	227.7 ppm	1.81	123.1 - 402.5	68.2 -727.5	30.0	1000.0
	Y	26.9 ppm	1.50	17.9 - 40.5	11.9 - 60.9	10.0	150.0
	Sc	12.1 ppm	1.50	8.0 - 18.2	5.3 - 27.4	5.0	50.0
	Nb	11.3 ppm	1.47	7.6 - 16.6	5.2 - 24.5	N	30.0
	B	73.7 ppm	1.72	42.8 - 126.9	24.9 -218.6	N	150.0
	La	41.4 ppm	1.63	25.5 - 67.3	15.7 -109.5	10.0	100.0
	Ga	10.3 ppm	2.45	4.2 - 25.3	1.7 - 62.1	N	30.0
	Yb	3.4 ppm	1.52	2.2 - 5.1	1.5 - 7.8	1.0	10.0
	Be	2.4 ppm	1.51	1.6 - 3.7	1.1 - 5.6	N	10.0
	Nd	too few values			N	150.0 ppm	
Miscellaneous Economic Elements	Ag	too few values				N	3.0 ppm
	Bi	too few values				N	70.0 ppm
	Mo	too few values			N	30.0 ppm	

* Central Range = geom.mean/geom. dev. to geom. mean x geom. dev.

**Expected Range = geom. mean/(geom.dev.)^2 to geom. mean x (geom. dev.)^2

G = > greater than accompanying value (upper limit of detection)

L = > less than accompanying value (lower limit of detection)

N = > not detected in a sample

TABLE II

Analytic results for miscellaneous elements not shown in general element groups of TABLE I.

Element	Number of samples element was detected in	Limit of detection (lower limit except for Si)	Element	Number of samples element was detected in	Limit of detection (lower limit except for Si)
Ag	5	0.7 ppm	Hf	0	50.0 ppm
As	3	100.0 ppm	In	0	1.0 ppm
Au	0	7.0 ppm	Li	0	100.0 ppm
Bi	2	7.0 ppm	Re	0	7.0 ppm
Cd	0	7.0 ppm	Ta	0	50.0 ppm
Mo	5	2.0 ppm	Th	0	150.0 ppm
P	54	0.1 %	Tl	0	3.0 ppm
Pd	0	1.0 ppm	Pr	0	20.0 ppm
Pt	0	5.0 ppm	Nd *	3	20.0 ppm
Sb	8	20.0 ppm	Sm	0	50.0 ppm
Sn	23	2.0 ppm	Eu	0	1.5 ppm
Te	0	300.0 ppm	Gd	0	5.0 ppm
U	0	150.0 ppm	Tb	0	100.0 ppm
W	0	10.0 ppm	Dy **	0	20.0 ppm
Si***	179	10.0% upper limit	Ho	0	5.0 ppm
Ce	19	50.0 ppm	Er	0	30.0 ppm
Ga	151	0.7 ppm	Tm	0	2.0 ppm
Ge	0	7.0 ppm	Lu	0	15.0 ppm

* Looked for only when La or Ce is found

** Looked for only when Y is >50 ppm

***Si was a major component in all samples analyzed, i.e., >10.0%. However, exact values cannot be assigned above this limit.

TABLE III

Lists most closely related or disrelated elements according to the correlation coefficients between their log values.

GA	
La	.4950
Se	.4047
Ti	.3806

Fe	
Cu	.8323
Ni	.8101
Zn	.7868
Mn	.7738
Co	.7503
Ti	.7251
Sc	.6326
B	-.3164*

Mg	
Ca	.5861
Co	.5151
Ni	.4949
Fe	.3884
Ti	.3884
Sc	.3565
Cr	.3331

Ca	
Mg	.5861
Sr	.5469
Sc	.3371
Nb	-.3232*

Ti	
Fe	.7251
Sc	.7180
Mn	.6617
Ni	.6153
Zn	.5717
Cu	.5682
Cr	.5623
Y	.5435
Yb	.5181
Co	.5067

Mn	
Fe	.7738
Zn	.6657
Ti	.6617
Cu	.6612
Y	.6103
Ni	.5954
Yb	.5729
Sc	.5571

B	
K	.4929
Ba	.4508
Al	.4328
Na	.4109
Nb	.2884
La	.2815
Ni	-.5464*
Co	-.4110*
Fe	-.3164*

Ba	
K	.8040
Na	.6847
Sr	.6241
Al	.6092

Be	
La	.3720
Yb	.3388
Sc	.3351
Cu	.3211
Ti	.3058

Co	
Ni	.8263
Fe	.7503
Cu	.6296
Zn	.5982
B	-.4110*
K	-.3177*

Cr	
Ni	.6132
Ti	.5623
Sc	.5274
Fe	.4796
Co	.3879

Cu	
Fe	.8823
Zn	.8023
Ni	.6833
Mn	.6612
Co	.6296

La	
Sc	.5572
Sn	.5539
Ba	.5508
V	.5189
K	.5171
Ga	.4950
Zr	.4933
Ti	.4473

Nb	
B	.2884
Ca	-.3232*

Ni	
Co	.8263
Fe	.8101
Cu	.6833
Ti	.6153
Zn	.6142
Cr	.6132
Mn	.5954
B	-.5464*

Pb	
Cu	.5114
Zn	.4194
Y	.3701
Fe	.3106
Mn	.2615
Na	-.4041*

Sc	
Ti	.7180
Fe	.6326
V	.5790
La	.5572
Mn	.5571
Cu	.5470
Cr	.5274

Sr	
K	.6994
Na	.6863
Al	.6140
Ba	.6241
La	.5539
Cu	.5469

V	
Sc	.5790
La	.5189
Cu	.4801
Yb	.4589
Zn	.4584
Ti	.4352
Fe	.4039

Y	
Mn	.6103
Yb	.5678
Fe	.5563
Ti	.5435
Cu	.4842
Zr	.4552
Sc	.4335

Zn	
Cu	.8023
Fe	.7868
Mn	.6657
Ni	.6142
Co	.5982
Ti	.5717
Yb	.5713

Zr	
La	.4933
Y	.4552
Ti	.4059
K	.3778
Ba	.3694

Al	
Na	.8348
K	.6999
Sr	.6140
Ba	.6092
B	.4328

Na	
Al	.8348
K	.7935
Sr	.6863
Ba	.6847
B	.4109
Pb	-.4041*

K	
Ba	.8040
Na	.7935
Al	.6999
Sr	.6994
La	.5171
B	.4929
Co	.3177*

Yb	
Mn	.5729
Zn	.5713
Y	.5678
Fe	.5294
Cu	.5112
Ti	.5181
V	.4589
Sc	.4278

*Extreme negative correlation.

TABLE IV

Correlation coefficients between element log values

```
D0101 CORRELATION ANALYSIS - USGS STATPAC (04/27/77)                                                   DATE   4/11/79

ARRAY OF CORRELATION COEFFICIENTS -
                         1          2          3          4          5          6          7          8          9         10
                     GA PPM-S   FE   %-S   MG   %-S   CA   %-S   TI   %-S   MN PPM-S   B   PPM-S   BA PPM-S   CO PPM-S   CR PPM-S

  1 GA PPM-S          1.0000     0.3289     0.1181     0.1505     0.3806     0.1154    -0.0253     0.1866     0.2649     0.3128
  2 FE    %-S         0.3289     1.0000     0.3884     0.2678     0.7251     0.7738    -0.3164    -0.0398     0.7503     0.4796
  3 MG    %-S         0.1181     0.3884     1.0000     0.5861     0.3884     0.2669    -0.2313    -0.1395     0.5151     0.3331
  4 CA    %-S         0.1505     0.2678     0.5861     1.0000     0.2823     0.1458    -0.0424     0.0475     0.2837     0.2014
  5 TI    %-S         0.3806     0.7251     0.3884     0.2823     1.0000     0.6617    -0.1365     0.0932     0.5067     0.5623
  6 MN PPM-S          0.1154     0.7738     0.2669     0.1458     0.6617     1.0000    -0.2643    -0.1461     0.5187     0.3113
  7 B  PPM-S         -0.0253    -0.3164    -0.2313    -0.0424    -0.1365    -0.2643     1.0000     0.4508    -0.4110    -0.2177
  8 BA PPM-S          0.1866    -0.0398    -0.1395     0.0475     0.0932    -0.1461     0.4508     1.0000    -0.2254     0.2336
  9 CO PPM-S          0.2649     0.7503     0.5151     0.2837     0.5067     0.5187    -0.4110    -0.2254     1.0000     0.3879
 10 CR PPM-S          0.3128     0.4796     0.3331     0.2014     0.5623     0.3113    -0.2177     0.2336     0.3879     1.0000
 11 CU PPM-S          0.2418     0.8323     0.2714     0.2434     0.5682     0.6612    -0.2482     0.0008     0.6296     0.3522
 12 LA PPM-S          0.4950     0.3369     0.0688     0.2879     0.4473     0.2424     0.2815     0.5508     0.1032     0.3629
 13 NB PPM-S          0.1875    -0.0777    -0.2974    -0.3232     0.0435    -0.0686     0.2884     0.1651    -0.1894    -0.0039
 14 NI PPM-S          0.3090     0.8101     0.4949     0.2480     0.6153     0.5954    -0.5464    -0.1467     0.8263     0.6132
 15 PB PPM-S          0.0227     0.3106    -0.2186     0.0812    -0.0118     0.2615    -0.0271    -0.0241     0.2152    -0.2529
 16 SC PPM-S          0.4047     0.6326     0.3565     0.3371     0.7180     0.5571     0.0724     0.3589     0.3984     0.5274
 17 SR PPM-S          0.3097     0.0081     0.1979     0.5469     0.1885    -0.1694     0.1981     0.6241    -0.0661     0.3323
 18 V  PPM-S          0.0446     0.4039     0.2333     0.1561     0.4352     0.3714     0.2196     0.3529     0.2090     0.3407
 19 Y  PPM-S          0.2224     0.5563     0.1480     0.2392     0.5435     0.6103     0.0590    -0.0607     0.4272     0.1015
 20 ZN PPM-S          0.2140     0.7868     0.1528     0.0466     0.5717     0.6657    -0.1722     0.0552     0.5982     0.2692
 21 ZR PPM-S          0.2732     0.2547     0.1485     0.2224     0.4059     0.2388     0.1497     0.3694     0.1450     0.3005
 22 AL    %-S         0.2245     0.0585     0.2193     0.2679     0.2162    -0.1887     0.4328     0.6092     0.0046     0.2365
 23 NA    %-S         0.2528    -0.0524     0.1963     0.2352     0.1629    -0.2520     0.4109     0.6847    -0.1178     0.3354
 24 K     %-S         0.1800    -0.1536     0.0225     0.2076     0.0296    -0.2734     0.4929     0.8040    -0.3177     0.1947
 25 YB PPM-S         -0.0617     0.5294    -0.0234     0.0692     0.5181     0.5729     0.1397     0.1760     0.2138     0.1956
 26 BE PPM-S          0.1098     0.2741    -0.0618     0.0194     0.3058     0.2558     0.0945     0.2710     0.0144     0.1313
```

Table IV cont.

```
D0101 CORRELATION ANALYSIS - USGS STATPAC (04/27/77)                                                          DATE    4/11/79

ARRAY OF CORRELATION COEFFICIENTS - CONT.
                     11           12           13           14           15           16           17           18           19           20
                  CU PPM-S     LA PPM-S     NB PPM-S     NI PPM-S     PB PPM-S     SC PPM-S     SR PPM-S     V  PPM-S     Y  PPM-S     ZN PPM-S

  1 GA PPM-S       0.2418       0.4950       0.1875       0.3090       0.0227       0.4047       0.3097       0.0446       0.2224       0.2140
  2 FE    %-S      0.8323       0.3369      -0.0777       0.8101       0.3106       0.6326       0.0081       0.4039       0.5563       0.7868
  3 MG    %-S      0.2714       0.0688      -0.2974       0.4949      -0.2186       0.3565       0.1979       0.2333       0.1480       0.1528
  4 CA    %-S      0.2434       0.2879      -0.3232       0.2480       0.0812       0.3371       0.5469       0.1561       0.2392       0.0466
  5 TI    %-S      0.5682       0.4473       0.0435       0.6153      -0.0118       0.7180       0.1885       0.4352       0.5435       0.5717
  6 MN PPM-S       0.6612       0.2424      -0.0686       0.5954       0.2615       0.5571      -0.1694       0.3714       0.6103       0.6657
  7 B  PPM-S      -0.2482       0.2815       0.2884      -0.5464      -0.0271       0.0724       0.1981       0.2196       0.0590      -0.1722
  8 BA PPM-S       0.0008       0.5508       0.1651      -0.1467      -0.0241       0.3589       0.6241       0.3529      -0.0607       0.0552
  9 CO PPM-S       0.6296       0.1032      -0.1894       0.8263       0.2152       0.3984      -0.0661       0.2090       0.4272       0.5982
 10 CR PPM-S       0.3522       0.3629      -0.0039       0.6132      -0.2529       0.5274       0.3323       0.3407       0.1015       0.2692
 11 CU PPM-S       1.0000       0.4102      -0.1300       0.6833       0.5114       0.5470       0.0144       0.4801       0.4842       0.8023
 12 LA PPM-S       0.4102       1.0000       0.1089       0.1760       0.2100       0.5572       0.5539       0.5189       0.3886       0.3333
 13 NB PPM-S      -0.1300       0.1089       1.0000      -0.0983      -0.0720      -0.0297      -0.0829       0.0931       0.0139       0.0700
 14 NI PPM-S       0.6833       0.1760      -0.0983       1.0000       0.1626       0.4481       0.0041       0.2766       0.3516       0.6142
 15 PB PPM-S       0.5114       0.2100      -0.0720       0.1626       1.0000      -0.0439      -0.0772       0.0053       0.3701       0.4194
 16 SC PPM-S       0.5470       0.5572      -0.0297       0.4481      -0.0439       1.0000       0.3238       0.5790       0.4335       0.5294
 17 SR PPM-S       0.0144       0.5539      -0.0829       0.0041      -0.0772       0.3238       1.0000       0.2163      -0.0675      -0.1362
 18 V  PPM-S       0.4801       0.5189       0.0931       0.2766       0.0053       0.5790       0.2163       1.0000       0.2237       0.4584
 19 Y  PPM-S       0.4842       0.3886       0.0139       0.3516       0.3701       0.4335      -0.0675       0.2237       1.0000       0.4121
 20 ZN PPM-S       0.8023       0.3333       0.0700       0.6142       0.4194       0.5294      -0.1362       0.4584       0.4121       1.0000
 21 ZR PPM-S       0.1452       0.4933       0.1213       0.2615       0.0857       0.3509       0.3286       0.2401       0.4552       0.1914
 22 AL    %-S     -0.0534       0.3294       0.2116      -0.0162      -0.2630       0.3365       0.6140       0.3314      -0.0457      -0.0332
 23 NA    %-S     -0.1747       0.3754       0.2021      -0.0615      -0.4041       0.3212       0.6863       0.2713      -0.1440      -0.1644
 24 K     %-S     -0.1474       0.5171       0.1445      -0.1998      -0.1277       0.2040       0.6994       0.2661      -0.1034      -0.1840
 25 YB PPM-S       0.5112       0.3746       0.1340       0.3027       0.2547       0.4278      -0.0703       0.4589       0.5678       0.5713
 26 BE PPM-S       0.3211       0.3720       0.0378       0.0884       0.1790       0.3351       0.2056       0.2900       0.2444       0.2771
```

Table IV. cont.

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                                                          DATE    4/11/79



D0101 CORRELATION ANALYSIS - USGS STATPAC (04/27/77)


ARRAY OF CORRELATION COEFFICIENTS - CONT.
                   21         22          23          24          25          26
                 ZR PPM-S   AL    %-S   NA    %-S   K     %-S   YB PPM-S    BE PPM-S
  1 GA PPM-S     0.2732     0.2245      0.2528      0.1800     -0.0617      0.1098
  2 FE    %-S    0.2547     0.0585     -0.0524     -0.1536      0.5294      0.2741
  3 MG    %-S    0.1485     0.2193      0.1963      0.0225     -0.0234     -0.0618
  4 CA    %-S    0.2224     0.2679      0.2352      0.2076      0.0692      0.0194
  5 TI    %-S    0.4059     0.2162      0.1629      0.0296      0.5181      0.3058
  6 MN PPM-S     0.2388    -0.1887     -0.2520     -0.2734      0.5729      0.2558
  7 B  PPM-S     0.1497     0.4328      0.4109      0.4929      0.1397      0.0945
  8 BA PPM-S     0.3694     0.6092      0.6847      0.8040      0.1760      0.2710
  9 CO PPM-S     0.1450     0.0046     -0.1178     -0.3177      0.2138      0.0144
 10 CR PPM-S     0.3005     0.2365      0.3354      0.1947      0.1956      0.1313
 11 CU PPM-S     0.1452    -0.0534     -0.1747     -0.1474      0.5112      0.3211
 12 LA PPM-S     0.4933     0.3294      0.3754      0.5171      0.3746      0.3720
 13 NB PPM-S     0.1213     0.2116      0.2021      0.1445      0.1340      0.0378
 14 NI PPM-S     0.2615    -0.0162     -0.0615     -0.1998      0.3027      0.0884
 15 PB PPM-S     0.0857    -0.2630     -0.4041     -0.1277      0.2547      0.1790
 16 SC PPM-S     0.3509     0.3365      0.3212      0.2040      0.4278      0.3351
 17 SR PPM-S     0.3286     0.6140      0.6863      0.6994     -0.0703      0.2056
 18 V  PPM-S     0.2401     0.3314      0.2713      0.2661      0.4589      0.2900
 19 Y  PPM-S     0.4552    -0.0457     -0.1440     -0.1034      0.5678      0.2444
 20 ZN PPM-S     0.1914    -0.0332     -0.1644     -0.1840      0.5713      0.2771
 21 ZR PPM-S     1.0000     0.2784      0.3000      0.3778      0.3322      0.2169
 22 AL    %-S    0.2784     1.0000      0.8348      0.6999      0.0953      0.1454
 23 NA    %-S    0.3000     0.8348      1.0000      0.7935      0.0077      0.0699
 24 K     %-S    0.3778     0.6999      0.7935      1.0000      0.0875      0.2228
 25 YB PPM-S     0.3322     0.0953      0.0077      0.0875      1.0000      0.3388
 26 BE PPM-S     0.2169     0.1454      0.0699      0.2228      0.3388      1.0000
```

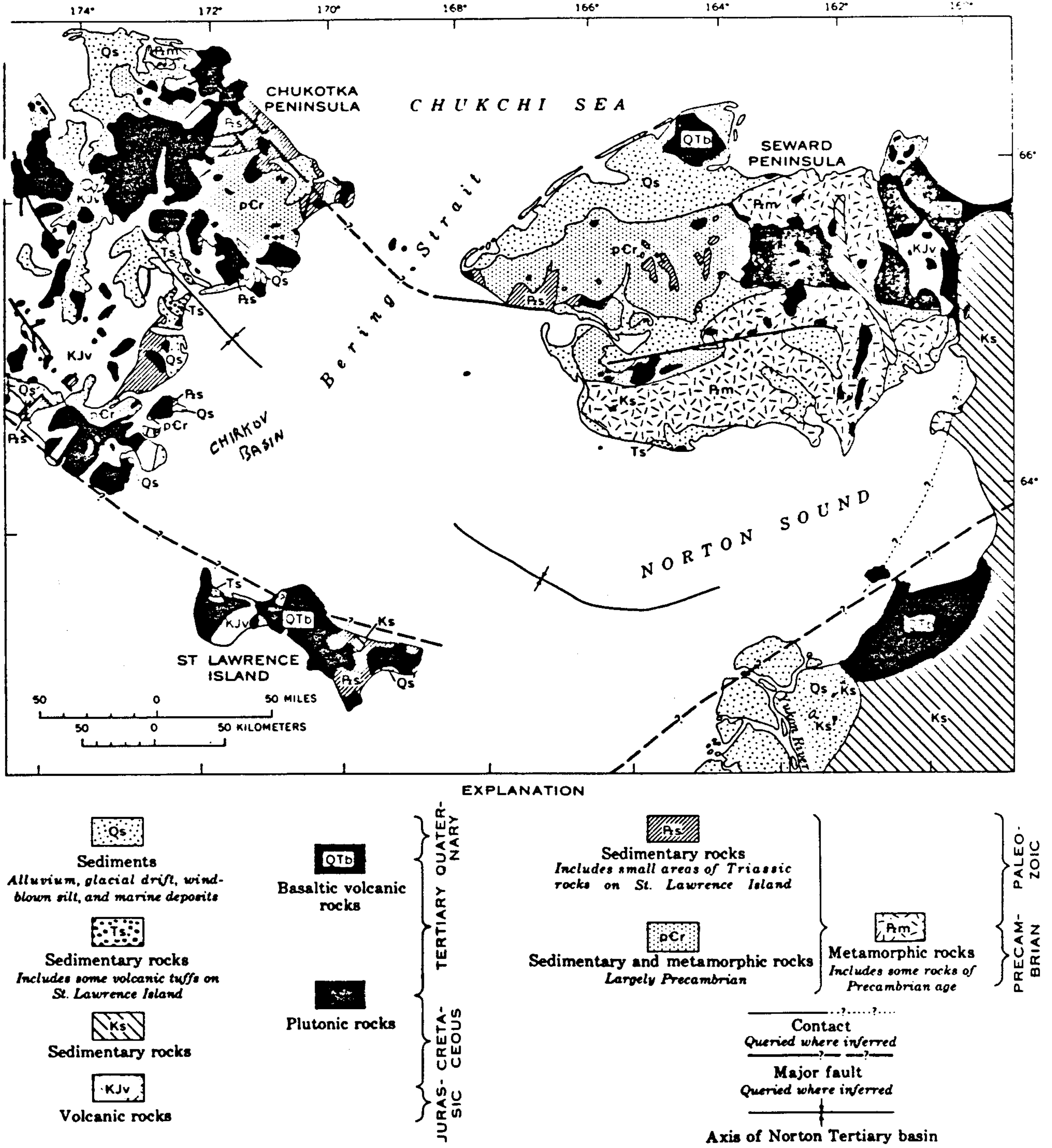

Figure 1. Generalized map of the northern Bering Sea region, (Nelson and Hopkins, 1972).

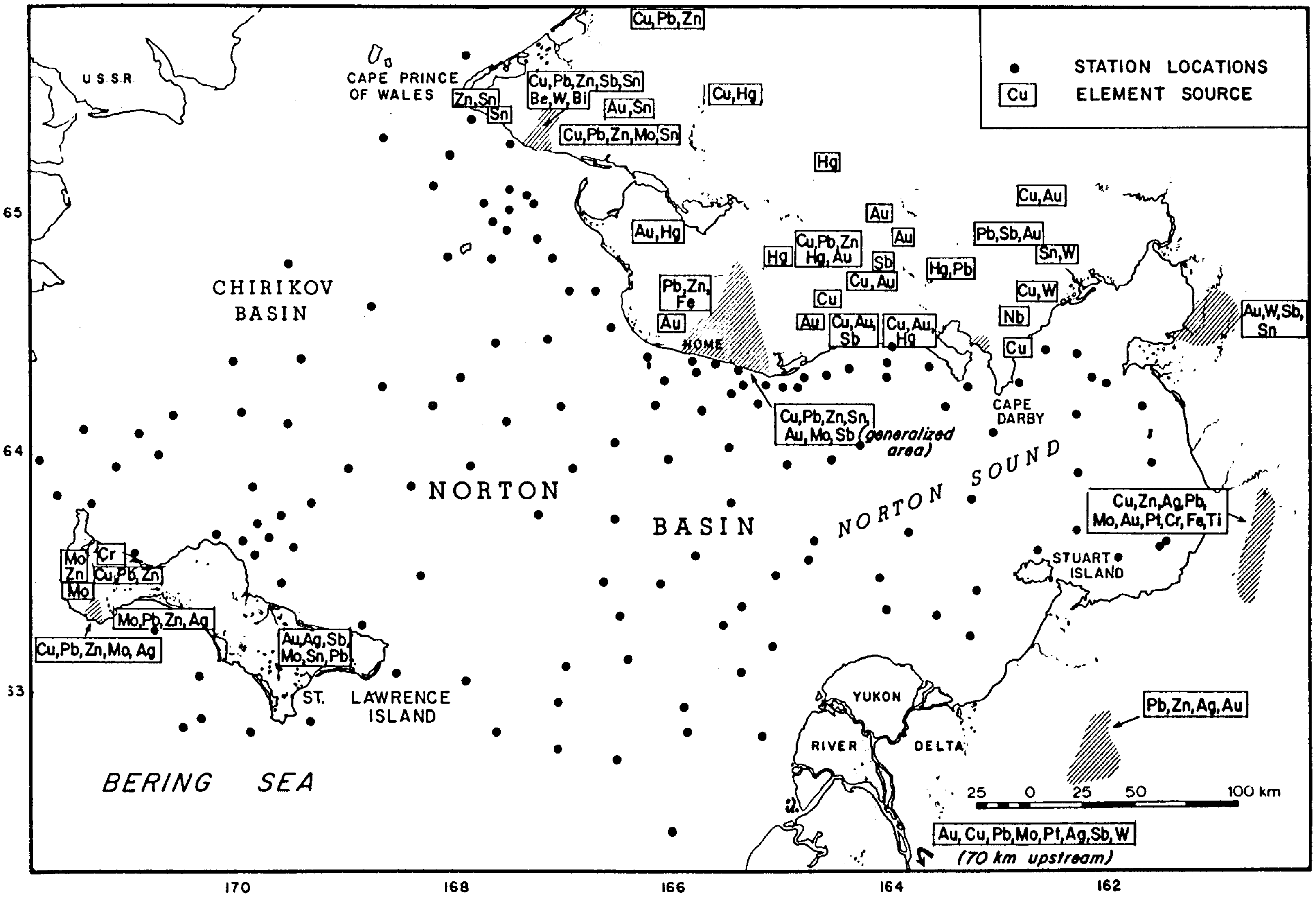

Figure 2. Offshore sampling locations and terrestrial sites of known mineralization for various elements.

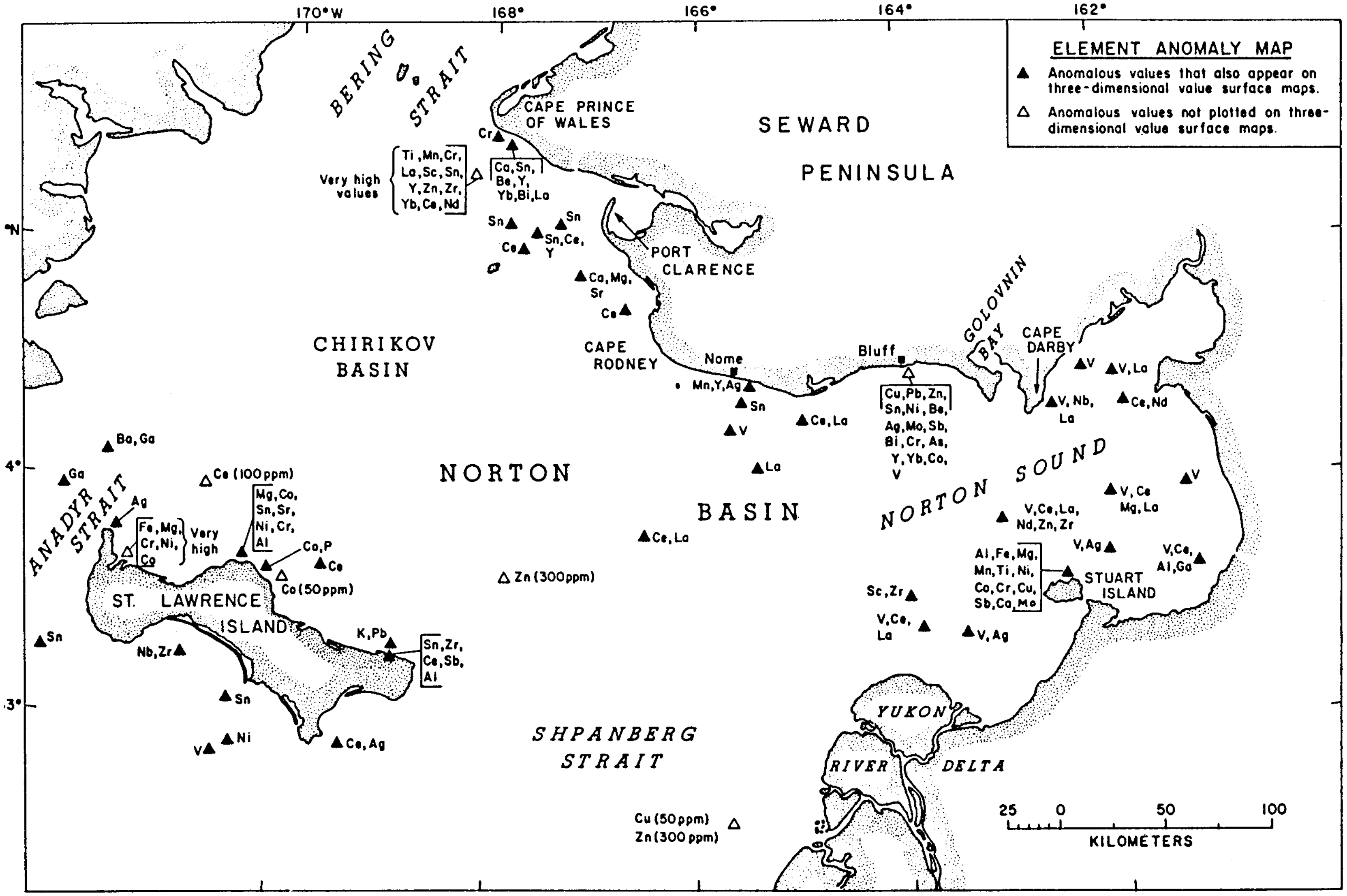

Figure 3. Map depicting significant anomalies defined as values falling outside the upper limit of the expected value range or as the highest few values (see Table I).

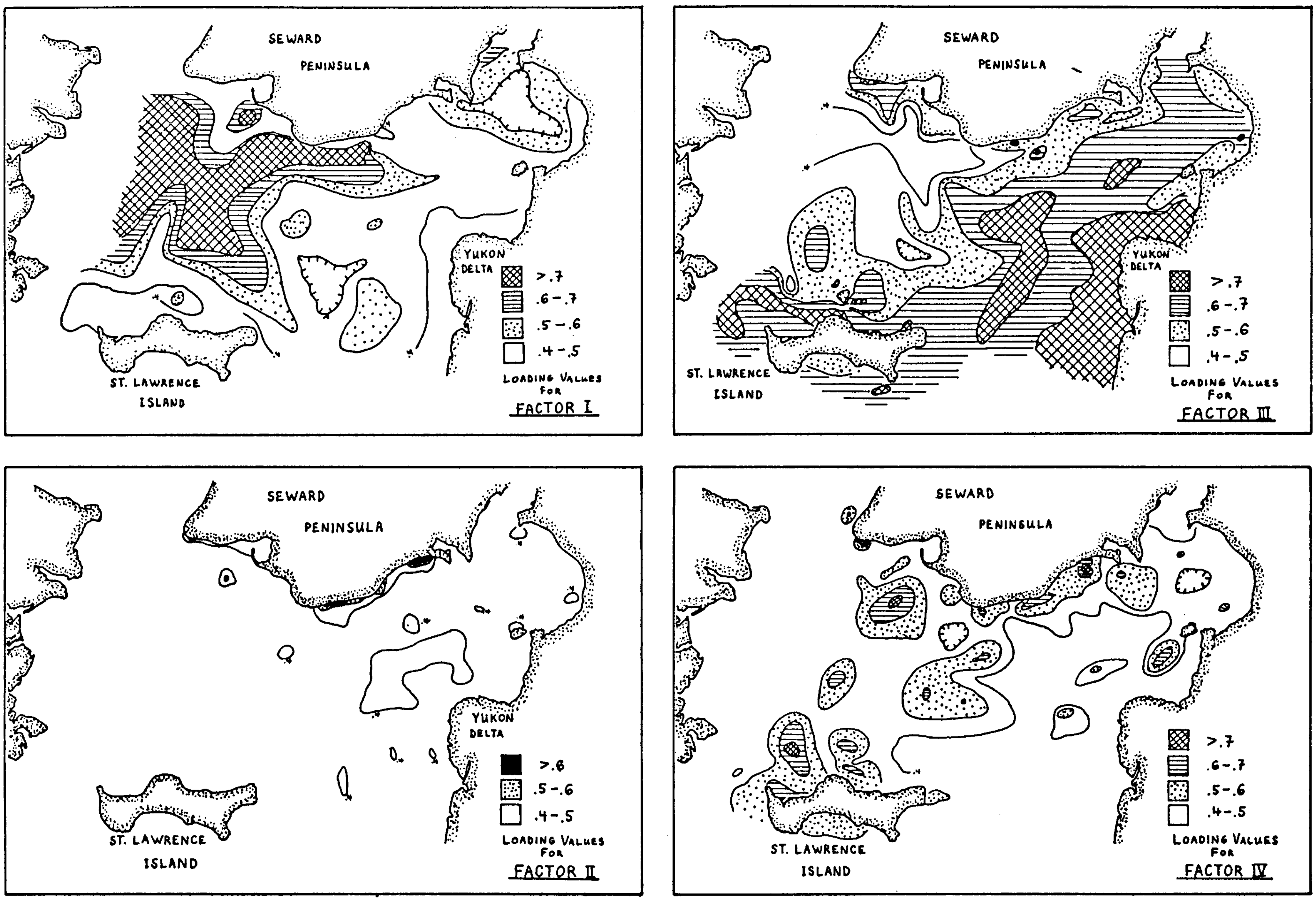

Figure 4. Distribution of Q-mode Factor loadings for the first four factors.

are some areas where the relict and modern sediments intersect creating a palimpsest mixture of the two (McManus et al., 1977). Much of the sediment coming from the Yukon and deposited in Norton Sound is thought to be re-suspended periodically and then flushed through the Bering Strait and deposited in the Chukchi Sea by normal and storm tides (Nelson and Creager, 1977). This is helped by currents which trend generally northwards to the Bering Strait and have velocities as high as 190 cm/sec in the Strait itself (Coachman, et al., 1976).

Water in the region is characterized by two fairly distinct masses. Colder, more saline waters dominate the central and western parts of the region. These are surrounded by a shoreward hugging mass of Alaskan coastal water which is warmer, less dense and generally moving along the eastern coast northward to the Bering Strait.

Significant mineralized deposits are found in several areas bounding this region (Fig. 2; Cobb, 1960a,b,c, 1962, 1964, and 1970; Eberlein and Menzie, 1978; Hudson and DeYoung, 1978, Hudson, et al., 1977; Hummel, 1977, Nelson and Hopkins, 1972, Nelson, et al., 1972; Overstreet, et al., 1974, 1978; Patton and Csejtey, 1971, 1972; and Sainsbury, 1969, 1975). Of particular importance are the gold placer deposits found in the Nome Bluff area. Gold placers are also located in various relict beach ridges or reworked glacial moraines presently submerged off the coast from Nome as well as off Chutkotka Peninsula and St. Lawrence Island (Nelson, Hopkins, 1972).

Lode deposits of economic interest occur in many areas surrounding Norton Basin. They include copper, lead, zinc, silver and molybdenum deposits in western and eastern St. Lawrence Island; tin and beryllium deposits of the Lost River ining district on the western tip of Seward Peninsula which also contain high concentrations of copper, lead, zinc, antimony, gold and molybdenum; the general area of the southern Seward Peninsula where there are numerous occurrences of gold, copper, lead, zinc, mercury, antimony, iron, and some tungsten and niobium; the lands to the east of Norton Sound where gold, tungsten, antimony, tin, copper, silver, lead, zinc, molybdenum, platinum, chromium and titanium are found; and the entire Yukon drainage basin where mineral concentrations containing high concentrations of most of the aforementioned elements are located.

All of the areas mentioned are drained by streams and rivers that have undoubtedly been contributing substantial amounts of mineralized sediment to Norton Basin for the past several thousand years.

V. SOURCES, METHODS, AND RATIONALE OF DATA COLLECTION

Two groups of samples were utilized for this study. The first group consists of samples collected on 3 different cruises during the years 1968, 1969, and 1970. These samples were originally collected to delineate sediment characteristics and faunal distributions in the region and to assess placer gold dispersal from Seward Peninsula sources (Nelson and Hopkins, 1972). They were taken using a 5 gallon galvanized steel Van Veen grab sampler which would normally penetrate the top 5-10 cm of bottom sediment. The resulting samples were given no special treatment and were stored at room temperature. The second group of samples were collected using a Soutar Van Veen grab sampler during 1976 and 1977 U.S.G.S. cruises of the U.S.G.S. R/V SEA SOUNDER. The Soutar grab sampler is teflon coated and causes minimal disturbance of surface samples. Subsamples were selected for trace element analysis from the top 1-2 cm of each sample collected using the Soutar sampler and were immediately frozen and kept frozen until analyzed in Menlo Park, California.

This sampling technique was developed by Ian Kaplan of UCLA for BLM/NOAA trace element study of sediments on the western North American outer continental shelf.

The average distance between samples is approximately 30 km. In an analysis of variance of samples from the central and southern Bering Sea, Gardner, et al., 1980, found this distance to be adequate to show statistically significant trends in sediment composition.

Samples, including pore water salts, were air dried at 110o C. Each sample was then homogenized and a one gram split of each sample was analyzed by the Analytical Laboratories Branch, U.S.G.S, for a suite of over 50 elements using semi-quantitative optical emission spectroscopy (Grimes and Marinzino, 1968).

To assess the precision and accuracy of the 6-step semi-quantitative optical emission spectrographic technique used in this study, replicate analyses were done on both U.S.G.S. rock standards and on subsamples of the sediment samples being studied. Additionally, several replicate subsamples were analyzed by neutron activation.

VI. ANALYTIC RESULTS

Semi-quantitative emission spectroscopy, although not as precise as other analytic techniques, yields values that are adequate to delineate regional trends. Care must be taken, however, to establish the limits of precision and accuracy for the technique as used with a particular type of sample to detect a particular element.

The precision of the 6-step emission spectroscopy technique is influenced by two factors: variability of the substance being analyzed and the variability introduced by the imprecision in the use of the technique or in the technique itself. To reduce errors due to sample variability, samples were ground to 230 mesh and homogenized. Sub-splits from the sample were then used for replicate analyses. The overall precision of the 6-step emission spectrographic technique was determined by running 5 to 8 replicate analyses on each of three samples. The subsamples used for the replicate analyses were submitted in a random sequence along with the other samples analyzed. The precision was calculated by averaging the percent difference between each replicate analysis and the mean value for all of the replicate analyses. Additional replicate analyses were run on subsamples from the same set of test samples by neutron activation as a further test of both the precision and accuracy of the emission spectrographic technique. Values of replicate analyses for all elements except zinc, were within 25 percent of the mean values for the replicate analyses, and replicate values for most of the elements fall within 15 percent of their mean (Patry, et al., 1977).

The accuracy of the 6-step emission spectographic analyses was tested by analyzing four U.S.G.S. standard rock samples of known element composition. Two analyses were made on each rock sample and the average of the two values was calculated for each of 30 elements. Then the percent difference between these values and the actual values for each rock was determined. Next, the percent differences for all four rock standards were averaged to give the average percent error between values yielded by the 6-step emission spectrographic technique and the known values for the rocks. Element values for Y, Ca, Ba, K, Cr, Cu, Na, Co, Nb, Ni, V, and Zn, as determined by emission spec, were within 30 percent of the established values for the rock standards. This group of elements is almost entirely within the bounds of the 'accepted' error for this analytic technique and therefore provides baseline data for the study area that is relatively free of analytic error. Values for eleven elements including Sr, Al, Sc, Zr, Ti, Ga, Pb, Fe, Mn, and Mg, were within 35 to 65 percent of the actual values for the rock standards and can still be considered reasonable baseline data for these elements. Two elements, Yb and B, had values varying by more than 80% from the known values. Values for these elements should be regarded as only gross estimates of their actual content in the sediment. Accuracy for the determination of eight elements, Ag, As, Bi, Mo, Nd, Sb, Sn, and Ce, could not be assessed because quantities present were too low to be detected by the analytic method. These elements were not statistically analyzed but where present above the detection limit, they were plotted as anomalous values. Si was eliminated because its values were all greater than the upper limit of detection of the analytic technique (Patry, et al., 1977).

The data was transformed into base 10 logarithms and the arithmetic means and standard deviations were determined for the log values. The arithmetic mean of the log values of a distribution is equivalent to the geometric mean of the original values and if the distribution approximates log normality, the geometric mean is the best measurement of the central tendency of the distributon (Table I; Miesch, 1967). The distributions in this study were presumed to approximate log normality. Correlation analyses relating element pairs were also run on the logs of the data values. Q-mode factor analysis was performed to examine significant relationships among samples and elements (Fig. 4, Tables V , VI , and VII). Most of the elements had no values less than the lower limit of detection. If an element had only one to three values above or below the upper or lower limit of detection, these indeterminate values were substituted with definite values set two class intervals above or below the value of the limit of detection. Nine elements (Ag, As, Bi, Mo, Nd, Si Sb, Sn, and Ce) had too few values for statistical treatment but enough values were obtained for Ag, Mo, and Sn to be plotted graphically.

TABLE V

Correlation coefficients between Q-mode Factor loading values and non-log element values.

```
D0101 CORRELATION ANALYSIS - USGS STATPAC (04/27/77)                                        DATE    3/23/78

ARRAY OF CORRELATION COEFFICIENTS -
                     1          2          3          4          5          6          7          8          9          10
                  factor1    factor2    factor3    factor4    GA PPM-S   FE    %-S  MG    %-S  CA    %-S  TI    %-S  MN PPM-S

  1 factor1        1.0000    -0.3258    -0.1758     0.0181    -0.5480    -0.5093    -0.4750    -0.4209    -0.3586    -0.3352
  2 factor2       -0.3258     1.0000    -0.2785    -0.4808     0.0926     0.6616     0.1630     0.1168     0.6328     0.6527
  3 factor3       -0.1758    -0.2785     1.0000    -0.1591     0.5729    -0.1304    -0.0144     0.1668     0.2239    -0.2894
  4 factor4        0.0181    -0.4808    -0.1591     1.0000     0.1481    -0.4933    -0.1958    -0.2655    -0.4254    -0.4867
  5 GA PPM-S      -0.5480     0.0926     0.5729     0.1481     1.0000     0.2323     0.0767     0.1157     0.3407     0.0346
  6 FE    %-S     -0.5093     0.6616    -0.1304    -0.4933     0.2323     1.0000     0.3534     0.1270     0.6022     0.8405
  7 MG    %-S     -0.4750     0.1630    -0.0144    -0.1958     0.0767     0.3534     1.0000     0.4199     0.2847     0.0851
  8 CA    %-S     -0.4209     0.1168     0.1668    -0.2655     0.1157     0.1270     0.4199     1.0000     0.2017     0.0055
  9 TI    %-S     -0.3586     0.6328     0.2239    -0.4254     0.3407     0.6022     0.2847     0.2017     1.0000     0.4214
 10 MN PPM-S      -0.3352     0.6527    -0.2894    -0.4867     0.0346     0.8405     0.0851     0.0055     0.4214     1.0000
 11 B  PPM-S       0.5392    -0.1656    -0.0089     0.1728     0.1575    -0.2368    -0.2685    -0.1292    -0.1006    -0.2229
 12 BA PPM-S       0.1990    -0.3470     0.7106    -0.1613     0.4000    -0.1194    -0.2644    -0.1561     0.0600    -0.1898
 13 CO PPM-S      -0.6072     0.5020    -0.1428    -0.2790     0.1962     0.7835     0.5335     0.1775     0.3948     0.6020
 14 CR PPM-S      -0.3911     0.2104     0.1073    -0.2136     0.1573     0.4351     0.6329     0.1227     0.4659     0.1228
 15 CU PPM-S      -0.3316     0.4444    -0.2692    -0.3765     0.0312     0.6852     0.0005    -0.0025     0.1593     0.6637
 16 LA PPM-S      -0.0977     0.1546     0.6073    -0.4107     0.5193     0.1447    -0.0687     0.1215     0.3340     0.0494
 17 NB PPM-S       0.1628    -0.0266    -0.1231     0.4103     0.1705    -0.1652    -0.2389    -0.3283    -0.0241    -0.1243
 18 NI PPM-S      -0.4219     0.2246    -0.1548    -0.2109     0.0263     0.5145     0.6984     0.0401     0.2242     0.2827
 19 PB PPM-S      -0.3033     0.3939    -0.3279    -0.3356    -0.0372     0.5928    -0.0839     0.0072     0.0383     0.6280
 20 SC PPM-S      -0.2070     0.4598     0.4683    -0.5150     0.4777     0.4371     0.1420     0.1943     0.6401     0.3225
 21 SR PPM-S      -0.2944    -0.2621     0.6476    -0.1438     0.3909    -0.0342     0.1171     0.5443     0.1646    -0.1729
 22 V  PPM-S       0.2703     0.2858     0.2886    -0.5579     0.1720     0.1910     0.0242    -0.0143     0.3205     0.1154
 23 Y  PPM-S      -0.2662     0.7176    -0.1753    -0.3921     0.1518     0.5309    -0.0513     0.2354     0.4335     0.6178
 24 ZN PPM-S      -0.3199     0.5440    -0.2229    -0.4407     0.1069     0.7869     0.0044    -0.0616     0.2700     0.7980
 25 ZR PPM-S      -0.0689     0.0418     0.0825    -0.0516     0.1167     0.0155    -0.0335     0.0277     0.1798    -0.0307
 26 AL    %-S      0.0527    -0.2436     0.5707     0.0729     0.4666    -0.0257     0.0199     0.1024     0.2603    -0.2648
 27 NA    %-S     -0.0308    -0.3275     0.6674     0.0416     0.5404    -0.0169     0.0233     0.0863     0.2389    -0.2490
 28 K     %-S      0.0796    -0.4179     0.5948    -0.0583     0.4125    -0.1494    -0.1554     0.0003     0.0118    -0.2329
 29 YB PPM-S       0.1620     0.5663    -0.1618    -0.5081     0.0283     0.4684    -0.1397    -0.0357     0.4097     0.5124
```

TABLE VI

A. Q-mode scaled varimax factor scores relating which elements are most correlative with each factor (in order of descending importance).

B. Lists elements most closely related to the first four factor loadings according to the correlations among their non-log values.

A.

Factor I	Factor II	Factor III	Factor IV
B 2.74	Y 2.05	La -2.02	Nb -2.40
V 2.10	Yb 1.78	Na -1.98	Ga -2.35
Yb 1.62	Ti 1.75	Ga -1.70	B -1.97
Ba 1.22	Fe 1.52	Ba -1.70	Al -1.67
Al 1.05	Sc 1.49	Sr -1.67	Na -1.38
	Cu 1.28	Sc -1.46	
	V 1.08	K 1.29	
	Mn 1.04	V -.93	
		Al -.86	

B.

Factor I	Factor II	Factor III	Factor IV
B .54	Y .72	Ba .71	Nb .41
V .27	Fe .66	Na .67	
Ba .20	Mn .65	Sr .65	*V -.56
Yb .16	Ti .63	La .61	*Sc -.52
	Yb .57	K .59	*Yb -.51
*Co -.61	Zn .54	Ga. 57	*Fe -.49
*Ga -.55	Co .50	Al .57	*Mn -.49
*Fe -.51	Sc .46	Sc .47	*Zn -.44
*Mg -.48	Cu .44	*Pb -.33	*Ti -.43
*Ni -.42			*La -.41
*Ca -.42	*K -.42		
*Cr -.39	*Ba-.35		
*Ti -.36	*Na-.33		
*Mn -.34			
*Cu -.33			
*Zn -.32			

*Extreme negative correlation.

TABLE VII

Q-mode varimax factor matrix associating samples into factor groupings.

```
00097  FACTOR ANALYSIS (Q-MODE)  - U S G S  STATPAC 06/07/77

Q Factor analysis on 25 col bu

VARIMAX FACTOR MATRIX


                         COMM.       1         2         3         4

  1  69ANC100           0.9484    0.4232    0.3825   -0.6168   -0.4924
  2  69ASC101           0.9440    0.4416    0.3271   -0.6588   -0.4562
  3  69ASC105           0.9773    0.4202    0.2779   -0.5858   -0.6167
  4  69ANC107           0.9481    0.4572    0.1810   -0.5552   -0.6310
  5  69ANC114           0.9585    0.4006    0.2533   -0.7559   -0.4031
  6  69ANC116           0.9727    0.4459    0.3677   -0.6634   -0.4455
  7  69ANC121           0.9322    0.4167    0.3968   -0.6592   -0.4082
  8  69ASC155           0.9613    0.5693    0.1800   -0.5227   -0.5758
  9  69ANC200           0.9300    0.5289    0.3561   -0.3572   -0.6292
 10  69ANC206           0.9646    0.4538    0.2277   -0.5654   -0.6222
 11  69ANC208           0.9632    0.4163    0.2146   -0.7042   -0.4980
 12  69ANC209           0.9499    0.4636    0.1901   -0.6528   -0.5221
 13  69ANC220           0.9368    0.4127    0.1696   -0.6747   -0.5315
 14  69ANC221           0.9680    0.3569    0.1194   -0.7602   -0.4984
 15  69ANC224           0.9364    0.3438    0.2519   -0.7037   -0.5095
 16  69ANC227           0.9097    0.3356    0.1820   -0.7413   -0.4632
 17  69ANC229           0.9336    0.4468    0.0843   -0.6401   -0.5632
 18  69ANC232           0.9720    0.4616    0.3126   -0.6604   -0.4745
 19  69ANC235           0.9514    0.4560   -0.0240   -0.5355   -0.6753
 20  69ANC247           0.9029    0.5502    0.2904   -0.5967   -0.3998
 21  70ANC7B            0.9609    0.5759    0.2251   -0.6379   -0.4144
 22  70ANC11B           0.8948    0.4364    0.2424   -0.5643   -0.5719
 23  70ANC13B           0.9458    0.5066    0.2030   -0.5994   -0.5372
 24  70ANC14B           0.9156    0.5066    0.2986   -0.6510   -0.3821
 25  70ANC15S           0.9610    0.5425    0.2433   -0.6660   -0.4050
 26  70ANC16S           0.9303    0.4445    0.0799   -0.7395   -0.4235
 27  70ASC20S           0.9261    0.4357    0.1942   -0.6840   -0.4804
 28  70ANC24S           0.9578    0.4122    0.1384   -0.6691   -0.5666
 29  70ANC27B           0.9337    0.5181    0.2702   -0.6696   -0.3794
 30  70ANC29S           0.9383    0.5582    0.3855   -0.6325   -0.2792
 31  70ANC32B           0.9757    0.4818    0.3486   -0.6964   -0.3701
 32  70ANC35S           0.9597    0.5424    0.3971   -0.5493   -0.4540
 33  70ANC40B           0.9432    0.4999    0.3090   -0.6018   -0.4854
 34  70ANC45S           0.9362    0.5548    0.3249   -0.5934   -0.4131
 35  70ANC47B           0.9337    0.5830    0.3417   -0.5284   -0.4448
 36  70ANC48B           0.9373    0.5555    0.3395   -0.6292   -0.3428
 37  70ANC53S           0.8663    0.4755    0.3627   -0.6375   -0.3198
 38  70ANC54S           0.9484    0.5384    0.2752   -0.5928   -0.4811
 39  70ANC56B           0.9460    0.4945    0.3379   -0.6486   -0.4083
 40  70ANC59T           0.9532    0.4870    0.3153   -0.6643   -0.4188
 41  70ANC61T           0.9266    0.4721    0.1501   -0.5394   -0.6247
 42  67ANC30            0.8690    0.5279    0.4974   -0.4106   -0.4176
 43  68AWF310           0.8950    0.4137    0.4762   -0.2763   -0.6486
 44  68AWF327           0.8661    0.4049    0.5763   -0.3370   -0.5065
 45  68AWF338           0.9619    0.3472    0.4583   -0.5557   -0.5680
 46  68AWF343           0.9319    0.3005    0.3751   -0.4177   -0.7256
 47  68AWF344           0.9537    0.3296    0.2750   -0.3425   -0.8076
 48  68AWF345           0.9547    0.3733    0.4562   -0.4144   -0.6599
 49  68AWF346           0.9133    0.3573    0.3553   -0.3988   -0.7073
```

Table VII cont.

50	68AWF350	0.9629	0.4113	0.4042	-0.6142	-0.5031
51	68AWF354	0.9516	0.3836	0.3658	-0.4953	-0.6522
52	68AWF355	0.9614	0.2864	0.3079	-0.4429	-0.7671
53	68AWF357	0.9739	0.4131	0.4332	-0.5483	-0.5612
54	68AWF410	0.9652	0.4131	0.3524	-0.6053	-0.5514
55	68AWF430	0.9464	0.4607	0.4339	-0.5155	-0.5292
56	68AWF440	0.9318	0.3728	0.3901	-0.5148	-0.6128
57	68AWF505	0.8597	0.4819	0.2095	-0.4516	-0.6161
58	68ANC30B	0.9547	0.4479	0.2959	-0.2083	-0.7894
59	68ANC61B	0.7867	0.2441	0.4051	-0.6690	-0.3398
60	68ANC709	0.7790	0.3230	0.2936	-0.6989	-0.3161
61	68ANC95B	0.9286	0.3070	0.0497	-0.6824	-0.6052
62	68ANC105	0.9189	0.2003	0.2794	-0.6621	-0.6020
63	68ANC112	0.9572	0.3260	0.1645	-0.7143	-0.5601
64	68ANC115	0.8643	0.0644	0.3589	-0.7140	-0.4706
65	68ANC118	0.9271	0.2252	0.3215	-0.7242	-0.4985
66	68ANC120	0.9278	0.3284	0.3170	-0.6561	-0.5377
67	68ANC126	0.9013	0.3785	0.1983	-0.6157	-0.5828
68	68ANC140	0.9207	0.3305	0.2739	-0.7270	-0.4561
69	68ANC154	0.9565	0.3945	0.1499	-0.5947	-0.6517
70	68ANC166	0.9550	0.5444	0.1272	-0.3336	-0.7289
71	68ANC179	0.9630	0.4315	0.4627	-0.5643	-0.4943
72	68ANC181	0.6896	0.3151	0.2304	-0.4730	-0.5599
73	68ANC182	0.7059	0.6045	0.1876	-0.3397	-0.4358
74	68ANC187	0.9552	0.7767	0.3260	-0.3369	-0.3636
75	68ANC190	0.2377	0.2429	0.0879	-0.3257	-0.2547
76	68ANC200	0.9855	0.7714	0.2255	-0.3393	-0.4738
77	68ANC212	0.9527	0.7923	0.2554	-0.2870	-0.4212
78	68ANC215	0.9290	0.6878	0.0987	-0.5117	-0.4293
79	68ANC231	0.9559	0.6885	0.2961	-0.5342	-0.3299
80	68ANC233	0.9644	0.7508	0.3190	-0.4152	-0.3557
81	68ANC234	0.9749	0.7168	0.4826	-0.4212	-0.2255
82	68ANC240	0.9616	0.6988	0.3902	-0.5404	-0.1703
83	68ANC241	0.9604	0.7254	0.3452	-0.4834	-0.2852
84	68ANC244	0.9608	0.7342	0.4107	-0.3938	-0.3132
85	68ANC248	0.9450	0.6889	0.3396	-0.5418	-0.2480
86	68ANC251	0.9441	0.7140	0.4263	-0.3571	-0.3536
87	68ANC76B	0.9643	0.7788	0.1157	-0.3990	-0.4303
88	68ANC79B	0.9259	0.7315	0.0777	-0.4545	-0.4221
89	68ANC839	0.8958	0.6669	0.1483	-0.5800	-0.3045
90	68ANC148	0.9128	0.6197	0.2206	-0.6148	-0.3195
91	68ANC156	0.9196	0.6771	0.0916	-0.4854	-0.4660
92	68ANC158	0.9298	0.6897	0.0385	-0.5289	-0.4158
93	68ANC160	0.9347	0.7136	0.0897	-0.4858	-0.4260
94	68ANC163	0.9380	0.7013	0.1127	-0.4868	-0.4433
95	68ANC169	0.9581	0.7503	0.2086	-0.2989	-0.5121
96	68ANC194	0.9382	0.7383	0.2261	-0.4120	-0.4151
97	68ANC214	0.9341	0.7696	0.1105	-0.2665	-0.5086
98	68ANC218	0.9431	0.7240	0.2095	-0.3586	-0.4964
99	68ANC221	0.9782	0.5222	0.2021	-0.5020	-0.6424
100	68ANC223	0.8672	0.5486	0.2991	-0.4402	-0.5320
101	68ANC225	0.9577	0.4280	0.4083	-0.6715	-0.3960
102	69ANC102	0.9520	0.5282	0.3186	-0.5835	-0.4806
103	69ANC104	0.9427	0.5190	0.2885	-0.6475	-0.4134
104	69ANC110	0.9483	0.4746	0.3688	-0.5990	-0.4778
105	69ANC111	0.9826	0.5322	0.2469	-0.7074	-0.3714
106	69ANC112	0.9611	0.4927	0.4057	-0.6827	-0.2960
107	69ANC113	0.9761	0.5112	0.2272	-0.7182	-0.3838
108	69ANC115	0.9590	0.4929	0.3073	-0.6860	-0.3888
109	69ANC117	0.9817	0.4617	0.3162	-0.5951	-0.5607

Table VII cont.

110	69ANC119	0.9573	0.4507	0.3894	-0.6482	-0.4270
111	69ANC205	0.9750	0.3932	0.2409	-0.6342	-0.6002
112	69ANC211	0.9485	0.4283	0.1794	-0.6123	-0.5983
113	69ANC218	0.9444	0.3355	0.0940	-0.7666	-0.4851
114	70ANC28	0.9794	0.4698	0.2464	-0.6882	-0.4737
115	70ANC38I	0.9619	0.5256	0.2684	-0.4585	-0.6352
116	70ANC42I	0.9727	0.5306	0.2564	-0.5538	-0.5646
117	70ANC51	0.9664	0.5337	0.3643	-0.5537	-0.4922
118	70ANC52I	0.9699	0.4673	0.3150	-0.6362	-0.4975
119	70ANC57I	0.9510	0.5293	0.3472	-0.5384	-0.5103
120	70ANC60	0.9771	0.4312	0.2863	-0.5677	-0.6221
121	69ANC120	0.9785	0.4103	0.3880	-0.6828	-0.4398
122	68ANC38	0.9534	0.5340	0.4619	-0.5668	-0.3655
123	68ANC89	0.9299	0.3639	0.0614	-0.6984	-0.5531
124	68ANC15	0.6726	0.4328	0.3754	-0.3558	-0.4666
125	68ANC23	0.8771	0.4001	0.1920	-0.3137	-0.7627
126	68PR23	0.7044	0.3410	0.5527	-0.4380	-0.3013
127	69ANC127	0.9288	0.5259	0.5832	-0.2720	-0.4880
128	69ANC130	0.9336	0.4822	0.6779	-0.2361	-0.4310
129	69ANC145	0.8808	0.5048	0.2053	-0.4436	-0.6221
130	69ANC147	0.9073	0.4125	0.4665	-0.3157	-0.6480
131	68AWF801	0.8641	0.2954	0.8409	-0.1481	-0.2185
132	68AWF802	0.7666	0.1953	0.8215	-0.2112	-0.0950
133	68AWF807	0.8339	0.0931	0.8944	-0.1420	-0.0717
134	68AWF827	0.5930	0.0293	0.7592	-0.1209	-0.0338
135	69ANC85	0.7732	0.0829	0.4862	-0.6355	-0.3551
136	69ANC86	0.3821	-0.1003	0.4880	-0.2841	-0.2307
137	69ANC95	0.7883	0.1965	0.4825	-0.6085	-0.3829
138	69A5C97	0.8668	0.2828	0.4972	-0.6231	-0.3891
139	68ANC302	0.7034	0.3949	0.3192	-0.4779	-0.4660
140	68ANC304	0.8314	0.4120	0.2272	-0.6094	-0.4885
141	68ANC307	0.8992	0.3947	-0.0038	-0.6653	-0.5485
142	68ANC309	0.9053	0.3274	0.0545	-0.7469	-0.4871
143	68ANC216	0.9539	0.5533	0.2698	-0.4974	-0.5723
144	68ANC235	0.9410	0.5004	0.4194	-0.5074	-0.5072
145	69ANC204	0.9306	0.5730	0.1613	-0.5032	-0.5684
146	69ANC207	0.9716	0.4669	0.2338	-0.7072	-0.4459
147	69ANC223	0.9668	0.4421	0.1071	-0.7505	-0.4434
148	69ANC230	0.9778	0.5789	0.0915	-0.4893	-0.6283
149	69ANC245	0.9505	0.5858	0.2288	-0.5193	-0.5343
150	69ANC252	0.9125	0.5596	0.3766	-0.5227	-0.4292
151	69ANC255	0.9838	0.5897	0.1446	-0.4297	-0.6561
152	70ANC58H	0.9349	0.5320	0.3934	-0.6332	-0.3100
153	M131032	0.9666	0.4302	0.4735	-0.7269	-0.1703
154	M131033	0.8264	0.5580	0.5431	-0.4786	-0.2260
155	M131034	0.9500	0.6335	0.2132	-0.3338	-0.6260
156	M131036	0.5672	0.1702	0.2717	-0.6376	-0.2405
157	M131037	0.9312	0.6037	0.3913	-0.3729	-0.5239
158	M131038	0.9499	0.4790	0.4085	-0.6896	-0.2791
159	M131039	0.9473	0.5429	0.2660	-0.5197	-0.5583
160	M131040	0.9628	0.4795	0.4457	-0.6432	-0.3469
161	M131041	0.9207	0.3196	0.4762	-0.7256	-0.2555
162	M131042	0.9703	0.4903	0.4222	-0.6961	-0.2590
163	M131043	0.9545	0.4090	0.4931	-0.6481	-0.3522
164	M131044	0.9611	0.4793	0.4695	-0.6693	-0.2510
165	M131045	0.9821	0.4390	0.4918	-0.7040	-0.2277
166	M131046	0.9843	0.4023	0.3589	-0.7529	-0.3561
167	M131047	0.9418	0.3364	0.4083	-0.7642	-0.2792
168	M131048	0.9797	0.3698	0.3793	-0.7891	-0.2766
169	M131049	0.9728	0.4587	0.3965	-0.7315	-0.2648

Table VII cont.

170	M131050	0.9535	0.5231	0.3978	-0.6951	-0.1961
171	M131051	0.9812	0.4966	0.4042	-0.7183	-0.2348
172	M131052	0.8930	0.4699	0.3032	-0.7200	-0.2489
173	M131053	0.9741	0.4610	0.3655	-0.7673	-0.1980
174	M131054	0.9671	0.4966	0.2958	-0.6839	-0.4065
175	M131055	0.9704	0.3806	0.2975	-0.7991	-0.3139
176	M131056	0.9670	0.5309	0.2372	-0.6532	-0.4497
177	M131057	0.9307	0.4832	0.2691	-0.6349	-0.4709
178	M131059	0.9561	0.4526	0.4419	-0.6690	-0.3292
179	M131064	0.9384	0.4293	0.3202	-0.7184	-0.3682
		VARIANCE	24.232	11.842	33.379	22.489
		CUM. VAR	24.232	36.074	69.453	91.942

Concentrations of twenty-six elements were all below detection limits (Table II). Two elements, Ga and P, had a considerable number of values that were less than the lower limits of detection.

Computer software developed by the Dynamic Graphics Company, Berkeley, California (Dynamic Graphics Surface Display Library) was used to display the geochemical values. For each element (Figs. 5-66) there is a two-dimensional contour map of the value-surface and a three-dimensional mesh plot of the value-surface shown at an oblique perspective to the land surface.[1] A single viewing perspective of 20° degrees to the horizontal and looking NNW was chosen for all of the three-dimensional mesh plots because the uniformity was found to enhance the ease with which one can compare plots for different elements. The value surface of each three-dimensional plot was made to decrease to zero as it impinged on a rough polygonal outline of surrounding coastlines. To further help viewer orientaion, a map view showing the coastal outline in the same perspective as the three-dimensional plot was generated above the three-dimensional plot.

The Dynamic Graphics software used to generate the plotting grids from which the two- and three-dimensional map plots are made, employs an iterative technique to solve biharmonic equations which produces a surface of least tension passing through all the data points. It is this surface which is contoured or graphically represented by a mesh pattern. Contour intervals for the two-dimensional contour plots are chosen automatically by the program which makes the selection based on the maximum, minimum and distribution of values encountered.

VII. DISCUSSION

A. Petroleum Indicators

High concentrations of V and Ni in sediments near petroleum seeps have been attributed to contamination of the sediments by high concentrations of

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[1] A microfiche plate displaying lists and map-plots of element concentrations and locations is available on request.

these elements as chelated porphyrins in the oils and tars of the seeps (Reed and Kaplan, 1977; Yen, 1975). Therefore, relatively high concentrations of V and Ni together in a particular area might indicate the presence of thermogenic hydrocarbons.

The one known gas seep in Norton Basin is located roughly 35 km south of Nome. At this site concentrations of Ni in surface sediment are not anomalously high but concentrations of V are up to 200 ppm, more than two geometric deviations higher than the geometric mean for V in sediment of the northern Bering Sea region (Figs. 5$\overset{6}{,}$7,8; Table I). But the high V values in the gas-seep area may be a result of being located in the region of Yukon Holocene sedimentation because equally high values are found quite generally throughout this area. The lack of both Ni and V anomalies at the Norton Sound Seep is in keeping with the fact that it is primarily a CO_2 gas seep with only traces of low molecular weight thermogenic hydrocarbons (Kvenvolden, et al., 1979).

Additional sediment samples were collected in a grid surrounding the gas seep in order to look for possible chemical differences between sediment in the gas seep area and sediments in surrounding areas. The samples were analyzed for 54 elements including V and Ni. The average concentrations of V and Ni in these samples are 68.8 ppm and 18.8 ppm respectively, which are lower than backgound V and Ni concentrations for this region (Table I).

It is clear that the V and Ni values for the detailed sampling grid do not support thermogenic origin of the anomalous hydrocarbons found in this area. There was a seven-year difference between the collection time of the grid of samples and the first group of samples in the gas-seep area. Differences in the V and Ni content of these two sets of samples may reflect a basic change in the sediment due perhaps to the large storm surge of 1974 (Fathauer, T.F., 1975).

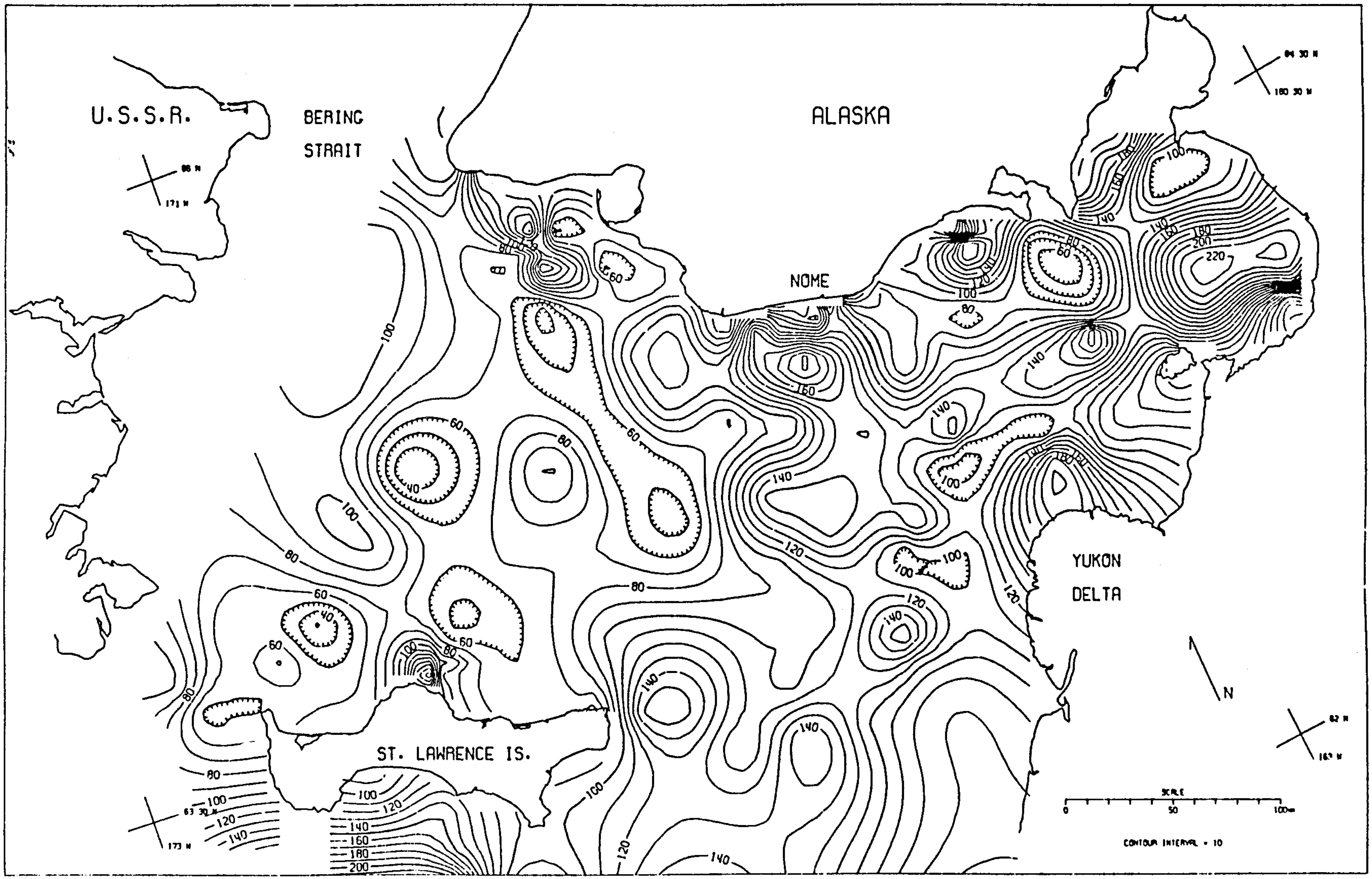

FIG 5 V PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

NORTON BASIN PERSPECTIVE VIEW

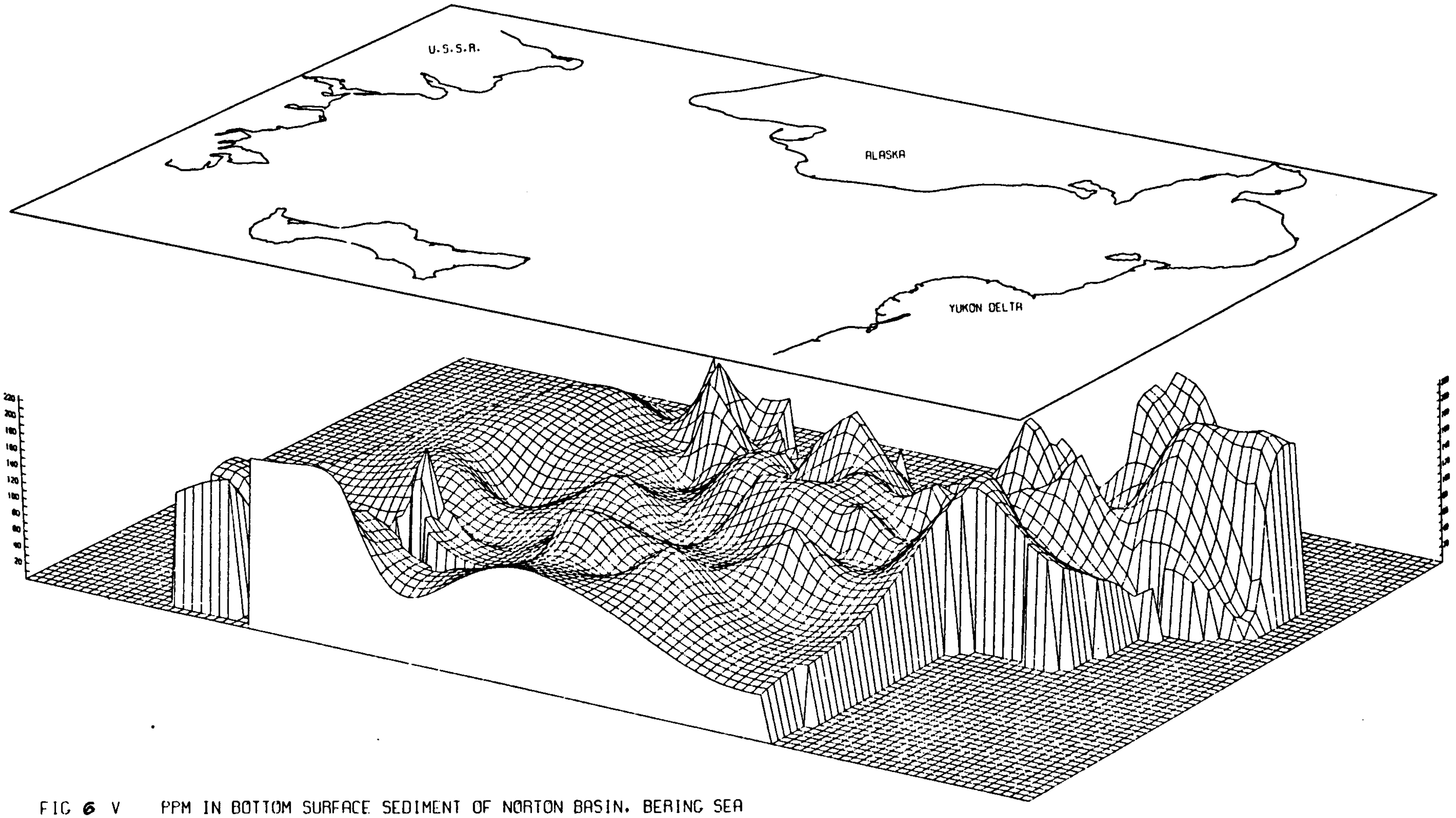

FIG 6 V PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

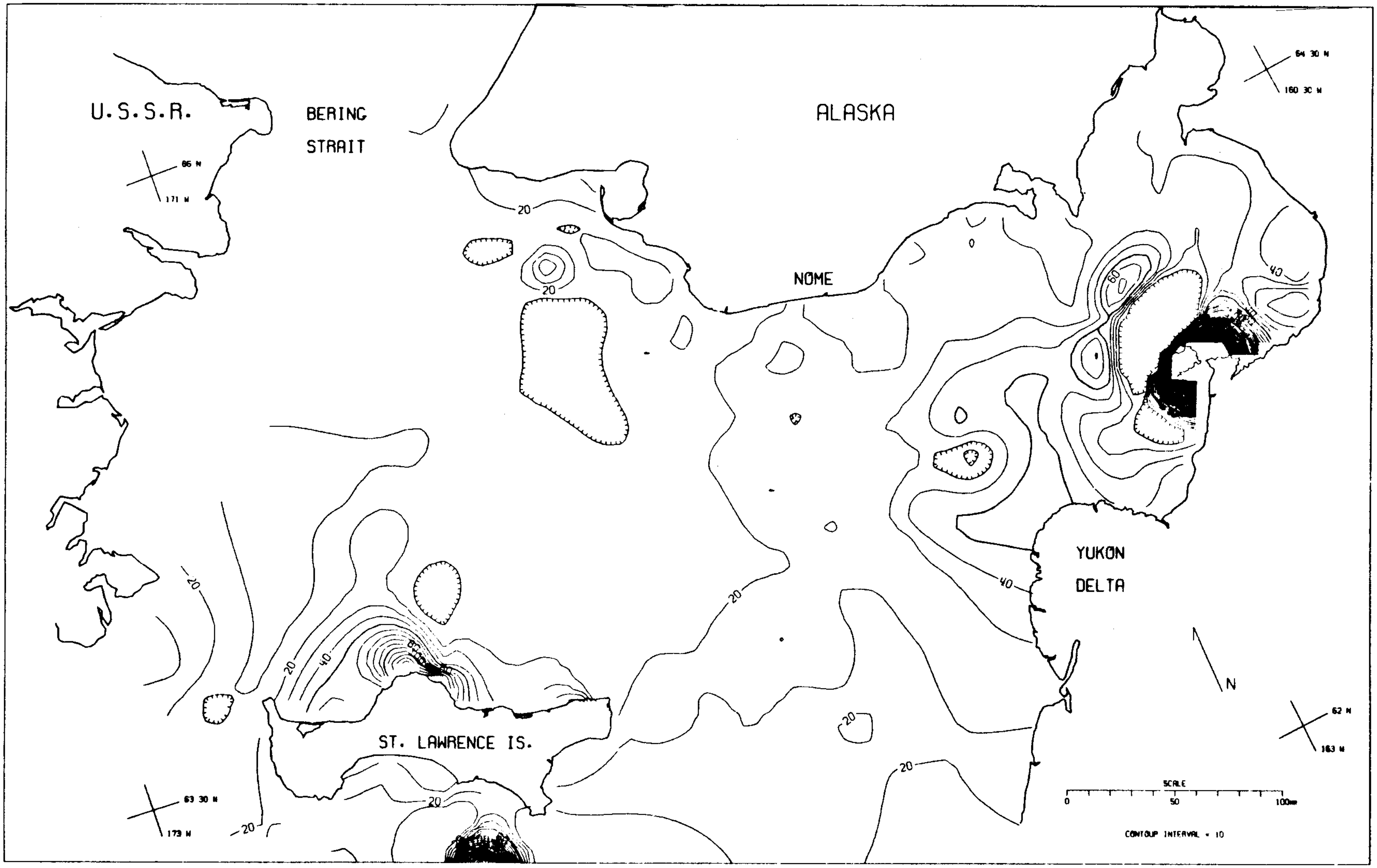

FIG 7 NI PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

NORTON BASIN PERSPECTIVE VIEW

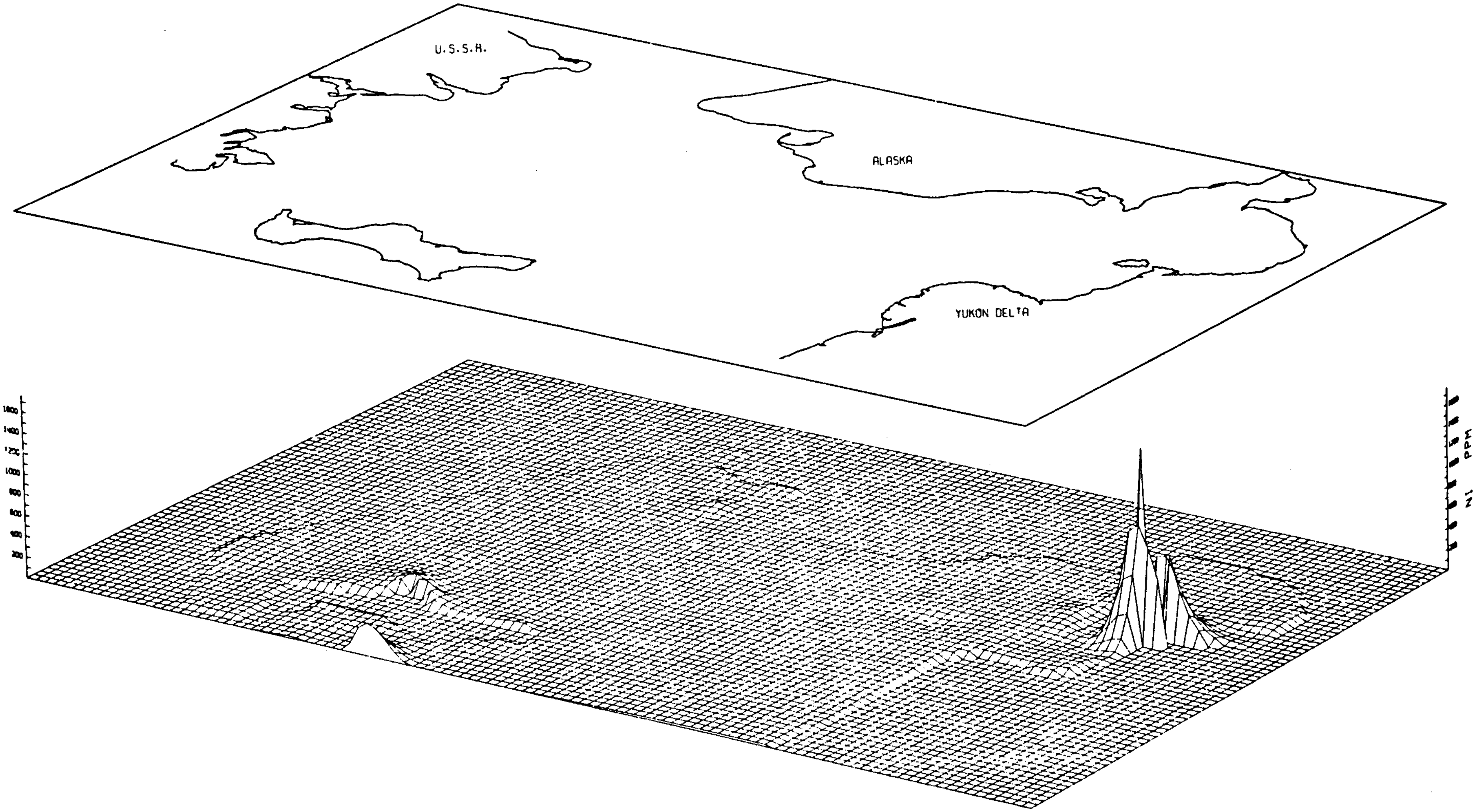

FIG 8 NI PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

Sediments in an area located approximately 40 km west of the southern tip of St. Lawrence Island had V and Ni concentrations of 200 and 100 ppm (Fig. 3). Both of these values are higher than the expected ranges for V and Ni (Table I). These relatively high values coupled with the fact that the sample locations are at some distance from any possible land source could be taken as sufficient evidence to warrant a closer examination of this area for hydrocarbons.

B. Heavy Metals

General Characteristics

Sn, Cr, Zr, and Ce are treated as a group because they are found in minerals which are heavy and stable enough to be mechanically concentrated into placer deposits. Au and Hg, etc., are not considered in this report because their distribution is described in other published reports (Nelson and Hopkins, 1972; Nelson et al., 1975-1977).

Previous studies including those by Venkatarathnam, 1971; Sheth, 1971; and McManus et al., 1976, have looked at the distribution of heavy minerals in the Norton Basin region but these studies were either limited to a small area or involved only mineral concentrates from a portion of the sand-size range.

The degree to which a heavy mineral is concentrated in placers is dependent on winnowing forces and the magnitude of the density and size differences between the heavy mineral and the containing sediment. For example, if the heavy mineral particles in a sediment are relatively uniform in size, the mineral may be evenly distributed throughout hydraulically-equivalent sediment. Concentration can begin to take place only when the hydraulic balance between the particle size and density for the various mineral constituents of a sediment becomes unequal. An example would be when mechanical and chemical forces wear down heavy mineral particles in a sediment at a slower rate than the other mineral constituents of the sediment.

Once a given heavy mineral has been concentrated, the main factor influencing whether the concentration will be detected is the sampling interval. If the sampling interval was chosen primarily to detect significant areal variability in an average suite of elements, it may be too large to detect significant variability in specific heavier elements that tend to change in concentration over shorter distance. Also, the sampling interval may be entirely adequate to pick up general variability of the heavy element as it is distributed in sediments from a particular provenance but it may miss smaller scale variability caused by localized hydraulic fractionation (Flores and Shideler, 1978).

Zr

Relatively high concentrations of Zr are found in sediments surrounding the Yukon Delta, in Norton Sound, and around St. Lawrence Island (Figs. 9 and 10). This contrasts with the much lower values in Chirikov Basin. The presence of relatively higher concentrations of Zr in Yukon-derived sediment is probably because the Yukon River passes through a terrain which is composed mainly of sialic rocks, predominant contributers of zircon (Mason and Berry, 1968). A comparison of our contoured value-surface map for Zr and Venkatarathnam's percentage distribution maps (1971) of the heavy-mineral zircon in the 1-2.75 and 2.75-4.0 phi size-range show that his areas of high values generally correspond with the high value areas of our 2-dimensional map. This is particularly true off the NE Cape of St. Lawrence Island where his values as well as ours are highest. Our data also show persistently high concentrations for Zr off the western and southern parts of St. Lawrence Island. Probable sources for these high values are sediments derived from quartz-monzanite plutons which are found over much of St. Lawrence Island.

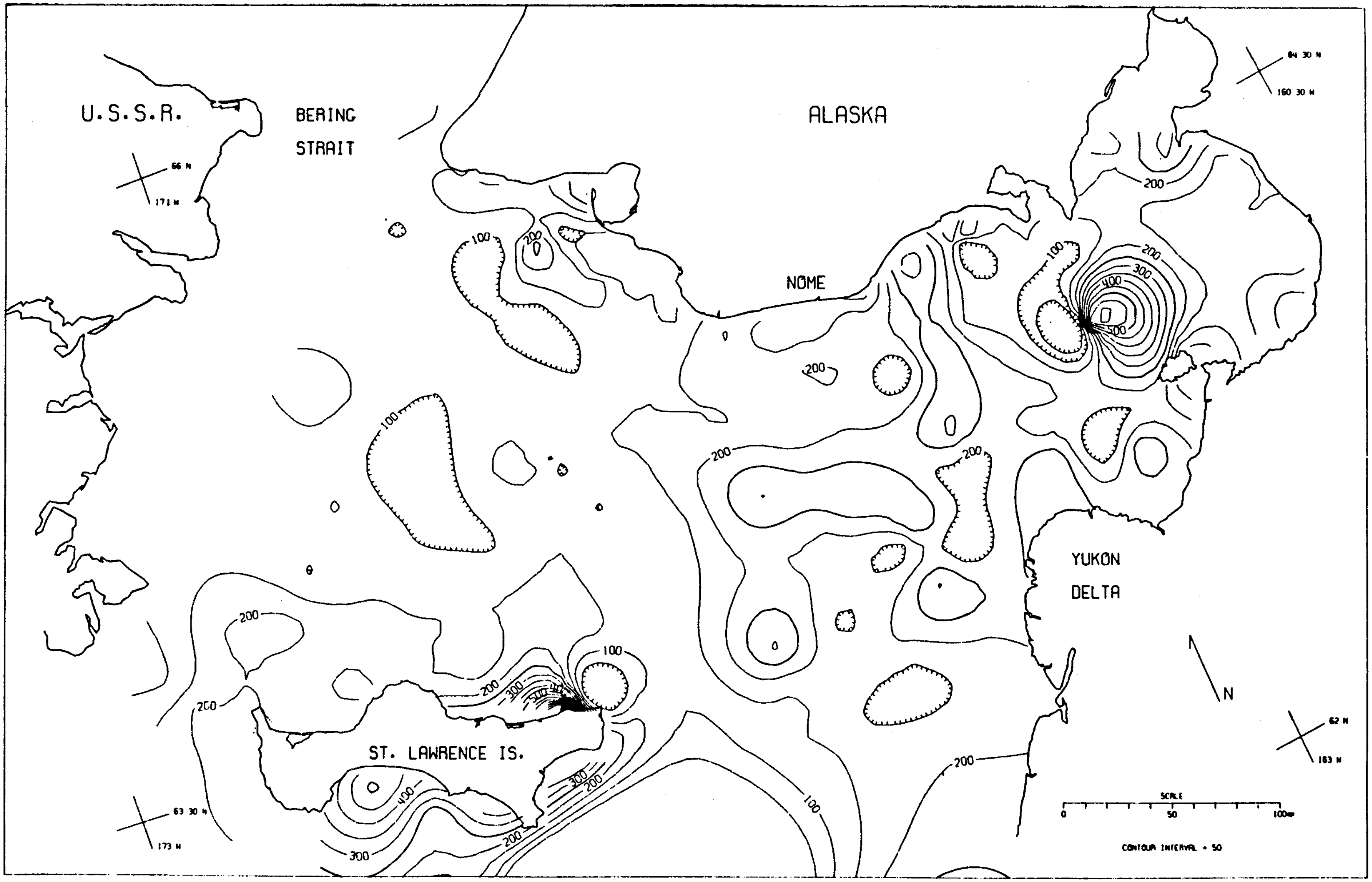

FIG 9 ZR PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

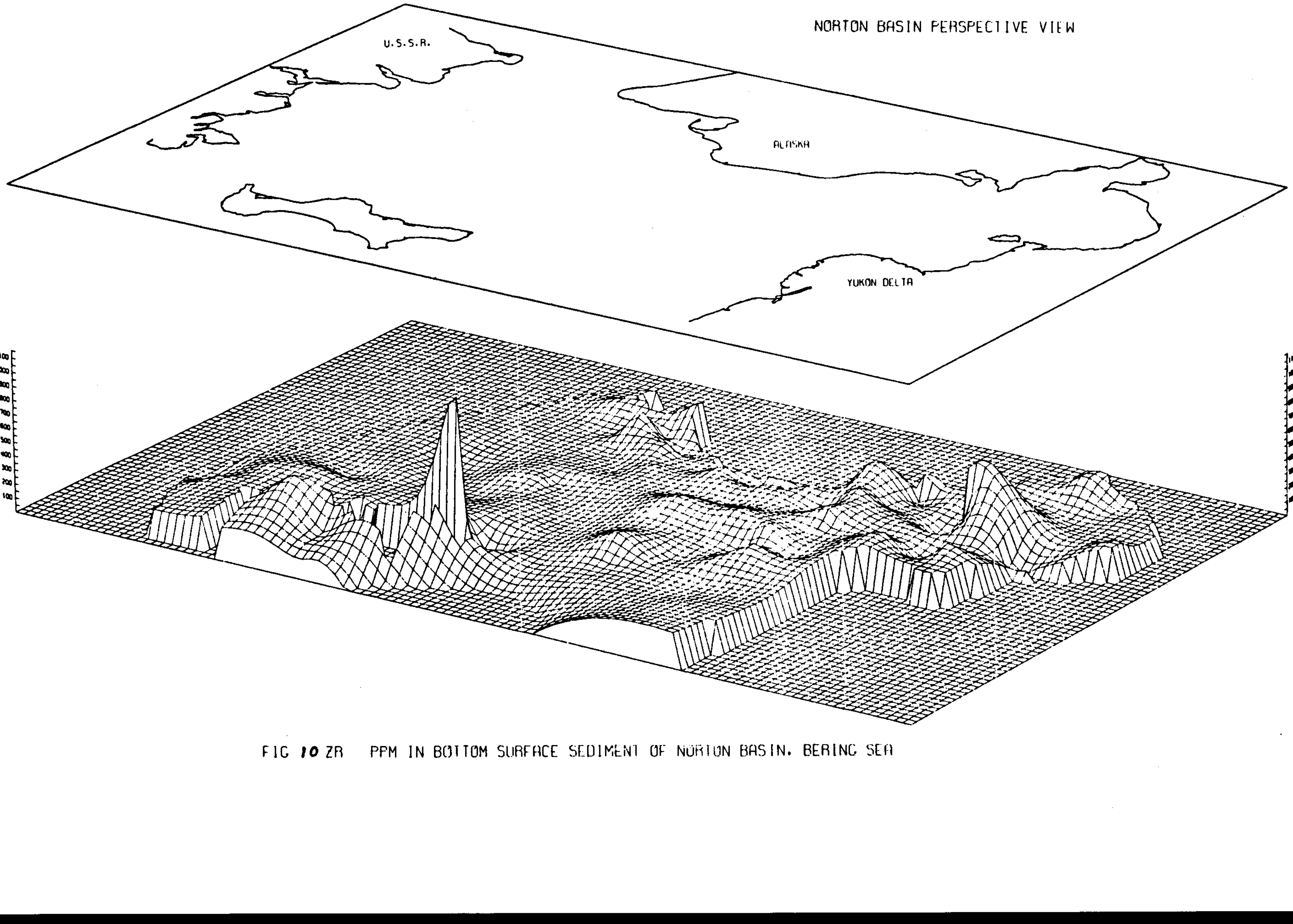

FIG 10 ZR PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

A strong Zr concentration occurs in a sample from the central part of Norton Sound, relatively far from land. Sediment analyzed at this locale was taken from a depth of about 10 meters and, according to McManus et al., 1976, in an area of generally higher sand content than the rest of Norton Sound. The lack of a nearby land source and the lack of generally high values in similar surrounding sediments might suggest that this sample may contain hydraulically concentrated zircon in a zone of coarser sediment. Strong tidal currents pass through this area (Cacchione and Drake, 1978) and may concentrate the heavier zircon grains.

Another sample with a high concentration of Zr was found 30 km south of Cape Prince of Wales (see Fig. 3; this sample is not represented on the value-surface maps). The Zr content in sediment from this location is as great as in any other sample in this study and the concentrations of Ti, Mn, Cr, La, Sc, Y, Zr, Yb, Nd, Ce, Sn and Zn are also greater than the expected ranges for these elments.

Venkatarathnam reports high concentrations of heavy minerals in the 2.75-4.0 phi size-range from this area, especially further south and east in the sand wave region west of Port Clarence. Similar concentrations are found in Anadyr and Shpanberg Straits. It is probable that the high speed currents in these areas have concentrated heavy minerals there. The high concentrations of various elements in the sample 30 km south of Cape Prince of Wales may represent a significant anomaly and may indicate deposits heretofore undetected and of considerable economic potential.

Sn

Sn concentrations in 156 of the 180 samples analyzed were below the limit of detection of 2 ppm. The highest values occurred close to Tin City on the southwest coast of Cape Prince of Wales; lesser anomalies were found in the area of King Island, Port Clarence, Bluff, Cape Rodney, the western and north-central coast of St. Lawrence Island, half way between Cape Prince of Wales and St. Lawrence Island, and the aforementioned sample from 30 km south of Cape Prince of Wales (Figs. 11 and 12). The highest concentrations of Sn, near Tin City, are obviously derived from the same mineralized formation which gave Tin City its name. Anomalies near Bluff, north central St. Lawrence Island, and Cape Rodney-Nome areas also appear to be related to adjacent onshore mineralization. The isolated high concentrations off of the NW tip of St. Lawrence Island may have been hydraulically concentrated. High values off Pt. Clarence and in the area of King Island are in an area of high currents and sand dune fields that also may represent an area of tin concentration.

Cr

The distribution of Cr in the Norton Basin is uniform except in the areas of Stuart Island, St. Lawrence Island, and Cape Prince of Wales (Figs. 13 and 14). These locations have relatively high concentrations of Cr, some of which are greater than one geometric deviation above the geometric mean.

All of these anomalies, except the sample site 30 km south of Cape Prince of Wales discussed earlier, are located close to igneous outcrops on land. Cape Prince of Wales is the site of granitic plutons that are cut by occassional mafic dikes. Gabbro and metagabbro bodies are also found throughout the same region. Stuart Island, the adjacent peninsula and the central portion of St. Lawrence Island are composed largely of alkali olivine basalts. Because chromite ($FeCr_2O_4$), which is the principal mineral of chromium, is thought to form as a magmatic segregation in ultrabasic rocks and is usually associated with olivine, there is probably a direct connection between anomalous values of Cr offshore, and the adjacent mafic igneous outcrops on land.

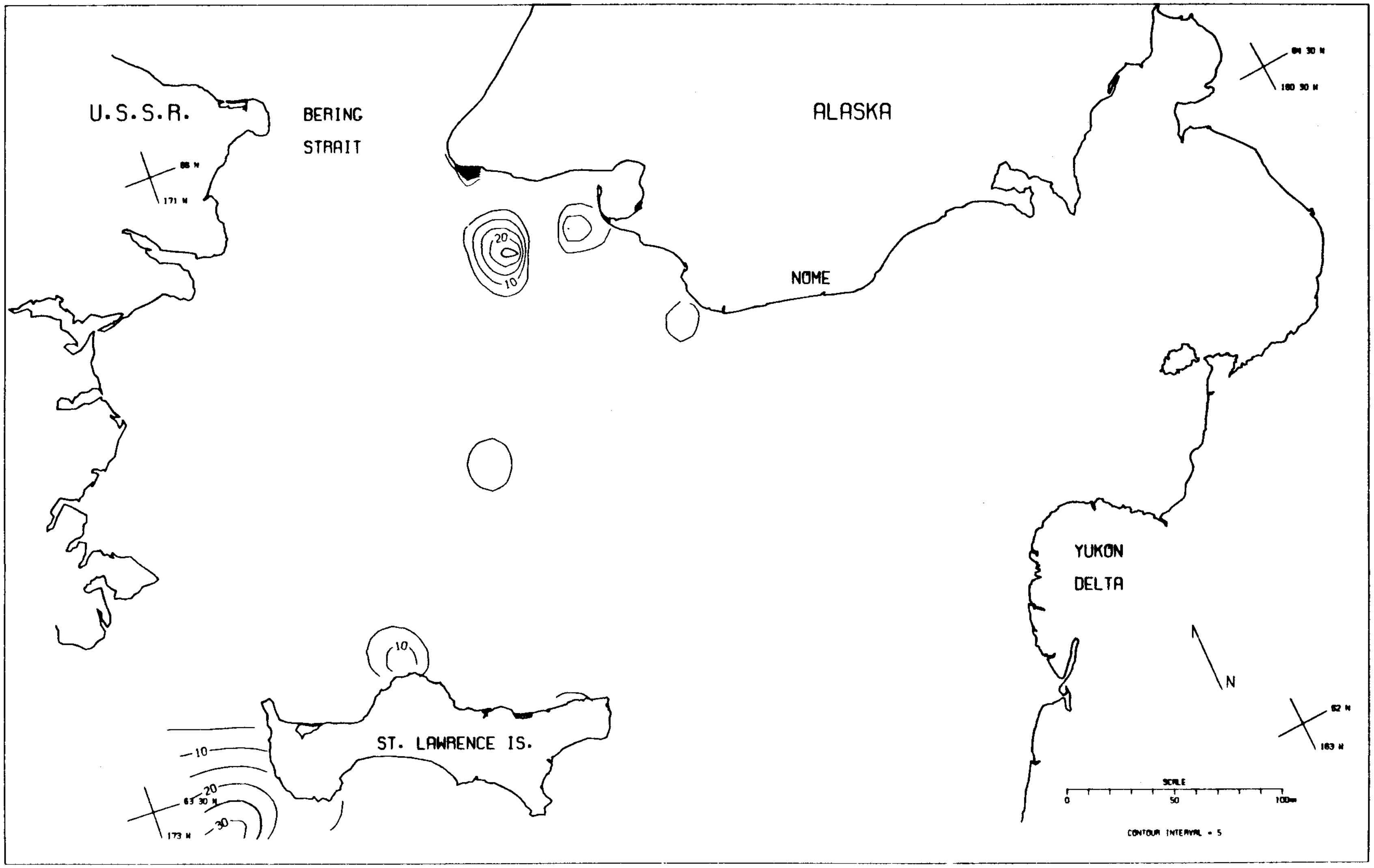

FIG 11 SN PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

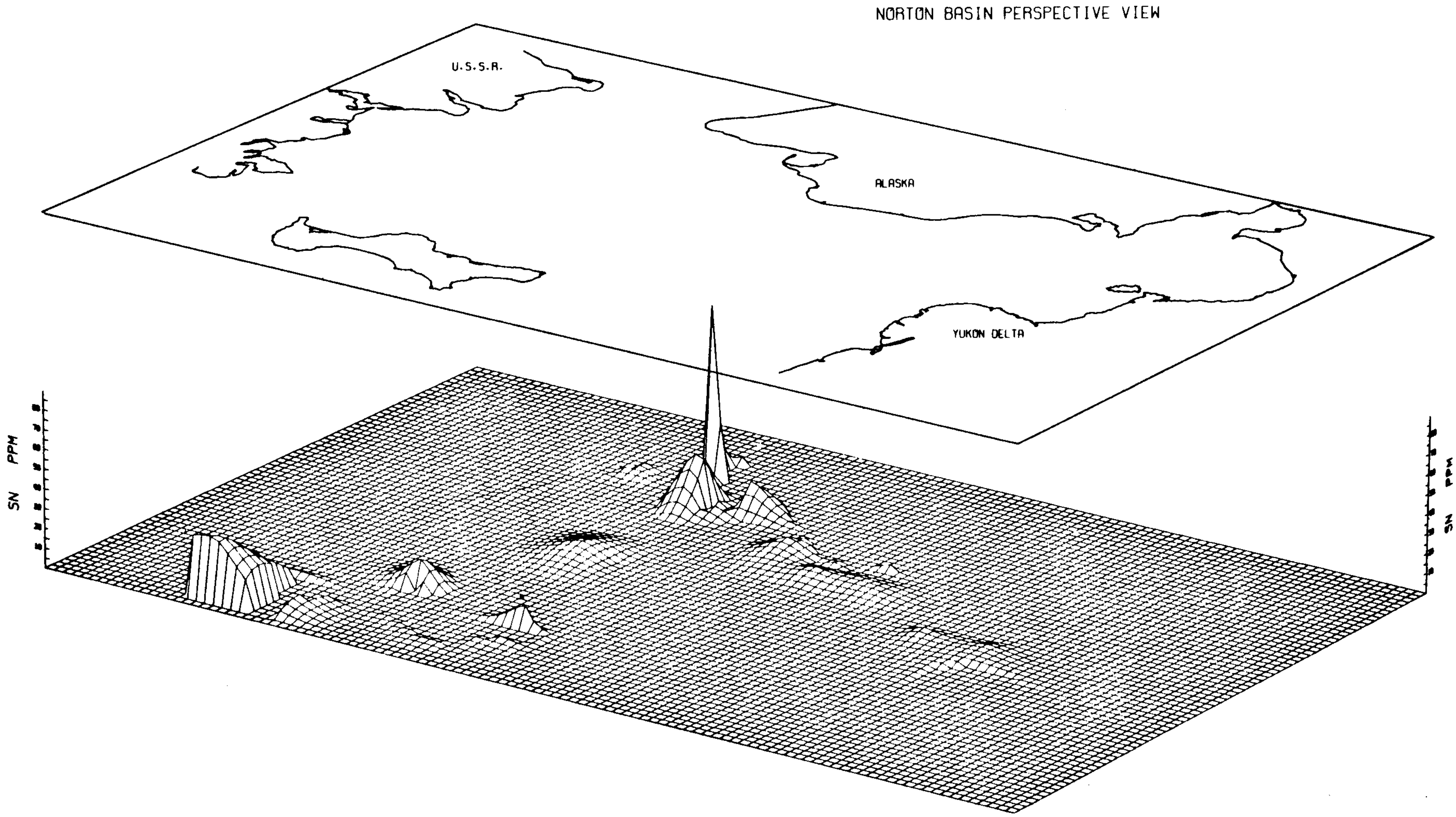

FIG 12 SN PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

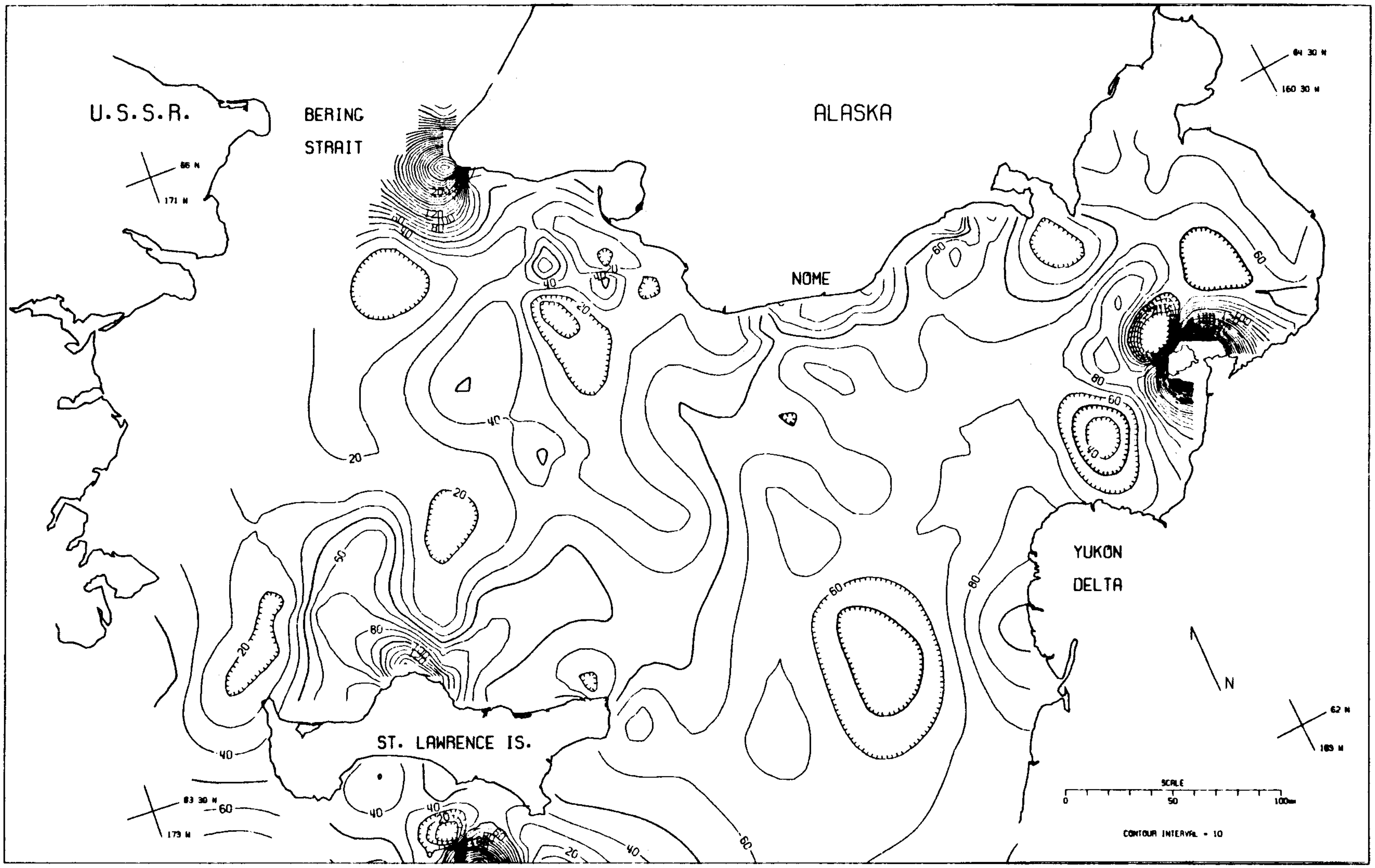

FIG 13 CR PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

NORTON BASIN PERSPECTIVE VIEW

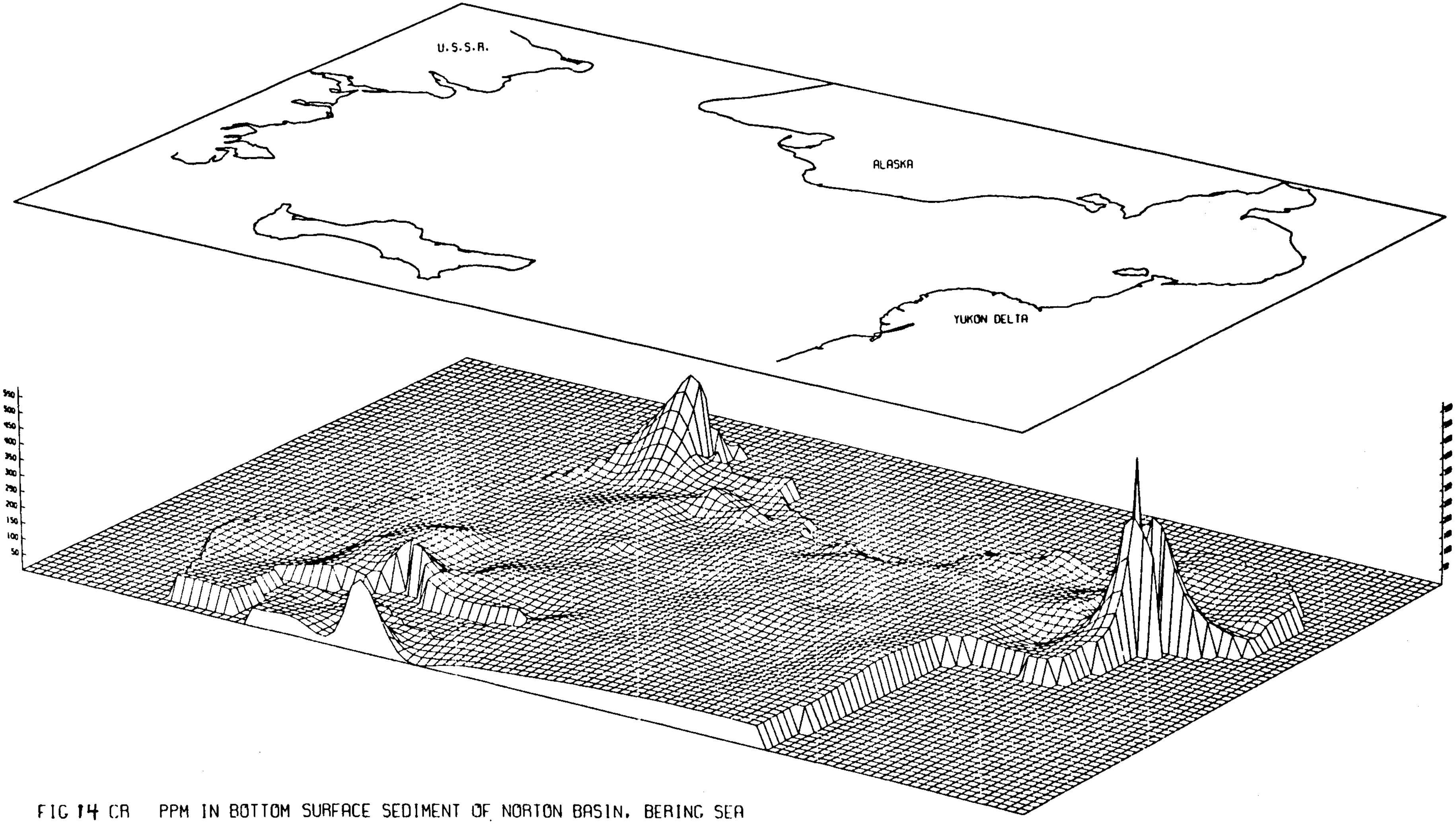

FIG 14 CR PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

Nelson and Hopkins found an abundance of harzburgite among rock fragments collected in dredge hauls in Akeftapak Bay off the NNE end of St. Lawrence Island (Patton and Csejtey, 1972). Semi-quantitative emission spectrographic analysis of some of these harzburgite samples yielded chromium values as high as 2,000 to 10,000 ppm. Patton and Csejtey also reported very high chromium values in the lower reaches of streams feeding into Akeftapak Bay. From this evidence, Patton and Csejtey infer the presence of an ultramafic body existing just below a thin veneer of sediment at this location. However, samples from the same area in our study did not have high concentrations of Cr. The distance between the dredge haul site and the nearest sampling site used in this study is 14 km. The fact that our study did not detect the dredge haul anomalies illustrates the importance of selecting the right sampling interval when attempting to delineate concentrations of heavy minerals and their associated heavy metals.

<u>Ce</u> (and associate Lanthanides, <u>La</u> and <u>Nd</u>)

Ce (cerium) is a heavy metal classified with a group of chemically similar elements called the lanthanides. The lanthanides usually occur together and their most common source mineral is monazite which is a fairly rare and complex phosphate occuring as an accessory mineral in granites, gneisses, aplites, and pegmatites. Monazite is resistant to chemical attack and is often concentrated in sands, particularly beach placers (Bateman, 1965; Sienko and Plane, 1961). The presence of cerium and other lanthanide elements in the same samples would be strong evidence for the presence of monazite in the samples.

La (lanthanum) and Ce anomalies on our maps (Figs. 15, 16, and 49, 50) generally coincide. The only real difference is that La has a much lower limit of detection than Ce and therefore shows much greater definition in the

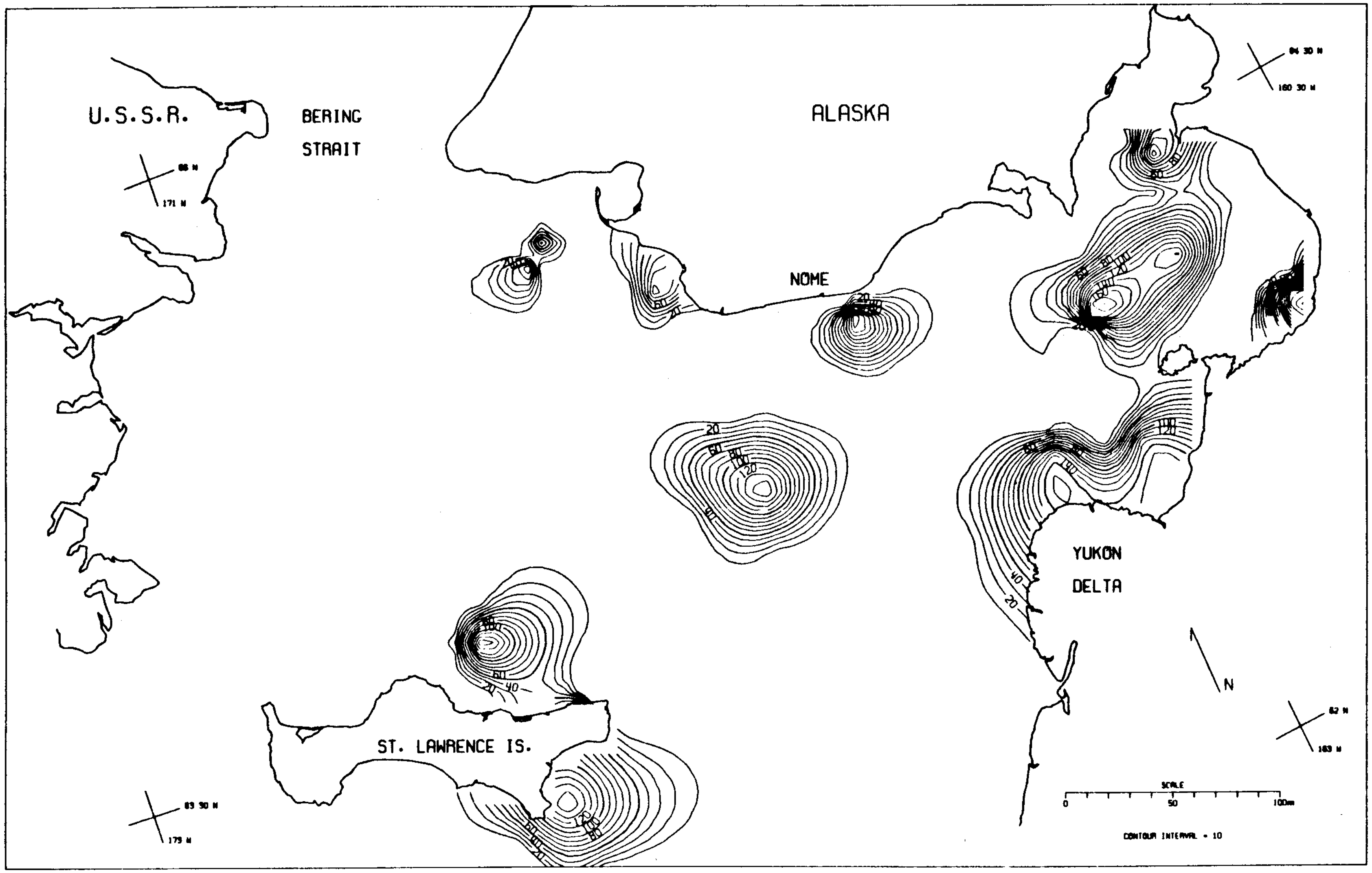

FIG 15 CE PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN. BERING SEA

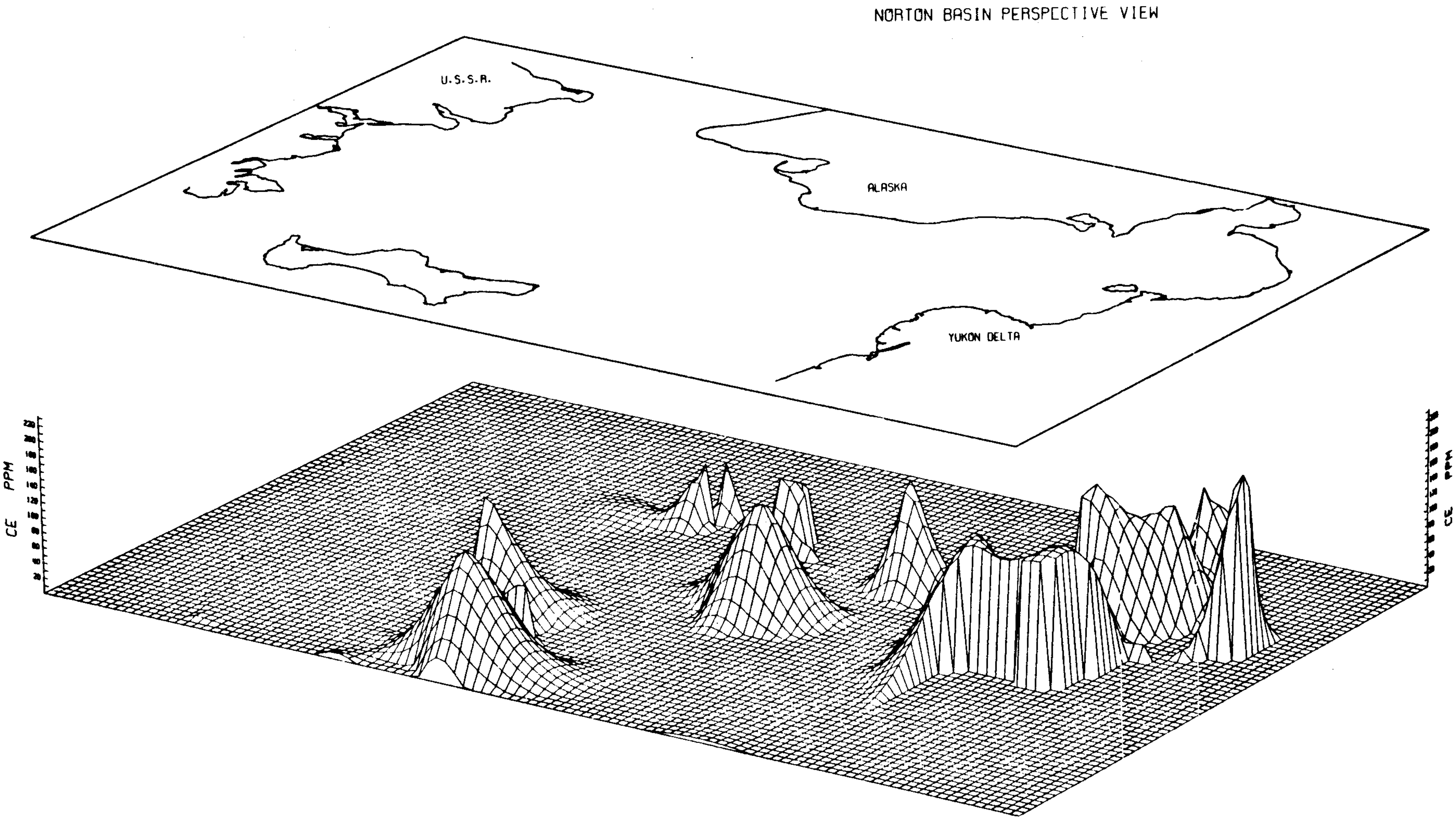

FIG 16 CE PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

lower value range. Neodymium (Nd), another lanthanide, was detected in three raw bulk samples and these three samples also had anomalously high concentrations of La and Ce. It is clear that these three elements occur together. Additional evidence that the containing mineral for these elements is monazite is the detection of Ce and Nd in analyses of mechanical concentrates of samples used in the study (not reported here). Analyses from raw bulk samples of the same sample set show either an absence of Ce or Nd or much lower values. This indicates that these elements are present in a heavy mineral like monazite that may be hydraulically concentrated.

The highest concentratios of Ce, La, and Nd are in a sample 30 km south of Cape Prince of Wales. Their presence together lends support to the probability that the sample had indeed been concentrated. Areas where monazite has been reported in this region are from Brooks Mountain, Ear Mountain, and Gold Run on the eastern Seward Peninsula (Cobb, 1970). High concentrations of Cerium in sediment west of Cape Rodney may be related to the Gold-Run location.

C. Potentially Toxic Elements

Of the potentially toxic elements considered in this report, only Cu, Pb, and Zn have sufficient numbers of values greater than their lower limits of detection to calculate meaningful statistics or to plot their value surfaces. Cd (cadmium) was not detected in any sample analyzed. Sb (antimony) was detected only in beach samples taken near Bluff, the NE Cape of St. Lawrence Island, and from Stuart Island; As (arsenic) was detected only in the beach samples from Bluff. Anomalous values are not found offshore from these beach areas. The values for Sb and As in these samples are several orders of magnitude higher than their limits of detection by the 6-step emission spectrographic technique and can therefore be considered to be anomalous. The map depicting source areas (Fig. 2) for some of the more economically important elements of this study shows Bluff to be a known area of concentrations of As.

Distribution of Cu, Pb, and Zn surface values in shelf sediments of Norton Basin are generally similar, including anomalously high values off St. Lawrence Island, along the southern coast of the Seward Peninsula, and throughout Norton Sound. The maps for Cu and Zn show much greater similarity to each other, however, than to the map for Pb (Figs. 17, 18, 19, 20, 21, and 22). Statistically, Pb correlates better with Cu and Zn than with any other element represented in the study (Table III), but Cu and Zn have a much higher correlation between themselves (.8023) than with Pb which supports the relative visual similarity between the maps of these elements.

A significant trend that appears in value-surface maps of both Cu and Zn is the generally higher values in Norton Sound compared to Chirikov basin. High values for Cu and Zn form a halo surrounding the Yukon Delta and the western edge of the halo trends due north along a line extending from the southern edge of the Yukon Delta towards the Bering Strait. The location of this halo coincides closely with the area of maximum deposition of Yukon-derived sediment in Norton Sound (Nelson and Creager, 1977). The gradation of Cu and Zn values away from the delta and the generally higher concentrations of these elements in Norton Sound suggest a source and dispersal coincident with Yukon-derived sediment. The Yukon River flows through an area highly mineralized in these elements and thus appears to be the dominant source for minerals bearing these elements.

Another significant aspect of the distribution of Cu, Zn and Pb is the presence of localized high values generally close to certain coastal areas. All three elements have their highest concentrations in beach samples taken near

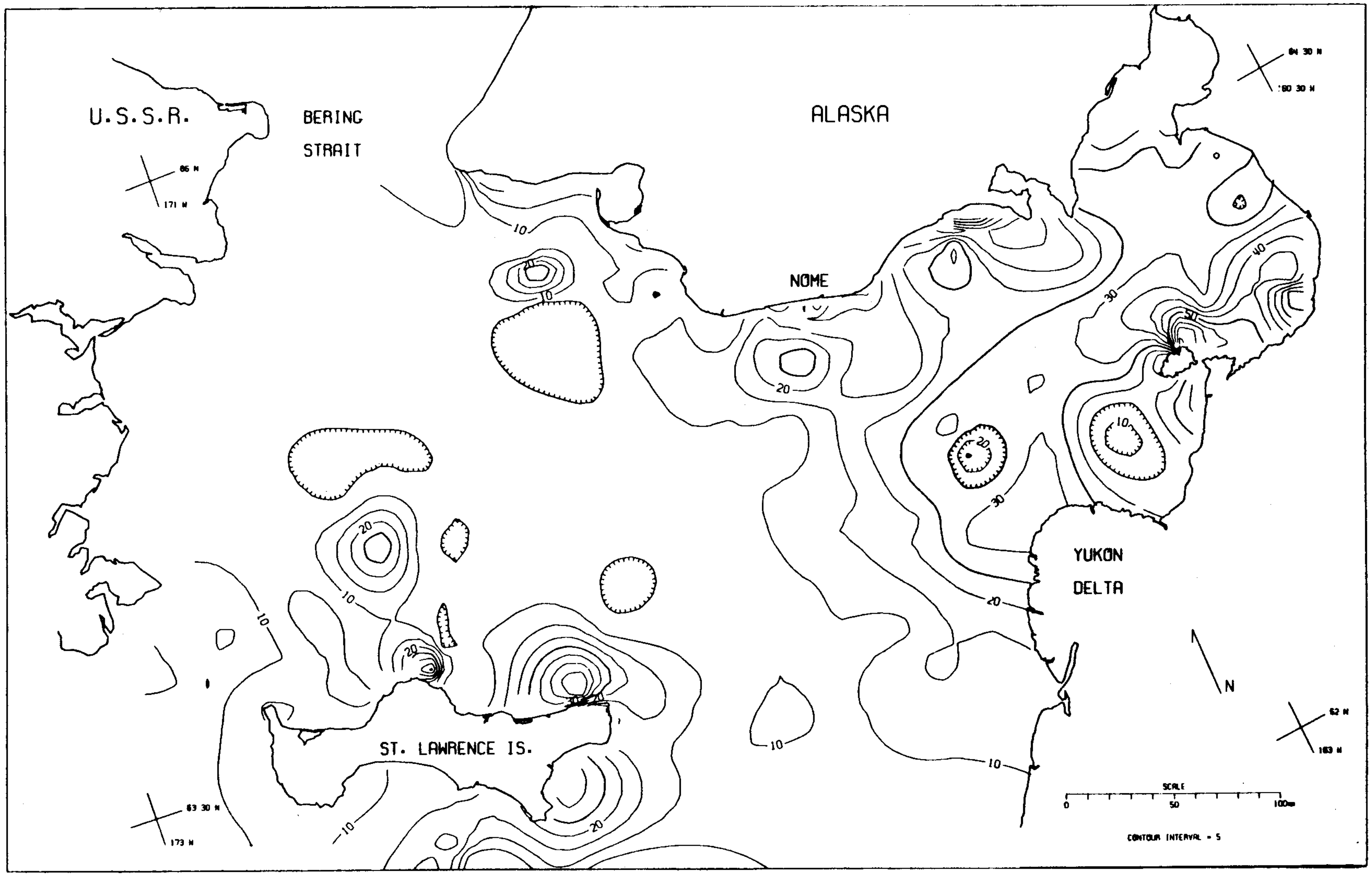

FIG 17 CU PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

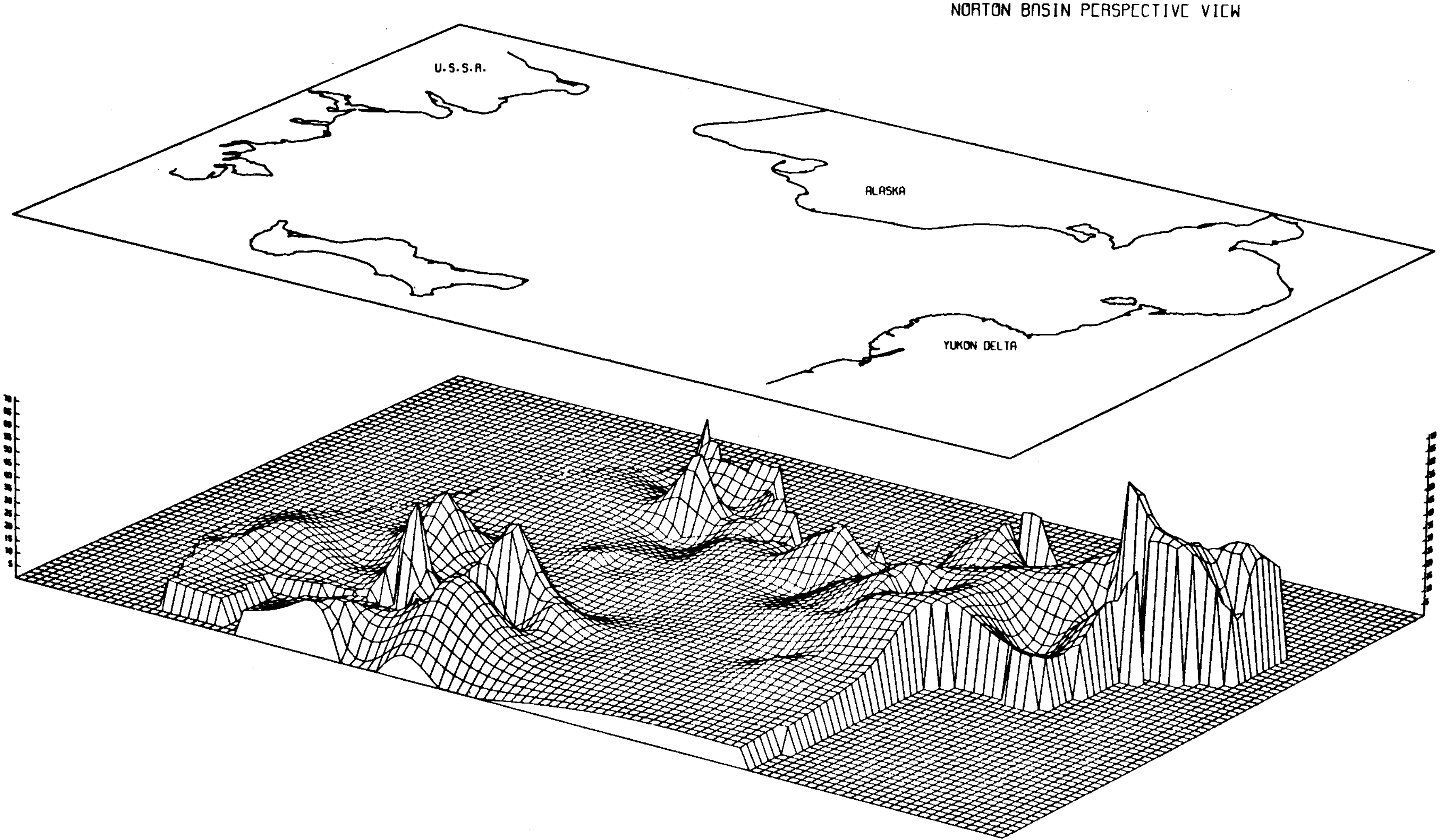

FIG 18 CU PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

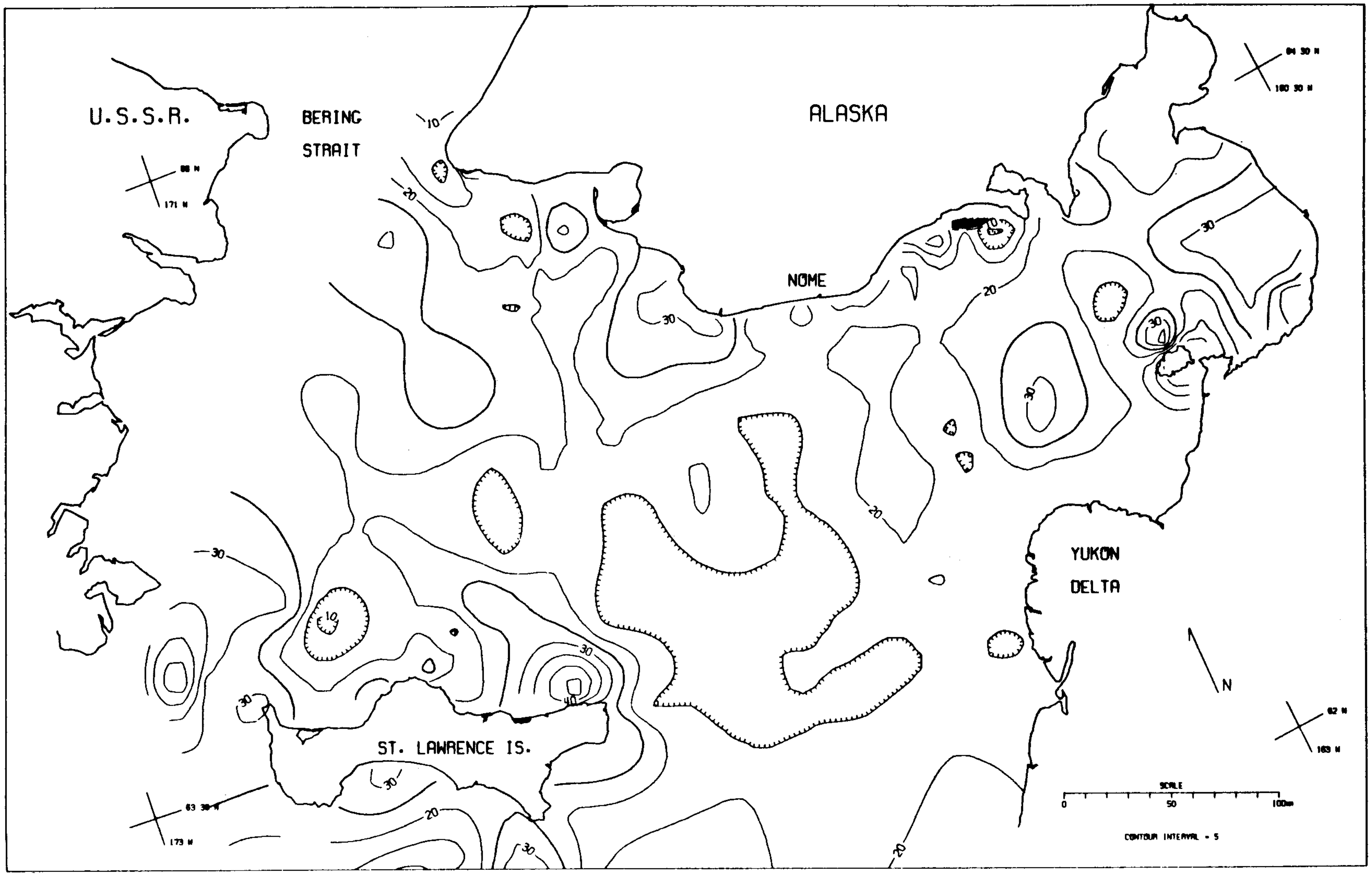

FIG **19** PB PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

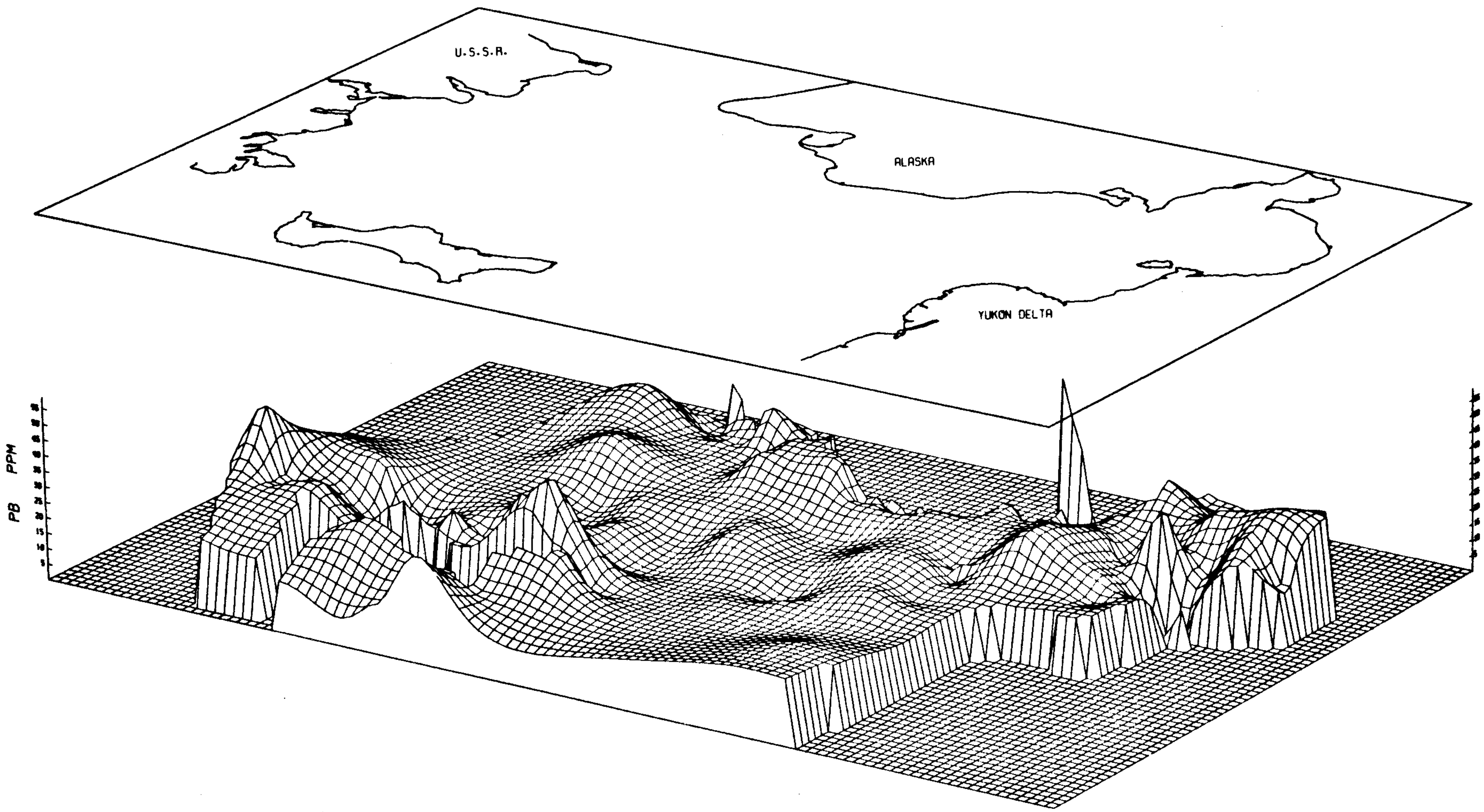

FIG **20** PB PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

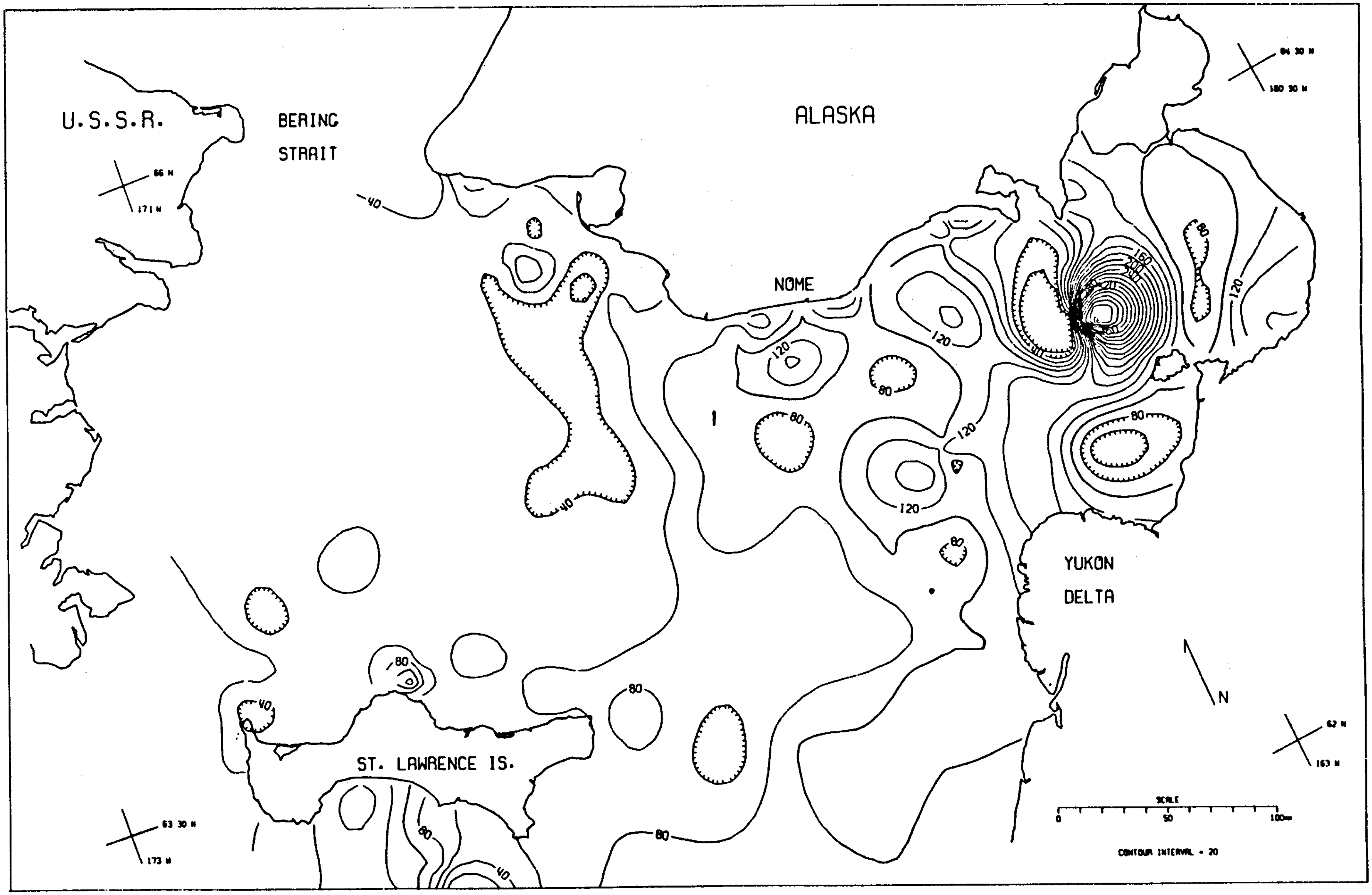

FIG 21 ZN PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

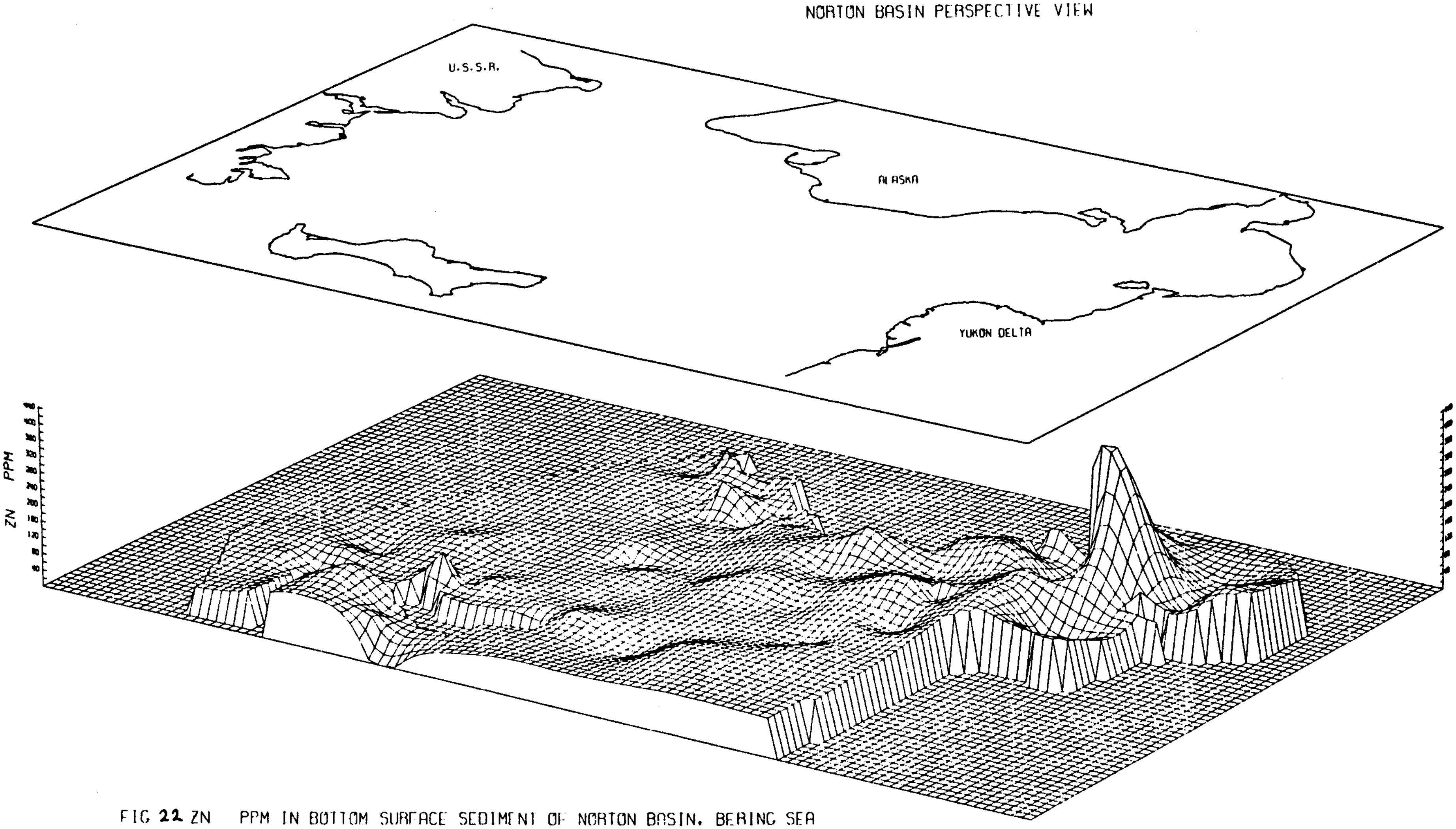

FIG 22 ZN PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

Bluff, Alaska (not completely represented on value surface maps.) Pb and Cu show a continuation of these high values up to 20 km offshore from Bluff. Unlike Cu and Zn, and except for values from the Bluff beach samples, Pb deviates little from the geometric mean throughout Norton Basin; although fairly high values can be seen adjacent to Stuart Island and the eastern tip of St. Lawrence Island. Cu is also concentrated near Stuart Island and the eastern tip of St. Lawrence Island. In addition, high concentrations are found off the southern coast of eastern St. Lawrence Island and off the north-central projection of the island as well as off Nome and in an area around King Island. High Zn concentrations occur off south-central and north-central St. Lawrence Island. Concentrations of Zn are also relatively high concentrations off Nome, in a sample taken 30 km south of Cape Prince of Wales, and along the eastern edge of Norton Sound, but are greatest (except for the Bluff beach samples) in the central part of eastern Norton Sound. This last Zn anomaly is rather puzzling and does not appear to be related to dispersal of Yukon sediment or to the nearshore high values that seem to be caused by concentration in sediment derived from immediately adjacent land areas.

In summary, the toxic elements discussed here apparently have their highest values in relatively localized beach areas close to known terrestrial sources or are clearly derived from the sediments eroding from nearshore areas close to probable higher concentrations of these elements. Other elevated concentrations offshore are probably related to general sediment dispersal within the region and the possible placer concentration of those elements aggregated in heavy minerals. An example of high values over a broad area which are probably related to sediment type/source terrains are the regionally high values of Cu and Zn over Norton Sound.

D. Chemical-Environmental Change Indicators

Though the evidence cited below indicates concentrations of Fe, Mn, and Co in Norton Basin sediments are source related, they are singled out here because they are more responsive to changing oxidation/reduction environments than most of the other elements under discussion. Ba is included because of its use as a drilling mud and the resulting potential contamination of sediment where it is used.

The value-surface maps for Fe, Mn and Co are quite similar (Figs. 23, 24, 25, 26, 27, and 28). The most obvious correlations are the high anomalous values each map shows in the areas of the volcanics of north-central St. Lawrence Island and Stuart Island. Anomalies in these volcanogenic areas have also been found for Cu, Ni, and Cr (other mafic-associated elements) as has already been pointed out. The other obvious correlation is the wide area with high values surrounding the Yukon Delta in particular and Norton Sound in general.

High values surrounding the Yukon Delta, much of Norton Sound, and northward toward the Bering Strait seem to fall mainly within the area defining the prevalence of modern Yukon sediment. The generally high values in this region probably are directly related to Yukon source sediments which are in part derived from the input of mafic volcanic terrain in the river drainage basin. Anomalous values of Fe, Mn or Co resulting from concentrated precipitates of these elements are not readily apparent. This could only be determined by taking a closer look at the exact mineral species containing Fe and Mn.

The highest Mn value was detected in a sample from 30 km south of Cape Prince of Wales that has been previously discussed. This sample is considerably removed from land and it is probable that its high Mn values are

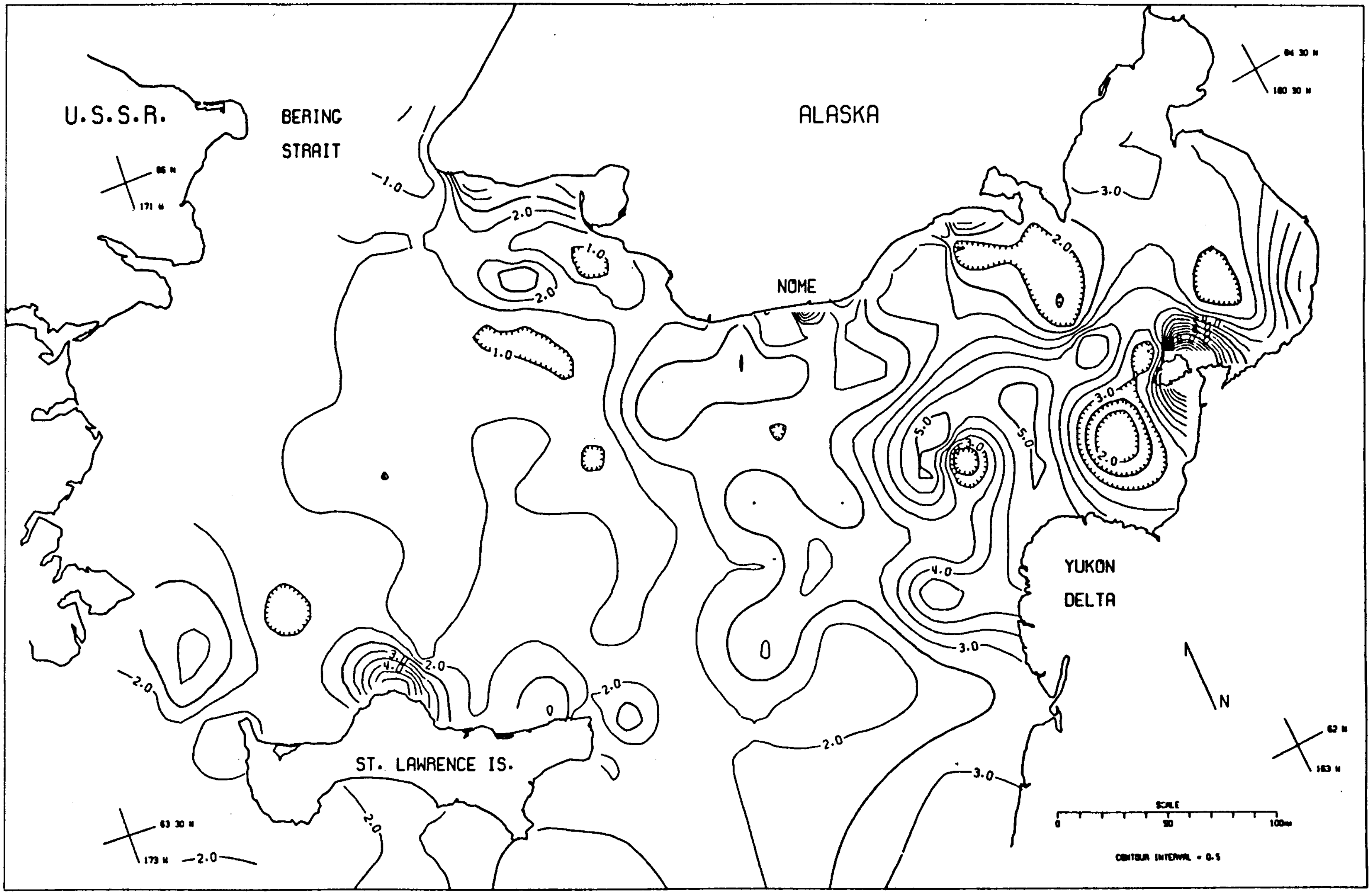

FIG 23 FE % IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

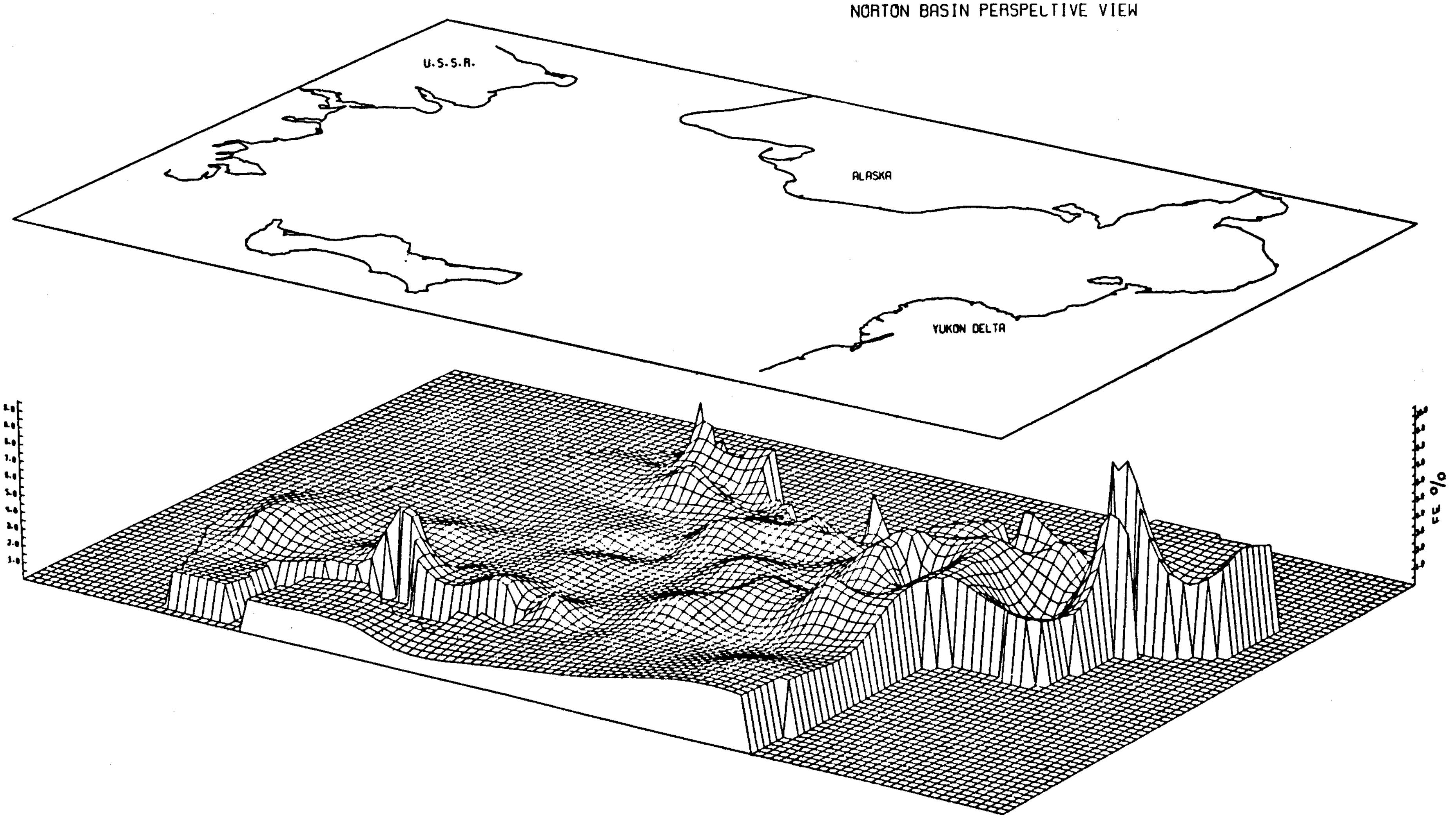

FIG 24 FE %   IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

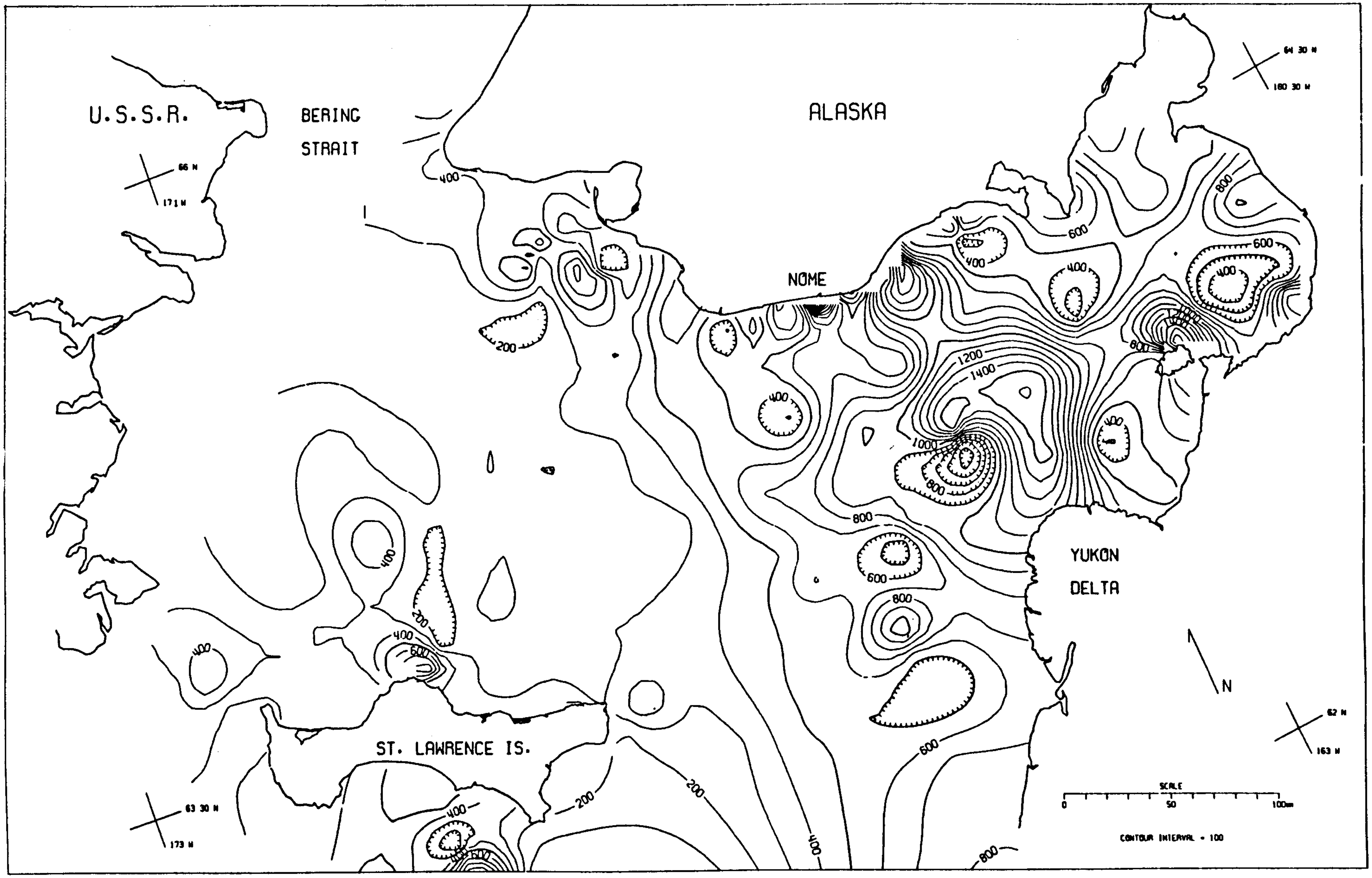

FIG 25 MN PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

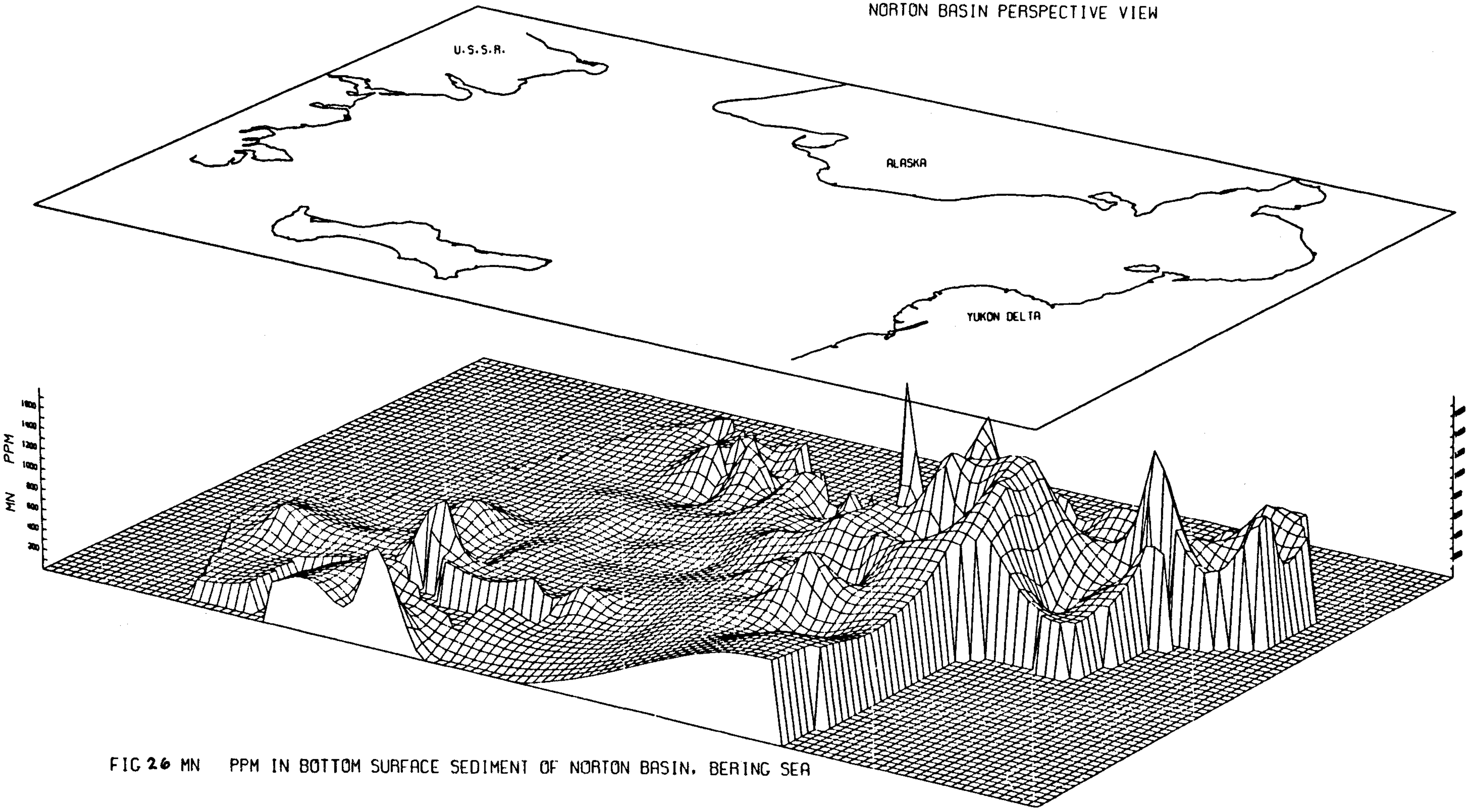

FIG 26 MN PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

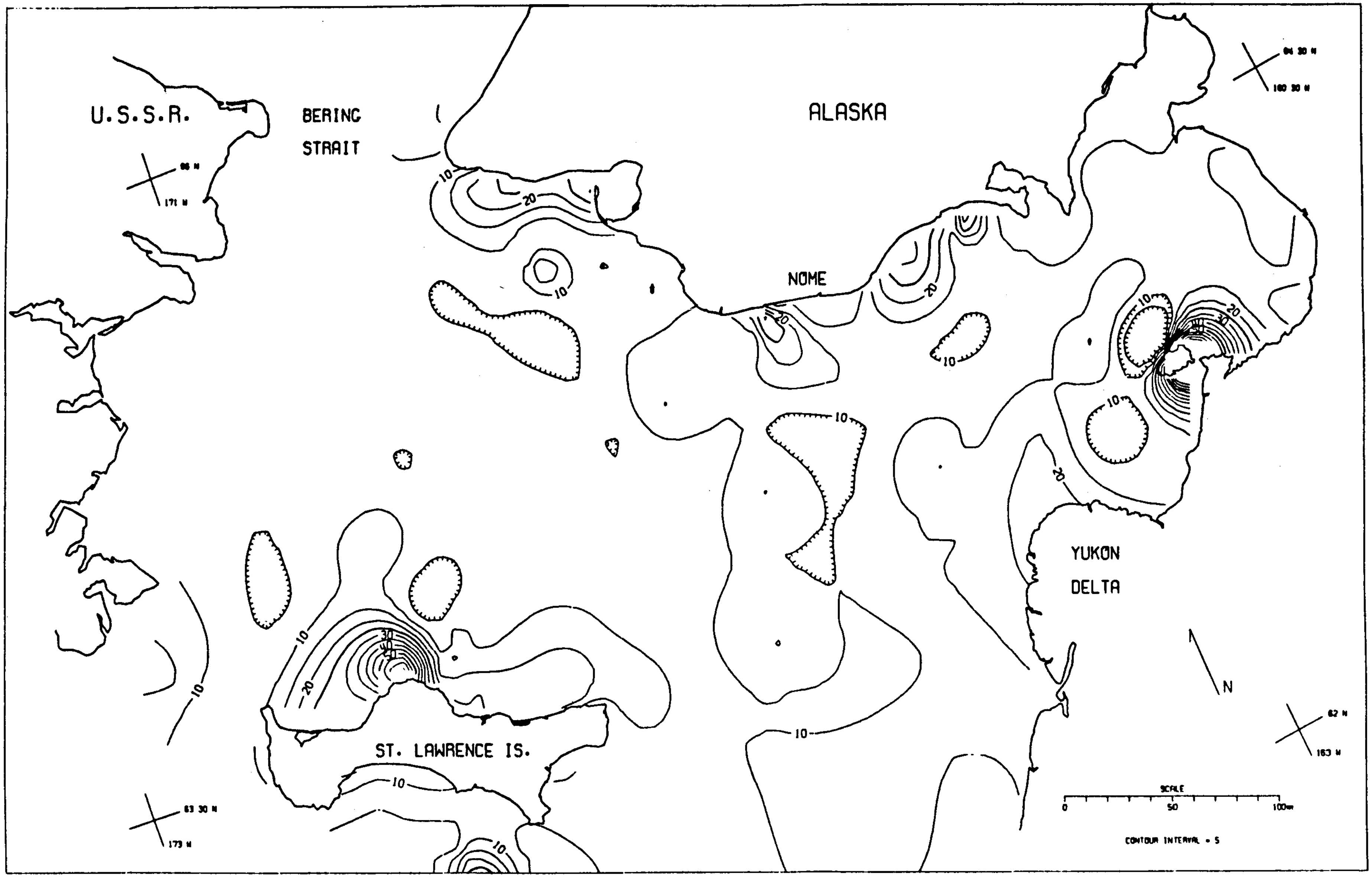

FIG 27 CO PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

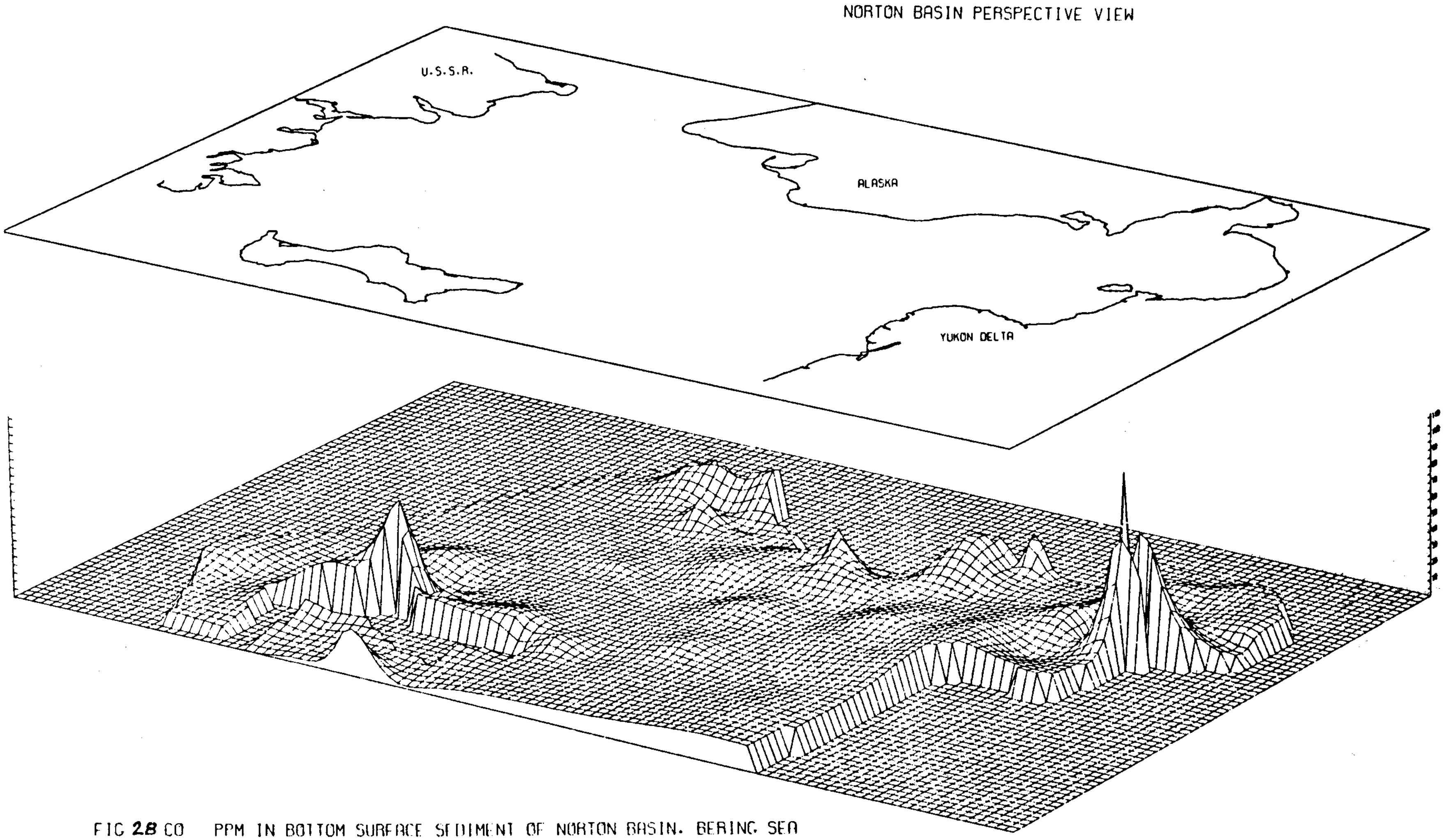

FIG **28** CO PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN. BERING SEA due to mechanical concentration rather than having been directly derived from volcanic terrain.

The value surface maps for Ba show slightly anomalous values surrounding the Yukon Delta, in addition to high values near Stuart Island and at various locations along the southern coast of Seward Peninsula (Figs. 29 and 30). The highest anomalies are just off the southern edge of St. Lawrence Island and in the middle of Anadyr Strait. The general increase in concentrations of a number of elements in this area surrounding the delta has already been noted and seems to be related to the Yukon sediment source and dispersal pattern. The anomalies near Stuart Island and the southern coast of Seward Peninsula appear as lobes coming off the land and may be correlated with sediment sources from igneous rocks in those areas. The origin of the high values close to St. Lawrence Island are more obscure. None of the elements that correlate with Ba have outstanding anomalies in the Anadyr Strait and only Sr has high values off the southern edge of St. Lawrence Island. The value of 1500 ppm in Anadyr Strait is equal to .15% and could reflect a source for Ba mineralization on the point of the Chukotka Peninsula.

E. Major Elements

All samples used in this study were analyzed for all of the major elements Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, and P. Values for Si, however, were higher than the upper limit of detection (10%) in every sample analyzed and are not reported here.

Value-surface maps for major elements show some of the general element distribution patterns already discussed. Mn, Fe, and Ti have higher values surrounding the Yukon Delta and in Norton Sound relative to the Chirikov Basin (Figs. 23, 24, 25, 26, 31, and 32). Ca, Mg, Na, K, and Al show a similar trend to some degree (Figs. 33, 34, 35, 36, 37, 38, 39, 40, 41, and 42). Each

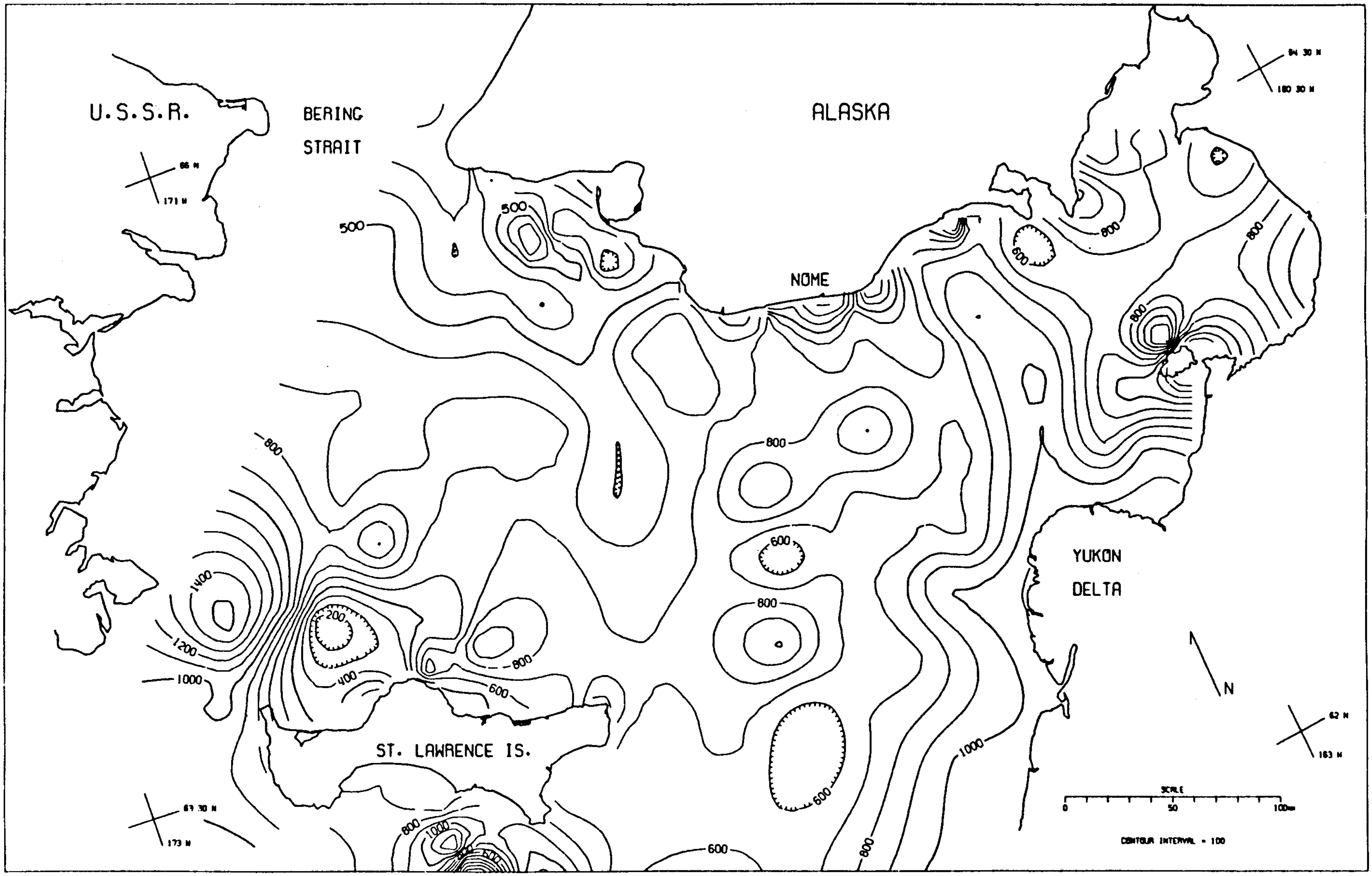

FIG 29 BA PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

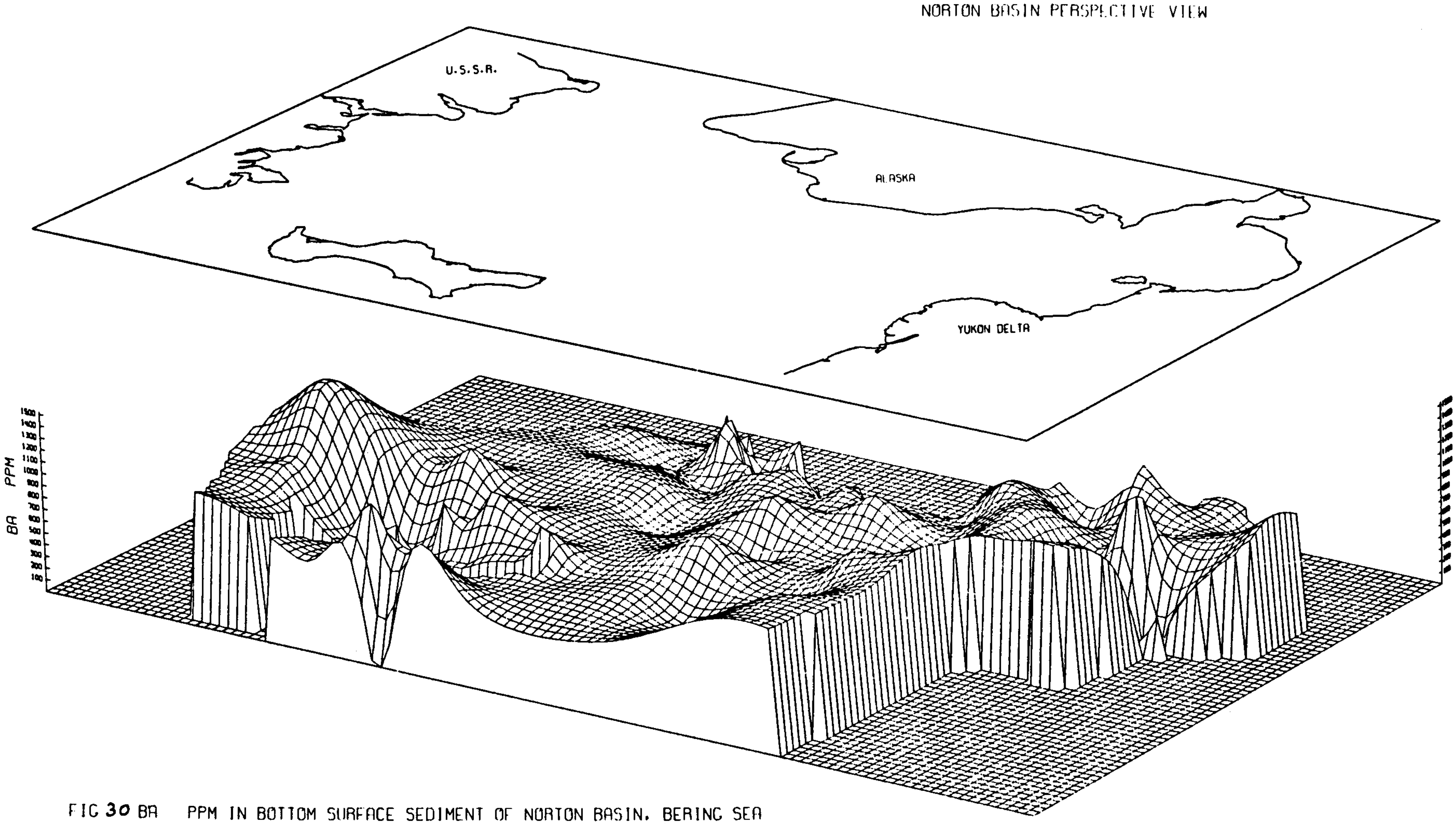

FIG 30 BA PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

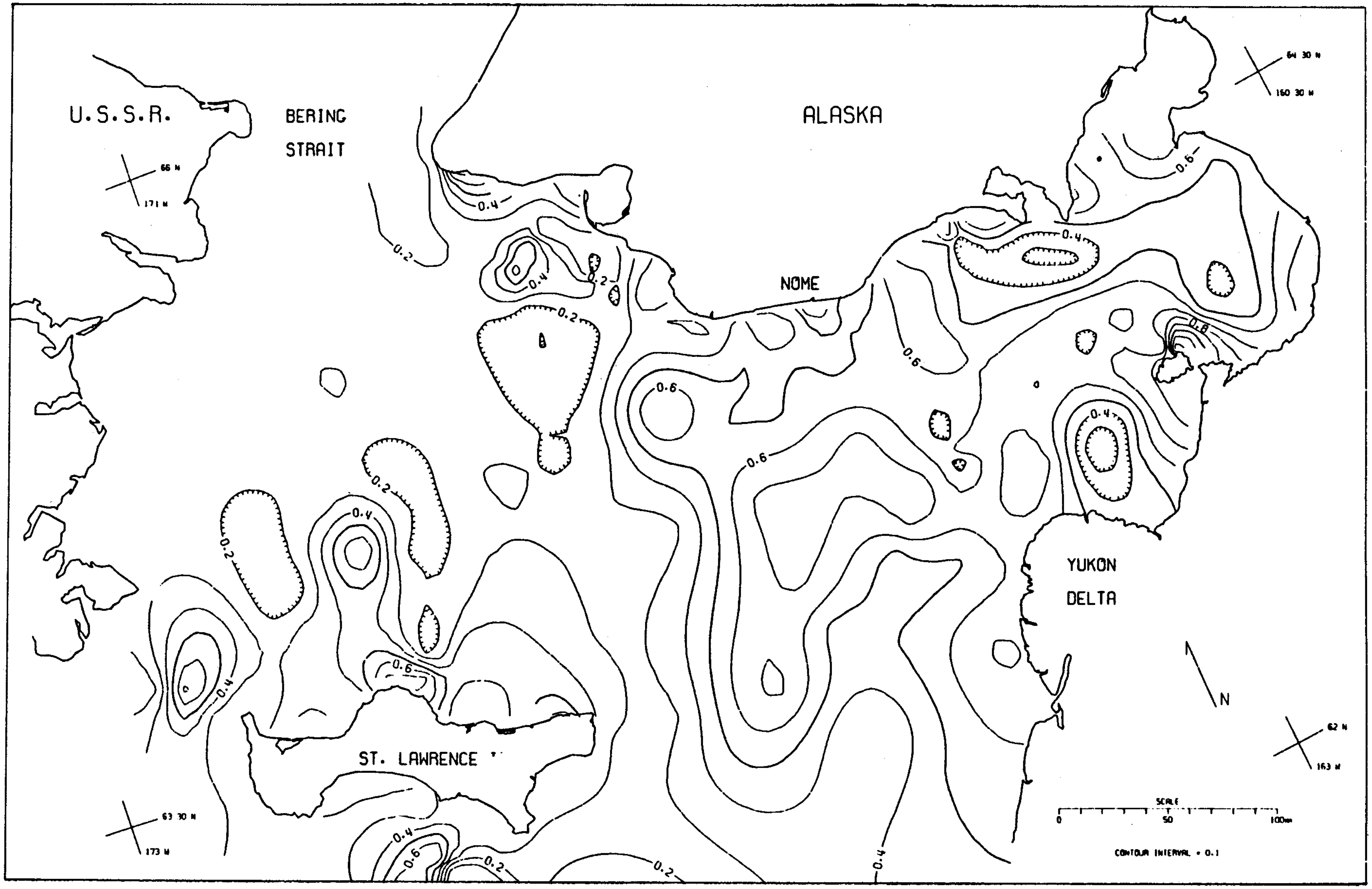

FIG 31 TI % IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

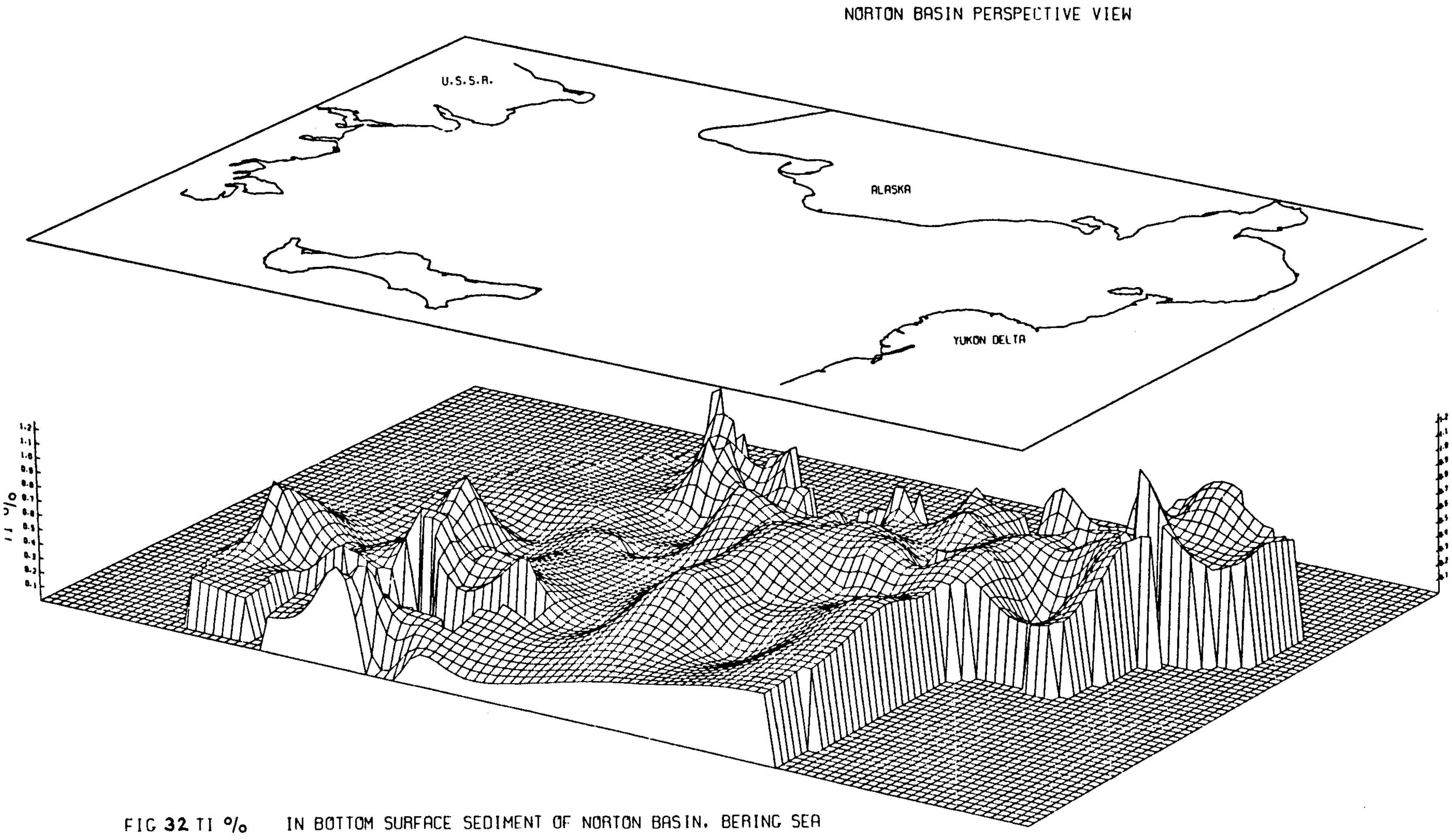

FIG 32 TI % IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

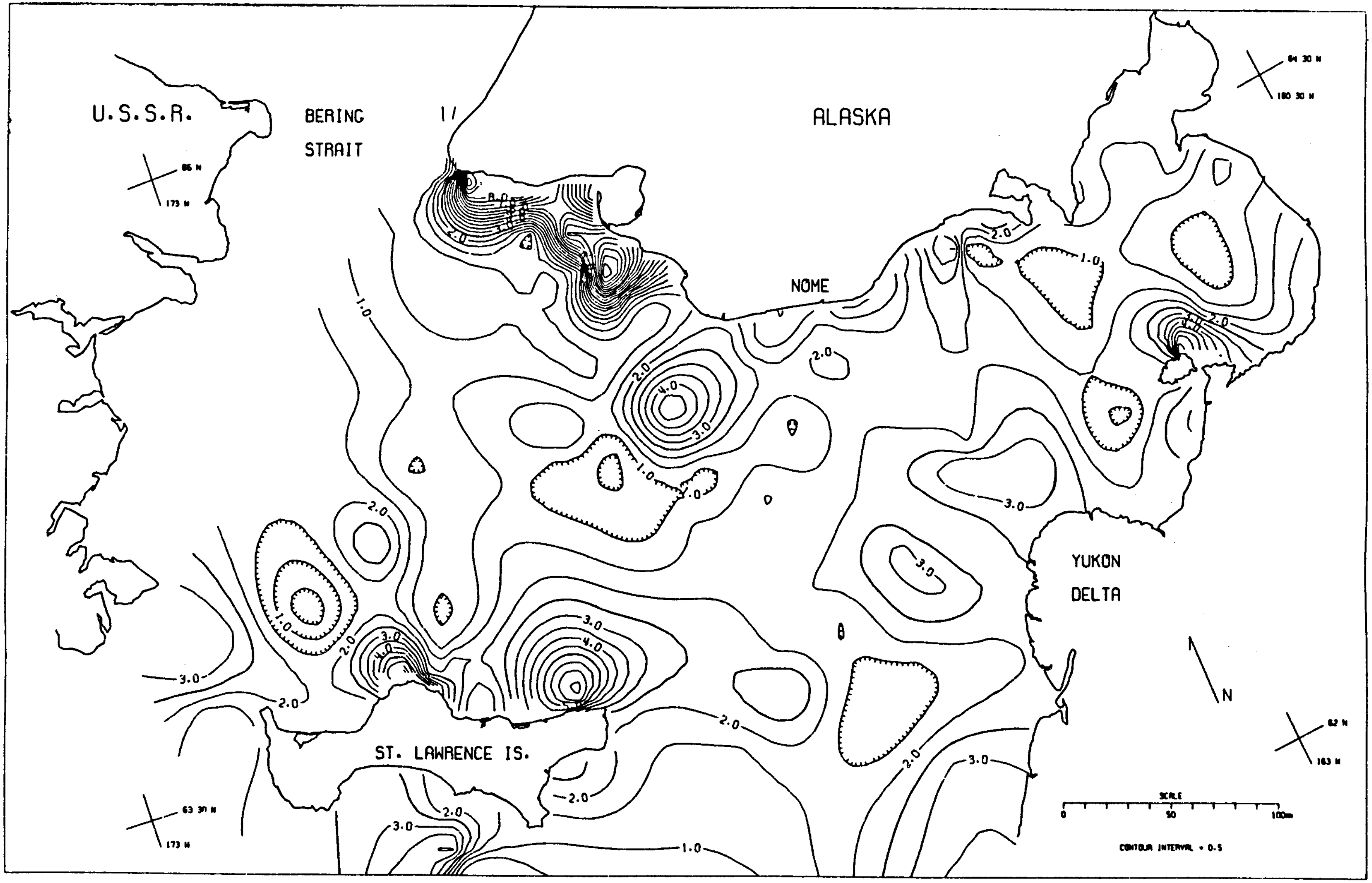

FIG 33 CA IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN. BERING SEA

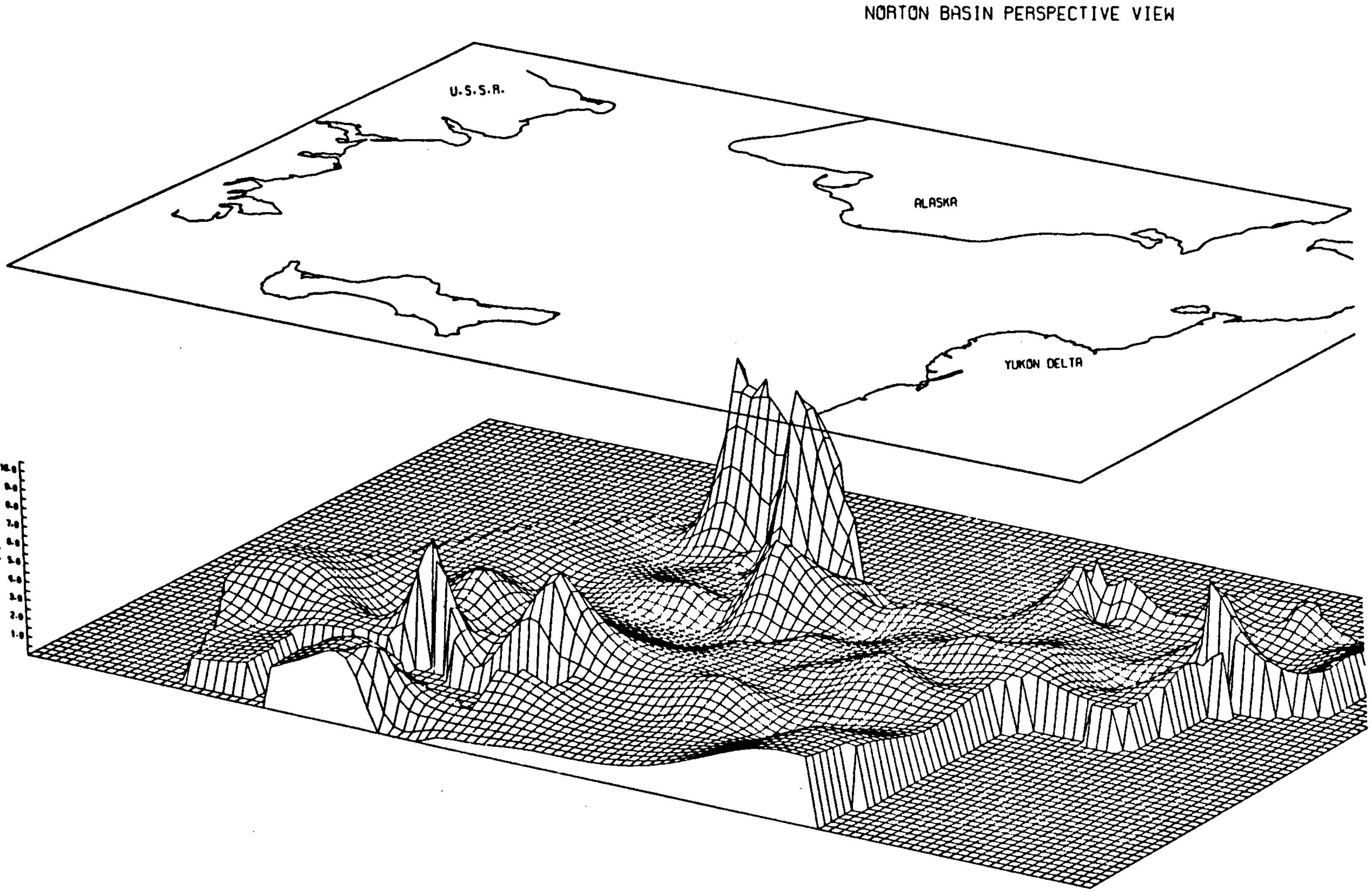

FIG 34 CA %   IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

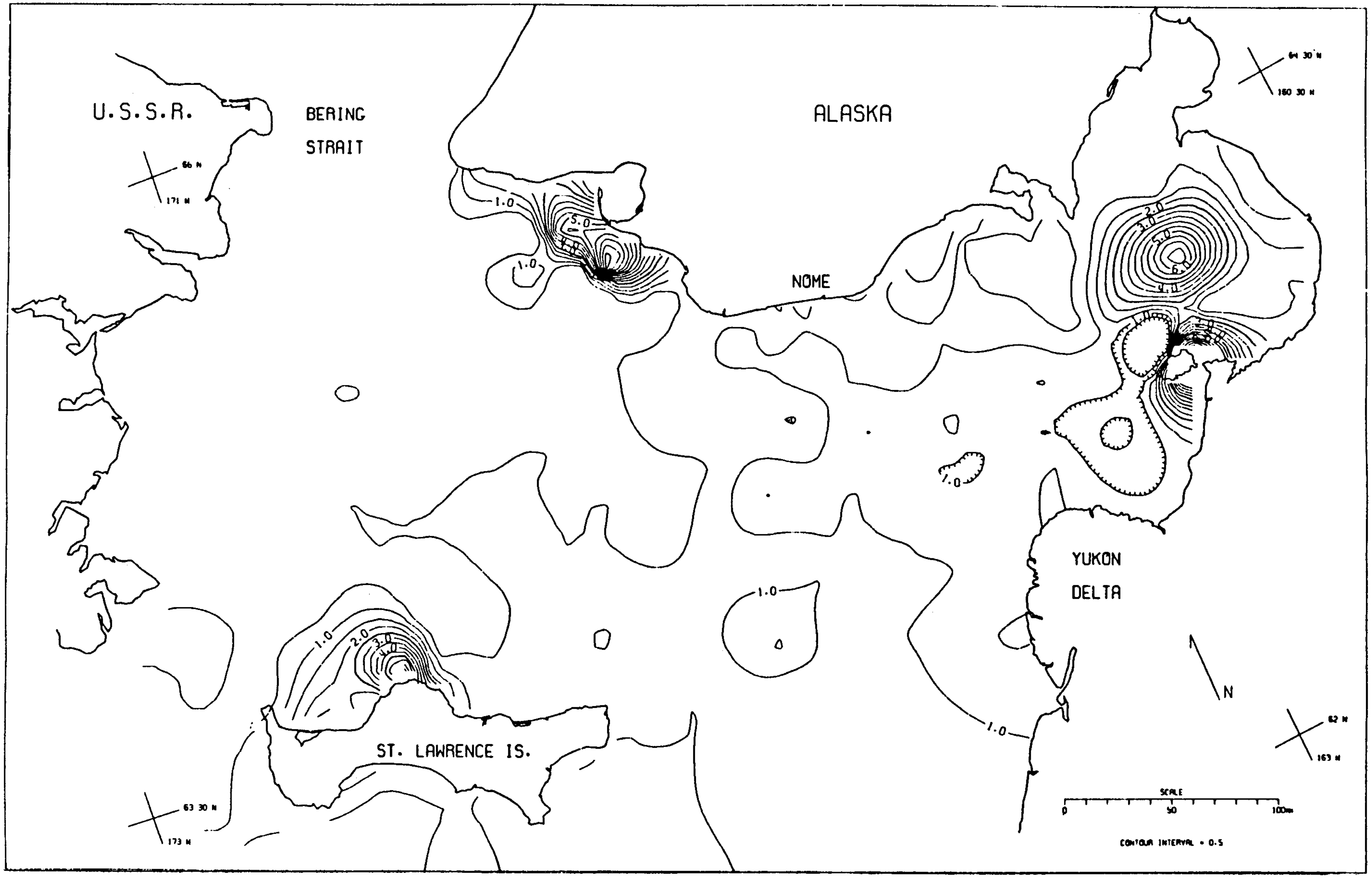

FIG 35 MG % IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

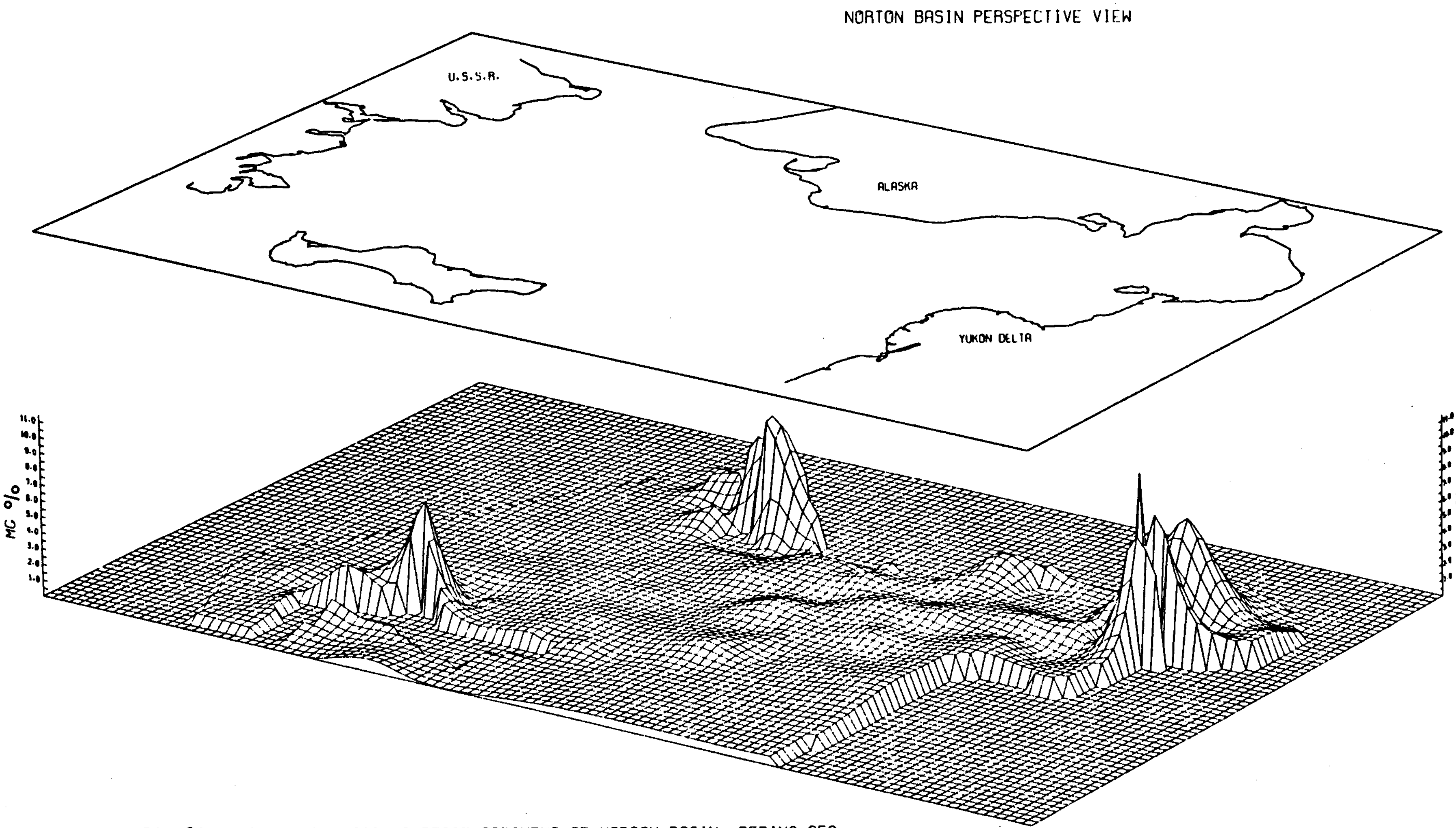

FIG 36 MC % IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN. BERING SEA

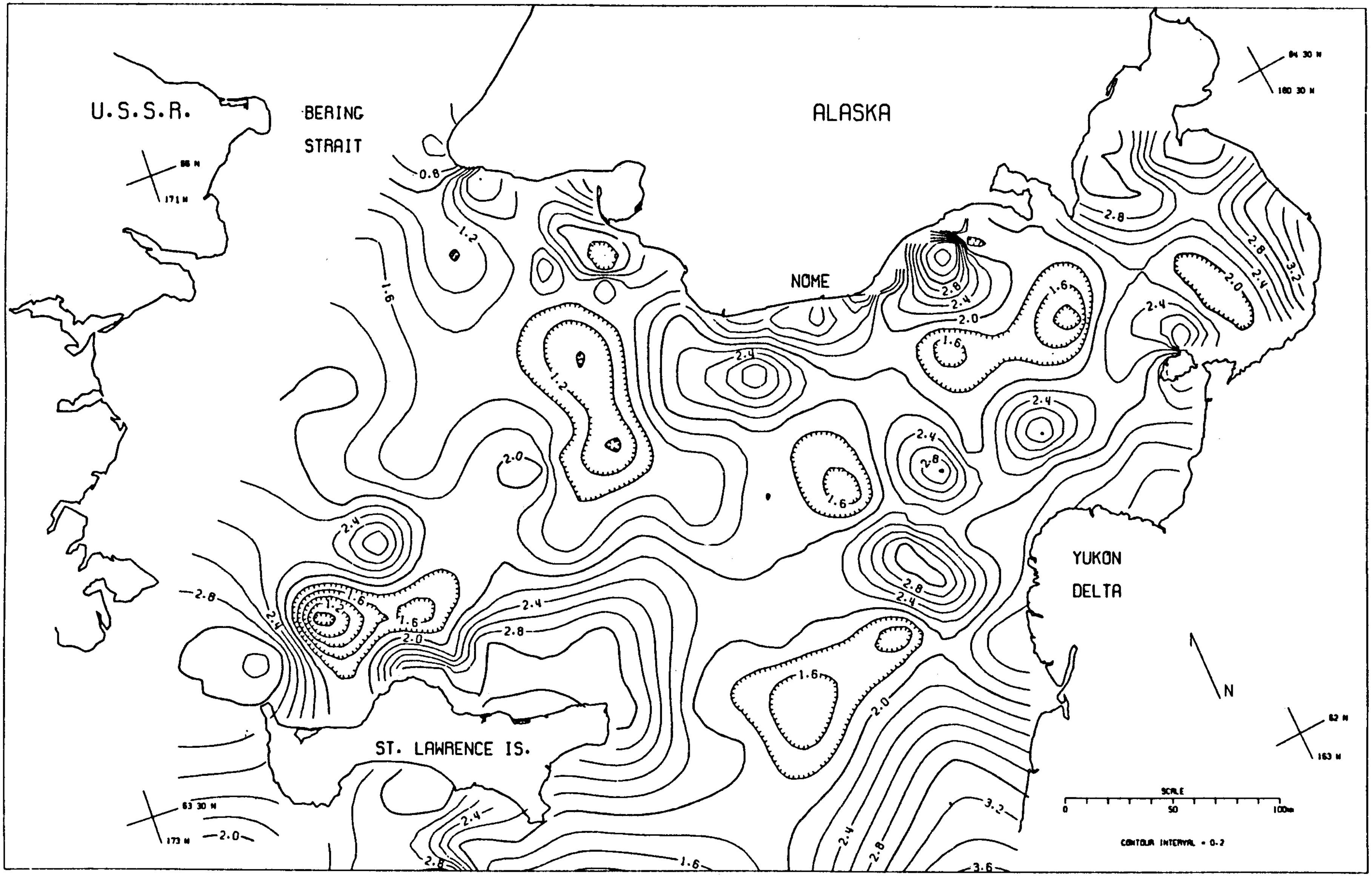

FIG 37 NA % IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

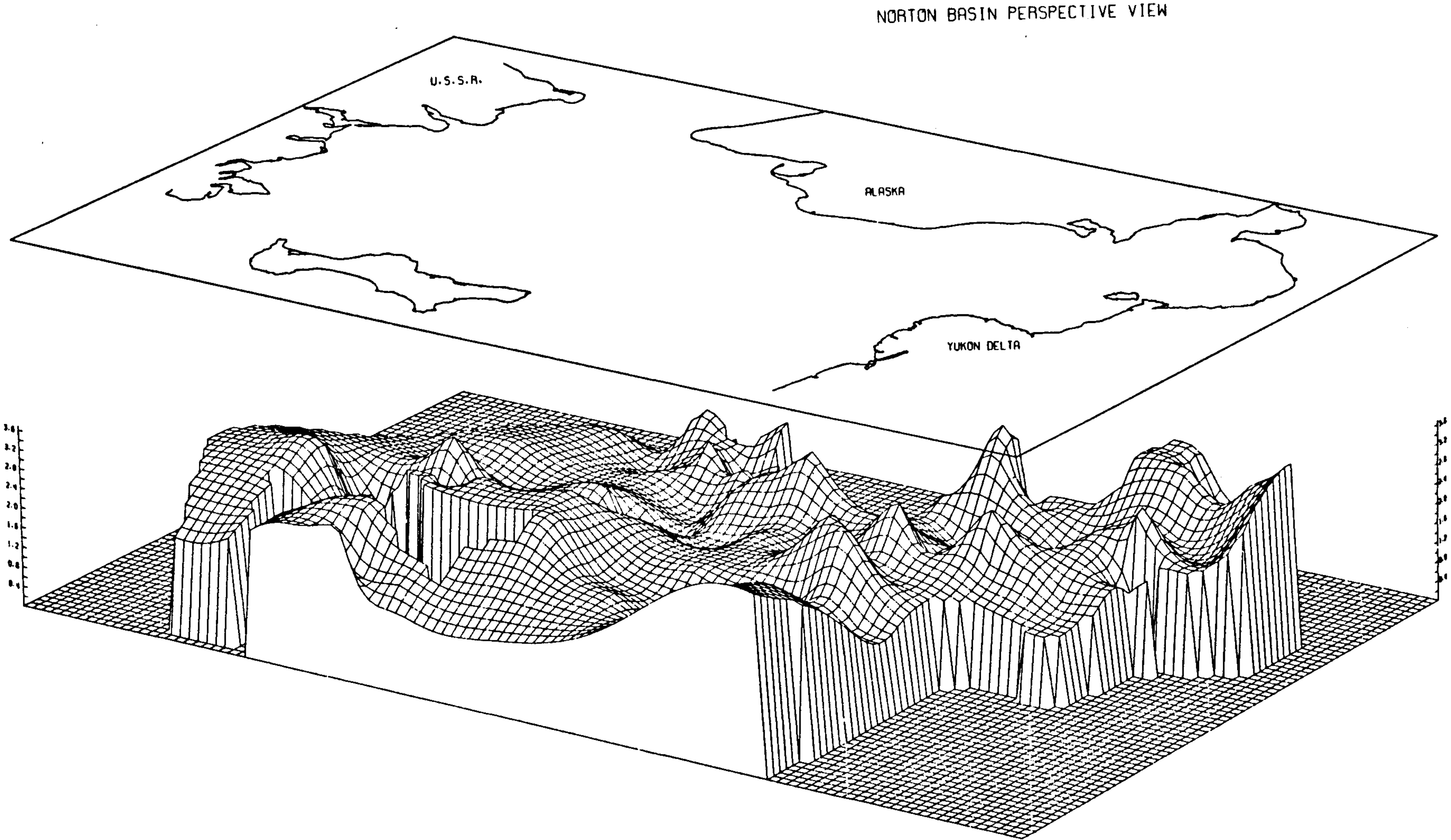

FIG 3B NA % IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

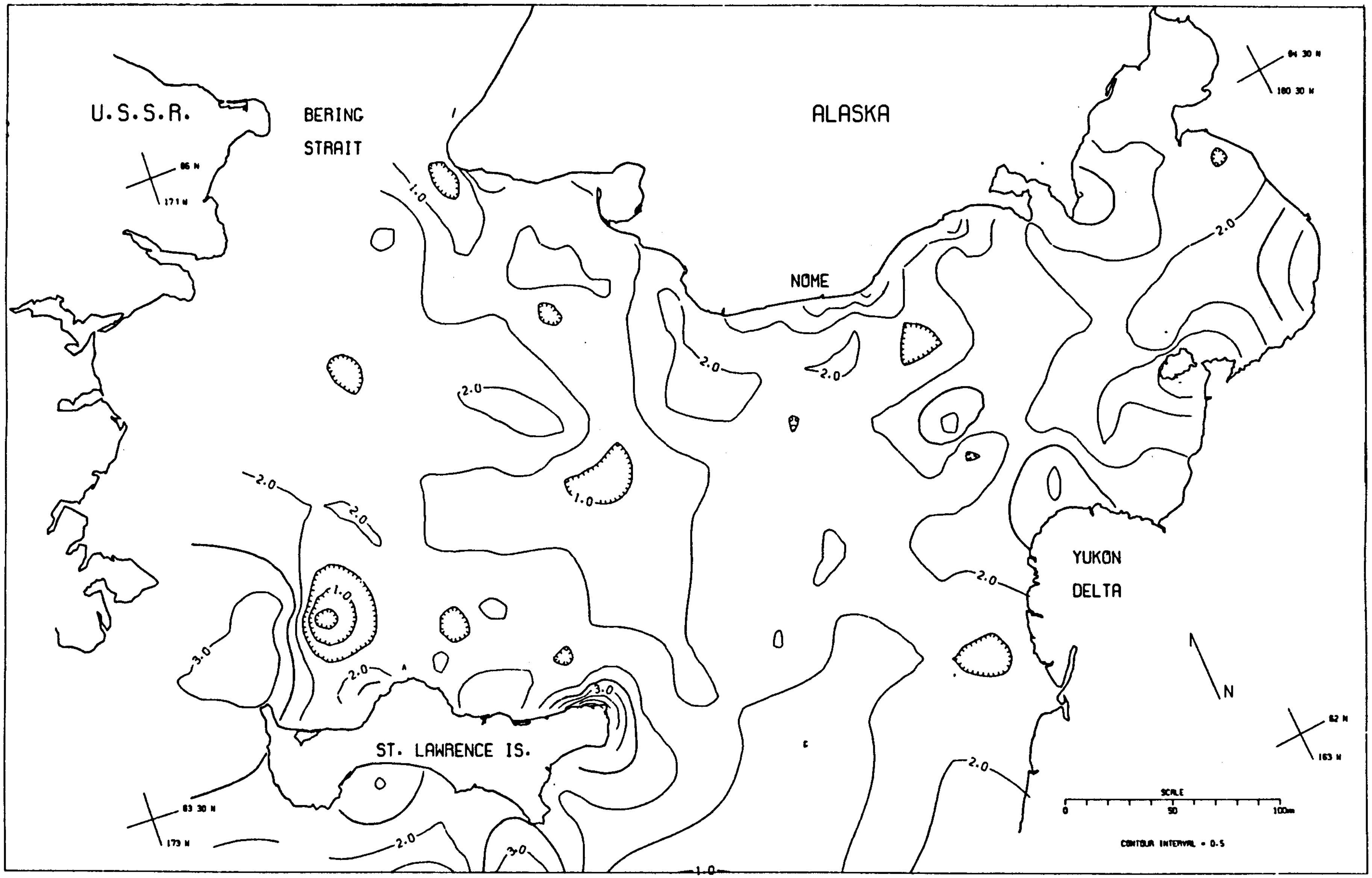

FIG 39 K % IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

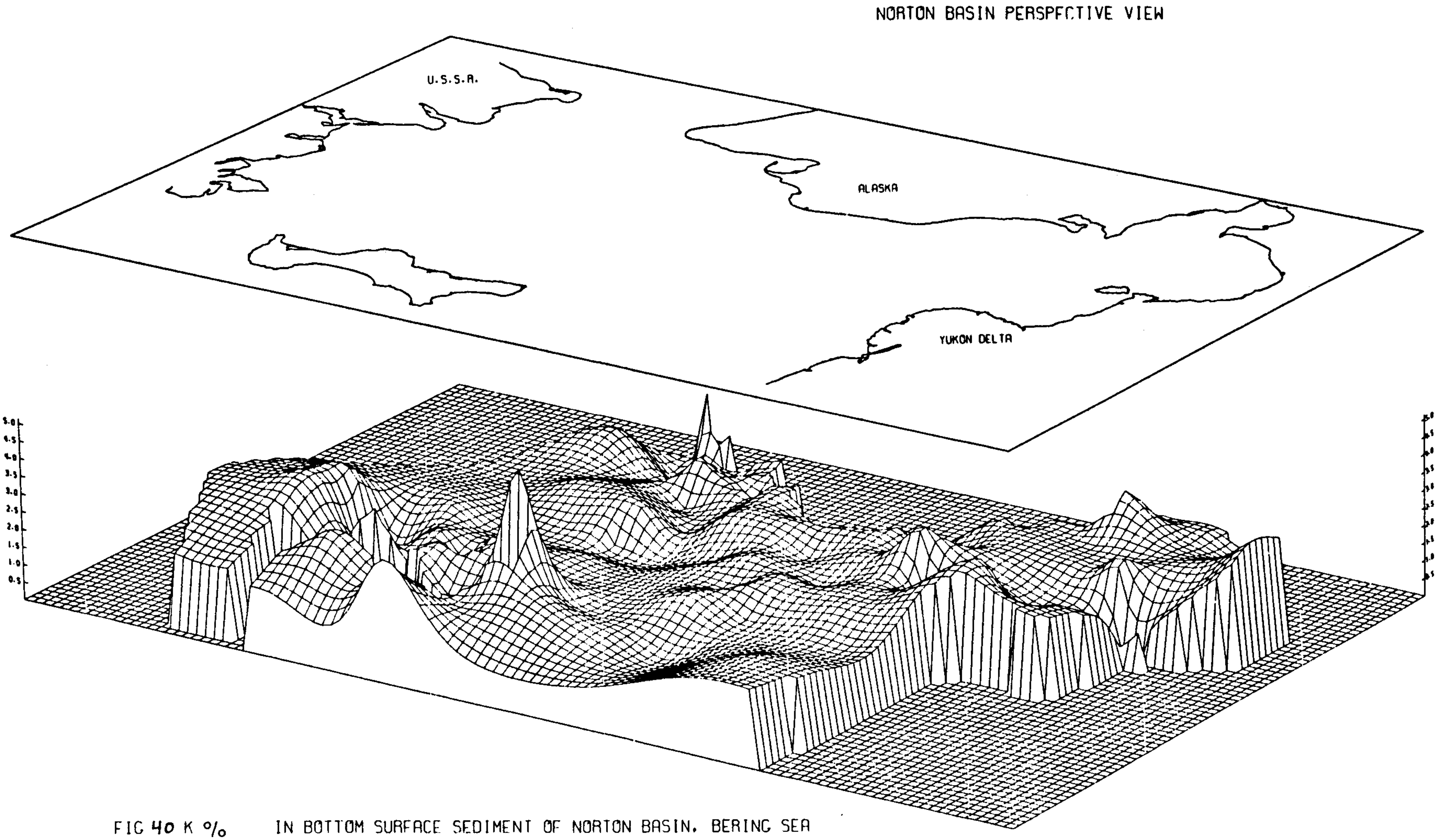

FIG 40 K % IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

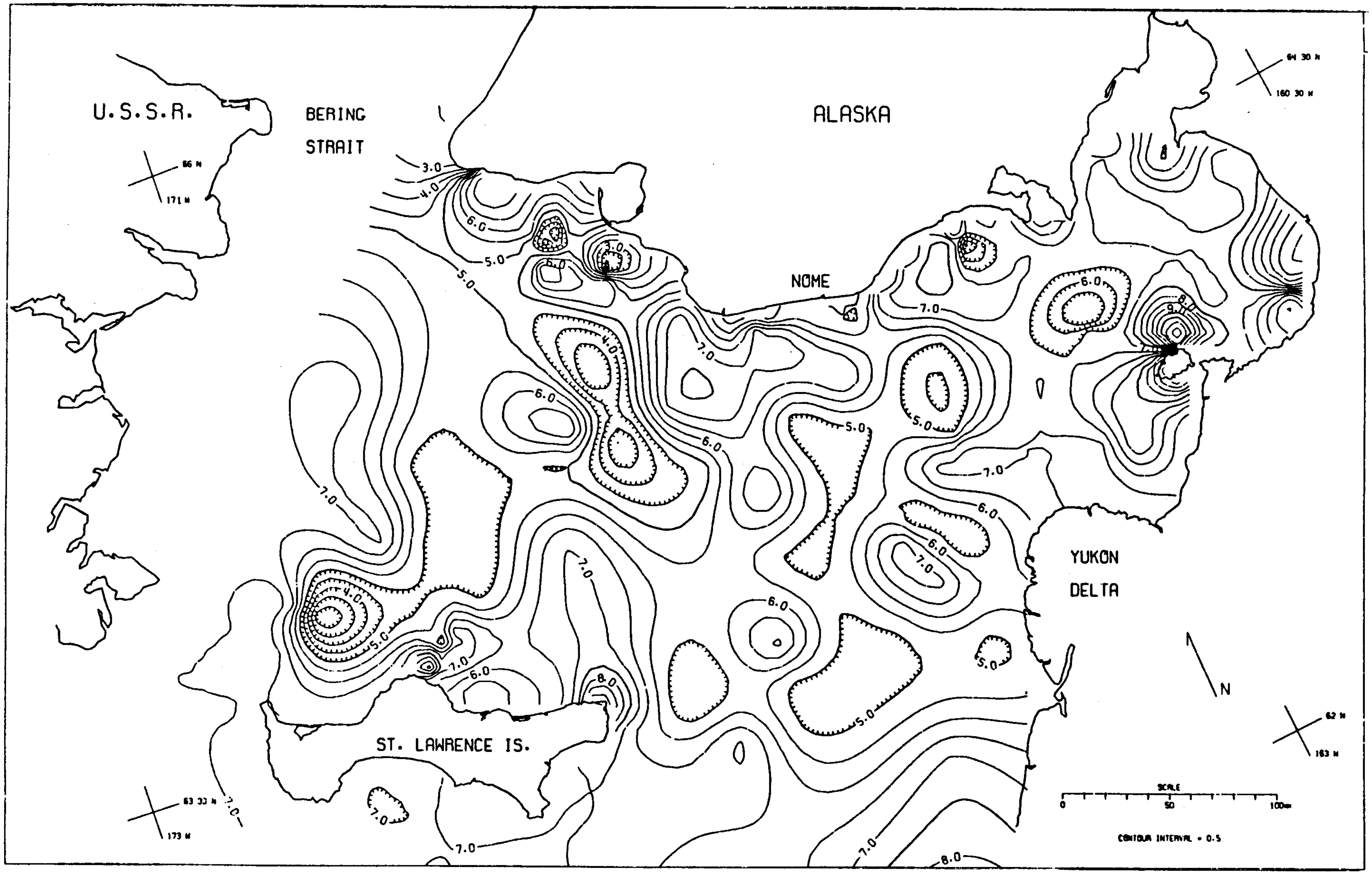

FIG 41 AL % IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

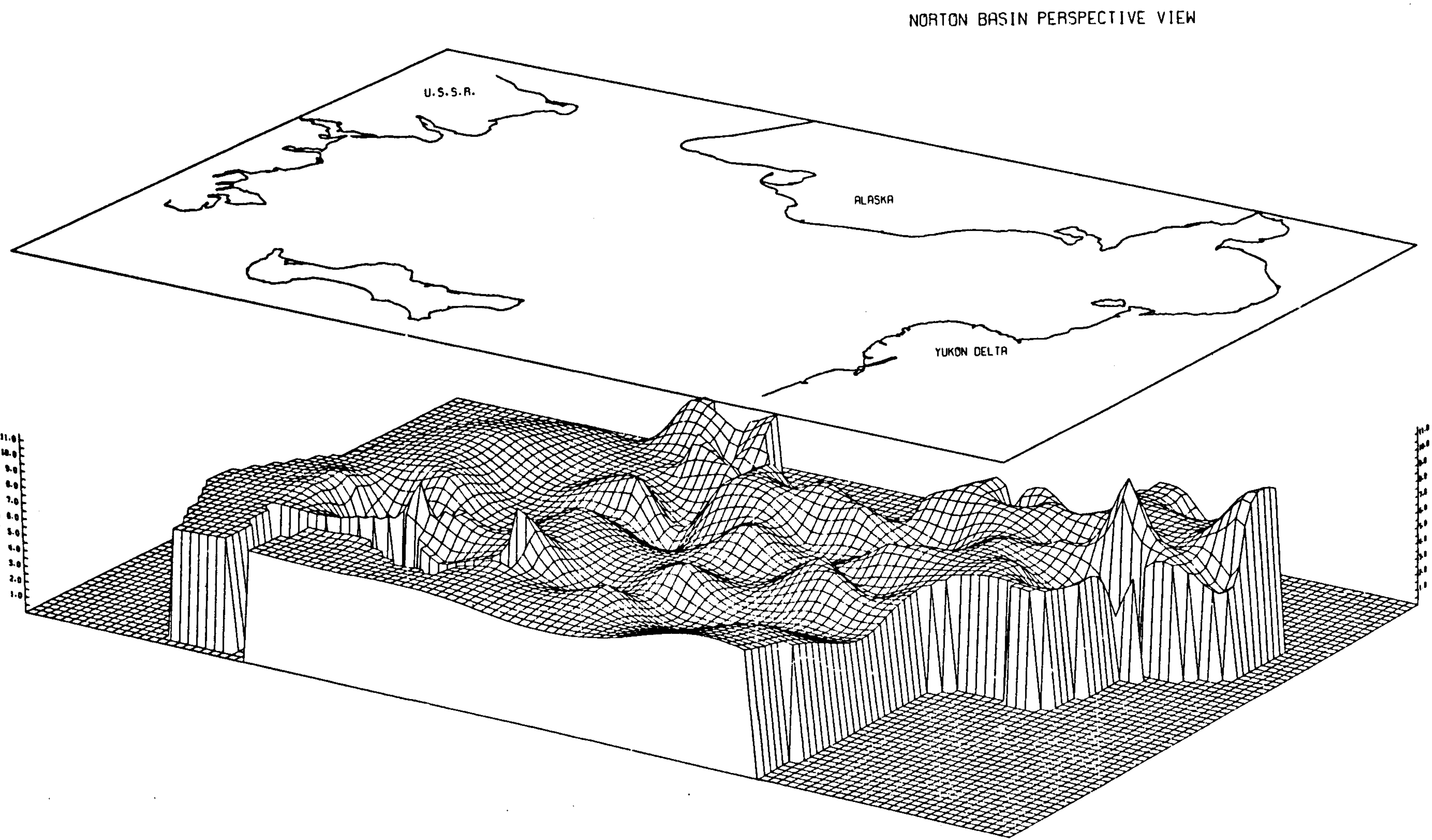

FIG 42 AL% IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

element also has anomalously high values shown as lobes that appear to be coming from nearby land sources.

Areas with higher Ti concentrations generally correspond to areas with high concentrations of Mn and Fe which have already been shown to be associated with the volcanics of Stuart Island and St. Lawrence Island. This is expected because Ti is relatively high in basaltic rock types. The highest Ti value is from the sample previously discussed that comes from a possible placer 30 km south of Cape Prince of Wales.

Concentrations of Ca and Mg are also high near the Stuart Island and St. Lawrence volcanics, but they are highest offshore from the southern coast of Cape Prince of Wales and south of Port Clarence. High concentrations of Ca and Mg in these last areas probably are related to the limestone formations found on Cape Prince of Wales and in outcrops reported on the sea floor south of Port Clarence (Nelson et al. in preparation,; Nelson and Hopkins, 1972). Sr anomalies, normally associated with limestone, exist in the same areas.

Value-surface maps for Na, K, and Al are more varied than maps of the other major elements. They consist of alternating high and low values and show only slight regional differences. The anomalies that do seem to originate from land sources appear broader in areal extent than some of the less common elements already discussed. The sample containing highest concentrations of K is off of the NE Cape of St. Lawrence Island and is probably derived from granitic bodies that are found there. Samples with highest concentrations of Al are from the areas of Stuart Island and eastern Norton Sound and are probably derived from basalts.

P (phosphorus) was detected in only 54 samples, and was not used in the correlation analysis. The lower limit of detection is .10% which is somewhat higher than concentrations found in average shales and sandstones (Mason, 1966). Elevated concentratios of P are found in the eastern portion of Norton Sound, in a few patches surrounding the Yukon Delta and in a swath running through eastern Anadyr Strait and hooking to north of St. Lawrence Island. The highest concentration of P occurs in a sample from an enclosed basin just off the northeast coast of St. Lawrence Island. This high value may be related in some way to the reducing conditons of the enclosed basin (Mason, 1966).

F. Minor Elements

The minor elements Sr, Sc, La, Ga, Nb, Nd, B, Y, Yb, and Be correlate with other elements. Sr is normally associated with limestone and, as expected, high concentrations of Sr correspond quite closely to the Ca anomalies previously mentioned. However, correlation coefficients are higher between Sr and K, Na, Ba, and Al than between Sr and Ca (see Tables III and IV). The association of Sr with Ba is common. The association of Sr with K, Na, Al, and Ca suggests a possible relationship with feldspar where Sr and Ba substitute for K.

Sc (scandium) correlates most closely with Ti, Fe, V, La and Mn and exhibits the same general distribution as these elements, with higher values grading off the Yukon to lower values in Chirikov Basin (Figs. 47 and 48). The association of Sc with La and Nd is common and the usual mineral containing them is monazite (Figs. 49 and 50). Ga (gallium) also shows some association with La, Sc, and Ti. The highest values of Ga are in Anadyr Straits and the eastern end of Norton Sound (Figs. 51 and 52).

Nb (niobium) exhibits no correlation with any other element. The highest concentrations are in samples from off Cape Darby in Norton Sound and southwest of St. Lawrence Island (Figs. 53 and 54). The anomaly off Cape Darby correlates with the highest Nb anomalies detected in western Alaska

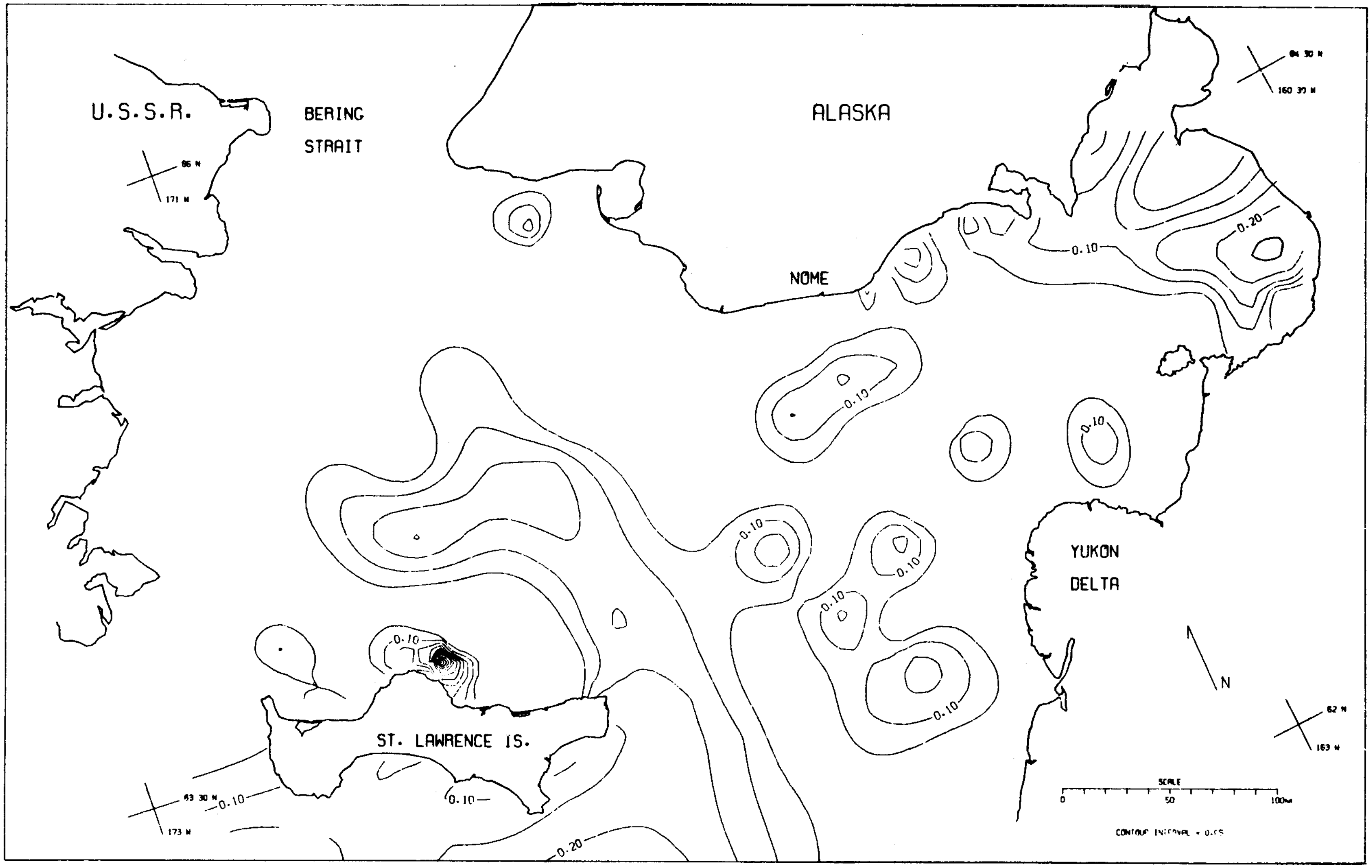

FIG 43 P PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

NORTON BASIN PERSPECTIVE VIEW

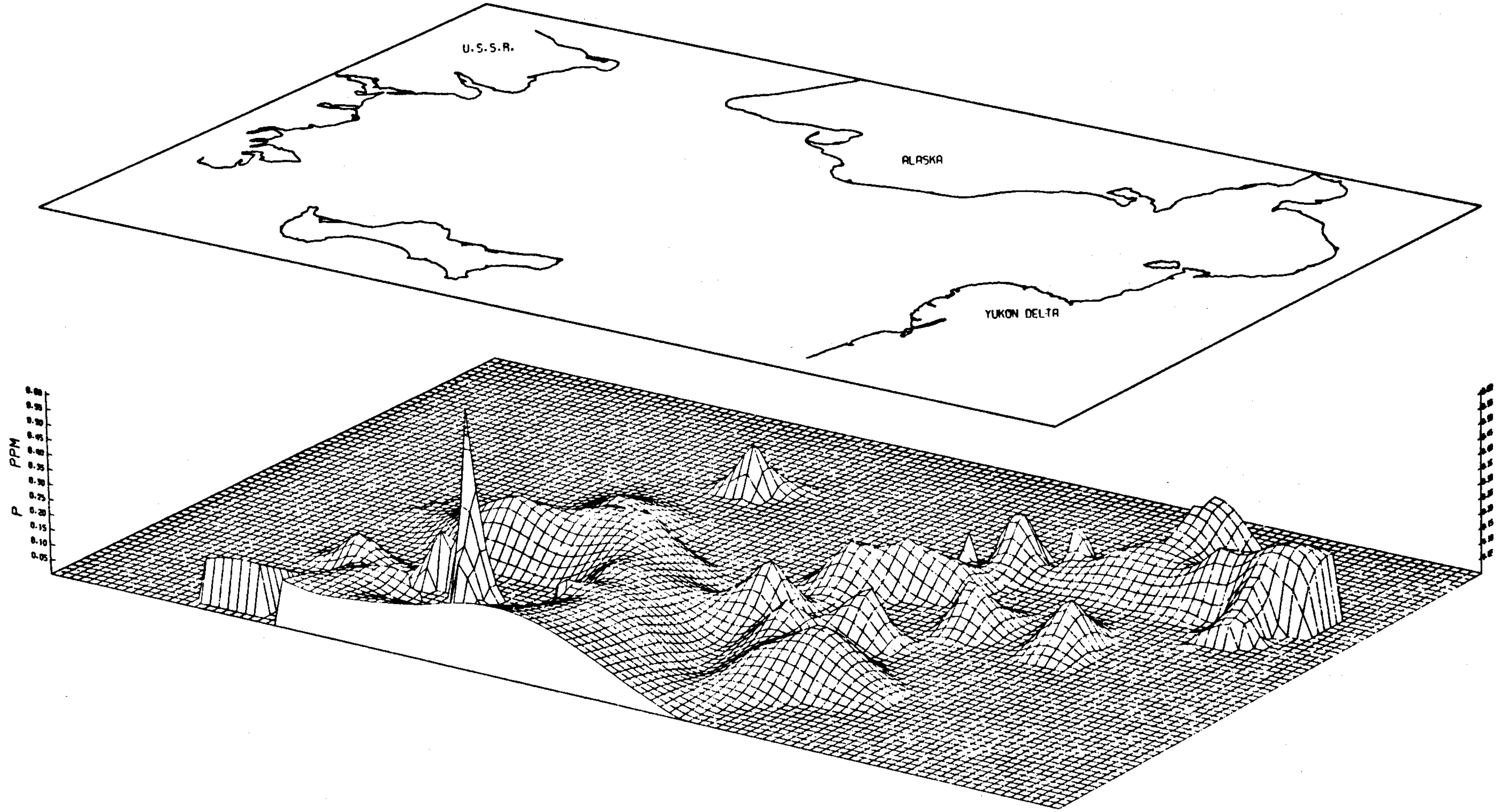

FIG 44 P PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN. BERING SEA

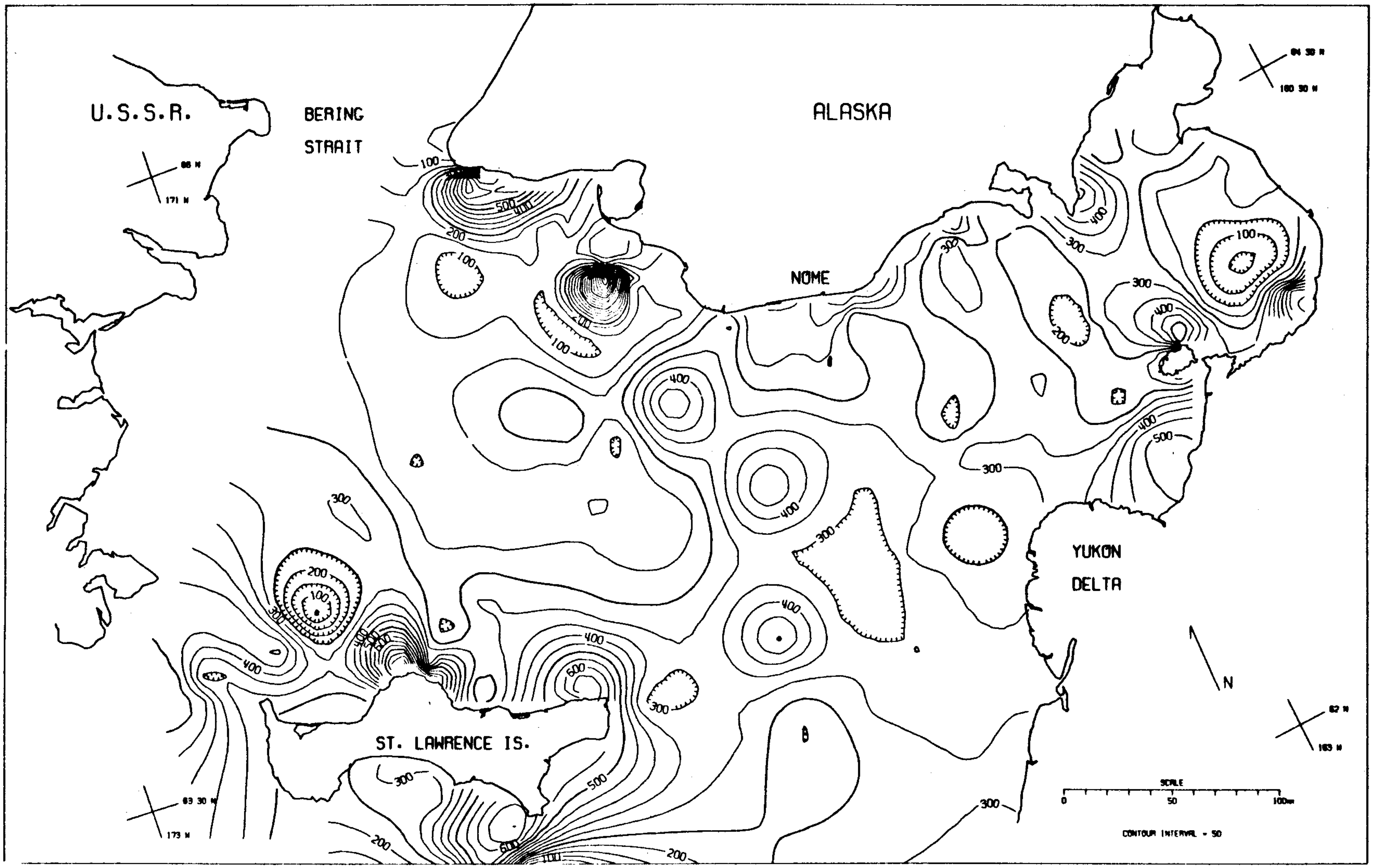

FIG 45 SR PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

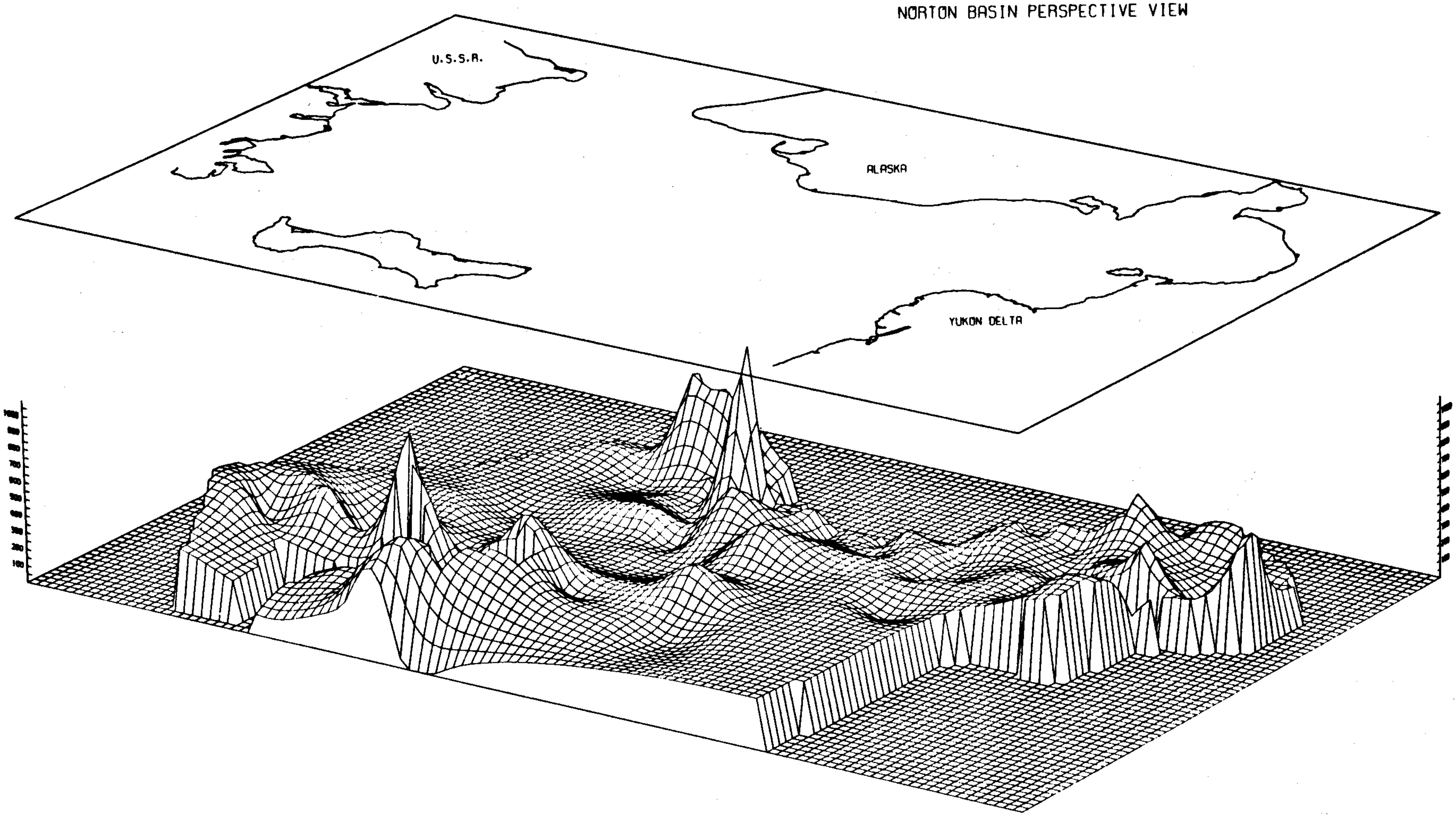

FIG 46 SR PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN. BERING SEA

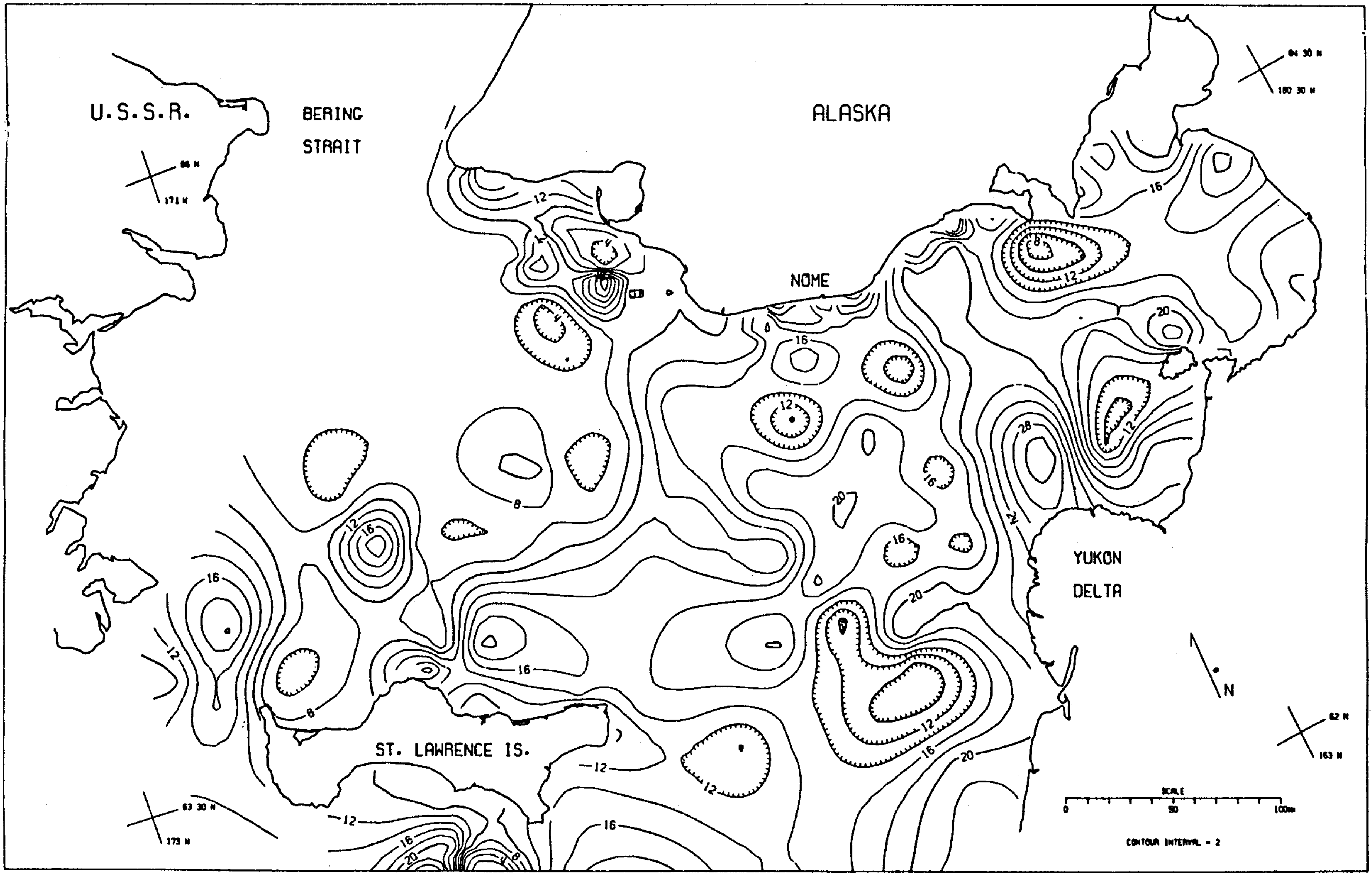

FIG 47 SC PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

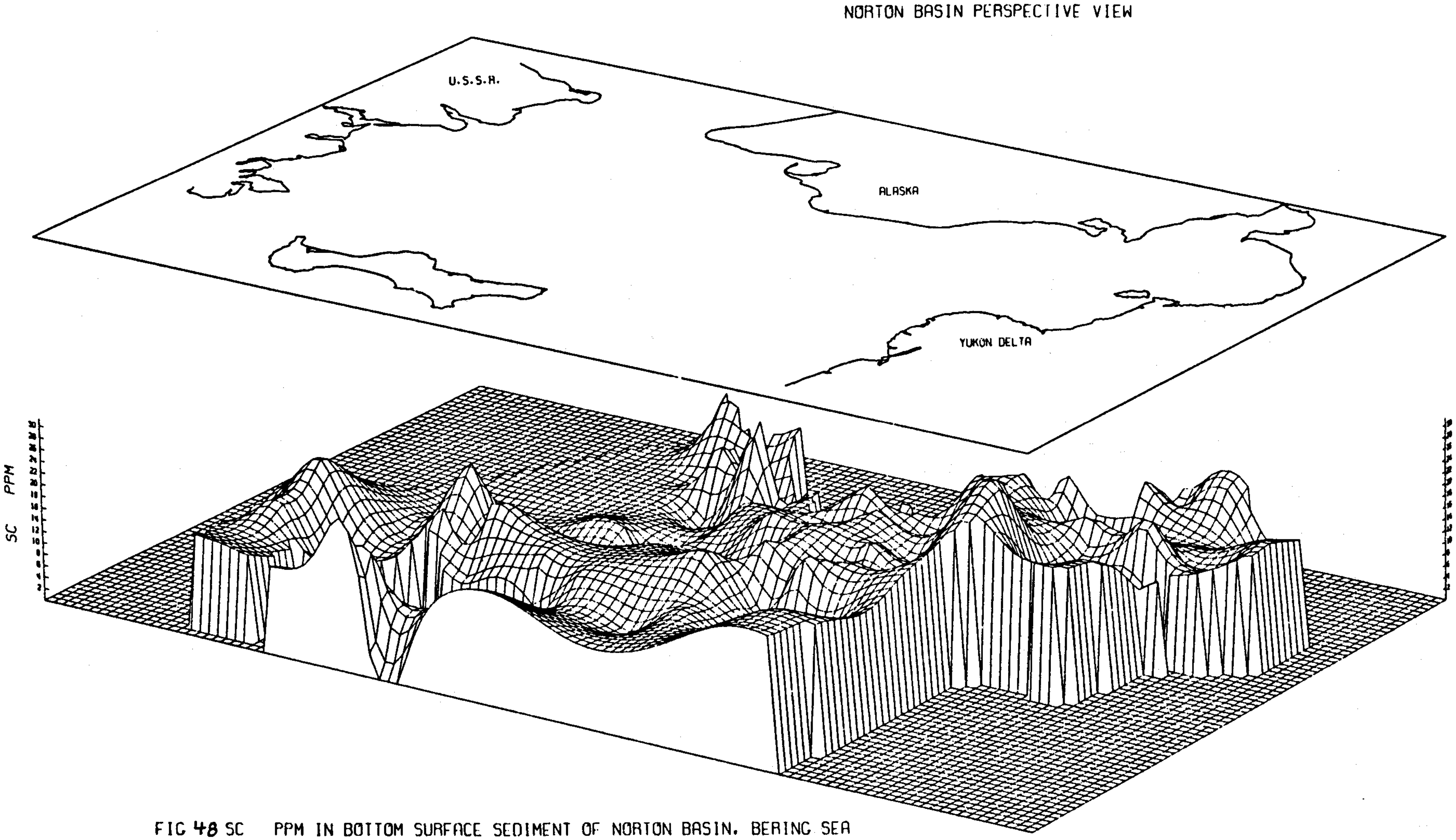

FIG 48 SC PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN. BERING SEA

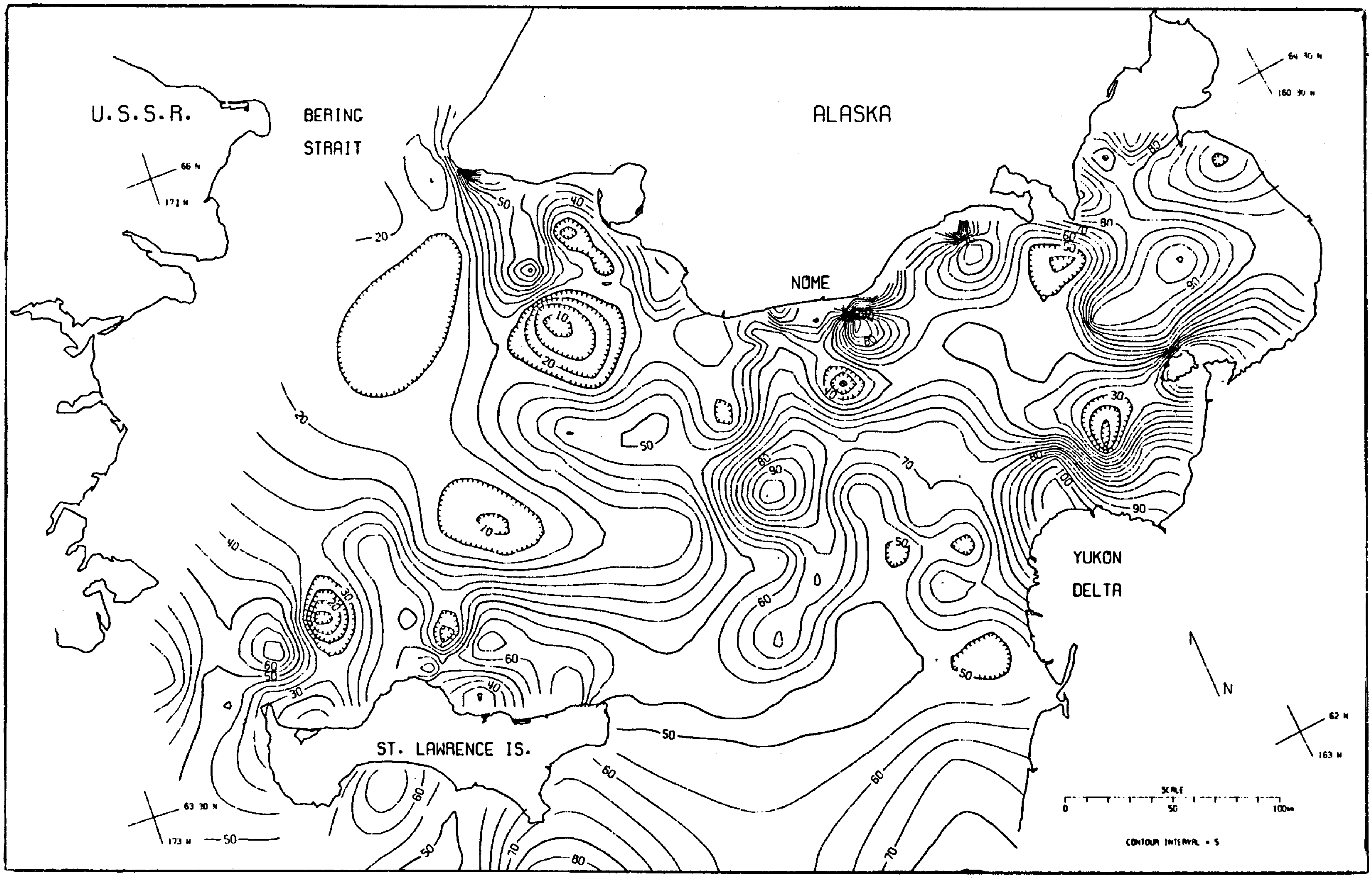

FIG 49 LA PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

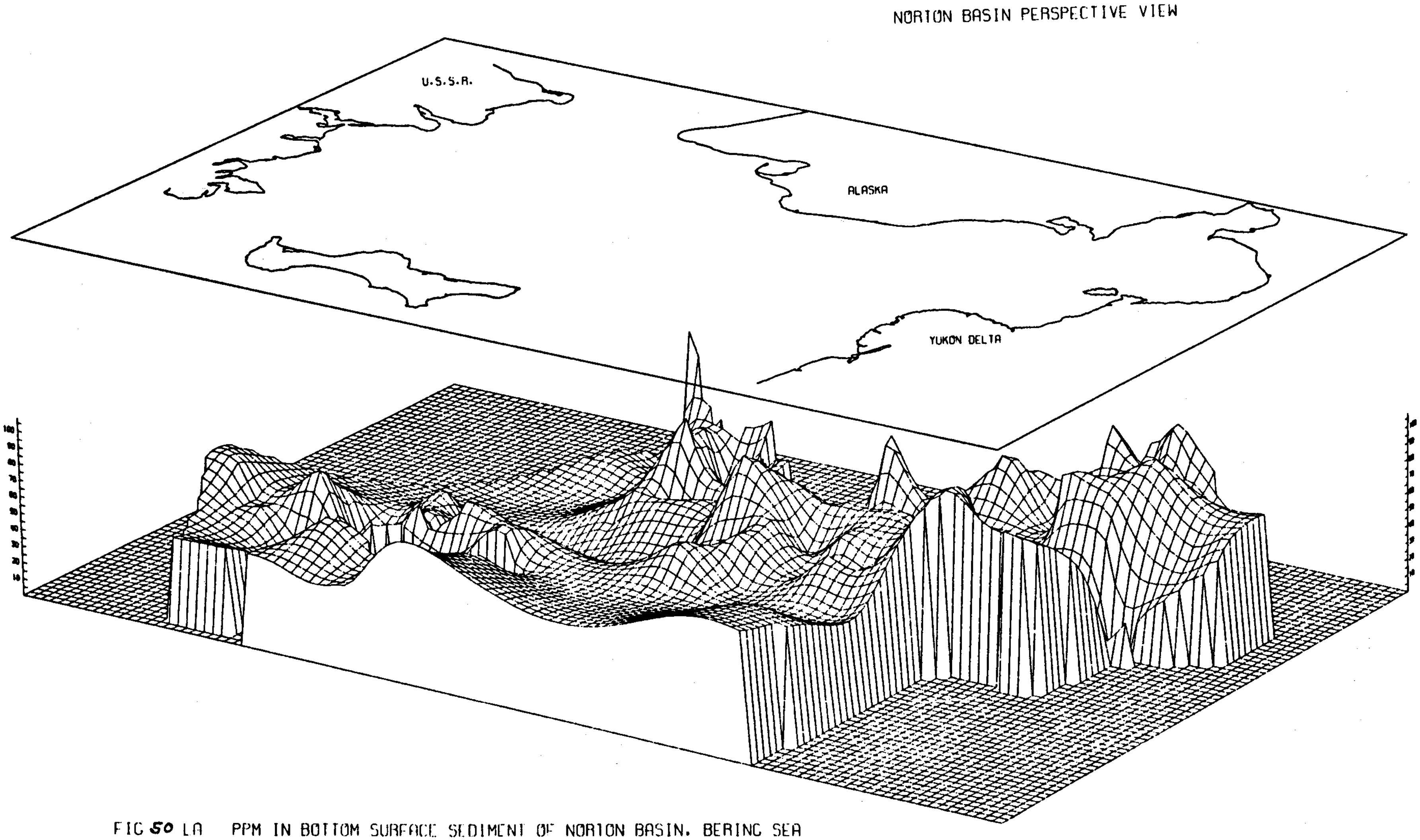

FIG 50 LA PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

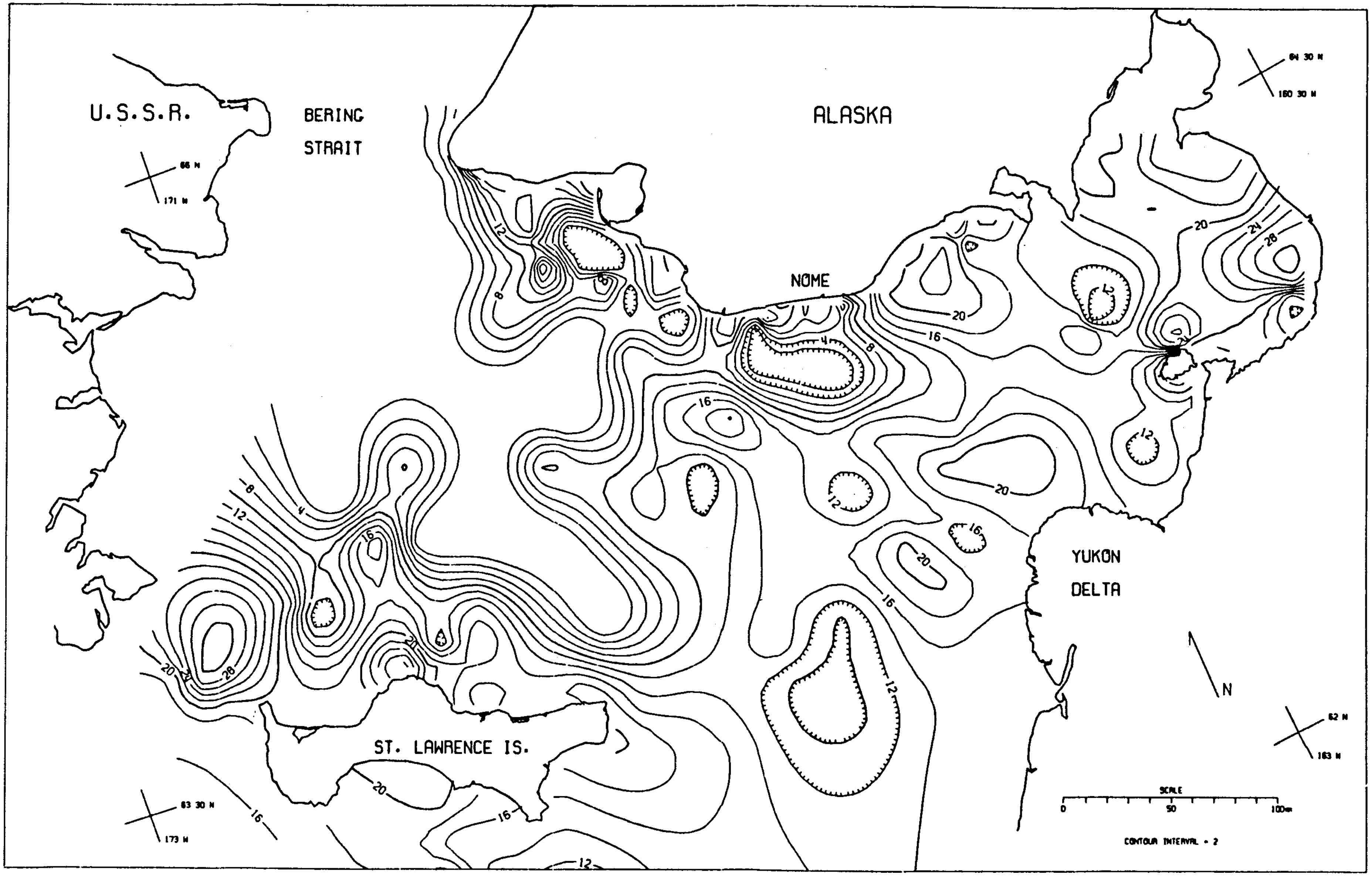

FIG 51 CA PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

NORTON BASIN PERSPECTIVE VIEW

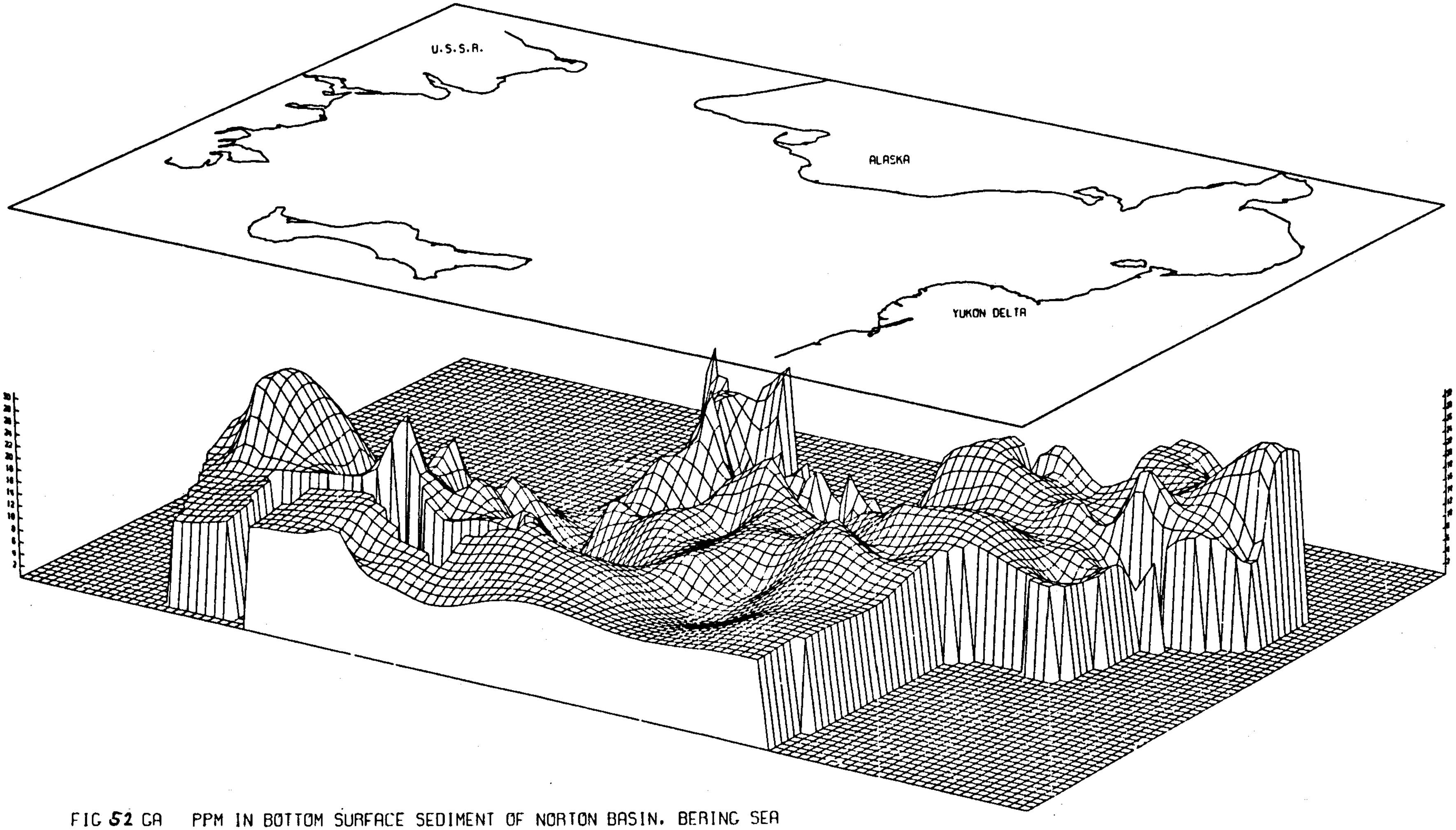

FIG 52 GA PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

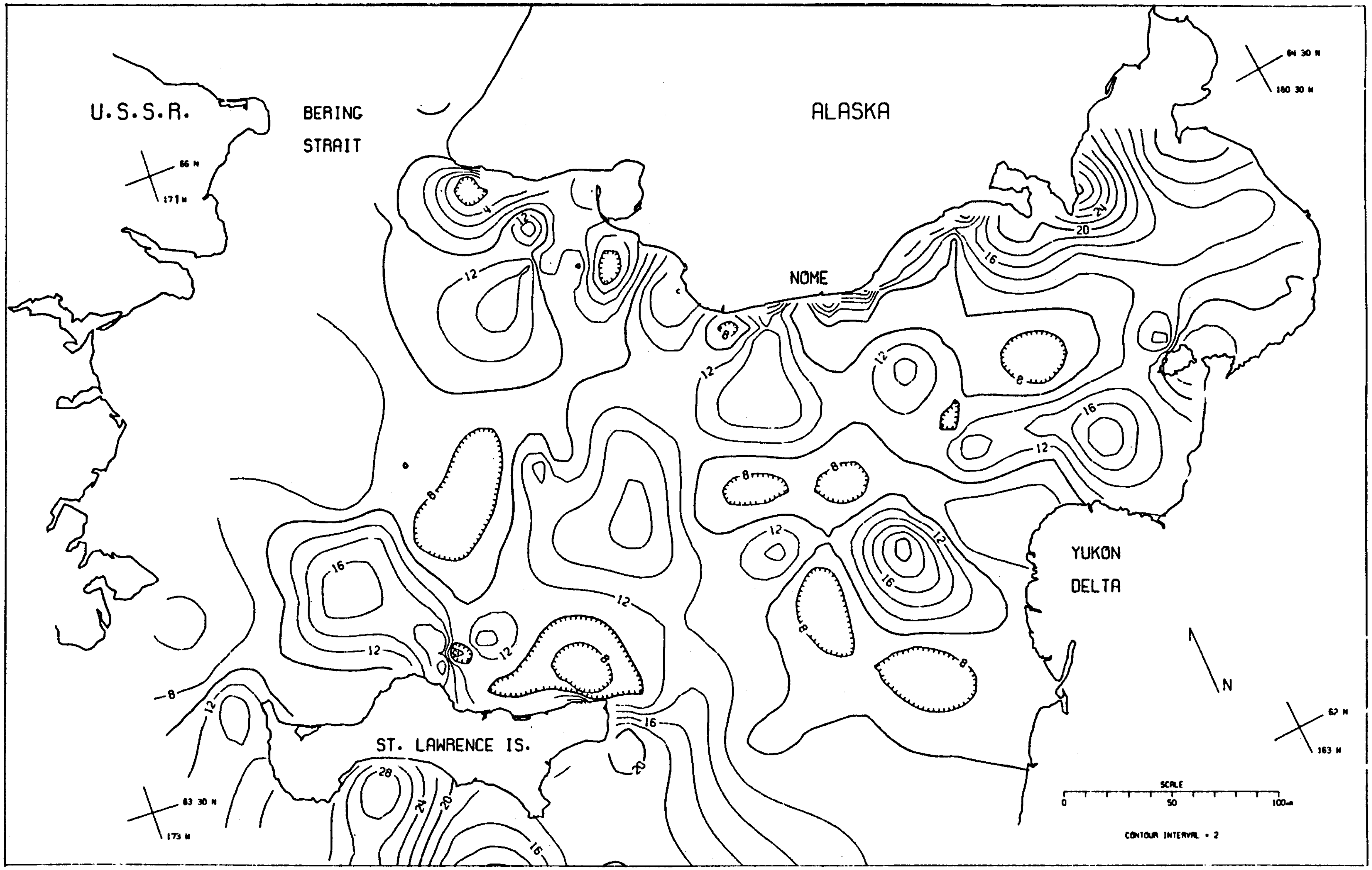

FIG 53 NB PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

NORTON BASIN PERSPECTIVE VIEW

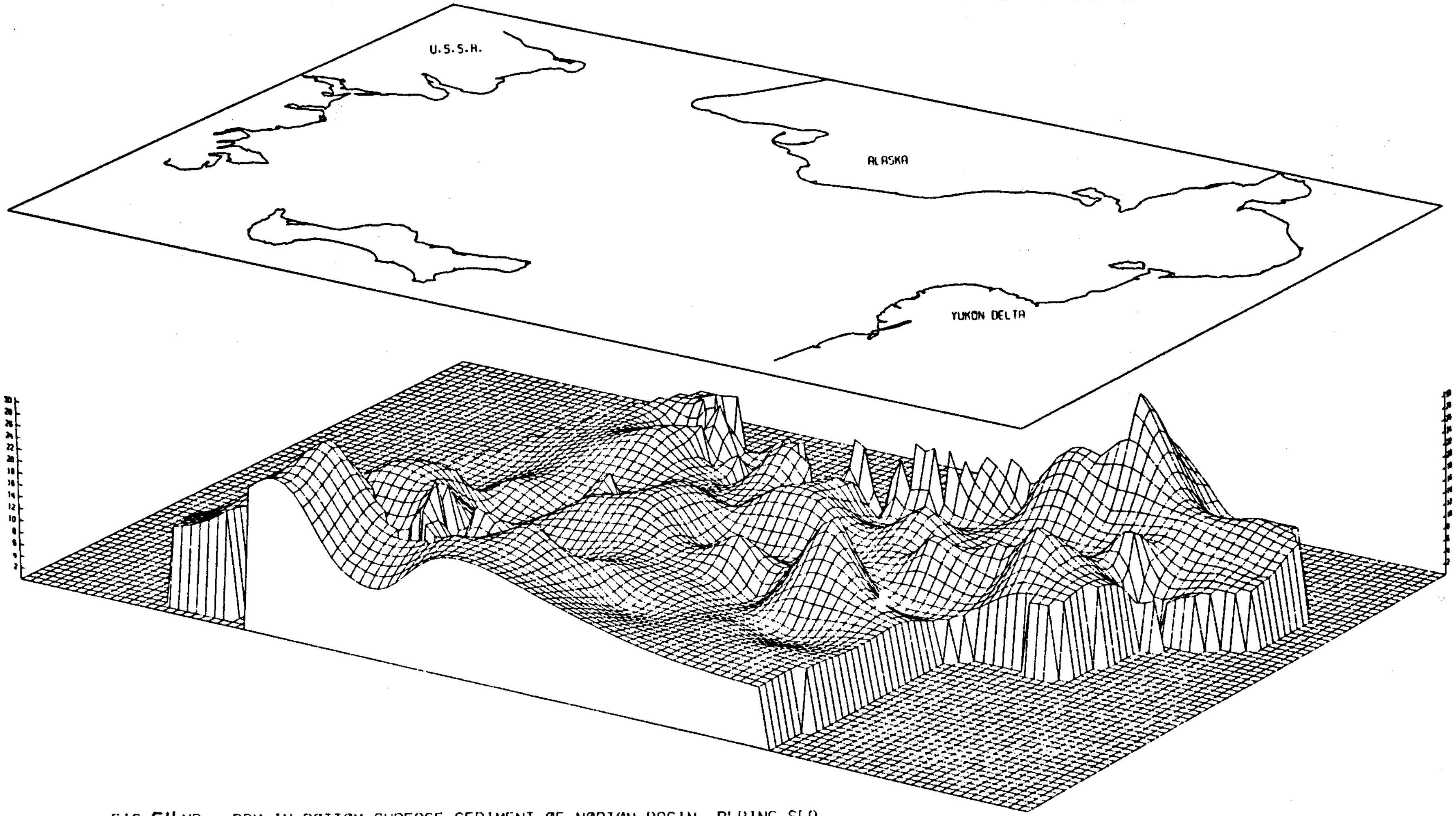

FIG 54 NB   PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

found on the Darby Peninsula (Miller and Grybeck, 1973).

B (boron) is most closely correlated with K and Ba. High concentrations are located at the eastern end of Norton Sound, off Cape Darby, off the coast from Bluff, off Cape Rodney, and southwest of St. Lawrence Island (Figs. 55 and 56).

Y (yttrium) follows the pattern of elements with generally high concentrations in sediment surrounding the Yukon Delta and Norton Sound and low concentrations in sediment from the Chirikov Basin (Figs. 57 and 58). It correlates most closely with Mn, Fe, and Ti which also follow this pattern. Very localized high anomalies are found off Cape Prince of Wales, Nome, and Bluff.

Yb (yterbium) correlates most closely with Mn, Zn, and Y but has no pronounced trends except for the general trend of high values in Norton Sound, and low values in Chirikov Basin (Figs. 59 and 60). A few very high concentrations occur in sediment off Cape Prince of Wales, at various localized points off the southern coast of Seward Peninsula, in the general area of eastern Norton Sound, and NNE of St. Lawrence Island.

Beryllium (Be) correlates closest with La, Yb, and Sc with high concentrations in eastern Norton Sound, along the southern coast of the Seward Peninsula, and off the southwest and southeast coasts of St. Lawrence Island. Highest concentrations occur in samples from just off Tin City at Cape Prince of Wales and one close to Stuart Island. These two high values as well as other high values that appear as lobes coming off the land indicate that specific mineralized terrains are probable sources. This is confirmed for Cape Prince of Wales where extensive economic grade beryllium deposits have been reported by Sainsbury, 1969, in the central York Mountains.

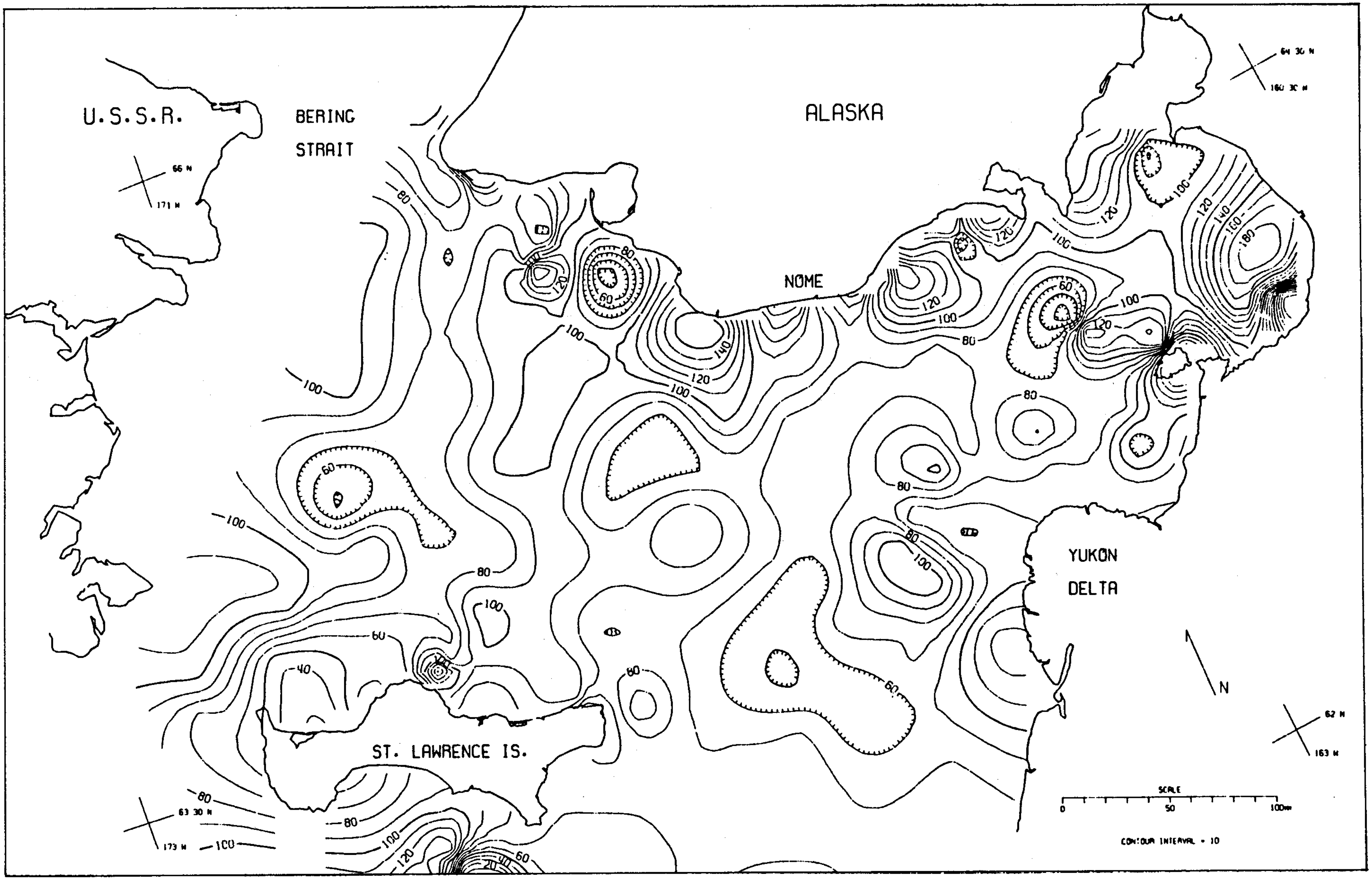

FIG 55 B PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

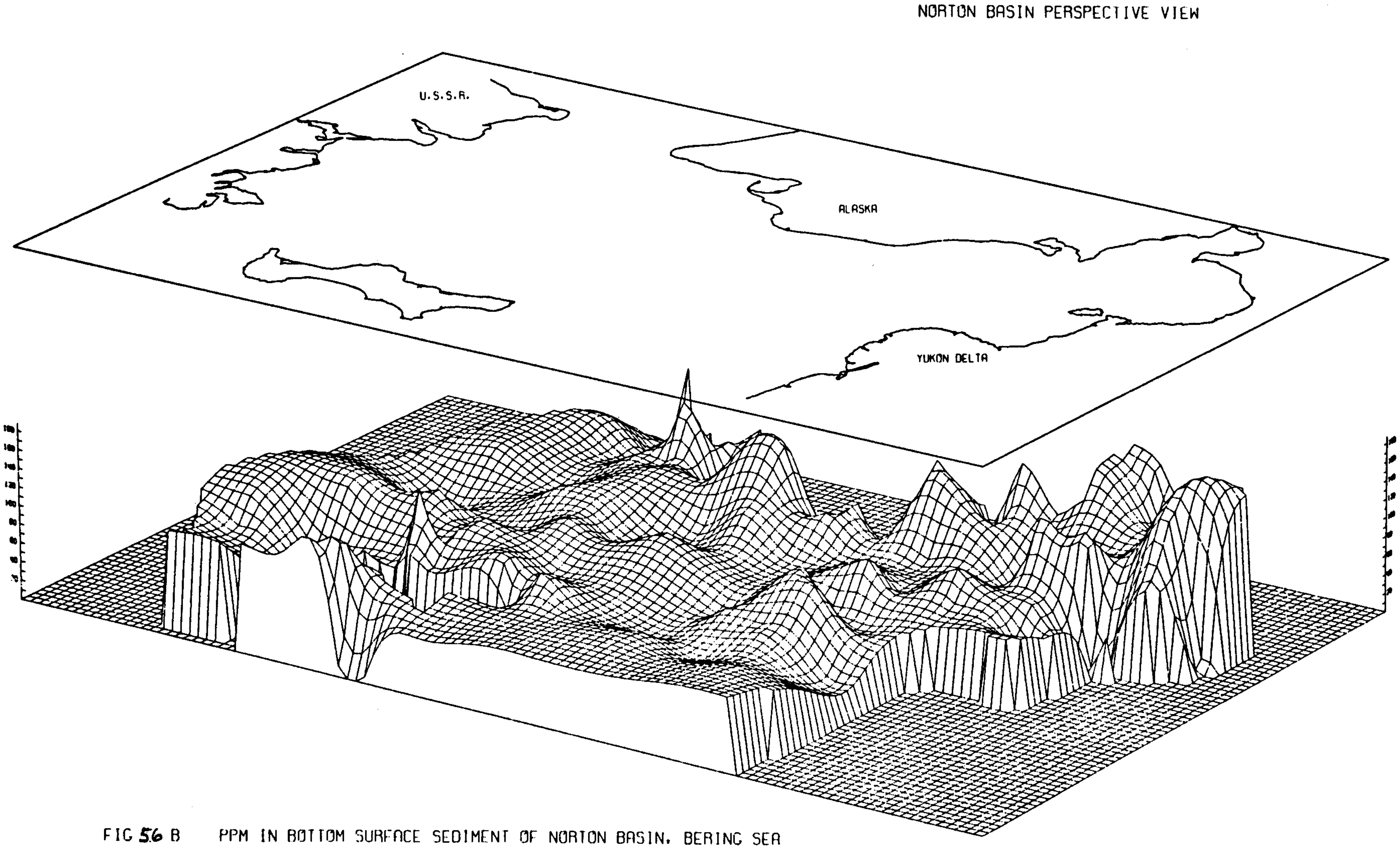

FIG 56 B PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

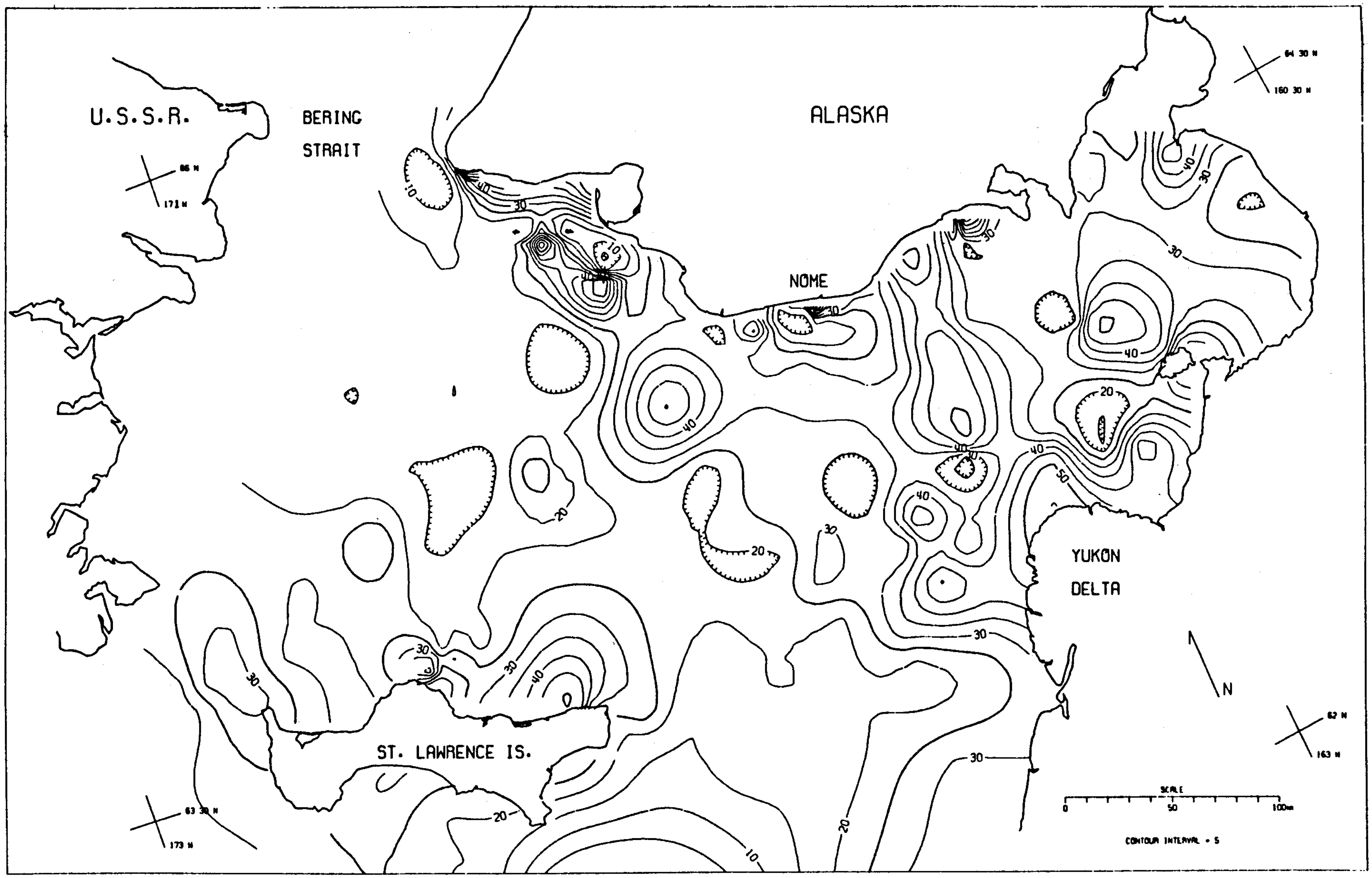

FIG 57Y PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

NORTON BASIN PERSPECTIVE VIEW

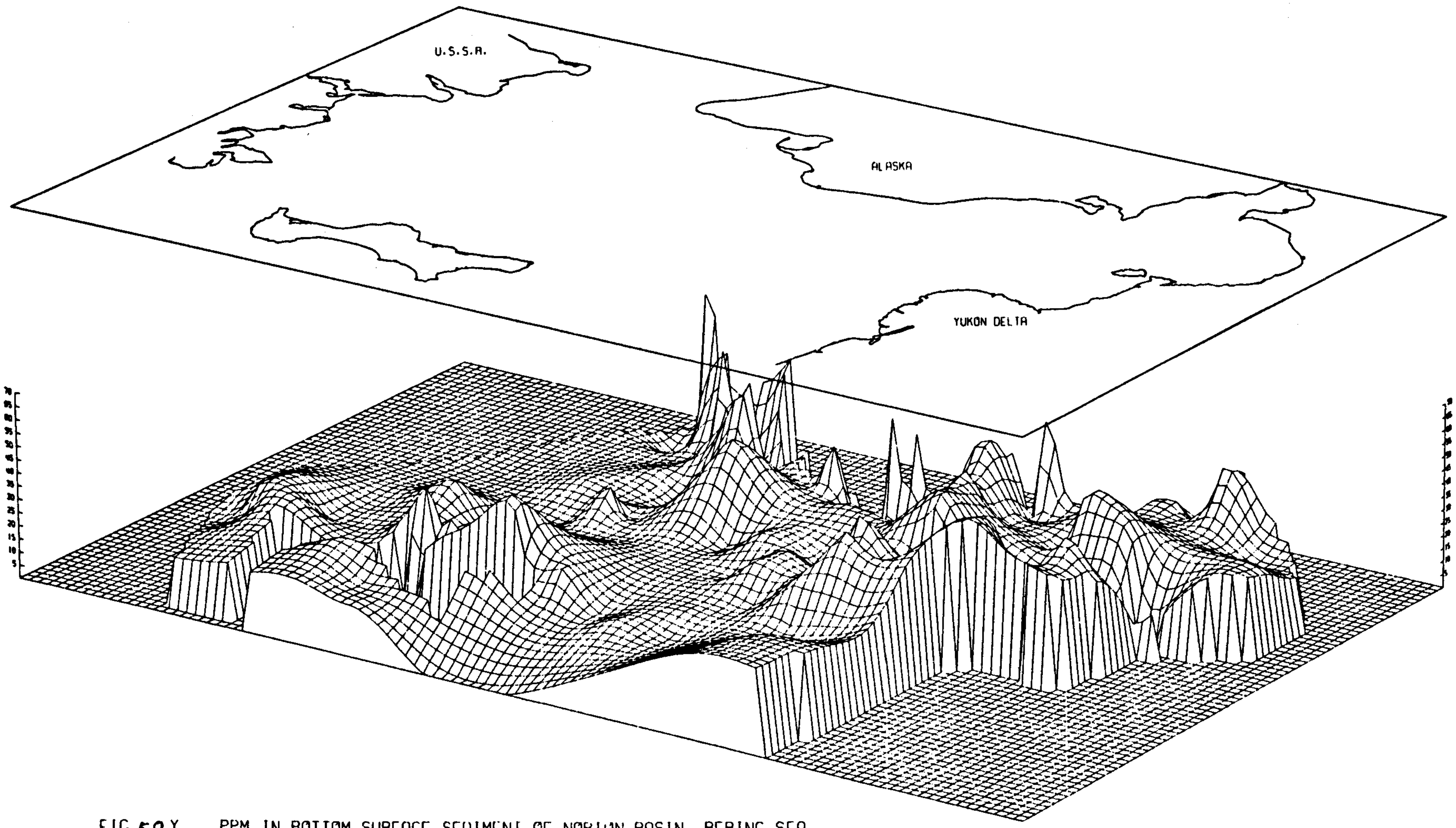

FIG 58 Y PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

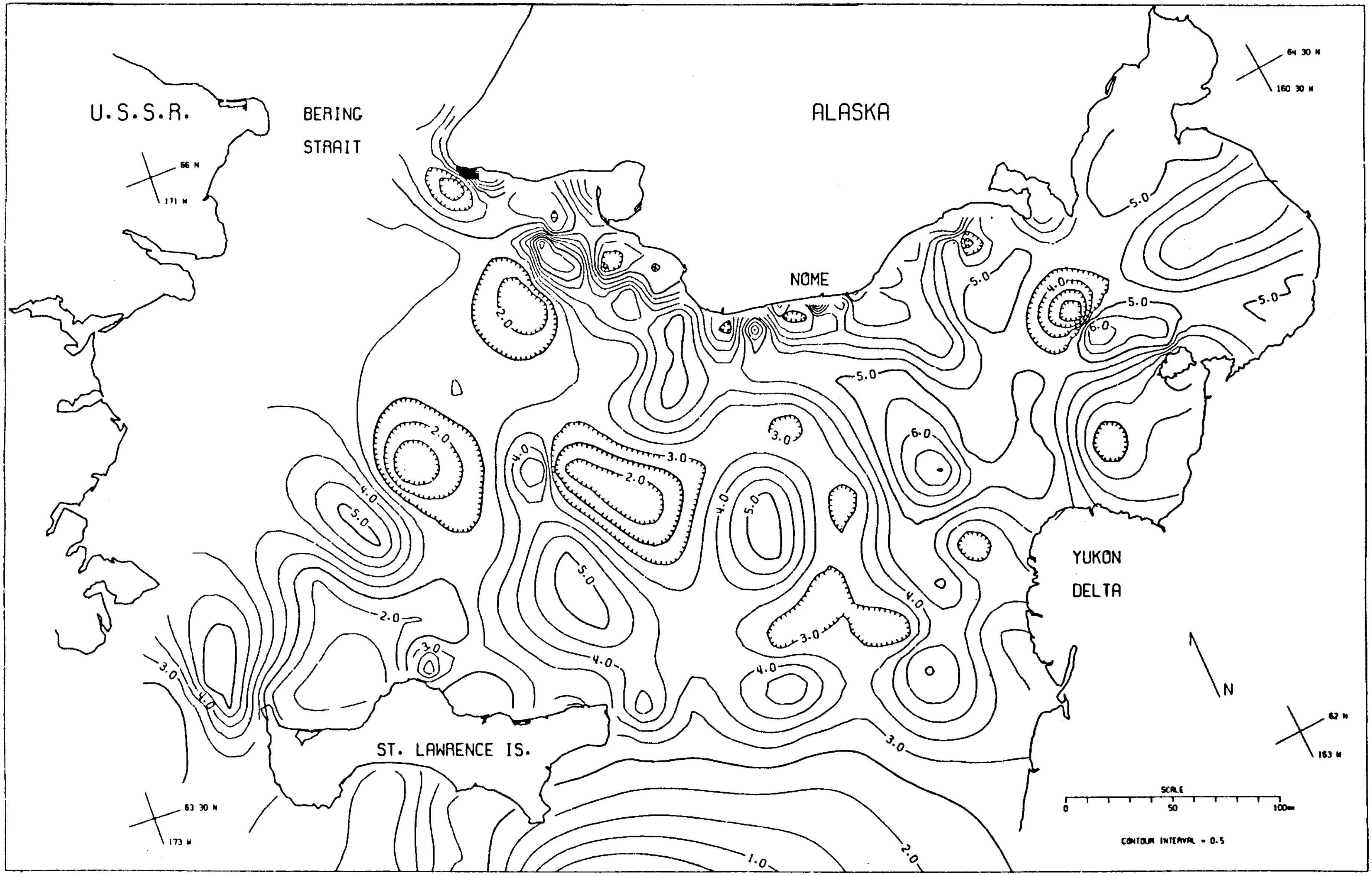

FIG 59 YB PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN. BERING SEA

NORTON BASIN PERSPECTIVE VIEW

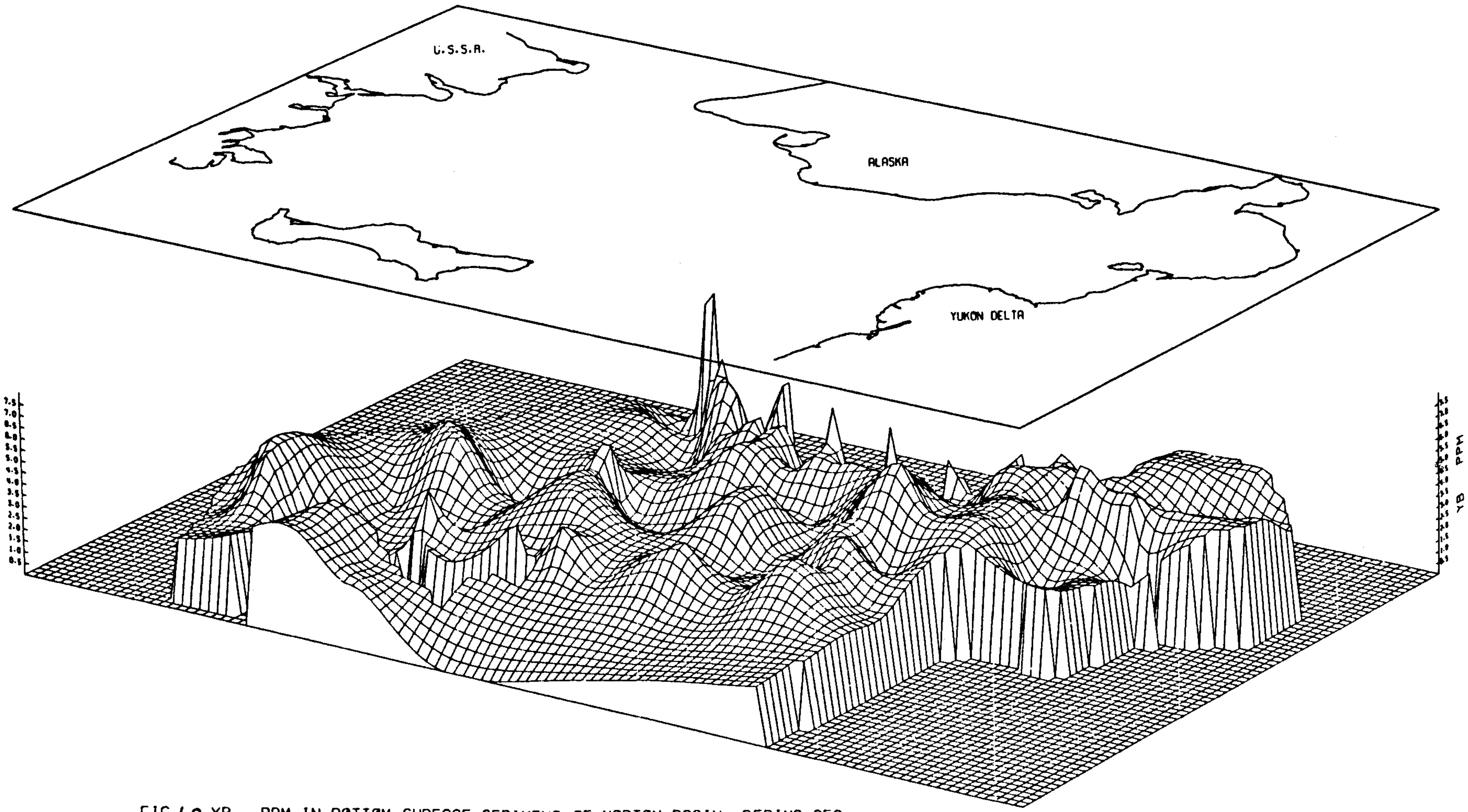

FIG 60 YB PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

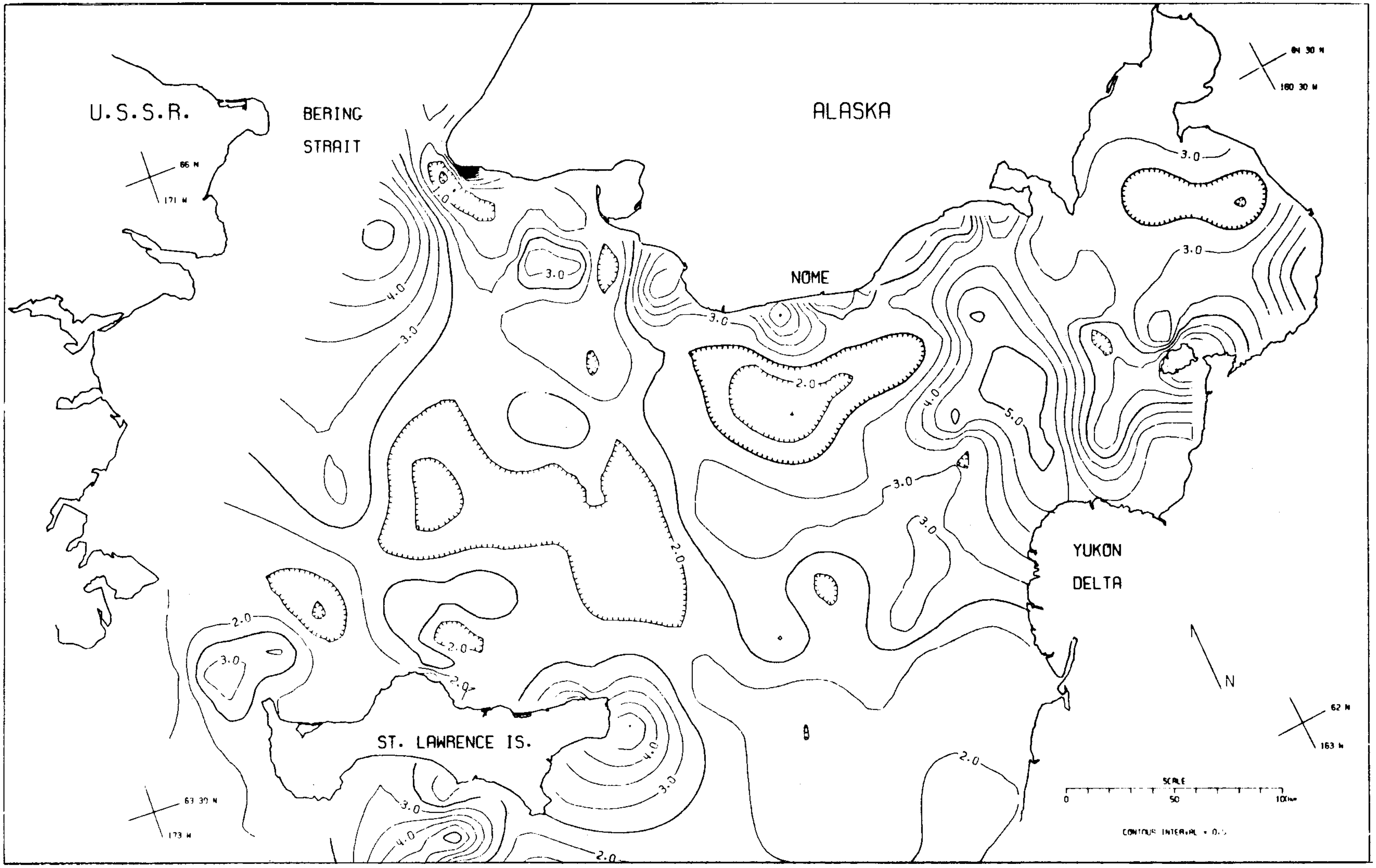

FIG 61 BE PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

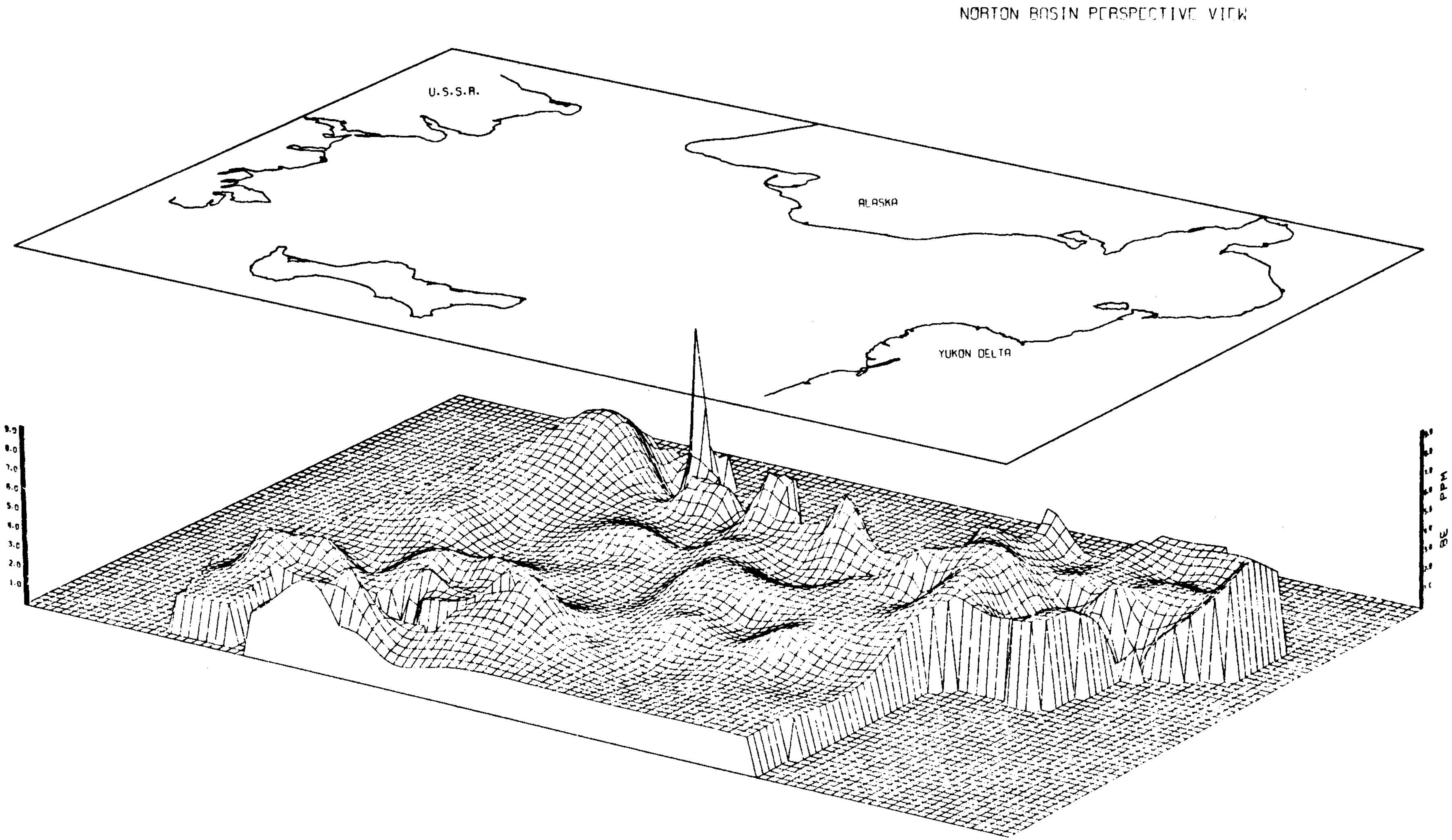

FIG 62 BE PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

G. Other Miscellaneous Economic Elements

Au was not detected in any of the samples analyzed. This was to be expected because the lower limit of detection for Au using the emission spectographic method, is 7 ppm (7000 ppb). A study by Nelson and Hopkins, 1972, has shown that average Au concentrations in open Bering Sea sediments are about 2-3 parts per billion (ppb), and the highest nearshore concentrations found in relict gravel and selected ruby sands, ranged from 556 to 2,118 ppb.

Ag was detected in only 8 of the 180 samples and 3 of these samples could not be assigned a reasonable quantitative value. Some of the samples containing Ag concentrations were from off the NW Cape and the southern tip of St. Lawrence Island (Figs. 63 and 64). Mineralization containing appreciable amounts of Ag has been reported on both ends of St. Lawrence Island and could be the source for for Ag in these samples. Relatively high values were also found near Stuart Island and close in to the Yukon Delta. In addition, Ag was detected in a few samples from off Nome and Cape Nome. High concentrations of Ag (3 ppm) were found in beach samples from Bluff but these values were not plotted on the value-surface maps.

Mo concentrations in all but 5 samples were below the limit of detection of 2 ppm. The highest values were detected in Bluff beach samples (30 ppm) (Figs. 65 and 66). Another high value was found in a Stewart Island beach sample (2 pm) and the presence of Mo was detected off Cape Rodney. Mo mineralization has been reported inland from the coast of eastern Norton Sound and in the Nome area.

Bi was below the limit of detection of 7 ppm in all but 2 samples. The highest value of 70 ppm was in a sediment sample close to the Lost River Mining District on Cape Prince of Wales that also had an anomalously high Sn concentration. Bi is often found in association with Sn ores and is known to

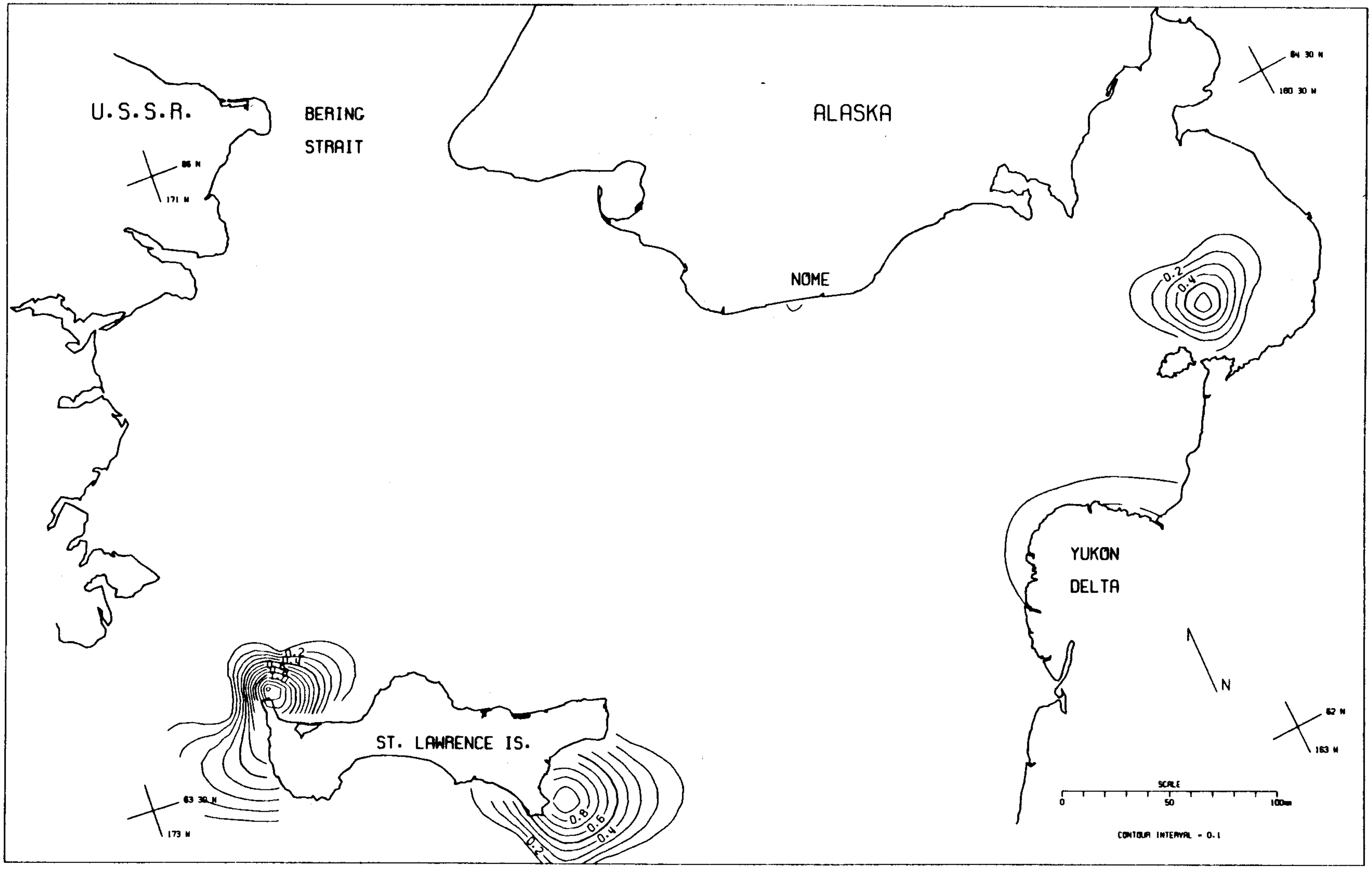

FIG 63 AG PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

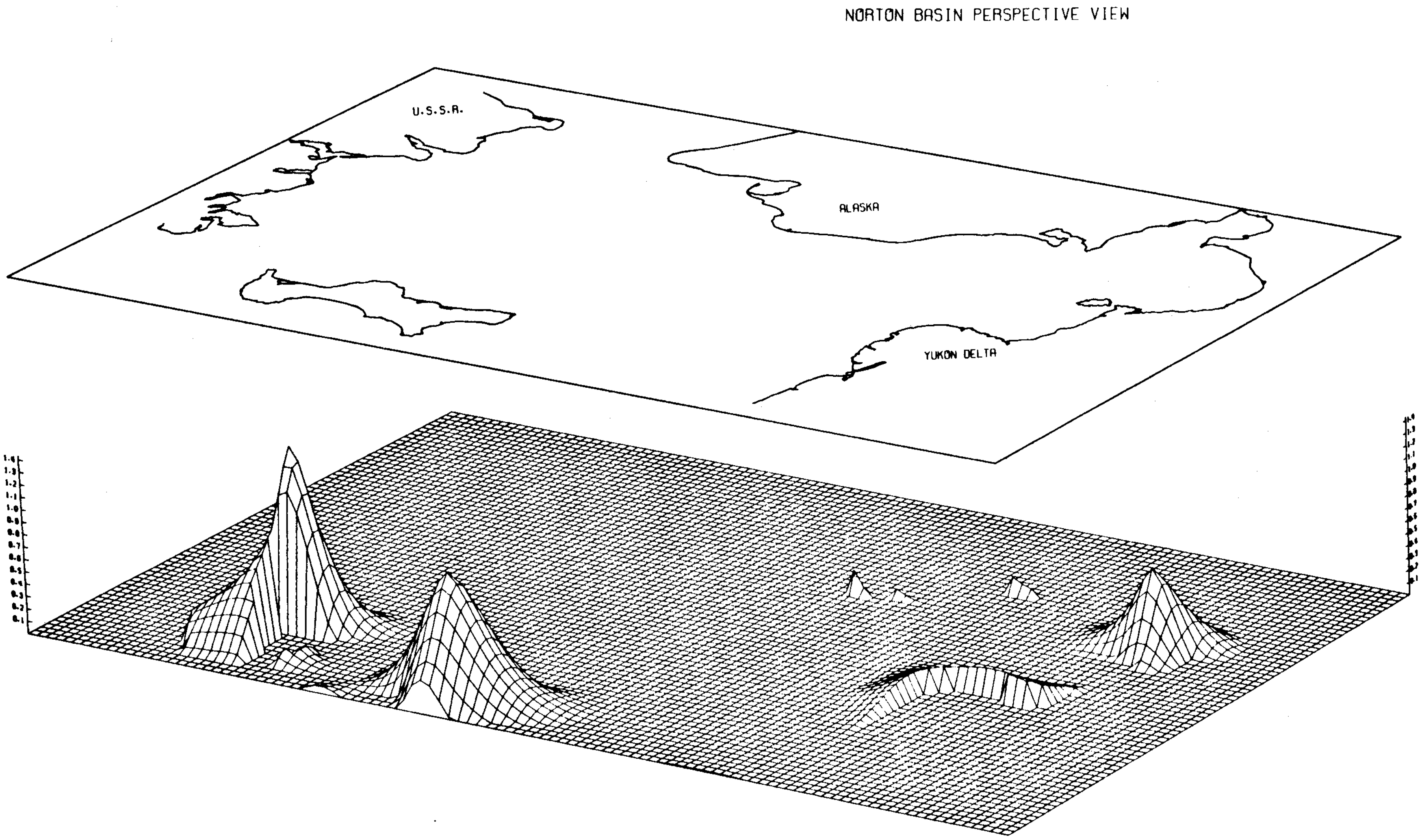

FIG 64 AG PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

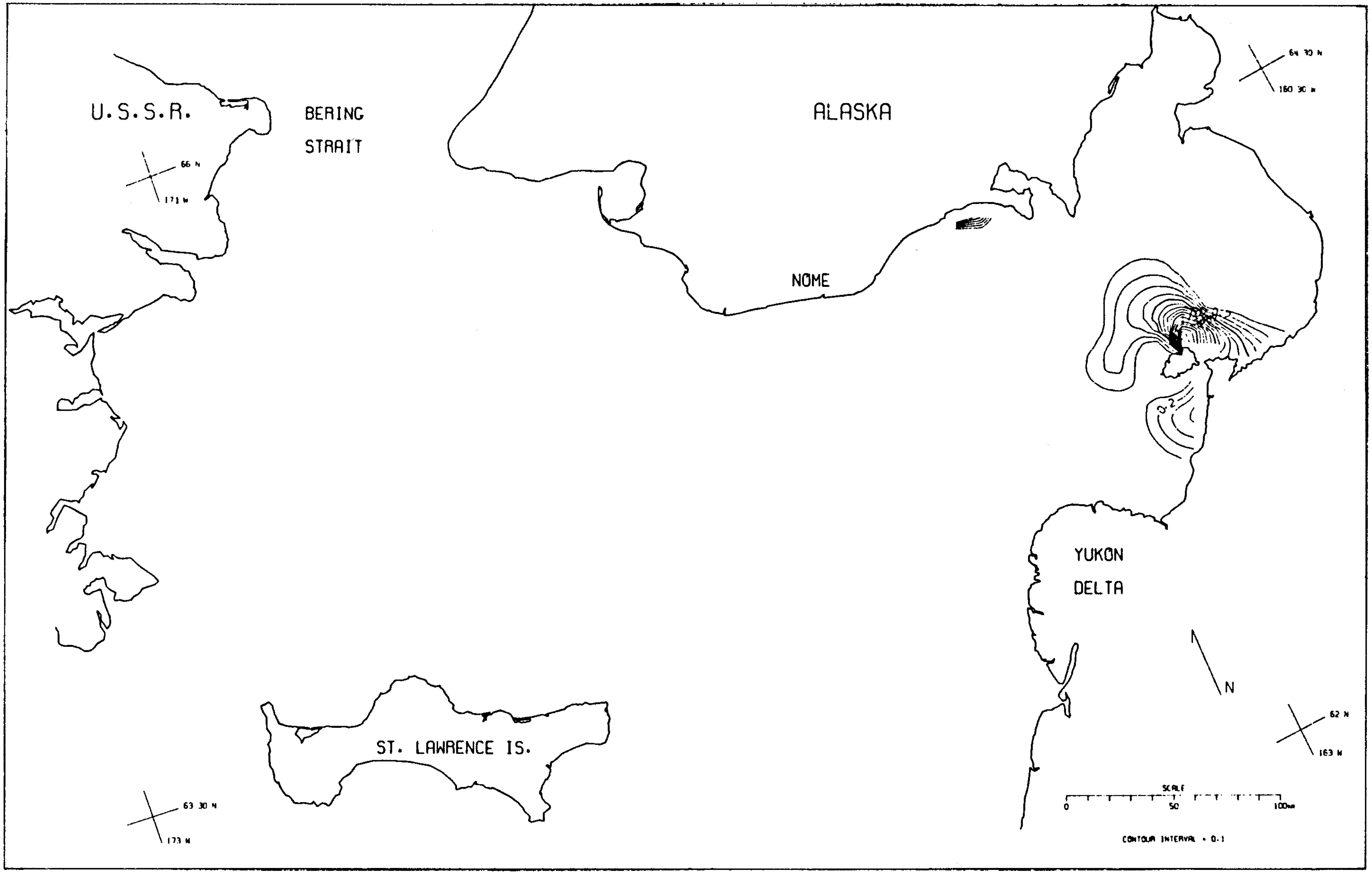

FIG 65 MO PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN. BERING SEA

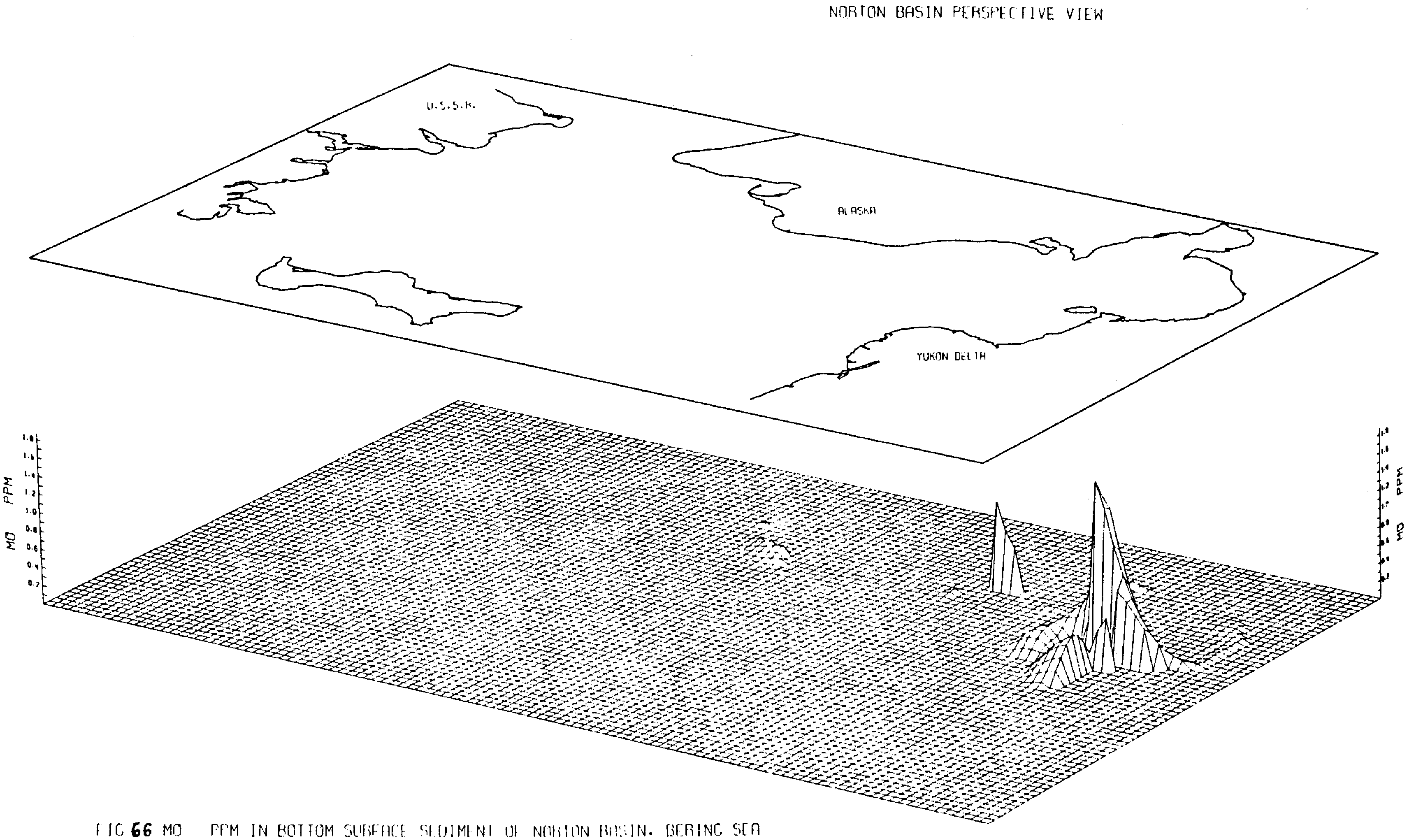

FIG 66 MO PPM IN BOTTOM SURFACE SEDIMENT OF NORTON BASIN, BERING SEA

occur in the form of bismuthinite as one of the main mineral constituents of a skarn zone associated with the Sn and Be deposits at Lost River (Sainsbury, 1969). A sample from off the known mineralized area of Bluff contained Bi; this sample also had high concentrations of Cu, Pb, Zn, Mn, Sb, and As.

H. Q- Mode Factor Analysis

Q-mode analysis was employed to discover possible relationships between groups of samples. The basic algorithms used in the Q-mode analysis are from Klovan and Imbrie (1971) and Imbrie (1963). A more complete description of the program is in Van Trump (1975).

The raw data was first transformed to proportions or the value range of each element so that the transformed values would lie between 0 and 1.

Four factors from the Q-mode varimax factor matrix were found to explain 92% of the variance between samples (see Table VII) and only these four factors seemed to be related to sediment characteristic and geologic background. Of these factors, Factor III was judged to include the most important sample group because it explained 33.4% of the variance between samples. Factor I explained 24.3%, Factor IV explained 22.5% and Factor II with a variance of 11.8%, encompassed the fewest samples.

Samples with the highest loadings (>.7) for Factor III were found in an apron around the Yukon Delta and in patches in the west-central part of Norton Sound and NNW of St. Lawrence Island and in Anadyr Strait (Fig. 4). Samples with intermediate loadings (.6 to .7) values were found in a wide apron around the Yukon Delta, throughout most of Norton Sound, around the northern, eastern, and southern coasts of St. Lawrence Island, and south of Cape Prince of Wales.

Samples with the highest loadings for Q-mode Factor I, which explained the second highest percentage of variance, were from an area that generally has low loadings for Factor III, namely the Chirikov Basin region (Fig. 4). Samples with the highest loadings for Factor II are from along the coast between Cape Rodney and Golovnin Bay, just off Cape Prince of Wales and near King Island. Samples with the highest loadings for Factor IV are from patches north of St. Lawrence Island, from random areas throughout Norton Basin, and from areas just off the south coast of the Seward Peninsula.

Scaled varimax factor scores (Table VI) were computed for each element during the Q-mode analysis in order to determine the elements that are most correlative with each factor group. As an additional check of the relationship between samples and to highlight possible negative relationships between factors, correlation coefficients were computed between element values and factor loadings for all the samples (Tables III and V). Both the Q-mode scaled varimax factor scores and the correlation coefficients between varimax factor loadings and element values indicate that samples with high loadings for Factor III contain relatively high concentrations of Ba, Na, Sr, La, K, Ga, Al, and Sc. B, V, and Yb are concentrated in Factor I samples; Factor II loadings correlate most closely with Y, Fe, Mn, Ti, Yb, Zn, Co, Sc, and Cu. The only element that seems to correlate somewhat with Factor IV is Nb and its most negative r values (Table V) are almost the same as the elements that belong to Factor II which indicates it may simply be the negative of Factor II.

The area of sediments with high factor loadings for Factor III of the Q-mode analysis (0.5 and above) corresponds closely to the area covered predominantly by Yukon Holocene sediment, although samples with high loadings for Factor III are also found north of St. Lawrence Island and in Anadyr Strait. The elements used in grouping samples in this factor are primarily those elements that are most abundant in sialic rock types. Na cannot readily be regarded as an artifact of residual pore water salts because it increases in concentration in sediments closer to the hyposaline runoff of the Yukon River. The occurrence of high loadings for Factor III in areas not covered by Yukon sediments probably indicates that the sediments in these areas are similar to Yukon-type sediment and that they also originated in sialic rock terrain.

Samples with high loadings for Q-mode Factor I are from areas where modern Yukon sediment is absent but where Holocene transgressive sands of mixed origin are found. This general area covers the region of Chirikov Basin, but there does not seem to be any clear relationship between the elements of this factor and the sediments of the region.

Samples with highest loadings for Factor II of the Q-mode analysis are from very close to the Nome-Bluff strand line and off of Cape Prince of Wales and King Island, regions of highly mineralized mafic rocks. Factor II is therefore grouping sediments derived from these terrains. This is borne out by the association of several mafic-related elements to Factor II, particularly Ti, Fe, Co, and Mn.

The contoured surface of Factor IV shows a rough correlation with areas reported to be covered by relict glacial debris and lag gravel, particularly in a lobe extending NE of St. Lawrence Island (McManus et al., 1977). Otherwise, its significance is not readily apparent, except as a negative factor to Factor II.

It is not altogether clear why some of the minor elements should be grouped with a particular factor or why, in some cases, they should be related to one another through their r values. These relationships should be regarded with caution.

VII. CONCLUSIONS AND NEED FOR FURTHER STUDY

Measured concentrations of Y, Ca, Ba, K, Cr, Cu, Na, Co, Nb, Ni, V, and Zn are within 30% of reported values for rock standards and are therefore reliable baseline data. Measured concentrations of Sr, Al, Sc, Zr, Ti, Ga, Pb, Fe, Mn, and Mg were within 35-65% of the reported values for rock standards and can probably be regarded as providing reasonable baseline data. The elements Ag, As, Bi, Mo, Sb, Sn, P, Ce, and Nd had too few concentrations above detection limits to say anything about the accuracy of their measurement. Concentrations of Si were higher than the upper limit of detection in every sample. All concentrations of Au, Cd, Pd, Pt, Te, U, W, Ge, Hf, In, Li, Re, Ta, Th, Tl, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Lu were below limits of detection.

High concentrations of V and Ni have been noted in sediment in the areas of hydrocarbon seeps. Concentrations of these elements in samples from a grid covering a probable thermogenic gas seep 35 km south of Nome however, were no different than background concentrations for these elements in the northern Bering Sea. Lack of V and Ni anomalies for this gas seep may only mean that the seep source is of a light hydrocarbon gas type that does not result in high Ni and V values as do some heavy hydrocarbon petroleum seeps. Samples 40 km west of the southern tip of St. Lawrence Island contains high concentrations of V and Ni and their location warrants a closer study for hydrocarbon seeps. Other high concentrations of Ni occur in sediments in the vicinity of Stuart Island and off the north and south coasts of St. Lawrence Island and are related to the basaltic volcanics in these areas, not petroleum sources.

Pb, Cu, Zn, As, Sb, and Cd are considered to be potentially toxic when found in sufficient concentrations. Presently, the highest values of any of these elements are derived from highly mineralized onshore locations, for example, Cu and Zn off St. Lawrence Island, Nome, and Bluff beaches, and high Cu values off Stuart Island. The few values detected for Sb and As are in sediment derived from areas of onshore mineralization near Bluff, the NE tip of St. Lawrence Island, and just off Stuart Island. Both Cu and Zn have relatively high values in areas off the Yukon Delta and in Norton Sound that correspond to the areas covered by Yukon Holocene sediment.

Concentrations of Pb vary little from the geometric mean but there are some relatively high concentrations off Bluff beach, Stuart Island, and the eastern tip of St. Lawrence Island.

Because Zr, Sn, Cr, and Ce are commonly found in heavy minerals, high concentrations of these elements may well indicate placer as well as primary lode occurrences of these minerals. Anomalously high Zr values were found off the NE Cape and the western portions of St. Lawrence Island and probably originated from zircon-containing quartz monzanitic rocks on the island. Concentrations generally above the mean were found in the area of Yukon Holocene sediment. The highest values for Sn are found close to Tin City and are related to the tin mineralization there. Detection of Sn in samples near Bluff and Cape Rodney-Nome areas again may be related to tin mineralization known to exist in these areas. Samples containing detectable concentrations of Sn in the areas of King Island, Port Clarence, and in the Anadyr Strait may be from tin placer deposits concentrated by the relatively high currents there. High Cr concentrations were found in sediment off Stuart Island, Cape Prince of Wales and north-central St. Lawrence Island and appear to be related to basalts or granites containing ultra-mafic dikes that are sources of chromite. Samples with high Ce values also have high La values and often have high Nd values, suggesting that the heavy mineral monazite concentrated as a placer mineral and may be the source of these elements. Because monazite is probably the primary carrier of Ce and related elements and because it is concentrated in placer deposits, it promises to be a good indicator of sediment dispersal trends.

A sediment sample from 30 km south of Cape Prince of Wales contains the greatest amounts of Cr, Zr, Ce, Ti, Mn, La, Sc, Y, Yb, and Nd of all the samples analyzed and also contains a high concentration of tin. Because of these high concentrations and because the sample contains high values of La and Nd which are commonly found with Ce in the heavy mineral monazite, this sample may represent an area of placer deposits the existence and extent of which should be explored. Future studies of Sn, Zr, Cr, and Ce and associated heavy minerals should use sampling intervals close-spaced enough to detect significant variations caused by hydraulic concentration. Mechanical concentration of samples before analysis would also help to enhance existing trends.

Fe, Mn, Co, and Ba were considered together as chemically or environmentally-sensitive elements but in this study the evidence indicates their concentrations are source related. Fe, Mn, and Co all show high values near the volcanics of Stewart Island and north-central St. Lawrence Island. These elements also correlate with Cu, Zn, V, Y, and Zr, with generally high values in the areas of Yukon Holocene sedimentation and generally low values in Chirikov Basin. Co, however, does not follow this trend as closely as Fe and Mn. Concentrations of Ba above the mean are found generally throughout the area of Yukon sediment distribution but also are found close to Stuart Island and at various locations along the southern coast of the Seward Peninsula. The maximum concentration of Ba (.15%) is found in a sample from the Anadyr Strait and is unique in that other concentrations of other elements that usually correlate with Ba are not similarly high at this location.

Of the major elements, Ti is closely associated with Fe and Mn, discussed above, all of which have generally high concentrations in Yukon sediment with very high concentrations in areas close to the volcanics of Stuart Island and St. Lawrence Island. Ca and Mg are relatively high in Yukon sediment and sediment close to the volcanic areas mentioned. However, sediment with the highest concentrations of Ca and Mg was probably derived from the limestone formations in the Cape Prince of Wales and Port Clarence areas. Values for Na, K, and Al exhibit more erratic variation than values for the other major elements and the anomalies of Na, K and Al that appear to originate from land sources and are broader in areal extent. Concentrations of P occur in patches in eastern Norton Sound, Anadyr Strait, and surrounding the Yukon Delta. The highest concentration of P was in a sample from an enclosed basin NE of St. Lawrence Island and could be a result of reducing conditions in the basin.

Of the minor trace elements that are not usually regarded as potentially toxic, Sc correlates closest with Ti, Fe, V, La, and Mn. Yttrium correlates closest with Mn, Fe, and Ti. Yb correlates closest with Mn, Zn, and Y. Concentrations of Sc, Y, and Yb are all highest in Yukon sediment and lowest in Chirikov Basin sediment. Nb exhibited maximum concentrations in sediment off Cape Darby where the highest Nb anomalies on land in western Alaska have been found. Nd was detected in two samples from Norton Sound and in samples of sediment north of King Island, samples that also have high concentrations of La and Ce. These elements probably exist in the mineral monazite. Slightly higher values of Be can be found just off the coasts enclosing Norton Basin but maximum offshore values near Cape Prince of Wales correlate with economic Be deposits there.

Of the economically important elements, Ag, Mo, and Bi, detectable Ag concentrations occur in samples offshsore from terrestrial Ag mineralization sites on St. Lawrence Island, near Stuart Island, and close to the Yukon Delta. Highest concentrations of Mo were found off the Bluff beach mineralization, Bi was detected in samples off the Cape Prince of Wales mineralization area that has associated Bi.

A contour map of the Q-mode factor loadings for Factor III outlines an area corresponding to the distribution of Yukon Holocene sediment plus areas in Anadyr Strait and north of St. Lawrence Island. Scaled varimax factor scores and cross correlation between factor loadings and element concentrations indicate that Factor III is best characterized by elevated concentrations of Ba, Na, Sr, La, K, Ga, Al, and Sc. The significance of this element grouping is that these elements tend to be concentrated in sialic rock types. Samples with high loadings for Factor I of the Q-mode analysis generally corresponds with the area of relict sediment in the Chirikov Basin. Samples with high loadings for Factor II of the Q-mode analysis occur off the coast from Bluff, Nome, and Tin City, suggesting a strong influence from the mineralization in these areas. This is confirmed by high correlations between loadings for this factor and concentrations of Fe, Mn, Ti, Co, Zn, Sc, Cu, Y, and V. Factor IV of the Q-mode analysis does not have any strong relation to sediment or mineral characteristics but shows some correlation with areas of known glacial debris.

REFERENCES

Bateman, A.M., 1965, Economic Mineral Deposits: John Wiley and Sons, Inc., New York, 916 p.

Cacchione, D.A., and Drake, D.E., 1978, Sediment transport in Norton Sound-Northern Bering Sea, Alaska, in: Environmental Assessment of the Alaskan Continental Shelf, Annual Report of Principal Investigators for the year ending March, 1978: Environmental Research Laboratory, Boulder, Colorado, NOAA, U.S. Dept. of Commerce, v. 12, p. 308-450.

Coachman, L.K., Aagaard, K., and Tripp, R.B., 1976, Bering Strait: The regional physical oceanography: Seattle, Washington, University Press, 186 p.

Cobb, E.H., 1960, Sb, bismuth and mercury occurrences in Alaska: U.S. Geological Survey, Mineral Investigations, Resource Map MR-11.

________, 1960a, Chromite, cobalt, nickel, and platinum occurrences in Alaska: U.S. Geological Survey, Mineral Investigations Resource Map MR-8.

________, 1960b, Copper, lead, and zinc occurrences in Alaska: U.S. Geological Survey, Mineral Investigations, Resource Map, MR-9.

________, 1960c, Molybdenum, tin, tungsten occurrences in ALaska: U.S. Geological Survey, Mineral investigations, Resource Map MR-10

________, 1962, Lode gold and silver occurrences in Alaska: U.S. Geological Survey, Mineral Investigations, Resource Map MR-32.

________, 1964, Iron occurrences in Alaska: U.S. Geological Survey, Mineral Investigations, Resource Map MR-40.

________, 1970, Uraniam, Thorium, and Rare-Earth elements of Alaska: U.S. Geological Surey, Mineral Investigations, Resources Map MR-56.

Cohen, A.C., Jr., 1959, Simplified estimators for the normal distribution when samples are singly censored or truncated: Technometrics, v. 1, no. 3, p. p. 217-237.

Dean, W., Gardner, J., and Vallier, T., 1978, Inorganic geochemistry and sedimentology of surface sediments, outer continental shelf, southern Bering Sea, Alaska: International Sedimentological Congress, Israel.

Eberlein, G.D., Chapman, R.M., Foster, H.L., Gassaway, J.S., 1977, Map with table showing known metalliferous and non--metalliferous mineral deposits in central Alaska: U.S. Geological Survey Open-file Report 77-168-D.

________, Menzie, W.D., 1978, Maps and tables describing areas of metalliferous mineral resource potential of central Alaska: U.S. Geological Survey Open-file Report 78-1-0.

Fathauer, T.F., 1975, The great Bering Sea storms of 9-19 November, 1974 Weatherwise Magazine, American Meterological Society, v. 28, p. 76-83.

Flores, R.M., Shideler, G.L., 1978, Factors controlling heavy-mineral variations on the south Texas outer continental shelf, Gulf of Mexico: Journal of Sedimentary Petrology, v. 48, p. 269.

Grimes, D.J., and Marinzino, A.P., 1968, U.S. Geological Survey, Circular 591.

Hudson, T., Miller, M.L., Pickthorn, W.J., 1977, Map showing metalliferous and selected non-metalliferous mineral deposits, Seward Peninsula, Alaska: U.S. Geological Survey, Open-file Report 77-796B, 46 p.

________, DeYoung, J.H., Jr., 1978, Maps and tables describing areas of mineral resource potential, Seward Peninsula, Alaska: U.S. Geological Survey, Open-file Report 78-1-C, 62 p.

Hummel, C.L., 1977, Review of exploration geochemical surveys on Seward Peninsula, Western Alaska: U.S. Geological Survey Open-file Report 77-796D, 28 p.

Imbrie, J., 1963, Factor and vector analysis programs for analyzing geologic data: Office of Naval Research Technical Report 6, Geography Branch, p. 83.

Klovan, J.E. and Imbrie, J., 1971, Algorithm and FORTRAN IV Program for large-scale Q-mode Factor analysis and calculations of Factor scores: Mathematical Geol. 3, p. 61-77.

Kvenvolden, K.A., Weliky, K., Nelson, C.H., DesMarais, D.J., 1979, Submarine seep of carbon dioxide in Norton Sound, Alaska: Science, v. 205, No. 4412, p. 1264.

Mason, B., 1966, Principles of Geochemistry: John Wiley and Sons, Inc., New York, 329 p.

________, Berry, L.G., 1968, Elements of Mineralogy: W. H. Freeman and Company, San Francisco, California, 550 p.

McManus, D.A., Venkatarathnam, K., Hopkins, D.M., Nelson, C.H., 1977, Distribution of bottom sediments on the continental shelf, northern Bering Sea: U.S. Geological Survey Professional Paper 759-C, p. C1-C31.

Meisch, A.T., 1967, Methods of computation for estimating geochemical abundance: U.S. Geological Survey Professional Paper 574-B, p. B1-B15.

Miller, T.P., Grybeck, D., 1973, The geochemical survey of the eastern Solomon and southeastern Bendeleben Quadrangles, Seward Peninsula, Alaska: U.S. Geological Survey Open-file Report.

Nelson, C.H., Hopkins, D.M., 1972, Sedimentary processes and distribution of partiulate gold in the northern Bering Sea: U.S. Geological Survey Professional Paper 689, 27 p.

________, Pierce, D.E., Leong, K.W., Wang, F., 1975, Mercury distribution in ancient and modern sediment of northeastern Bering Sea: Marine Geology 18C, p. 91-104.

________, and Creager, J.S., 1977, Sediment budgets and displacement of Yukon River sediments from Berng Sea in the late Holocene.

________, Larsen, B.R., Larsen, M., Thor, D.R., Sedimentary characteristics of the Norton Basin sea floor, U.S. Geological Survey Open-file Report (in prep.).

Overstreet, W.C., Hamilton, J.C., Boerngen, J.G., Rosenblum, S., Marsh, W.R., and Sainsbury, C.L., 1974, Minor elements in nonmagnetic concentrates from Alaska: U.S. Geological Survey/G.D. 74-039, National Technical Information Service, PB-238'989, 434 p.

Patry, J.J., Larsen, B.R., Nelson, C.H., Heropoulos, C., 1977, Trace metal content of bottom sediment in northern Bering Sea: Quarterly Report of Principal Investigators, April-June 1, _in_: Environmental Assessment of the Alaskan Continental Shelf, Environmental Research Laboratory, Boulder, Colorado, NOAA, U.S. Dept. of Commerce, Contract RK6-6074, 10 p.

Patton, W.W., Jr., and Csejtey, B., Jr., 1971, Preliminary Geologic Investigations of eastern St. Lawrence Island, Alaska: U.S. Geological Survey Open-file report 52 p.

________, ________, 1971, Preliminary Geologic Investigations of western St. Lawrence Island, Alaska: U.S. Geological Survey Professional Paper 684-C, p. C1-C15.

________, ________, 1972, Analysis of stream-sediment and rock samples from St. Lawrence Island, Alaska, 1966-1971: U.S. Geological Survey Open-file Report, 78 p.

Peratis, A., et al., 1978, User Manual for the Surface Display Library: Dynamic Graphics, Inc., Berkeley, California.

________, et al., 1978, User Manual for the Surface Gridding Library: Dynamic Graphics, Inc., Berkeley, California.

Reed, W.E., Kaplan, I.R., 1977, The chemistry of marine petroleum seeps: Journal of Geochemical Exploration, No. 7., p. 255-293.

Sainsbury, C.L., 1969, Geology and Ore Deposits of the Central York Mountains, western Seward Peninsular, Alaska: U.S. Geological Survey Bulletin 1287, 101 pages.

________, 1975, Geology, ore deposits, and mineral potential of the Seward Peninsula, Alaska: U.S. Bureau of Mines, Open-file Report, 108 p.

Sheth, M., 1971, A heavy mineral study of Pleistocene and Holocene sediments near Nome, Alaska: U.S. Geological Survey Open-file Report, 82 p.

Sichel, H.S., 1947, An experimental and theoretical investigation of bias error in mine sampling, with special reference to narrow gold reefs: Laudon, Inst. Mining Metallulrgy Trans., v. 56, p. 403-474.

Sienko, M.J., Plane, R.A., 1961, Chemistry: McGraw Hill Book COmpany, Inc., New York, 673 p.

Van Trump Jr., G., 1975, Factor analysis (Q-mode)-STATPAC, Program D0097: U.S. Geological Survey Computer Program Documentation (unpub.).

Venkatarathnam, K., 1971, Heavy minerals on the continental shelf of the northern Berng Sea: U.S. Geological Survey Open-file report, 93 p.

Yen, T.F., 1975, The role of trace metals in petroleum: Ann Arbor Science Publishers, Ann Arbor, Michigan, 221 p.

ASPECTS OF SIZE DISTRIBUTIONS, CLAY MINERALOGY, AND GEOCHEMISTRY OF SEDIMENTS OF THE BEAUFORT SEA AND ADJACENT DELTAS, NORTH ARCTIC ALASKA

by

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Final Report
Outer Continental Shelf Environmental Assessment Program
Research Unit 529

September 1982

ACKNOWLEDGEMENTS

This research was supported by the Bureau of Land Management through interagency agreement with the National Oceanic and Atmospheric Administration under which a multiyear program responding to the needs of petroleum development of the Alaskan continental shelf is managed by the Outer Continental Shelf Environmental Assessment Program. Some of the data integrated in this report were generated through research grants from the Office of Marine Geology, U.S. Geological Survey, Menlo Park, through contract No. 14-08-0001-14827, by the State of Alaska appropriation to the Institute of Marine Science, University of Alaska, Fairbanks, the U.S. Environmental Protection Agency (Grant R801124-03), and the NOAA Alaska Sea Grant Office.

Grateful thanks are due J. A. Dygas, R. W. Tucker, M. D. Sweeney, J. Helmericks, L. H. Larsen, and H. V. Weiss for their help in sample collection and studies in the field. I am indebted to P. W. Barnes and E. Reimnitz for providing grab and vibrocore samples, and to T. Osterkamp for the ice core samples. I have profited from a number of discussions with D. M. Hopkins on various aspects of the study. Identification of microfossils in the vibrocores was done by R. Nelson, K. McDougall, E. Brouwers, and L. Marincovich, and this help was kindly arranged through D. M. Hopkins. The grain size analyses on the vibrocore samples were kindly run by Wieslawa Wajda. The sedimentation rate measurements and investigations on the erratic boulder petrology are part of joint studies with H. V. Weiss and T. C. Mowatt, respectively. The section on the geochemical partitioning of metals constitutes part of the ongoing M.S. thesis work of M. D. Sweeney. I appreciate the help and encouragement received from the OCSEAP Arctic Project Office particularly from G. Weller, W. Sackinger, and D. Norton, and from J. H. Kravitz of the NOAA-OCSEAP Office (Boulder, Colorado). Logistic support in the field was coordinated through D. L. Brooks. The meticulous attention and assistance from Helen Stockholm and her colleagues from the Publications Department of the Institute of Marine Science, in the preparation of this report, is gratefully acknowledged.

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INTRODUCTION

This report concerns primarily with the description of the surficial or near surficial sediments of the continental shelf of the Alaskan portion of the Beaufort Sea. The distributional patterns of the granulometric, clay mineralogic and chemical compositions of the surficial sediments are displayed on maps. The characteristics of the size distributions of particles are discussed in light of the present hydrodynamic and ice conditions and on the limited knowledge of the late Pleistocene history of the Beaufort Sea continental shelf. Clay mineral compositions are discussed in terms of the possible terrigenous sources and their dispersal by prevailing currents. Baseline concentrations and yearly fluxes of a suite of metals pertaining to sediments are established. An attempt is made to understand the partitioning patterns of the metals in various sediment fractions.

In this report an effort is made to relate the granulometric composition of surficial sediments to potential engineering hazards in the Alaskan Beaufort Sea. However, some of the foregoing discussions must be considered somewhat speculative, in view of the fact that no specific complementary measurements of the engineering properties of substrates were made. The potential usefulness of mapping the surficial geology of any marine area, to provide a basis for presenting and understanding some of the hazards that may be associated with engineering construction activities, was lucidly discussed (with special reference to the Canadian Arctic) elsewhere by Pelletier (1979).

Additional discussions in this report refer to the sedimentation rate measurements in the lagoons, possible mechanism for the unusual concentrations of sediments in sea-ice, and the origin and stability of the barrier island-lagoon systems.

This report should provide baseline data to detect and, possibly also provide criteria to predict impacts of anthropogenic activities in the North Arctic Alaska.

Salient features of the regional climate, geology and hydrography for the Beaufort Sea nearshore, North Arctic Alaska were earlier summarized by Naidu and Mowatt (1974) and Northern Technical Services (1981), and therefore these will not be repeated here.

MATERIALS AND METHODS

All data available since 1972 (Dygas *et al.*, 1971; Tucker, 1973; Barnes, 1974; Alexander *et al.*, 1975; Naidu, 1979, 1982; and Naidu and Mowatt, 1974, 1975a, 1975b, 1976 and 1982) on the size distributions of sediments were collated and integrated into this paper. The textural data gathered by Carsola (1954), however, were purposely excluded because the calculation of grain size statistical parameters by him were based on Inman's method (1952), which was significantly different than those adopted since 1970 (e.g., Folk and Ward, 1957). This synthesis is based on size analysis of 330 grab or core top sediment samples from the open Beaufort Sea (Fig. 1), and about 100 analyses of grab sediment samples and 10 vibrocore samples from the deltaic environment (e.g., lagoons, sound, bays, beaches, dunes, etc.). The locations of the latter suite are shown in Figures 2a, 2b, 3, 4 and 5a. The granulometric analyses were achieved by the usual sieve-pipette technique (Folk, 1968). Each of the values of gross textural attributes (e.g., percentages of gravel, sand, silt, clay

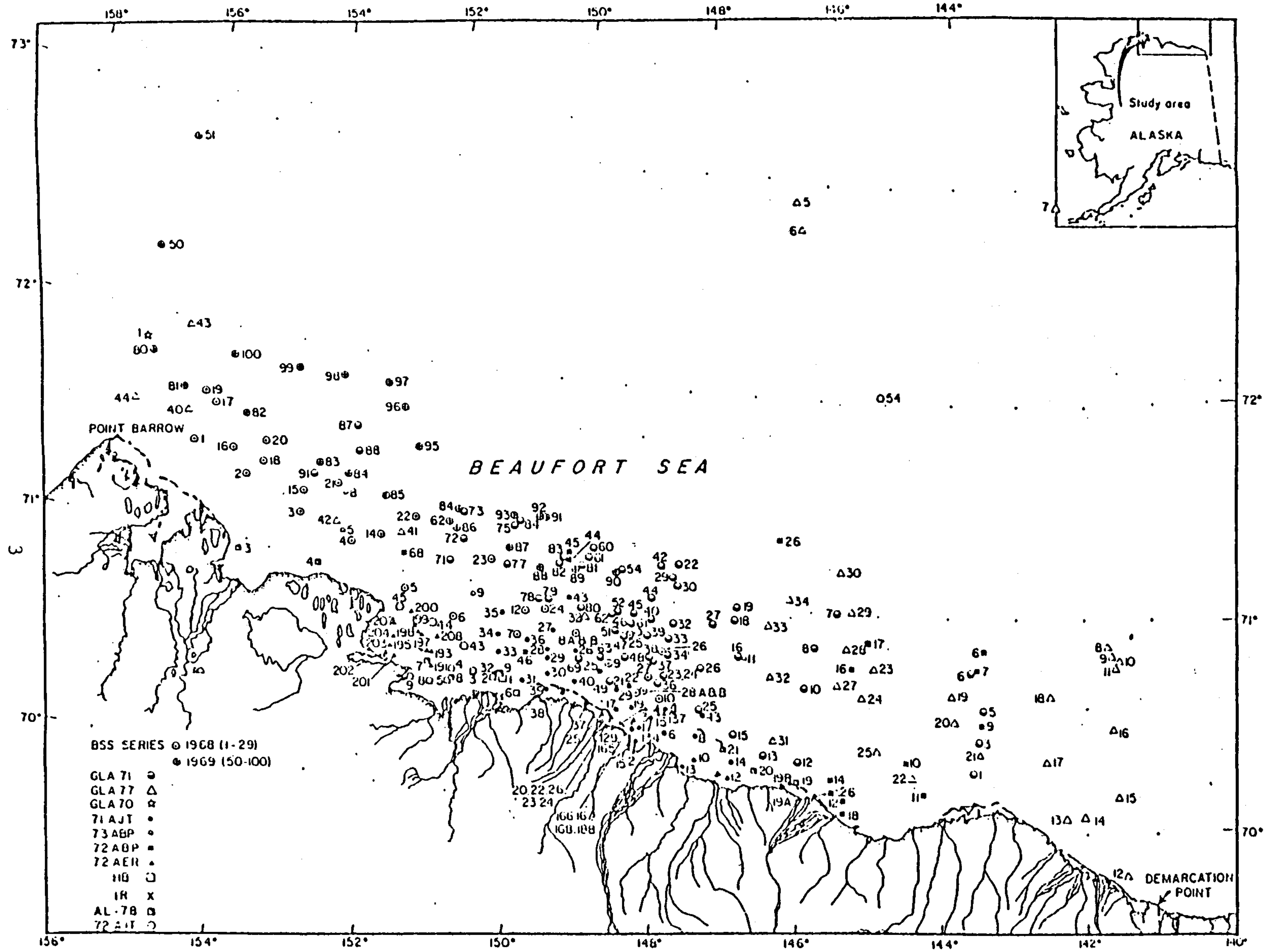

Figure 1 . Station locations for Beaufort Sea.

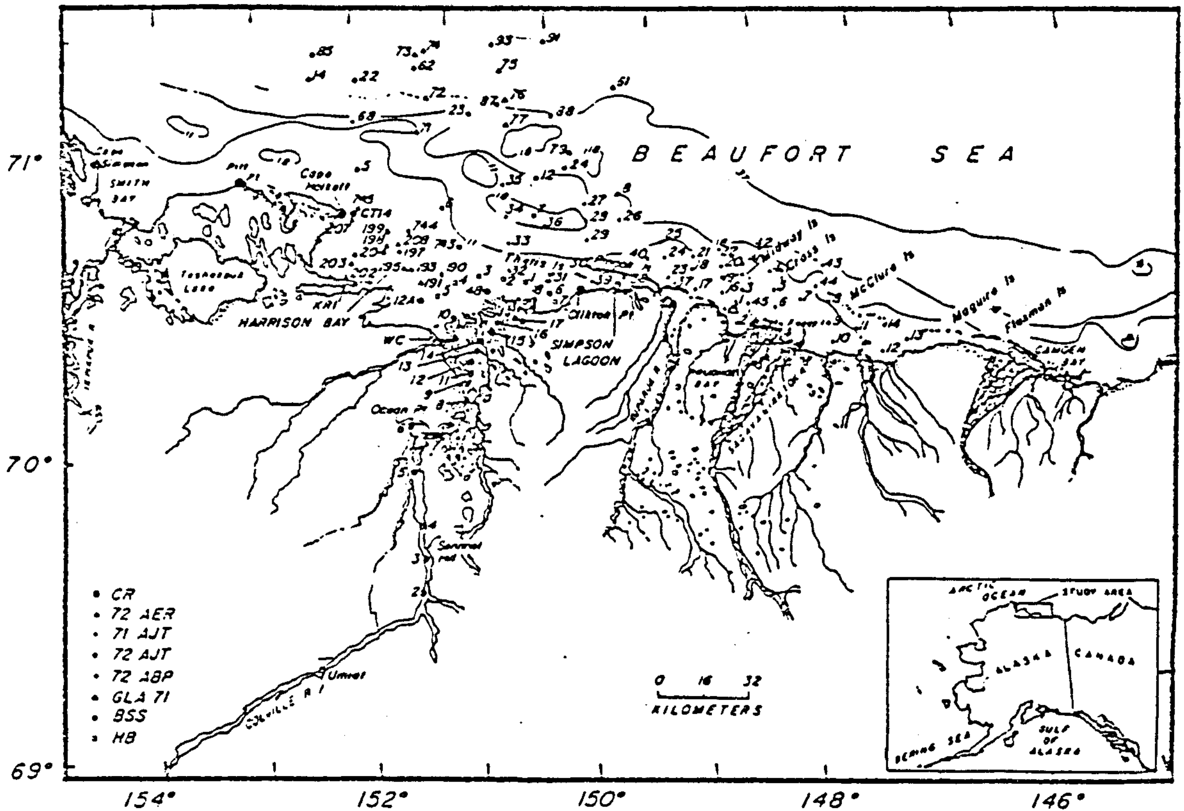

Figure 2a. Map of the North Slope of Alaska. showing the deltaic area of study and locations of sediment samples. The depth contours are in meters.

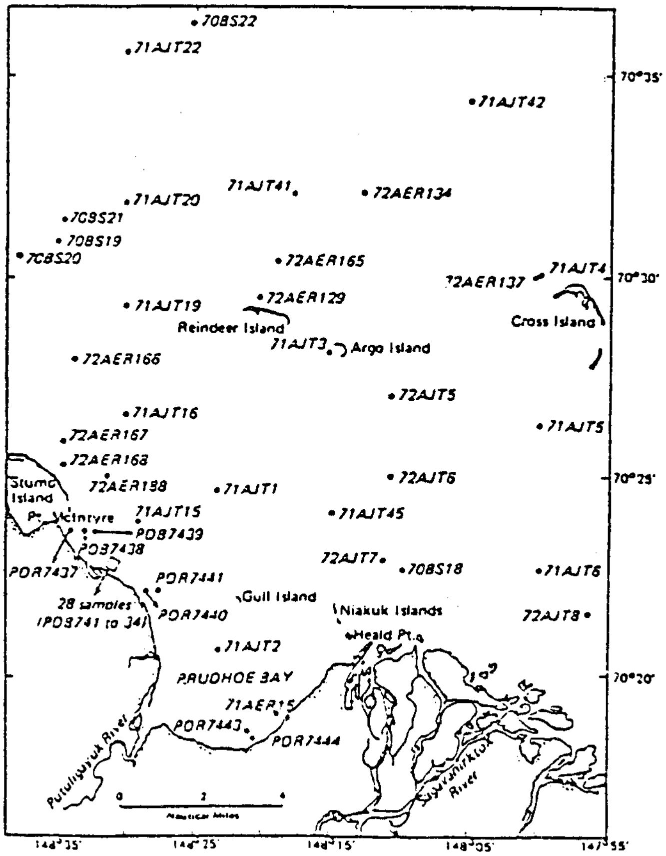

Figure 2b. Locations of sediment samples in the Prudhoe Bay and adjacent shallow marine environment of north arctic Alaska.

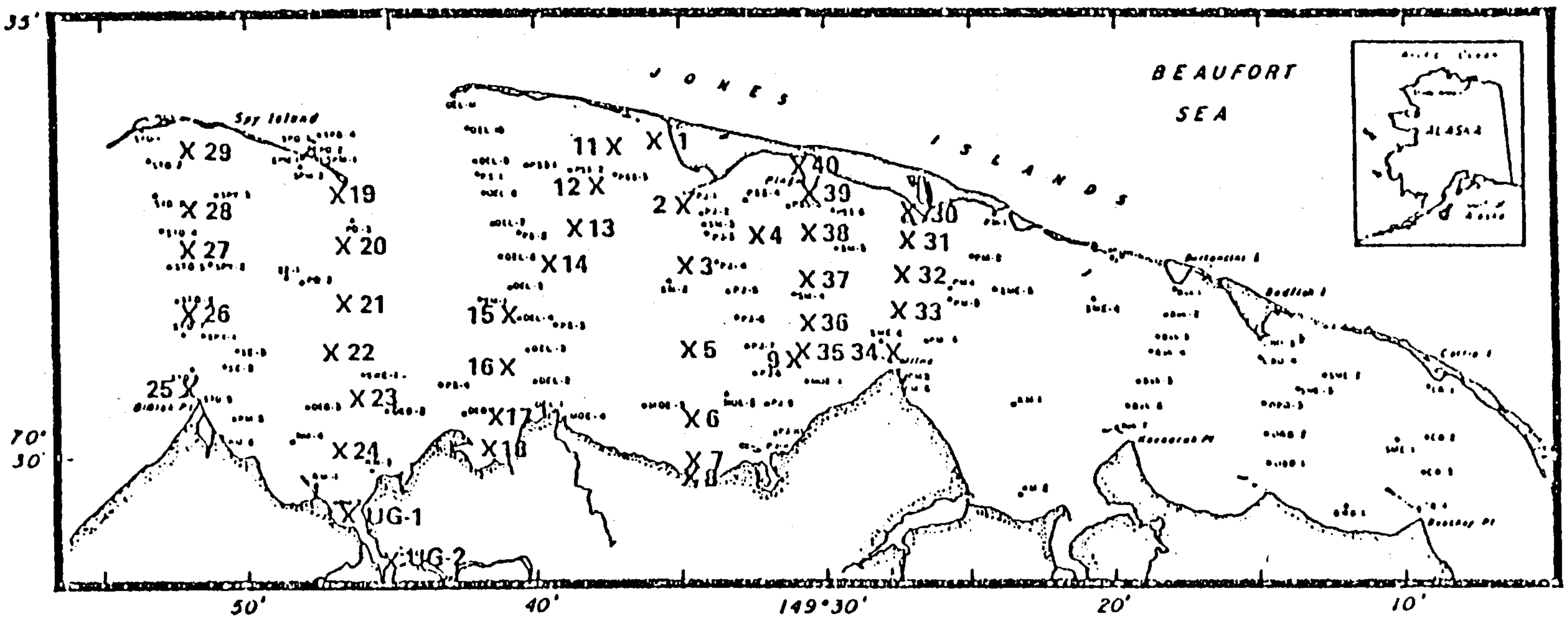

Figure 3. Sample locations in Simpson Lagoon. Locations depicted by heavy crosses indicate samples collected in Summer 1977. The remaining samples were collected by Tucker (1973) and size analysis data on them are already available.

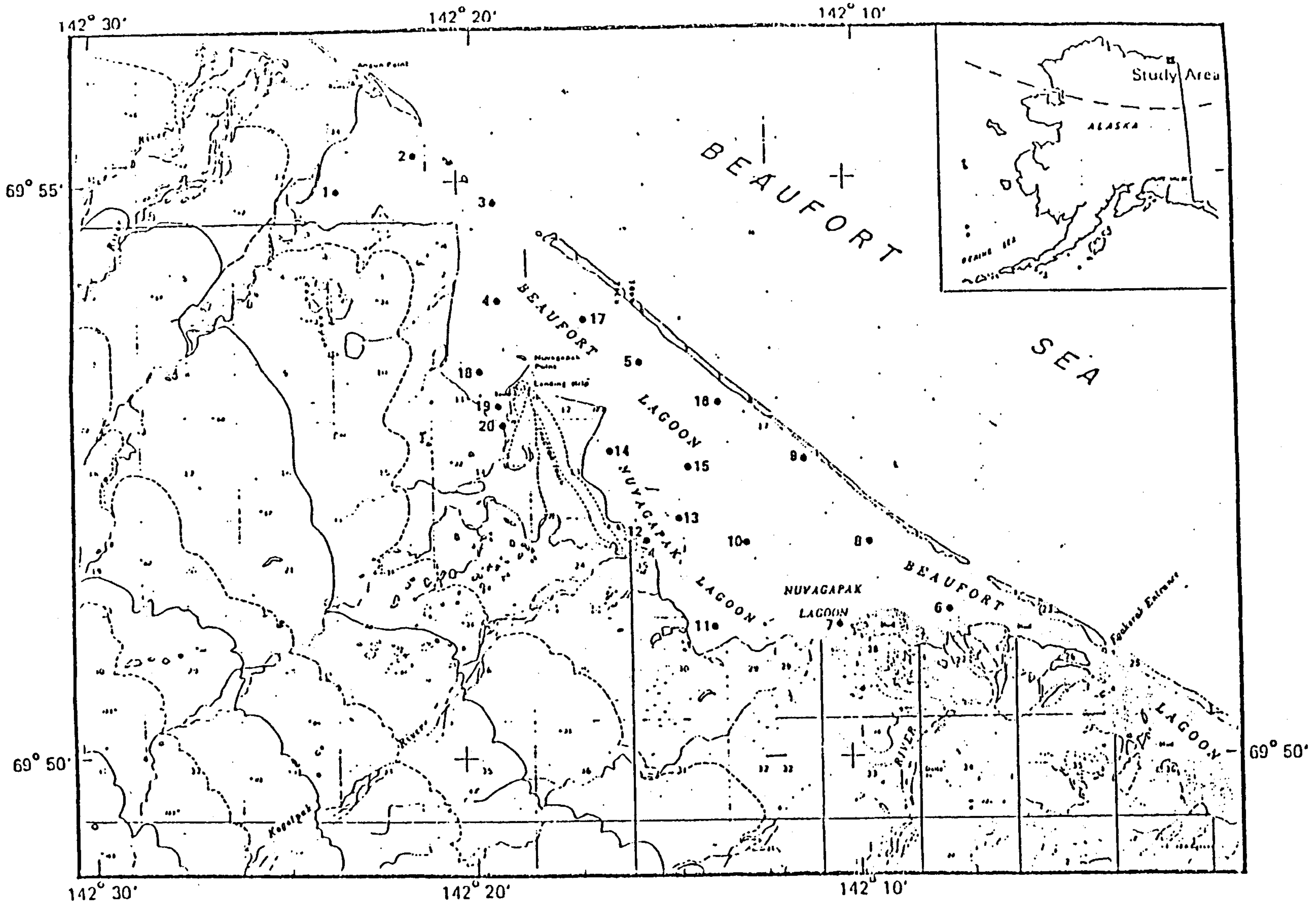

Figure 4. Map showing the locations of sediment samples from the Beaufort Lagoon, north arctic Alaska.

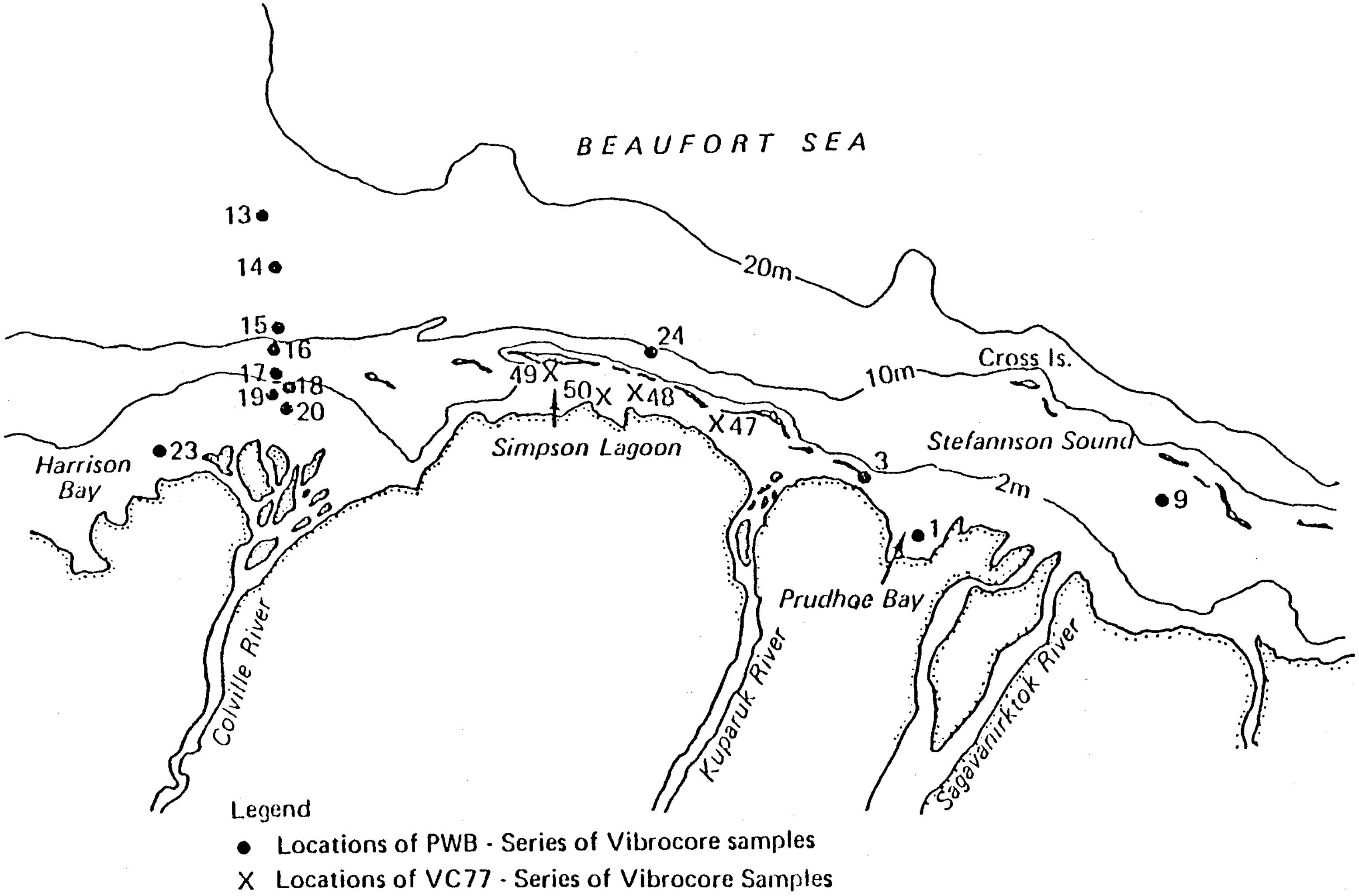

Figure 5a. Locations of vibrocore sediment samples that have been collected by Drs. P. W. Barnes and E. Reimntz of the U.S. Geological Survey in 1976 and 1977. Splits of core samples from locations depicted by heavy dots have been provided to us for study.

and mud) as well as two conventional grain size statistical parameters, mean size and graphical standard deviation (after Folk and Ward, 1957) were digitally transferred onto maps of the Beaufort Sea and isopleths plotted.

The clay mineral analytical procedures were discussed in detail elsewhere (Naidu and Mowatt, 1974); therefore, only a brief description follows. The sediment was initially treated with H_2O_2 to remove organic matter, and then dispersed in deionized-distilled water into suspensions. Dispersion was achieved by repeated washing. The < 2 μm equivalent spherical diameter (e.s.d.) size fraction from each of the sediment suspensions was separated by settling techniques. The < 2 μm fractions were smeared on glass slides (Gibbs, 1965) and air dried. Prior to, as well as following glycolation by vapor phase exposure for 24 hours, the slides were run for clay mineral analysis on a Phillips-Norelco X-ray diffractometer with a scintillation detector, using Ni-filtered copper K_α radiation.

Criteria adopted for the identification of the various clay minerals were outlined elsewhere (Mowatt *et al.*, 1974; Naidu and Mowatt, 1974). The Expandable Group included all clay minerals that expanded upon glycolation and displayed a basal diffraction peak in the vicinity of 17 Å. Given the large number of samples involved, and the reconnaissance nature of this initial work, we have refrained from attempting to resolve further the various expandable mineral phases (e.g., vermiculites, mixed-layer phases, etc.) besides smectite that might be embraced within the above group. However it should be noted that some of the expandable clay mineral components exhibit characteristics similar to materials described by Weaver (1958a) in Ordovician Womble Shale of southeastern Oklahoma, and, hence are most likely "degraded" (depotassicated) detrital illites. This is substantiated by studies (Mowatt *et al.*, 1974) on several unglycolated and glycolated clay samples that were initially saturated with either 1N $MgCl_2$ or KCl solutions. Although we recognize the potential value of more detailed characterization (Hayes, 1973), no attempt was made to resolve and quantify the more complex mixed-layer clay mineral phases, minor amounts of which appear to be present in some samples as illite-smectite or illite-chlorite, with varying amounts of "vermiculite". The term "illite" is used primarily in the sense of Brindley (in Brindley and Brown, 1980, p. 182), but includes various micas in the < 2 μm particle size range as well. Despite certain limitations, in particular with regard to interpretation of mixed-layering, the method adopted by Biscaye (1965) was followed for semi-quantitative estimation of clay minerals. The relative abundances of chlorite and kaolinite were estimated on the basis of the 3.5 Å region diffraction peaks (Biscaye, 1964). Overall analytical precision was ± 5 percent. The relative abundances of the various clay minerals and the kaolinite/chlorite ratios were digitally transferred onto maps of the Beaufort Sea and isopleths plotted.

Carbonate in the sediment was determined manometrically (Hülsemann, 1966). Organic carbon abundance in the sediment was calculated from the difference between total carbon and carbonate carbon. Total carbon was estimated in a LECO, TC-12 automatic carbon determinator.

Baseline trace element analyses were performed on gross sediment samples. For this purpose a representative portion of the gross sediment sample was taken, dried at 110°C and pulverized into fine powders using an agate mortar and pestle. Subsequent elemental analyses were on 10% HNO_3

solutions of HF-HNO_3 digests of sediments (Rader and Grimaldi, 1961), by atomic absorption spectroscopy using a Perkin-Elmer, Model 603, unit. Analytical precision for the gross metal analysis was better than 12%, and the accuracy was checked with reference to U.S.G.S. Standard rock powders G-2, AGV-1 and BCR-1 (Table 1).

Selective leaching experiments (see results section) were done on lightly disaggregated sample splits to acquire information on the partitioning of eight metals (e.g. Fe, Mn, Zn, V, Cr, Co, Cu and Ni) among the sediment constituents. The metal analyses were performed using the Model 603, and the Perkin-Elmer Model 5000 unit with HGA 500 graphite furnace.

Thin sections of 105 selected rock chip specimens of erratic boulders and cobbles strewn along the beaches and coastal plain were studied under a petrographic microscope, and the rock identification was supplemented by X-ray diffraction analysis as appropriate. The depositional rates were derived from ^{210}Pb measurements as a function of core depth, using the approach described by Koide *et al.* (1972). The method for ^{210}Pb analysis was similar to that described by Nittrouer *et al.* (1979). Coarse fractions (> 62 μm) and microfossils of various sections of two of the vibrocore samples (V-48 and V-49) were studied under a binocular microscope. Representative microfossil specimens were submitted to Dr. D. M. Hopkins of the U.S. Geological Survey (Menlo Park) for identification by the survey personnel.

In attempting to understand the processes of sediment entrainment in sea ice of lagoons and sounds, four samples of ice cores were taken from the Stefansson Sound, and 6- to 7-cm long continuous sections of the ice

TABLE 1

AVERAGE CONCENTRATIONS (μg/g, except for Fe which is in 10^4 μg/g) OF SOME HEAVY METALS IN STANDARD U.S. GEOLOGICAL SURVEY ROCKS: AGV-1, BCR-1, & G-2.

U.S.G.S. Standard Sample	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
AGV-1								
This Study -1		9.6		4.67	15.0	13.0	59.2	99
This Study -2	127	12.8	767	4.79	14.6	14.5		
Reported Literature Values								
Flanagan, 1969	121	12.9	728	4.76	15.5	17.8	63.7	112
Flanagan, 1973	125	12.2	763	4.73	14.1	18.5	59.7	84
Range (Flanagan, 1969)	70-171	8-45	640-870	4.26-5.21	10-30	11-27	52-83	64-304
BCR-1								
This Study -1		10.7			33.7	5.9	17.5	136
This Study -2	500	14.6	1425	8.98-8.94	35.7	6.4		
Reported Literature Values								
Flanagan, 1969	384	16.3	1350	9.44	35.5	15.0	22.4	132
Flanagan, 1973	399	17.6	1406	9.37	38	15.8	18.4	120
Range (Flanagan, 1969)	120-700	8-45	1040-1600	9.02-9.97	29-60	8-30	7-33	94-278
G-2								
This Study	38	10	258	1.58	15	17	7.6	88
Reported Literature Values								
Flanagan, 1969	37	9.0	265	1.93	4.9	6.4	10.7	74.9
Flanagan, 1973	35.4	7.0	260	1.85	5.5	5.1	11.7	85
Range (Flanagan, 1969)	26-60	5-29	180-360	1.53-2.44	2-21	2-14	<2-17	42-138

cores were split, thawed and the particle concentrations analyzed. One red/dark pink granite sample from the Flaxman Island was submitted to Dr. D. L. Turner of the University of Alaska for dating by the K-Ar method. Representative portions of two basal peats, one separated at 150 cm from the top of the vibrocore V-49, and the other from under an 84-cm overburden of sand and gravel exposed in a section at the seaward beach of the spit west of Pingok Island, were dated by the C-14 method.

For the estimation of sedimentation rates in Simpson Lagoon seven short (15 to 33 cm long) core samples were collected from the western and central lagoon (Fig. 5b). All cores were obtained from more than 2 m depth to avoid sampling of sediment sequences that might have been disturbed by ice gouging. The westernmost core sample was retrieved by a Phleger gravity corer and the others by a manually driven unit. Sedimentation rates were derived without benefit of correction for the quantity of background-supported ^{210}Pb. Such a correction was not possible because background-supported ^{210}Pb concentrations could not be obtained as the cores were quite short and facilities for direct measurement of ^{226}Ra were not available with us for every core split. Thus, the rates presented represent upper limits of sedimentation.

GRANULOMETRIC COMPOSITION

Continental Shelf Sediments

The broad regional variations in the granulometric compositions of the Beaufort Sea substrate are graphically displayed in Figures 6 to 12.

Generally, the middle and outer continental shelf areas are carpeted by poorly-sorted sandy muds (with almost equal proportions of silt and

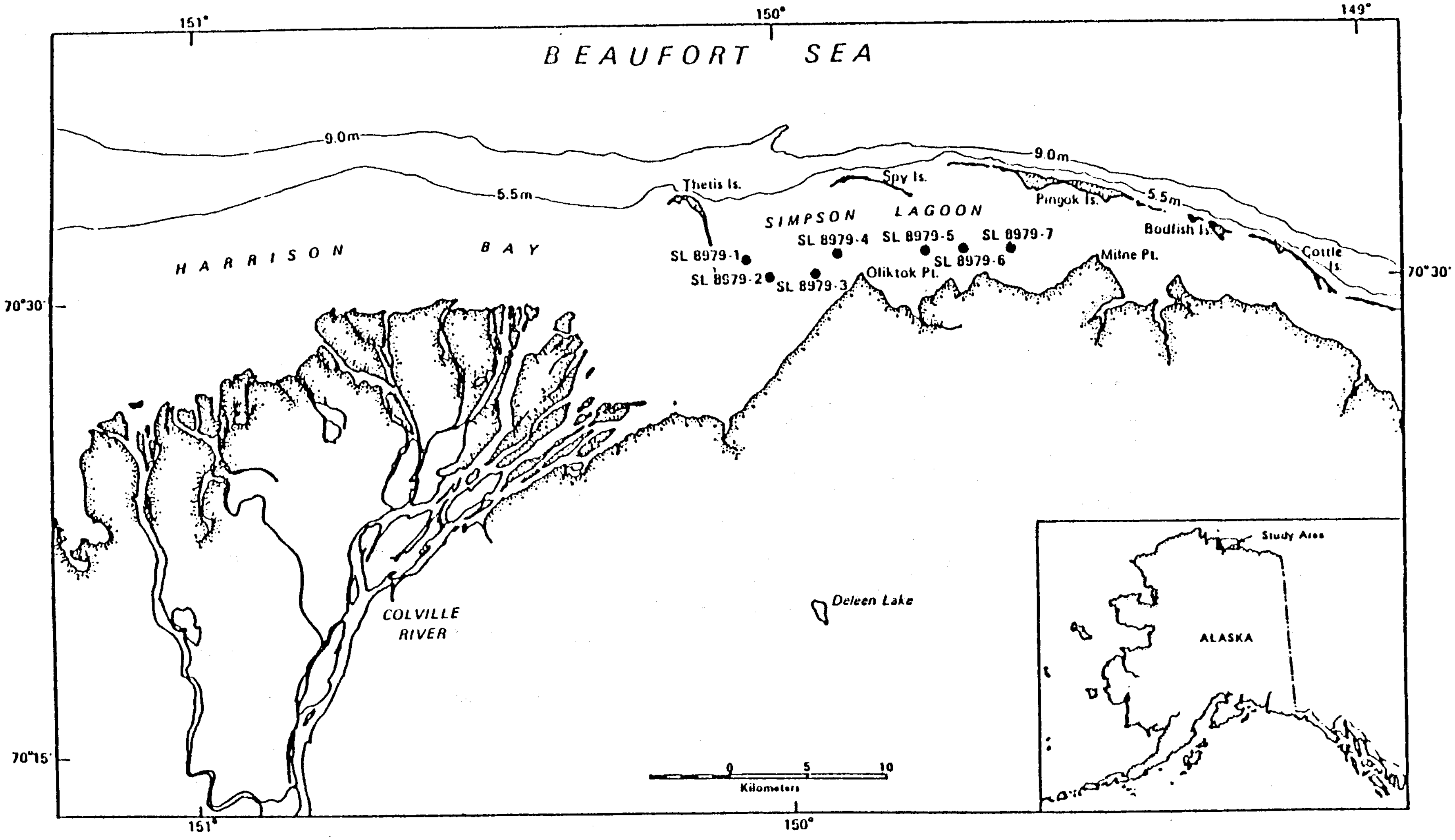

Figure 5b. The area of study showing locations of the core samples in the Simpson Lagoon, east Harrison Bay and Deleen Lake.

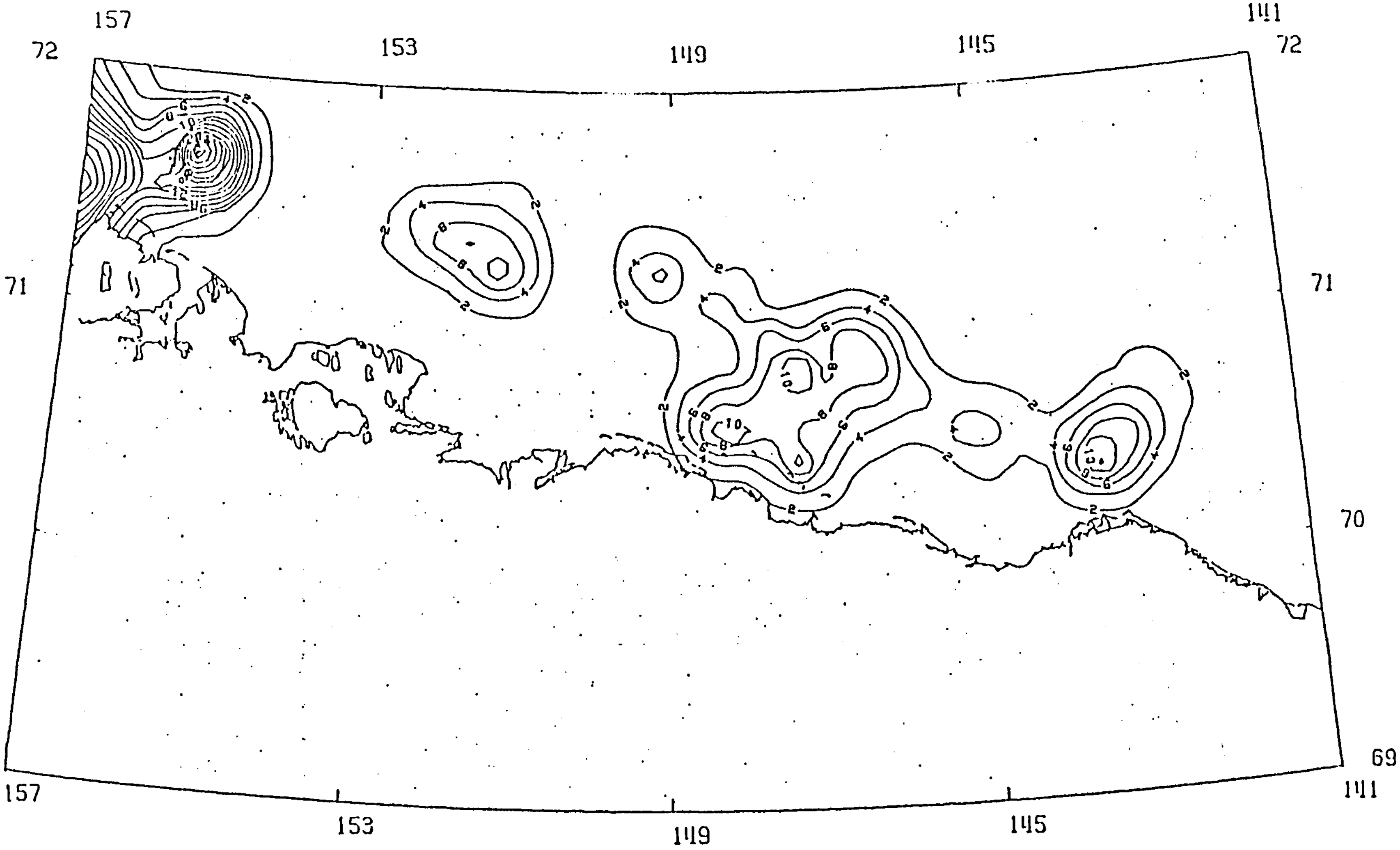

Figure 6. Map of the Beaufort Sea showing the distribution of gravel concentrations (wt. %).

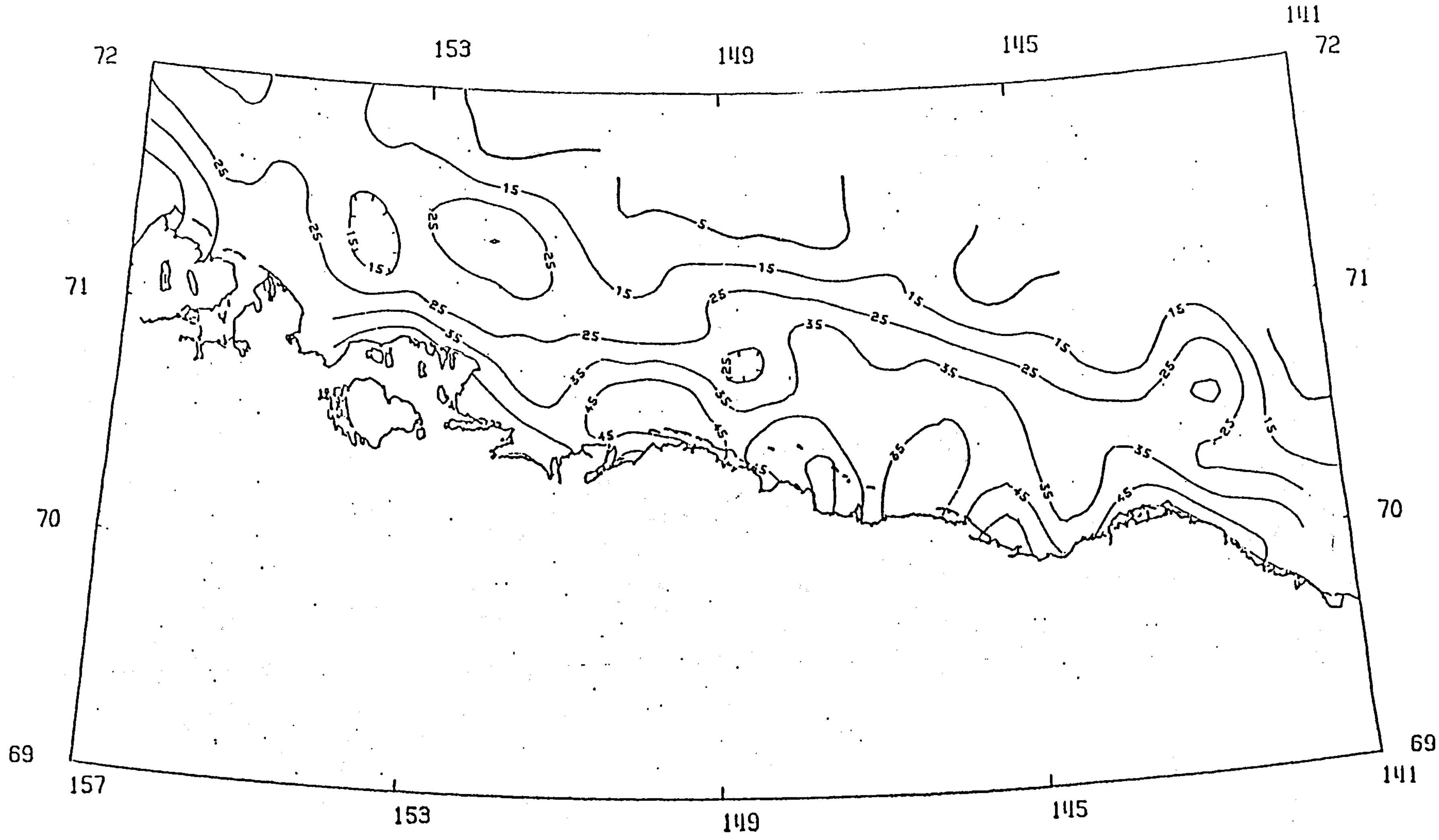

Figure 7. Map of the Beaufort Sea showing the distribution of sand (wt. %).

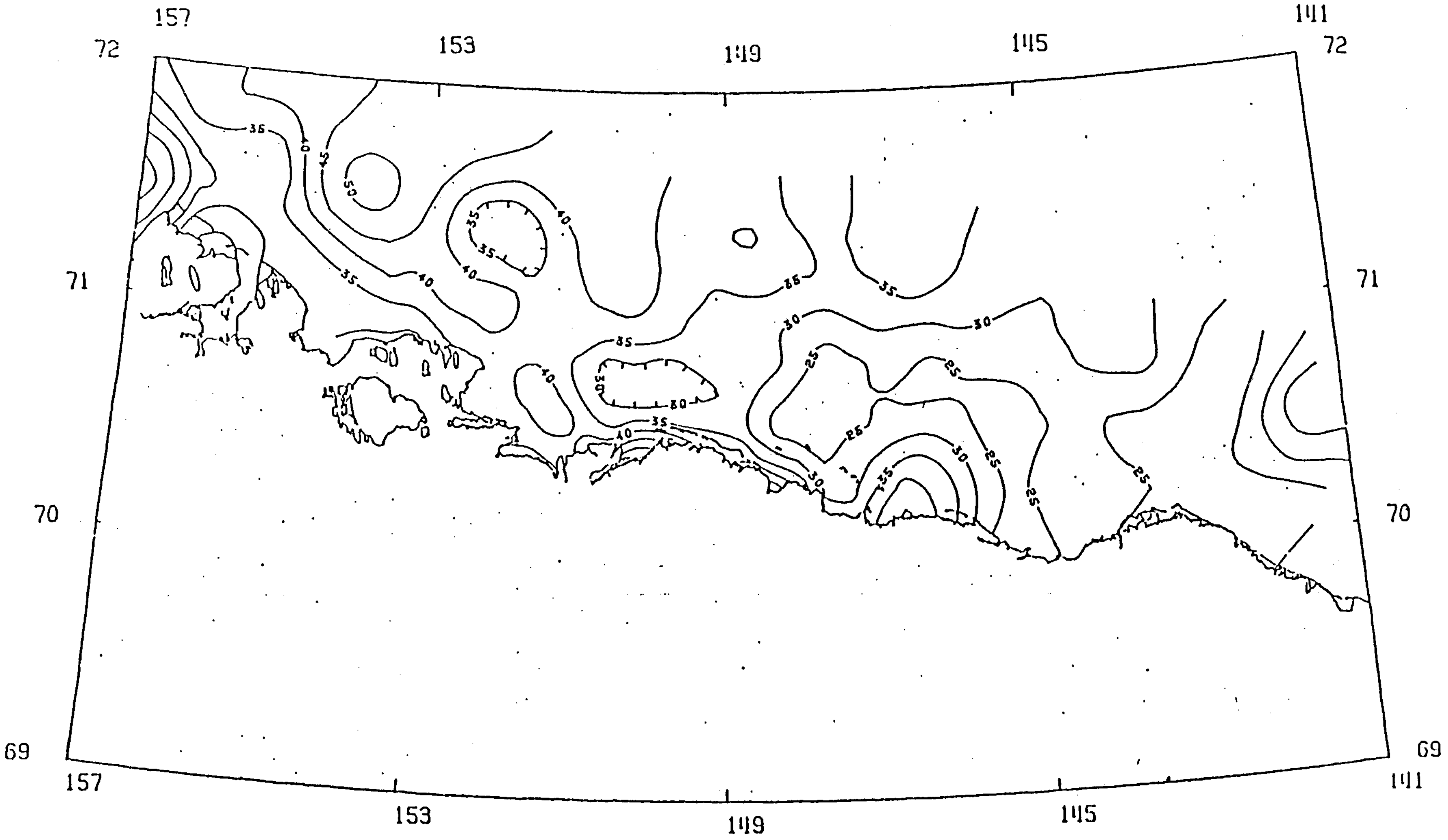

Figure 8. Map of the Beaufort Sea showing the distribution of silt (wt. %).

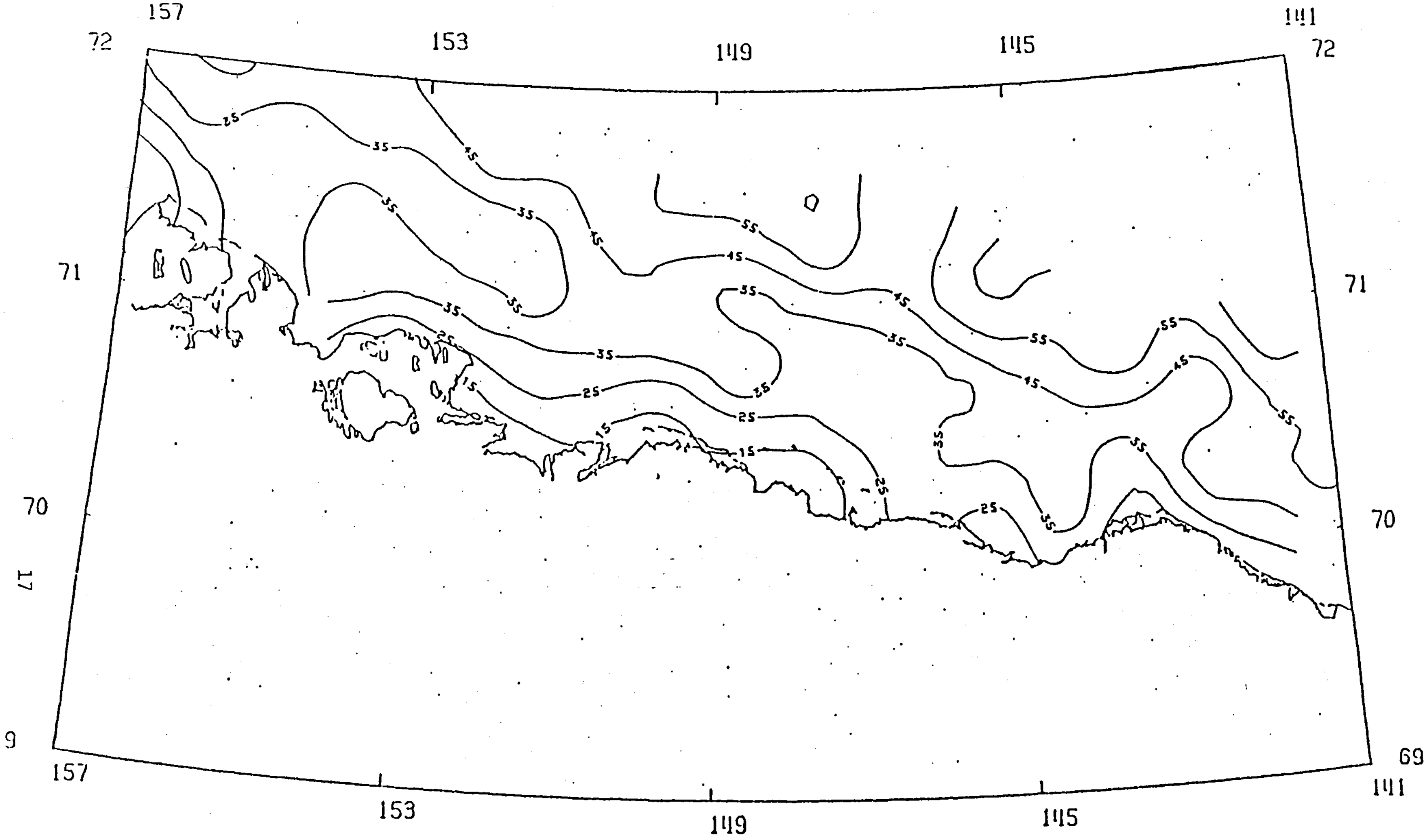

Figure 9. Map of the Beaufort Sea showing the distribution of clay (wt. %).

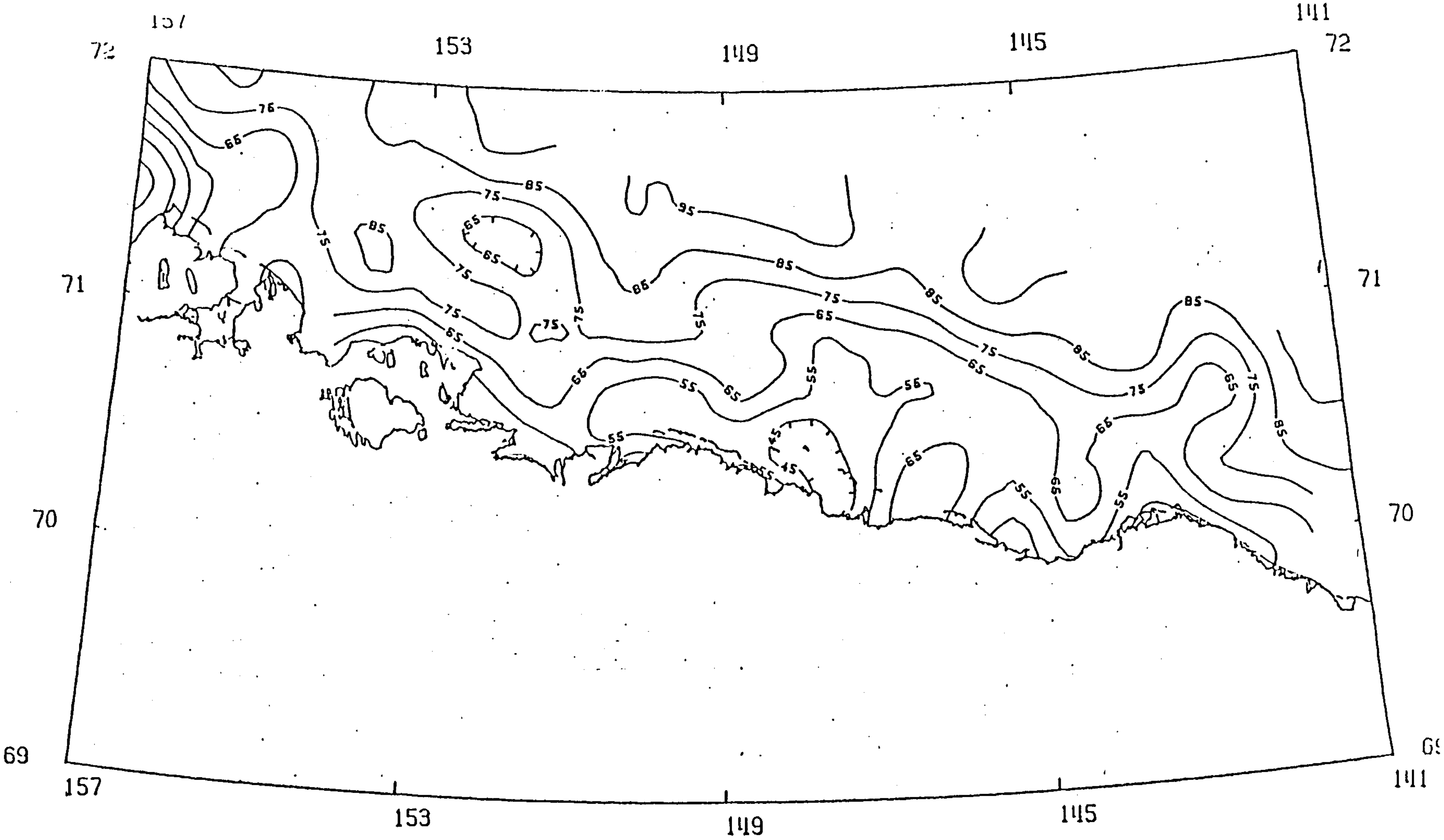

Figure 10. Map of the Beaufort Sea showing the distribution of mud (wt. %).

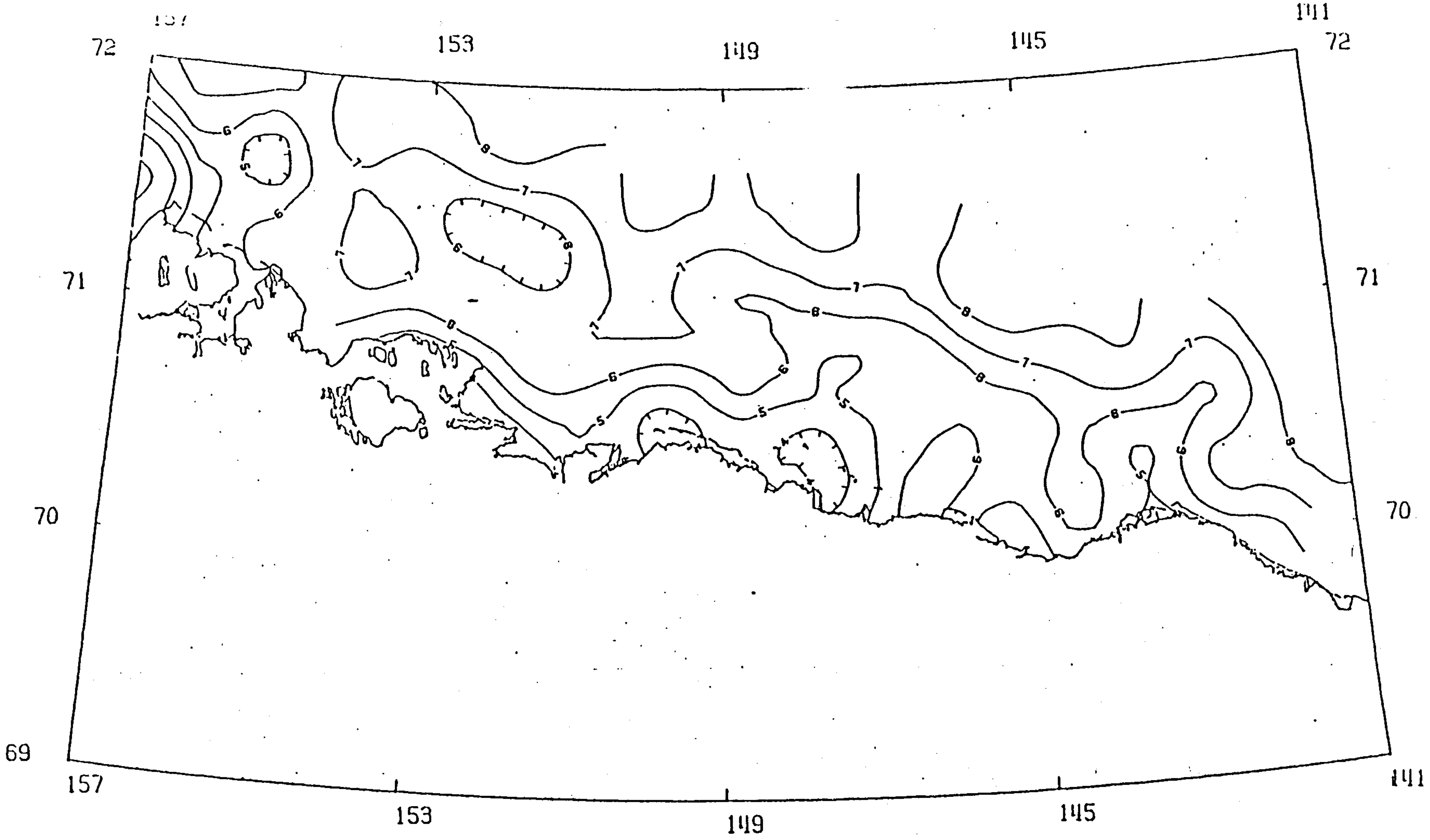

Figure 11. Map of the Beaufort Sea showing the variation of the phi mean size (M_z) of the sediments.

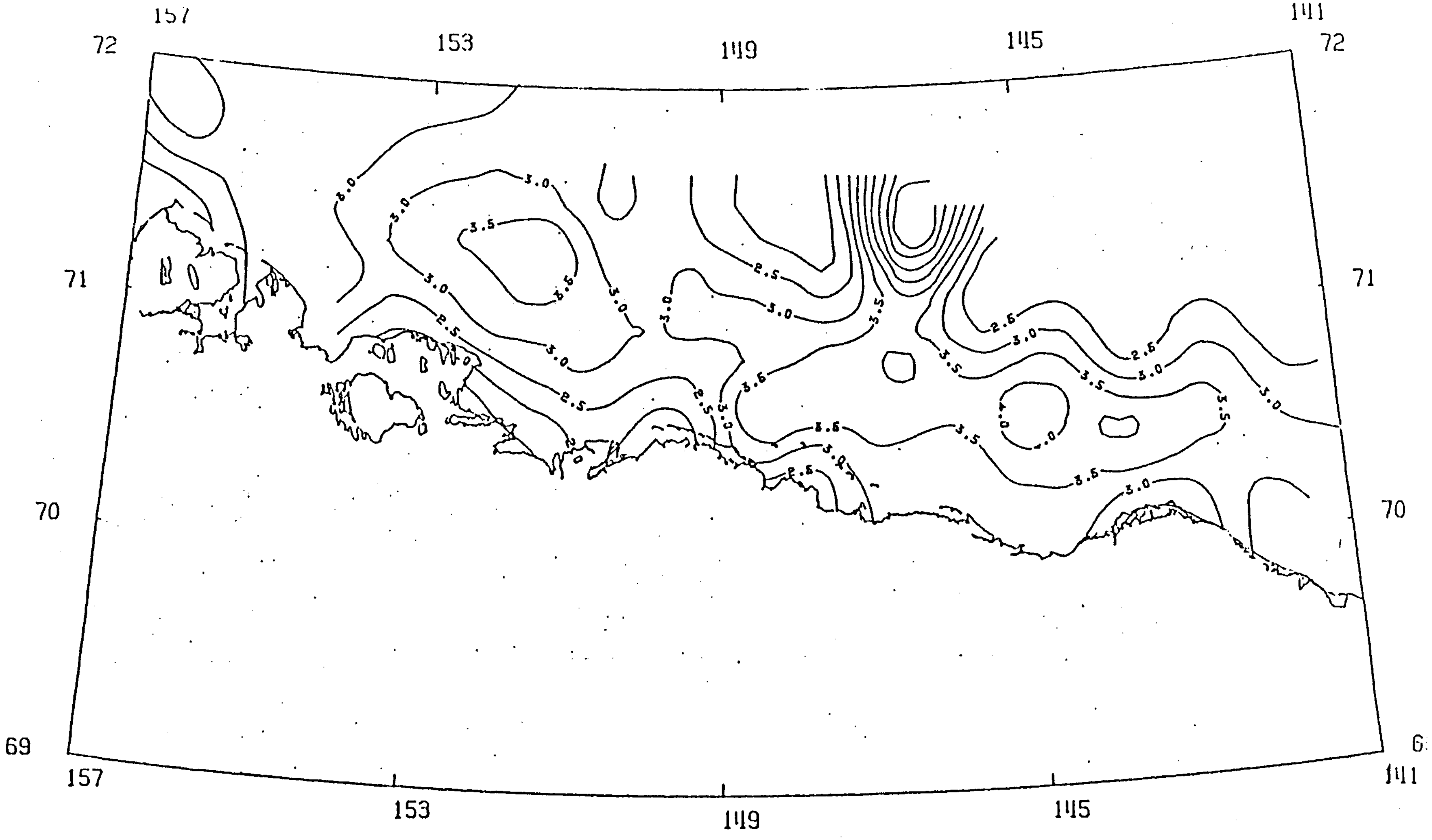

Figure 12. Map of the Beaufort Sea showing the variation in sorting of sediments.

clay). Invariably size distribution curves of these sediments are positive-skewed to nearly symmetrical and platykurtic. The inner shelf and inland bays are characterized by silty-sand to sandy-silt substrate with minor clay and occasional gravel-size particles. No unequivocal lithological gradation is observed across the Beaufort Sea shelf. There are a few extensive regions within the middle shelf of the eastern Alaskan Beaufort Sea where significant amounts of gravel are encountered (Fig. 6). Naidu (1974) and Naidu and Mowatt (1974) have discussed the various possible modes of origin of these gravel deposits. The consensus of the above authors and the majority of geologists working in the Beaufort Sea area would seem to suggest that the gravels are ice-rafted deposits. However, some differences in opinion exist as to whether the gravels are contemporaneously transported by ice or are relict ice-rafted clastics laid down during Pleistocene higher sea-levels. I believe that for the most part the gravels on the Beaufort Sea shelf are relict. This conclusion is primarily based on the observations that the transport presently of gravel by ice-rafting is insignificant (Naidu, 1974). Furthermore, several of the gravels have a thick, horizontal rim of Fe-Mn encrustations (Naidu, 1974) implying that these gravels have been lying undisturbed on the Beaufort Sea floor for quite a while. These relict deposits have remained exposed on the shelf surface because they have not been blanketed by contemporary muds and/or sands. In this context I agree with Carsola's (1954) contention that the eastern shelf of the Alaskan Beaufort Sea is essentially devoid of supply of mud from the Mackenzie River. Likewise it would also seem that although large volumes of terrigenous mud are being ice-rafted offshore from the Alaskan coast, the transport and deposition of this mud is apparently bypassed in the shelf area of the Alaskan eastern Beaufort Sea. It is believed that the western Beaufort is the depositional site for the coastal-derived mud. Thus, it would seem that the presence of relatively higher amounts of gravel in the eastern shelf perhaps does not reflect a state of unusually higher wave-current regime in that area. Therefore, engineering construction in this area may not be faced with any special problems at least as far as hydrodynamic conditions are concerned. However, the occurrence of the gravels may offer greater resistance and thus impede drilling operations or pile driving. Nowhere on the shelf outcrops of rocks were encountered, which means that for foundation concerns special care must be exercised in designing shallow engineering structures.

The poorly-sorted nature of the central and outer continental shelf sediments are probably a resultant of reworking and mixing of various sedimentary units that is brought about by ice gouging action (Reimnitz and Barnes, 1974; Reimnitz *et al.*, 1972, 1973, 1977) and bioturbation. I am, however, not aware how frequently any area on the Beaufort Sea shelf is exposed to the bulldozing effect of grounded ice, although some attempts have been made to estimate this by Barnes and Reimnitz (1979). This later information would be of potential use in the designing of offshore engineering structures, for the effects of ice keel dragging and undercutting by ice gouging, and the possible subsequent burial of pipelines, cables, as well as footings (that may be placed on the sea floor) by the gouged sediment could be substantial.

No volumetric estimates are available on the gravel deposits of the Beaufort Sea continental shelf as a potential source for building material. Considering the extensive deposits more readily available on the adjacent coastal plain (in paleofluvial channels), I believe that exploitation of the shelf gravels, at least at present, may not prove very cost effective. Additionally, although the gravel deposits on the shelf seem to be quite extensive they occur typically as haphazard patches interspersed between stiff muddy deposits. Consequently, systematic exploitation of such deposits may pose a problem. In another context effects of any future dredging operation associated with gravel mining on the Beaufort Sea ecosystem are unknown, but could very well have deleterious impact on the ecosystem.

In the continental shelf of the Alaskan Beaufort Sea patchy deposits of an "over-consolidated", stiff mud are quite frequently observed either on the shelf surface or a few centimeters below. These muds have also been frequently encountered in the nearshore between the Reindeer Island and the Prudhoe Bay. Presumably these deposits are relict and their unusual stiff nature has been commonly attributed to progressive dewatering of the mud resulting from alternate freezing and thawing of the substrate brought about perhaps by periodic ice loading in the past. However, as far as I know no emphirical data are available to substantiate such a contention. At any rate it would seem important to note that these stiff muddy substrates which apparently do not exhibit thixotropic characteristics may provide a more favorable foundation for offshore engineering structures. However, in another context these areas may be specially hazardous. Because of the higher impermeability of the stiff muds, the surface of permafrost zone may be relatively shallower under these muds.

Recapitulation of the Pleistocene depositional history of the Beaufort Sea continental shelf region has been somewhat thwarted, primarily because of the absence of some typical submarine geomorphic clues (e.g. terraces/benches, paleofluvial channels, etc.) that can be related to episodes of climatically induced sea-level oscillations. The Pleistocene paleogeography of the adjacent shelf areas (e.g. Chukchi, east Siberian and Laptev Seas) are presumably better understood. However, it would seem unreasonable to extrapolate data from the latter areas to the Beaufort Sea, for the glacial history of the different shelf areas were probably not the same. I believe that the reconstruction of the Pleistocene history of the Beaufort Sea would be quite crucial to the development of any model to predict the distribution of permafrost in the coastal and upper continental margin areas of the Beaufort Sea. I am aware of the progress made on studies along this direction by Dr. D. M. Hopkins (RU 204 and 473), but do feel that serious data gaps still exist.

One of the justifications for carrying out size analysis of surficial sediments and preparing lithological maps was to identify different benthic substrate habitats for the Beaufort Sea. However, whether such habitats can actually be delineated or not on basis of sediment granulometric distributions can only be verified in cooperation with the benthic zoologists (e.g. Dr. A. G. Carey, RU 6). My responsibility was to generate the necessary grain size statistical parameters for sediment samples that were jointly collected with the biological samples, and this task has been fulfilled. I assume that sufficient number of sedimentological and benthic data sets are available for several of the stations that a meaningful attempt can be made to correlate the two. The outcome of such a comparative study will be of great potential use to managers who may look for guidelines applicable to the Beaufort Sea, to predict the changes in benthic communities resulting from possible large-scale alteration in substrate sediment budgets triggered by anthropogenic activities (e.g. causeway, dock, offshore island constructions, etc.).

Deltaic Sediments

Grain size statistical parameters for contemporary sediment samples from several subfacies of the deltaic complex in North Arctic Alaska were determined.

Results of the granulometric analysis of the various subenvironments are summarized in Table II. Evidently the deposits of the lagoon, bay and open shallow marine environments cannot be differentiated on the basis of the conventional grain size statistical parameters. However, the coastal beach, dune and deltaic plain sediments have distinctive lithologies. It is contended that with the exception for coastal dune (Table II) gross textural relationships do not seem to be rigorously definitive with regard to delineating paleosedimentary subfacies of polar deltas and this endorses our earlier observations (Naidu and Mowatt, 1975, 1976). The distinctive granulometric composition of North Slope coastal beaches is predominantly attributable to a local unique provenance (e.g., gravel-enriched Quaternary Gubik Formation underlying coastal tundra), rather than solely to depositional processes prevailing in the polar region. Naidu and Mowatt (1975, 1976) have suggested that other criteria, such as the overall three-dimensional framework of the deltaic sequences and sediment structures may be more reliable means to reconstruct the paleogeography of the shallow-marine and coastal areas of the Beaufort Sea. These restrictions must mean that any attempts to develop models on the basis of the geological history,

TABLE II. SUMMARIZED DATA ON THE TEXTURE OF RECENT DELTAIC SEDIMENTS ON, THE NORTH SLOPE, ARCTIC ALASKA. DESCRIPTIVE GRAIN SIZE PARAMETERS CALCULATED BY FOLKS (1958) METHOD

Environment	Gross Texture	Md (ϕ)	M_z (ϕ)	σ_I	Sk_I	K_G
River Channel	Gravelly-sand to clayey-sand	-3.4 to 5.6	-2.4 to 5.9	Very poorly to poorly sorted	Positive to very positive	Platykurtic to extremely leptokurtic
Tundra Deltaic Plain (Marsh)	Structureless peaty organic muck, with sparse inorganic particles, and occasional frost-heaved gravels and eolian sand	-	-	-	-	-
Mainland Coastal Beach	Gravel-gravelly-sand, and sand	-2.8 to 1.3	-2.8 to .06	Poorly sorted (many); moderately sorted (few)	Continuous range from positive to negative	Platykurtic (predominantly) to leptokurtic
Bay	Sand, silty-sand and sandy-silt	2.8 to 6.6	2.9 to 6.8	Very poorly sorted to poorly sorted; few well sorted	Continuous range from positive to negative	Platykurtic to very leptodurtic
Lagoon	Sand, sandy-silt, silty-sand, and sand-silt-clay	2.2 to 6.2	2.1 to 7.0	Very poorly sorted; few well sorted	Most positive, few nearly symmetrical	Highly variable mesokurtic to extremely leptokurtic
Coastal Dune	Medium to fine sand	1.8	1.8	Well to very well sorted	Nearly symmetrical	Mesokurtic
Barriers	Gravel, gravelly-sand, and sand	-2.5 to -8.0	-1.5 to -8.0	Well sorted to very poorly sorted	Very positive to very negative	(Not available)
Open Marine (Delta front platform?)	Sand-silt-clay to silty-clay	2.2 to 8.3	1.2 to 8.1	Very poorly sorted	Most positive, few very positive	Platykurtic to extremely leptokurtic

to predict the distribution of permafrost in the Beaufort Sea coastal area, will be faced with difficulties.

Further discussion on the characteristics of the granulometric compositions of lagoon sediments of North Arctic Alaska are included in latter sections of this report.

STRATIGRAPHIC STUDIES ON CORE SAMPLES

In this section are discussed the depositional processes in the marine facies of the Colville Delta area (Fig. 5) as inferred from examination of the stratigraphic variations in lithology of short unconsolidated cores (Figs. 13 and 14). It would seem that in the proximal end of the prodelta (?) sediments are deposited under fluctuating hydrodynamic conditions. This is evident from the presence of alternate bands and laminations of relatively high and low sand contents as displayed in cores PWB76-18, 19, 20 and 23. It is possible that the highly sandy layers reflect deposition at intensified wave action during storms. Additionally, it is suggested that in the area of the shelf from where these cores were retrieved reworking of sediments by bioturbation and/or ice gouging has not prevailed in recent times. This is inferred from the lack of stratigraphic homogeneity in the four core samples. However, the core PWB76-1 (Fig. 13), which was retrieved from the Central Prudhoe Bay (Fig. 12) at 3 m water depth, consists essentially of homogenous clayey silt with no evidence of sediment layering on basis of textural and/or structural analysis. This would obviously mean that sediments of the Prudhoe Bay have either not been completely free from reworking by ice gouging, or deposition in the bay has continued under similar hydrodynamic conditions during recent times.

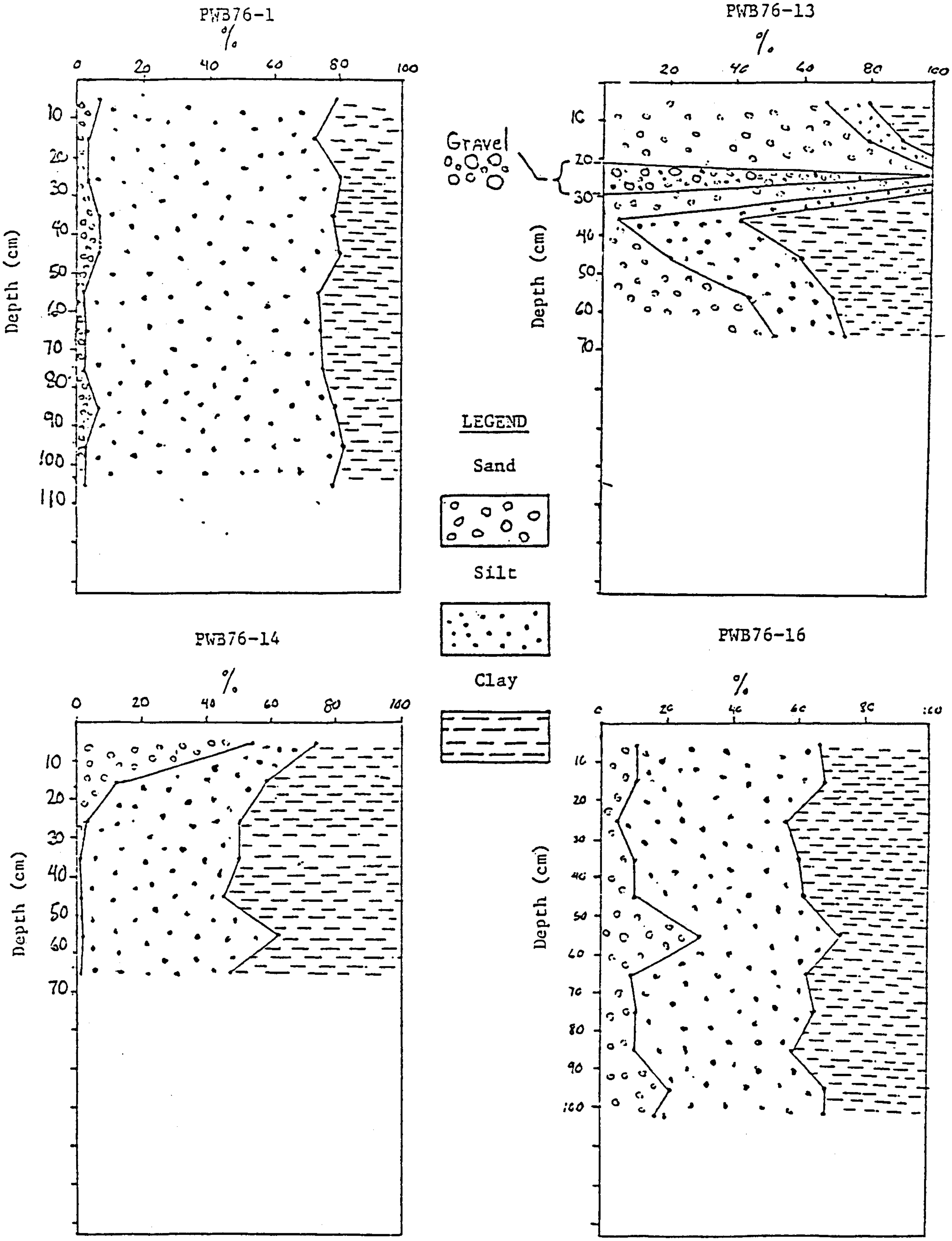

Figure 13. Variation of sediment texture with depth of PWB76 core samples.

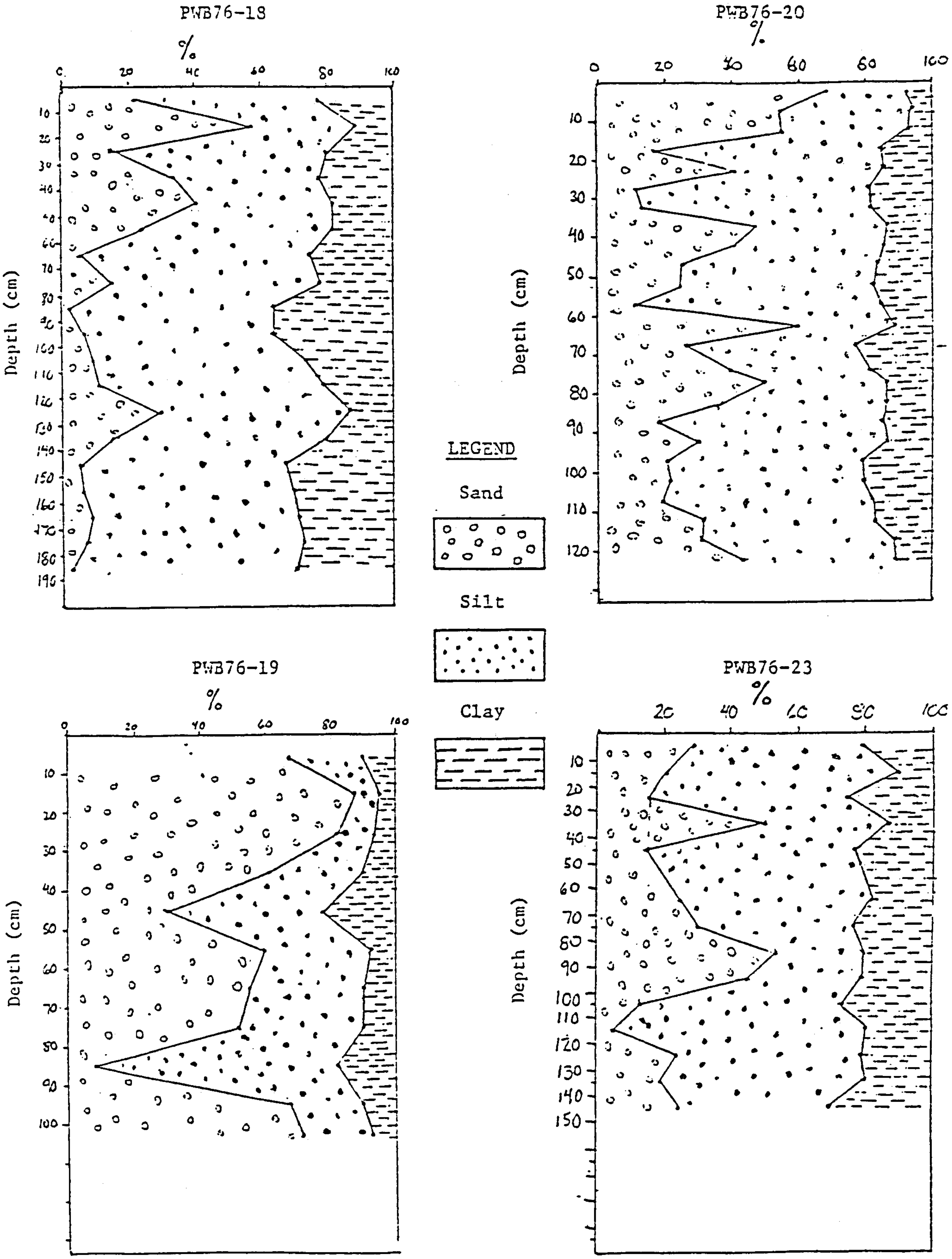

Figure 14. Variation of sediment texture with depth of PWB76 core samples.

^{210}Pb stratigraphic studies on a sediment core collected from the central Prudhoe Bay show no definite exponential decrease in ^{210}Pb down the core, which seem to substantiate that reworking of sediments perhaps by ice gouging in the area has been quite intense. This would imply that cautionary steps must be taken to mitigate possible undercutting by ice on engineering structures and submarine pipe lines that may be emplaced in this and similar shallow marine areas.

The granulometric analysis on a suite of core samples shows that the overall volume of gravel are generally low within the surficial 1 to 2 m sediment sequences from the Beaufort Sea nearshore. On the basis of this restricted sampling it would seem that the prospect for potential gravel deposits in the nearshore for economic exploitation is generally not very high.

BARRIER ISLAND-LAGOON SYSTEM OF THE ALASKAN NORTH ARCTIC COAST

Geomorphic Characteristics

A number of chains of barrier islands border the Beaufort Sea coast of Alaska (Figs. 1b and 2a). In the west a chain designated as the Plover Islands extends eastward of the barrier spit anchored to Pt. Barrow. Two chains of barrier islands stretch westward from west of the Sagavanirktok River and Canning River mouths. There is a third interspersed chain east of the Canning Delta that continues up to Demarcation Point.

By conventional definition, barrier islands, barrier spits and bay barriers are offshore subaerial depositional features of current/wave action. Therefore, offshore lands such as mud islands, erosional remnants of relict coastal plains, subaerial reefs, volcanic islands, and sea stacks *sensu stricto* are not barrier islands. Following this definition some offshore islands along the Beaufort Sea coast, such as Pingok, Bertoncini, Bodfish, Flaxman, Tigvariak and perhaps also Cottle are not barrier islands. Unlike the barrier islands, the latter islands for the most part have much higher relief, up to 5 m above mean sea level (a.m.s.l.), and are remnants of ancient coastal plain as suggested by the presence of an active tundra blanket, a stratigraphy similar to the adjacent coastal plain and continuous permafrost. Long barrier spits have subsequently extended laterally to some of these islands. Thus, in this paper unless otherwise stated, discussions will not be apropos to the tundra-blanketed islands.

The islands are typically low (1 to 3 m above MHW), with lengths ranging from 100 m to 27 km and are elongated parallel to the coastline. The notable exception to the latter pattern is the island chain extending due west of the Canning River mouth, the alignation of which progressively deviates farther away from the coast towards the west. Generally the seaward beaches of the Alaskan arctic barriers are straight; it is only following an occasional storm that beach cusps and/or ridge-runnel physiography is observed along the barrier islands. There are, however, a number of microrelief features typically associated with the ice-stressed beaches of the Arctic. For the most part these are elongated sand/gravel ridges resulting from landward bulldozing of beach deposits by overriding ice or movement of the deposit from backshore to foreshore by shifting ice at spring thaw. Furrows resulting from ice gouging are seen across the beaches; low mounds of gravel piling ('kaimoos') are also observed and believed to have formed from in-place ablation of shorefast ice entrained with gravel and/or storm-ice foots. These features were more thoroughly characterized by Rex (1964) and Greene (1970).

The barrier islands are separated from one another by tidal inlets (or channels), the depths of which can vary between less than 1 m to about 6 m (e.g., Egg Island inlet). The dimensions of the lagoons — semi-enclosed bodies of waters encompassed by the barrier islands and the mainland coast — can vary widely. The widths may extend from a few hundreds of meters to 4 km, whereas the length may continuously stretch up to 40 km. The lagoons are typically 1 to 3 m deep. The semi-enclosed body of water encompassed by the Midway-McClure-Stockton-Maguire group of islands and the mainland coast east of the Canning River Delta (Figs. 1b and 2a) is relatively wider, more extensive and deeper (about 5.5 m average depth; 10 m maximum depth) than the typical adjacent lagoons. Additionally, the hydrodynamic conditions in this littoral water body are influenced to a greater extent by the open marine environment. It would, therefore, seem more appropriate to class such an environment as a sound rather than a lagoon. Following this reasoning, this water body is presently called Stefansson Sound. However, such a definition should not construe that Stefansson Sound has dimensions comparative to some well-known larger sounds elsewhere (e.g., Pamlico and Long Island Sounds in the U.S. east coast) and its usage in this paper is purely descriptive. Review of the open literature clearly demonstrates that there can be marked variability in the dimensions, geomorphology, sediment characteristics and the physicochemical and biological facies between the barrier island-lagoon systems of different regions of the world. Glaesser (1978) contended that barrier islands are typically developed along marginal sea and trailing edge (passive or non-subductive) coasts (Inman and Nordstrom, 1971; Davies, 1973). Hayes (1979), from his worldwide experience, classified barrier island morphology as a function of tidal current and wave energy, and concluded that the development of barriers are more extensive in coastal areas where the tidal range is less than 4 m and that are wave dominated. Furthermore, Hayes (1976, 1979) noted a distinct morphological difference between barriers from microtidal (0-2 m tidal range) and mesotidal (2-4 m tidal range) coastal belts. The generalizations asserted by Glaesser (1978) and Hayes (1979) can be extended to the North Arctic coast of Alaska only to a limited extent. The latter coast with a mean tidal range of less than 16 cm do indeed have extensively developed barrier island-lagoon systems. However, along the Beaufort Sea coast of the Arctic some significant deviations are observed from the ideal geomorphic model related to barrier islands of microtidal areas of the temperate coasts. Presence of a "hot dog" morphology, storm-surge washover terraces and fans, as well as large flood-tidal deltas and a paucity of tidal inlets, are claimed as typical features of barriers of microtidal provinces (Hayes, 1979). However, presence of these features is not substantiated in the Beaufort Sea. It is of interest to note that occurrence of the washover terraces and fans were reported by Hayes (1979, p. 11) in an adjacent microtidal area of the Alaskan arctic (e.g., Kotzebue Sound, along the Alaskan Chukchi Sea coast).

Another notable feature of the Beaufort Sea barrier island system is the lack of any definite pattern of lateral variations in the interbarrier inlet widths, or degree of downdrift offsets. A close examination of LANDSAT images and aerial photographs of the Beaufort Sea coast discloses that in the majority of cases the relatively wider end of the barrier islands is disposed toward the downdrift of the net littoral currents. The foregoing observations on the north-Alaskan barriers are in contrast to the conclusions on barrier islands of mesotidal coasts (Hayes, 1976, 1979). Additional peculiarities of the north-arctic barrier islands are the virtual absence of some of the depositional subfacies such as the sand dunes at barrier crests, fringing salt marshes (with halophytic vegetation), tidal channels and flats on the lagoonward shores, and beach ridges. These subfacies are commonly well evolved in temperate and tropical barrier islands (Shepard and Moore, 1955; Chapman, 1960; Shepard, 1960; Allen, 1965; Dickinson *et al.*, 1972; Hayes and Kana, 1976; Hill and Hunter, 1976; Godfrey *et al.*, 1979; and McCann, 1979), and several of the facies are reported to be developed as well in the barriers along the microtidal southern coast of Gulf of St. Lawrence, Canada (McCann, 1979).

The tundra-covered islands are, as mentioned earlier, significantly different from the barrier islands. The lagoonward beaches of the tundra islands are generally irregular and the lower foreshores are blanketed by slushy, peaty deposits. The seaward shore (excluding that of the barrier spit) may or may not have a clearly defined beach. When a seaward beach is well developed, as on Pingok and Bodfish Islands, it is quite similar to the barrier island beach. Alternately, when the seaward beach is virtually absent (e.g., Flaxman Island) the shoreline is characterized by steep coastal bluffs.

The foregoing suggests that the barrier islands of North Arctic Alaska have a number of unique characteristics. Because the barrier island-lagoon environment in the North Alaskan Arctic is quite extensive, it was necessary to restrict the sedimentologic and geomorphic studies to a few type areas. The Jones Island-Simpson Lagoon situated along the central Beaufort Sea coast of Alaska (Fig. 1b) represents a type area off gently sloping coastal plain adjacent to an extensive deltaic complex, whereas the Icy Reef-Beaufort Lagoon in the eastern end of the study area represents a type area off a relatively steep coastal plain with less widespread deltation. Stefansson Sound, which is the only representative of the so-called sound environment along the above coast, is situated between the two type areas of barrier island-lagoon systems (Fig. 1b).

Reasons for Arctic Barrier Island Peculiarity

In the preceding section it was contended that the barrier islands along the Beaufort Sea coast have geomorphic characteristics that do not conform to the model generally outlined by Hayes (1976; 1979) for barrier islands of microtidal coasts of the tropical and temperate climatic belts. The uniqueness of the Beaufort Sea barriers is considered part of a local phenomenon that cannot be extended to the entire ice-stressed circum-coastal regime of the Arctic. It is suggested that the very unusual characteristics of the Beaufort Sea barriers are most likely related to the prevalence in the area of low annual current/wave energy. The Beaufort Sea coast is subjected to a mean astronomical tidal range of less than 16 cm, and the tidal current velocities in the tidal inlets are also suggested to be generally low (less than 6 to 7 cm sec^{-1}). The absence of flood tidal deltas may be ascribed to the net seaward flow of bottom currents (of tidal and fluvial outflow origin), and by implication an overall sediment transport from the lagoon to the open sea. Because of the unusually low tidal range it is contended that development of extensive tidal flats and salt marshes is particularly hampered on the lagoonward shores of the north Alaskan barriers. There is, as yet, no comprehensive statistical data base available on the wave climate for the Beaufort Sea coast. Preliminary data gathered by Wiseman *et al.* (1973) and Dygas and Burrell (1976) suggested that the wave field in ice-free seasons is dominated generally by wind-waves with 1.9 to 3.0-second period, that are punctuated by occasional swells with 8.0 to 10.0-second period and heights of 1.5 to 2.0 m impinging on the Beaufort Sea coast. However, storm-surges with heights ranging from 1.5 to 3.0 m a.m.s.l. are known to occur at about 25 to 50 years intervals (Reimnitz and Maurer, 1978). One of the primary reasons for the prevalence generally of the low wave energy, and less frequent storm-surge annually in the north Alaskan Arctic, is to be attributed to the extended period of ice cover. For eight to nine months in a year the Beaufort Sea is blanketed totally by ice, while during the summer three months open water may extend only within the 10-15 km inshore. The total fetch for wave generation is thus effectively much reduced in the Beaufort Sea in comparison to the ice-free tropical-temperate microtidal coasts. Therefore, except during periods of rare storms when the barrier islands can be completely inundated by sea (Reimnitz and Maurer, 1978), the potential development of the washover terraces and fans is generally inhibited in the North Arctic barriers.

In another context the lack of washover features can perhaps also be accounted for in the presence of numerous tidal inlets between the Beaufort Sea barriers. The inlets, by serving as suitable channels to transfer portions of the storm-surges into the lagoons, would concurrently minimize the possibility of surges passing over barriers. We also suspect that the prolonged ice-stress conditions in some, as yet, unknown way deviates the barrier morphology from the ideal 'hot dog' type, and better understanding of the role of ice will be a part of our future study.

Thus, it is quite evident that the model of barrier island formation, as stipulated by Hayes (1976, 1979), did not adequately take into account the possibility that there can be a marked variation in the model because of the role of ice in microtidal coasts such as those of North Arctic Alaska. The close resemblance of the West Arctic Alaskan barriers to the 'hot dog' prototype, and the association of washover terraces and fans with them (e.g. barriers of Kotzebue Sound) are considered by us as atypical features of the barriers of intensely ice-stressed microtidal coasts. The above 'abnormality' is attributable perhaps to relatively much intense storm-surge and wind-wave actions in that particular arctic area. In comparison to the Beaufort Sea, the Alaskan Chukchi Sea is known to have a much wider ice-free marginal zone in summer (Wiseman *et al.*, 1973) plus a significantly shorter duration of ice cover annually.

The absence of sand dunes on the Beaufort Sea barrier islands is an additional peculiarity in contrast to barrier islands of temperate-tropical coasts. Some of the prerequisites for the development of sand dunes on barrier islands are the presence of (1) and adequate source of sand on the seaward beach, (2) net onshore winds with thresholds adequate to transfer the beach sand to the dune site at the backshore, (3) vegetation and/or some other barriers to promote the accumulation of the onshore transported sand, and, (4) sufficient exposure of the beach sands, in a dry state, for onshore winds to pick them up. The availability of the beach sand, in turn, is effected by a number of more primary hydrodynamic and geomorphic factors that control the overall sediment budget at the beaches (e.g. the competency, capacity and rate of alongshore sediment drift, barrier configuration with respect to the wind-wave fronts, the volume of sediment exported periodically from the beaches and across the barriers by storm-surge washovers, etc.). We contend that the chief reasons for the virtual absence of sand dunes on the North Arctic barriers are the lack of vegetation and prolonged exposure of the beach sands to wind transport, notwithstanding that there is adequate volume of beach sand as a source and a net strong onshore wind. It is conceivable that because of the prolonged annual ice cover the total onshore transport of sand by wind is considerably reduced in comparison with ice-free barrier regions. McCann (1979, p. 49) referring to Owens (1974, 1975) maintained that barrier elevations and extent of dunes on barriers are closely associated with longshore sediment transport rates. Although along the Beaufort Sea barriers some short-term littoral transport rates were estimated (Wiseman *et al.*, 1973; Burrell *et al.*, 1975), these data are grossly inadequate to take into serious consideration in context of Owens' contentions.

Granulometric Compositions of Lagoon Substrates

The areal variations in the granulometric characteristics of the Simpson Lagoon substrate are displayed in Figure 15 whereas those of the Beaufort Lagoon (Fig. 4) were reported by Naidu (1980, 1981).

Following the classification scheme of Folk (1954), it is surmised that Simpson Lagoon sediments are very poorly sorted, slightly gravelly, muddy sands to slightly gravelly, sandy muds with the mean size generally in the silt category. In addition, the sediments display very positive- to positive-skewed (fine-skewed) and platykurtic to leptokurtic size distributions. Some broad areal variations in the gross texture were identified within Simpson Lagoon (Tucker, 1973; Naidu, 1981). From trend

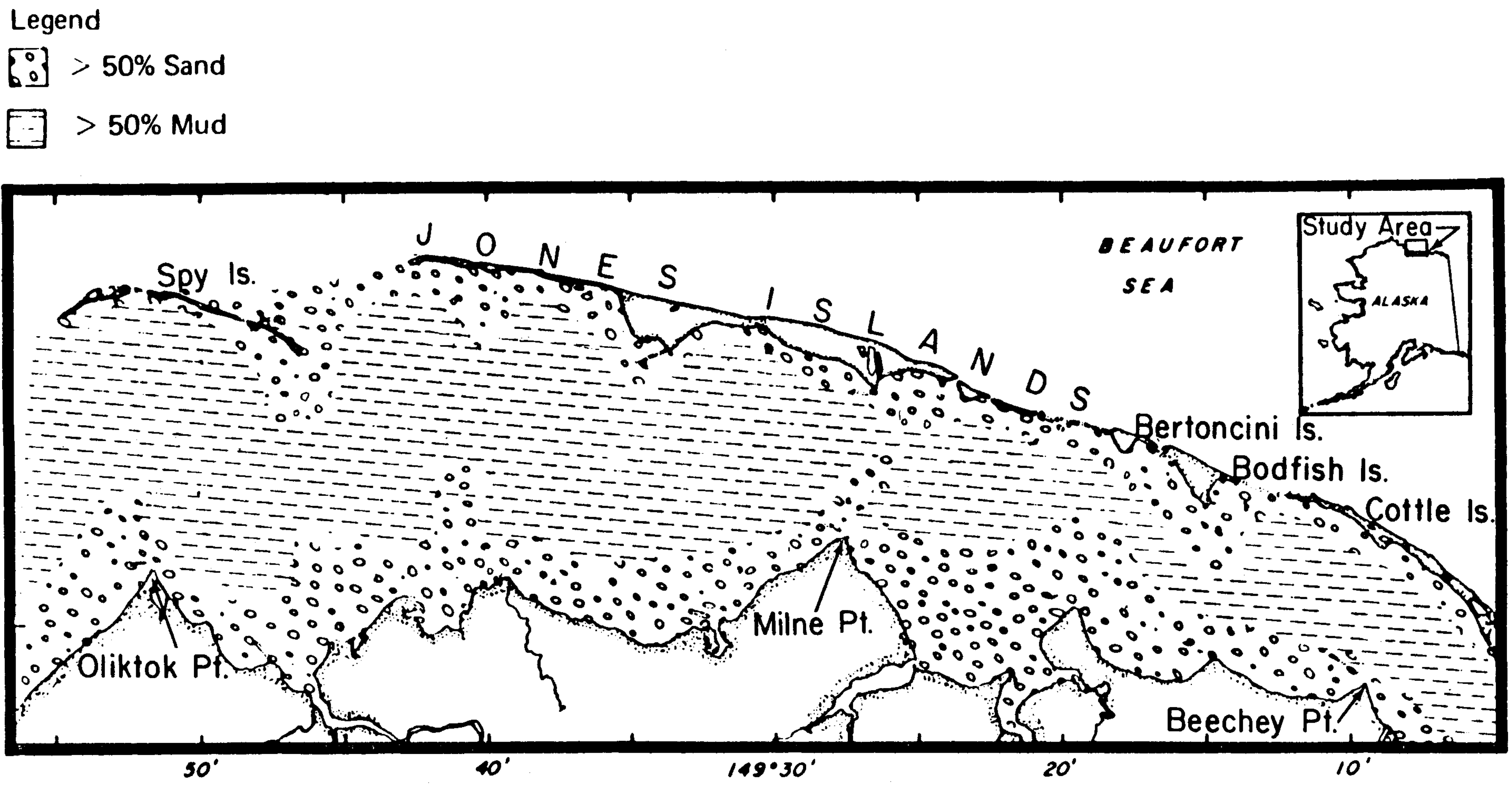

Figure 15. Characteristics of substrate lithology in Simpson Lagoon.

surface analysis, Tucker (1973) concluded that there is a net decrease in the mean size of sediments from the nearshore shallower portion to the deeper central lagoon. Substantiating this trend is the areal variation in the sand and mud contents (Fig. 15). No definite regional patterns, however, were noted in the sorting and skewness values of size distributions. For the most part, Beaufort Lagoon sediments have textures quite similar to those of Simpson Lagoon; the only notable difference is in the virtual absence of gravel-size particles in Beaufort Lagoon. The Stefansson Sound substrate varies widely between muddy sands and sandy muds with occasional minor amounts of gravel and clean sands. Generally, the sediments are very poorly sorted, and strongly fine-skewed with the mean size between fine sand to fine silt. The above generalization on the Stefansson Sound substrates, which is based on analysis of grab samples, does not convey the actual situation, for the sound is widely strewn with boulders up to 1 m wide (K. Dunton, personal communication). In places, the course debris is sufficiently concentrated to form discrete boulder patches. All deposits of the barrier islands as well as those of the seaward beaches of the tundra islands are poorly to very poorly sorted, and consist either of gravelly sands, sandy gravels or clean gravels; the gravels are generally in the pebble size category. The mainland coastal beach sediments have similar size distributions. More precise size analysis data show that these sediments are either gravels, gravelly sands or sands that have poor to very poorly sorted, coarse- to fine-skewed and platykurtic size distributions. Exposures of boulders are restricted to beaches and onshore areas of the tundra islands and mainland coast, in addition to Stefansson Sound in the area of study.

Longitudinal sections of the four vibrocores from central Simpson Lagoon are displayed in Figure 16, and stratigraphic variations of the textures of two of the vibrocores are further shown in Tables III and IV. The lithology and structure between the four cores vary widely. In core V-49 the basal section (140-150 cm) is constituted mostly of finely divided and fluffy peat intermixed with fine sand, silt and occasional fossil residues of the freshwater gastropod *Valvata* and the pelecypod *Psidium*. Overlying this section is a 65-cm sequence of cross-bedded, silty fine sand with a few pelecypod shells of *Cyrtodaria kuriana* and *Serripes groenlandicus* (at 120-130 cm core section). This bed, in turn, is overlain by a 75-cm sequence of clayey to sandy silt displaying typical mottled structure in the base and laminated deposits the rest of the core. Core V-48 which shows more dramatic stratigraphic changes in lithology (Fig. 16) apparently is devoid of any freshwater sediment sequence. The lower 55 cm is a section with typical mottled structure with a number of the ostracod *Heterocyprideis sorbyana* Jones, 1886. There is a 20-cm laminated silty sand sequence intercalated between two layers (60 to 90 cm and 110 to 115 cm) constituted chiefly of gravels and pelecypod fragments. The top 60 cm of this core is a homogenous silty sand. Stratigraphic analysis on cores V-47 and V-50 have not been completed. Presence of a laminated layer, however, is obvious in the top 50 cm of core V-50, whereas the rest of this core and the entire core V-47 are apparently structureless and consist of homogenous clay-silt-sand. Examination of the vibrocore samples suggests that any designing of piling or footing driven into lagoon substrate must provide allowance for possible soft, peaty, muddy substrate.

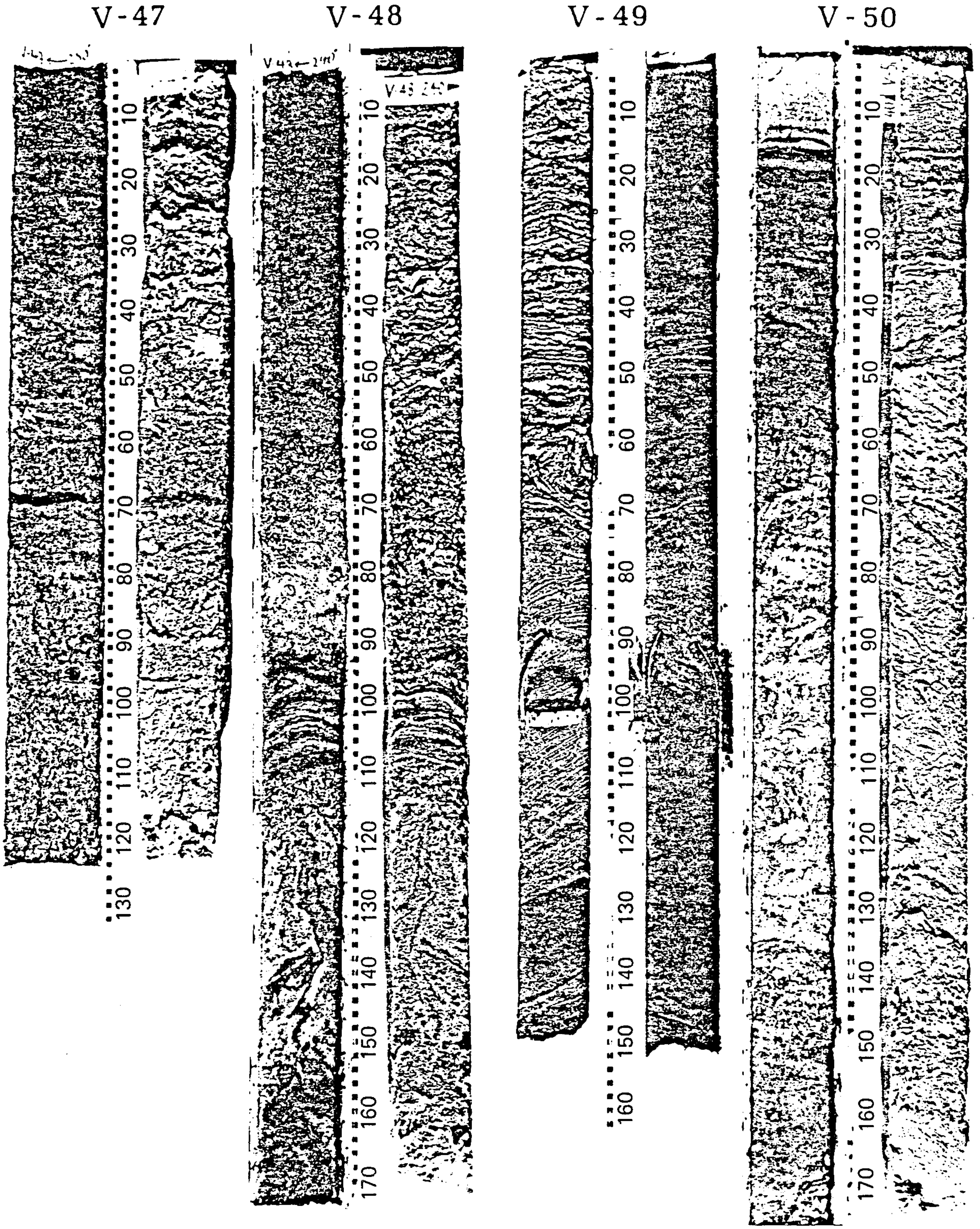

Figure 16. Vertical sections of vibrocore samples from Simpson Lagoon showing variations in sediment structure.

TABLE III

Stratigraphic Variations in the Sediment Texture in the Vibrocore Sample V-48 from Simpson Lagoon

Core Section (cm)	Gravel %	Sand %	Silt %	Clay %	Md	M_z	δ_I	Sk_I	K_G
0- 10	-	21.20	68.28	12.52	5.21	5.45	2.16	0.19	1.20
10- 20	-	13.60	77.24	9.16	5.03	5.42	1.73	0.33	1.38
20- 30	-	26.55	68.02	5.42	4.76	4.91	1.94	0.09	1.18
30- 50	1.42	28.80	65.96	3.83	4.41	4.68	1.92	0.15	1.09
40- 50	3.74	33.25	59.40	3.61	4.30	4.31	2.15	0.03	0.92
50- 60	2.55	69.38	25.58	2.49	2.06	2.35	1.94	0.65	0.95
60- 64	0.39	67.95	27.83	3.83	2.75	3.69	2.08	0.61	1.09
64- 70	0.08	75.81	21.48	2.62	2.66	3.17	1.72	0.55	1.31
70- 75	3.21	65.16	29.36	2.26	2.97	3.10	1.84	0.11	1.42
75- 95	100	-	-	-	-	-	-	-	-
95-100	-	100	-	-	-	-	-	-	-
110-120	0.31	75.64	23.50	0.55	3.40	3.29	1.25	0.06	1.55
120-130	0.75	72.14	24.75	2.36	3.23	3.18	1.43	0.13	1.41
130-140	0.71	71.48	25.18	2.62	3.15	3.20	1.48	0.24	1.37
140-150	0.18	64.36	33.11	2.35	3.53	3.45	1.40	0.13	1.44
150-160	-	67.09	30.71	2.20	3.36	3.36	1.45	0.19	1.33
160-165	-	56.13	40.12	3.75	3.79	4.03	1.79	0.23	1.39

TABLE IV

Stratigraphic Variations in the Sediment Texture in the Vibrocore Sample V-49 from Simpson Lagoon

Core Section (cm)	Gravel %	Sand %	Silt %	Clay %	Md	M_z	δ_I	Sk_I	K_G
0- 10	-	15.35	78.55	6.10	4.72	5.16	1.46	0.47	1.08
10- 20	0.14	9.05	81.31	9.50	5.21	5.54	1.74	0.40	1.38
20- 30	-	5.52	86.79	7.69	5.91	5.90	1.38	0.13	1.40
30- 40	0.09	25.73	61.03	13.15	5.29	5.38	2.24	-0.02	2.56
40- 50	-	48.91	46.38	4.71	4.11	3.98	2.07	0.03	0.92
50- 60	0.73	64.26	31.39	3.63	2.78	3.73	2.12	0.58	1.03
60- 70	-	30.45	63.11	6.45	4.94	4.77	2.16	-0.02	1.03
70- 80	0.54	73.72	23.21	2.54	2.38	3.02	1.82	0.54	1.08
80- 90	0.67	99.33	-	-	1.87	1.85	0.49	-0.06	1.10
90-100	0.09	99.91	-	-	2.10	2.15	0.47	-0.15	1.21
100-110	0.12	99.88	-	-	2.39	2.39	0.39	-0.01	0.92
110-120	-	100.00	-	-	2.11	2.05	0.71	-0.17	0.91
120-130	0.46	92.02	5.98	1.53	2.19	2.12	1.00	0.02	1.46
130-150	1.70	51.25	26.13	20.92	3.69	4.18	2.63	0.21	1.22

Evolution of the Barrier Islands and the Associated Lagoons

Our studies relating to the evolution of the barrier islands along the Alaskan Beaufort Sea coast are not complete as yet. At this point in time we have rudimentary knowledge of the direction of alongshore net mass sand transport, which is based largely on the morphology of the barrier spits and long-term migration patterns of barrier islands. Studies were recently extended on the stratigraphy of vibrocore samples. Without adequate knowledge of the paleogeographic history of the inshore area, wave refraction patterns, sources and transport pathways of sand-sized particles, and submarine bottom profiles off the islands, it would be difficult for us to elucidate the barrier island evolution.

Field observations would seem to suggest that the Pingok, Bertoncini, Bodfish, Flaxman and other tundra blanketed islands are Pleistocene relict coastal highlands. In contrast to the above, islands with sand and/or gravel substrates, which are more abundant along the Beaufort Sea coast, are most likely resultants of contemporary marine constructive processes. By conventional definition* they are to be considered modern, notwithstanding that the gravel and sand constituting them may have been reworked from older residual deposit (e.g. deposit left from erosion of ancient tundra islands and/or coastal bluffs). The presence of several bars, hundreds of meters long and elongated roughly parallel to the Beaufort Sea coast, suggests that at least some of the barriers might have grown subaerially from bars as a result of progressive sediment accretion via alongshore drift. Incidentally, Wiseman *et al.* (1973) have reported the formation of several

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*For conventional definitions of relict, contemporary (or modern and palimpsest deposits, refer to Swift *et al.* (1971).

bars in the Beaufort Sea inshore as a result of standing wave action. Although evolution of the barriers can be addressed from several stand points (refer to Schwartz, 1973 for a review), our approach has been restricted to gathering geological evidences.

At the beginning of the investigations it was felt that the interpretation of the stratigraphic changes in both lithology and structure of the Simpson Lagoon cores (Fig. 16) would be a straight-forward simple effort, and that the recapitulation of the Holocene paleogeography of the North Slope coastal area and thus the origin of the barrier islands would not be too difficult to follow. However, it would seem that the recent paleogeographic history of the Simpson Lagoon area has been quite complex. This is indicated by the stratigraphic dissimilarities observed between the four cores that were collected from not-too-widely-apart locations within the lagoon. In spite of this fact, identification of the progressive changes in lithology, structure and coarse fractions of sediments in two core samples retrieved from Simpson Lagoon due southeast and south of Pingok Island (cores V-48 and V-49 in Fig. 5a), and coastal retreat measurements (Naidu *et al.*, 1982), have provided us with sufficient data that can be used to recapitulate the paleogeographic scenario pertaining to the lagoon evolution.

Basal sections of core V-49 suggest that the Simpson Lagoon region due west and south of the tundra islands was dominated in the recent geologic past by low-lying tundra coastal plain with a number of freshwater coastal lakes and/or ponds very similar to that of the present time. These lakes supported the freshwater gastropod *Valvata* and the pelecypod *Psidium*, and provided a relatively quiescent environment for growth of freshwater marsh vegetation and/or accumulation of terrigenous plant debris, now represented as a basal peat. As suggested by the carbon-14 date of the basal peat sample (separated at approximately 150 cm from the top of core V-49), the afore mentioned coastal plain with lakes dominated the above area around 4500 years B.P. Some time thereafter, it is believed that the lakes were occasionally breached and came to be in tidal communication with the sea either through tidal channels and/or heightened wave surge, as implied by a modest presence of faunal residues such as *Cyrtodaria kurriana, Serripes groenlandicus* and species of estuarine and/or marine foraminifera and ostracods (Table V) intercalated with seeds of a number of freshwater plants (e.g., *Chara, Hippuris vulgaris* L., and *Potamogeton* over the basal peat layer (at 120-130 cm below the V-49 core top, Fig. 16). The breached lakes then progressively coalesced and eventually were inundated by sea water (most likely coincident with subsidence of the lake beds resulting from subsurface permafrost thawing, and synchronous with the progressive deglacial rise in sea level).

Pingok Island and the adjacent tundra-blanketed islands delineated the inundated lakes from the open sea to form the present Simpson Lagoon. Obviously the upper 70 cm of muddy sediments in core V-49 are contemporary lagoonal deposits, whereas the sandy cross-bedded sequences between 70 cm and 145 cm in core V-49 most probably represent beach facies of the ancient shallow lagoon.

It is uncertain how much time elapsed between the formation of the lacustrine peat and marine inundation at the site of core V-49. Based solely on mean coastal retreat of 1.1 m yr^{-1}, about 2500 years are required to inundate Simpson Lagoon to this point according to the model of coastal bluff retreat (Naidu *et al.*, 1982). This implies a hiatus of 2000 years. Alternately, coastal retreat then may have been slower than the present mean rate, and Simpson Lagoon may have been inundated to the site of core V-49 shortly after 4500 y.B.P.

TABLE V

Species of Foraminifera and Ostracods in Some Sections of Vibrocore Samples of Simpson Lagoon, and in recent Sediments of Beaufort Lagoon

CORE V-48

120-130 cm;	Foraminifera:	*Elphidium excavatam alba*
		Elphidium incertum
		Elphidium Orbiculare
		Buccella frigida
		Polymorphina suboblongata
130-140 cm;	Ostracod:	*Heterocyprideis sorbyana*

CORE V-49

120-130 cm;	Ostracods:	*Rabilimis septentrionalis*
		Paracyprideis pseudopunetillata
		Eucytheridea bradii
		Cytheretta edwardsi
		Candona rectangulata
		Illyocypris bradii
	Foraminifera:	*Elphidium excavatum alba*

Beaufort Lagoon (Recent Sediments)

Foraminifera:	*Elphidium excavatum alba*
	Buccella frigida
	Polymorphina suboblongata
	Elphidium nanum
Ostracod:	*Paracyprideis pseudopunctillata*
	Cytheromorpha macchesneyi

The evolutionary history of eastern Simpson Lagoon has been complex and, perhaps, this is true for all lagoon areas of north-arctic Alaska that are now encompassed by barrier islands. It is probable that core V-48 did not extend sufficiently deep to encounter coastal plain deposits. A lack of any well-defined freshwater deposits, and the presence of well-preserved foraminifera and ostracod tests throughout core V-48 imply that eastern Simpson Lagoon was probably in tidal communication roughly at the time when the western lagoon was part of a coastal plain. This interpretation is consistent with the coastal bluff retreat model discussed by Naidu *et al.*, 1982. Again, based on mean coastal retreat of 1.1 m yr^{-1}, only about 1500 years are required to inundate Simpson Lagoon to the site of core V-48. Regardless of when inundation occurred, it is possible that inundation of site V-48 preceded inundation of site V-49 by approximately 1000 years. The mottled structure as displayed in the lower 50 to 55 cm layer of gravelly silty sand of the core is suggestive of intense bioturbation of substrate some time in the past. The occurrence, however, of a well-defined, thin gravel layer between 75 cm and 95 cm of V-48 and sandwiched between gravelly silty sands connotes that the depositional process in the eastern lagoon was briefly punctuated by the formation of a transient gravel bar, barrier island or barrier spit.

Stability and Growth Rate of the Pingok Island Barrier Spit

It is now reasonably well documented that almost all barrier islands along the Alaskan Beaufort Sea coast have undergone some degree of temporal geomorphic changes, irrespective of the nature of the islands whether they are tundra blanketed or not. The changes in the configuration of some of the islands over a few decades (from 1906 to 1974) have been assessed by Wiseman *et al.* (1973), Barnes *et al.* (1977), Lewellen (see Hopkins *et al.*, 1977 and Naidu *et al.*, 1982). The relatively short-term changes within one summer season for the Pingok-Leavitt island have been documented by Wiseman *et al.* (1973) and Dygas *et al.* (1972). A review of the above literature shows that the lateral growth rates of the barrier spits of the various islands are significantly different, and within any one summer great fluctuations in the above rate can be noted. However, there is a general consensus among most geologists working in the Beaufort Sea coast that the net alongshore drift of sediments along that coast is toward the west.

One of the many research objectives, embodied in RU 529, was to look for evidences that might assist in assessing the long-term net alongshore sediment transport direction, as well as to estimate the long-term growth rate of barrier spits along the Alaskan Beaufort Sea coast. In attempting to fulfill the latter objective, field surveys on Pingok Island were conducted. During the course of this survey a peat formation was encountered on the seaward beach at the proximal end of the sand-gravel barrier spit extending to the west of the Pingok Island (e.g., the Leavitt Island). Evidently the peat deposit was not a remnant of an old collapsed coastal bluff, because it was quite an extensive contiguous formation. At the high-water mark where a vertical section of the north shore of the spit was exposed, the peat was observed to lie under an overburden of 84 cm of sand and gravel. Apparently the same peat layer extended continuously under the barrier spit, as suggested by the detection of another peat deposit under 79 cm of sand-gravel over-burden in a trench in the center of the barrier spit. It was assumed that a radiocarbon date on a sample of the upper layer of the peat would indicate the geologic age when the sandy-gravel barrier spit most likely started to grow westward from the Pingok Island*. The peat sample thus dated provided an age of 2600 years B.P., implying that the barrier spit was geologically quite a young formation. Additionally, on the basis of this date and the approximate 5.5 km length of the spit (included the Leavitt Island) as recorded in 1977 it would seem that the average long-term linear growth rate of the spit on a steady state basis was around 2 m/year. Further, assuming that the average thickness and width of the spit (as estimated in 1977) was 1 m and 140 m respectively, it would seem that the long-term accretion rate of the spit volume was in the order of approximately 280 m^3/year.

It is interesting to compare the growth rates for the western Pingok Island spit that we have estimated on long-term basis and those reported earlier by Wiseman *et al.* (1973) on a seasonal basis. The latter estimated the spit growth rate in summer 1972 based on evidences gathered in the field, as well as taking into consideration data from Dygas *et al.* (1972).

The linear growth rate of the Pingok barrier spit, as cited by Wiseman *et al.* (1973) was 6 m/year while the rate for volumetric increase was about 7.1 x 10^3/summer. These accretion rates of the barrier spit in question are considerably higher than our figures. It would be of interest to check what portions of the total length and volume of the spit accretion in summer could be ascribed to catastrophic storm action and what portions to normal current/wave action. It would also be of importance to estimate the decrease

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*This contention assumes that the upper portion of the peat and the sand-gravel unit lying over it are more or less a continuous sequence of sediments and that there was no great depositional time gap between the sedimentary units.

in the spit areal size consequent to ice bulldozing during the ice stress season. As observed by us as well as several others, occasional storm surges can bring about large-scale degradation (e.g., in the order of 10-15 m) along some beach stretches, with almost concomitant progradation at other beach sites along the Beaufort Sea barriers. The sum total resultant of the storm and ice-ploughed actions on the sediment "budget" of the spit is unknown, but is conceivable that the two counteracting processes will eventually amount to net spit growth rates which are relatively much lower than the estimates that were provided by Wiseman *et al.* (1973) on a seasonal basis. It is, therefore, no wonder that Wiseman *et al.* (1973) have observed only a modest change in the spit length west of Pingok (tundra) Island between 1908 and 1972 (e.g., 64 years). Presently it would seem imperative that additional long-term data must be gathered before more precise estimates can be provided of the barrier spit growth rate on the Pingok Island.

In conclusion, barrier islands of the North Arctic coast of Alaska are a dynamic component of the geomorphology of the above coast. Migration and growth rates of these islands vary widely (perhaps between 1 to 30 m) and their lateral growth on a long-term basis is determined by sand nourishment via the net westward littoral drift. No reliable, quantitative estimate of the littoral drift are available presently. Without the latter data and complementary information on the wave energy flux as well as wave diffraction patterns, it would be difficult to predict what may be the possible impacts on the physical integrity of the barrier island-lagoon-inlet composite, consequent to building of causeways, offshore islands and docks, and dredging. It is quite conceivable that the overall sediment budget in the Beaufort Sea littoral zone may be so significantly perturbed as a result of the above anthropogenic activities that large-scale erosion of some barriers followed by unusually high deposition of the eroded sediments at inlets or other barriers may finally alter the circulation pattern in the adjacent lagoons and nearshore. This could ultimately lead to deleterious effect on the ecosystems of the adjacent lagoon and the nearshore. At present there is a serious data gap pertaining to littoral transport estimates. Perhaps these estimates must be obtained on a site specific basis or for various stretches of the Beaufort Sea coast, because the rate of migration and growth of the various barrier islands vary widely and thus data from one coastal area to another can not simply be extrapolated.

In another context, the highly migratory nature of the barriers and adjacent bars implies that any pipelines, cables and footings emplaced on the sea bottom surface of the inshore areas may be buried.

STRUCTURE AND ORIGIN OF TURBID PLUMES IN COASTAL AREAS IN LATE SUMMER

Satellite images clearly display that movement of turbid plumes along the nearshore lagoons and bays of North Alaskan Arctic was either in the form of long continuous plumes or disconnected irregular streaks and wedges. With the exception of the Tigvarik Island area where an eastward moving turbid gyre was apparent, along the rest of the Alaskan Beaufort Sea coast the nearshore turbid plume was invariably seen to move westward. The latter water movement was impelled by the prevailing westward littoral currents. However, it would seem that the tongues of turbid plumes in the lagoons and bays in mid and late summer (i.e., late July-September) could not, to any large extent, be ascribed to fluvial discharge and/or thermoerosion of coastal bluffs and barriers. No such direct association was apparent from detailed scrutiny of several multi-year satellite images, although invariably extensive turbid plumes do occur in the vicinity of large river mouths. It is important to note that waters relatively free from suspensions (about 1 mg/l) are discharged in late summer from mouths of the major distributary channels, while presence of relatively turbid waters can be delineated at some distance off the mouths. Additionally, the satellite images displayed that the parcels of lagoon waters extending up to a few meters away from the coastal bluffs and barrier islands were observed to be relatively less turbid than the rest of the lagoon. A notable example was the Dease Inlet region. All of these observations led us to suspect that in mid and late summer when the fluvial outflow was low, much of the turbidity in coastal waters could be associated to resuspension of the cohesionless substrate particles from shallow-water regions by wave induced agitation. Since the region slightly off the river mouths are generally more shallow and are constituted of unconsolidated clays it was not surprising that relatively high turbid waters are associated with such areas. Subsequent to resuspension the particles are carried westward in the form of a turbid plume.

No estimates are available on the concentrations of sediment particles that are resuspended off the river mouths by waves in late summer. I have documented for 1981 summer the concentrations of suspended particles on water samples that were collected from certain known geographic locations of the Beaufort Sea nearshore and which coincided with the LANDSAT satellite passages overhead in that region. These ground truth data on suspensates were forwarded to Dr. W. J. Stringer of the Geophysical Institute, University of Alaska (Fairbanks). Dr. Stringer will be generating density-sliced

LANDSAT images synchronising for those days and time when our water samples were collected. Hopefully, correlating the image densities with the ground truths on suspensate concentrations reliable criteria would be developed to provide with a means to infer the concentrations of particles off the river mouths.

It is contended that the quantification of the concentration of particles resuspended naturally by wave-induced turbulence may have important bearing in attempting to predict the possible ecological impacts of increased turbidity resulting from anthropogenic activities such as dredging and occasional discharge of drilling spoils. Will the concentrations of particles that are naturally resuspended be similar to those in the discharged spoils? If no significant difference can be identified between the two then the above-mentioned anthropogenic activities may not pose a serious environmental hazard in the Beaufort Sea. Alternately, if substantial differences in the suspended loads are shown then environmental managers will be compelled to regulate the rate and volume of discharge of dredge and drilling spoils to closely match natural situations of water turbidity.

Our investigations has led us to believe that any initial deposition of fine-grained dredge or drilling spoils (and perhaps also any inorganic or organic pollutant scavenged by naturally depositing mud) will be periodically resuspended from the inshore areas of the Beaufort Sea, during the open-water season by wave-induced turbulence. Because such resuspended particles will be quickly redispersed and laterally diffused by the littoral currents the initial deposition of any pollutants may not pose a permanent hazard to benthic communities of the inshore areas. This seems to be substantiated by the field and complementary laboratory studies conducted by

Northern Technical Services, Anchorage (1981) on drilling effluents in the Reindeer Island site of the Beaufort Sea. However, any large-scale resuspension of pollutant charged substrate at the freeze-up period may get entrained and concentrated in the sea-ice, with possible deleterons effect on the frazil organisms in the sea-ice.

SEDIMENT DYNAMICS STUDY

Tripod Experiments

It was only recently that serious process-response sedimentological investigations were initiated for the Beaufort Sea nearshore. Results of preliminary sediment dynamic studies were reported by Naidu (see 1979 to 1981 Annual Reports Submitted to OCSEAP). Our progress was limited by quite frequent losses of instruments which were not specifically designed for work under ice-stressed conditions. The instrumented package on a tripod — the Sediment Dynamics Sphere (SDS) — which was used by us was originally designed by the University of Washington (Lahore *et al.*, 1977), to obtain time-series hydrodynamic parameters in context with sediment dynamic studies, in ice-free continental shelf area. This instrument was subsequently redesigned by us to operate satisfactorily in the arctic; the fabrication of the latter prototype model was completed and is ready to be deployed. We believe, therefore, that we have now the right type of instruments to pursue sediment dynamic studies in the Alaskan Arctic. Limited investigations would seem to suggest that the processes of sediment entrainment, transport and deposition in summer 1979 in the Simpson Lagoon were not the same as those which prevailed in summer 1978. Plotting of the summer 1978 time-series data exhibited apparent correlations between wind strengths and suspensate concentrations at the

Milne Pt. tripod station. On the basis of those correlations, Naidu (1979) suggested that the threshold of wind to induce wave-current sediment resuspension in Simpson Lagoon at the tripod station was about 8 m/sec. That conclusion does not seem to be well substantiated by the summer 1979 data which indicate quite suspension-free waters at 10.5 to 13 m/sec winds at the tripod station (about 2.9 m water depth) in the Simpson Lagoon. It is to be noted that in 1979 the spring break-up was unusually earlier, and in middle and late summer (August-September) abnormally high sediment-laden fluvial discharge was observed. Implication of these unusual events, if any, on summer 1979 suspended load budgets could not be assessed because of lack of LANDSAT images for the period.

Conceptual Model for Sediment Concentration in Frazil Sea-ice of North Arctic Alaska

The presence of sediments in frazil sea-ice, in concentrations 2 to 3 orders of magnitude higher than in ambient coastal waters, has been an enigma to investigators working on sea-ice problems in the nearshore of Beaufort Sea. The question that has been time and again raised refers to the mechanism which leads to the entrapment of sediments in ususual concentrations in the ice. Many ideas were presented (refer to Schell, 1980 for detailed discussion on the subject), but none seem to have offered a satisfactory answer. A commonly held notion has been that occurrence of storms during the incipient freeze-up period is critical to entrain large quantities of sediments into the water column, and that the subsequent fixation of the suspended particles on ice could account for the unusual particle concentration in the sea-ice (Barnes *et al.*, 1982). However, the exact mechanism for such fixation was not defined by the above authors. The other ideas prescribed took into consideration adfreezing of suspended charged waters, which would seem untenable in most cases. It is hard to believe that in the Beaufort Sea nearshore intensified wave action during occasional storms is capable of suspending fine sediments in concentrations as much as 200 to 750 mg/ℓ — the levels generally observed in sea-ice*. Alternate concepts for the unusual sediment accumulation in sea-ice refer to possible anchor ice sediment entrainment, or to occasional 'ducking' and sediment scraping by highly fragmented frazil ice by storm surge wave action. The lack of any textural correlation between sediments of substrate and overlying sea-ice for any specific inshore region, does not seem to add much credence to the thesis of sea-ice scraping bottom sediments. Additionally, the occasional scrapping process would tend to be manifested in sediments occurring as streaks, blebs, and bands in an otherwise clean sea-ice, which are definitely not observed.

In the following is presented a hypothesis that might explain the processes leading to the unusual sediment concentrations in sea-ice. During freeze-up period** when continuous fluxes of suspended particles, borne in laterally moving currents of water impinge on highly porous, undulating slushy*** sea-ice the particles are assumed to retain by the mesh of slushy ice crystals. It is further contended that as the sea-ice grows, fresh surfaces are successively exposed for continuous retention of suspended sediment particles. Moreover, occurrence of storms during freeze-up time would seem to be a critical factor for the sediment accumulation at the vicinity

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*The extremely turbid water debouching from the North Slope rivers generally has between 70-100 mg/ℓ of suspended particles, and this fluvial plume stands out in LANDSAT images. None of the LANDSAT images during freeze-up time (or storms) show such turbid waters offshore.

**After the formation of pan-cake ice.

***Slushy and rough nature of sea-ice seems critical for particle adherence.

of sea-ice/water interface, because higher water turbulence will maintain the slushy nature of the accreting sea-ice surface in addition to providing larger fluxes of suspended particles for potential accumulation at the surface. For particles to accumulate at concentration levels equivalent to those generally observed in the ice (i.e., 200 to 750 mg/ℓ) it would be crucial that the concentrations, supply and accumulation rates of particles at the sea-ice/water interface are sustained at a certain optimum level and are commensurate with the sea-ice growth rate. It would seem that in the Beaufort Sea nearshore the critical particle supply and accumulation rates are adequately carried, as suggested by the followup computations. Assuming that during freeze up period the mean suspensate concentration in the nearshore waters is about 1 mg/ℓ, mean current strength is at 10 cm/sec, and the slush-ice accretion rate is about 1 cm/day, it is estimated that the maximum possible sediment accumulation on sea-ice will amount to about 850 mg/ℓ. However, it is most likely that the suggested sediment accumulation process is less than 100 percent efficient. Assuming that the process is only 25 percent efficient it would still be possible to satisfactorily explain, within the said process framework, the nearly 200 mg/ℓ sediment concentrations generally observed in frazil sea-ice.

The general lack of sediment concentrations in the lower segments of sea-ice is perhaps attributable to the process by which those segments are formed. Accretion of sea-ice in the lower portions presumably occurs as relatively smooth, horizontal, and consolidated sheets rather than as porous, undulating slush. The lack of slushiness seems to be promoted by relatively tranquil waters, which in turn obviously results from the lack of fetch sometime after the initial frazil ice formation. It is surmised that the horizontal consolidated sheets do not offer as effective a surface as the rough surface of slush ice for sediment accumulation.

The hypothesis presented above is of course conceptual in nature, and must be verified by laboratory experiments conducted in freezing tanks and supplemented by correlation of time-series hydrographic measurements during freeze-up period and chronologic characterization of the ice structure and concentration of particles in sea-ice. At any rate, understanding of the processes which lead to the concentration of sediments in sea-ice will certainly have implication on several environmental related problems (e.g., pollutant entrapment by ice; the relevance of sediment in sea-ice to light attenuation and hence spring primary productivity, etc.).

Sedimentation Rates

Several gravity and box core samples were taken to estimate the upper limit of sedimentation rates, based on ^{210}Pb dating techniques, for the Simpson Lagoon, Prudhoe Bay, Harrison Bay, a coastal lake, continental shelf and continental slope of the Beaufort Sea (Fig. 5b). In the eastern margin of Harrison Bay the rate ranged between 0.60 cm yr^{-1} and 1.64 cm yr^{-1}, and in the Simpson Lagoon there was a net decrease from 0.82 cm yr^{-1} in the western end to 0.52 cm yr^{-1} in the central lagoon due south of Pingok Island (Fig. 17). The lateral variations in the sedimentation rates within the continuous bay-lagoon region was obviously a reflection of the volume of deposition of the Colville River debris. No meaningful rate could be obtained for the continental shelf, central and western Harrison Bay, and central Prudhoe Bay because of a lack of a clear-cut net linear exponential decay in ^{210}Pb. Presumably, reworking of sediments by ice-gouging and bioturbation

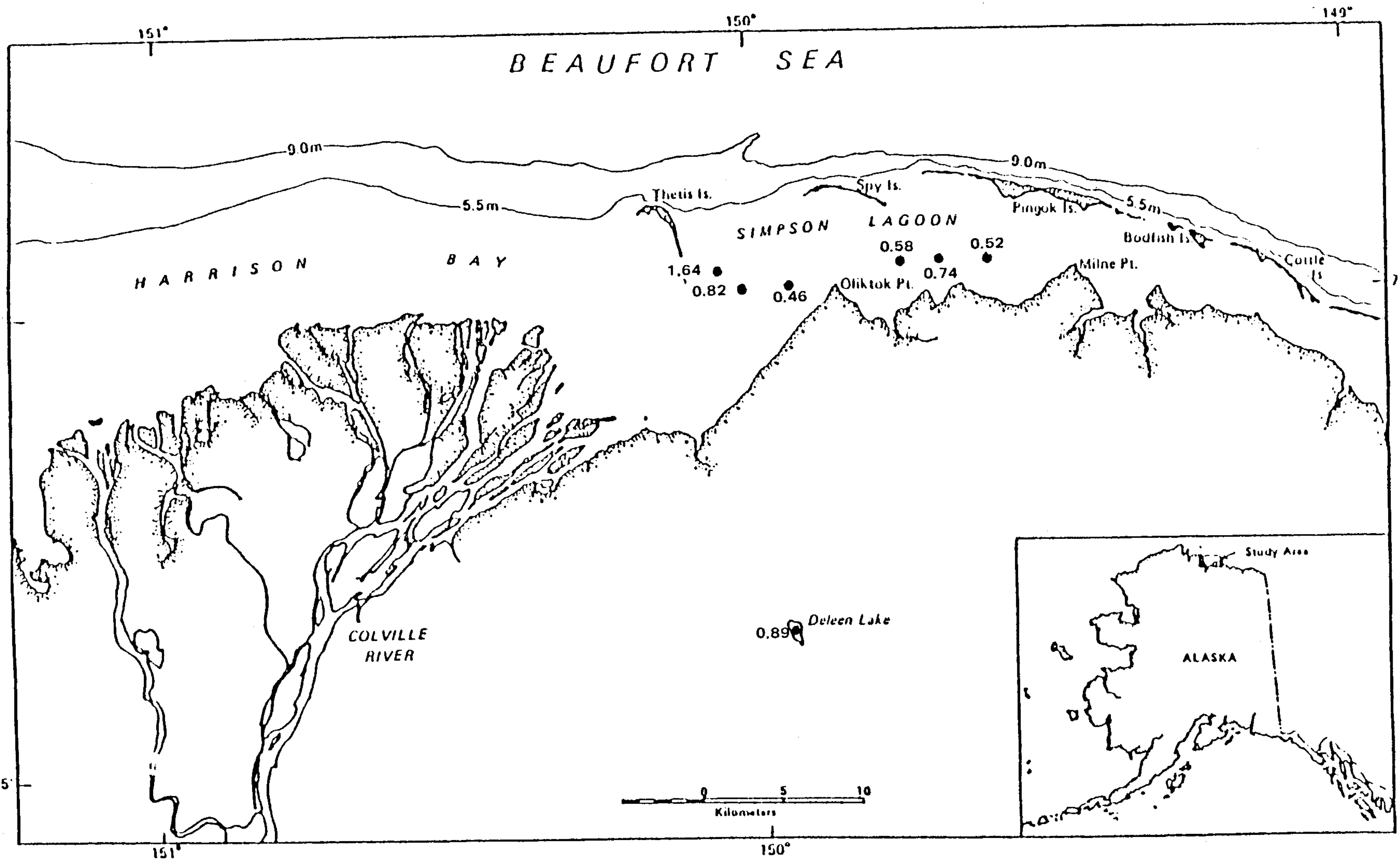

Figure 17. Sedimentation rates (cm/yr) in the Deleen Lake, east Harrison Bay and Simpson Lagoon, based on ^{210}Pb method.

homogenized the ^{210}Pb stratigraphy in the above regions. In the continental slope the sedimentation rate was relatively low (i.e., between 0.70 to 0.45 mm yr^{-1}). In the coastal lake the rate was about 0.89 cm yr^{-1}.

Our ^{210}Pb stratigraphic work suggests that with the exception of some semi-enclosed bodies of coastal waters, such as the lagoons, the sediments of the Beaufort Sea for the most part are subjected to frequent reworking and redistribution by ice-gouge action. The undisturbed nature of the lagoon sediments was additionally attested to in upper sections of vibrocore samples (Fig. 16), which clearly display the preservation of primary sedimentary structures and sediment sequences that are sharply delineated. On the basis of these observations it would seem that any pollutant that may be scavenged by, or codeposited with, the substrate marine sediments they would frequently be remobilized from subsurface layers and thus could be exposed periodically to biological communities. The common notion that sediments are generally a very effective means to permanently scavenge pollutants may have a limited relevance to the arctic shallow marine area.

Estimation of the baselines of sedimentation rates for various depositional sites would seem to be crucial in developing criteria to detect possible changes in sediment budgets and metal fluxes resulting from industry-related coastal activities. As discussed earlier, the ^{210}Pb technique in the north arctic would seem to offer a limited means to estimate these rates and fluxes and, as such other methods must be explored.

Sources and Origin of Erratic Boulders on Alaskan Beaufort Sea Coast

Results of the detailed petrographic studies on 105 separate samples of boulder chips and visual inspection of hundreds of samples in the field have enabled us to define the composition of the boulders that are scattered on the beaches of the Pingok, Bodfish and Flaxman Islands, and on the coastal plain in the vicinity of Prudhoe Bay and lower Canning River of North Arctic Alaska. Petrographically the coastal boulder and cobble specimens are diabases, volcanics, granites, clastic sedimentary rocks, carbonates, cherts and metamorphic (medium- to high-grade) rocks. Detailed descriptions of these rock types are included in Mowatt and Naidu (1974) and Naidu (1979). Based on knowledge of known rock types in the Brooks Range, Davidson, British and Romanzof Mountains and the MacKenzie River drainage area it would seem most unlikely that the boulder samples had their source in the hinterland of Northern Arctic Alaska or the adjacent Northwest Canada (i.e., MacKenzie Valley). Besides, no conceivable mode of transport can be invoked to explain the means of moving boulders from the far hinterland highlands to the Beaufort Coast. The lower area of the coastal plain of the North Slope was not glaciated by mountain glaciers during the last two glacial epochs and therefore, the boulders are not ancient morainic debris from the Alaskan Arctic. Possible fluvial transport of the boulders seems unacceptable considering the presence of glacial striae on some of the boulders and the angular nature of the boulders, and the long travel distances that might have been involved. Additionally, representatives of some of the typical lithologies among the boulder assemblages were not observed in the present fluvial bed loads of the North Slope rivers.

Based on the unique lithologic assemblage and the relatively old age of three separate samples of a red/dark pink granite (i.e., 1.6*, 2.1* and

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*Ages kindly provided by S. Rawlinson from his unpublished reports.

2.4 billion years), and the regional geology of the archipelago and shield areas of Canada (Geol. Soc. Canada, 1970), it is contended that the boulders probably have a major source in the region due south of the Coronation Gulf of Northwest Territories, Canada (i.e., east of the Great Slave and Great Bear Lake Provinces). In the past, we had believed that the Ellesmere Island in the Canadian Archipelago could have been an important additional provenance for the boulder deposits. However, this notion is not consistent with the virtual absence of dolomites and limestones on the ice island T-3 (Stoiber *et al.*, 1956), and the common presence of boulders of these two rock types along the Alaskan Arctic coast. It is generally contended that the ice island T-3 calved from the Ellesmere Island ice shelf. We have not ruled out other possible source areas such as Northern Greenland (Hopkins, 1978a) for the coastal boulders in question. It is suggested that only further detailed geological mapping of the various potential areas will help resolve the boulder source(s).

The scenario which has been drawn in attempting to define the transport mechanics of the erratic boulders to the Alaskan arctic coast, dwells upon the theme that the boulders were ice-rafted by large bergs (Leffingwell, 1919; Naidu, 1974; Mowatt and Naidu, 1974) presumably some time during interglacial interval(s) when sea-level was at least 3 or 4 meters higher than the present (Naidu, 1974; Hopkins, 1978a,b). Hopkins (1979) further contended that with a synchronous rise in sea-level during the Pelukian Transgression (last interglacial) the above icebergs were calved and set free (with the boulder burden associated with them) from an ice shelf that presumably extended into the arctic continental shelf from northern Keewatin and south-central Elizabeth Islands of Canada

(Hughes *et al.*, 1977; Denton and Hughes, 1981; Hopkins, 1979). Lately I have become quite skeptical of the ice-rafted concept, because of the difficulty in accepting the incursion of large bergs with deep drafts into inshores of the Alaskan Beaufort Sea. It would seem that bergs, sufficiently large to be able to carry big boulders, would have been grounded around the continental shelf margin of the ancient Beaufort Sea just the way some of the larger ice islands (with mean thickness of about 17 m) do moving inshore in present time. Alternatively, the ice-rafting concept would imply that the ancient Beaufort Sea shelf was tectonically or isostatically depressed during the interglacial transgression when the boulders were ice-rafted and deposited at the North Alaskan Arctic coastal area. However, there is no substantiative evidence to support that the above coastal area has been tectonically very active.

In light of the foregoing context, I have been tempted to entertain an alternative idea. It is quite possible that the erratic boulders of the Alaskan Arctic coast were borne and transported by a continental ice sheet rather than icebergs. I contend that such a sheet was a distal tongue of the much larger Laurentide ice complex (Flint, 1943). Conceivably, such a sheet had extended at the height of the Wisconsinan glaciation (late Würm; around 18,000 y.B.P.) across the Northwest Territories (Canada) and along the southern margin of the Beaufort Sea continental shelf, as well as the adjacent coastal hinterland via the Coronation Gulf, Dolphin and Union Straits, and had an outlet into the Beaufort Sea at Amundsen Gulf. It is further conceivable that the boulders which were carried by such an ice were stranded as residual lag deposits at more or less their present sites of occurrence upon the melting of the Wisconsinan ice sheet. The possibility that such an ice sheet extended into the Beaufort Shelf is apparently implied by the successive inferred positions of glacial ice margins during the Wisconsin for North America (Prest, 1969; Denton and Hughes, 1981). It has been speculated by Prest (1969) that the retreating margin of the North American ice was at the vicinity of the mouth of the Amundsen Gulf around 14,000 years ago. Therefore, it would not seem unreasonable to assume that at the height of the late Würm glacial epoch (i.e., centered around 18,000 y.B.P.) the Wisconsinan ice might have extended farther out perhaps along the present Beaufort Sea coast and the adjacent hinterland and, thus, carried the train of boulders along with it. The foregoing scenario, although perhaps somewhat simplistic, nevertheless would seem to be more credible than the ice-rafting idea. It is suggestive that Prest's (1969) map showing the speculative ice-marginal positions during recession of the Wisconsinan ice-sheet complex may be somewhat out dated (see Hughes *et al.*, 1977; and Hopkins, 1979 for further discussion and additional references). If this is true, then the timing of the suggested extension of the Wisconsinan ice-sheet into the Beaufort Sea shelf may have to be revised (perhaps to early Wisconsin). More recently Hughes *et al.* (1981) offered explicit evidence to show that Laurentide ice lobes had in fact engulfed the coastal region of northeastern Yukon Territory in late Wisconsin time. Therefore, the proposed idea of transport of the boulders by an ice sheet rather than icebergs, remains for serious consideration.

CLAY MINERALOGY OF THE BEAUFORT SEA

The predominant clay mineral in the < 2 μm fraction was illite (45-70%) with relatively minor amounts of glycol expandable minerals, kaolinite, chlorite and mixed-layered phases. The dispersal patterns of the expandable minerals and the kaolinite/chlorite ratios in the continental shelf of the Beaufort Sea are exhibited as Figures 18,19 and 20, and the distribution of illite is shown in Figure 21 and was discussed elsewhere (Naidu and Mowatt, 1982). Significant regional variations existed in the concentrations of the expandable minerals in the Beaufort Sea. The marine facies of the Colville Delta had the highest concentrations (30 percent or slightly more) followed by a net seaward decrease to less than 10 percent off the delta. The adjacent nearshore region north of the Kuparuk and Sagavanirktok Deltas, the outer continental shelf of the Alaskan Beaufort Sea and the entire shelf off the Mackenzie Delta had a general paucity of expandable minerals. It is notable that a narrow isolated band, extending east-west in the central continental shelf off the Canning River, had relatively more (20 to 28 percent) expandable minerals (Figs. 18 and 19). Although no systematic downstream variations in the expandable minerals was recognized within the lower 170 km of Colville River (Mowatt *et al.*, 1974; Naidu and Mowatt, 1975), a definite net decrease in the concentrations of these mineral phases was identified seaward from the contemporary subaerial part of the Colville Delta (Fig. 22). An illite-enriched belt extended eastward of Point Barrow into the Beaufort Sea and was confined to the nearshore up to the western margin of the Colville Delta (Fig. 21). Subsequent lateral variations in illite abundances were sharply delineated along the coasts of the major deltaic systems of North Arctic Alaska. For example, sediments with relatively low (38 to 40 percent) illite were restricted to the marine facies of the Colville Delta including Harrison Bay, whereas a sharp increase (> 60 percent) was apparent off the Kuparuk and Sagavanirktok Rivers (Fig. 21). Coinciding with the relatively

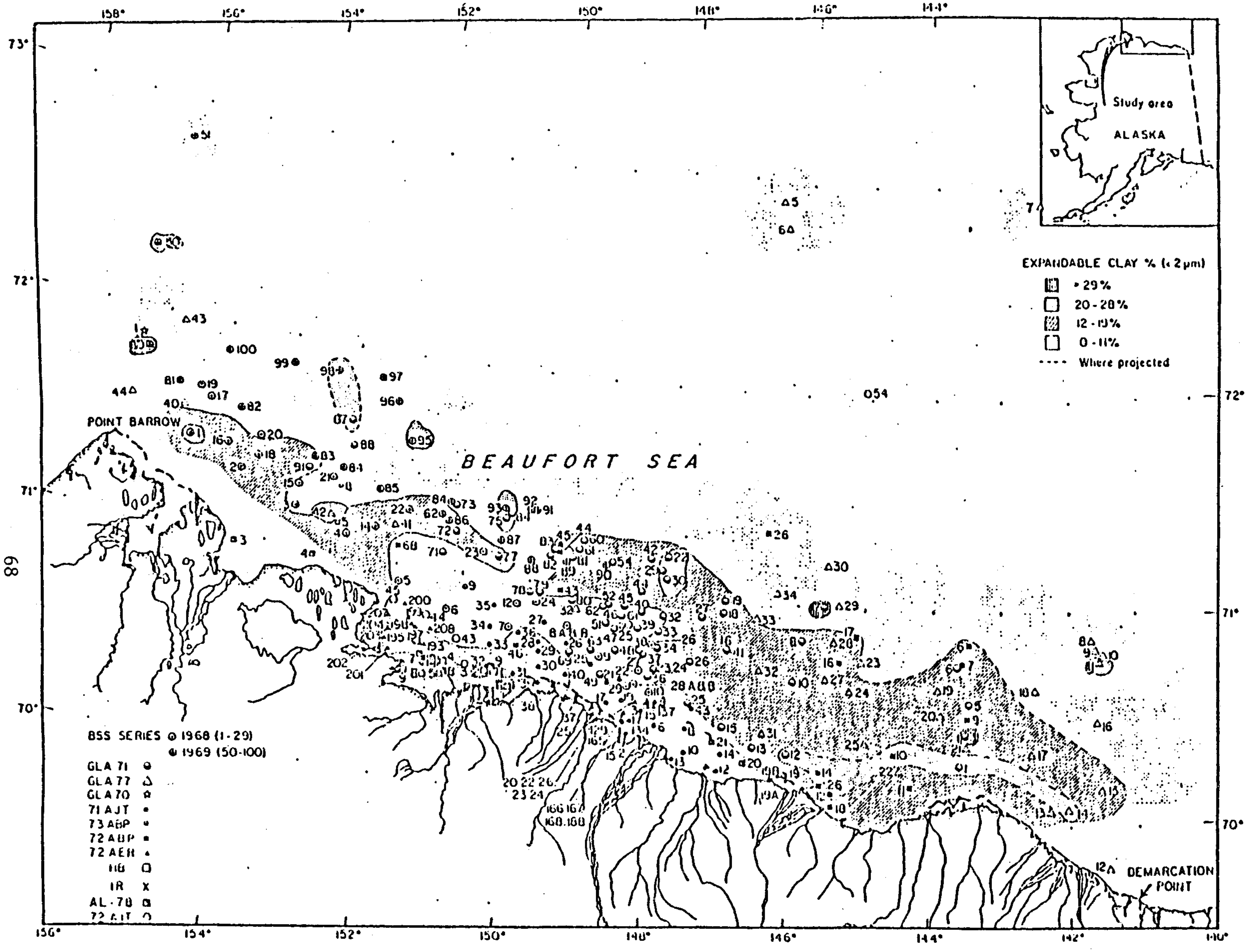

Figure 18. Expandable clay mineral distribution in Beaufort Sea surface sediments.

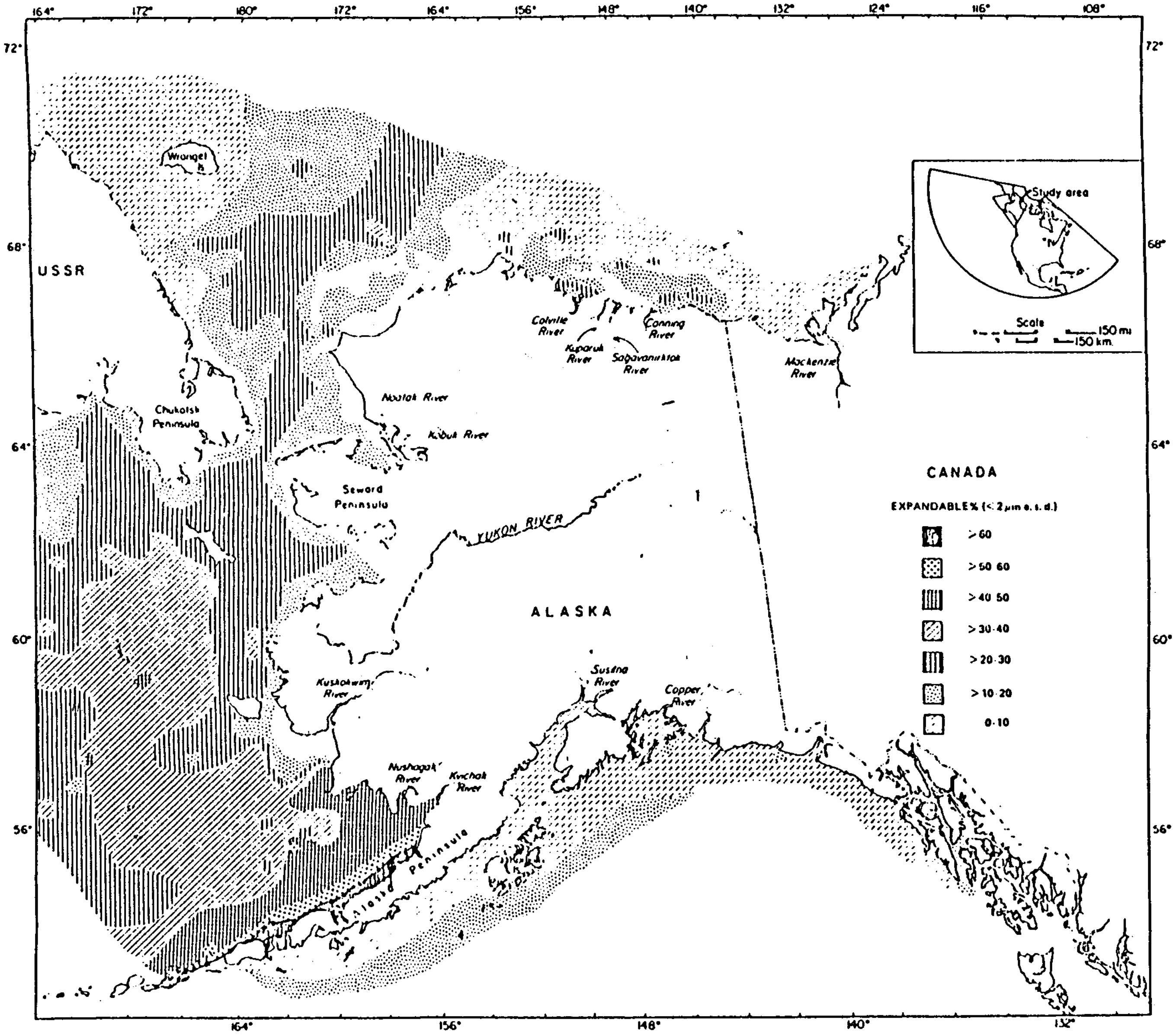

Figure 19. Distribution of the expandable clay mineral group in marine surface sediments of Alaska (After Naidu and Mowatt, 1982).

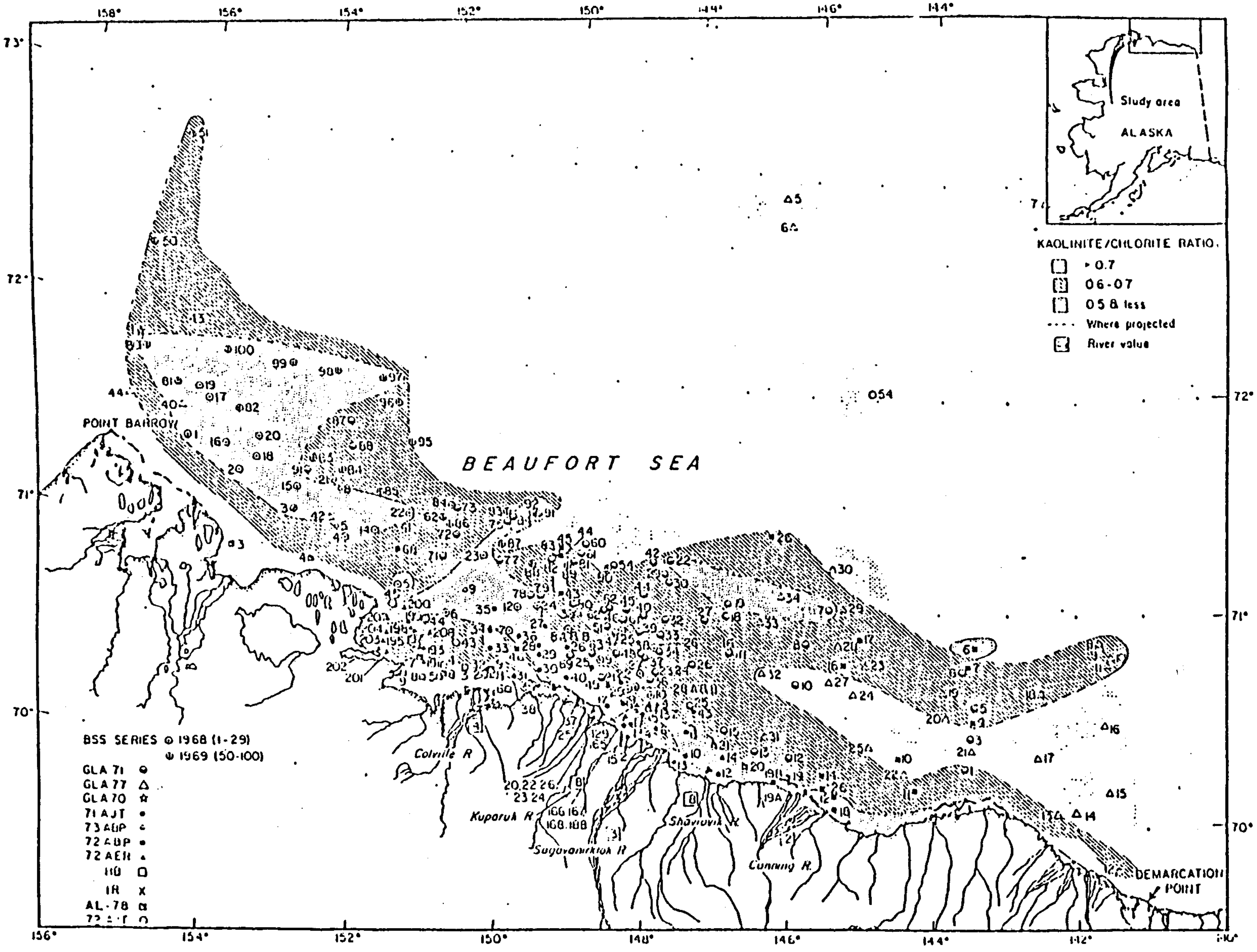

Figure 20. Kaolinite/chlorite ratio distribution in Beaufort Sea surface sediment.

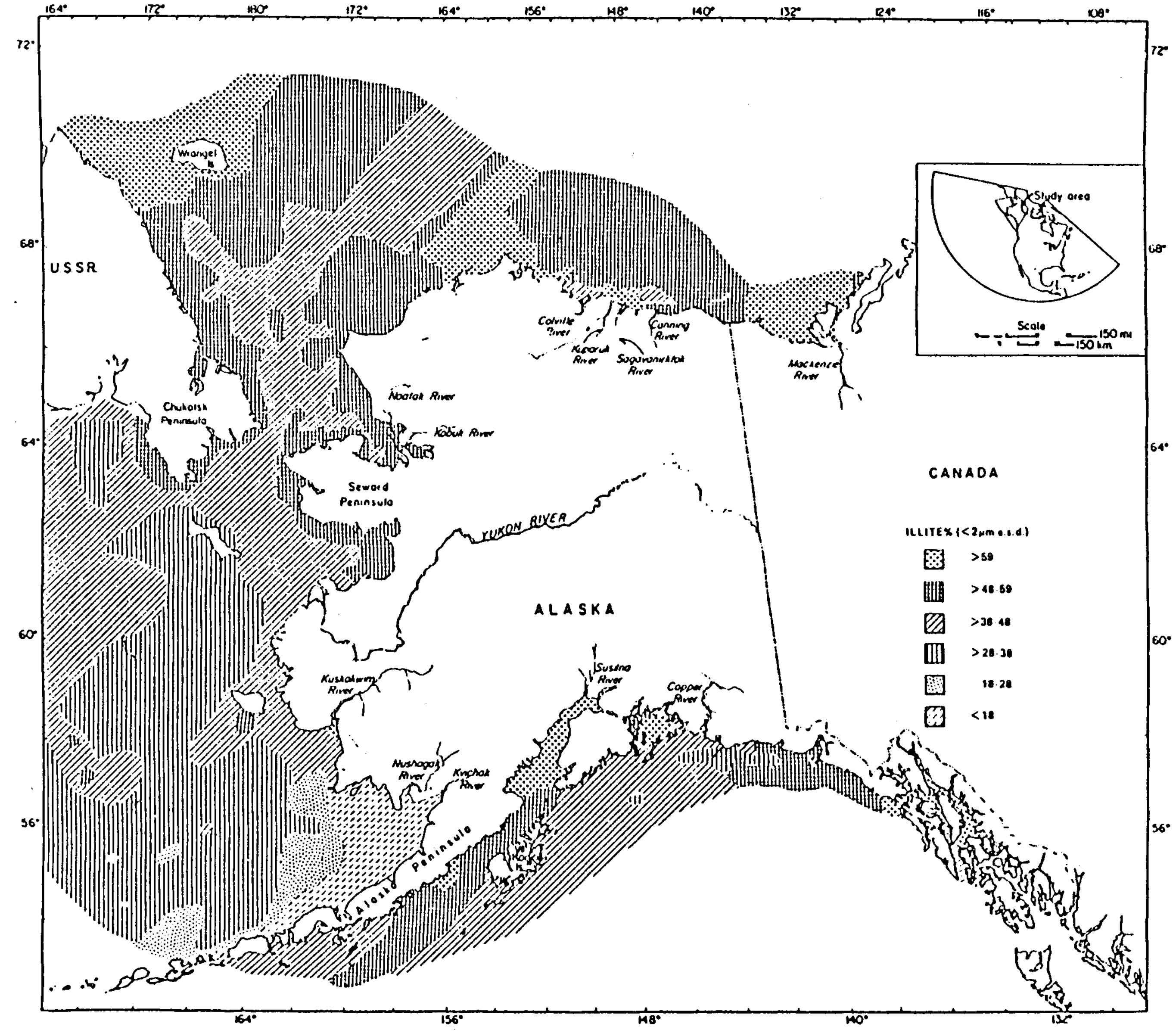

Figure 21. Distribution of illite in marine surface sediments of Alaska (after Naidu and Mowatt, 1982).

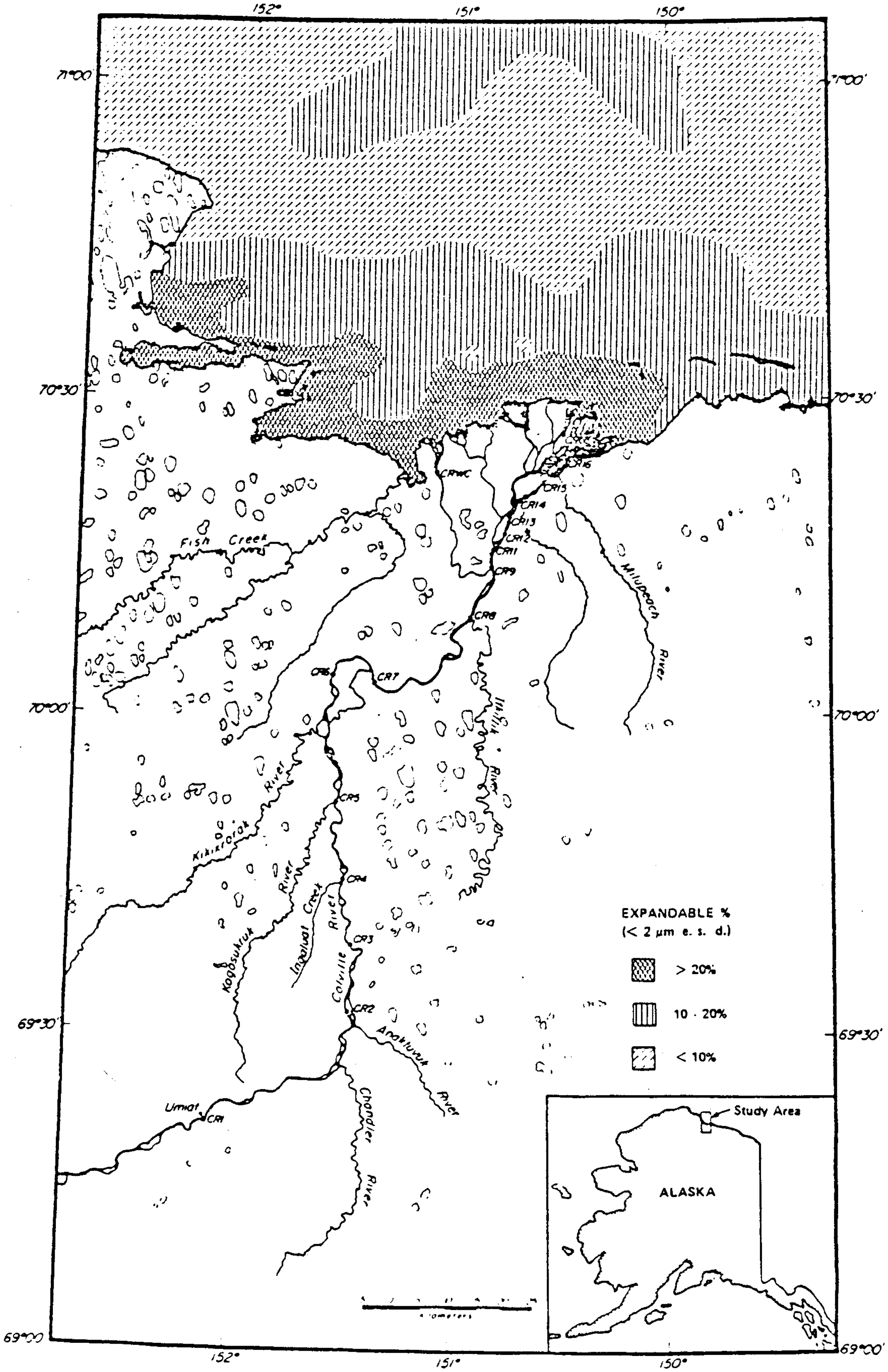

Figure 22. Variations in the expandable clay mineral distribution in the Colville Delta (after Naidu and Mowatt, 1982).

increased abundance of expandable minerals was an isolated, eastwest elongated band of low amounts of illite in the middle continental shelf north of the Canning River. The rest of the Beaufort Sea shelf was blanketed by moderately high (48 to 59 percent) amounts of illite (Fig. 21).

Additional clay mineral studies on the Colville deltaic sediments showed, as in case of the expandable minerals, no systematic downstream pattern of variation along the lower 170 km of the Colville River (Mowatt *et al.*, 1974; Naidu and Mowatt, 1975). However, an unequivocal net increase in illite seaward from the contemporary subaerial part of the Colville Delta are noted (Fig. 23).

The concentrations of kaolinite in the < 2 μm fraction of sediments ranged from 10 to 15 percent. The kaolinite/chlorite ratios (Fig. 20) seem to have offered a useful means to identify the relative variations of the two minerals. In the Beaufort Sea, the ratios were generally high throughout (> 0.5) as compared to the rest of the Alaskan shelves (Naidu and Mowatt, 1982), although appreciable lateral variations were observed in the ratios (Fig. 20). There was a net seaward decrease from the Colville River mouth. A band with the highest ratio (> 0.7) extended westward from the Kuparuk River, whereas the lowest ratios were identified adjacent to the coast of the Sagavanirktok and Canning Deltas, and extended up to Barter Island. In the central Beaufort Sea shelf, the lowest ratio extended northeast of Point Barrow, whereas a tongue of sediments with the highest kaolinite/chlorite ratios existed off the Canning River-Barter Island area.

The observed clay mineral distribution patterns on the inner continental shelf of Alaska (especially the Simpson Lagoon area, Fig. 24) generally can be attributed to various terrigenous sources, and to the subsequent dis-

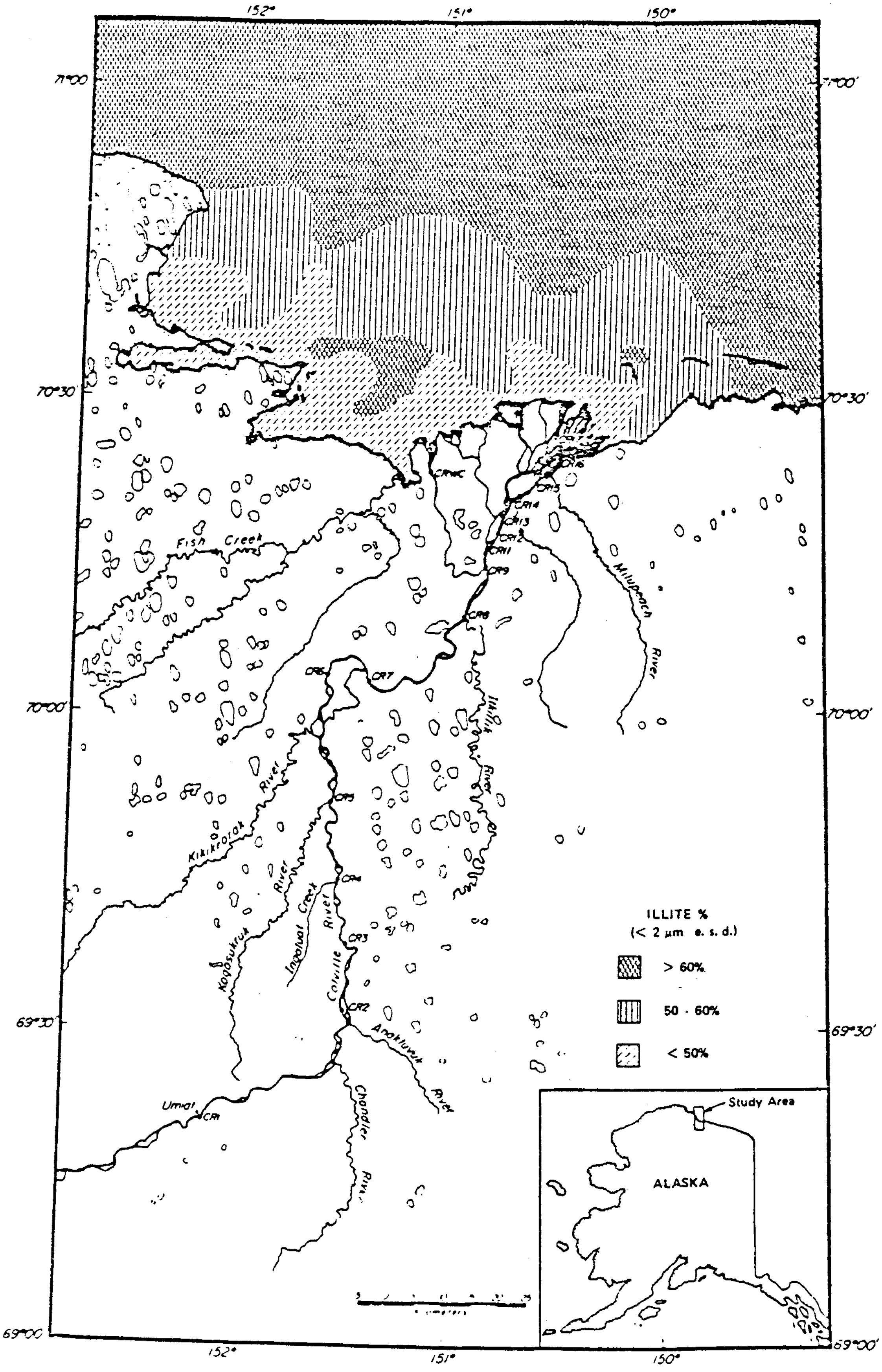

Figure 23. Variations in illite in the Colville Delta (after Naidu and Mowatt, 1982).

LEGEND

- ▩ Colville Influx, Almost Entirely (90%)
- ░ Predominantly Colville (85%); with minor influx of Kuparuk (10%) & Sagavanirktok Rivers (5%)
- ☰ Predominantly Kuparuk River (80%) with minor Sagavanirktok River Influx (15%) & Colville River (5% or less).

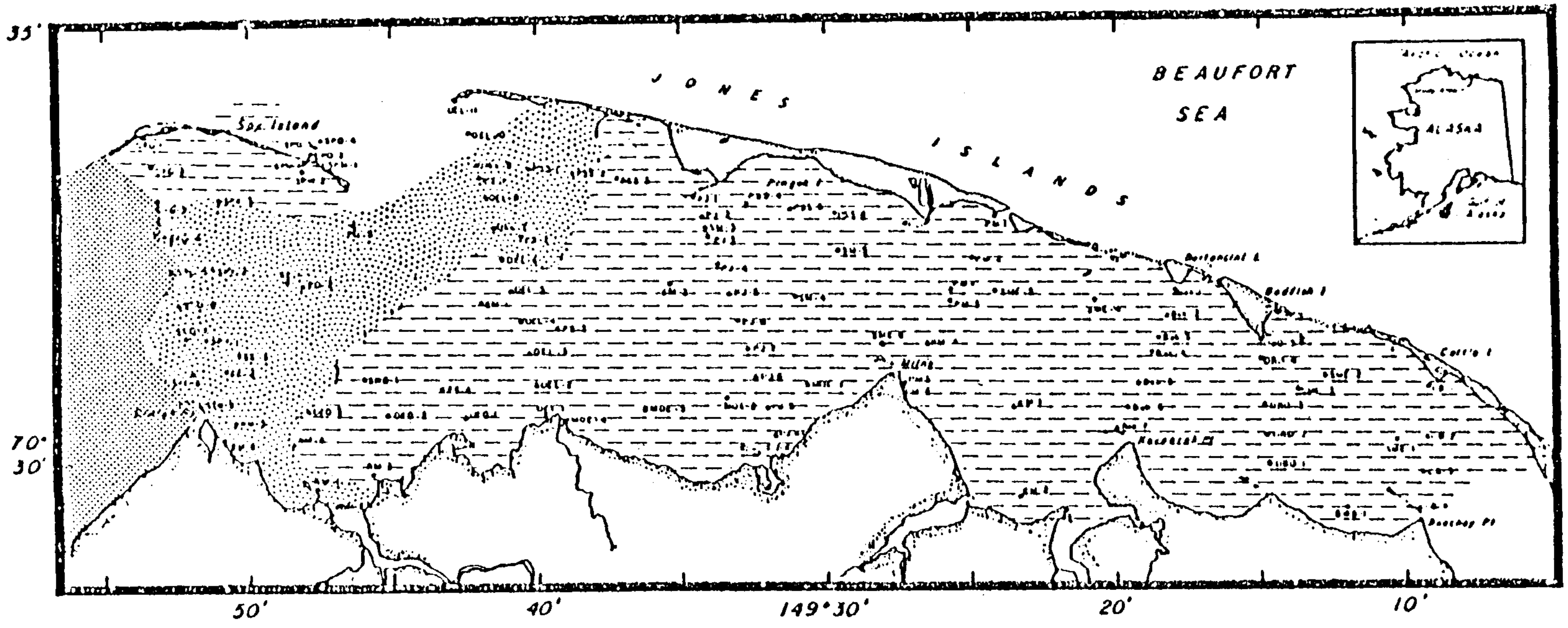

Figure 24. Sources of fine-grained (mud fraction) fluvial sediments* based on detailed clay mineral analysis.

*Sources of mud from coastal bluffs and barriers not considered.

persal of the clays to the depositional sites by the prevailing current systems, rather than to chemical reactions between detrital clays and cations in sea water (Naidu and Mowatt, 1982).

A number of investigators (Biscaye, 1965; Griffin *et al.*, 1968; Rateev *et al.*, 1969) have shown that broad latitudinal trends existed in the distribution of kaolinite and chlorite in the world's oceans. Such trends were related to the generation of characteristic clay mineral assemblages under different pedogenic processes associated with latitudinal variations in climate. Our studies in the Beaufort Sea of Alaska would seem to show that the latitudinal trends in the distribution patterns of the clay minerals, as suggested by the above authors, were not maintained, for the concentrations of kaolinite and the kaolinite/chlorite ratios were similar to those found at middle latitudes. It was suggested (Naidu *et al.*, 1971) that this apparent discrepancy was related to the reworking of kaolinite-bearing sedimentary rocks of Northern Alaska, and the subsequent supply of kaolinite to the adjacent Beaufort Sea.

In the Beaufort Sea, with the exception of the coastal area, the clay mineral assemblages do not appear to provide unequivocal means to elucidate the sources and depositional sites of fine-grained sediments in the middle and outer continental shelf areas. The patchy distribution of clay minerals in the central and outer continental shelves are presumably attributable to the highly seasonal nature of sedimentary regimes, ice-cover effects, the haphazard transport of clays by ice-rafting, and the occasional reworking and redistribution of sediments resulting from ice gouging, all of which are phenomena peculiar to the arctic sedimentary regime (Reimnitz and Barnes, 1974; Reimnitz *et al.*, 1977). The identification of an extensive, isolated area of sediment, with unexpectedly low illite (Fig. 21), accompanied by relatively high proportions of expandable clay minerals (Figs. 18 and 19) and high kaolinite/chlorite ratios, in the outer eastern shelf of the Alaskan Beaufort Sea (north and east of the Canning River delta) has proved to be an enigma. Initially, we were led to believe that the clay deposit was a contemporary sediment originally derived from the Colville River. This conclusion was based on the presence of large amounts of expandable clay minerals in the Colville River bedload (Naidu and Mowatt, 1982) as well as in the deltaic sediments off the river mouth. Currents with a net eastward vector and of sufficient strength (up to 100 cm/sec; average 40 cm/sec) were reported to prevail in the central and outer continental shelf of the Beaufort Sea (Johnson, 1956; Hufford, 1973; Mountain, 1974). Conceivably therefore, clay size particles from the Colville Delta could be transported readily to the Alaskan sector of the Eastern Beaufort Sea. However, the isolated and discontinuous position relative to the Colville Delta strongly suggests that the deposit was relict. A possible source in the Mackenzie River was considered unlikely, for there are relatively high proportions of illite and low concentrations of expandable mineral phases in the Mackenzie bedload and also in the deltaic sediments off the river mouth (Naidu and Mowatt, 1982). In addition, the distribution pattern of illite (Fig. 21) does not support a significant westward flux of Mackenzie River clays.

In the coastal Alaskan part of the Beaufort Sea the lateral variations in clay mineral assemblages were shown by Naidu and Mowatt (1974, 1982) to reflect the differences in the clay mineral suites of the major rivers of the North Slope of Alaska and to show limits of westward littoral transport of the clays from the various fluvial outfalls. The presence of a net westward littoral drift in the above area was confirmed by investigations based on nearshore current measurements and experiments involving drifters (Wiseman *et al.*, 1973; Dygas and Burrell, 1976; Barnes and Toimil, 1979; Matthews, 1981).

In attempting to explain the seaward decrease in expandable clay minerals relative to illite, we have considered possible authigenic and diagenetic changes in clay mineral suites resulting from changing salinities, particularly in light of the experimental data gathered by Whitehouse *et al.* (1960), in addition to our own studies on Colville River clays (Mowatt *et al.*, 1974). Naidu and Mowatt (1975, 1982) suggested that the observed variations in the clay mineral assemblages of Colville Delta are largely due to "reconstitution" (Weaver, 1958a, 1958b) of some of the expandable material by K^+ adsorption by degraded (depotassicated) illites and/or by mixed-layered illite/smectite that had intercalated degraded illite phases. The proposed mineral reconstitution probably occurred through a process of halmyrolysis as some of the expandable clay minerals were passed from non-saline to the saline environment. This further seemed likely considering that a portion of the expandable minerals (other than the depotassicated illites) of the Colville River are predominantly well-defined smectite, derived principally from the Uniat Bentonite, thoroughly characterized by Anderson and Reynolds (1966). The conversion of such a smectite to illite in the contemporary marine environment is difficult to conceive, particularly in light of thermodynamic arguments (Eberl and Hower, 1976), and the character of illites and mixed-layer illite/montmorillonites (Hower and Mowatt, 1966).

In summary, our ability to fingerprint the clay mineral assemblages of the various fluvial systems of the North Slope offers a unique criterion to interpret the disposition of paleochannels, and also of paleocurrent directions, for the Beaufort Sea nearshore. Additionally, based on our studies, it would seem that dispersal patterns and depositional sites of any pollutants that would be scavenged by clay minerals and discharged from specific discharge points, can be predicted for the Beaufort Sea inner continental shelf.

SEDIMENT GEOCHEMISTRY

Organic Carbon and C/N Ratios: The average concentrations (by dry weight %) of organic carbon and nitrogen and the average C/N ratios of marine sediments for various environments of the North Alaskan Arctic are presented in Table VI. The distribution pattern of organic carbon in the Beaufort Sea and the Simpson Lagoon are shown in Figures 25 and 26 respectively. The C/N ratios of the arctic deltaic sediments are slightly higher than the 8 to 12 ratios that were reported as typical for the low-latitude deltaic sediments. A net decrease in the C/N ratios of sediments from the nearshore to deeper waters are recognized. It is surmised that the latter variations are most likely attributable to seaward decrease in the proportion of terrigenous organic detritus as opposed to marine detritus. This is consistent with the pattern of seaward variations in the stable isotope ratios ($\delta\ ^{13}C$) of total organic carbon in continental margin sediments of Beaufort Sea (Gearing *et al.*, 1977).

Organic carbon in the particulate and dissolved phases of a few water samples were analyzed. The content of particulate organic carbon (POC) in the Colville River fresh-water regime was 0.54 mg ℓ^{-1}, whereas in the lower saline or brackish portion it was about 0.34 mg ℓ^{-1}. In the east Harrison Bay and Simpson Lagoon the POC values were 0.28 and 0.31 mg ℓ^{-1}, respectively. The dissolved organic carbon (DOC) in the Colville River and east Harrison Bay waters were 4.4 and 2.9 mg ℓ^{-1}, respectively.

TABLE VI

AVERAGE CONTENTS (BY DRY WT. %) OF ORGANIC CARBON AND NITROGEN, AND AVERAGE C/N RATIOS OF COASTAL TUNDRA PEAT, AND SURFICIAL SEDIMENTS OF THE CONTINENTAL MARGIN OF THE BEAUFORT SEA AND CANADA BASIN

Environment	Organic Carbon	Nitrogen	C/N Ratios
Harrison Bay	0.88	0.08	11.7
Simpson Lagoon	1.12	0.08	13.2
Open Beaufort Sea Shelf (21 m to 64 m)	0.73	0.08	9.0
Continental Slope (64-1000 m)	0.89	0.12	7.0
Deep-Sea (>1000 m)	0.81	0.17	5.2
Coastal Tundra Peat*	-	-	19.0*

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*Average of C/N ratios of several samples provided by Dr. D. Schell (personal communication).

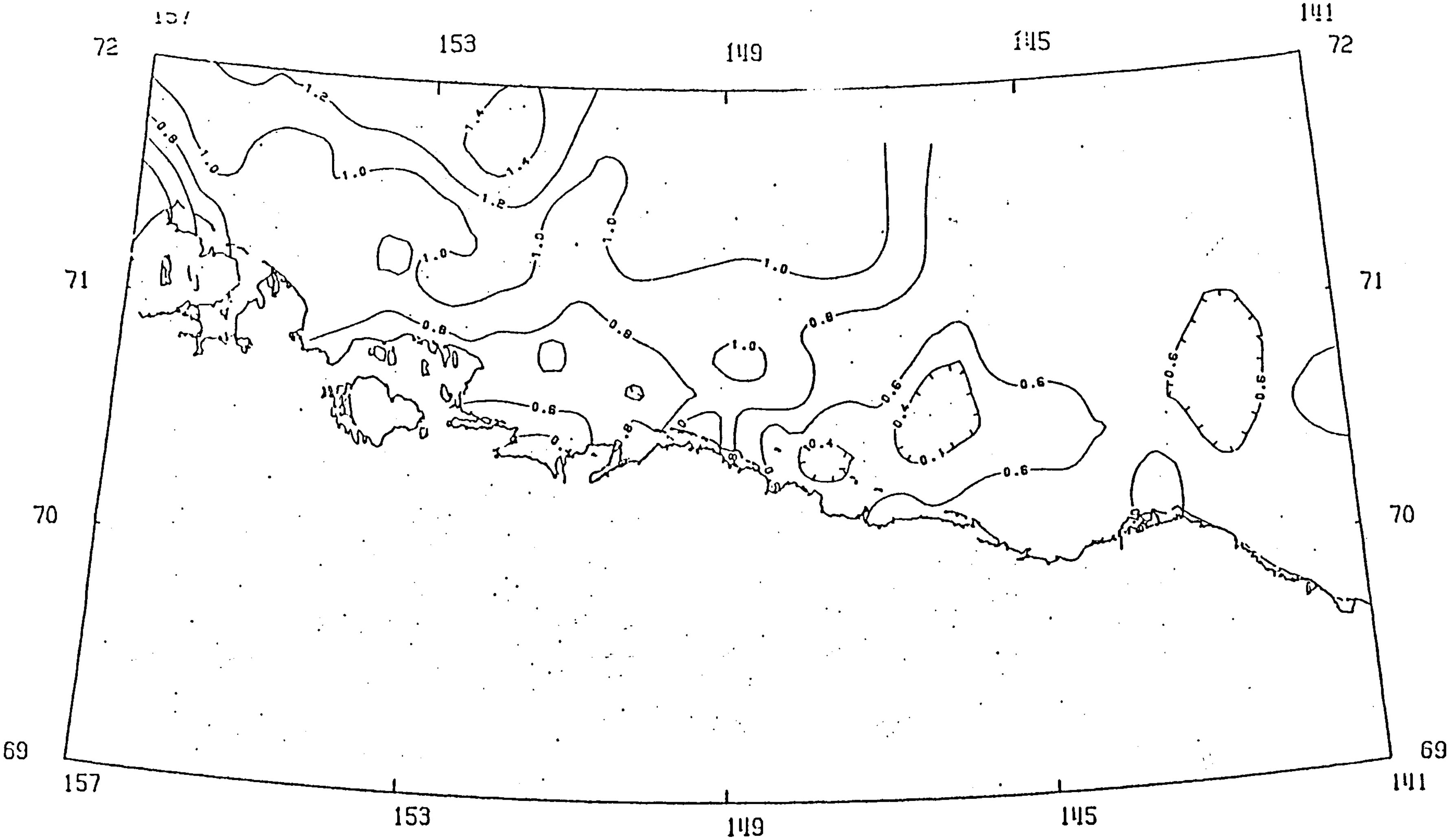

Figure 25. Map of the Beaufort Sea showing the distribution of organic carbon (wt. %) in bottom sediments.

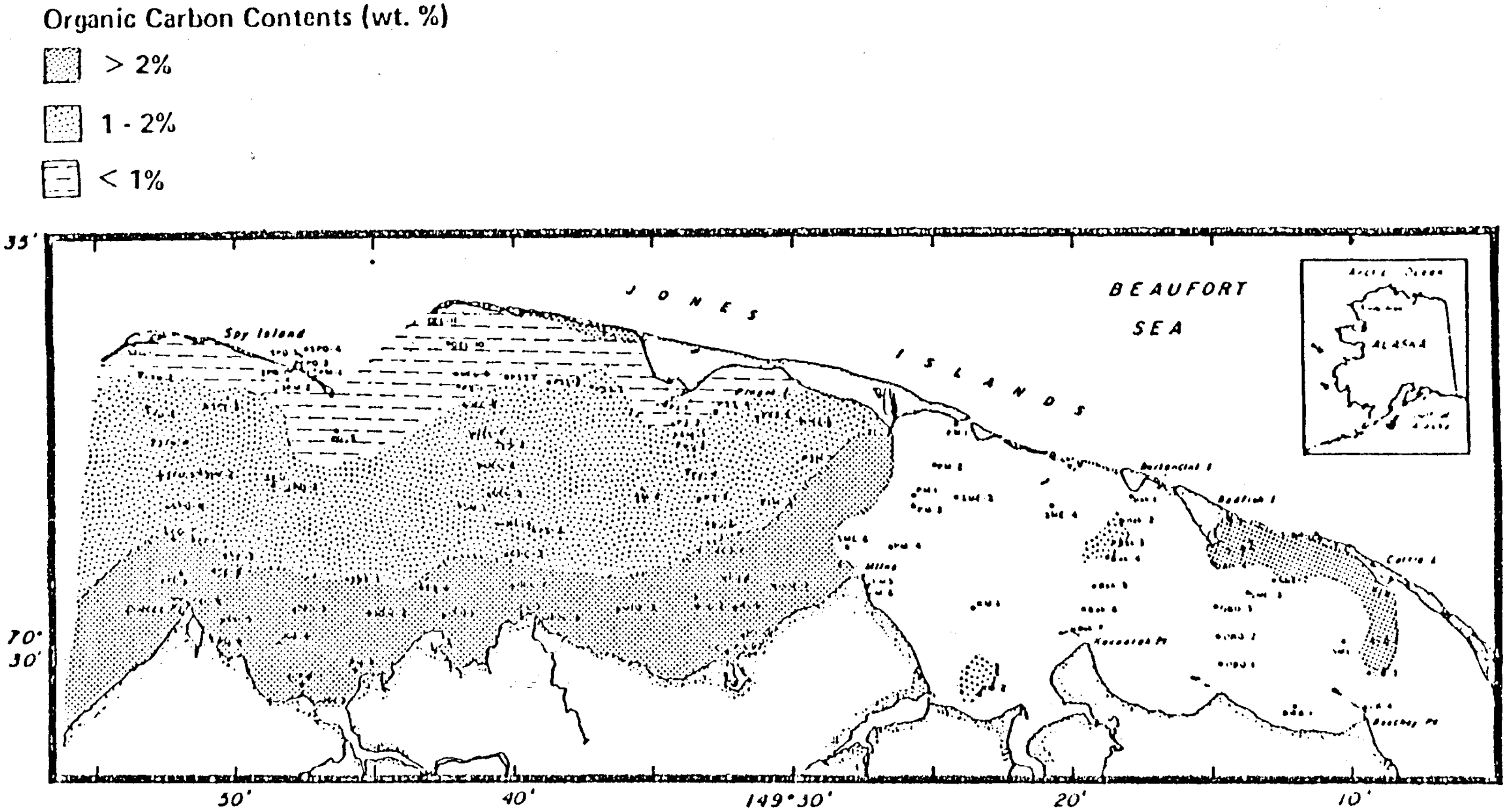

Figure 26. Organic carbon contents (dry weight percent) in substrate sediments in Simpson Lagoon.

Carbonate Contents: The distributional pattern of carbonate contents (dry weight %) in bottom sediments of the Beaufort Sea are illustrated in Figure 27. A net seaward decrease in carbonate contents is apparent.

Heavy Metal Geochemistry: The baseline average concentrations of eight metals (e.g., Fe, Mn, Cu, Co, Cr, Ni, V and Zn) in gross sediments and "readily" mobilized sediment fractions in four depositional facies (e.g., continental shelf, Harrison Bay, Simpson and Beaufort Lagoons) of the Beaufort Sea are compared in Table VII. More detailed fractionation patterns of the metals for six different Simpson Lagoon sediments are shown in Tables VIII to XIII. The distributional patterns of the eight metals surface sediments of Beaufort Sea are displayed in Figures 28 to 35.

An abbreviated reaction description, for data presented in Tables VIII to XIII, with the corresponding sediment constituent presumably under attack is shown for each treatment. The seven-step treatment scheme is similar to the scheme used by Gupta and Chen (1975, among many others), in basic form and rationale. The more easily leached metal phases (or the more "readily" mobilized fractions) are selectively removed first and the relatively more stable forms are attacked in successive steps.

The references for treatments adopted were:

Idealized Fraction	References
Exchangeable	Jackson, 1958
Carbonates	Sibbesen, 1977
Organic Complex	Giovannini and Sequi, 1976
Manganese and Easily Reducible Oxides	Daly and Binnie, 1974
Moderately Reducible and Crystalline Iron Oxides	Coffin, 1963
Remaining Nonsilicates, Sulfides and Organics	Agemian and Chau, 1977; Olade and Fletcher, 1974

TABLE VII

AVERAGE CONCENTRATIONS (μg/g, EXCEPT Fe WHICH IS IN 10 μg/g) OF SOME HEAVY METALS IN THE TOTAL (T) AND THE ACETIC ACID-HYDROXYLAMINE HYDROCHLORIDE EXTRACTS (E), WITH CALCULATED PERCENT EXTRACTABLE QUANTITIES (%E) FROM 54 SIMPSON LAGOON, 19 BEAUFORT LAGOON, 7 BEAUFORT SEA SHELF AND 7 HARRISON BAY SEDIMENTS

	V			Cr			Mn			Fe			Co			Ni			Cu			Zn		
Environment	T	E	%E	T	E	%E	T	E	%E	T	E	%E	T	E	%E	T	E	%E	T	E	%E	T	E	%E
Simpson Lagoon	70	4	6	45	1	2	260	130	50	2.0	.22	11	8	2	25	23	3	14	17	3	18	76	13	17
Beaufort Lagoon	100	9	9	55	1.6	3	400	200	50	2.8	.31	11	10	3.5	35	30	3	10	27	4	15	80	15	19
Beaufort Sea Shelf	140	10	17	85	1.6	2	560	230	40	4.1	.42	10	16	3.9	24	40	3.7	9	33	8	24	112	21	19
Harrison Bay	108	14	13	67	2.5	4	410	180	44	2.8	.57	20	10	2.5	25	28	4.5	16	30	7	23	80	22	28

TABLE VIII

AVERAGE CONCENTRATIONS (μg/g) OF SOME HEAVY METALS IN EXTRACTS FROM A SEVEN-STEP, TWO-STEP, AND SINGLE CHEMICAL TREATMENT, AS WELL AS TOTAL DISSOLUTION OF SL877-2 (SAND SEDIMENT, SIMPSON LAGOON)

EXTRACTION PROCEDURE[a]	IDEALIZED FRACTION TARGET	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
I. Seven-Step Treatment[b]									
1. 0.2 N $MgCl_2$ - triethanolamine; pH 8.1; 5 minutes	Exchangeable	0.13	0.02	9	3	0.02	0.07	0.23	
2. Cation exchange resin in nylon net bag; pH 5; 8 hours	Carbonates	0.12	0.12	20	40	0.18	0.5	0.6	2.5
3. Acetylacetone in benzene (5:95); 200 hours	Organic complex	0.2	0.03	15	200	0.15	0.03	1	
4. 0.1 M hydroxylamine-HCl in 0.01 M HNO_3 (pH 2); 30 minutes	Manganese and easily reducible oxides	0.2	0.03	15	100	0.2	0.2	0.37	2
5. 0.2 M acid ammonium oxalate; pH 3.3 buffered; 2 hours	Amorphous iron oxides	1.7	0.15	5	1,100	0.2	0.4	1	2
6. 5% sodium dithionite in 0.2 M citrate buffer (pH 4.8); 30 minutes; 50°C	Moderately reducible and crystalline iron oxides	2	0.5	12	2,100	0.8	0.8	0.3	
7. 2% $KClO_3$ in 0.5 N HCl; pH 0.3; 24 hours	Remaining nonsilicates; authigenic sulfides, organic complex	0.55	0.2	5	400	0.25	0.9	1	
Extractable Total		4.9	1.05	81	3,943	1.8	2.9	4.5	
Concentrated HF (48%) and HNO_3 (70%) digestion (1:1)[c]	Residual, resistant minerals	NA	16.35	35	5,000	NA	3.2	4.4	11.6
Sum Total			17.4	116	8,943		6.1	8.9	
II. Two-Step Treatment[d]									
1. 0.1 M hydroxylamine-HCl in 0.01 M HNO_3 (pH 2); 30 minutes	Exchangeable, carbonates, easily reducible oxides								
2. 0.5 N HCl; pH 0.3; 12 hours	Iron oxides, organic complex, authigenic sulfides								
Extractable Total									
III. Single Treatment[e]									
1 M hydroxylamine-HCl in 25% acetic acid; pH 1.5; 4 hours	Exchangeable, carbonates, manganese oxides, some iron oxides	2.0	0.44	80	1,100	0.66	1.0	1.1	3.0
IV. Single Total Dissolution[c]									
Concentrated HF-HNO_3 digestion (1:1)	Entire sediment	36	21	146	9,500	3.6	11	11	28

[a] Temperature of 25°C unless otherwise specified.

[b] Sequence modified after Gupta and Chen, 1975 (see text for details).

[c] Rader and Grimaldi, 1961.

[d] As suggested in this study (see text for details).

[e] Chester and Hughes, 1967.

TABLE IX

AVERAGE CONCENTRATIONS (μg/g) OF SOME HEAVY METALS IN EXTRACTS FROM A SEVEN-STEP, TWO-STEP, AND SINGLE CHEMICAL TREATMENT, AS WELL AS TOTAL DISSOLUTION OF SL877-13 (SILT SEDIMENT, SIMPSON LAGOON)

EXTRACTION PROCEDURE[a]	IDEALIZED FRACTION TARGET	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
I. Seven-Step Treatment[b]									
1. 0.2 N MgCl$_2$ - triethanolamine; pH 8.1; 5 minutes	Exchangeable	0.25	0.06	37	15	0.05	0.23	0.7	
2. Cation exchange resin in nylon net bag; pH 5; 8 hours	Carbonates	0.6	1	70	150	0.3	1.8	2.7	9
3. Acetylacetone in benzene (5:95); 200 hours	Organic complex	0.5	0.05	60	400	0.3	0.02	3	
4. 0.1 M hydroxylamine-HCl in 0.01 M HNO$_3$ (pH 2); 30 minutes	Manganese and easily reducible oxides	0.5	0.05	37	85	0.15	0.2	0.2	1.3
5. 0.2 M acid ammonium oxalate; pH 3.3 buffered; 2 hours	Amorphous iron oxides	4	1	28	4,500	0.8	2	4.5	8
6. 5% sodium dithionite in 0.2 M citrate buffer (pH 4.8); 30 minutes; 50°C	Moderately reducible and crystalline iron oxides	3.7	1	40	4,050	2	3.5	1.3	
7. 2% KClO$_3$ in 0.5 N HCl; pH 0.3; 24 hours	Remaining nonsilicates; authigenic sulfides, organic complex	3.45	3.5	28	3,000	1	4.5	2.6	
Extractable Total		13	6.66	300	12,200	4.6	12.25	15	
Concentrated HF (48%) and HNO$_3$ (70%) digestion (1:1)[c]	Residual, resistant minerals								
Sum Total									
II. Two-Step Treatment[d]									
1. 0.1 M hydroxylamine-HCl in 0.01 M HNO$_3$ (pH 2); 30 minutes	Exchangeable, carbonates, easily reducible oxides								
2. 0.5 N HCl; pH 0.3; 12 hours	Iron oxides, organic complex, authigenic sulfides								
Extractable Total									
III. Single Treatment[e]									
1 M hydroxylamine-HCl in 25% acetic acid; pH 1.5; 4 hours	Exchangeable, carbonates, manganese oxides, some iron oxides	5.1	1.8	300	3,700	3.0	5.0	3.5	18
IV. Single Total Dissolution[c]									
Concentrated HF-HNO$_3$ digestion (1:1)	Entire sediment	79	60	467	26,400	9.2	29	23	88

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[a] Temperature of 25°C unless otherwise specified.

[b] Sequence modified after Gupta and Chen, 1975 (see text for details).

[c] Rader and Grimaldi, 1961.

[d] As suggested in this study (see text for details).

[e] Chester and Hughes, 1967.

TABLE X

AVERAGE CONCENTRATIONS (μg/g) OF SOME HEAVY METALS IN EXTRACTS FROM A SEVEN-STEP, TWO-STEP, AND SINGLE CHEMICAL TREATMENT, AS WELL AS TOTAL DISSOLUTION OF SL877-18 (PEATY, SILTY SAND SEDIMENT, SIMPSON LAGOON)

EXTRACTION PROCEDURE[a]	IDEALIZED FRACTION TARGET	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
I. Seven-Step Treatment[b]									
1. 0.2 N $MgCl_2$ - triethanolamine; pH 8.1; 5 minutes	Exchangeable								
2. Cation exchange resin in nylon net bag; pH 5; 8 hours	Carbonates	3.7	0.14	16	660	1.2	2.5	3.4	10.5
3. Acetylacetone in benzene (5:95); 200 hours	Organic complex	1	0.06	1	1,000	0.25	0.05	4.7	
4. 0.1 M hydroxylamine-HCl in 0.01 M HNO_3 (pH 2); 30 minutes	Manganese and easily reducible oxides	1.3	0.1	12	250	0.3	0.7	0.2	2.5
5. 0.2 M acid ammonium oxalate; pH 3.3 buffered; 2 hours	Amorphous iron oxides	5	0.9	7	4,000	0.7	3	4.6	5
6. 5% sodium dithionite in 0.2 M citrate buffer (pH 4.8); 30 minutes; 50°C	Moderately reducible and crystalline iron oxides	1.3	0.9	10	1,500	1.4	1.7	0.7	
7. 2% $KClO_3$ in 0.5 N HCl; pH 0.3; 24 hours	Remaining nonsilicates; authigenic sulfides, organic complex	2	2	16	2,080	1.3	3.5	2.1	
Extractable Total		14.5	4.2	70	9,500	5.2	11.6	16	
Concentrated HF (48%) and HNO_3 (70%) digestion (1:1)[c]	Residual, resistant minerals								
Sum Total									
II. Two-Step Treatment[d]									
1. 0.1 M hydroxylamine-HCl in 0.01 M HNO_3 (pH 2); 30 minutes	Exchangeable, carbonates, easily reducible oxides	5	0.5	44	670	1.3	3	5	16
2. 0.5 N HCl; pH 0.3; 12 hours	Iron oxides, organic complex, authigenic sulfides	8	1.6	23	4,810	1.7	4	8.5	19
Extractable Total		13	2.1	67	5,480	3	7	13.5	35
III. Single Treatment[e]									
1 M hydroxylamine-HCl in 25% acetic acid; pH 1.5; 4 hours	Exchangeable, carbonates, manganese oxides, some iron oxides	6.7	1.7	60	4,100	3.1	6.1	2.3	22
IV. Single Total Dissolution[c]									
Concentrated HF-HNO_3 digestion (1:1)	Entire sediment	74	54	163	19,300	8.7	27	20	78

[a] Temperature of 25°C unless otherwise specified.

[b] Sequence modified after Gupta and Chen, 1975 (see text for details).

[c] Rader and Grimaldi, 1961.

[d] As suggested in this study (see text for details).

[e] Chester and Hughes, 1967.

TABLE XI

AVERAGE CONCENTRATIONS ($\mu g/g$) OF SOME HEAVY METALS IN EXTRACTS FROM A SEVEN-STEP, TWO-STEP, AND SINGLE CHEMICAL TREATMENT, AS WELL AS TOTAL DISSOLUTION OF SL877-23 (SANDY SILT SEDIMENT, SIMPSON LAGOON)

EXTRACTION PROCEDURE[a]	IDEALIZED FRACTION TARGET	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
I. Seven-Step Treatment[b]									
1. 0.2 N $MgCl_2$ - triethanolamine; pH 8.1; 5 minutes	Exchangeable	0.4	0.2	20	10	0.03	0.2	0.8	
2. Cation exchange resin in nylon net bag; pH 5; 8 hours	Carbonates	1.5	0.6	80	300	0.7	2.5	2.5	13
3. Acetylacetone in benzene (5:95); 200 hours	Organic complex	0.4	0.2	20	400	0.2	0.05	3.5	
4. 0.1 M hydroxylamine-HCl in 0.01 M HNO_3 (pH 2); 30 minutes	Manganese and easily reducible oxides	0.4	0.1	20	200	0.3	0.5	0.2	3.5
5. 0.2 M acid ammonium oxalate; pH 3.3 buffered; 2 hours	Amorphous iron oxides	4	1	20	4,000	1	2	5	6
6. 5% sodium dithionite in 0.2 M citrate buffer (pH 4.8); 30 minutes; 50°C	Moderately reducible and crystalline iron oxides	3	1	40	5,000	1.7	3	1.5	
7. 2% $KClO_3$ in 0.5 N HCl; pH 0.3; 24 hours	Remaining nonsilicates; authigenic sulfides, organic complex	1.5	2	20	1,800	0.7	3	2.5	
Extractable Total		11.2	5.1	220	11,710	4.6	11.3	16	
Concentrated HF (48%) and HNO_3 (70%) digestion (1:1)[c]	Residual, resistant minerals		60	80	13,000		15	5.5	37
Sum Total			65.1	300	24,710		26.3	21.5	
II. Two-Step Treatment[d]									
1. 0.1 M hydroxylamine-HCl in 0.01 M HNO_3 (pH 2); 30 minutes	Exchangeable, carbonates, easily reducible oxides	1.5	0.2	151	170	0.8	0.3	0	3.1
2. 0.5 N HCl; pH 0.3; 12 hours	Iron oxides, organic complex, authigenic sulfides	8.8	2.5	84	4,700	2.5	7	12.2	25.4
Extractable Total		10.3	2.7	235	4,870	3.3	7.3	12.2	28.5
III. Single Treatment[e]									
1 M hydroxylamine-HCl in 25% acetic acid; pH 1.5; 4 hours	Exchangeable, carbonates, manganese oxides, some iron oxides	4.4	1.2	215	2,480	2.7	4.7	2.7	15
IV. Single Total Dissolution[c]									
Concentrated HF-HNO_3 digestion (1:1)	Entire sediment	70	56	380	20,900	8.4	27	21	93

[a] Temperature of 25°C unless otherwise specified.

[b] Sequence modified after Gupta and Chen, 1975 (see text for details).

[c] Rader and Grimaldi, 1961.

[d] As suggested in this study (see text for details).

[e] Chester and Hughes, 1967.

TABLE XII

AVERAGE CONCENTRATIONS (µg/g) OF SOME HEAVY METALS IN EXTRACTS FROM A SEVEN-STEP, TWO-STEP, AND SINGLE CHEMICAL TREATMENT, AS WELL AS TOTAL DISSOLUTION OF SL877-28 (CLAYEY SILT SEDIMENT, SIMPSON LAGOON)

EXTRACTION PROCEDURE[a]	IDEALIZED FRACTION TARGET	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
I. Seven-Step Treatment[b]									
1. 0.2 N $MgCl_2$ - triethanolamine; pH 8.1; 5 minutes	Exchangeable	0.3	0.07	10	7	0.03	0.2	0.7	
2. Cation exchange resin in nylon net bag; pH 5; 8 hours	Carbonates	1.3	0.3	30	300	0.42	3	4	8
3. Acetylacetone in benzene (5:95); 200 hours	Organic complex	1.3	0.06	5	600	0.15	0	4	
4. 0.1 M hydroxylamine-HCl in 0.01 M HNO_3 (pH 2); 30 minutes	Manganese and easily reducible oxides	1.8	0.04	20	83	0.10	0.2	0.2	1
5. 0.2 M acid ammonium oxalate; pH 3.3 buffered; 2 hours	Amorphous iron oxides	5	1	20	4,100	1.2	3.5	6	8
6. 5% sodium dithionite in 0.2 M citrate buffer (pH 4.8); 30 minutes; 50°C	Moderately reducible and crystalline iron oxides	4.3	0.7	45	4,900	2	3.5	1.2	
7. 2% $KClO_3$ in 0.5 N HCl; pH 0.3; 24 hours	Remaining nonsilicates; authigenic sulfides, organic complex	2.5	2	30	2,700	1	4	3.5	
Extractable Total		16.5	4.17	160	12,690	4.9	14.4	19.6	
Concentrated HF (48%) and HNO_3 (70%) digestion (1:1)[c]	Residual, resistant minerals								
Sum Total									
II. Two-Step Treatment[d]									
1. 0.1 M hydroxylamine-HCl in 0.01 M HNO_3 (pH 2); 30 minutes	Exchangeable, carbonates, easily reducible oxides								
2. 0.5 N HCl; pH 0.3; 12 hours	Iron oxides, organic complex, authigenic sulfides								
Extractable Total									
III. Single Treatment[e]									
1 M hydroxylamine-HCl in 25% acetic acid; pH 1.5; 4 hours	Exchangeable, carbonates, manganese oxides, some iron oxides	5.1	1.8	114	2,740	2.3	4.3	2.8	16
IV. Single Total Dissolution[c]									
Concentrated HF-HNO_3 digestion (1:1)	Entire sediment	93	62	290	26,700	9.3	32	23	100

[a] Temperature of 25°C unless otherwise specified.

[b] Sequence modified after Gupta and Chen, 1975 (see text for details).

[c] Rader and Grimaldi, 1961.

[d] As suggested in this study (see text for details).

[e] Chester and Hughes, 1967.

TABLE XIII

AVERAGE CONCENTRATIONS (μg/g) OF SOME HEAVY METALS IN EXTRACTS FROM A SEVEN-STEP, TWO-STEP, AND SINGLE CHEMICAL TREATMENT, AS WELL AS TOTAL DISSOLUTION OF UG-1 (PEATY, CLAYEY-SILT SAND SEDIMENT, SIMPSON LAGOON)

EXTRACTION PROCEDURE[a]	IDEALIZED FRACTION TARGET	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
I. Seven-Step Treatment[b]									
1. 0.2 N $MgCl_2$ - triethanolamine; pH 8.1; 5 minutes	Exchangeable	0.4	0.05	17	30	0.03	0.25	0.55	
2. Cation exchange resin in nylon net bag; pH 5; 8 hours	Carbonates	1	0.5	34	220	0.47	4.3	2.5	12
3. Acetylacetone in benzene (5:95); 200 hours	Organic complex	0.4	0.05	10	200	0.1	0.05	2	
4. 0.1 M hydroxylamine-HCl in 0.01 M HNO_3 (pH 2); 30 minutes	Manganese and easily reducible oxides	0.4	0.05	11	170	0.2	0.7	0.05	2.5
5. 0.2 M acid ammonium oxalate; pH 3.3 buffered; 2 hours	Amorphous iron oxides	2.6	0.85	7	3,000	0.5	2	3.5	6
6. 5% sodium dithionite in 0.2 M citrate buffer (pH 4.8); 30 minutes; 50°C	Moderately reducible and crystalline iron oxides	4	1.5	26	3,700	1.7	2.7	1.2	
7. 2% $KClO_3$ in 0.5 N HCl; pH 0.3; 24 hours	Remaining nonsilicates; authigenic sulfides, organic complex	2	2.2	12	1,400	0.5	3	2	
Extractable Total		10.8	5.2	117	8,720	3.5	13	11.8	
Concentrated HF (48%) and HNO_3 (70%) digestion (1:1)[c]	Residual, resistant minerals								
Sum Total									
II. Two-Step Treatment[d]									
1. 0.1 M hydroxylamine-HCl in 0.01 M HNO_3 (pH 2); 30 minutes	Exchangeable, carbonates, easily reducible oxides								
2. 0.5 N HCl; pH 0.3; 12 hours	Iron oxides, organic complex, authigenic sulfides								
Extractable Total									
III. Single Treatment[e]									
1 M hydroxylamine-HCl in 25% acetic acid; pH 1.5; 4 hours	Exchangeable, carbonates, manganese oxides, some iron oxides	3.5	0.7	90	1,500	2.1	4	0.4	12
IV. Single Total Dissolution[c]									
Concentrated HF-HNO_3 digestion (1:1)	Entire sediment	56	46	211	16,500	6	21	16	65

[a] Temperature of 25°C unless otherwise specified.

[b] Sequence modified after Gupta and Chen, 1975 (see text for details).

[c] Rader and Grimaldi, 1961.

[d] As suggested in this study (see text for details).

[e] Chester and Hughes, 1967.

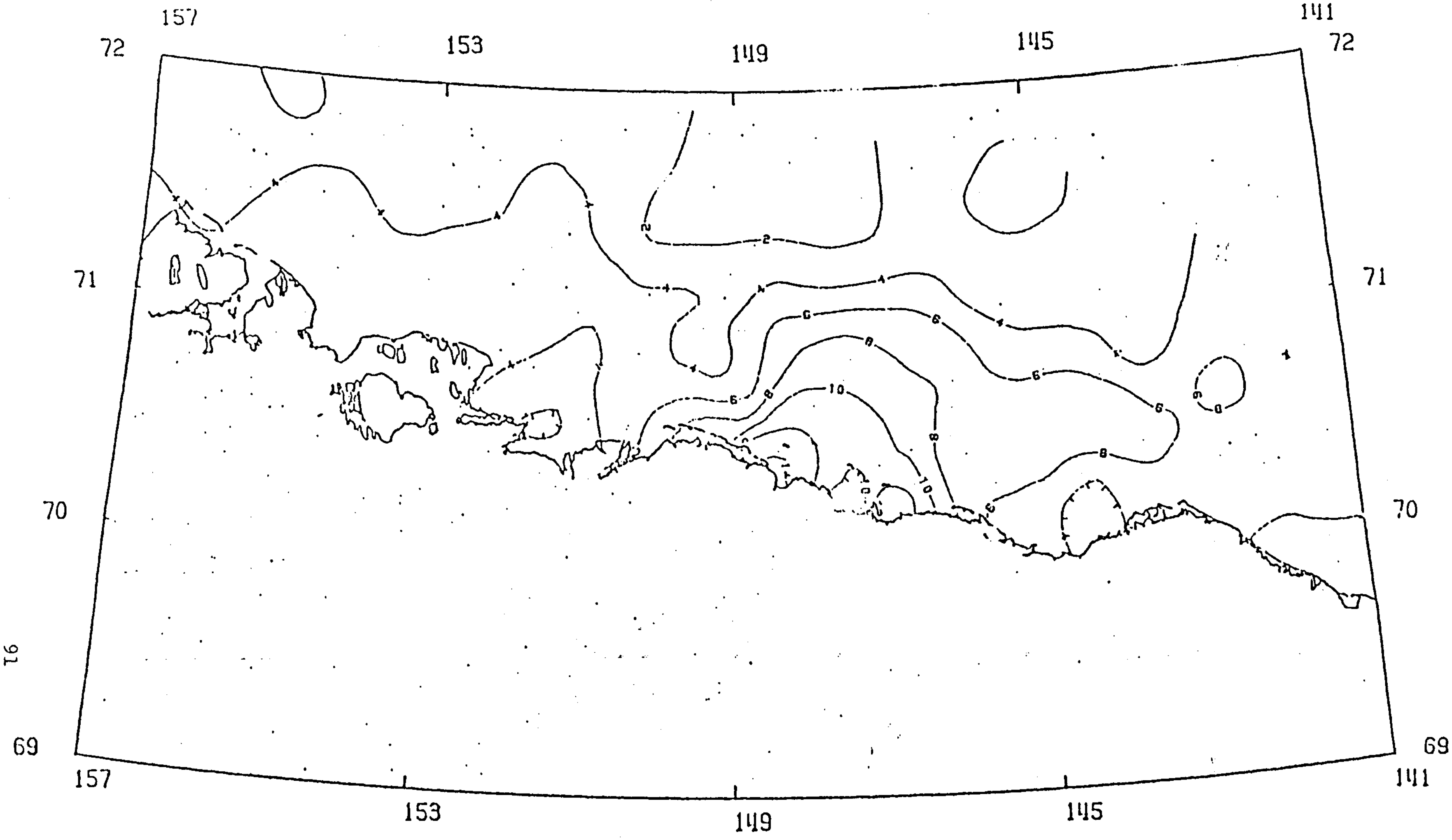

Figure 27. Map of the Beaufort Sea showing the distribution of carbonate (wt. %) in bottom sediments.

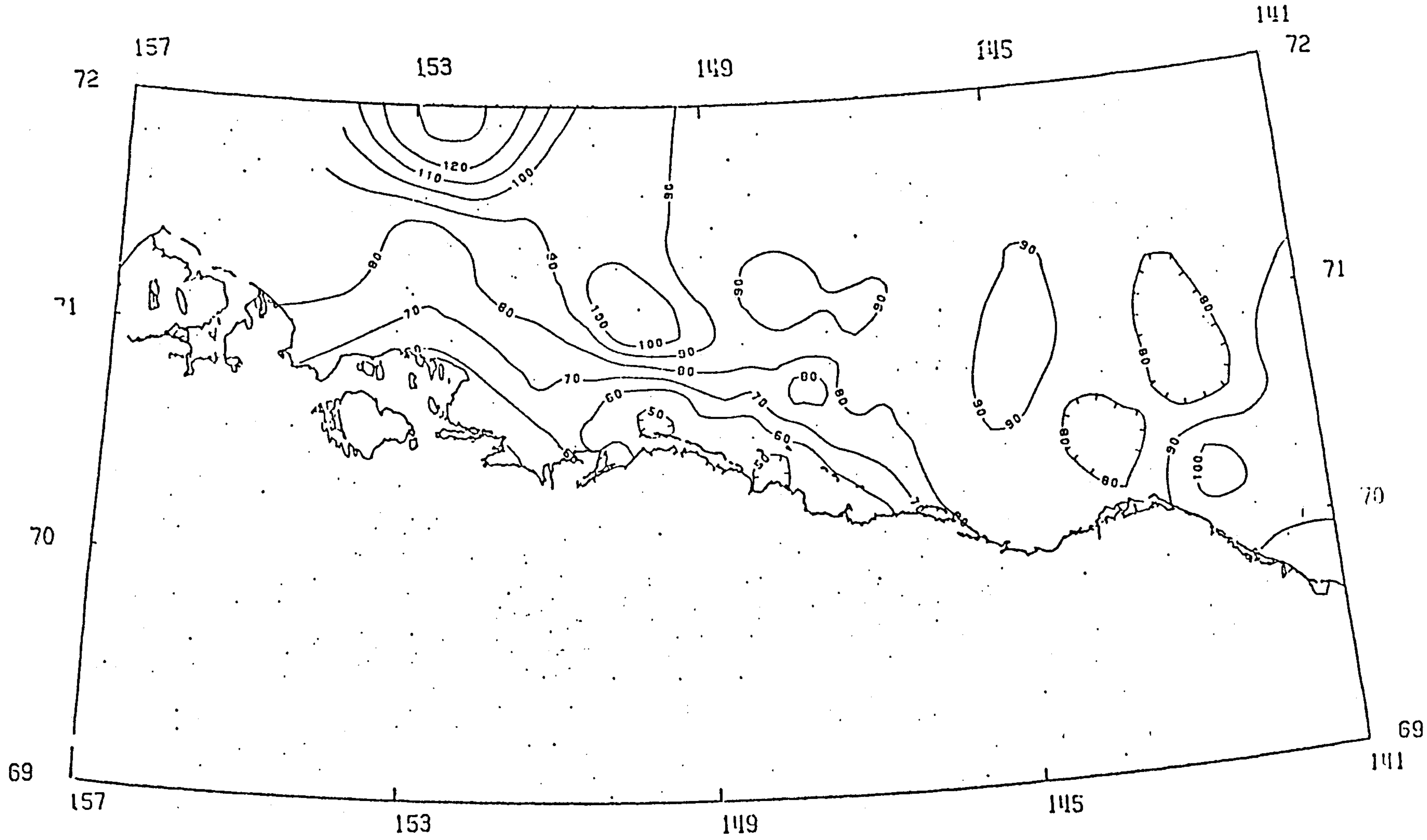

Figure 28. Map of the Beaufort Sea showing the variations in the concentrations (μg/g) of chromium in bottom sediments.

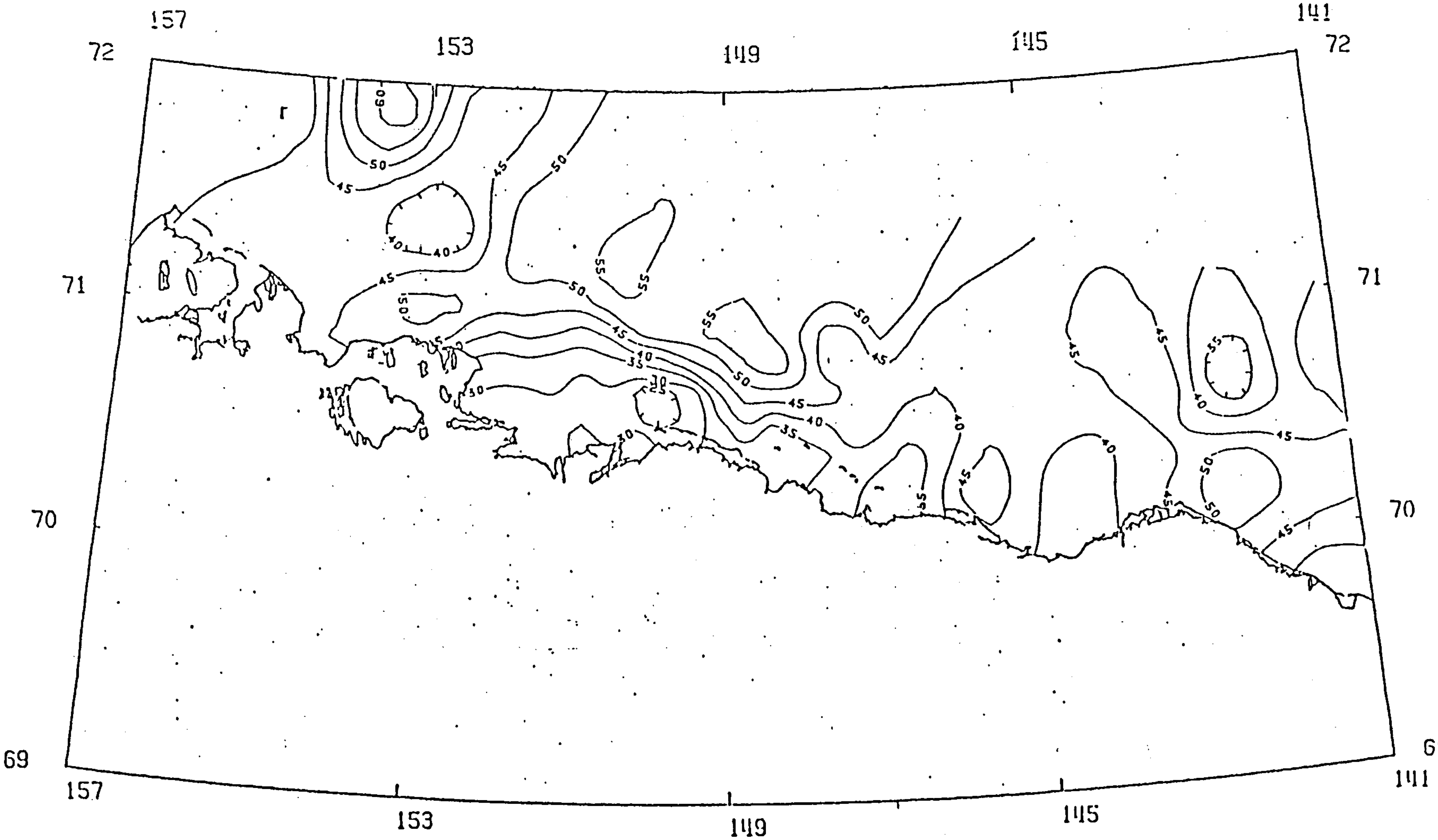

Figure 29. Map of the Beaufort Sea showing the variation in the concentrations (μg/g) of nickel in bottom sediments.

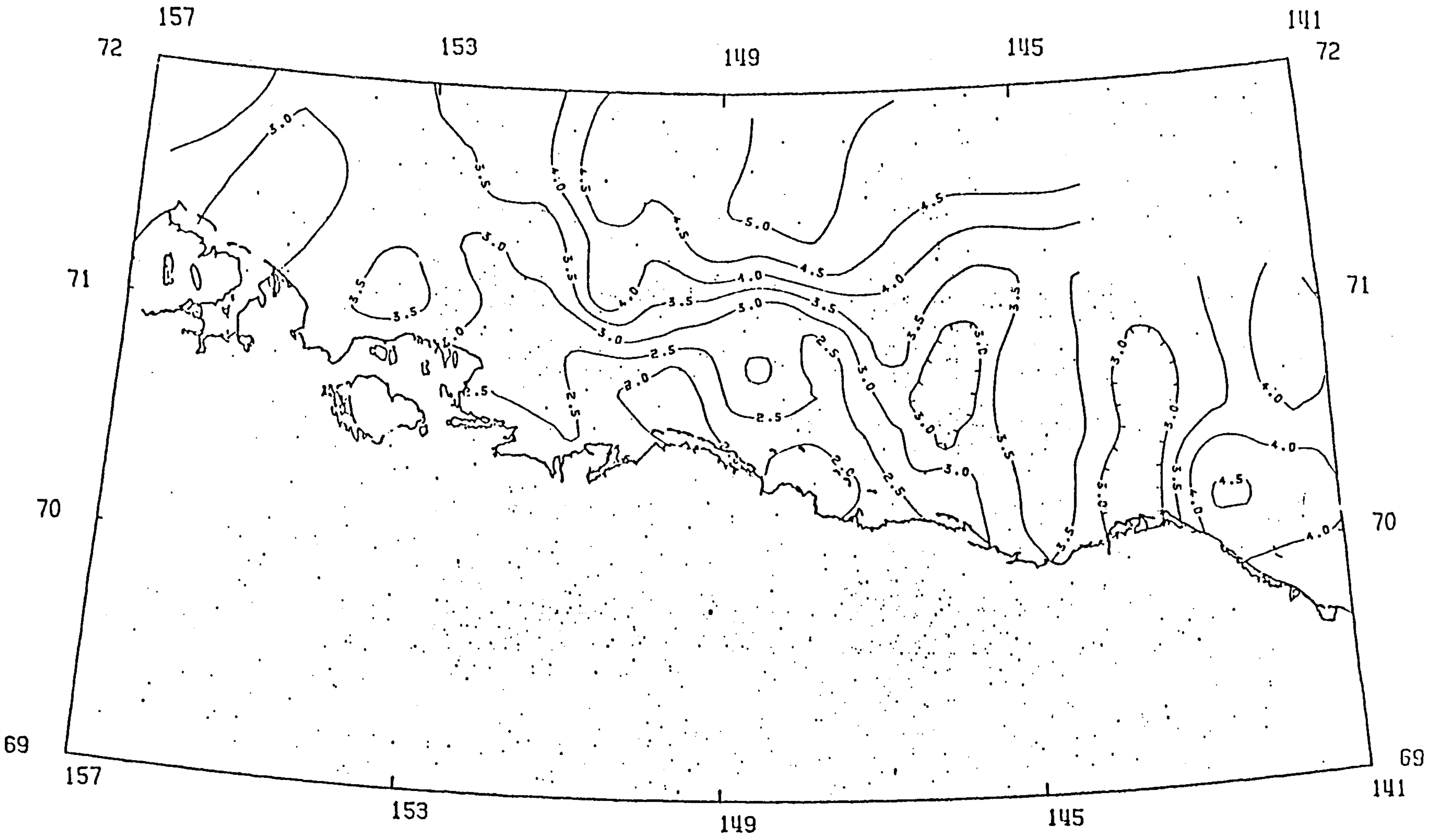

Figure 30. Map of the Beaufort Sea showing the variation of the concentrations ($10^4 \times \mu g/g$) of iron in bottom sediments.

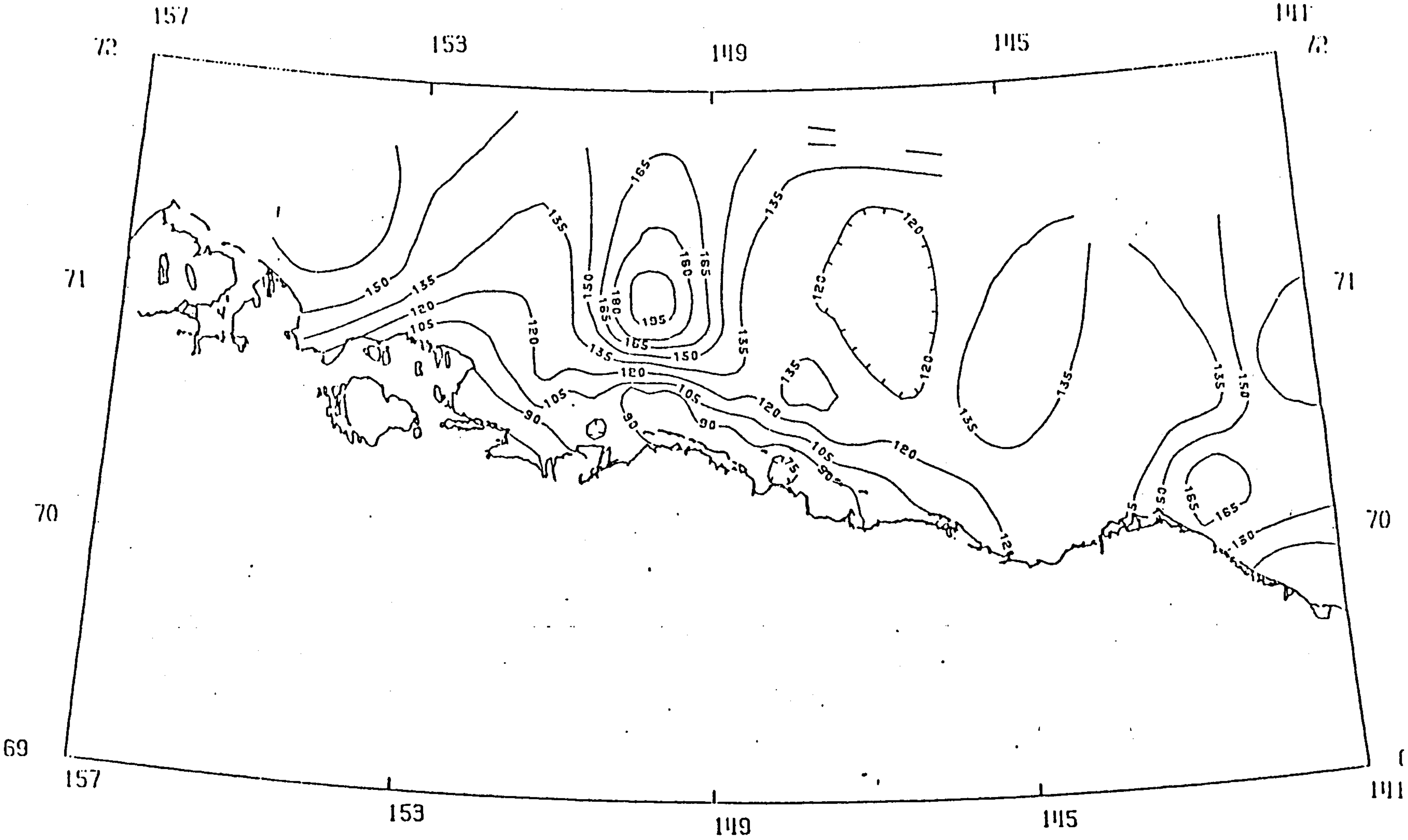

Figure 31. Map of the Beaufort Sea showing variation in the concentrations (μg/g) of vanadium in bottom sediments.

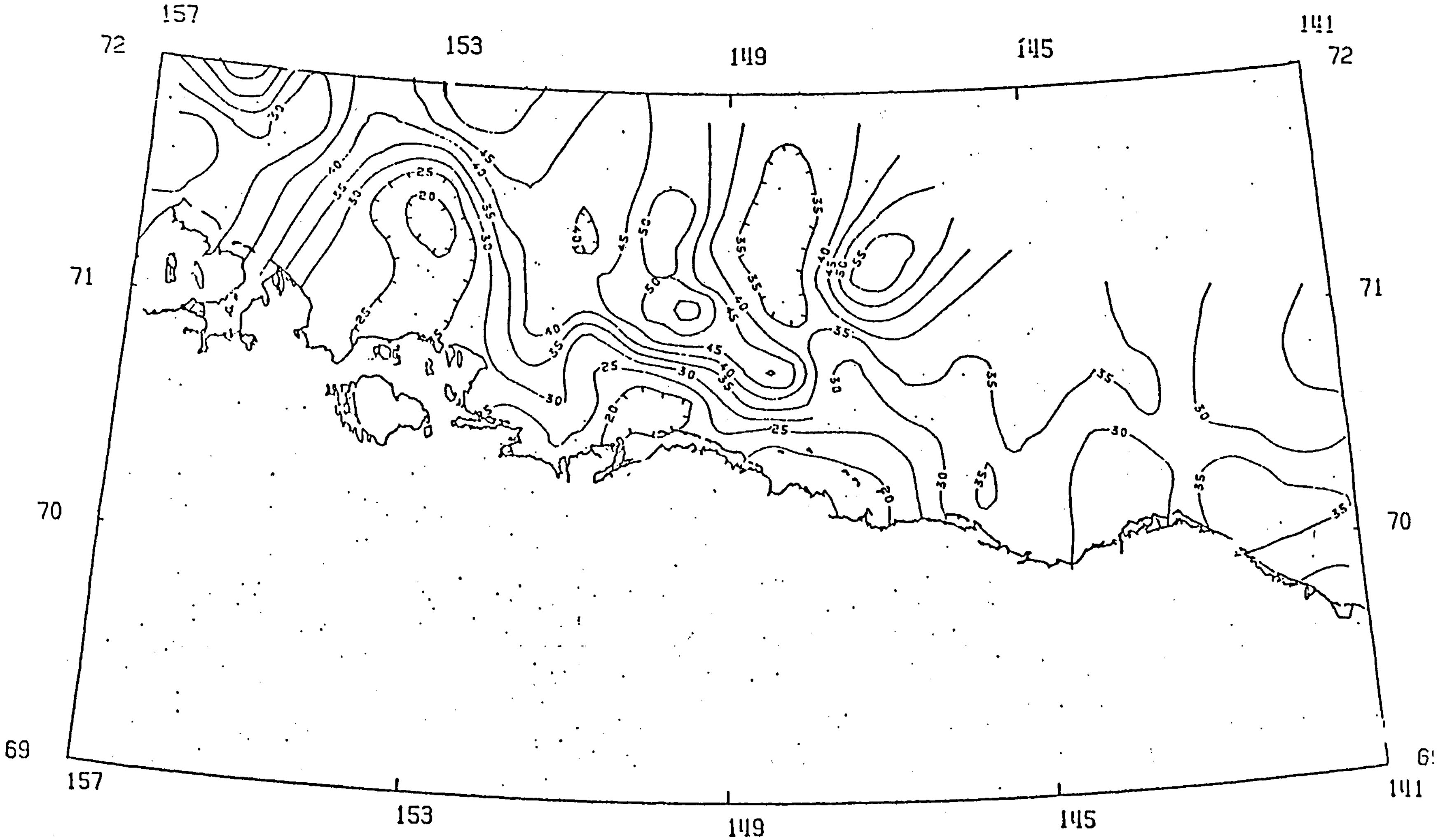

Figure 32. Map of the Beaufort Sea showing variation in the concentrations (μg/g) of copper in bottom sediments.

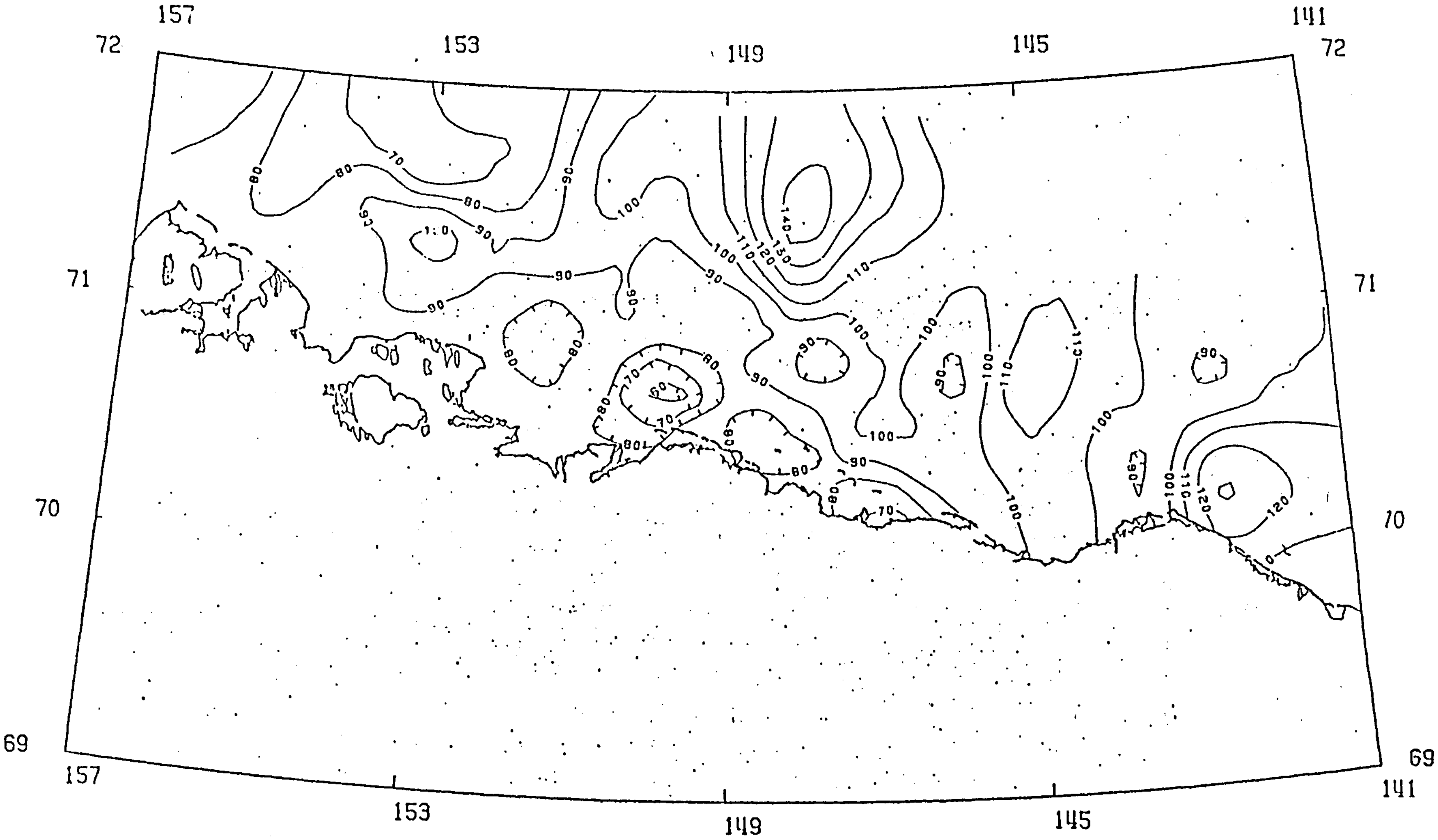

Figure 33. Map of the Beaufort Sea showing variation in the concentrations of zinc in the bottom sediments.

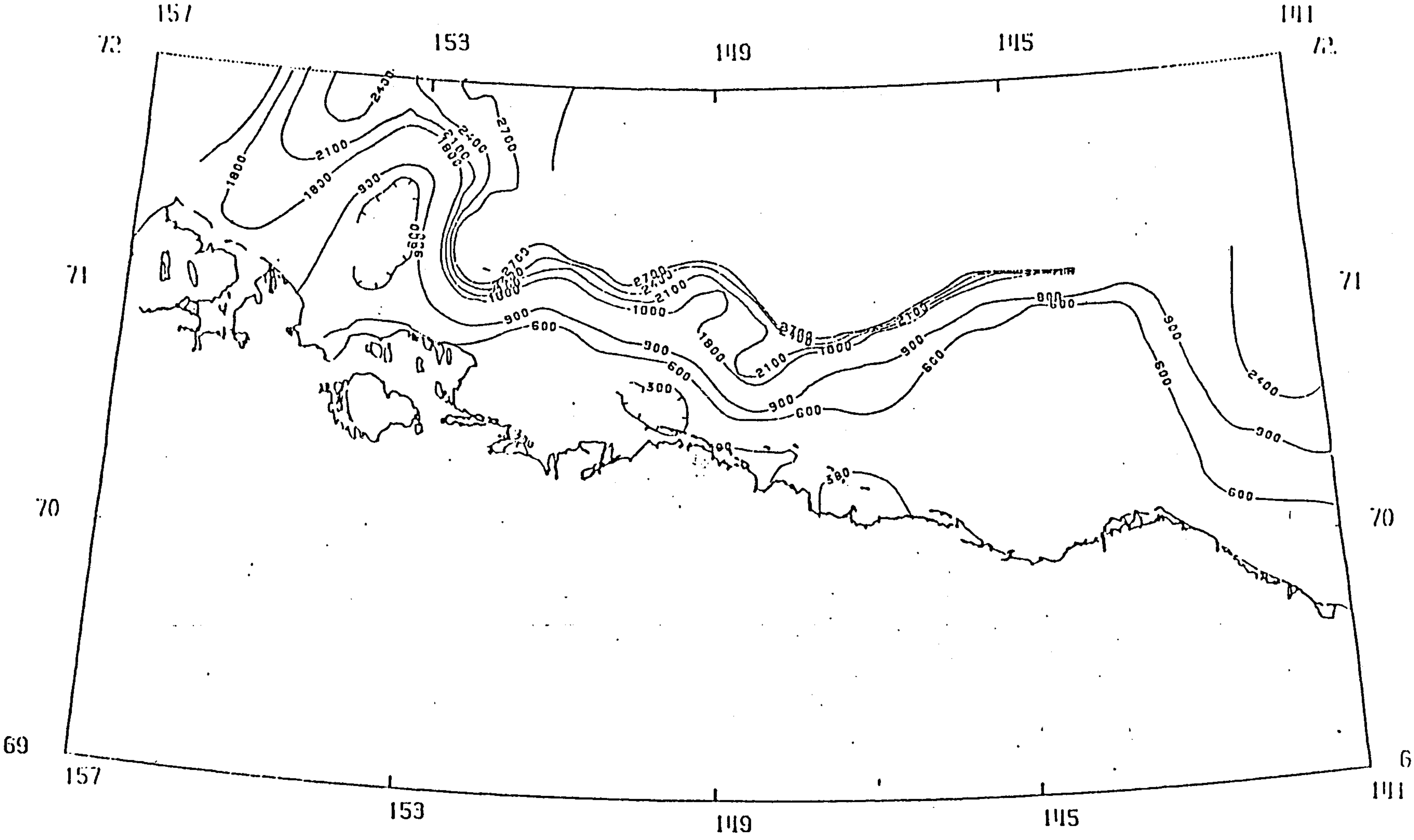

Figure 34. Map of the Beaufort Sea showing variation in the concentrations of manganese in bottom sediments.

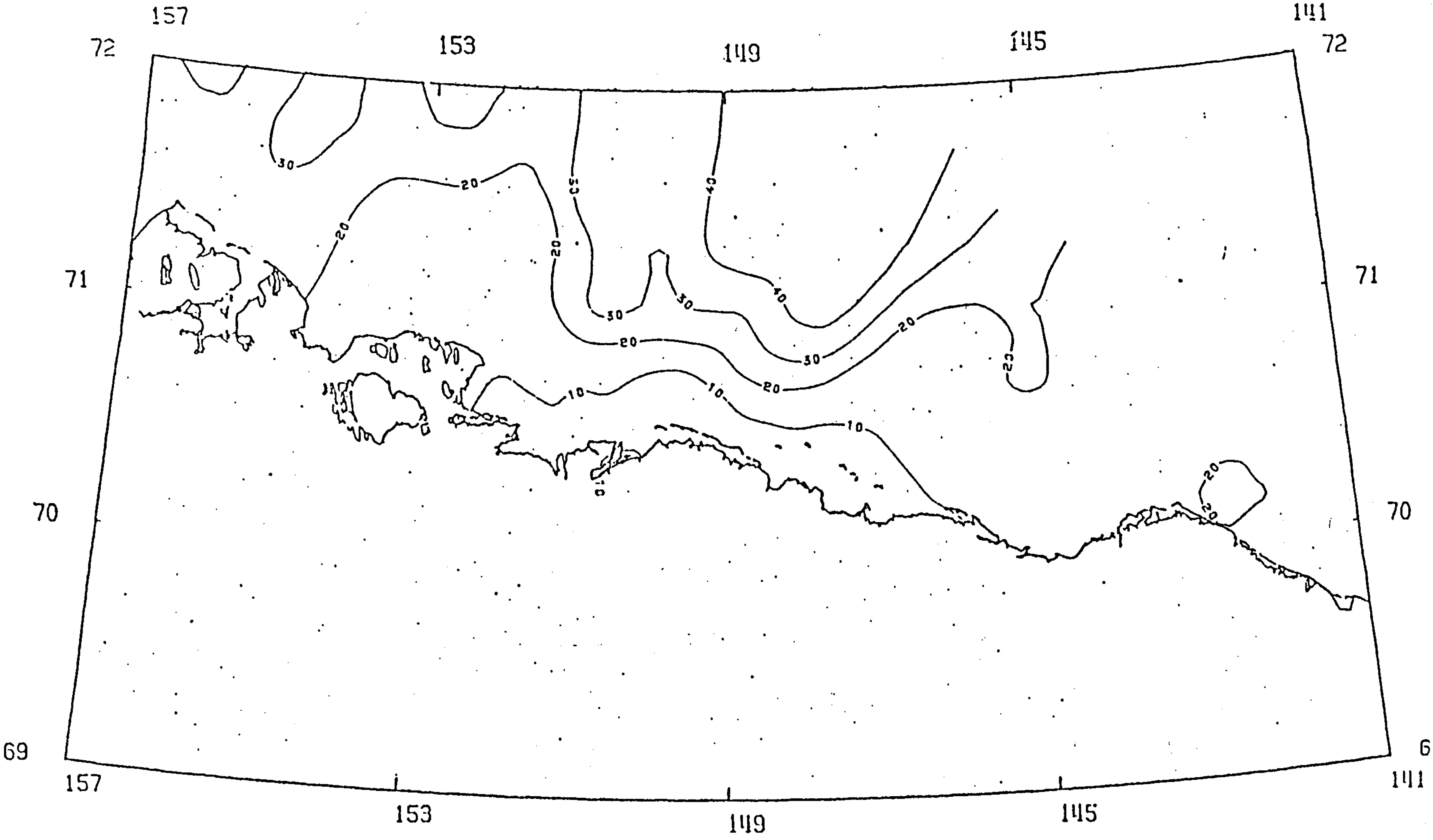

Figure 35. Map of the Beaufort Sea showing the variation in the concentrations (µg/g) of cobalt in bottom sediments.

A two-step abridgement of the above six steps is also shown for two of the six samples. Here, the very complex sediment assemblage was simplified into two categories: easily leachable and moderately leachable.

The single treatment was the familiar hydroxylamine hydrochloride-acetic acid procedure of Chester and Hughes (1967).

The foregoing laboratory investigations, and the interelement and the elemental-lithological correlation matrix (Table IX) have assisted in understanding the partitioning of the eight metals in the sediments.

The bulk of the iron occurred in the last steps of the sequential scheme, i.e., oxalate, dithionite, HCl, and HF-HNO_3 treatments. Approximately half of the total iron was non-residual, i.e., removed into the seven extractions. The oxalate, dithionite, and HCl steps account for 90% of the non-residual iron. Therefore, most of the available iron required a moderate to strong chemical attack to be released from the sediment. While the remaining elements showed great variation in the proportion of residual to non-residual partitioning, they generally followed iron's non-residual distribution pattern among the various leachates.

Iron oxides appeared to account for a large share of the nonsilicate metal partitioning. Note, however, the abundance of metals removed by step 2 (cation exchange resin). This implies that a significant amount of the metals can be released from sediments merely by a small lowering of the pH of the environment.

Copper displayed the most distinctive extraction behaviour of all the trace elements. It showed the least association with oxides phases. Relatively more copper was removed by the weaker treatments and it had the highest non-residual proportion of the eight metals studied (up to 80%).

TABLE XIV

CORRELATION COEFFICIENTS[a] FOR CHEMICAL AND TEXTURAL COMPOSITIONS[b] OF 54 SIMPSON LAGOON SEDIMENTS, ARCTIC COAST OF NORTHERN ALASKA

	D	Sd	St	Cl	Mu	CO_3	OC	NE Fe	E Fe	NE Mn	E Mn	NE Zn	E Zn	NE V	E V	NE Cr	E Cr	NE Ni	E Ni	NE Cu	E Cu	NE Co	E Co
D																							
Sd	-0.630																						
St	0.638	-0.987																					
Cl	0.465	-0.829	0.762																				
Mu	0.630	-1.000	0.987	0.829																			
CO_3	0.490	-0.843	0.829	0.712	0.843																		
OC	0.249*	-0.546	0.520	0.587	0.546	0.413																	
NE Fe	0.676	-0.944	0.917	0.841	0.944	0.776	0.520																
E Fe	0.513	-0.841	0.820	0.767	0.841	0.687	0.600	0.844															
NE Mn	0.647	-0.887	0.874	0.793	0.887	0.709	0.546	0.934	0.839														
E Mn	0.353*	-0.696	0.682	0.613	0.696	0.671	0.499	0.680	0.744	0.709													
NE Zn	0.655	-0.817	0.783	0.771	0.817	0.705	0.473	0.847	0.720	0.817	0.580												
E Zn	0.405	-0.813	0.761	0.886	0.813	0.745	0.603	0.776	0.814	0.692	0.598	0.704											
NE V	0.585	-0.876	0.835	0.897	0.876	0.785	0.569	0.916	0.771	0.815	0.608	0.846	0.852										
E V	0.465	-0.853	0.816	0.882	0.853	0.670	0.575	0.846	0.899	0.794	0.631	0.726	0.892	0.832									
NE Cr	0.596	-0.924	0.889	0.908	0.924	0.727	0.568	0.937	0.829	0.898	0.617	0.827	0.843	0.918	0.914								
E Cr	0.399	-0.796	0.774	0.724	0.796	0.716	0.531	0.737	0.863	0.744	0.717	0.661	0.764	0.683	0.825	0.726							
NE Ni	0.587	-0.929	0.894	0.898	0.929	0.788	0.552	0.933	0.817	0.888	0.659	0.821	0.824	0.908	0.882	0.950	0.756						
E Ni	0.313*	-0.755	0.726	0.750	0.755	0.656	0.667	0.709	0.792	0.664	0.732	0.589	0.806	0.729	0.798	0.746	0.811	0.732					
NE Cu	0.301*	-0.680	0.653	0.721	0.680	0.585	0.618	0.674	0.709	0.718	0.574	0.635	0.764	0.693	0.709	0.723	0.616	0.701	0.684				
E Cu	0.482	-0.694	0.652	0.701	0.694	0.659	0.284*	0.749	0.634	0.673	0.567	0.660	0.754	0.698	0.704	0.724	0.579	0.736	0.498	0.579			
NE Co	0.453	-0.717	0.692	0.675	0.717	0.623	0.439	0.757	0.548	0.676	0.433	0.557	0.585	0.730	0.628	0.736	0.473	0.728	0.474	0.588	0.607		
E Co	0.468	-0.778	0.759	0.709	0.778	0.626	0.635	0.777	0.866	0.753	0.772	0.671	0.763	0.729	0.815	0.770	0.797	0.754	0.903	0.649	0.565	0.473	

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[a] Spearman nonparametric correlation problem. All coefficients are significant at or above the 99.9% confidence level.

* These coefficients are significant only at the 95% confidence level.

[b] The prefix "E" to the heavy metals connotes the amount of the metal extractable by an hydroxylamine hydrochloride-acetic acid leaching procedure (Chester & Hughes, 1967). The prefix "NE" connotes the amount of the metal not extracted by the same reagent. D, Sd, St, Cl, Mu, CO_3, and OC are abbreviations for depth, sand + gravel, silt, clay, mud, carbonate, and organic carbon, respectively.

A comparison of the two-step with the seven-step treatment results revealed the additive effect of several chemical attacks on the sediment particles: The seven-step sum was greater for every element except manganese. Also, was observed that the number of steps, the severity and duration of treatments, would modify the amount of metals leached. There was no firm leachable value, it was relative to the scheme and treatments employed.

Relevance of the Geochemical Studies on Metal Pollutant Behaviour

The foregoing sequential extraction data may be used as a potential means to estimate the proportion of each of the eight metals that can be mobilized into the seawater of the Beaufort Sea by changing the pH and oxidation-reduction potential of the sedimentary environment. Whether the perturbation is an oil spill or dredge spoil dispersed in the nearshore arctic environment, it would appear that only a minor portion of the total metal content in the marine substrate would be potentially available for release into the water column. Most likely, the direct physical and chemical effects of an oil spill and/or dredge spoil (e.g., water turbidity change, sedimentation rate change, etc.) to the environment would be far more important than any small increases in dissolved metallic species mobilized from the natural bottom material. The rate of release of the metals and their concentration gradient between the sediment and the entire water column, the nature of the metal species released, and the circulation characteristics, as well as turbulence, to diffuse and remove the supplementary metal must be understood before one can realize the relationship of the total released metal to the overall variations of dissolved metals in time and space.

The current fluxes of the eight metals into the Simpson Lagoon are listed in Table XV. The metal inventories, their partitioning patterns and fluxes would provide a bench mark to monitoring of pollution in the Beaufort Sea shelf and adjacent coastal areas.

TABLE XV

AVERAGE FLUXES (μg cm^{-2} yr^{-1}, EXCEPT Fe WHICH IS IN 10^4 μg cm^{-2} yr^{-1}), FOR TOTAL (T) AND ACETIC ACID-HYDROXYLAMINE HYDROCHLORIDE EXTRACTABLE (E) HEAVY METALS IN SIMPSON LAGOON SEDIMENTS

V		Cr		Mn		Fe		Co		Ni		Cu		Zn	
T	E	T	E	T	E	T	E	T	E	T	E	T	E	T	E
90	5.6	60	1.2	340	165	2.6	.29	9.6	2.5	30	4.2	22	4.0	100	17

REFERENCES

Agemian, H. and A. S. Y. Chau. 1977. A study of different analytical extraction methods for nondetrital heavy metals in aquatic sediments. *Arch. Environ. Contam. Toxicol.* 6:69-82.

Alexander, V., D. C. Burrell, J. Chang, R. T. Cooney, C. Coulon, J. J. Crane, J. A. Dygas, G. E. Hall, P. J. Kinney, D. Kogl, T. C. Mowatt, A. S. Naidu, T. E. Osterkamp, D. M. Schell, R. D. Siefert and R. W. Tucker. 1975. Environmental Studies of an Arctic Estuarine System. Corvallis, Oregon: United States Environmental Protection Agency, Final Report EAP-660/3-75-026. 536 pp.

Allen, J. R. L. 1965. Late Quaternary Niger Delta and adjacent areas: sedimentary environments and lithofacies. *American Association Petroleum Geologists Bulletin* 49:547-600.

Barnes. P. W. 1974. Preliminary results of marine geological studies off the northern coast of Alaska. *In* Huffort *et al.* (eds.), *An Ecological Survey in the Beaufort Sea.* Washington, D.C.: United States Coast Guard Oceanographic Unit. Oceanographic Report CG373-64:183-227.

Barnes, P. and E. Reimnitz. 1979. Ice gouge obliteration and sediment redistribution event: 1977-1978, Beaufort Alaska. U.S. Geol. survey Open File Rept. 79-848. 22 pp.

Barnes, P. W. and L. J. Toimil. 1979. Maps showing inner shelf circulation patterns, Beaufort Sea, Alaska. Map MF-1125, U.S. Geol. Surv., Denver, Colorado.

Barnes, P. W., E. Reimnitz and D. Fox. 1982. Ice rafting of fine-grained sediment, a sorting and transport mechanism, Beaufort Sea, Alaska. *J. Sedimentary Petrology* 52 (in press).

Biscaye, P. E. 1965. Mineralogy and sedimentation of recent deep-sea clay in the Atlantic Ocean and adjacent seas and oceans. *Geol. Soc. Amer. Bull.* 76:803-832.

Brindley, G. W. 1980. Order-disorder in clay mineral structures. *In* G. W. Brindley and G. Brown (eds.), *Crystal Structures of Clay Minerals and Their X-ray Identification.* Monograph No. 5, Mineralogical Society, London. pp. 125-195.

Burrell, D. C., J. A. Dygas and R. W. Tucker. Beach morphology and sedimentology of Simpson Lagoon. *In* Alexander *et al.* (eds.), *Environmental Studies of an Arctic Estuarine System.* Corvallis, Oregon: United States Environmental Protection Agency, Final Report EPA-660/3-75-026: 45-141.

Carsola, A. J. 1954. Recent marine sediments from Alaskan and northwest Canadian Arctic. *Bull. Amer. Assoc. Petrol. Geol.* 38:1552-1586.

Chao, T. T. 1972. Selective dissolution of manganese, oxides from soils and sediments with acidified hydroxylamine hydrochloride. *Soil Sci. Soc. Amer. Proc.* 36:764-768.

Chapman, V. J. 1960. *Salt Marshes and Salt Deserts of the World.* London: Interscience Publishers. 392 pp.

Chester, R. and M. J. Hughes. 1967. A chemical technique for the separation of ferro-manganese minerals, carbonate minerals and adsorbed trace elements from pelagic sediments. *Chem. Geol.* 2:249-262.

Coffin, D. E. 1963. A method for the determination of free iron in soils and clays. *Can. J. Soil Sci.* 43:7-17.

Daly, B. K. and H. J. Binie. 1974. A leaching method for the extraction of acid oxalate--soluble aluminum and iron from soil in conjunction with cation exchange leachings. *Comm. in Soil Sci. and Plant Anal.* 5(6): 507-514.

Denton, G. H. and T. J. Hughes. 1981. *The Last Great Ice Sheets.* New York: John Wiley and Sons. 484 pp.

Dickinson, K. A., H. L. Berryhill, Jr. and C. W. Holmes. Criteria for recognizing ancient berrier coastlines. *In* J. K. Rigby and W. K. Hamblin (eds.), *Recognition of Ancient Sedimentary Environments.* Tulsa: Society of Economic Paleontologists and Mineralogists. Special Publ. 16. pp. 192-214.

Dygas, J. A. and D. C. Burrell. 1976. Response of waves and currents to wind patterns in an Alaskan lagoon. *In* D. W. Hood and D. C. Burrell (eds.), *Assessment of the Arctic Marine Environment.* Occ. Publ. 4, Inst. Mar. Sci., Univ. Alaska, Fairbanks. pp. 263-285.

Dygas, J. A., R. Tucker and D. C. Burrell. 1972. Geological report on the heavy minerals, sediment transport, and shoreline changes of the barrier islands and coast between Oliktok Point and Beechy Point. *In* P. J. Kinney *et al.* (eds.), Baseline Data Study of the Alaskan Arctic Aquatic Environment. Inst. Mar. Sci. Rept. R72-3, Univ. Alaska, Fairbanks. pp. 61-121.

Dygas, J. A., R. Tucker, A. S. Naidu and D. C. Burrell. 1971. Preliminery sedimentological investigation of the Colville River and Oliktok Point coastal region. *In* P. J. Kinney, D. Schell, V. Alexander, A. S. Naidu, C. P. McRoy and D. C. Burrell (eds), Baseline Data Study of the Alaskan Arctic Aquatic Environments. Eight Month Progress 1970. Rept. R-71-4. Inst. Mar. Sci., Univ. Alaska, Fairbanks. pp. 48-82.

Eberl, D. and J. Hower. 1976. Kinetics of illite formation. *Geol. Soc. Amer. Bull.* 87:1326-1330.

Flanagan, F. J. 1969. U.S. Geological Survey Standards-II. First Compilation of Data for the New U.S.G.S. Rocks. *Geochim. Cosmochim. Acta* 33:81-120.

Flanagan, F. J. 1973. 1972 values for International Reference Samples. *Geochim. Cosmochim. Acta* 37:1189-1200.

Flint, R. F. 1943. Growth of the North American ice sheet during the Wisconsin age. *Geol. Soc. Amer. Bull.* 54:325-362.

Folk, R. L. 1968. *Petrology of Sedimentary Rocks.* Hemphills, Austin, Texas. 170 pp.

Folk, R. L. and W. C. Ward. 1957. Brazos River bar - a study in the significance of grain size parameters. *J. Sedimentary Petrology* 27: 3-26.

Gearing, P., F. E. Plucker and P. L. Parker. 1977. Organic Carbon stable isotope rations of continental margin sediments. *Marine Chemistry* 5:251-266.

Geological Society of Canada. 1970. Isotopic age map of Canada. Map 1256A.

Gibbs, R. 1965. Error due to segregation in quantitative clay mineral X-ray diffraction mounting techniques. *Am. Mineralogist* 50:741-751.

Giovannini, G. and P. Sequi. 1976. Iron and aluminum as cementing substances of soil aggregates. I. Acetylacetone in benzene as an extractant of fractions of soil iron and aluminum. *J. of Soil Sci.* 27:140-147.

Godfrey, P. J., S. P. Leatherman and R. Zarenba. 1979. A geobotanical approach to classification of barrier beach system. *In* S. P. Leatherman (ed.), *Barrier Islands: From the Gulf of St. Lawrence to the Gulf of Mexico.* New York: Academic Press. pp. 99-126.

Greene, H. G. 1970. Microrelief of an arctic beach. *J. Sedimentary Petrology* 40:419-427.

Glaesser, J. D. 1978. Global distribution of barrier islands in terms of tectonic setting. *J. Geology* 86(3):283-298.

Griffin, J. J., H. Windom and E. D. Goldberg. 1968. The distribution of clay minerals in the world ocean. *Deep-Sea Research* 15:433-459.

Gupta, S. K. and K. Y. Chen. 1975. Partitioning of trace metals in selective chemical fractions of nearshore sediments. *Environ. Letts.* 10(2):129-158.

Hayes, M. O. 1976. Transitional-coastal depositional environments. *In* M. O. Hayes and T. W. Kana (eds.), Terrigenous Clastic Depositional Environments. Tech. Rept. 11-CD. Columbia, South Carolina: Coastal Research Division, Dept. Geology, Univ. South Carolina. I-32-I-111.

Hayes, M. O. 1979. Barrier island morphology as a function of tidal and wave regime. *In* S. P. Leatherman (ed.), *Barrier Islands from the Gulf of St. Lawrence to the Gulf of Mexico.* New York: Academic Press. pp. 1-27.

Hayes, M. O. and T. W. Kana (eds.). 1976. Terrigenous clastic depositional environments: some modern examples. Columbia, South Carolina: Tech. Rept. 11-CRE, Coastal Research Division, Dept. Geology, Univ. Southern Carolina. II-84 pp.

Hayes, J. B. 1973. Clay petrology of mudstones, Leg 18, Deep Sea Drilling Project. *In* Initial Reports of the Deep Sea Drilling Project, Vol. 18. Univ. California, Scripps Inst. Ocng., La Jolla, Calif. pp. 903-914.

Hill, G. W. and R. E. Hunter. 1976. Interaction of biological and geological processes in the beach and nearshore environments, northern Padre Island, Texas. *In* R. A. Davis and R. L. Ethington (eds.), *Beach and Nearshore Sedimentation.* Tulsa: Society of Economic Paleontologists and Mineralogists. Special Publ. 24. pp. 169-187.

Hopkins, D. M. 1967. Quaternary marine transgressions in Alaska. *In* D. M. Hopkins (ed.), *The Bering Land Bridge.* Stanford Univ. Press, Stanford. pp. 47-90.

Hopkins, D. M. 1978a. The Flaxman Formation of northern Alaska: evidence for an arctic ice shelf. Proc. American Quaternary Assoc. (AMQUA), 5th Biennal mtg., Edmonton, Canada. Abstract. 214 pp.

Hopkins, D. M. 1978b. Offshore permafrost studies, Beaufort Sea, Alaska. Quarterly Rept. to OCSEAP, Environmental Assessment of the Alaskan Continental Shelf, BLM-NOAA. pp. 253-261.

Hopkins, D. M. 1979. Development of northern hemisphere ice sheets during the past 120,000 years: an aspect of the paleogeography of the Arctic Steppe biome. Paper prepared for Wenner-Gren Foundation, Burg Wartenstein Conf. #81, "Paleoecology of the Arctic Steppe-Mammoth Biome, Austria (1979).

Hopkins, D. M. *et al.* 1977. Earth Science Studies. *In* Beaufort Sea Synthesis Report. Environmental Impacts of OCS Development in Northern Alaska. OCSEAP Arctic Project Office, Univ. Alaska, Fairbanks. Special Bull. 15:43-72.

Hower, J. and T. C. Mowatt. 1966. The mineralogy of illites and mixed-layer illite-montmorillonites. *Am. Mineralogist* 51:825-854.

Hufford, G. L. 1973. Warm water advection in the southern Beaufort Sea, August-September 1971. *J. Geophy. Res.* 3:274-279.

Hughes, T., G. H. Denton and M. G. Grossward. 1977. Was there a late Würm arctic ice sheet? *Nature* 266:596-602.

Hughes, O. L., C. R. Harington, J. A. Janssens, J. V. Mattews, Jr., R. E. Morlan, N. W. Rutter and C. E. Schweger. 1981. Upper Pleistocene stratigraphy, paleoecology, and archaeology of the Northern Yukon Interior, Eastern Beringia: 1. Bonnet Plume Basin. *Arctic* 34:329-365.

Hülsemann, J. 1966. On the routine analysis of carbonates in unconsolidated sediments. *J. Sedimentary Petrology* 36:622-625.

Inman, D. L. 1952. Measures for describing the size distribution of sediments. *J. Sedimentary Petrology* 22:125-145.

Inman, D. L. and C. E. Nordstrom. 1971. On the tectonic and morphologic classification of coasts. *J. Geology* 79:1-21.

Jackson, M. L. 1958. Exchangeable cations of calcareous soils. *In: Soil Chemical Analysis*. Prentice-Hall, Inc. pp. 88-89.

Johnson, M. W. 1956. The plankton of the Beaufort and Chukchi Sea area of the Arctic and its relation to the hydrography. Arctic Inst. North America. Tech. Paper No. 1. 32 pp.

Koide, M. and K. W. Bruland. 1975. The electrodeposition and determination of radium by isotope dilution in sea water and in sediments simultaneously with other natural radionuclides. *Anal. Chim. Acta* 75:1-19.

Koide, M., K. W. Bruland and E. D. Goldberg. 1972. Th-228/Th-232 and Pb-210 geochronologies in marine and lake sediments. *Geochim. Cosmochim. Acta* 37:1171-1187.

Lahore, H., D. Morrison, G. Peterson, R. Roark and R. Sternberg. 1977. *Users's Guide to the Sediment Dynamics Data Acquisition System.* Seattle: Dept. Oceanography, Univ. Washington. 82 pp.

Leffingwell, E. de K. 1919. The Canning River region, northern Alaska. U.S. Geol. Surv. Prof. Paper 109. 251 pp.

McCann, S. B. 1979. Barrier islands in the Southern Gulf of St. Lawrence, Canada. *In* S. P. Leatherman (ed.), *Barrier Islands: From the Gulf of St. Lawrence to the Gulf of Mexico.* New York: Academic Press. pp. 29-63.

Matthews, J. B. 1981. Observations of surface and bottom currents in the Beaufort Sea near Prudhoe Bay, Alaska. *J. Geophy. Res.* 86:6653-6660.

Mountain, D. G. 1974. Preliminary analysis of Beaufort shelf circulation in summer. *In* J. C. Reed and J. E. Sater (eds.), *The Coast and Shelf of the Beaufort Sea.* Arctic Inst. North America, Arlington, Virginia. pp. 27-42.

Mowatt, T. C. and A. S. Naidu. 1974. Gravels from the Alaskan Continental Shelf, Beaufort Sea, ARctic Ocean: petrologic character, and implications for sediment source and transport. Open File Rept. 43. Div. of Geological and Geophysical Surveys, State of Alaska, Fairbanks. 12 pp.

Naidu, A. S. 1974. Sedimentation in the Beaufort Sea: a synthesis. *In* Y. Herman (ed.), *Marine Geology and Oceanography of the Arctic Seas.* Springer-Verlag, N.Y. pp. 173-190.

Naidu, A. S. 1978. Sediment characteristics, stability, and origin of the barrier island-lagoon complex, north-arctic Alaska. *In: Environmental Assessment of the Alaskan Continental Shelf.* Annual Rept. of the Principal Investigators, March 1978. Vol. 10. National Oceanic and Atmospheric Administration, Boulder, CO. pp. 628-686.

Naidu, A. S. 1979. Sources, transport pathways, depositional sites and dynamics of sediments in the lagoon and adjacent shallow marine region, northern arctic Alaska. *In: Environmental Assessment of the Alaskan Continental Shelf.* Annual Rept. of the Principal Investigators, March 1979. Vol. 8. National Oceanic and Atmospheric Administration, Boulder, CO. pp. 98-181.

Naidu, A. S. 1980. Sources, transport pathways, depositional sites and dynamics of sediments in the lagoon and adjacent shallow marine region, northern arctic Alaska. *In: Environmental Assessment of the Alaskan Continental Shelf.* Annual Rept. of the Principal Investigators, March 1980. Vol. 7. National Oceanic and Atmospheric Administration, Boulder, CO. pp. 3-67.

Naidu, A. S. 1981. Sources, transport pathways, depositional sites and dynamics of sediments in the lagoon and adjacent shallow marine region, northern arctic Alaska. *In: Environmental Assessment of the Alaskan Continental Shelf.* Annual Rept of the Principal Investigators, March 1981. National Oceanic and Atmospheric Administration, Boulder, CO. In press. 142 pp.

Naidu, A. S. and T. C. Mowatt. 1974. Aspects of size distributions, mineralogy, and geochemistry of deltaic and adjacent shallow marine sediments, north arctic Alaska. *In: An Ecological Survey in the Beaufort Sea.* U.S. Coast Guard Oceanog. Unit, Washington, D.C. Ocng. Rept CG 373-64:238-262.

Naidu, A. S. and T. C. Mowatt. 1975. Depositional environments and sediment characteristics of the Colville and adjacent deltas, northern Arctic Alaska. *In* M. L. S. Broussard (ed.), *Deltas: Models for Subsurface Exploration.* Houston Geol. Soc., Houston, Texas. pp. 284-309.

Naidu, A. S. and T. C. Mowatt. 1976. Significance of textural criteria in the recognition of ancient polar deltaic sediments. *In* T. C. Miller (ed.), *Recent and Ancient Sedimentary Environments in Alaska.* Alaska Geol. Soc., Anchorage, D1-D12.

Naidu, A. S. and T. C. Mowatt. 1982. Sources and dispersal patterns of clay minerals in surface sediments from the continental shelf areas off Alaska. *Bull. Geol. Soc. America.* In press.

Naidu, A. S. and H. V. Weiss. 1982. Sedimentation rate and Pb-210 atmospheric flux in an arctic coastal region. Submitted for publication.

Naidu, A. S., T. C. Mowatt, S. E. Rawlinson and H. V. Weiss. 1982. Barrier island-lagoon system of North Arctic Alaska: lithologies, depositional processes, evolution and stability. *In* P. W. Barnes, E. Reimnitz and D. Schell (eds.), *Arctic Shelf Physical and Biological Environment: with Examples from the Beaufort Sea.* Academic Press. In press.

Nittrouer, C. A., R. W. Sternberg, R. Carpenter and J. T. Bennett. 1979. The use of Pb-210 geochronology as a sedimentological tool: application to the Washington continental shelf. *Marine Geology* 31:297-316.

Northern Technical Services. 1981. *Beaufort Sea Drilling Effluent Disposal Study.* Anchorage, Alaska: NORTEC. 329 pp.

Olade, M. and K. Fletcher. 1974. Potassium chlorate-hydrochloric acid: a sulfide selective leach for bedrock geochemistry. *J. Geochem. Explor.* 3:337-344.

Owens, E. H. 1975. Barrier beaches and sediment transport in the southern Gulf of St. Lawrence. Proceedings 14th Coastal Engineering Conference (ASCE, New York), Vol. II. pp. 1177-1193.

Pelletier, B. R. 1979. Review of surficial geology and engineering hazards in the Canadian offshore. *Maritime Sediments* 15:55-91.

Prest, U. K. 1969. Retreat of Wisconsin and Recent ice in North America. Geol. Surv. Canada Map 1257A.

Rader, L. D. and R. S. Grimaldi. 1961. Chemical analysis for selected minor elements in Pierre Shale. U.S.G.S. Prof. Pap. 391-A, pp. A1-A45.

Rateev, M. A., Z. N. Gorbunova, A. P. Lisitsyn and G. L. Nosov. 1969. The distribution of clay minerals in the oceans. *Sedimentology* 13:21-43.

Reimnitz, E. and P. W. Barnes. 1974. Sea ice as a geologic agent on the Beaufort Sea shelf of Alaska. *In* J. C. Reed and J. E. Sater (eds.), *The Coast and Shelf of the Beaufort Sea.* Arctic Inst. North. Amer., Arlington, Virginia. pp. 301-353.

Reimnitz, E., P. W. Barnes and T. R. Alpha. 1973. Bottom features and processes related to drifting ice on the arctic shelf. U.S. Geol. Surv. Misc. Field Studies Map F-532.

Reimnitz, E., P. W. Barnes, T. Forgatsch and C. Rodeick. 1972. Influence of grounding ice on the arctic shelf of Alaska. *Marine Geology* 13: 323-334.

Reimnitz, E., P. W. Barnes, L. J. Toimil and J. Melchior. 1977. Ice gouge recurrence and rates of sediment reworking, Beaufort Sea, Alaska. *Geol.* 5:405-408.

Reimnitz, E. and D. K. Maurer. 1978. Storm surges in the Alaskan Beaufort Sea. U.S. Geol. Surv. Open File Rept. 78-593. 26 pp.

Rex, R. W. 1964. Arctic beaches, Barrow, Alaska. *In* R. L. Miller (ed.), *Papers in Marine Geology: Shepard Commemorative Volume.* New York: The Macmillan Company. pp. 384-400.

Schell, D. M. 1980. Beaufort Sea Winter Watch. Ecological Processes in the Nearshore Environment and Sediment-Laden Sea Ice: Concepts, Problems and Approaches. Fairbanks, Alaska: Arctic Project Office, Geophysical Institute, University of Alaska. 74 pp.

Schwartz, M. L. 1973. *Barrier Islands: Benchmark Papers in Geology.* Stroudsburg, Pennsylvania: Dowden, Hutchinson and Ross, Inc. 451 pp.

Shepard, F. P. 1960. Gulf coast barriers. *In: Recent Sedimentations, Northwestern Gulf of Mexico.* Tulsa: American Asso. of Petroleum Geologist. pp. 197-220.

Shepard, F. P. and D. G. Moore. 1955. Central Texas coast sedimentation: characteristics of sedimentary environments, recent history and diagenesis. Tulsa: American Asso. of Petroleum Geologists Bull. 39:1463-1593.

Sibbesen, E. 1977. A simple ion-exchange resin procedure for extracting plant-available elements from soil. *Plant and Soil* 46:665-669.

Stoiber, R. E., J. B. Lyons, W. T. Elberty and R. H. McCrehan. 1956. Petrographic evidence on the source area and age of T-3: Final Rept., AFCRC Contract No. AF19(604)-1075, Dartmouth College. pp. 58-72.

Swift, D. J. P., D. J. Stanley and J. R. Curray. 1971. Relict sediments on continental shelves: a reconsideration. *J. Geol.* 79:322-346.

Tucker, R. W. 1973. The sedimentary environment of an arctic lagoon. M.S. Thesis, Univ. Alaska. University Microfilms, Ann Arbor, Michigan. 96 pp.

Weaver, C. E. 1958a. The effects and geologic significance of potassium "fixation" by expandable clay minerals derived from muscovite, biotite, chlorite and volcanic material. *Am. Mineralogist* 43:839-861.

Weaver, C. E. 1958b. Geologic interpretation of argillaceous sediments. Part I, origin and significance of clay minerals in sedimentary rocks. *Amer. Assoc. Petrol. Geol.* 42:254-271.

Whitehouse, U. G., L. M. Jeffrey and J. D. Debbrect. 1960. Differential settling rates of clay minerals in saline waters. Proc. Seventh Nat. Clays and Clay Minerals Conf., Earth Sci. Monograph No. 5. pp. 1-79.

Wiseman, W. J., Jr., J. M. Coleman, S. A. Shu, A. D. Short, J. N. Suhayda, C. D. Walters, Jr. and L. D. Wright. 1973. Alaskan arctic processes and morphology. Baton Rouge: Coastal Studies Institute, Louisiana State Univ. Tech. Rept. 149. 171 pp.

HYDROCARBONS: NATURAL DISTRIBUTION AND DYNAMICS ON THE ALASKAN OUTER CONTINENTAL SHELF

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Final Report
Outer Continental Shelf Environmental Assessment Program
Research Unit 275

February 1981

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ABSTRACT

Determination of the ambient kinds and amounts of hydrocarbons in sediment, organisms and water of Alaska's continental shelf have shown that this area is generally free of petroleum. Measurements made in the Gulf of Alaska, Cook Inlet, the Bering Sea, Norton Sound, the Chukchi Sea, and the Beaufort Sea indicate that the hydrocarbons present are predominantly of modern biogenic origin. Where non-biogenic hydrocarbons have been observed, these appear to be associated with natural oil seeps, coal outcrops, long distance atmospheric transport of combustion particulates and local pollution sources such as a small boat harbor.

Two potential mechanisms for the transport of petroleum from the water column to the benthos have been investigated. Sorption of dissolved hydrocarbons by Alaskan suspended sediments is a highly inefficient process for transport to the bottom. Movement of oil droplets to the bottom after incorporation into zooplankton fecal pellets is a process of highly variable efficiency depending on location and season.

INTRODUCTION

In the early 1970's, the federal government of the United States began to actively consider petroleum exploration and development on Alaska's outer continental shelf (OCS). In order to better understand and anticipate the environmental consequences of petroleum related activities in this area, an extensive program of scientific research has been implemented. The overall goal of this research has been to provide reliable information about the present state of Alaska's marine environments and their probable responses to pollution induced stresses.

This Final Report covers one project commissioned by the Outer Continental Shelf Environmental Assessment Program (OCSEAP). As implied by this report's title, the project's objective was to study the natural distribution and dynamics of hydrocarbons in Alaskan OCS areas under consideration for petroleum exploration and development. Work on this project began in 1975 and continued through 1980. During this period, a considerable number of specific tasks have been accomplished. These include several groups of measurements which provide "baseline data sets", indications of the ambient kinds and amounts of hydrocarbons (in the approximate molecular weight range 200-400) present in water, biota and sediment prior to petroleum exploration. This project has also included studies of dynamic processes by which hydrocarbons are transferred from the water column to the sediments. These studies have provided the basis for the estimation of the quantitative extent of two such transfer processes under conditions likely to prevail in Alaskan marine environments.

This Final Report consists of two principal parts. Part One presents results obtained since the preparation of the most recent Annual Report. Hence, this part is essentially an Annual Report for the final six months of the project. Part Two is a review of information obtained over the entire course of the project. This review first treats each geographic area for which "baseline data sets" have been obtained and then addresses the dynamics of hydrocarbon transfer.

PART ONE: SUB-PROJECT REPORTS

I. HYDROCARBONS OF NORTHEAST GULF OF ALASKA SEDIMENTS

One of the first tasks addressed in the course of assessing the probable environmental consequences of petroleum exploration on Alaska's OCS was the measurement of the kinds and amounts of hydrocarbons in benthic sediments in the northeast Gulf of Alaska (Shaw, 1975). In view of the substantial progress in analytical methodology, which has been made since these sediments were first analysed, we decided to reanalyse northeast Gulf of Alaska sediment samples which has been collected in 1974 and 1975. By doing this, we hoped to gain two kinds of information: (1) more detailed and accurate information about the ambient kinds and amounts of hydrocarbons present in Gulf of Alaska sediments in the mid-1970's; and (2) information about the consequences of 5-6 year's storage on the hydrocarbon contents of the sediments. As it turns out, our results do not allow a neat separation of these kinds of information. Some of the ambiguities that arise here are probably generic to the reanalysis of archieved materials. Therefore, we discuss them in some detail as a model of the kinds of conclusions which can (and cannot) be drawn in this circumstance.

Methods

Sediments were collected at the times and places specified in Table I and Figure 1. All collections were made with a van Veen grab except Station 37 which, because of the greater water depth, was made with a Skipek grab. Samples were transferred from the interior of the grab (i.e., not material in contact with the grab itself) to pre-cleaned glass jars with aluminum foil lined lids. Samples were frozen within one hour of collection and stored at 0° to -30°C until analysis.

Approximately 80 g of accurately weighed homogeneous sediment were added to a solvent cleaned, tared cellulose extraction thimble (Whatman, 43x123 mm). Samples were reflux extracted using 150 ml distilled hexane plus 150 ml distilled methanol for 48 hours with stirring after 24 hours. The solvent was then separated from the sediment sample for further processing.

TABLE I

SEDIMENT SAMPLING STATIONS USED IN THIS STUDY

Station (GASS)	Position		Depth (m)	Collection Date	% Water	% TOM (dry)
	N	W				
1	59°50.2'	149°30.5'	263	July 74	61	-
6	59°07.2'	148°47.5'	151	July 74	44	3.9
25	59°02.5'	140°49.8'	179	May 75	38	4.2
28	59°26.5'	140°16.9'	239	May 75	54	4.0
30	59°44.1'	141°27.9'	43	February 75	30	1.1
37	59°16.2'	142°59.2'	1920	February 75	59	-
41	59°55.1'	142°39.5'	119	July 74	34	3.4
42	59°55.1'	143°51.2'	93	July 74	30	3.1
44	59°35.0'	143°54.2'	181	February 75	34	4.0
49	59°37.5'	145°10.0'	186	February 75	48	4.4
52	60°07.6'	145°06.5'	53	February 75	49	3.6
53	60°23.0'	146°54.0'	279	February 75	28	-
56	60°55.2'	146°36.8'	64	February 75	33	-
59	59°17.1'	146°14.0'	334	July 74	50	3.7

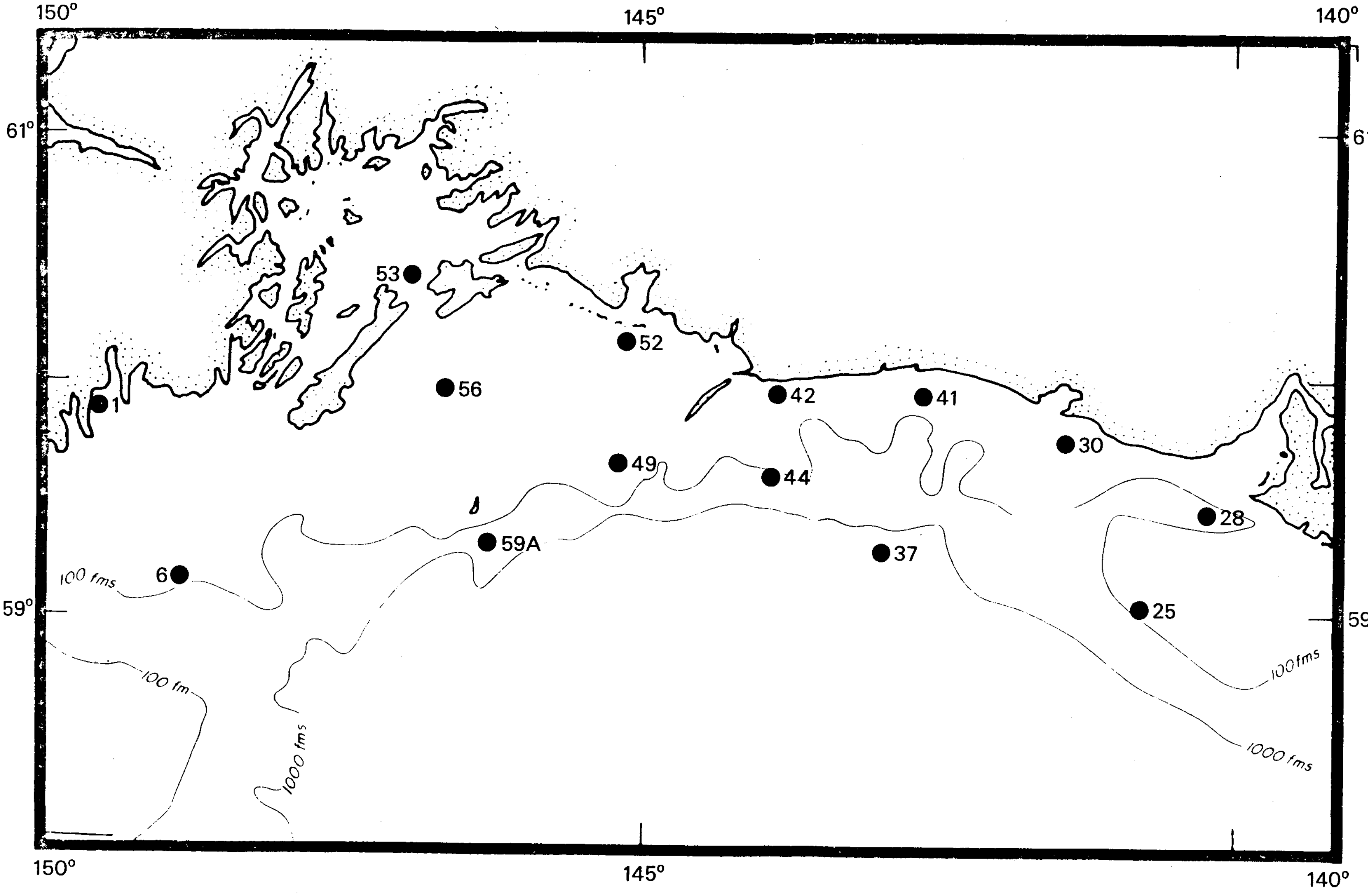

Figure 1. Sediment sampling stations used in this study.

The solvent mixture plus 50 ml distilled H_2O was extracted with 100 ml of distilled hexane 3 times, the hexane fractions collected, pooled, and dried overnight with Na_2SO_4 (baked, 500°C, 24 hours). Samples were decanted from the Na_2SO_4 and concentrated by rotary vacuum evaporation to 1.5 ml, then further concentrated to approximately 1.0 ml with a stream of ultrahigh purity N_2. Any residual sulfur that may have been present was removed by reaction with elemental copper.

The volume of the hexane extract was then determined by weighing the extract in a tared sample vial and computing from the density of the solvent. A 1% aliquot was air dried and weighed to determine non-saponifiable lipid content. All samples had 6-15 mg non-saponifiable lipid and each was eluted from a 9 mm I.D. x 27 cm column packed with 5 g of 6% deactivated silica (fully activated by baking at 120°C for 24 hours, deactivated with H_2O). Aliphatic hydrocarbons were eluted with 5 column pore volumes distilled hexane. Aromatic hydrocarbons were separated from the heavier weight esters by elution with 5 column pore volumes of 20% (V:V) methylene chloride in hexane.

The samples were analyzed on a Hewlett Packard 5710A gas chromatograph (GC) with flame ionization detector. The analytical column was a SCOT glass capillary column, 30 m x 0.7 mm I.D. coated with a slurry of OV-101 (SCOT column from Scientific Glass Engineering, Inc., Austin, Texas). Samples were concentrated to approximately 0.5 ml with a stream of ultrahigh purity N_2. Total hydrocarbon weight was determined by transferring the sample to a tared vial and determining solution volume from the density of the solvent. Peak areas were measured with a Hewlett Packard 3385A digital integrator. Detector response was calibrated daily by injections of a standard mixture of aliphatic and aromatic hydrocarbons in hexane.

Selected samples were analysed further using a computerized gas chromatograph-mass spectrometer (GC-MS) system (Hewlett Packard model 5930/5933). These analyses were carried out on the second fraction from the silica column clean up to determine concentrations of polycyclic aromatic hydrocarbons (PAH) and their alkyl homologs. For this, a quantitative internal standard of fully deuterated naphthalene was added to the sediment extract. With this, and an unlabeled external aromatic standard, PAH's were determined based on parent ion currents.

Results

Table II gives the sedimentary hydrocarbons of the 14 samples investigated as determined by flame ionization gas chromatography. These data include total saturates (operationally defined as hydrocarbons eluted with hexane in the silica gel clean up), total unsaturates (eluted with 20% methylene chloride in hexane), normal alkanes with 14 to 29 carbon atoms and the acyclic isoprenoids pristane and phytane. Pristane is the most abundant alkane in most of these samples. Pentadecane, heptadecane and nonadecane are also relatively abundant in most samples. Phytane was present in low relative concentrations in all samples except the two eastern most stations, 25 and 28. Most samples also contained normal alkanes with 20 to 29 carbon atoms; however, with little if any predominance of odd carbon chain lengths. Representative gas chromatograms are shown in Figure 2.

For seven of the sediment samples, the extract of unsaturates was further analysed by gas chromatography-mass spectrometry (GC-MS). Concentrations of aromatic hydrocarbons determined in this way are shown in Table III. This technique cannot distinguish among isomeric compounds. However, for seven aromatic ring systems, concentrations of compounds with 0 to 6 alkyl carbon substituents were determined. Table III also shows the highest aromatic hydrocarbon concentrations found in a blank determination (assumed sample size 50 g, dry weight). Other blanks run in the course of this work were generally one order of magnitude lower.

Discussion

For the purpose of this discussion, it is convenient to divide the sediments into two groups. The main group consists of Station 01, 06, 30, 37, 41, 42, 44, 49, 52, 53, 56 and 59 (Figure 1). The eastern group consists of Stations 25 and 28. Marine organisms contribute hydrocarbons to the sediments of both groups as evidenced by the presence of pentadecane, heptadecane, nonadecane and pristane. Terrigenous plant material is a minor contributor to

TABLE II

HYDROCARBONS IN NORTHEAST GULF OF ALASKA SEDIMENTS AS DETERMINED BY FLAME IONIZATION GAS CHROMATOGRAPHY EXPRESSED AS ng g^{-1} DRY WEIGHT BASIS

Pr = pristane, Ph = phytane, 14 = tetradecane, etc., t = trace

Station	Total Saturates	Total Unsaturates	14	15	16	17	Pr	18	Ph	19	20	21	22	23	24	25	26	27	28	29
01	11400	1100	130	240	150	170	400	140	60	240	120	140	100	200	140	146	100	160	t	-
06	8400	3500	80	140	90	100	230	100	40	140	90	110	220	230	210	220	140	160	80	t
25	1300	90	4	7	3	5	6	4	-	110	t	5	2	t	t	t	t	13	-	-
28	7300	160	10	20	10	10	20	10	-	10	10	20	10	20	t	40	t	50	-	-
30	830	180	14	20	18	20	40	22	9	24	22	23	25	25	49	47	36	36	t	-
37	1400	1300	80	100	60	60	140	50	20	60	30	30	50	60	40	40	20	20	t	-
41	3900	8100	69	110	76	83	190	72	29	73	58	54	50	68	52	51	28	t	t	-
42	7200	10600	130	170	89	93	250	82	37	88	71	71	66	61	51	110	75	93	t	t
44	14600	6600	64	93	64	68	18	66	26	78	64	68	59	100	86	89	60	75	t	t
49	3600	10400	32	95	84	110	320	110	58	160	110	120	110	160	150	160	130	200	93	120
52	5500	7600	31	66	36	44	120	35	18	52	31	26	25	26	20	25	18	32	33	45
53	4500	2000	38	74	41	50	120	38	16	64	36	41	35	78	47	84	36	14	t	46
56	4800	190	48	61	67	48	130	52	28	63	40	42	34	34	29	59	43	47	22	-
59	1100	1600	40	63	44	44	150	40	21	42	34	33	32	62	48	50	t	t	t	t

TABLE III

AROMATIC HYDROCARBON CONCENTRATIONS IN SEDIMENTS IN ng g^{-1} DRY WEIGHT BASIS.

Column headings indicate ring system and the number of alkyl carbon atoms

	$C_{10}H_8$							$C_{12}H_{10}$							$C_{13}H_{10}$							$C_{14}H_{10}$						
Station	0	1	2	3	4	5	6	0	1	2	3	4	5	6	0	1	2	3	4	5	6	0	1	2	3	4	5	6
01	5	26	78	92	47	9	1	12	39	50	51	53	59	10	19	42	137	22	10	4		123	164	150	70	29		
28	2	3	8	6				1	3	3					12	5						10	-	9	12	4		
42	25	71	137	135	63	28	9	22	54	68	79	77	-	23	23	63	54	32	47	36	23	159	220	182	108	50	16	5
49	19	57	101	107	56	29	15	17	46	61	65	80	67	39	29	55	70	59	45	29	33	161	233	179	114	51	17	
52	27	81	144	133	70	29	12	27	58	77	82	94	-	31	37	62	84	47	33	37	22	190	240	191	116	50	20	13
53	8	22	42	38	21	7	3	5	18	19	21	23	-	6	11	19	-	6				54	65	56	36	13	5	2
59	26	150	267	226	109	28	6	42	88	112	142	109	-	26	50	91	108	97	50	26	13	216	312	252	137	68	8	
High Blank	7	9	16	15	11	4		1	4	7	8	14	7	5	1	2	7					5	11	14	11	4	2	

TABLE III

CONTINUED

Station	$C_{16}H_{10}$							$C_{18}H_{12}$							$C_{20}H_{12}$						
	0	1	2	3	4	5	6	0	1	2	3	4	5	6	0	1	2	3	4	5	6
01	38	47	43	25	12			25	34	11	12				19	9					
28	6	6	5					6	6	12	6				16	10	9	6			
42	44	72	71	50	22	9	6	44	50	-	38	19	6		67	68	37	19			
49	47	75	80	65	57	40	23	46	55	58	68	38	19		78	66	54	35			
52	46	76	75	59	28	18	11	43	55	51	42	27	11		74	49	34	16			
53	16	24	23	17	8	4	2	16	17	16	13	9	4		28	21	13	5			
59	48	86	84	52	26	7	1	62	82	71	34	7	1		60	55	33	3			
High blank	3	5						1													

the sedimentary hydrocarbons as judged by the very slight predominance of odd chain length normal alkanes in the 20 to 29 carbon atom range.

The main group is distinct from the eastern group in that the former shows evidence of petroleum hydrocarbons. In the saturated fraction (Table II and Figure 2A) this evidence includes the presence of phytane and all normal alkanes from tetradecane through at least heptacosane with little if any dominance of odd carbon chain lengths. For the main group of sediments the presence of petroleum is further indicated by the wide variety of aromatic hydrocarbons in the 10-100 ng g^{-1} concentration range (Table III and Figure 2B). The most abundant aromatic compound in most homologous series has 2 or 3 alkyl carbon substituents. These concentrations are higher than observed in other sediments remote from petroleum sources (Laflamme and Hites, 1978) and this distribution among homologous alkyl series is indicative of fossil rather than combustion derived aromatic compounds (Laflamme and Hites, 1978; Shaw *et al.*, 1979).

The two stations of the eastern group are distinctly different (Tables II and III, Figure 2C and D). Phytane is not detectable. Some of the higher normal alkanes are absent or only present in trace amounts. Station 28 shows aromatics at concentrations comparable to the highest blank. Thus, it appears that if petroleum is present at all in the eastern group, its concentration is at least an order of magnitude lower than in the main group.

Having established the presence of petroleum hydrocarbons in the sediments analysed, it is appropriate to consider possible sources. In these archived samples, it will be necessary to give careful consideration to the possibility of contamination between collection and analysis. First, however, we will consider environmental sources of the petroleum.

One possible source of petroleum in the northeast Gulf of Alaska is a series of onshore oil seeps extending from the Malaspina forelands (landward of Station 30) to the Katalla area (landward of Station 52) (Blasko, 1976). Although it has not been shown that this oil seep region extends offshore, the regional geology of the area does not exclude this possibility (Sharma, 1979). The unknown and probably variable quantity of petroleum entering the Gulf of Alaska from these seeps would be moved westward by the

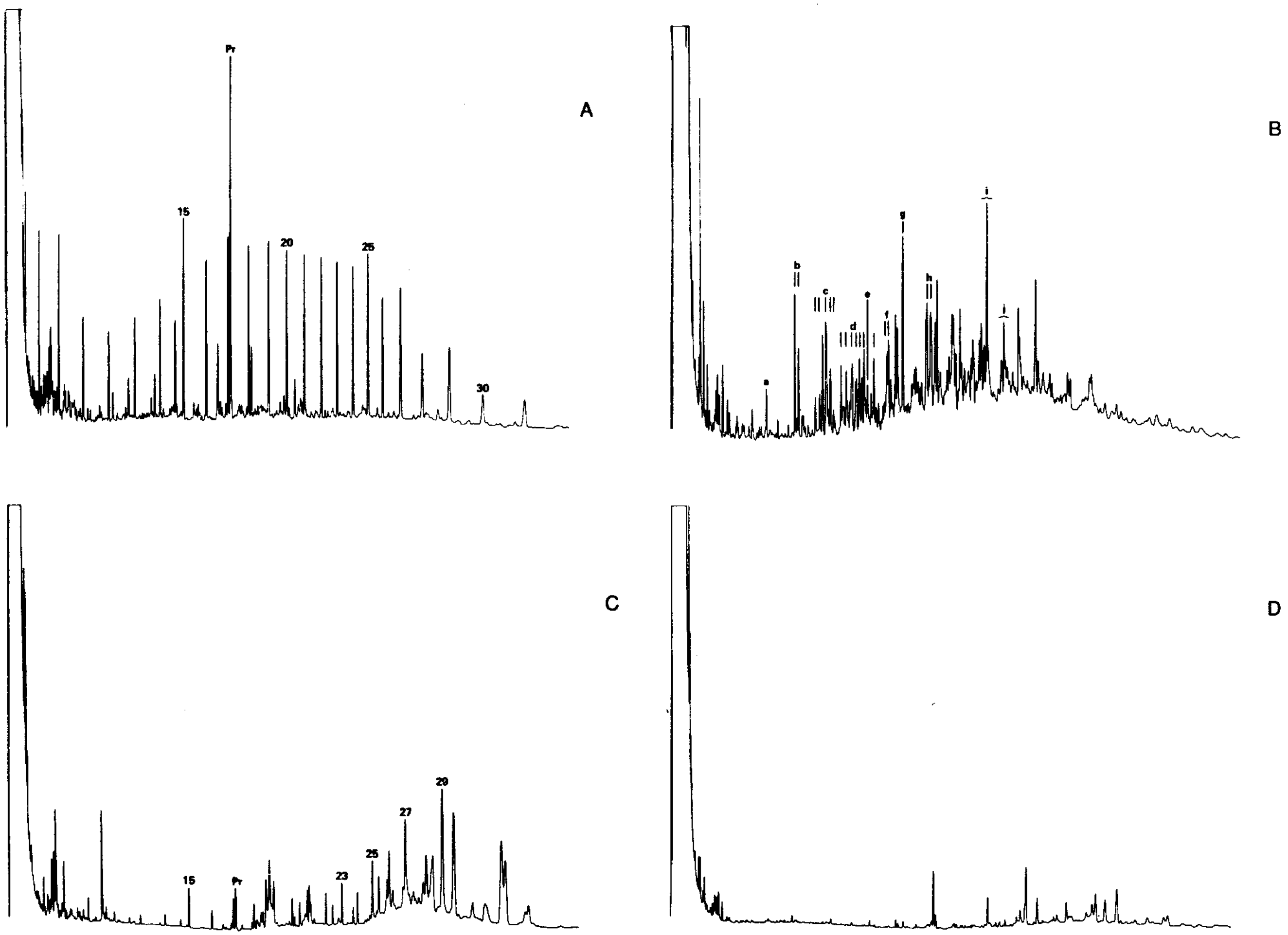

Figure 2. Representative gas chromatograms; A, Station 42 saturate fraction; B, Station 42 unsaturate fraction; C, Station 28 saturate fraction; D, Station 28 unsaturate fraction. In part B, a = naphthalene; b = methylnaphthalenes; c = C_2-naphthalenes; d = C_3-naphthalenes; e = fluorene; f = methylfluorenes; g = phenanthrene; h = methyl phenanthrenes; i = C_2-phenanthrenes; j = C_3-phenanthrenes.

general circulation of the area (Royer, 1979). Thus, petroleum from these seeps could be carried to the main group stations, but not the eastern group. This, of course, is the observed pattern. Although this source of petroleum to these sediments appears plausable, one puzzle persists. The petroleum in the main group sediments appears to be essentially unweathered. This is indicated by the high abundance of normal alkanes compared to the linear branched compounds, pristane and phytane, and by the absence of a prominent cycloalkane fraction (i.e., the lack of a large unresolved complex mixture). The sediments of the San Pedro Basin in the southern California borderland, a marine area of known oil seeps and anthropogenic petroleum additions, have an array of hydrocarbons much more characteristic of weathered petroleum (Venkatesan *et al.*, 1980). It is possible that this difference in degree of weathering is simply the result of environmental differences such as water temperature, oil seepage rate or microbial hydrocarbon degradation rate. But, the possibility that the hydrocarbons observed in the main group sediments are the result of contamination subsequent to collection also needs to be considered.

Given the logical basis of science, it is impossible to prove that contamination has not occurred in any sample where hydrocarbons are detected. The best that can be done is to present information which indicates that contamination is unlikely. In this way, we conclude that it is unlikely that contamination occurred during sediment extraction or analysis. This is based on two facts: (1) that three "system blanks" (complete analytical protocols executed without sediment sample) uniformly showed hydrocarbon levels well below those observed in the main group sediments, and (2) that, for the two eastern group sediments, a reasonable environmental explanation for the lower hydrocarbon concentrations exists (i.e., the observed distribution appears rational, not random). Two lines of evidence suggest that the likelihood of contamination during shipboard collection is also small. The main group sediment samples were collected on two separate cruises by different persons using different ships. Also, Station 37 was sampled using a Shipek grab, rather than the van Veen grab used elsewhere. The fact that none of these variables is reflected in the hydrocarbon distribution pattern argues against contamination during collection. However, it may be significant that the two eastern group samples were the only ones collected in May 1975 (Table I).

The remaining opportunity for contamination is during frozen storage between collection and analysis. For these samples, this storage period extended over five to six years. Although we have found no change in the hydrocarbons of intercalibration sediments re-analysed after 1.5 years storage, we have no previous experience with sediments stored for five or more years. The principal arguement against contamination during storage is the probabilistic one cited above as the second reason for doubting contamination during analysis. The arguement (which also can be used against contamination during storage) is that if contamination were random, it is unlikely that of the fourteen samples analysed, the particular two that are uncontaminated would be those two for which a reasonable environmental explanation of low hydrocarbon concentration exists. In fact, if one assumes two uncontaminated samples distributed at random, their probability of appearing at any particular pair is only about 0.005 or one in two hundred.

II. HYDROCARBONS OF NEARSHORE BEAUFORT SEA INVERTEBRATE ANIMALS

In the summer of 1977 a suite of sediment samples from the nearshore Beaufort Sea was collected for hydrocarbon analysis. We found that in addition to aliphatic hydrocarbons of biogenic origin these sediments contained aromatic hydrocarbons of both fossil and combustion origin (Shaw *et al.*, 1979). Given the presence of aromatic hydrocarbons in Beaufort Sea sediments it was of importance to determine whether these compounds are being transferred to the biota of the area.

In the summer of 1978 a suite of biota samples was collected from the nearshore Beaufort Sea to be analyzed with special attention given to the aromatic fraction.

Methods

Samples of approximately 10 g wet weight were digested in centrifuge tubes with 10 N NaOH at 90° for 3 hours and allowed to cool to room temperature (ca. 20°). Hexane was then added, the tube was resealed and then shaken vigorously for 2 minutes. The sample was then centrifuged at 2400 rpm for 10 minutes. The organic phase was subsequently removed with a 20 ml syringe and the extraction repeated twice. The hexane extract was dried over Na_2SO_4 and concentrated to 1-2 ml or a rotatory evaporator. This concentrate was further concentrated to 0.5 ml under N_2 before fractionation on a column of 5 g of silica gel (deactivated with 5% water). A saturate fraction was eluted with hexane and an aromatic fraction with 20% dichloromethane in hexane. Analysis of each fraction by gas chromatography was performed as described in the previous section.

Results and Discussion

Since the intent of this work was not only to obtain baseline information about the kinds and amounts of hydrocarbons in Beaufort Sea biota but also to assess the extent to which aromatic hydrocarbons previously identified in the area's sediments (Shaw *et al.*, 1979) are transferred to the biota, we attempted to obtain sessile or weakly motile organisms from locations whose sediments had previously been investigated. Although this objective was somewhat limited by logistic constraints, we were able to obtain sufficient data (Tables IV and V) to shed considerable light on the transfer question.

Three genera were investigated. The clams *Astarte* sp. were primarily *A. borealis* but included some *A. Montagui*. The clams *Liocyma* sp. were primarily *L. viridis* with a few *L. fluctuosa*. The isopods *Saduria* sp. were probably *Saduria entomon*. All of these invertebrates contain strikingly low concentrations of hydrocarbons. As shown in Table IV, pristane is the only identifiable alkane and squalene is the only identifiable olefin. These animals also contain small amounts of aromatic hydrocarbons as determined by gas chromatography-mass spectrometry (Table V). The suite of samples analyzed represents a considerable geographic range (Table IV) from Elson Lagoon just east of Barrow to Flaxman Island at the mouth of the Canning River. Although the size of this sample group was fairly small (13 analyses), the degree of uniformity in the results lends credence to generalizations drawn from this work.

TABLE IV

HYDROCARBONS IN BEAUFORT SEA ANIMALS AS DETERMINED BY GAS CHROMATOGRAPHY EXPRESSED AS $\mu g\ g^{-1}$ ON A WET WEIGHT BASIS

Sample number	Taxon	Position N	Position W	Location	Hydrocarbons Pristane	Aliphatic DUCM	Total aliphatic	Squalene	Total unsaturated
1	*Astarte* sp.	71°17.5'	156°20.8'	Elson Lagoon	-	-	-	0.19	0.45
2	*Astarte* sp.	71°17.5'	156°20.8'	Elson Lagoon	-	-	-	0.32	0.69
3	*Astarte* sp.	71°17.5'	156°20.8'	Elson Lagoon	-	-	-	0.13	0.31
4	*Astarte* sp.	71°17.5'	156°20.8'	Elson Lagoon	-	-	-	0.17	0.28
5	*Astarte* sp.	70°16.1'	147°38.0'	Tigvaviak Island	-	-	-	-	-
6	*Liocyma* sp.	71°17.5'	156°20.8'	Elson Lagoon	-	-	0.64	0.25	0.83
7	*Saduria* sp.	70°30.0'	148°04.0'	Cross Island	0.71	3.8	6.5	3.7	5.7
8	*Saduria* sp.	70°30.0'	148°04.0'	Cross Island	0.46	3.1	4.3	2.9	3.8
9	*Saduria* sp.	70°24.1'	148°32.6'	Stump Island	1.2	4.6	6.7	2.0	2.8
10	*Saduria* sp.	70°33.8'	149°30.0'	Pingok Point	1.1	-	1.6	3.6	5.7
11	*Saduria* sp.	70°33.8'	149°30.0'	Pingok Point	1.0	-	1.4	2.1	3.0
12	*Saduria* sp.	70°12.2'	146°41.4'	Challenge Entrance	1.3	-	2.6	1.3	6.6
13	*Saduria* sp.	70°11.2'	146°05.8'	Flaxman Island	0.5	-	0.8	1.4	3.4

TABLE V

AROMATIC HYDROCARBON CONCENTRATIONS IN BIOTA IN μg g^{-1} WET WEIGHT BASIS

Column headings indicate ring system and number of alkyl carbon atoms

Sample	$C_{10}H_8$				$C_{12}H_{10}$		$C_{13}H_{10}$		$C_{14}H_{10}$		$C_{16}H_{10}$		$C_{18}H_{12}$		$C_{20}H_{12}$	
	0	1	2	3	0	1	0	1	0	1	0	1	0	1	0	1
1	13	1.6	3.2	2.1	2.1	2.9			3.5	1.0	1.4		2.0		5.4	
2	14	1.7	2.4	1.5	1.7		0.54		2.6		0.8		0.1		0.2	
3	14	2.4	2.5	0.66	0.7		0.55		2.0	1.3	0.6		0.7		1.4	
4	31	7.2	7.9		2.8		2.4		4.5	4.2	3.1	2.2	1.6	1.3	3.3	
5	31	9.1	9.3	5.0	3.4		3.0		5.7		6.5	3.9		2.8		
6	23	11	16	38	2.7				5.7		3.0	1.8		3.2		
7	7.3	1.4	2.1		3.3	5.0	2.1	5.7	5.9	3.2						
8	21	6.4	3.1	1.7	1.0		0.8		2.4					0.9		
9	5.6	1.6	2.1	4.1	0.3			9.0	9.9							
10	13	3.2	3.5	1.0	1.3	1.9	0.6	1.7	2.1	0.9	0.6					
11	11				1.4			4.2	5.8		2.6			1.9		
12	8.3	4.0	5.2	2.3	3.4	2.5	0.9	2.0	1.6	1.5	0.6			0.6		
13	11	2.1	2.0	0.2	1.2	1.9	0.6	0.7	1.3	0.9	0.5					
Blank	7.2	0.7	0.3		0.7		0.2		0.7	0.3						

Our previous analyses of Beaufort Sea sediments indicated that the saturated hydrocarbon fractions were dominated by heptacosane and odd chain length normal alkanes with 23 to 31 carbon atoms whose respective probable origins are marine algae and terrigenous higher plants. None of these compounds were detected in any of the animal tissues analyzed. Since all three genera are consumers of particulate detritus, it seems reasonable to suppose that they are exposed to all of the hydrocarbons associated with the sediments. The fact that pristane (with its branched structure) is the only identifiable alkane which accumulates, may imply that normal alkanes are assimilated <u>and rapidly metabolized</u> by these organisms. The possibility of rapid metabolism is also consistent with the fact that only in *Saduria* were any aliphatic hydrocarbons whatever observed. In *Astarte* and *Liocyma* any aliphatics which may have been present were evidently below the detection limit of approximately 0.1 $\mu g\ g^{-1}$. Squalene, which was found in all but one of the samples is a common metabolic intermediate; it is probably produced by the animals themselves rather than acquired through the diet.

The sediments of this region contain arrays of aromatic hydrocarbons whose alkyl homolog ratios indicate contributions from both fossil and pyrolytic sources (Shaw *et al.*, 1979). In these biota, the concentrations of aromatic hydrocarbons are quite low; sometimes scarcely above the blank values of Table V. However, the fact that the aromatic hydrocarbons of these animals are generally restricted to structures with either no alkyl substitution or a single methyl group suggests that pyrolytically generated compounds are being incorporated but not fossil materials. However, at the low concentrations observed, this conclusion must not be considered tentative. Nevertheless, it is clear that the animals investigated do not have substantial accumulations of aromatic hydrocarbons.

Reference - Part One

Blasko, D. P. 1976. Oil and Gas Seeps in Alaska, North-central Gulf of Alaska. U.S. Bureau of Mines Report of Investigation, No. 8136.

Laflamme, R. E. and R. A. Hites. 1978. The Global Distribution of Polycyclic Aromatic Hydrocarbons in Recent Sediments, *Geochim. Cosmochim. Acta* 42:289-303.

Royer, T. C. 1979. On the Effect of Precipitation and Runoff on Coastal Circulation in the Gulf of Alaska. *J. Phys. Oceanogr.* 9:555-563.

Sharma, G. D. 1979. *The Alaskan Shelf: hydrographic, sedimentary and geochemical environment.* Springer, New York.

Shaw, D. G. 1975. Environmental Assessment of the Northeastern Gulf of Alaska: Chemical Oceanography (Hydrocarbons), University of Alaska, Institute of Marine Science, Final Report to NOAA, Department of Commerce.

Shaw, D. G., D. J. McIntosh and E. R. Smith. 1979. Arene and Alkane Hydrocarbons in Nearshore Beaufort Sea Sediments. *Estuar. Coastal Mar. Sci.* 9:435-449.

Venkatesan, M. I., S. Brenner, E. Ruth, J. Bouilla and I. R. Kaplan. 1980. Hydrocarbons in Age-Dated Sediment Cores and two Basins in the Southern California Bight, *Geochim. Cosmochim. Acta* 44: 789-802.

PART TWO: PROJECT REVIEW

This part of this final report summarizes and reviews the results obtained during the course of this project, July 1975 through September 1980. The intent here is not to repeat the detailed discussions which have been presented in Annual Reports, but rather to provide a concise summary of those discussions together with indications about which Annual Reports and other open literature sources should be consulted for further detail. In this section an abbreviated citation form for this project's Annual Reports has been adopted. Thus (77) is used to indicate the 1977 Annual Report. The complete bibliographic data for these reports as well as the publications and theses resulting from this work are listed at the end of Part Two.

I. GULF OF ALASKA

Water

A suite of 18 unfiltered surface water samples from the Gulf of Alaska continental shelf between Yakutat (140°W) and Unimak Island (164°W) collected in 1975 indicated that these waters had total hydrocarbon concentrations at or below the low parts per billion ($\mu g\ kg^{-1}$) level. No evidence of petroleum was detected (76). An additional 43 water samples from the same area in 1976 (77) were generally similar. These latter samples showed generally higher concentrations in spring than in winter suggesting biological origin and, in some cases, had a normal alkane array which we have subsequently concluded may be bacterial (Shaw and Wiggs, 1979). Although the precision of these analysis is low, it appears that the continental shelf waters of the Gulf of Alaksa are low in hydrocarbons and free of detectable petroleum.

Seston

Thirty-one surface tows covering 740 m^2 each were made in 1975 to determine the abundance of floating tar in the Gulf of Alaska (76). Of these, only two contained small amounts of tar. Of an additional 19 tows made in 1976 (77), only three contained tar. These data give an arithmetic mean concentration of tar on the continental shelf of 3.8×10^3 mg m^{-2}. This is two or more orders of magnitude less than the concentrations of tar reported along the world's major tanker routes.

Sediment

The results of the analysis of a suite of 14 sediment samples from the northeast Gulf of Alaska is described in detail in Part One of this report. These analyses indicate that some locations have small amounts of petroleum hydrocarbons, possibly the result of natural seepages in the area.

II. COOK INLET

Water

A suite of 20 unfiltered water samples was collected in lower Cook Inlet from Kennedy Entrance in the south to about Cape Ninilchik in the north and including both Kachemak and Kamishak Bays (77). The observed concentrations of total hydrocarbons ranged from 0.2 to 1.5 µg/kg and the gas chromatograms indicated biogenic rather than petroleum origin. A suite of 29 filtered water samples and suspended matter samples was collected (79) as part of a time series measurement for plankton and as a reconnaissance of the petroleum production area of upper Cook Inlet. Of the 29 samples analyzed, 20 showed no detectable hydrocarbons. For the 9 samples containing observable concentrations of hydrocarbons, the gas chromatograms suggest that the origin is clearly not petroleum and may be bacterial. The concentrations of hydrocarbons on suspended particulate matter were also low and appeared to be of bacterial and planktonic origin.

These results together with others presented here suggest that the intense tidal mixing of upper and central Cook Inlet rapidly disperse the petrogenic hydrocarbons which are added through oil production activities. Biogenic hydrocarbons (except for bacterial compounds which may be the result of contamination from the collecting ship) are also absent in the upper Inlet. This is in keeping with the low productivity of the region. In the lower portion of Cook Inlet where turbulence and suspended sediment load are lower and biological productivity is consequently higher, low concentrations of biogenic hydrocarbons were observed.

Seston

Twenty seston tows were made between Kennedy Entrance and Cape Ninilchik (77). Only one tow (740 m^2) contained a trace of floating tar (< 0.1 mg). This indicates that petroleum production and general commerce in Cook Inlet have not led to abundant floating tar there. This conclusion is reinforced by casual but extensive examination of stranded material on Cook Inlet beaches.

Sediments

Several determinations of hydrocarbons in sediments of Cook Inlet have been made (78, 79). These have primarily been intertidal materials from the lower part of the Inlet examined to provide background for biota analyses. Four sediment samples from Kachemak and Kamishak Bays were investigated (78) particularly to determine the character of aromatic hydrocarbons present. All four contained traces of aromatics whose alkyl homolog plots (Youngblood and Blumer 1975; Shaw *et al.*, 1979) indicated that both fossil (oil and coal) and combustion derived aromatics were present. A sample from Bluff Point (on the northern side of outer Kachemak Bay) was particularly rich in coal associated compounds. For comparison, a sediment sample from Port Valdez was also analyzed. It showed an alkyl homolog pattern indicative of only combustion derived aromatics. The aliphatic fractions of these samples showed arrays of normal alkanes typical of modern plants; there was no evidence of petroleum even in a sample from Iniskin Bay, one of the places within Kamishak Bay where natural oil seeps have been reported. Although the historic record of seeps in this area is extensive (Blasko, 1976), our work in Kamishak Bay has failed to detect any evidence of seeping petroleum in sediments, in organisms or visually as oil entering the marine environment. Additional intertidal sediment analyses (79) indicated that the area whose hydrocarbon composition is strongly influenced by coal is limited to the northern side of Kachemak Bay (Homer-Bluff Point) and that the influence is very much reduced on the southern side of Kachemak Bay (Kasitsna Bay).

An experimental analysis of analytical and environmental variability of the hydrocarbon content of intertidal sediments was carried out for Mud Bay near Homer (78). From this work, we concluded that laboratory variability is of roughly the same magnitude as environmental variability occurring over tens of meters.

Biota

Over the past three years (78, 79, 80), we have determined the hydrocarbon compositions of 41 specimens of attached plants and 51 specimens of benthic animals from lower Cook Inlet.

From this work three principal conclusions can be drawn.

1. The only location at which we have observed petroleum hydrocarbon residues is the small boat harbor at Homer. We have not examined organisms from other harbors of Cook Inlet (Kenai, Seldovia, etc.) but we expect that petroleum enters the biota at those locations also. However, we have examined organisms collected in the oil seep areas of Kamishak Bay. These, like the sediments from that area, show no indication of petroleum. We do not know whether this absence of oil residues indicates that oil seeping into Kamishak Bay is efficiently dispersed and degraded or that the seeps previously reported in the Iniskin Peninsula area have reduced their flow in recent years.

2. In the Coal Bay to Bluff Point area of northern Kachemak Bay an array of hydrocarbons associated with coal exposed in the area has to a limited extent, entered the detritus based food web. Hydrocarbons in this array include odd chain length normal alkanes with 21 to 31 carbon atoms and a group of abietic acid derived diterpenoids including retene, simonelite,

fichtelite, dehydroabietane and iosene. Although this same group of compounds is present in modern soils (Simoneit, 1977), our measurements (79) indicate that on the northern side of Kachemak Bay, this array is much more concentrated in detrital coal than in modern soil. Specimens of *Macoma balthica, Mytilus edulis* and *Strongylocentrotus droebachiensis* from this area showed all or part of this array. However, two factors complicate the situation: not every analysis of these species from this area showed the array and for those that did we do not know whether these hydrocarbons had been assimilated or were merely part of the gut contents.

3. By far the majority of the organisms examined contained only hydrocarbons consistent with contemporary biosynthetic origin. This included plant and animal materials from subtidal and intertidal locations in Kachemak Bay, Kamishak Bay and central Cook Inlet. In species for which hydrocarbon composition has been determined at other locations, the composition of Cook Inlet specimens were similar, at least in a qualitative sense. Quantitative differences within a species were observed between Cook Inlet and other locations, between locations in Cook Inlet and even between replicate analyses of materials collected at the same place and time. The most extensive example of this is our work with *Fucus distichus* (78, 79, 80). We expect that both seasonal and site-related differences contribute to this variation. We also concluded that variable hydrocarbon extraction efficiency probably related to an observed variability in efficiency of plant cell lysis contributes to the observed variability. However, the qualitative differences in hydrocarbon composition between petroleum contaminated *F. distichus* at Homer Spit and unoiled specimens collected at other locations were sufficient to make the two easily distinguishable.

III. BERING SEA

Biota

A considerable variety of organisms from the pelagic environment of the southeastern Bering Sea have been collected and analyzed (77, 78). The animals investigated include invertebrates, fish, birds and mammals. No hydrocarbons from petroleum or terrigenous plant sources were detected in any of the tissues analyzed. The analyses showed that the source of hydrocarbons in the Bering Sea pelagic environment is biosynthesis in that environment. This is in keeping with the current understanding of productivity and carbon flow in this area.

Seston

Twenty tows were made for floating tar in the southeast Bering Sea in 1975 (76). Only one of these revealed any tar. An additional 13 tows were made in Norton Sound in 1976 (77). No tar was found in any of these samples. Taken together these 33 tows imply an arithmetic mean concentration of 2.7×10^{-4} mg tar m^{-2} of the Bering Sea.

Water

Five analyses of unfiltered surface water were carried out on samples collected in Norton Sound in 1976 (77). These showed total hydrocarbon concentrations at or below the $\mu g\ kg^{-1}$ level. The analytical data indicated biogenic origin.

IV. CHUKCHI SEA

Water

Six analyses of unfiltered surface water were carried out on samples collected in 1976 (77). These showed total hydrocarbon concentrations at or below the $\mu g\ kg^{-1}$ level. The analytical data indicated biogenic origin.

Seston

Twelve surface tows of 740 m^2 each for floating tar were made in 1976 (77). No tar was found in any of these collections.

V. BEAUFORT SEA

Water

In 1976 (77), 14 surface water samples were collected in the Beaufort Sea from a U.S. Coast Guard Ice Breaker. Three of these samples showed evidence of petroleum hydrocarbons, but these may have been contamination from the collecting ship itself.

Sediment

A suite of 20 nearshore sediment samples was collected for hydrocarbon determination in 1977 (78). Analysis showed that, although the alkane composition suggests only biogenic sources, complex mixtures of polycyclic aromatic hydrocarbons are present. Among the stations analyzed, distributions of aromatic hydrocarbons characteristic of both pyrolytic and fossil sources were observed. The geographic distribution of pyrolytic compounds and other lines of evidence suggest that their source may be long distance transport of anthropogenic combustion products. Fossil aromatic hydrocarbons are present at some locations at sufficient concentrations to mask any pyrolytics which may be present.

Biota

As described in Part I of this report, a suite of 13 invertebrate animals from the nearshore Beaufort Sea was analyzed to determine the kinds and amounts of hydrocarbons present. These analyses showed low concentrations of a small number of biogenic hydrocarbons and very low concentrations of aromatic hydrocarbons from pyrolytic sources.

VI. THE ASSOCIATION OF PETROLEUM HYDROCARBONS AND SUB-ARCTIC SEDIMENTS - A POTENTIAL POLLUTANT TRANSFER MECHANISM

Based on published data as well as results from our own laboratory, we have developed a simple predictive model of the amount of petroleum likely to be transferred from the water column to the benthos by sorption and sedimentation with suspended sediments. Our model is based on experiments performed with naturally occurring glacially derived sediments from southcentral Alaska. Since these sediments are unlike many lower latitude sediments in that they are chemically unweathered and low in carbonates and organic carbon, our results will not necessarily apply to environments whose sediments are not glacial in origin. In applying these results to any environment it must also be recognized that they are concerned with a single process whereas in the environment other processes including evaporation, uptake, and degradation by biota, and photooxidation are simultaneusly occurring.

Several assumptions have been necessary in the development of the model and its application. In all cases for which we were not confident that we had accurate data, we chose values which lead to an over estimation of the extent of sediment-oil association. Thus the model represents an upper bound rather than an accurate prediction of the association. Even this approach leads to the prediction that interaction with suspended sediment can result in the sedimentation of only a small proportion of oil in seawater. Thus, we conclude that for the range of conditions investigated this process is not a major transport pathway for petroleum in the marine environment.

Sediment-hydrocarbon association experiments were carried out using particulate matter collected from the water column of the Gulf of Alaska and radio-labeled decane and biphenyl which were chosen to represent the two major compound classes in petroleum — the alkanes and the aromatics. The highest concentration of hydrocarbon tested was a biphenyl preparation of three times the saturated solution concentration; the range of concentrations examined was near or below saturation for both compounds. Thus, the model may only be applicable in environmental situations where petroleum is present in solution. Such situations might include permitted discharges or a spill at some distance from the slick itself. It is probably not appropriate to extrapolate the model to higher oil concentrations where most of the oil exists as droplets or larger particles. These may associate with sediments by mechanical coating giving quantitatively very different results than the dissolved fraction.

We assume that once sorbed to sediment, hydrocarbons never desorb. Work in our laboratory provided qualitative evidence that in fact substantial desorption occurs when an oiled sediment particle enters clean water.

We assume that the concentration of petroleum (in ppm) associated with sediment is 30 percent of the original aqueous concentration (in ppm). Our laboratory work showed that for either decane or biphenyl, this is roughly the percentage of hydrocarbon which associates with sediment when the water is initially saturated with hydrocarbon. Since decane and biphenyl are structurally quite different and since together they represent the two major classes of hydrocarbons in petroleum, we assume that this relation holds, at least crudely, for all oil. We do know that for subsaturation concentrations of biphenyl or decane, the percentage of hydrocarbon associated with sediment is smaller. However, for simplicity and in keeping with our upper bound approach we assume 30 percent applies at all concentrations. It is very important to note that 30 percent is the relation between the hydrocarbon concentrations in water and sediment. This is very different than saying that 30 percent of the petroleum is on the sediment since the amount of sediment in water rarely exceeds 1 g ℓ^{-1}.

We assume that the concentration of petroleum associated with sediment is independent of the concentration of suspended sediment (sediment load). Laboratory experiments have shown that this is the case for typical Alaskan sediment loads. This assumption means that in any particular application of the model, the concentration of petroleum which is carried to the benthos is unaffected by variation in sedimentation rate.

We can apply the model to actual or hypothetical discharges of dissolved hydrocarbons in southcentral Alaska to predict an upper bound for the amount of petroleum sorbed and sedimented by mineral particles. We have done this for the permitted discharge of treated ballast water at the trans-Alaska oil pipeline terminal at Port Valdez, Alaska. The operating permit for the ballast water treatment facility specifies the following effluent characteristics: petroleum, 8 ppm; daily discharge, 1.6×10^5 m^3.

If, as a quite unrealistic worst case, we assume no dilution at all, then the concentration of petroleum on sediment is predicted to be 2.4 ppm. Furthermore, we can estimate an upper bound to the total amount of hydrocarbon sedimented within Port Valdez. Shaw and Baker (1978) have reported seasonal sedimentation rates determined by sediment traps at several locations in Port Valdez. The highest sedimentation rate reported was 0.6 $mg/cm^2 \cdot hr$ during the summer at a station near the mouths of glacially fed rivers. If we assume that this sedimentation rate applies to the entire 105 km^2 area of Port Valdez, then the daily sedimentation is:

$$\frac{0.6\text{ mg}}{\text{cm}^2\cdot\text{hr}} \times \left(\frac{10^5\text{ cm}}{\text{km}}\right)^2 \times \frac{105\text{ km}^2}{\text{Port Valdez}} \times \frac{24\text{ hrs}}{\text{day}} \times \frac{1\text{ ton}}{10^9\text{ mg}} = 15 \times 10^3\text{ tons sediment}$$

If, as predicted above, this sediment contains 2.4 ppm of sorbed petroleum, then the total petroleum sorbed in a day is 0.036 tons. This can be compared to the total daily amount of petroleum discharged which is (assuming a density of 1 for the oil):

$$1.6 \times 10^5\text{ m}^3 \times 8 \times 10^{-6} \times \frac{1\text{ ton}}{\text{m}^3} = 1.28\text{ tons}$$

Thus only 0.036/1.28 or 3 percent of the oil is predicted to associate with sediment.

The most important point to note here is that in order to reach this prediction we consistently made assumptions which tend to overestimate the extent of oil-sediment interaction. The essential conclusion is therefore that interaction with sediments is not a major pathway for the dispersal of oil from a release such as the discharge of treated ballast water at Port Valdez.

Fjords, such as Port Valdez, with their fairly restricted circulation and relatively slow flushing rates provide the most favorable conditions in southcentral Alaska for sorption of oil by suspended sediments. In more open locations, mixing can be much more efficient. For instance, at one nearshore location in central Cook Inlet a dilution of 10^4 was observed within 25 m (Rosenberg *et al.*, 1969). A discharge at this location with the same hydrocarbon concentration as the Port Valdez ballast water treatment facility would, at 25 m from the outfall, result in a hydrocarbon on suspended sediment concentration of 240 ppt.

Our model probably cannot be extrapolated beyond the hydrocarbon concentration range and suspended sediment type for which it was developed. Even within its area of applicability the model deals with only a single physical process, not the sum of all petroleum dispersing processes in the marine environment. The model shows that sedimentation *via* sorption to suspended mineral particles is not a major pathway for the dispersion of petroleum in the marine environment.

VII. HYDROCARBON TRANSPORT *via* COPEPOD FECAL PELLETS - A POTENTIAL POLLUTANT TRANSFER MECHANISM

Copepods and other zooplankton non-selectively ingest small particles from the water column and excrete relatively large and therefore more rapidly sinking fecal pellets. Consequently, when oil droplets are present in the water column, copepods have the potential of enhancing the transfer of oil to the benthos. We have constructed a simple numerical model of this process in order to estimate its importance and its sensitivity to environmental variables under Alaskan conditions (Else, 1981).

The model is based on several assumptions:

- Copepods feed on food and oil particles in proportion to their concentration in the water. This is, there is no selectivity for or against oil.
- Behavior and metabolism (including fecal pellet production rate) are unchanged by the presence of oil.
- Each copepod feeds until it ingests its daily food ration necessary for maintenance; oil droplets ingested during this process will be excreted.
- The total ingested mass may not exceed twice the daily ration.
- Animals will cease to feed when the concentration of oil droplets exceeds that of food particles.

Using these key assumptions and published information about copepod abundance we have modeled the transfer of oil particles to the benthos as a function of season in the southern Bering Sea and at Port Valdez, Alaska.

The model predicts that, at the maximum, in the Bering Sea 200 mg of oil m^{-3} day^{-1} could be ingested by copepods and excreted as fecal pellets. A slightly smaller rate is predicted for Port Valdez. The times of year presenting greatest opportunities for this transfer are the spring bloom with high numbers of phytoplankton and zooplankton, and the summer. Summer months enable a greater percentage of the initial oil droplets to be ingested (as much as 60% the first day) than does the spring bloom situation, given an oil spill of equal magnitude. The low phytoplankton levels in winter months increase the chance of oil droplets outnumbering the food supply to such an extent that the animals will cease to feed. The increase in fecal matter mass due to the incorporation of oil is greatest in winter, and may quadruple the biogenic mass.

It appears that the importance of this mechanism for the transfer of spilled oil from the water column to the benthos in highly variable. At certain key seasons and locations this may be a major oil dispersal pathway; at others it is probably negligable.

References - Part Two

Blasko, D. P. 1976. Oil and Gas Seeps in Alaska, Alaska Peninsula, Western Gulf of Alaska. U.S. Bureau of Mines Report of Investigation, No. 8122.

Else, P. V. 1981. The Prediction of Hydrocarbon Transport *via* Copepod Fecal Pellets, M.S. Thesis, University of Alaska.

Rosenberg, D. H., K. V. Natarajan and D. W. Hood. 1969. Summary Report on Collier Carbon and Chemical Corporation Studies in Cook Inlet, Alaska; Part II November 1968-September 1969, Report No. 69-13 Appendix VI, University of Alaska, Institute of Marine Science.

Shaw, D. G. and B. A. Baker. 1978. Hydrocarbons in the Marine Environment of Port Valdez, Alaska, Environ. Sci. Technol. 12:1200-1201.

Shaw, D. G. and J. N. Wiggs. 1979. Hydrocarbons in Alaskan Intertidal Algae, Phytochem. 18:2025-2027.

Shaw, D. G., D. J. McIntosh and E. R. Smith. 1979. Arene and Alkane Hydrocarbons in Nearshore Beaufort Sea Sediments, *Estuar. Coastal Mar. Sci.* 9:435-449.

Simoneit, B. R. T. 1977. Ditepenoid Compounds and other Lipids in Deep Sea Sediments and their Geochemical Significance, *Geochim. Cosmochim. Acta* 41:463-476.

Youngblood, W. W. and M. Blumer. 1975. Polycyclic Aromatic Hydrocarbons in the Environment: Homologous series in soils and recent sediments, *Geochim. Cosmochim. Acta* 39:1303-1314.

Annual Reports of This Project

Shaw, D. G. 1976. Hydrocarbons: Natural distributions and dynamics on the Alaskan Outer Continental Shelf. Inst. Mar. Sci., Univ. of Alaska, Fairbanks. 120 p.

Shaw, D. G. 1977. Hydrocarbons: Natural distribution and dynamics on the Alaskan Outer Continental Shelf. Inst. Mar. Sci., Univ. of Alaska, Fairbanks. 217 p.

Shaw, D. G. 1978. Hydrocarbons: Natural distribution and dynamics on the Alaskan Outer Continental Shelf. Inst. Mar. Sci., Univ. of Alaska, Fairbanks. 92 p.

Shaw, D. G. 1979. Hydrocarbons: Natural distributions and dynamics on the Alaskan Outer Continental Shelf. Inst. Mar. Sci., Univ. of Alaska, Fairbanks. 49 p.

Shaw, D. G. 1980. Hydrocarbons: Natural distributions and dynamics on the Alaskan Outer Continental Shelf. Inst. Mar. Sci., Univ. of Alaska, Fairbanks. 22 p.

PUBLICATIONS RESULTING FROM THIS PROJECT

Open Literature

Gritz, R. L. and D. G. Shaw. 1977. A comparison of methods for hydrocarbon analysis of marine biota. *Bulletin of Environmental Contamination and Toxicology* 17:408-415.

Shaw, D. G. 1977. Pelagic tar and plastic in the Gulf of Alaska and Bering Sea. *The Science of the Total Environment* 8:13-20.

Shaw, D. G. 1977. Hydrocarbons in the water column. *In* Proceedings of Symposium on Fate and Effects of Petroleum Hydrocarbons in Marine Ecosystems and Organisms. Pergamon, New York. pp. 8-18.

Malinky, G. and D. G. Shaw. 1979. Modeling the Association of Petroleum Hydrocarbons and Sub-Arctic Sediments, in Proceedings of the Joint Conference on Prevention and Control of Oil Spills, American Petroleum Institute. Publ. No. 4308, Washington, D. C. pp. 621-623.

Shaw, D. G., D. J. McIntosh and E. R. Smith. 1979. Arene and Alkane Hydrocarbons in Nearshore Beaufort Sediments. *Estuarine and Coastal Marine Science* 9:435-449.

Shaw, D. G. and G. A. Mapes. 1979. Surface Circulation and the Distribution of Pelagic Tar and Plastic. *Marine Pollution Bulletin* 10:160-162.

Shaw, D. G. and J. N. Wiggs. 1979. Hydrocarbons in Alaskan Intertidal Algae. *Phytochemistry* 18:2025-2027.

Shaw, D. G. and J. N. Wiggs. 1980. Hydrocarbons in the Intertidal Environment of Kachemak Bay, Alaska. *Marine Pollution Bulletin* 11:297-300.

Theses

Malinky, G. A. 1979. Hydrocarbon Association to Sub-Arctic Suspended Sediment, M.S. Thesis, University of Alaska.

Else, P. V. 1981. (expected). The Prediction of Hydrocarbon Transport *via* Copepod Fecal Pellets, M.S. Thesis, University of Alaska.

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