

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<sub>3</sub> and 1 ml 30% Ultrex H<sub>2</sub>O<sub>2</sub>. Heated gently in water bath till cessation of reaction. Diluted to 25 ml with triple distilled water and analysed spectrophotometrically.

## 111. 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  
 ( $\mu\text{g/g}$  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
E 2		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  
0ss SURVEYOR MARCH 1978

Heavy metal contents of shrimp ( $\mu\text{g/g}$  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 ( $\mu\text{g/g}$  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.( )
		<.05	<.10	20.5	<5.0
38	Flat head	<.05	<.10	41.0	<5.0
		<.05	<.10	40.4	<5.(I
45a	Flat head	<.05	<.10	37.1	<5.0
		<.05	<.10	26.4	<5.( )

TABLE IV  
 LOWER COOK INLET  
 OSS SURVEYOR MARCH 1978

Heavy metal contents of king crab muscle tissue  
 Duplicate data ( $\mu\text{g/g}$  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	$25.8 \pm 1.0$	$0.13 \pm 0.02$	$12.8 \pm 0.6$	$1.41 \pm 0.15$
NBS Certified Value	$25 \pm 3$	$0.11 \pm 0.01$	$12 \pm 1$	$1.3 \pm 0.2$

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<sub>2</sub>O<sub>2</sub> extract of sediments (revised procedure)  
Mean of triplicate determinations (µg/g)

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

TABLE VII

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

HCl extract of sediments

Mean of triplicate determinations ( $\mu\text{g/g}$  dry weight)

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

AC 267 RES BAY HCL EXTRACTS STA 2.5

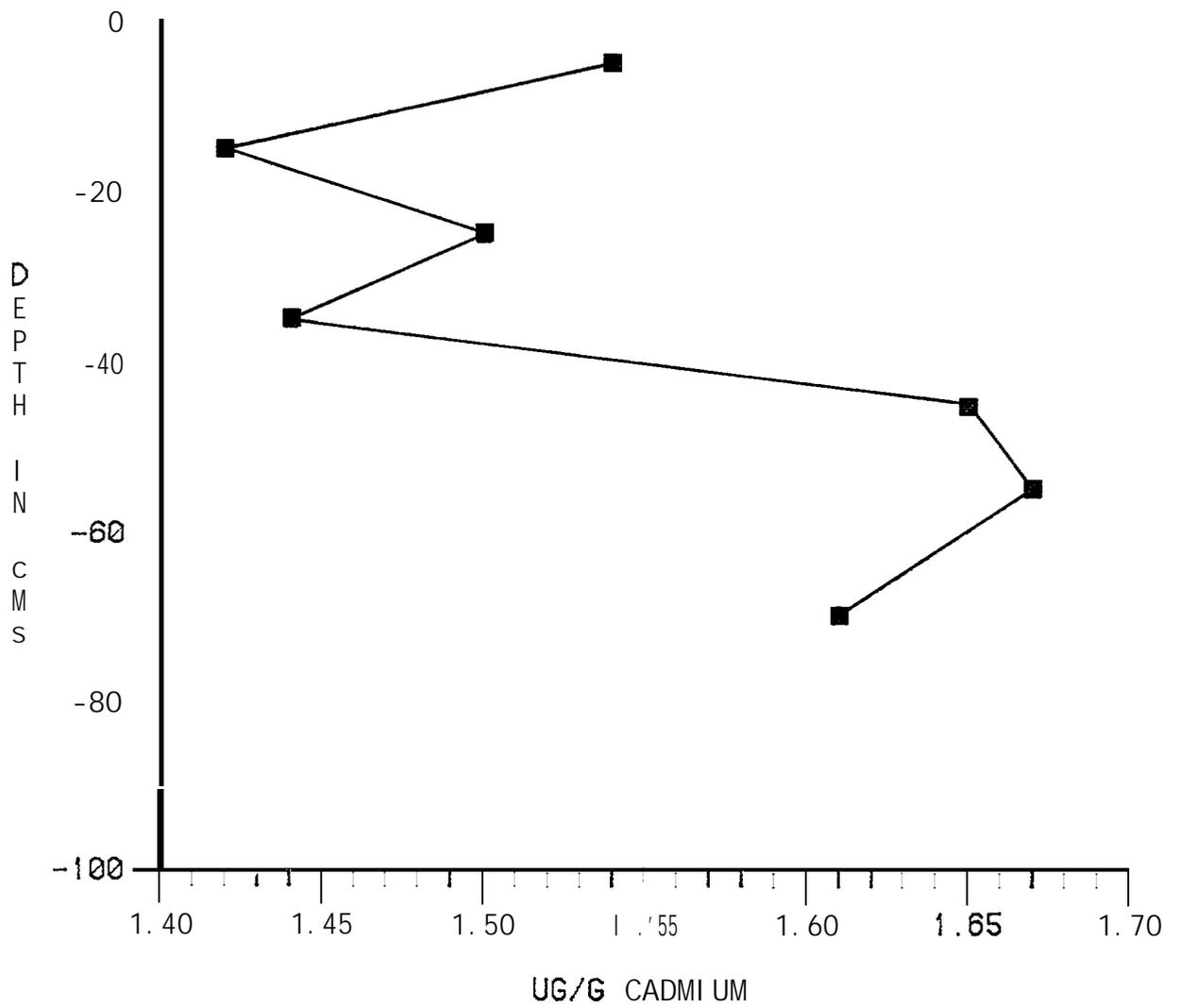


Figure 1.

AC 267 RES BAY HCL EXTRACTS STA 2.5

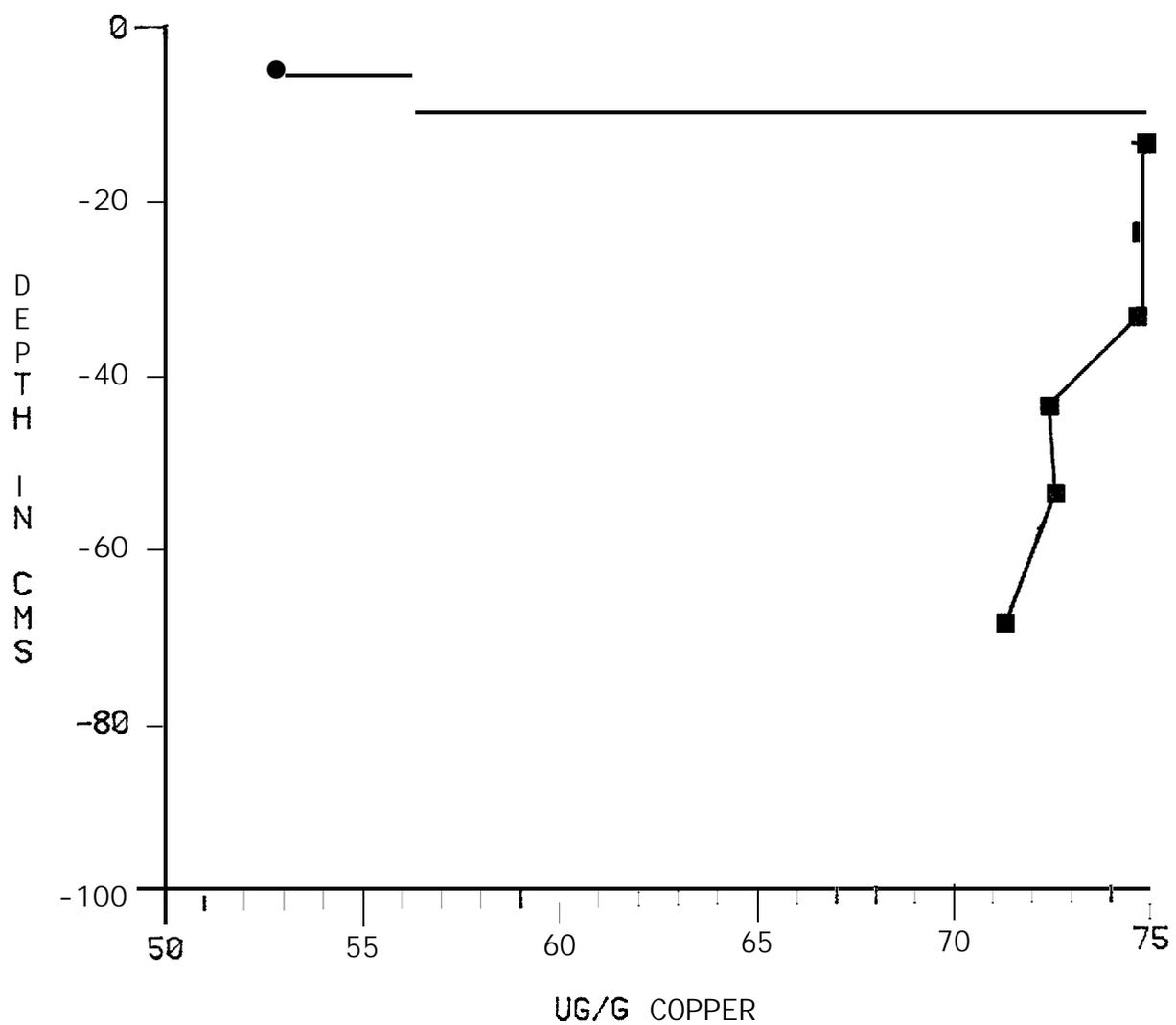


Figure 2.

AC 267 RES BAY HCL EXTRACTS STA 2.5

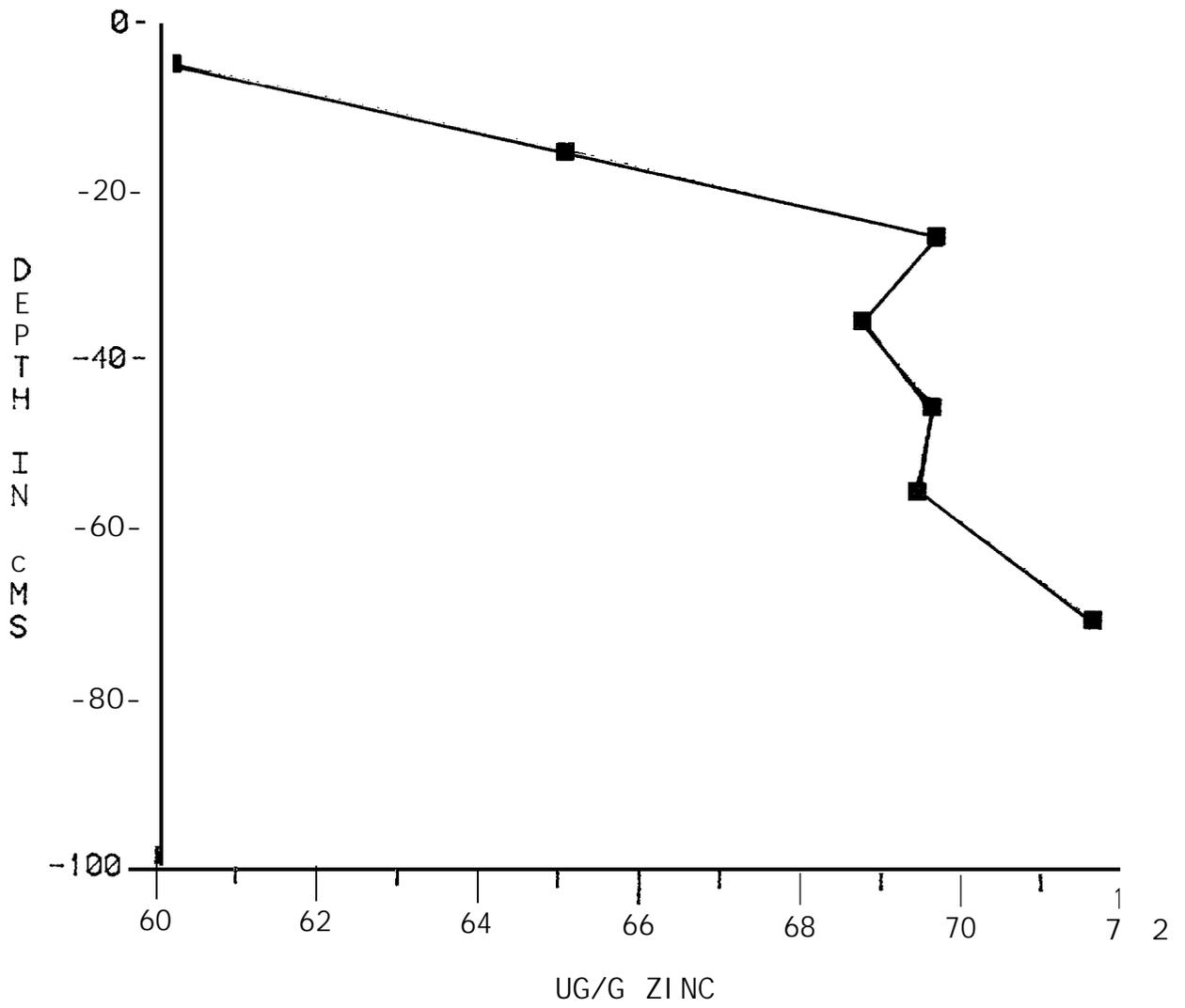


Figure 3.

AC 267 RES BAY HCL EXTRACTS STA 2.5

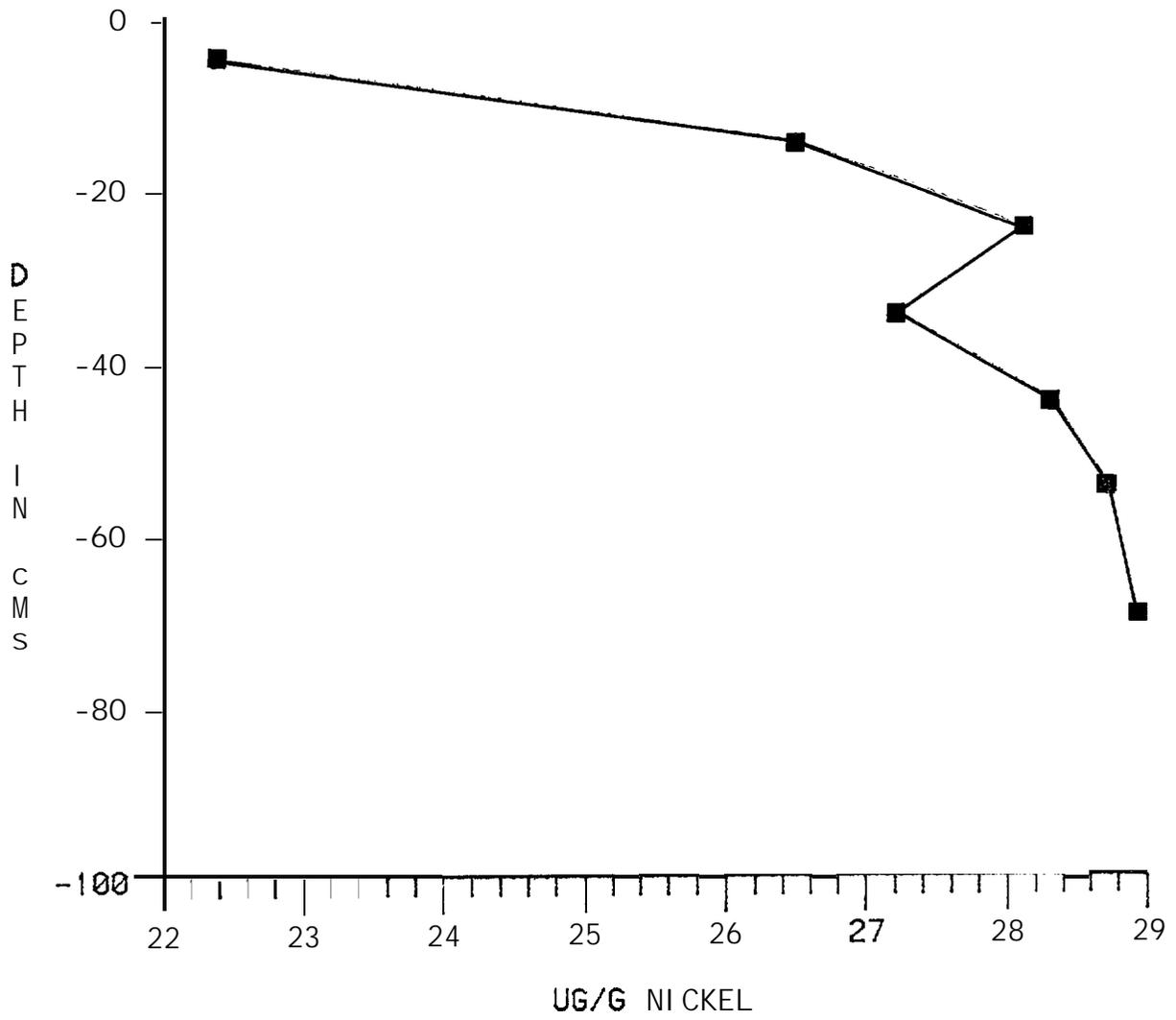


Figure 4.

AC 267 RES BAY HCL EXTRACTS STA 2.5

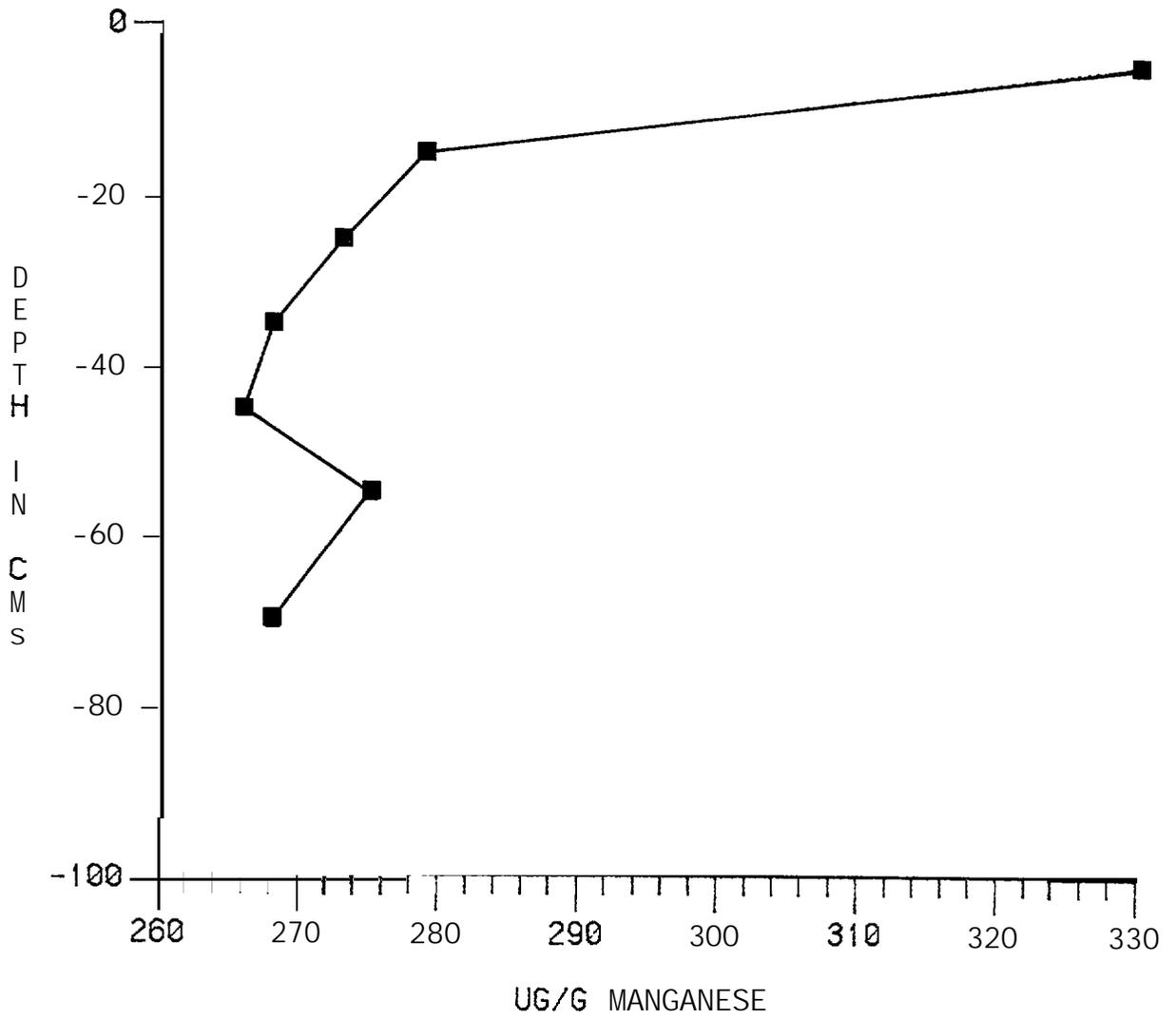


Figure 5.

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 **pollu-**  
t ion.

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 sub-contract 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 **sub-**project, 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 **biogeo-**chemical 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 particulate 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 (Aeons 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)			R
		A	B	c	
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	<b>RES-2.5</b>	0.21	10.91	2.08	0.999
260	RES-2. 5	- 2.00	10.80	2.15	0.995
262	<b>RES-2 .5</b>	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 (rein)	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  $\mu$ . The standard settings, however, have originally been determined to provide size intervals of 5  $\mu$  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  $\mu$  or 6  $\mu$  or 7  $\mu$ ).

- 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 microsphere 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

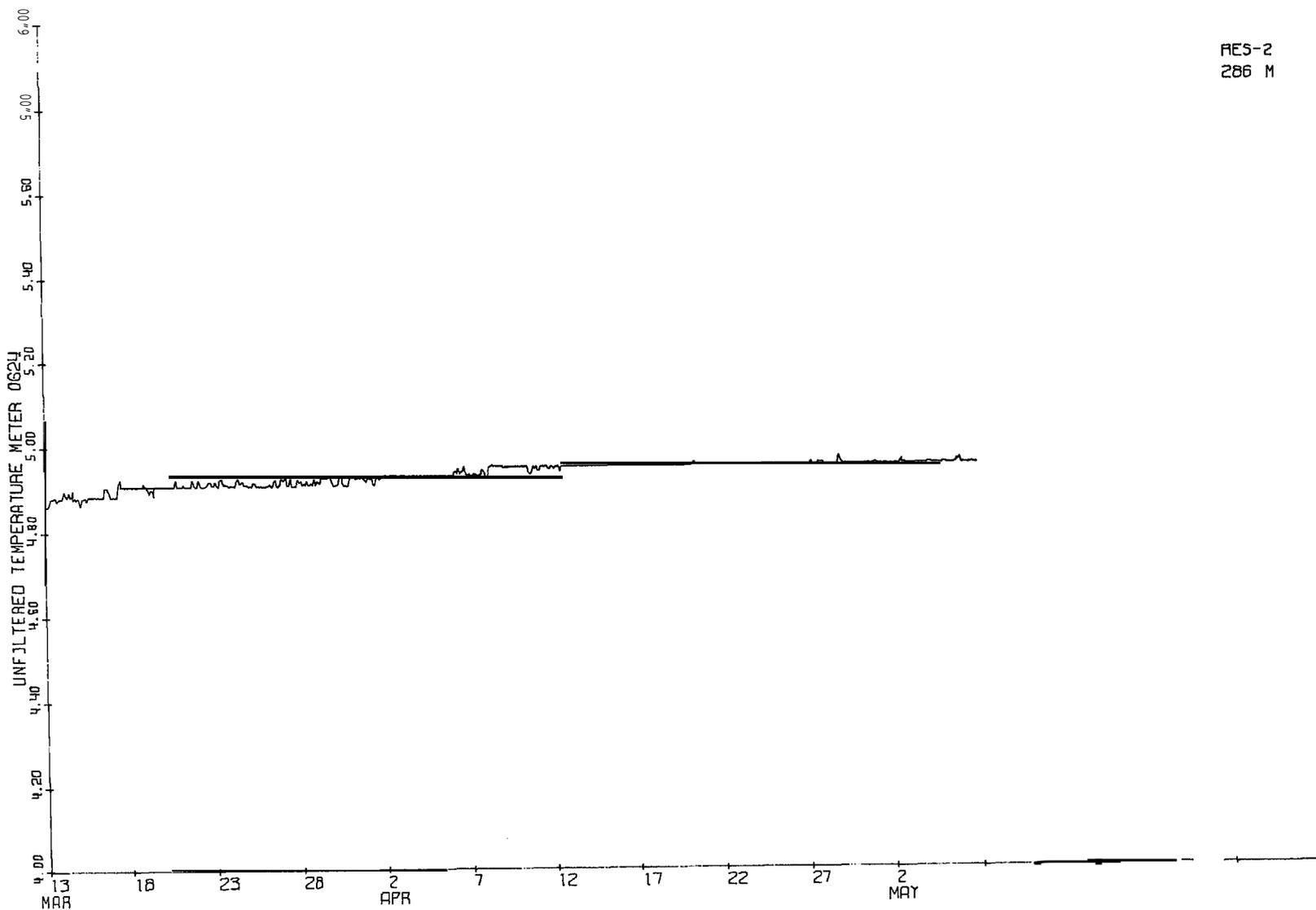


Figure 1.

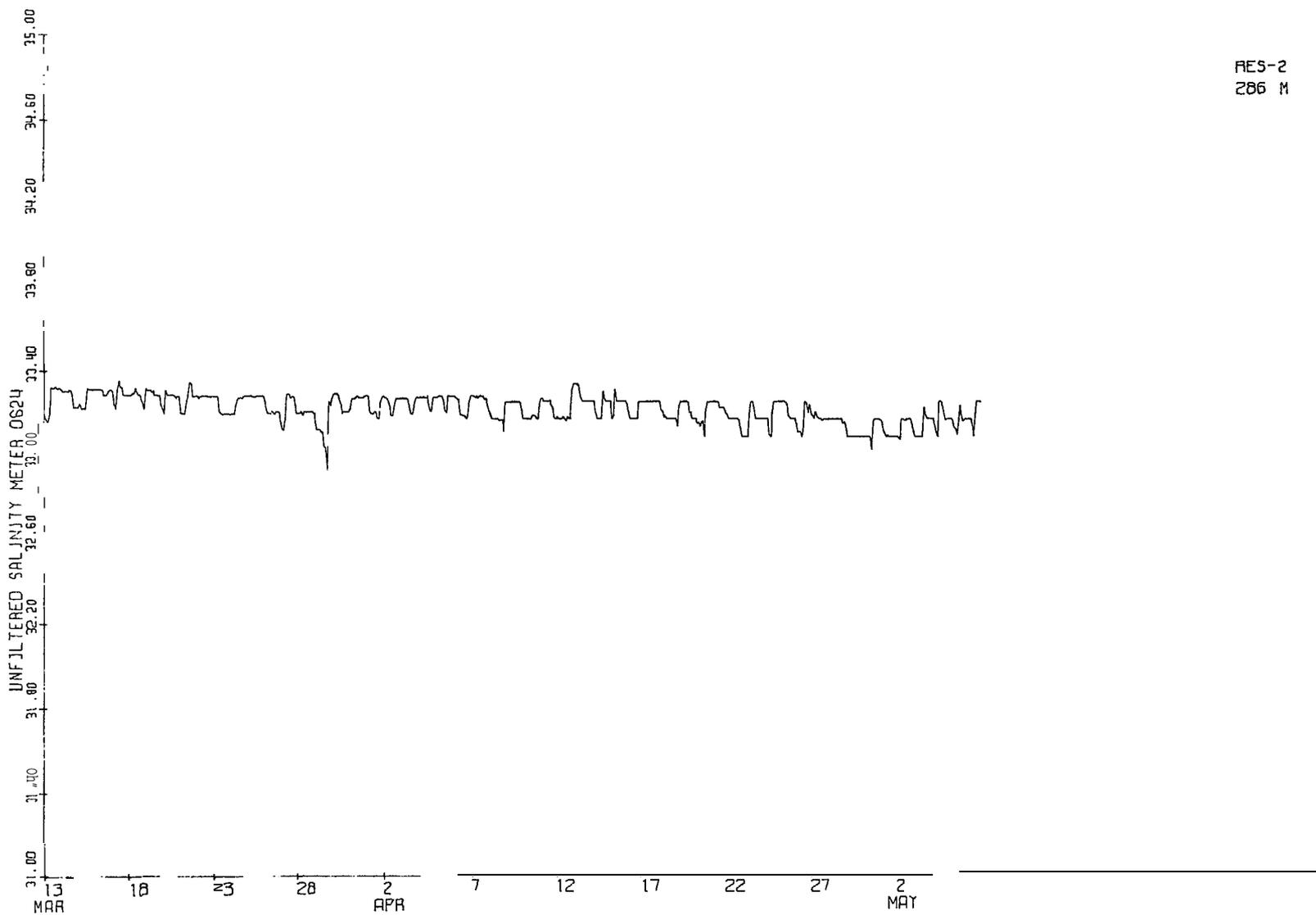
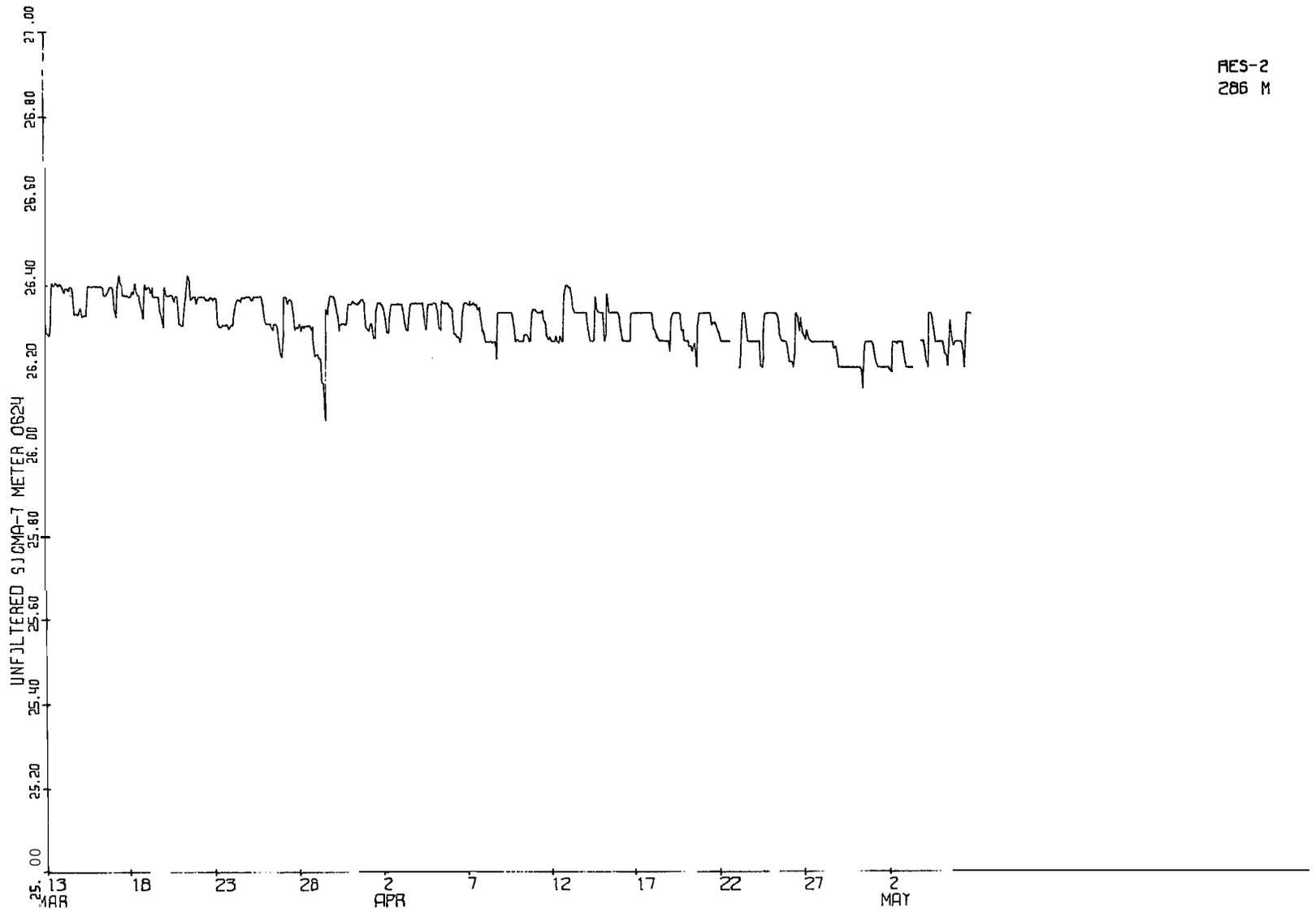
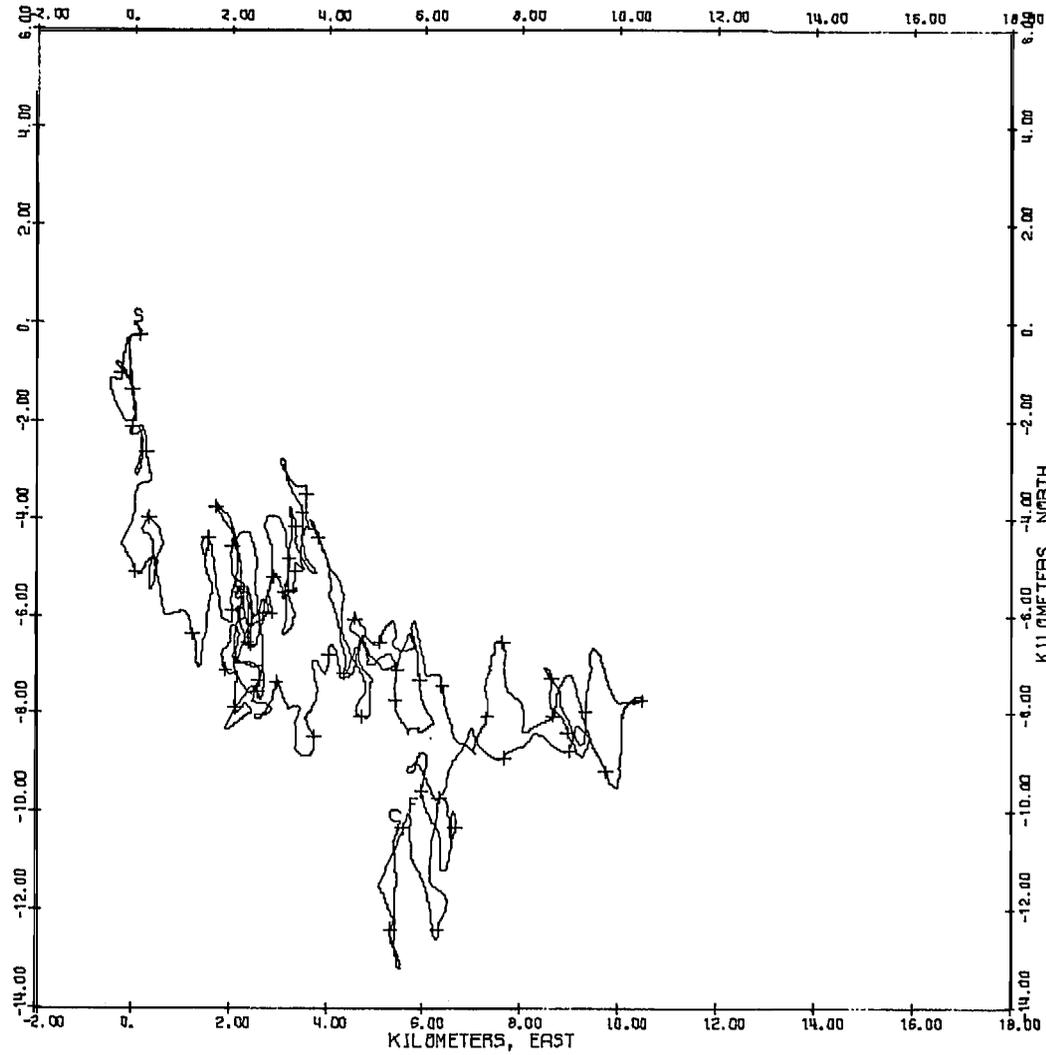


Figure 2.



AES-2  
286 M

Figure 3.



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

Figure 4.

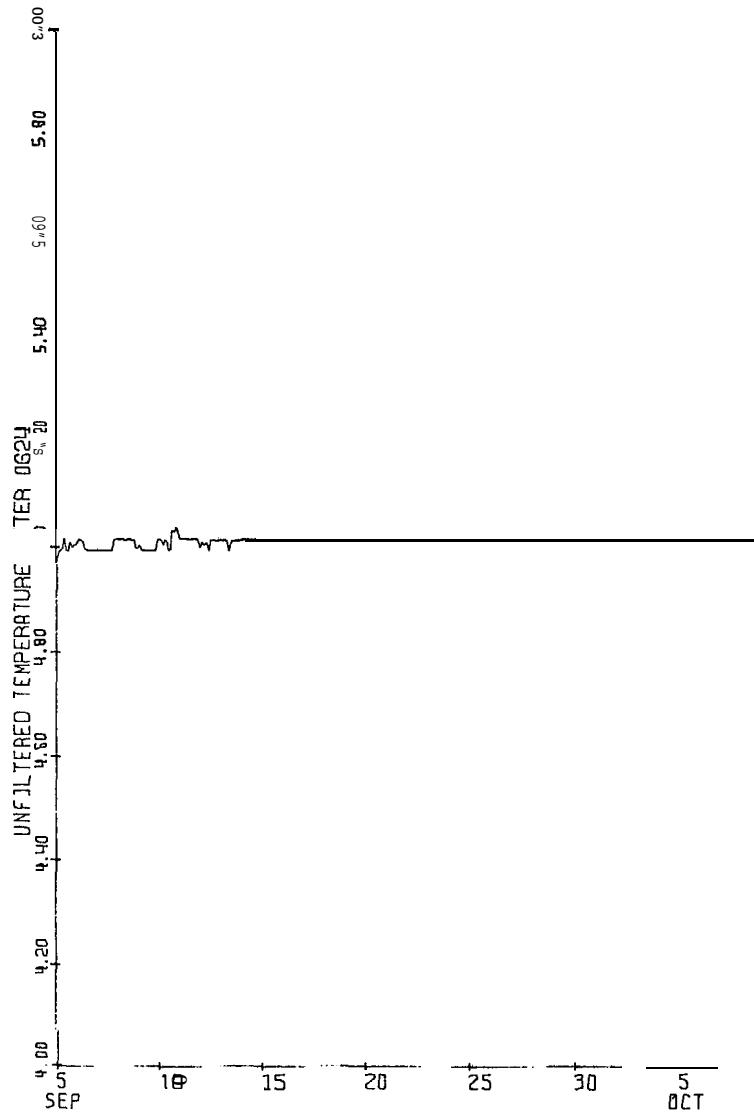


Figure 5.



Figure 6.

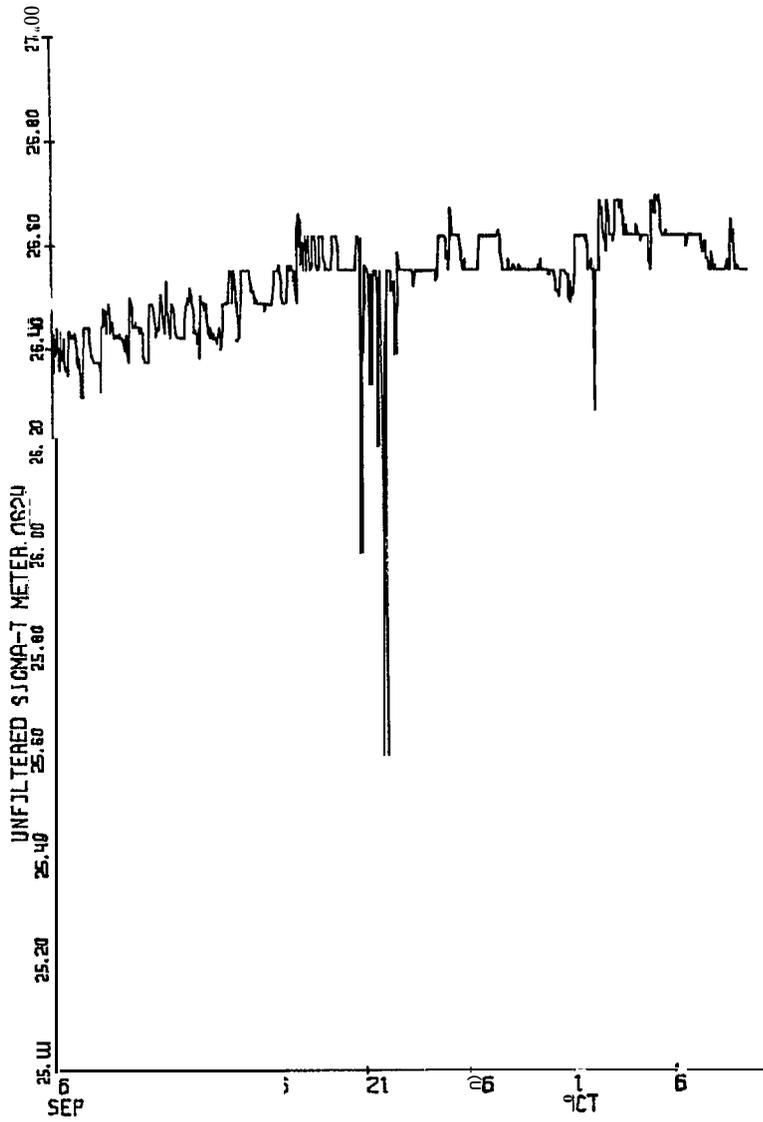
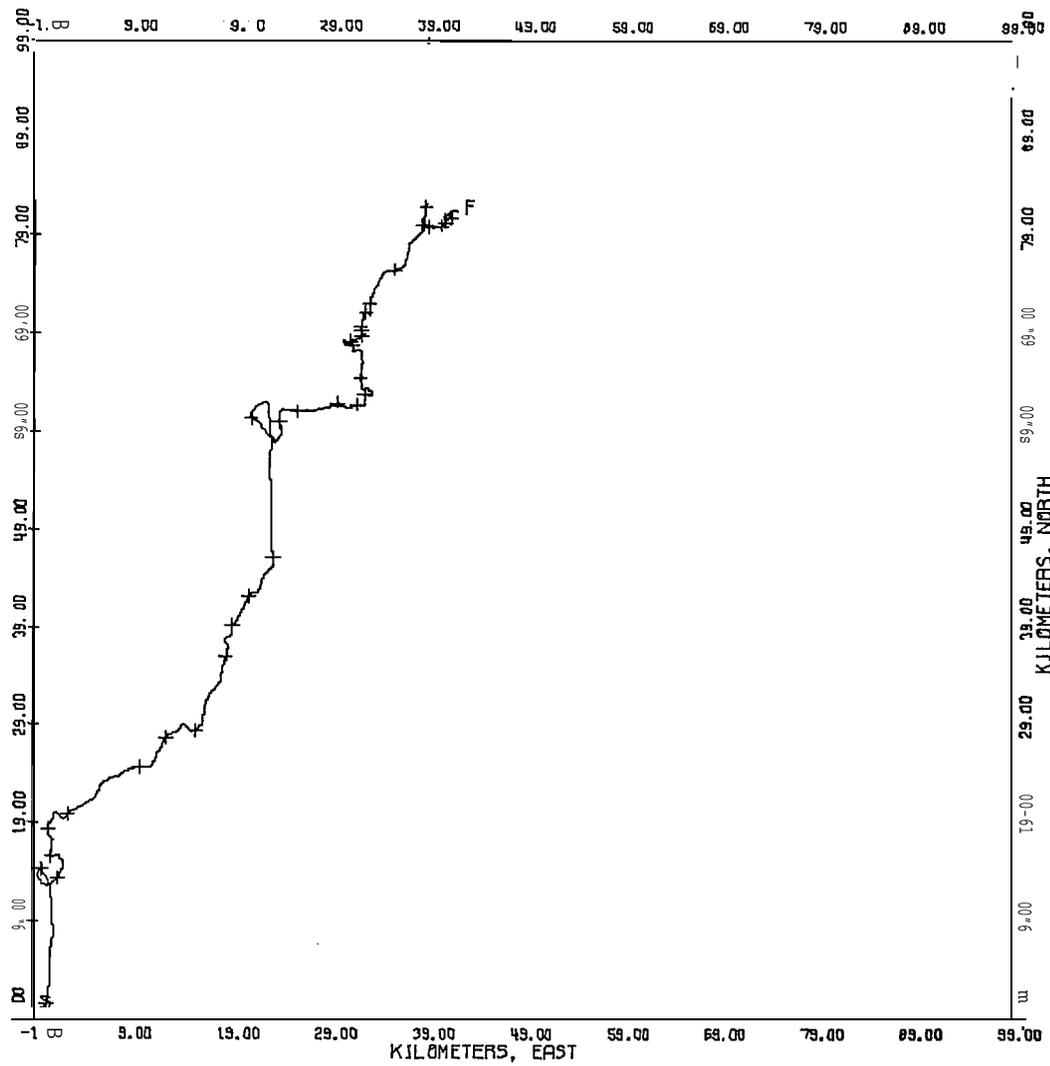


Figure 7.



RES-3  
 286 M  
 FIRST RECORD AT 1950 UT 5 SEP  
 1 DAYS BETWEEN TIC MARKS

Figure 8.

APPENDIX II

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

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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 4-1 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%.

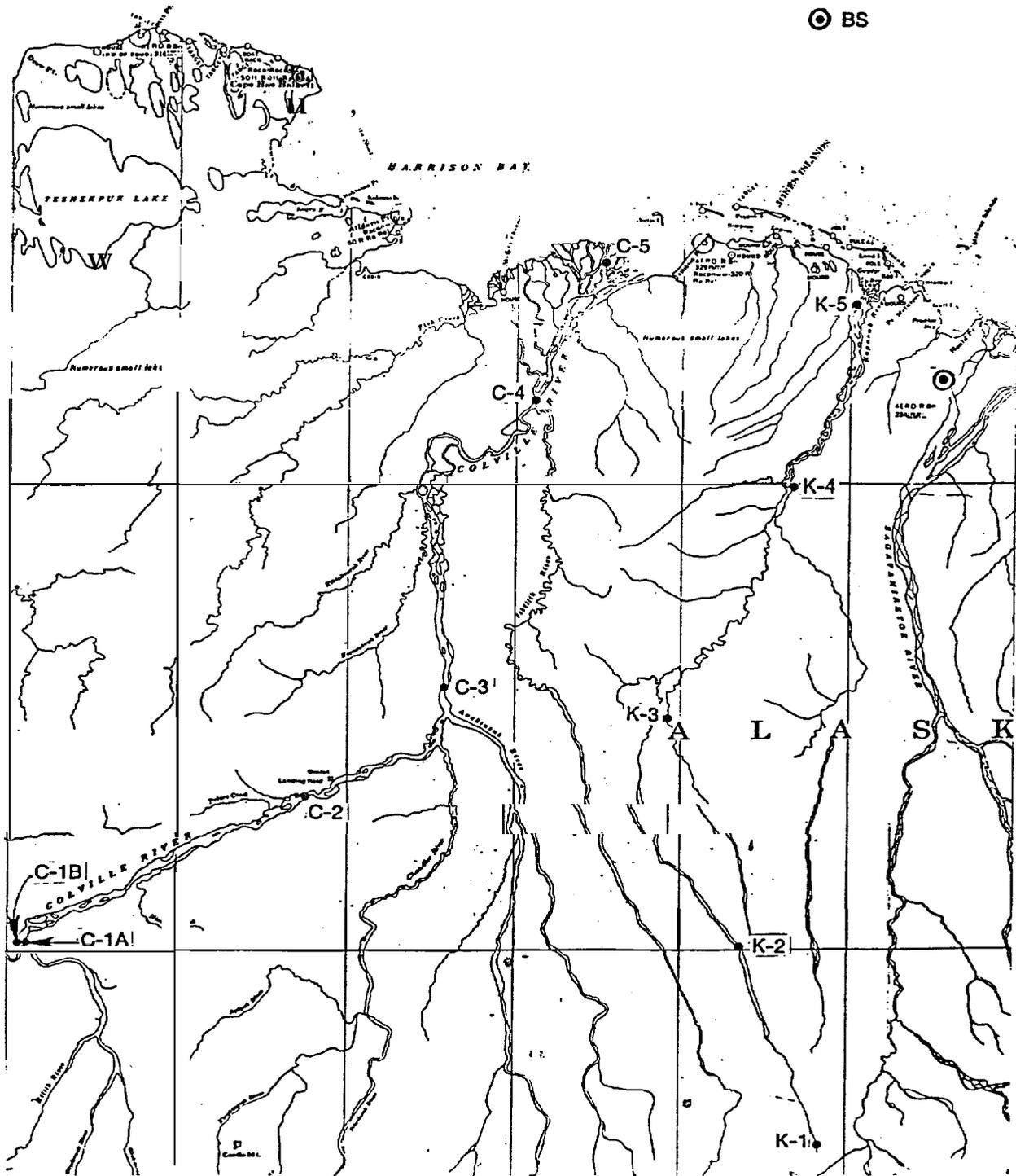
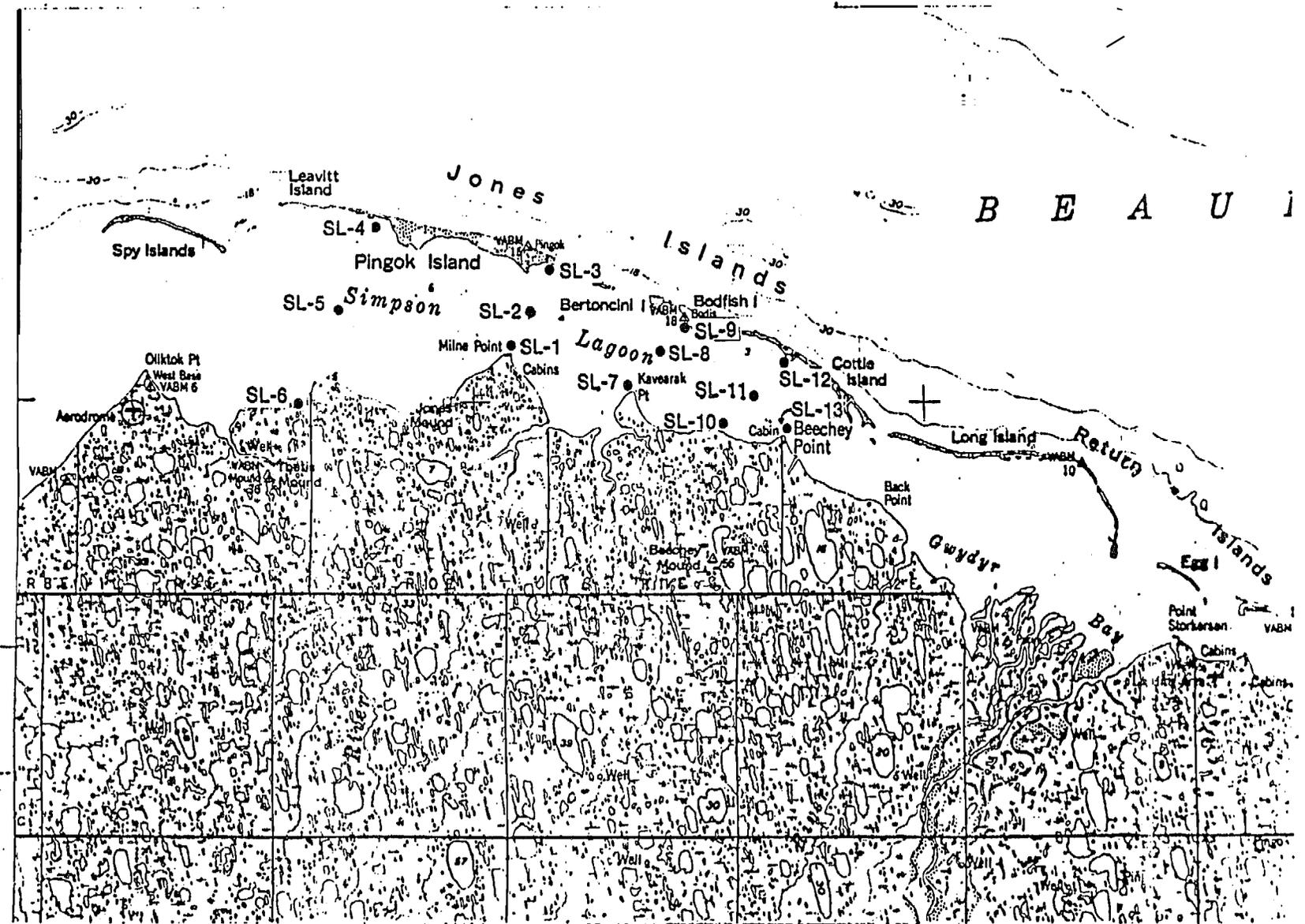


Figure 1.

47



## 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 **inter-calibration** 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 **co-crystallization** with 8-hydroxyquinoline (**oxine**). The crystals are irradiated with neutrons; following simple **radiochemical** purification steps, radio-induced  $^{64}\text{Cu}$  and  $^{56}\text{Mn}$  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  $\text{ml}^{-1}$  of cation in dissolved water. Comparators were 1 and 4  $\text{g}\cdot\text{ml}^{-1}$  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  $^{54}\text{Mn}$ . 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  $^{54}\text{Mn}$  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  $^{54}\text{Mn}$ , and the elements were cocrystallized as described above. ,

Data show that following the initial acidification,  $0.003 \pm 0.001$  and  $0.022 \pm 0.004$  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  $0.003 \pm 0.001$  and  $0.005 \pm 0.001$  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  $1 \times 10^{12}$  neutrons  $\text{cm}^{-2} \text{sec}^{-1}$ , and the specimens were rotated about the reactor core at  $1 \text{ rev/rein}^{-1}$ .

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  $^{54}\text{Mn}$  and, except for the **oxine** blank, they also received 250 mg of **oxine**.  $\text{H}_2\text{S}$  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 GuS 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  $^{54}\text{Mn}$ . Copper was precipitated as described above; the Mn comparator was brought to 50 ml with concentrated  $\text{HNO}_3$ , heated, and then treated with  $\text{KBrO}_3$ .

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  $^{64}\text{Cu}$  and  $^{56}\text{Mn}$ . The count rate was normalized for the  $^{54}\text{Mn}$  yield determined prior to irradiation and for the lapse of time from 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  $^{64}\text{Cu}$  and 847-keV photopeak of  $^{56}\text{Mn}$  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  $^{56}\text{Mn}$  and  $^{64}\text{Cu}$  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,  $2.5 \times 10^3$  and  $6.0 \times 10^4$  photopeak counts  $\text{min}^{-1}$  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- $\mu$ g level was 6%, while the error for manganese at the 0.16- $\mu$ g 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.  $^{52}\text{V}$  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  $\mu$ g/ml) was made from a commercial 100-ppm standard prepared from ammonium metavanadate. Other reagents used were of analytical reagent grade.

Instruments. The  $^{48}\text{V}$  tracer was gamma-counted with an NaI (Tl) well type detector coupled to a scaler. The neutron-induced  $^{52}\text{V}$  was measured with a 38-cm<sup>3</sup> 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  $^{48}\text{V}$  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  $^{49}\text{V}$  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  $\mu\text{l}$  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  $\mu\text{g}$  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  $3 \times 10^{12} \text{ n}\cdot\text{cm}^{-2}\text{ s}^{-1}$ . 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  $^{52}\text{V}$  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  $1.5 \times 10^4$  counts/ $\mu\text{g}$  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  $0.07 \pm 0.03$  ppb, and for the Colville River it was  $0.12 \pm 0.03$  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 ( $0.29 \pm 0.03$ ) and intermediate between the rivers and the Beaufort Sea. Except

Table 1.  
Concentration ( $\mu\text{g}/\text{kg}$ ) of V, Mn, **Cu**, and Fe in Waters.

<u>Source</u>	<u>Location*</u>	<u>Elements</u>				
		<u>V</u>	<u>Mn</u>	<u>Cu</u>	<u>Fe</u>	
Snow	1	0.08	3.0	0.3	20.8 $\pm 0.7$	
	2	0.08	2.2	0.9	24.8 $\pm 0.5$	
<b>Colville</b>						
River	<sup>A</sup>	0.07	5.2	1.0	42.7	
	<sup>B</sup>	0.12	2.7	2.3	<b>106.0</b>	
	<b>2</b>	0.11	4.0	<b>1.5</b>	<b>42.5</b>	
	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		
<b>Kuparuk</b>						
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	<b>1.2</b>	8.7	
<b>Simpson</b>						
Lagoon	1	0.26	16.9	1.2	6.9	
	2	0.29	21.9	1.5	<b>8.7</b> $\pm 0.3$	
	3	0.30	20.9	1.1	<b>9.5</b>	
	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	<b>1.1</b>	7.6	
	12	0.34	18.0	1.0	<b>3.1</b>	
	13	0.28	17.9	1.3	8.5 $\pm 0.2$	
<b>Beaufort</b>						
Sea	<u>Depth (m)</u>					
	<b>BS</b>	<b>3</b>	<b>0.50</b>	3.2	2.1	(111)
		20	<b>1.04</b>	0.5	0.4	6.9
	35	1.13	1.7	0.8	<b>14.1</b>	

\*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  $0.6 \pm 0.3$  ppb. This analysis agrees with contemporary deposits (post-1945) at the Dye-3 and Camp Century sites in Greenland (5). The average determination was  $1.0 \pm 0.2$  ppb and  $1.7 \pm 0.6$  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 ( $1.3 \pm 0.2$  ppb) and not distinctly different from the rivers.

#### Iron

The assay of iron on the snow samples was  $22.8 \pm 2.0$  ppb. By comparison with this result and excluding a single non-representative sample (774 ppb) the Kuparuk River was relatively depleted in this element ( $10.3 \pm 6.8$  ppb): on the other hand water from the Colville River was enriched ( $58.6 \pm 24.6$  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  $2.6 \pm 0.4$  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  $18.5 \pm 1.6$  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.

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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 meteorological 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 estuaries – 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.

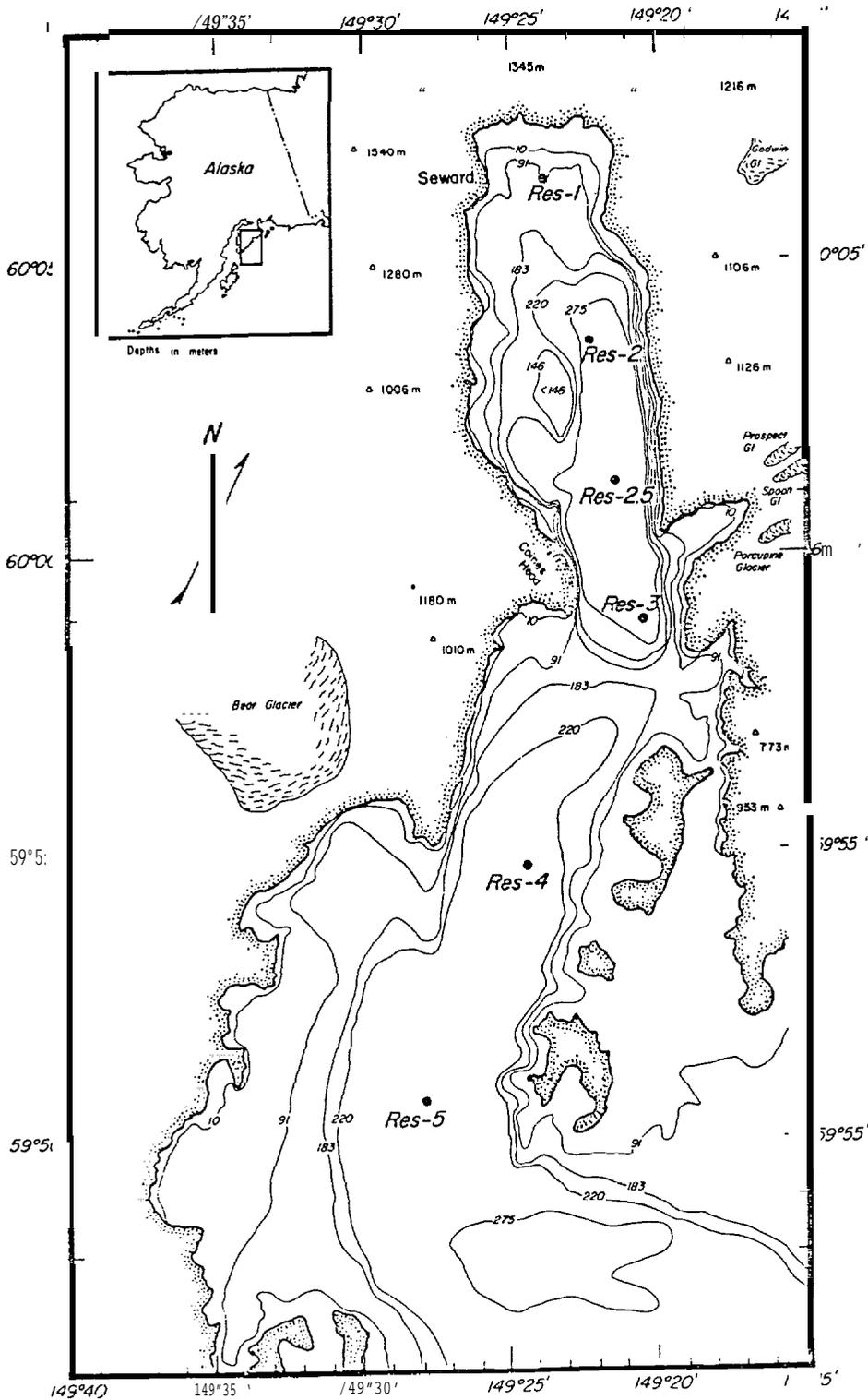


Figure 1. Resurrection Bay, southcentral Alaska, showing location of standard stations.

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 circulations. This freshwater inflow is markedly seasonal (Figure 2; more recent data are not available) with a maximum in late summer-fall ( $> 500 \text{ m}^3 \text{ sec}^{-1}$ ) 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

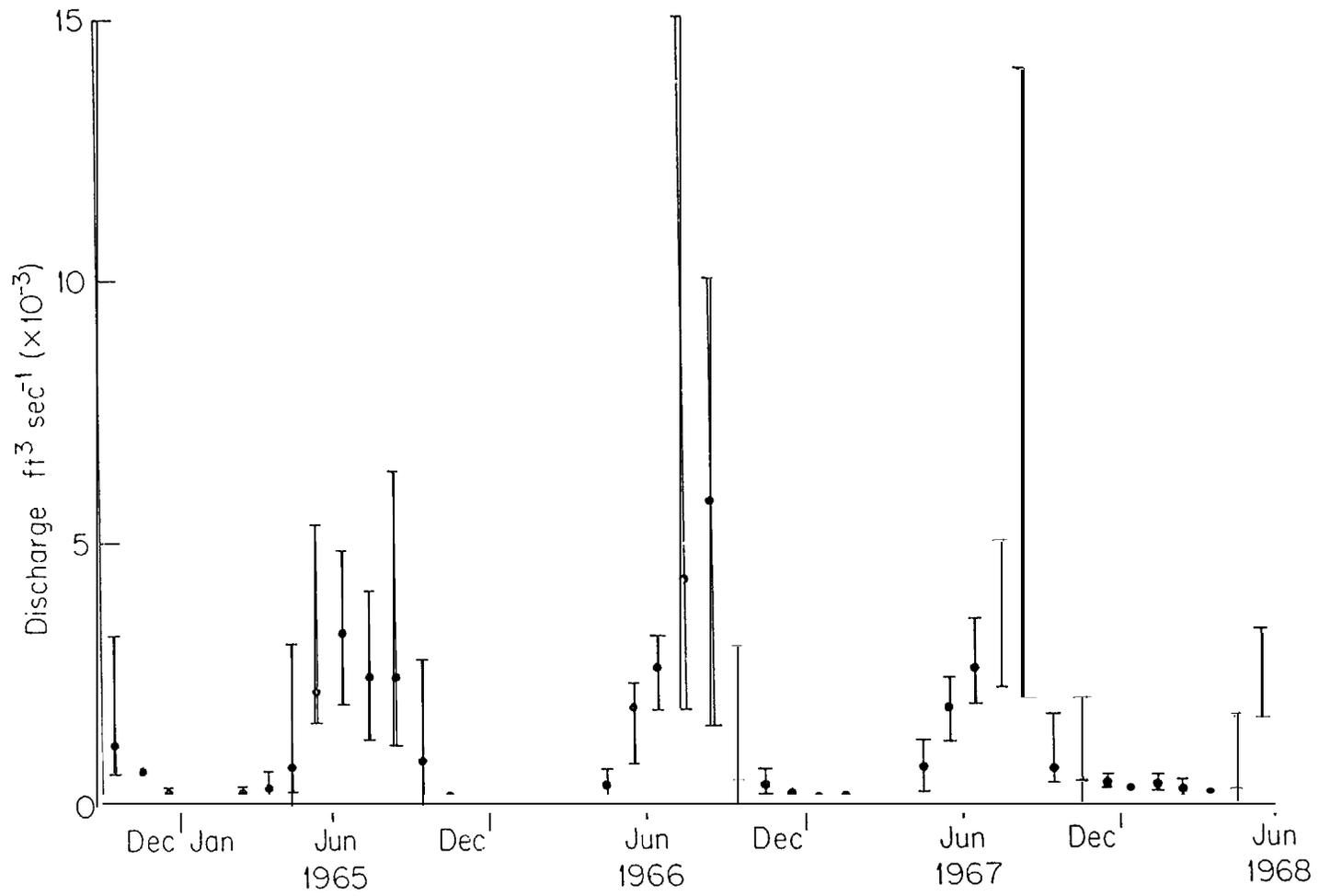


Figure 2. Seasonal discharge of Resurrection River 1965-68 (unpublished USGS data).

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 is advected over shallow sills to replace the enclosed basin water in the

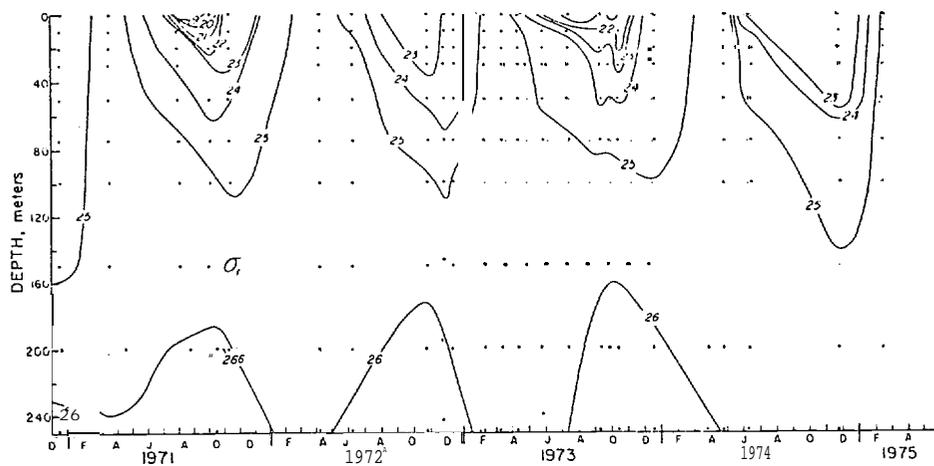


Figure 3. Seasonal density distribution at Station Res 5 (after Royer, 1975).

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

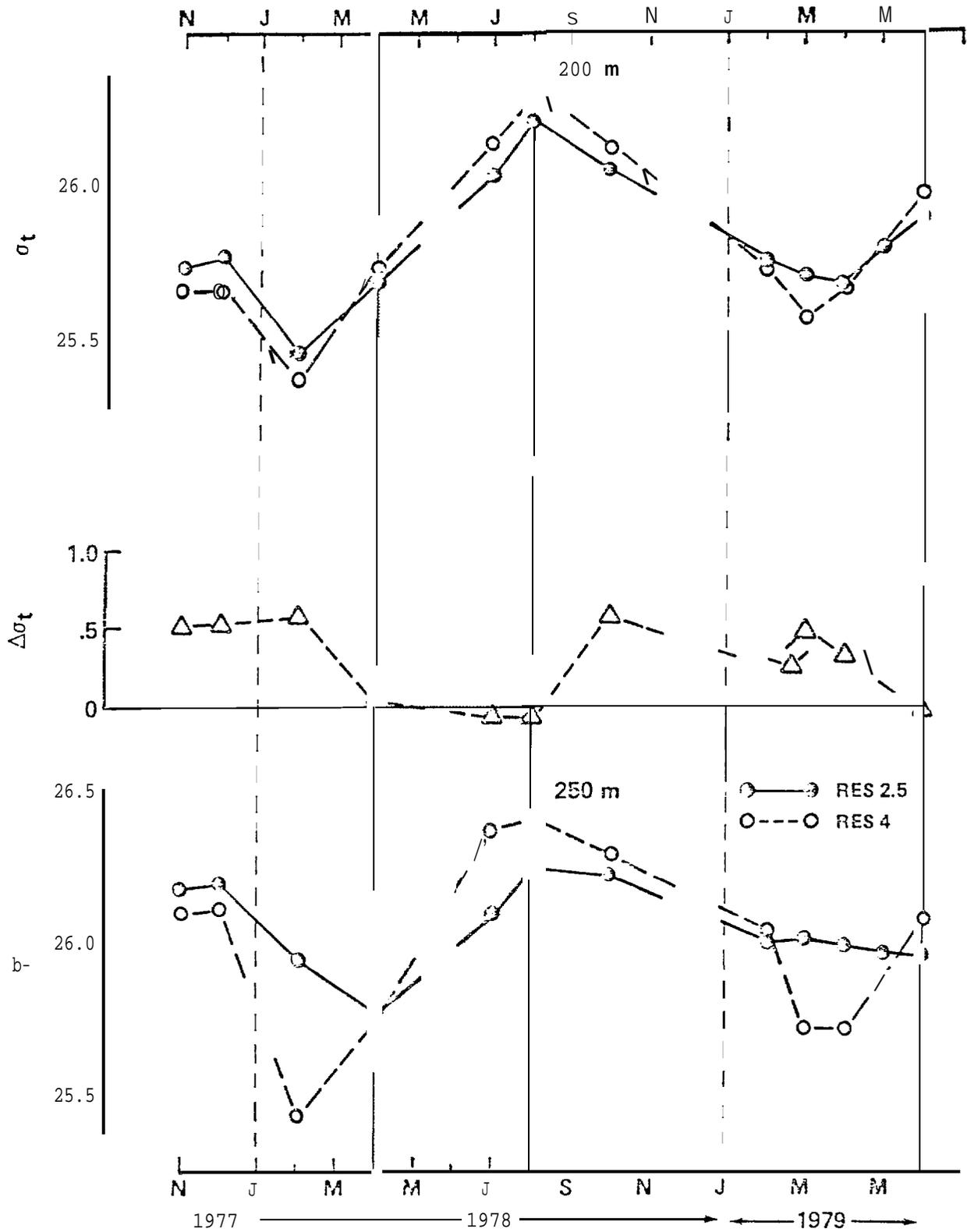


Figure 4. Density distribution at sill height (200 m) and depth (250 m) at Stations Res 4 and 2.5, November 1977-June 1979. The screened area in this and subsequent figures designates the primary annual basin flushing period (from  $\Delta\sigma_t$ ; see text).

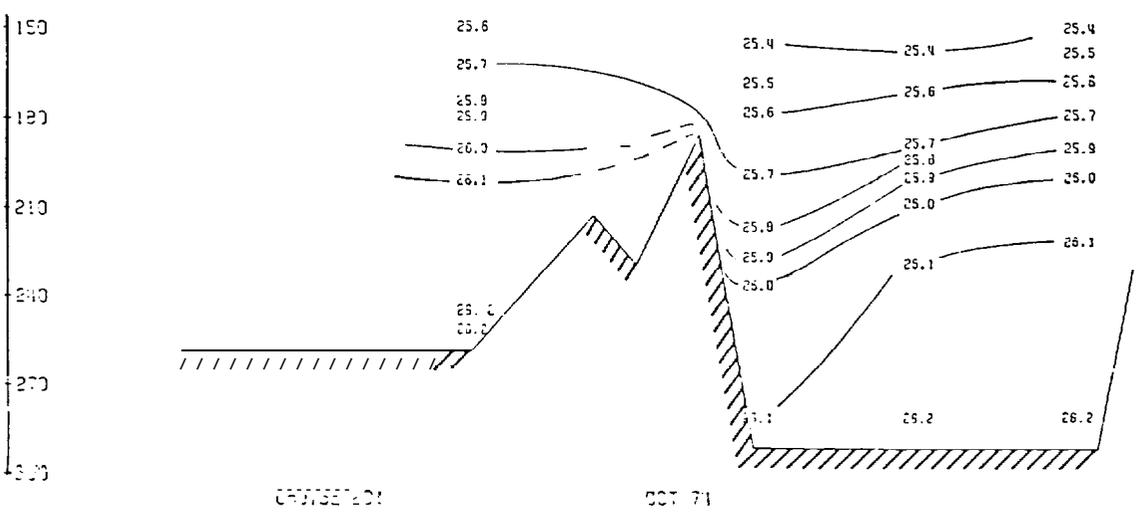
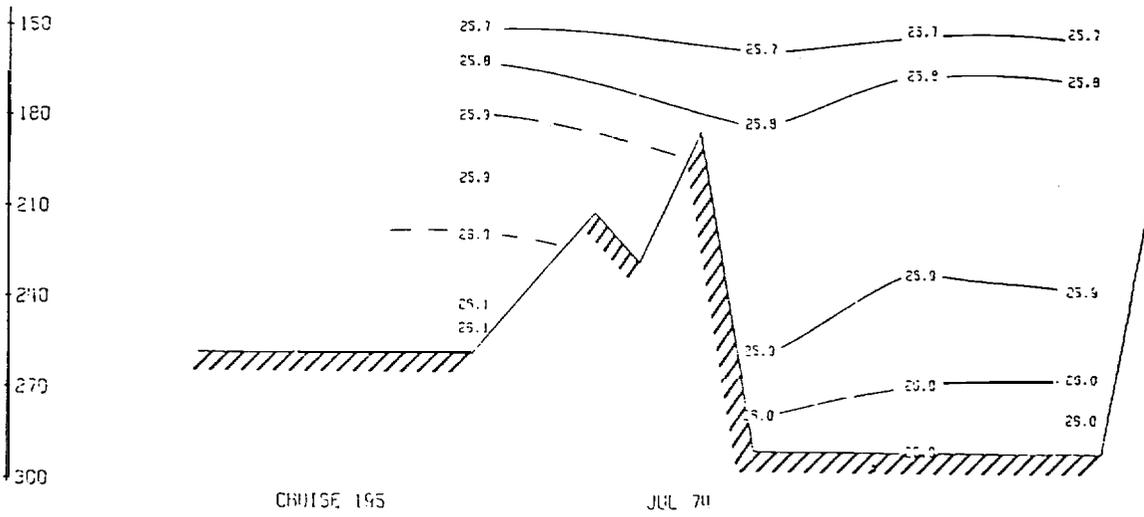
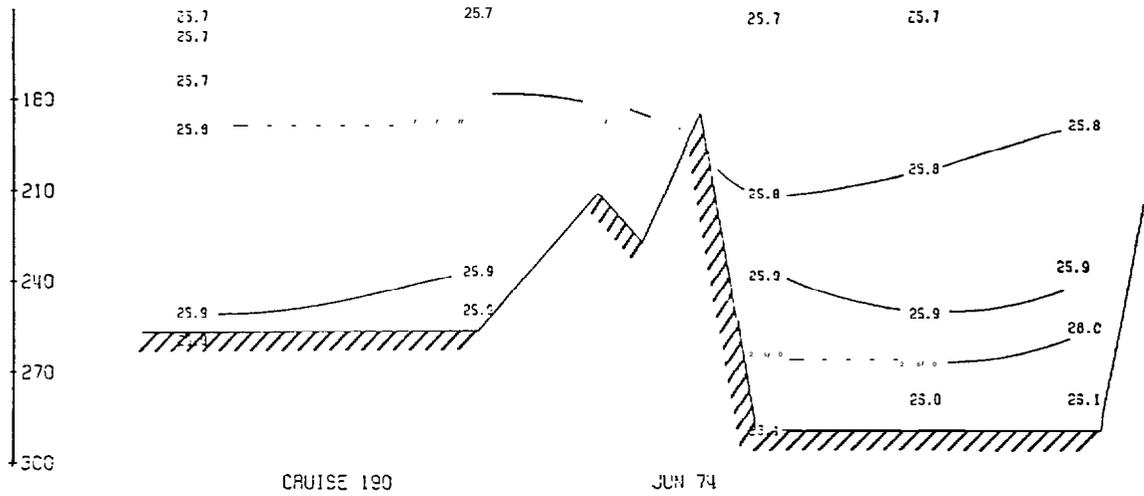


Figure 5. Longitudinal density profiles: summer-winter 1974.

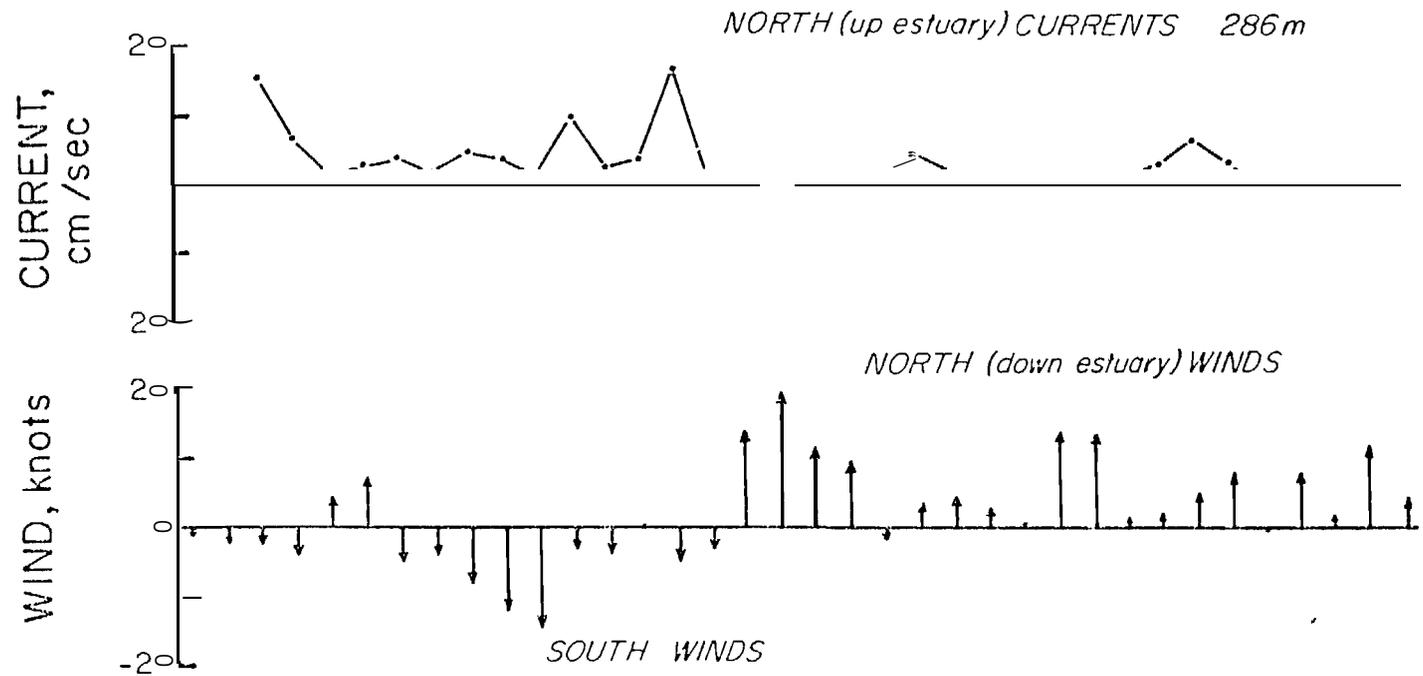


Figure 6. N-S current vectors at depth (286 m) in the basin during major water renewal period (September 5= October 8, 1973) and prevailing (N-S) winds.

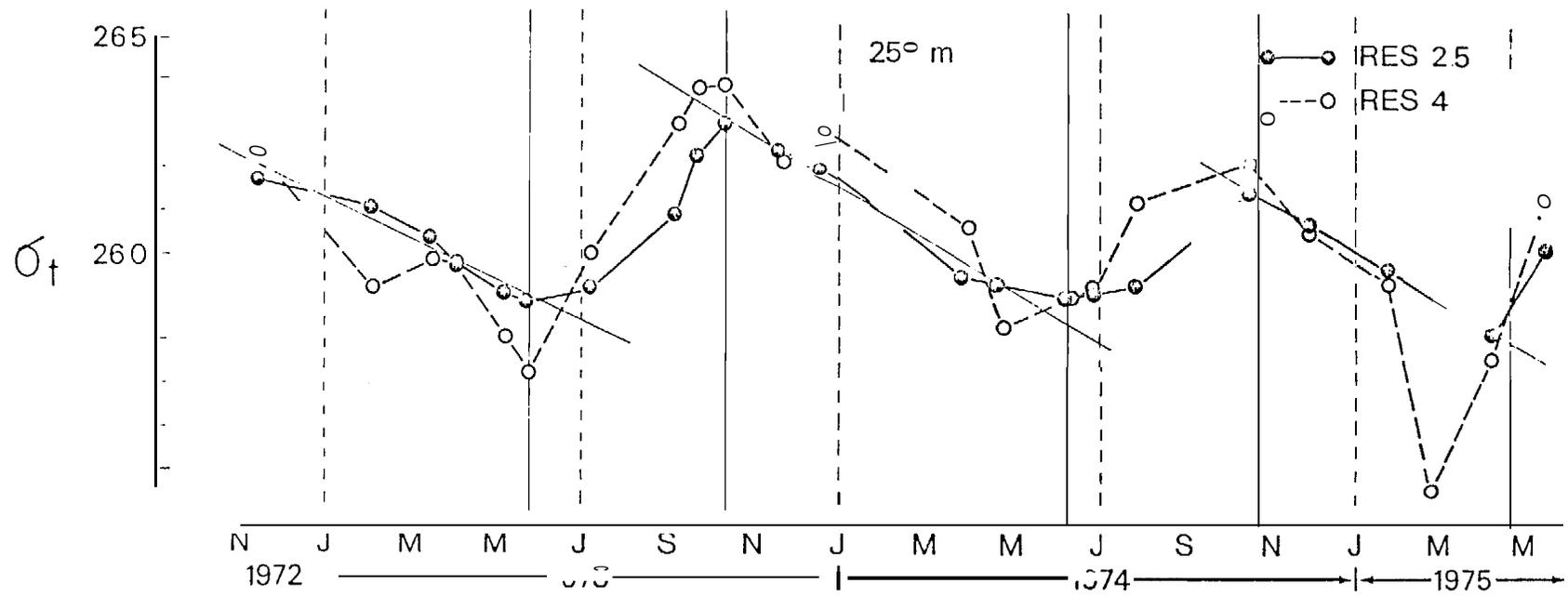


Figure 7. Density distribution at 250 m within and outside the sill, November 1972-May 1975.

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  $\sigma_t$  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.

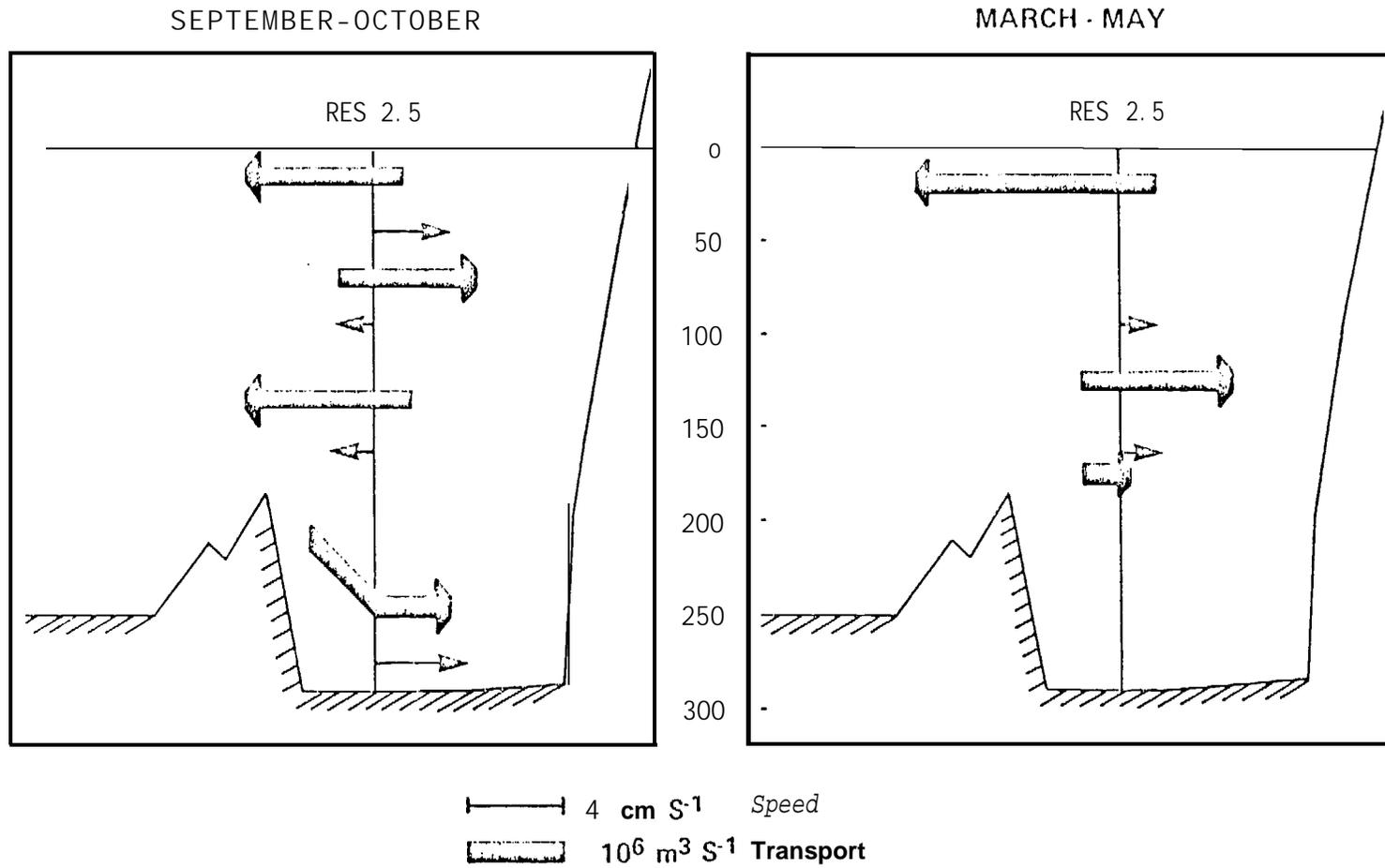


Figure 8. Schematic of proposed principal winter-summer (1973) circulation patterns in Resurrection Bay.

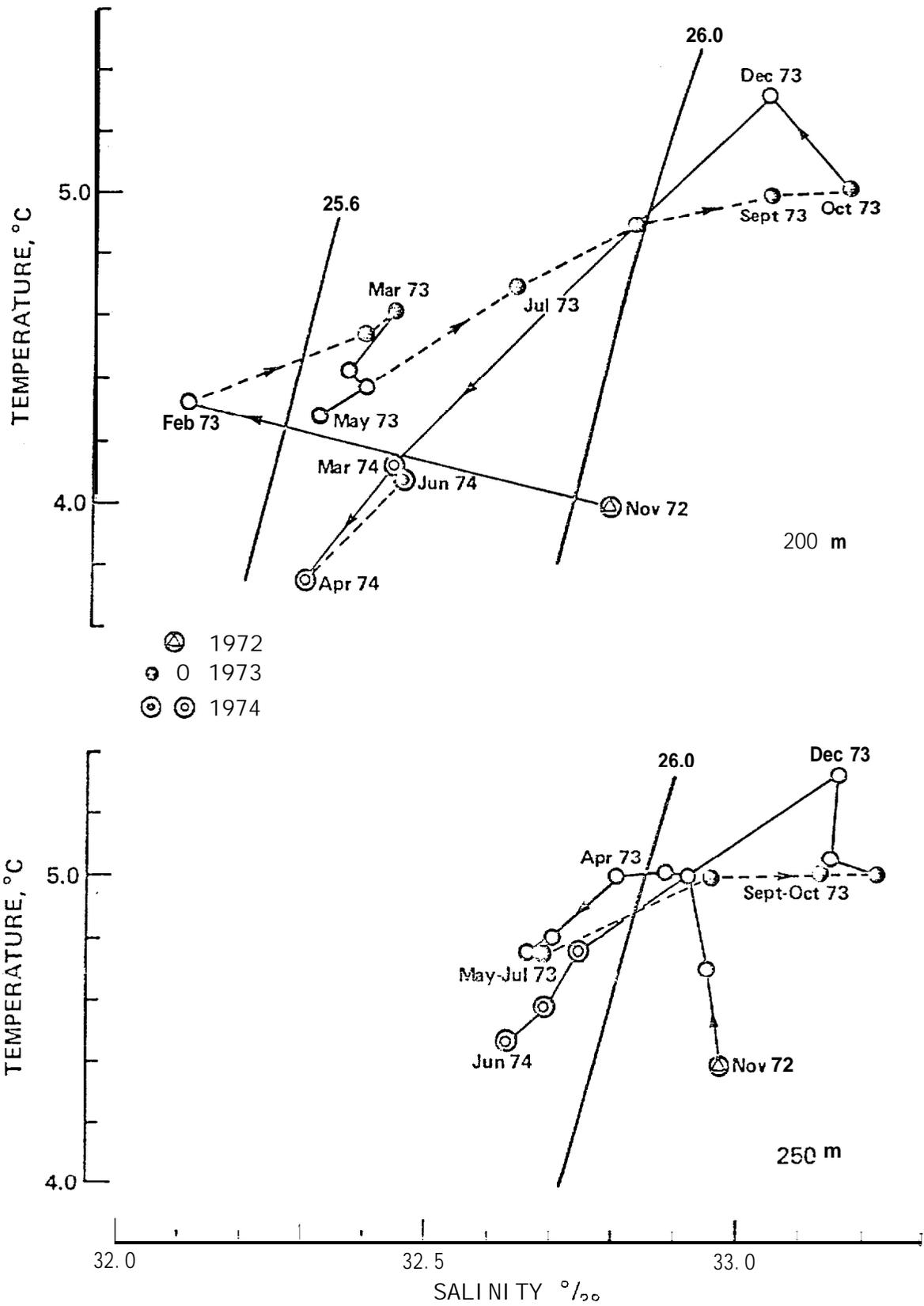


Figure 9. Time series  $\sigma_t$  at 200 and 250 m at Res 2.5, November 1972-June 1974. •---e shows periods of influx of denser water.

## 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  $\sigma_t$  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  $\text{cm}^2 \text{sec}^{-1}$  (mean of 3.9  $\text{cm}^2 \text{sec}^{-1}$ ).

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.

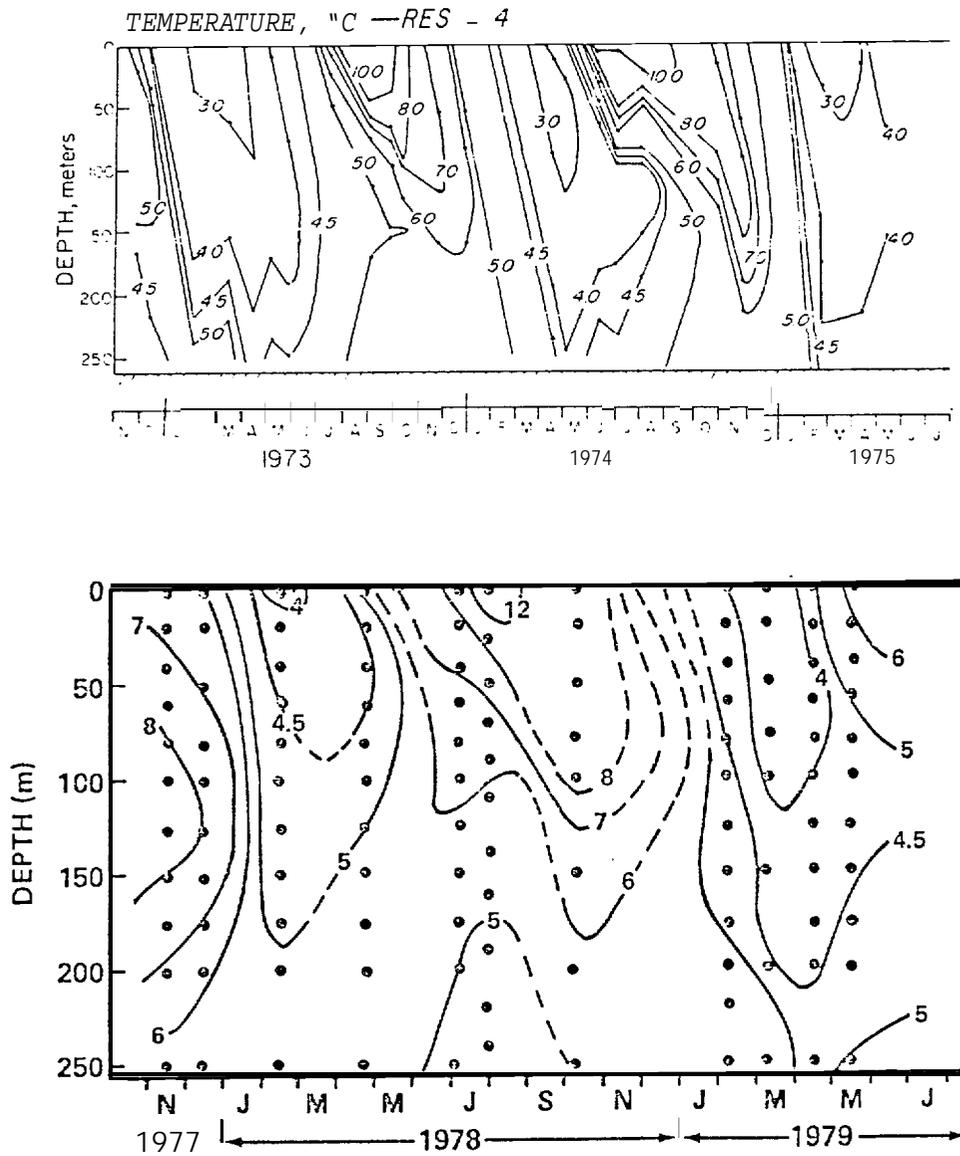


Figure 10. Temperature distribution outside the sill (Res 4) through the periods November 1972-May 1975 and November 1977-May 1979.

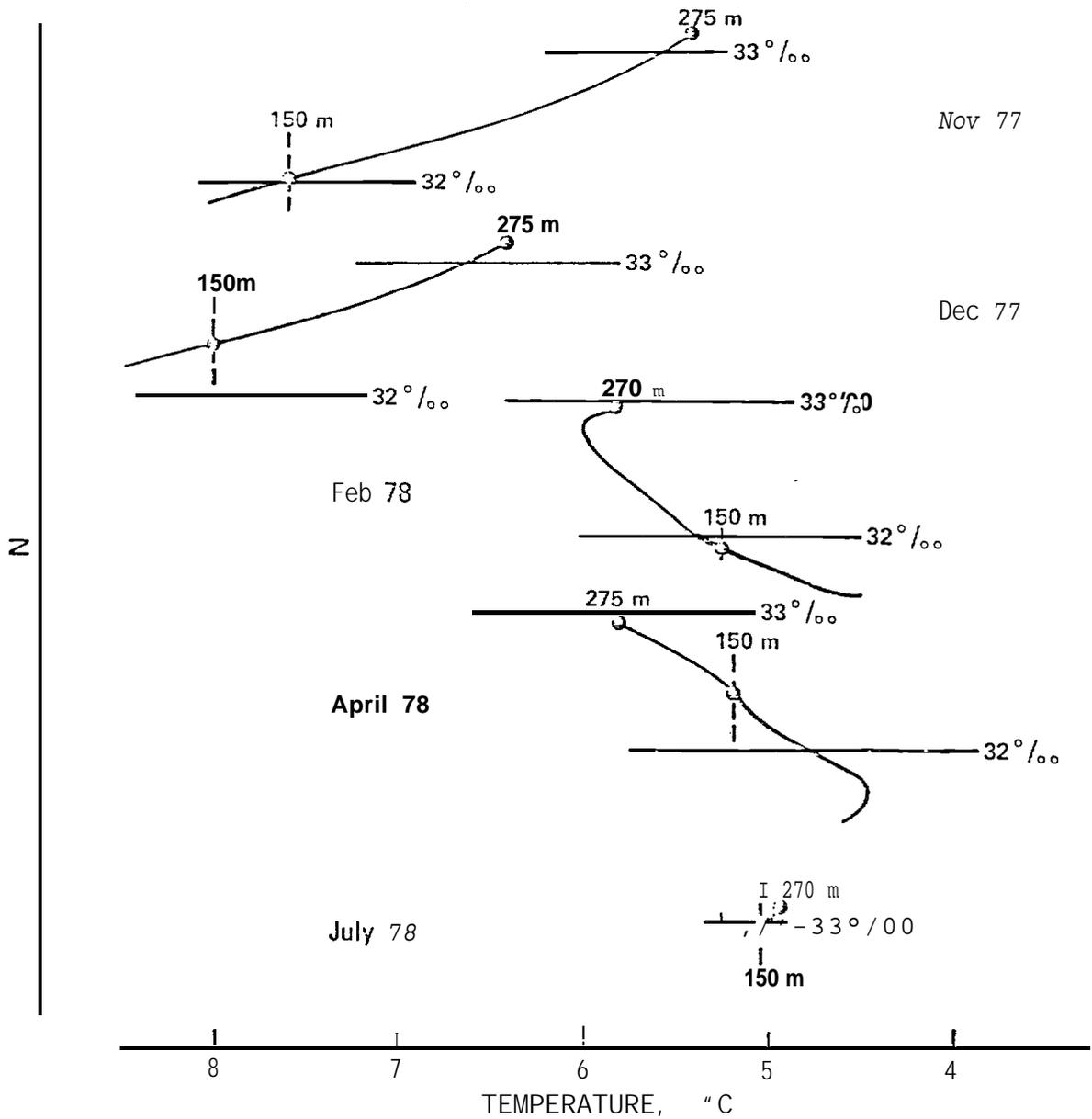


Figure 11. Seasonal T-S character of the basin winter (Res 2.5 below 150 m). November 1977-July 1978.

## 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  $< 1 \text{ ml } \ell^{-1}$  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 1, 1975 period of  $37 \text{ ml } \text{cm}^{-2} \text{ yr}^{-1}$ . Of this, from the surface sediment nitrate gradient, Heggie and Burrell (1979) estimated that oxygen is consumed in the sediment at around  $0.5 \text{ ml } \text{cm}^{-2} \text{ yr}^{-1}$ . 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  $19 \text{ moles C m}^{-2} \text{ yr}^{-1}$ , up to 60% of which may be accounted for in the deep water by applying

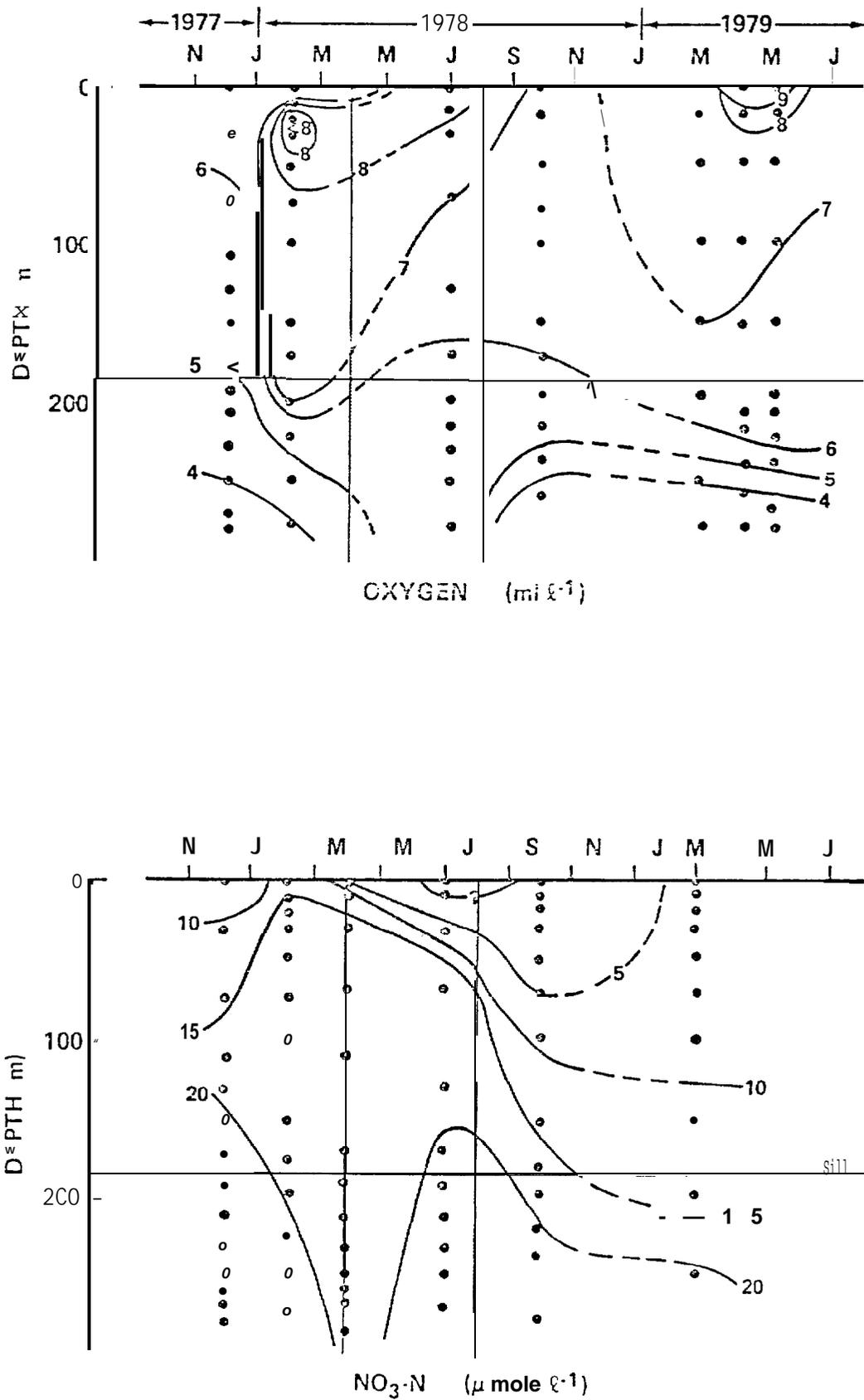


Figure 12. Distribution of dissolved oxygen (ml l<sup>-1</sup>) and nitrate (μM NO<sub>3</sub>-N) at Res 2.5, 1977-79.

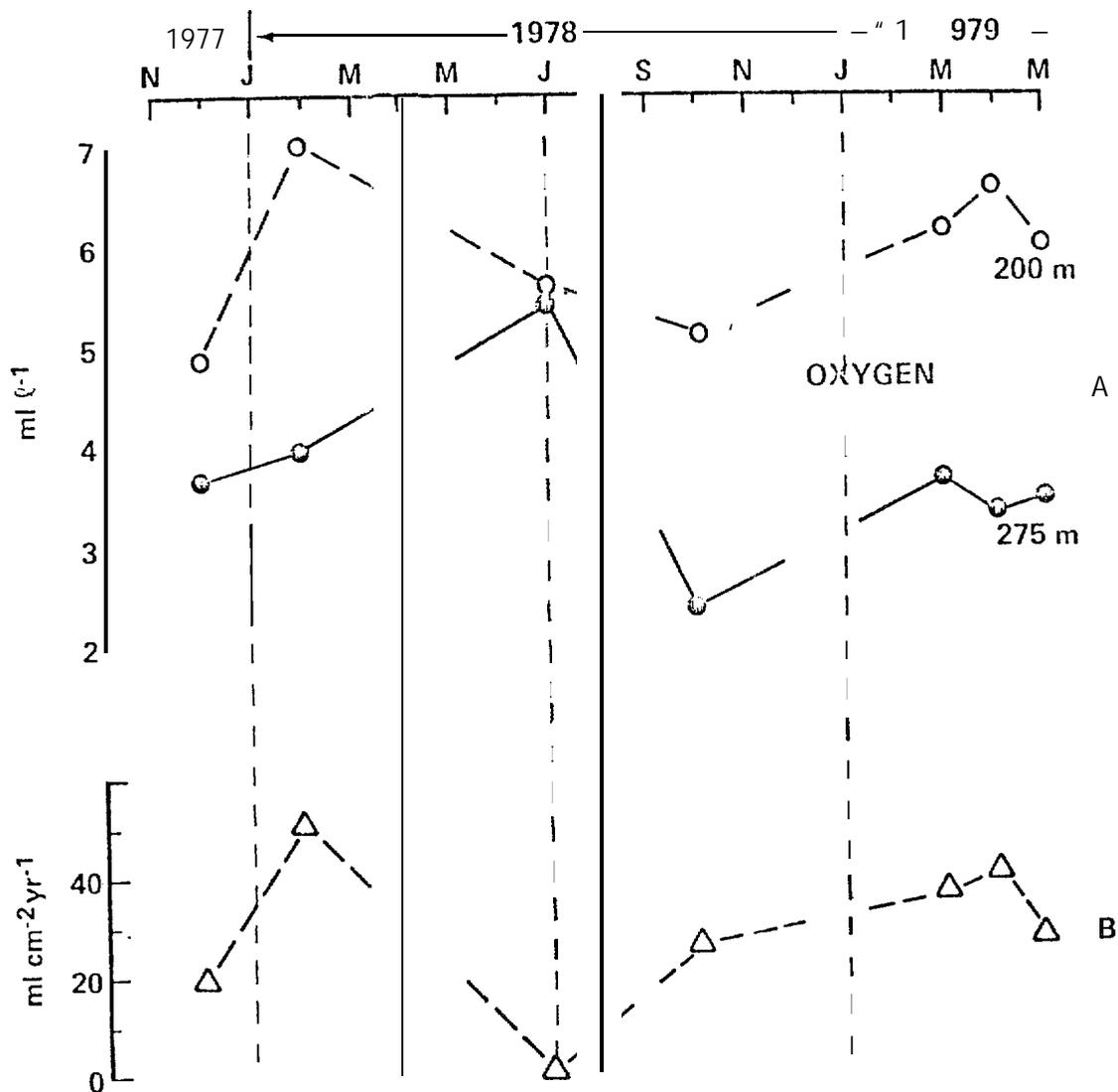


Figure 13. A. Dissolved oxygen concentrations ( $\text{ml l}^{-1}$ ) at 200 and 275 m at Res 2.5, November 1977–May 1979. B. Oxygen flux based on linear gradient between 200 and 250 m and  $K_2$  of  $3.5 \text{ cm}^2 \text{sec}^{-1}$ .

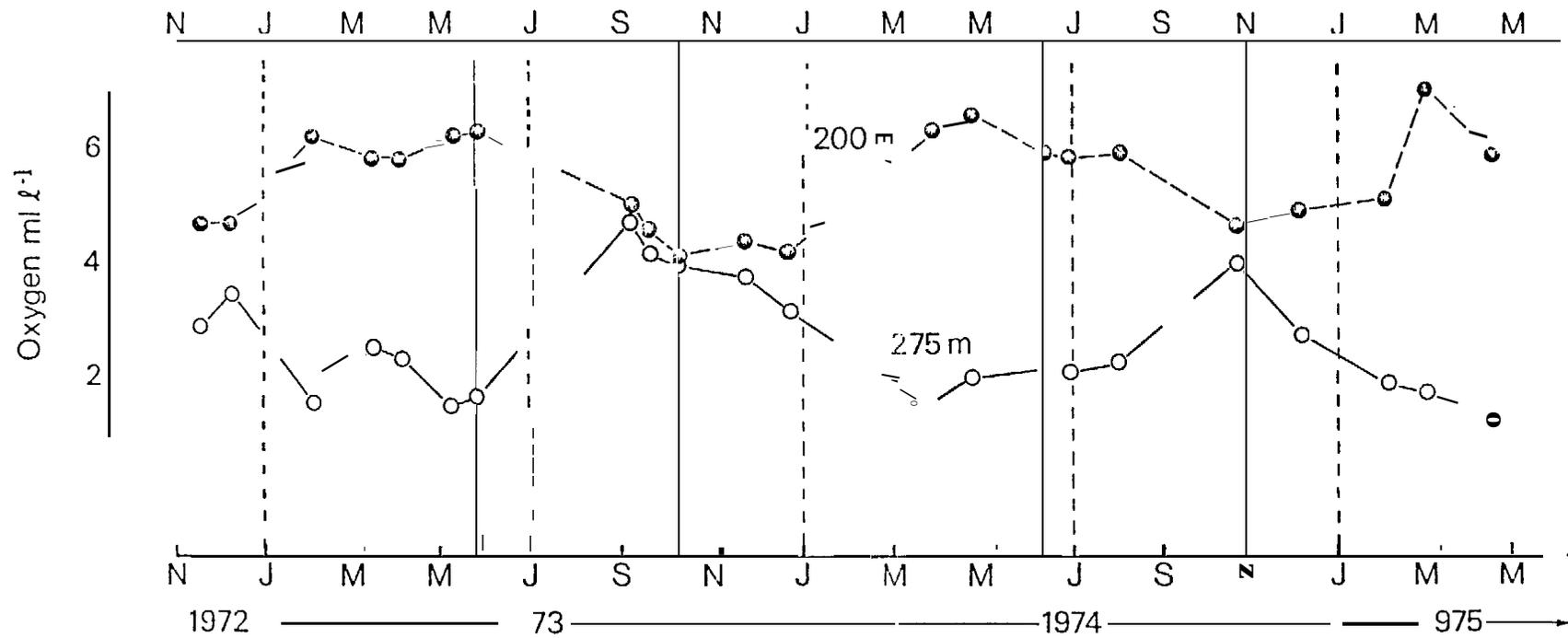


Figure 14. Dissolved oxygen concentrations ( $\text{ml l}^{-1}$ ) at 200 and 275 m at Res 2.5, November 1972–April 1975.

"Redfield stoichiometry" for the organic material. The distribution of carbon in the basin is highly seasonal, however. Discrete (0.4  $\mu\text{m}$  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  $10^{-3} \text{ cm sec}^{-1}$  (Owens *et al.*, 1979) yields corresponding downward fluxes at these seasons of 36 and 15  $\text{g C m}^{-2} \text{ yr}^{-1}$ . This range is some order of magnitude less than the computed mean annual surface productivity - an upper limit to the *insitu* 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  $\sim 1.0$  and  $\sim 2.5 \text{ ml l}^{-1}$  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

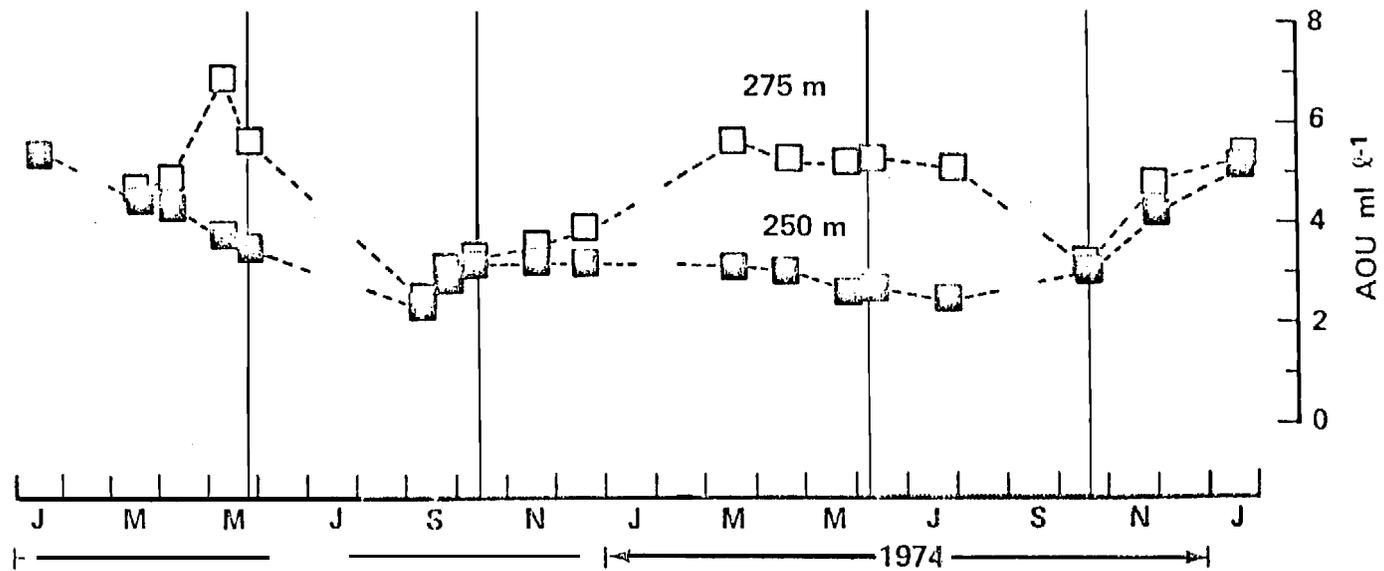


Figure 15. Time series (apparent) oxygen utilization at 250 and 275 m within the basin (Res 2.5), January 1973-January 1975.

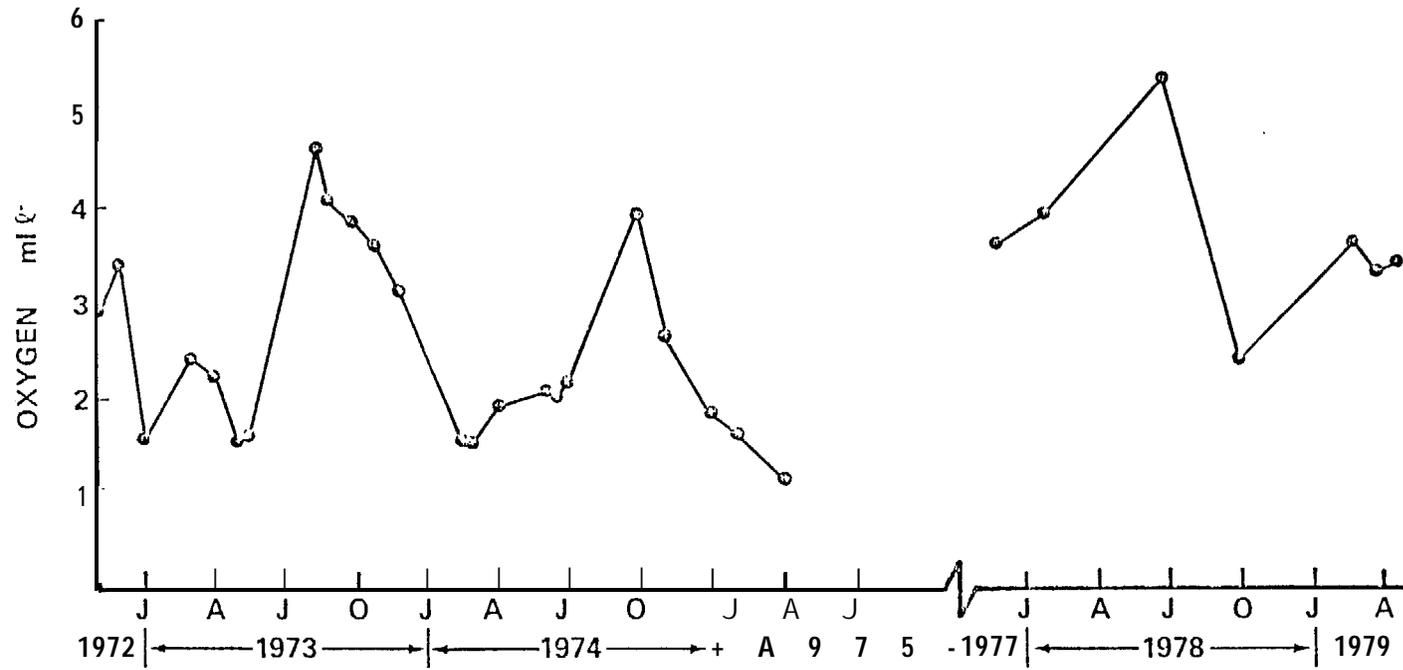


Figure 16. Seasonal dissolved oxygen contents ( $\text{ml l}^{-1}$ ) close to the basin floor (275 m at RES 2.5).

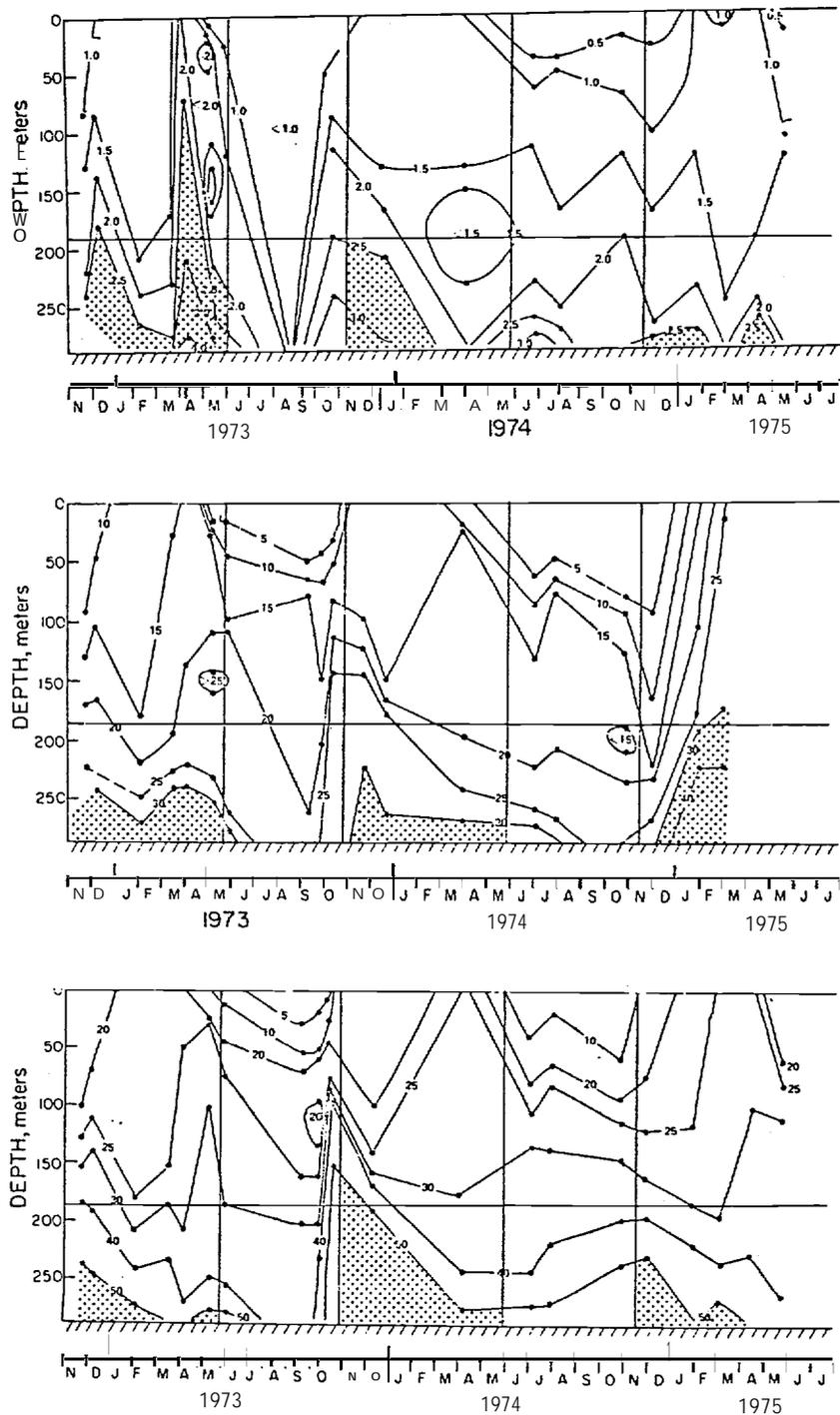


Figure 17. Seasonal distribution of (a) phosphate (b) nitrate (c) silicate at Res 2.5, November 1972–May 1975 after Heggie *et al.* (1977). Horizontal division marks sill depth.

that of oxygen. (Figure 12 also illustrates this behavior for  $\text{NO}_3\text{-N}$  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.

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APPENDIX IV

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

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Geophysical Institute  
University of Alaska

## General

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

## 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 chromatography 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 **piaszelenol** compounds which can be detected by gas **chromatographic** detectors (or by calorimeters 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 **piaszelenol** 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.