Calvin J. Lensink

Environmental Assessment of the Alaskan Continental Shelf

Annual Reports of Principal Investigators for the year ending March 1980

Volume III: Effects
Contaminant Baselines

U.S. DEPARTMENT OF COMMERCE
National Oceanic & Atmospheric Administration
Office of Marine Pollution Assessment

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DISCLAIMER

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EFFECTS

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LETHAL AND SUBLETHAL EFFECTS ON SELECTED ALASKAN MARINE SPECIES AFTER ACUTE AND LONG-TERM EXPOSURE TO OIL AND OIL COMPONENTS

by

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OUTER CONTINENTAL SHELF ENERGY ASSESSMENT PROGRAM
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I. EXECUTIVE SUMMARY:

Sensitivity of Arctic Species to Oil

The research was addressed to the question: Are arctic organisms more sensitive to oil than subarctic animals. To answer this, we first determined the sensitivity of six benthic arctic animals (2 fish, 4 invertebrates) to oil and oil components and compared results with previously generated sensitivity data with subarctic animals. Second, we determined the effect of temperature on the sensitivity of arctic animals to oil and their ability to acclimate to temperature change.

Arctic animals were sensitive to oil. Although direct comparisons of arctic and subarctic animal sensitivity are difficult due to different bioassay methods used, arctic animals appear to be equal in sensitivity to oil as subarctic animals. The fish were more sensitive than the invertebrates and were comparable to pink salmon (subarctic species). Arctic animals were highly adaptable to temperature changes although there were no effects of temperature on the sensitivity of arctic animals to oil.

These results indicate little difference in sensitivity of arctic and subarctic animals to oil. However, lower environmental temperatures in the arctic would result in oil persisting longer after a spill due to lower volatility and biodegradation of oil components and possibly because oil would become trapped and immobilized in ice. There are fewer species in the arctic and food chains are very short. If a species is affected, there would be few replacement species (opportunists). Therefore, the arctic habitat is probably more vulnerable, and once changed, less able to adjust, even though individual species are generally very hearty and tolerant of natural environmental extremes and limited amounts of pollution.

II. INTRODUCTION

General Nature and Scope of Study

The research was addressed to the general question, what are the effects of petroleum hydrocarbons on arctic animals and the relationship of these results to previously completed work with subarctic organisms. It involved acute and long-term toxicity testing of arctic animals collected from the Beaufort Sea.

Our studies can be broken down into two basic themes: (1) determination of the sensitivity of selected benthic arctic animals to oil and oil components; and (2) effects of temperature on the sensitivity of arctic animals to oil. We wished to determine if arctic animals are more and if temperature was a major factor in sensitivity.

OCSEAP funding on effects studies began at Auke Bay in FY 1975 and has continued through FY 1980. This report describes progress on OCSEAP funded studies only.

Specific Objectives

The specific objectives in FY 1979 were changed from the proposal due to logistical and animal availability problems. The OCSEAP contractor responsible for collecting animals, LGL, was conducting field work at Prudhoe Bay and was unable to collect the variety of species we desired. We determined the acute toxicity of oil and naphthalene to four species of crustaceans and two species of fish. We determined the long-term toxicity of oil and naphthalene to an arctic amphipod carrying eggs; we compared the sensitivities of arctic and subarctic animals to oil; we determined the nonacclimatized and acclimatized responses to temperature of arctic organisms; and we determined the effects of temperature to sensitivity of arctic animals to oil.

Relevance to Problems of Petroleum Development

The FY 1979 program on the sensitivity of arctic animals to oil has a great deal of relevance to problems of petroleum development in Alaska. A significant part of both current and future potential petroleum development in Alaska is taking place and will be taking place in the Arctic. Because low temperature is an important factor in making the arctic environment a stressed habitat, data on the effect of temperature on animal sensitivity is needed. For changes in temperature affected the sensitivities to oil and aromatics in a non-uniform or predictable way (Korn et al. 1979) and affects on arctic species could be more extreme at the extreme temperatures they live at.

Current State of Knowledge

Prior to this little was known about the sensitivity of arctic organisms to oil except for a few amphipod species. Unfortunately, much of this work has used methods that preclude comparisons between studies. No investigator has tested arctic and subarctic species; consequently comparisons between arctic and subarctic animals are not available. There was no previous information on effects of temperature on the sensitivity of arctic organisms to oil.

We now have an understanding of effects of temperature on arctic animals, effects of temperature on sensitivity of arctic animals to oil, and the comparative sensitivity of arctic vs. subarctic animals to oil.

Progress of FY 1979 Studies
October 1, 1978 to September 30, 1979

Four invertebrate and two fish species were tested in a series of bioassays to determine: (1) sensitivity of arctic animals to acute exposures of oil and naphthalene; (2) sensitivity of an arctic amphipod carrying eggs to long-term exposures of oil and naphthalene; (3) temperature tolerance of acclimated and nonacclimated arctic animals; and (4) effects of temperature on the sensitivity of arctic animals to naphthalene.

III METHODS

Collection and Handling

All specimens were collected near Prudhoe Bay, Alaska with a single exception, the amphipod *Anonyx nugax* (0.209 g ± 0.045, 18.93 mm ± 1.29), which was collected in Auke Bay, Alaska. The arctic species available for testing were: the amphipods *Boeckosimus nanseni* (0.095 g ± 0.024, 14.73 mm ± 1.37), and *Gammaracanthus loricatus* (0.305 g ± 0.067, 26.42 mm ± 1.84), and a sculpin, *Oncocottus hexacornis* (1.88 g ± 0.68, 6.8 cm ± 0.7).

Collections were made April 1979 and May 1979. Animals were shipped to Auke Bay by air (less than 10 hours) in oxygen filled bags on ice. Mortalities in handling and shipment were negligible, except one species of smelt, who sloughed scales due to handling, and began dying after arrival at Auke Bay. These animals were never tested.

Prior to experimentation, animals were held in partially recirculating "living streams" at approximately 2° C. and a salinity of 30°/oo. The mysids were not fed directly, but apparently fed on algae blooming in the holding tank. Cod were fed Oregon moist pellets and tetramine, sculpin accepted some tetramine and pink salmon roe as food, and amphipods were fed chopped fish. Although the tests were generally completed within six weeks of arrival, we maintained several species in the lab for up to five months.

Flow-through Techniques

The toxicants employed in comparative sensitivity experiments were Cook Inlet crude oil and naphthalene. Temperature effects employed naphthalene only.

Flow-through techniques were employed except for tests involving the mysid, *Mysis*, which are "larvae" size, and not practical to expose in our flow-through set up. The WSF of the crude oil was generated by constantly percolating water at 1 l/min. through a stable oil slick in a glass cylinder (16 cm dia. x 0.9 m). Oil was added to the lower surface of the slick at 1.5 ml/min., and allowed to overflow from the upper surface at the same rate. Slick depth was approximately 10 to 20 cm. Stock solutions of naphthalene were generated by forcing water through naphthalene flakes in a 4 l flask.

Toxicants plus dilutant seawater were fed into test containers through a dosing manifold. Turnover times (99% replacement) were 80 min. for B. nanseni and A. nugax tests, and a 4.5 h for all others. Temperatures ranged from 1.5 to 9.6°C. Amphipods were fed during exposures; fish and mysids were not. The number of organisms per dose ranged from 12-15 (standard to 80).

Tests ranged from 8 days plus a 3-day recovery period (standard procedure) to 40 days. Mortality observations were 2, 4, and 8 h, and daily thereafter. Gravid Boeckosimus females were exposed for 40 days to oil and naphthalene to determine if there are long-term effects on hatching and survival of larvae.

Water samples were collected daily from each test concentration for analysis. Toxicants were detected with UV spectrometry at 219 nm (naphthalene) using 1 cm cuvetts or gas chromatography (oil). Naphthalene samples were measured directly, but for the GC analysis, 750 ml of water were extracted with a total of 50 ml dichloromethane (in two 25 ml agitations with a 30 min. separation).

The mysids were exposed to static doses of naphthalene and Cook Inlet crude WSF; n = 12/dose. The exposure duration was 96 h; the mysids were redosed daily. The temperature was 4.4°C throughout the test periods.

Analysis of Data

Results were analyzed with the following methods; logit analysis (mortality data) Spearman-Karber method (when logit analysis was not possible), least squares regressions and polynomial regressions (mortality data), and analysis of variance followed by the Scheffe test (LD50's).

Temperature Techniques Tolerance Tests

The temperature tolerances were determined for two arctic amphipods (Boeckosimus nanseni and Gammaracanthus loricatus), an arctic mysid (Mysis relicta), and a local amphipod (Anonyx nugax). Temperature sensitivity tests were conducted in 5 l aquaria with a turnover rate of 3 h (99% replacement). Controls were maintained at approximately the original holding temperatures. The animals were fed every other day throughout the experiment.

There were two types of temperature tolerance tests: acclimatized and nonacclimatized. In the acclimatized tests, the temperature was increased slowly at the rate of 0.5°/day ± 1.4°C/day. Three replicates of approximately 20 animals were tested for A. nugax, B. nanseni, and M. relicta; n = 11 for G. loricatus. Mortality data were collected daily. The experimental duration was 41 days.

In the nonacclimatized tests, the organisms were subjected to sudden temperature changes. (Any given animal was tested only once in this manner.) Rapid temperature jumps were + 5°, + 10°, + 15°, and 20°C. Two replicates of 10 animals were tested for each species. Temperatures remained constant for 24 h, then continued to increase at the rate above, since the two phases were conducted simultaneously. Mortality data were collected at 24, 48, and 96 h, for the second phase animals.

IV RESULTS AND DISCUSSION

Sensitivities to Toxicants

Toxicity of Cook Inlet Crude Oil WSF to Arctic Species

Median lethal doses ranged from 1.569 to 3.843 ppm total aromatics. The arctic cod (*B. saida*) was the most sensitive species tested. *A. nugax*, (collected from Auke Bay) and *M. relicta* were intermediate in sensitivity, and *B. nanseni* was the most resistant. Maximum oil doses were insufficient to establish LC50's for the arctic sculpin (*O. hexacornis*) and *G. loricatus*. (Table 1)

B. nanseni did not begin to respond to the WSF until 13 to 16 days of exposure. Response stablized after 23 days of exposure. *M. relicta* responded most rapidly (4 h) followed by *B. saida* (2 days), then *A. nugax* (6 days). *G. loricatus* and *O. hexacornis* did not respond during 8-day exposures.

Toxicity of Naphthalene to Arctic Species

In general, LD50's ranged from 1.00 ppm to 5.26 ppm naphthalene. *B. nanseni* was found to be significantly more resistant to naphthalene than *A. nugax*, *O. hexacornis*, and *B. saida* ($P = 0.05$) by treating the LD50's from all test temperatures as replicates. The species tested tend to fall into two groups: *A. nugax* (Auke Bay), *O. hexacornis*, and *B. saida* were more sensitive; *B. nanseni* and *G. loricatus* were more resistant. *M. relicta* was intermediate in sensitivity. These relationships were consistent with interspecies comparisons at discrete test temperatures. (Table 2)

Long-term Amphipod Larval Survival Test

Boeckosimus gravid females exposed for 40 days to naphthalene and oil showed that eggs and larvae were equally sensitive as the adults. If the adults survived, then eggs hatched and larvae developed normally.

The relative tolerances are not surprising. The amphipod collected from Auke Bay was consistently more sensitive than the other amphipods. The arctic cod was more sensitive than the arctic sculpin. These results, for comparable species, roughly relate to similar sensitivities we have measured in subarctic species that we have tested with the same toxicants. The arctic species may be equal or slightly more tolerant, but are certainly not uniquely more sensitive than subarctic species.

Sensitivity to Temperature

Nonacclimatized Temperature Response

The resistance to temperature extremes from most resistant to least was: G. loricatus M. relicta B. nanseni A. nugax (Auke Bay). All differences were significant at P = 0.05. Nonacclimatized median lethal temperatures ranged from 9.74° ± 0.18°C to 16.50° ± 0.00°C, and were about 66% of the acclimatized temperatures.

Acclimatized Temperature Response

G. loricatus was the most resistant organism. Differences between the other three organisms could not be distinguished statistically, but responses were similar to the nonacclimatized response. Medial lethal temperatures, which were approximately 85% of the maximum lethal temperatures, ranged from 17.16° ± 0.68°C. to 24.01° ± 1.00°C. Maximum lethal temperatures also reflected these trends (Table 3).

The arctic amphipods were surprisingly tolerant of temperature and were consistently more tolerant than A. nugax which was collected in Auke Bay. Although the species from Auke Bay lives in an environment that has a yearly average temperature higher than the arctic species, the arctic species are exposed to higher extremes transiently in the shallow inshore arctic waters. The daily temperature can change rapidly from temperatures above 10°C. to nearly 0°C if the waters are subjected to a northern wind. Consequently, the arctic species are adapted to a rugged environment and our comparative tests at about 4°C were well within the temperatures they tolerate.

Hydrocarbon Sensitivity as a Function of Temperature

Sensitivities of B. nanseni, A. nugax, B. saida, and O. hexacornis to naphthalene were examined to determine the relationship between test temperatures and toxicity. O. hexacornia showed a uniform increase in tolerance as the temperature increased: no overall trends were distinguishable with the other species.

Hydrocarbon toxicity was also compared to temperature sensitivity. The most sensitive amphipod, A. nugax from Auke Bay, was also the least tolerant of high temperatures. However, further correlation between temperature tolerance and sensitivity to hydrocarbons was not consistent.

Interpretation of Results

Final interpretation of results will occur in two manuscripts being prepared and due to be completed in winter 1980. Results indicate the following:

Table 1. Median tolerance limits of arctic species exposed to Cook Inlet Crude oil WSF

Species	Temperature °C + SD	LC50 (ppm + CI) Days	
		4	8
A. nugax	3.5 ± 0.3		2.260 ± 0.093
G. loricatus	2.0 ± 0.5		>1.729
O. hexacornis	2.0 ± 0.5		>1.729
B. saida	2.0 ± 0.5	1.569 ± 0.040	1.659 ± 0.040
M. relicta	4.4	2.60 ± 0.52	
B. nanseni	3.4°	5.462 ± 0.553	4.879 ± 0.33

Table 2. Median Tolerance Limits of Arctic Animals Exposed to Naphthalene at Varying Temperatures

Species	Temperature °C ± sd	LC50 (ppm ± CI 4 Days	8
B. nanseni	4.8 ± 0.5		5.26 ± 0.12
	5.0 ± 1.8		3.36
	6.9 ± 0.4	4.02 ± 0.12	2.49 ± 0.05
	9.6 ± 0.3	2.88 ± 0.09	2.28 ± 0.09
	$\bar{X}$=6.6 ± 2.2	3.45 ± 0.57	3.35 ± 0.24
A. nugax	4.8 ± 0.5	2.70 ± 0.10	1.95
	6.9 ± 0.4	2.06 ± 0.05	1.20 ± 0.07
	9.6 ± 0.3	1.84	1.52 ± 0.07
	$\bar{X}$=7.1 ± 2.4	2.20 ± 0.13	1.56 ± 0.11
G. loricatus	2.05 ± 0.5	2.29	2.09
O. hexacornis	1.5 ± 0.2	1.06	1.00
	2.0 ± 0.5	1.07	1.07
	6.4 ± 1.1	1.63	1.63
	8.5 ± 1.3	1.82	1.74
	$\bar{X}$=4.6 ± 3.4	1.40 ± 0.11	1.36 ± 0.11
B. saida	1.5 ± 0.2	1.52 ± 0.04	1.46 ± 0.04
	2.0 ± 0.5	1.24 ± 0.09	1.24 ± 0.09
	6.4 ± 1.1	1.55	1.46 ± 0.05
	8.5 ± 1.3	1.22 ± 0.17	1.22 ± 0.17
	$\bar{X}$=4.6 ± 3.4	1.38 ± 0.05	1.35 ± 0.04
M. relicta	4.4	2.0	

Table 3. Acclimated (temperature increased 1-2° daily) and non-acclimated (temperature increased 10° daily) median lethal temperatures of artic marine animals

Species	ACCLIMIZED	NON-ACCLIMIZED
	Median lethal temperature	Median lethal temperature
A. nuggi	17.15 ± 0.68	9.74 ± 0.18
M. relicta	17.25 ± 3.73	14.72 ± 0.20
B. nanseni	20.56 ± 0.31	11.00 ± 0.00
G. loricatus	24.01 ± 1.00	16.50 ± 0.00

1. It is difficult to compare the sensitivity of subarctic and arctic animals because most previous subarctic organism tests were static exposures compared to the continuous-flow arctic tests. However, based on several close comparisons, arctic and subarctic are similarly sensitive to oil. Arctic species are NOT uniquely sensitive.

2. Arctic animals are more tolerant to temperature changes than subarctic animals due to the extreme environment in which they live.

3. The sensitivity of arctic animals is not affected by temperature, apparently because arctic animals are not stressed as much by temperature extremes.

4. The eggs and larvae of <u>Boeckosimos</u> are similarly sensitive to oil and naphthalene as the adults. Long-term exposure had no effect.

Problems Encountered

It was our goal to collect and test more species including Euphasids, isopods and Ciscos. LGL tried to locate and collect these other species but was unsuccessful even though they spent a lot of time in the field on this task and on their own OCSEAP contract. We successfully shipped and tested all animals that LGL collected with the exception of smelt.

A laborious 40-day continuous exposure of gravid <u>Boeckosimos</u> to oil WSF and naphthalene were successfully completed. A good 40-day TLm was generated. There were no long-term effects on egg survival or larval survival. There was much effort for negative results.

Progress on FY 1980

<u>Objective</u>: Determine the vulnerability of pink salmon eggs and alevins to Cook Inlet crude oil during a simulated intertidal cycle.

<u>Progress</u>: Exposures of eggs and alevins to oil began in November and were completed in March. Exposure regimes include intermittent oil exposures to fresh and seawater and is intended to simulate an oil exposure to eggs and alevins spawned in the intertidal zone.

Samples were taken periodically for histological examination and for GC analyses of tissues. Water samples from the exposures were measured twice daily by UV and once daily by GC.

Analyses of length, wet weight, dry weight are not expected to be completed until fall 1980. The exposures to eggs failed, but the 30-day exposure to alevins was successful and there were visual differences between the exposure groups.

Estimate of Funds Expended for FY 1980

	Annual Plan	Costs to 31 March 1980
Salary Costs (Base + Benefits + Cola)	$ 79.3	$ 79.3 [1]
Travel	9.5	0.6
Contracts	8.6	.7
Equipment and Supplies	10.4	12.6
Other Direct and Indirect Costs	27.2	27.2 [1]
	$135.0K	$120.4K

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[1] Salary costs projected through 30 September 1980.

SUBLETHAL EFFECTS OF PETROLEUM HYDROCARBONS AND TRACE METALS, INCLUDING BIOTRANSFORMATIONS, AS REFLECTED BY MORPHOLOGICAL, CHEMICAL, PHYSIOLOGICAL, PATHOLOGICAL, AND BEHAVIORAL INDICES

by

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A. SUMMARY OF OBJECTIVES

The overall objective of this program is to assess potential effects of petroleum and petroleum-related operations on marine organisms indigenous to Alaskan waters. Several principal objectives were addressed by this research unit (OCSEAP RU 73) during the contract period. These were:

(1) Determine the effects of crude petroleum (Prudhoe Bay and Cook Inlet) on the development of embryos and larvae of salmon, of a representative species of Alaskan flatfish, and of Osmeridae (capelin, smelt).

(2) Continue studies on pathological effects resulting from long-term exposure of juvenile flatfish to sediments contaminated with petroleum.

(3) (a) Determine if exposure to Cook Inlet crude oil (CICO)-contaminated sediment alters disease resistance in juvenile flatfish and in a representative Alaskan crustacean species and (b) conduct preliminary studies on the effect of petroleum/dispersant mixtures on disease resistance of juvenile salmon.

(4) (a) Continue studies on the uptake of aromatic hydrocarbons by flatfish and (b) identify potentially damaging petroleum hydrocarbons and their oxidized products.

(5) Determine the effects of CICO on the ability of salmon fry to avoid predation.

(6) Determine the concentrations of specific hydrocarbons in water, sediment, and tissues of exposed organisms in order to relate the presence of these components to biological effects.

B. SUMMARY OF CONCLUSIONS

The conclusions of this program are summarized according to disciplinary areas. Several aspects of the studies have been completed while others are continuing.

Behavior

Exposure of chum salmon (*Oncorhynchus keta*) fry to the saltwater-soluble fraction (SWSF) of CICO at a concentration of about 0.4 ppm for one week altered the behavior (reduced schooling, lethargy), but did not result in differential consumption of these fry by coho salmon (*O. kisutch*) predators, in comparison to controls.

Chemistry

Benzo[a]pyrene (BP) was readily taken up from both diet and oiled sediment by pleuronectid fish. The release of metabolites of BP from tissues of the flatfish was much slower than that of naphthalene metabolites.

Benzo[a]pyrene was extensively metabolized by flatfish liver into reactive intermediates that bind to DNA. Binding of metabolites of polynuclear aromatic hydrocarbons (PAH) to the genetic material, DNA, is a very important step in the events leading to genetic damage and tumor formation.

Thus, it is likely that BP, which is a minor component of petroleum, may accumulate in tissues of benthic organism to a significant level and may, on the basis of our findings that mutagenic intermediates were formed *in vivo*, initiate steps toward mutagenesis and neoplasia.

Pathology

Pathological Changes in Flatfish from Exposure to Oil-Contaminated Sediment

Experiments have been conducted during the past three years in which three species of flatfish, English sole (*Parophrys vetulus*), rock sole (*Lepidopsetta bilineata*), and starry flounder (*Platichthys stellatus*), were exposed to Prudhoe Bay crude oil (PBCO)-contaminated sediments for periods of 2 wk to 4 mo. Initial concentrations of PBCO mixed with sediment ranged from 0.2 to 1.0% (v/v), and two basic types of sediment (sandy and silty) were employed. Release of petroleum hydrocarbons was more than 10-fold greater from the sandy-type sediment than from the silty-type. Also, the three flatfish species differed substantially in the amount of petroleum-derived aromatic hydrocarbons found in tissues. PBCO-related pathological effects were not observed in rock sole or starry flounder exposed to contaminated sediments for 1 and 2 mo, respectively. Oil-exposed English sole were routinely observed to have reduced hemoglobin concentrations and lower hematocrits during the first month of exposure. Histopathological changes were seen in livers of all three species but they were frequently detected in control as well as oil-exposed individuals.

Changes observed in oiled sediment-exposed flatfish in these studies appear to be reversible and not directly life-threatening, although they may reflect damage that can reduce survival in natural environments.

Physiology

A substantial number (42%) of the eggs of chum salmon exposed to the SWSF of weathered PBCO throughout embryonic development died; however, the effect of oil exposure was even more manifest following hatching. Alevin mortality was observed (up to 82%) that was generally reflective of the total duration of exposure to oil as both embryos and alevins. Exposure of newly hatched alevins to the SWSF of weathered PBCO increased the mortality of fish at this developmental stage by more than 100%, compared to controls.

Two species of flatfish [sand sole (*Psettichthys melanostictus*) and English sole] eggs and larvae were exposed to fresh PBCO, weathered PBCO "mousse," and the SWSF of weathered PBCO. Fresh PBCO and the weathered "mousse" of PBCO layered on the water surface generally induced high embryo mortality. Eggs exposed to the SWSF of weathered PBCO did not undergo extremely high mortality, but most larvae exhibited morphological abnormalities. Histological changes were also evident in oil-exposed larvae (disruption of olfactory cilia and abnormal epidermal cell mitochondria).

Exposure of surf smelt (*Hypomesus pretiosus*) eggs to the SWSF of weathered CICO also resulted in reduced hatching success and there was evidence of necrosis in the eye and brain of some of the surviving larvae.

C. IMPLICATIONS WITH RESPECT TO OCS OIL AND GAS DEVELOPMENT

Findings from this program have clear implications with respect to petroleum effects on aquatic species and consequently to OCS oil and gas development. Most of the studies were designed as laboratory experiments with emphasis, as much as feasible on oil exposures of marine organisms in flowing-seawater tanks. Controlled studies with experimental designs of the types reported here are indispensible parts of a total program directed at understanding effects of petroleum on the marine environment. It is primarily through controlled experiments such as these that petroleum can, with a high degree of accuracy, be identified as causing specific effects. In addition, through these types of studies the relative susceptability or resistance of important species to petroleum components can be established, as can the precise nature of petroleum-induced abnormalities. The laboratory results can then be used to design directed field studies, to formulate hypotheses for testing petroleum impacts on marine species and ecosystems, and as a basis for developing best estimates of petroleum impacts on the environment.

Implications of studies conducted in this period for each disciplinary area are presented below.

Behavior

Pink (O. gorbuscha) and chum salmon fry spend several months in coastal estuaries before going to sea and at this life stage they are extremely vulnerable to predation by other salmonid fishes. Predator-prey studies in progress are designed to determine if fry are affected by petroleum differentially from adult predators so that they suffer substantially increased predation. Increased predation would imply severe effects of this type could result from petroleum released into Alaskan nearshore areas at certain times of the year.

Chemistry

Pleuronectid fish were able to take up BP from oiled sediment and diet and convert it extensively into mutagenic and carcinogenic metabolites. The results also show that metabolites of BP were retained in tissues of flatfish over a much longer period than naphthalene and its metabolites. It is apparent, therefore, that although aromatic hydrocarbons having four or five rings are minor components of petroleum, they can be bioconcentrated in tissues of demersal organisms to levels potentially leading to the onset of deleterious biological effects. Studies conducted under OCSEAP have clearly demonstrated that aromatic hydrocarbons are extensively converted to a variety of oxidized products in the marine environment. Therefore, if tissues, water, and sediment samples are analysed for PAH alone, and not for the oxidized products, erroneous conclusions will be reached. The presence of PAH and their metabolites in edible tissues (e.g. muscle) can also have a serious impact on consumer acceptability of fish.

Pathology

Pathological Changes in Flatfish From Exposure to Oil-Contaminated Sediment

Laboratory sediment-associated PBCO exposures have thus far resulted in few clearly serious pathological effects in juvenile and adult flatfish of three arctic and subarctic species. Whether or not fish exposed to similarly contaminated sediments could under natural conditions successfully compete for food, reproduce, escape predators, and perform a number of other vital functions and activities is still not known.

Physiology

Fresh and weathered oil exposure would, based on these studies, result in high mortality of flatfish embryos and larvae. In addition, flatfish eggs exposed to fresh and weathered PBCO were frequently ruptured. This was unexpected and made it difficult to evaluate precise numbers of eggs lost in the laboratory experiments. This effect may be of importance in field sampling of pelagic eggs in the vicinity of an oil-contaminated area; ruptured eggs would likely not be detected with the result that the pollutant impact could be underestimated.

Exposure of chum salmon and surf smelt eggs to the SWSF of weathered crude oil also resulted in reduced survival. The presence of weathered "mousse" in, or the removing of intertidally stranded oil from, spawning areas would be expected to promote even greater embryo mortality as a result of direct oil toxicity, suffocation, and physical disruption.

II. INTRODUCTION

A. GENERAL NATURE AND SCOPE OF STUDY

The responses of marine organisms to environmental contaminants are reflected in a number of changes detectable at organismic levels as well as at organic, tissular, cellular, subcellular, and molecular levels. The general scope of this study is to detect petroleum-related effects at various levels in marine species and evaluate their implications for survival and well-being of the animals.

B. SPECIFIC OBJECTIVES

In the interdisciplinary approach used in this study, there is a series of objectives to evaluate the effects of petroleum on marine organisms. The specific objectives of research performed during the current reporting period of April 1, 1979 to March 31, 1980 for individual disciplines are as follows:

Behavior

(1) Determine if exposure of salmonid fry to the SWSF of CICO affects normal behavior, specifically the ability to avoid predation.

Chemistry

(1) Determine concentrations of radioactively labeled hydrocarbons (e.g., BP) in various tissues of flatfish exposed to dietary BP or to sediment containing BP and PBCO.

(2) Study biotransformation of BP by flatfish liver into potentially mutagenic and carcinogenic metabolites.

Pathology

(1) Determine the frequency and nature of pathological changes occurring in flatfish as a result of exposure to oil-contaminated sediments.

(2) Determine if exposure to CICO petroleum-contaminated sediments alters disease resistance in very young individuals of a species of Alaskan flatfish and in a representative crustacean species.

Physiology

(1) Evaluate the effect of weathered PBCO on chum salmon embryo and alevin development.

(2) Evaluate the effect of fresh and weathered PBCO on the development of embryos and larvae of two species of flatfish.

(3) Evaluate the effect of weathered CICO on the development of embryos and larvae of surf smelt.

C. RELEVANCE TO PROBLEMS OF PETROLEUM DEVELOPMENT

When petroleum is transported in or obtained from coastal or offshore areas, inevitably petroleum hydrocarbons and associated trace metals escape into the marine environment. These materials, at some level, have a potential for producing critical damage to marine resources. This damage by crude oil components can take several forms (Blumer, M., Testimony before Subcommittee on Air and Water Pollution, Senate Comm. on Public Works, Machias, Maine, 8 Sept. 1970):

1. Direct kill or organisms through coating and asphyxiation.
2. Direct kill through contact poisoning of organisms.
3. Direct kill through exposure to water-soluble toxic components of oil at some distance in space and time from the accident.
4. Destruction of the generally more sensitive juvenile forms of organisms.
5. Incorporation of sublethal amounts of oil and oil products into organisms resulting in reduced resistance to infection and other stresses. Also, this may result in failure to reproduce.
6. Destruction of the food sources of higher species.
7. Exposure to long-term poisons, e.g., carcinogens.
8. Low-level effects that may interrupt any of the numerous events necessary for the feeding, migration, and propagation of marine species and for the survival of those species which stand higher in the marine food web.
9. Contamination of marine food resources to make then unfit for human consumption.

Studies of OCSEAP RU 73 are largely concerned with indirect, long-term effects of petroleum such as those detailed in items 4, 5, 7, and 8. These effects are much more difficult to detect and evaluate than those related to acute exposures, but may over a period of time have even greater impact on marine biota.

III. CURRENT STATE OF KNOWLEDGE

BEHAVIOR

Salmonid fry are preyed upon by a number of fish species including larger salmonids. The five species of Pacific salmon (Oncorhynchus sp.) as well as dolly varden (Salvelinus malma) and steelhead trout (Salmo gairdneri) are indigenous to the Lower Cook Inlet-Kodiak region. Pink and chum salmon are hatched in intertidal or lower reaches of the streams and enter the marine environment as fry, whereas coho (O. kisutch) and chinook (O. tshawytscha) salmon, steelhead trout, and dolly varden, enter as juveniles and are much larger when they leave their natal streams. Pink and chum fry spend several months in the coastal estuaries before going to sea and this is the life history stage when they are extremely vulnerable to predation by other salmonids.

Prevailing surface currents in Lower Cook Inlet are such that petroleum development in the lease area may create chronic oil pollution in the numerous coastal inlets where pink and chum fry spend the first months of their existence. Laboratory observation of coho juveniles and chum fry exposed to low levels (<1 ppm) of SWSF of PBCO revealed drastically altered behavior--lethargy, reduction in feeding, and loss of schooling (Craddock, personal observations). Any of these behavioral modifications could lead to a change in normal predator-prey relations.

Predator-prey studies proposed for FY80 involve exposure of salmonid fry and/or their predators to oil and oil-dispersant mixtures and testing of subsequent interactions. Laboratory studies of this nature have been conducted successfully in evaluating other environmental pollutants such as the effect of thermal stress on predator-prey interaction of salmon juveniles and fry, and the effects of light on the vulnerability of heat-stressed fry to predators (Sylvester 1973; Coutant 1973). A search of the literature, however, has revealed few studies of the effects of the SWSF of crude oil on salmon behavior, and no studies were found on oil effects on predator-prey relationships.

CHEMISTRY

A considerable portion of the oil entering the marine environment ultimately settles in the bottom sediment (Wharfe 1975; Gilfillan et al. 1976; Krebs and Burns 1977). In a recent study Herbes and Schwal (1979) showed that aromatic hydrocarbons having more than three rings persisted in sediments resulting in accumulation of these hydrocarbons following repeated simulated spills; lower molecular weight hydrocarbons were more efficiently biodegraded by microorganisms. Surveys of sediment in Washington State and British Columbia reveal that BP, a known carcinogen in mammals, can be present at up to 5-10 ppm (Dunn 1979; McCain et al. 1980) and analyses of tissues of benthic organisms, such as worms or clams, from these areas revealed the presence of a variety of aromatic hydrocarbons including BP. Interestingly, livers of flatfish obtained from these areas did not show detectable concentrations of BP (McCain et al. 1980) However, Dunn (1979) has reported a correlation between the high levels of BP in sediment and high hepatic arylhydrocarbon hydroxylase activity in flatfish.

It is likely that BP is taken up and extensively metabolized by these fish so that its presence in tissues can no longer be detected by currently available techniques which can detect only the parent hydrocarbon.

In general, metabolic products of aromatic hydrocarbons are not amenable to detection by standard analytical techniques. Previous work from our laboratories (Roubal et al. 1977; Collier et al. 1978; Varanasi et al. 1979) using radio-labeled naphthalene has shown that metabolic products of this hydrocarbon are retained in tissues of fish over a longer period than the parent hydrocarbon. Therefore, it is possible that when analyses of tissues of fish from petroleum-contaminated areas do not show detectable concentrations of hydrocarbons, metabolic products of petroleum related hydrocarbons may still be present in these tissues. Studies with mammals have shown that certain metabolites of higher molecular weight hydrocarbons (phenanthrene, BP, benzanthrancene) are toxic and damage DNA by reacting with it. Binding of these reactive metabolites with DNA leads to potential genetic damage and tumor formation (Brookes 1977). Therefore, it is important to determine if fish take up these hydrocarbons from the environment and convert them to damaging metabolites.

PATHOLOGY

Pathological Changes in Flatfish from Exposure to Oil-Contaminated Sediment

In previous experiments reported by members of OCSEAP RU 73 (McCain et al. 1978), English sole exposed to sediment-associated PBCO for 4 mo took up substantial amounts of petroleum hydrocarbons and developed the following apparently oil-related changes: (1) During the first month, when sediment and tissue levels of aromatic hydrocarbons were highest, 50% of the exposed fish and none of the controls had severe hepatocellular lipid vacuolization (HLV), with greater than two-thirds of the cytoplasm of hepatocytes occupied by lipid vacuoles; (2) the number of fish weighing less than their initial weight was significantly different ($P = 0.05$) in the experimental than in the control groups after 4 mo of exposure; and (3) Although no control fish died except those purposely sacrificed, and all control fish looked normal during the 4-mo experiment, 18% of the oil-exposed fish died or were moribund and appeared extremely emaciated. In a more recent publication, McCain and Malins (1980) reported experiments in which three species of flatfish (starry flounder, rock sole, and English sole) were exposed to crude-oil-contaminated sediments for periods ranging from 1 to 4 mo. English sole was the only species to undergo significant adverse effects, including liver structure aberrations and hematological changes.

There are a few reports of oil-related pathological changes in other species of marine fishes. For example, Payne et al. (1978) observed that cunner (Tautogolabrus adspersus) exposed to a surface slick of crude oil for 6 mo had lower testes-somatic indices (0.81) than did controls (1.33). The eye lens diameter of oil-exposed cunner was also significantly greater than that of controls. In another study, mummichogs (Fundulus heteroclitus) exposed for 15 days to recirculated seawater solutions of 2.0 to 0.02 µg/g naphthalene developed histopathological changes in a variety of organs (DiMichele and Taylor 1978). Major types of damage were sensory cell necrosis and localized tissue ischemia.

Effects of Petroleum on Disease Resistance

Disease occurs when complex interactions among the host, the environment, and the infectious agent are perturbed. Any reduction in efficiency of host defense mechanisms (i.e., immunosuppression) can upset this balance in favor of the pathogen and lead to infectious disease. Exposures to petroleum hydrocarbons and associated heavy metals have been previously demonstrated to cause immunosuppression in laboratory mammals (see Hodgins et al. 1977, for review); however, there is a paucity of information on the effects of these compounds on marine animals.

In previous laboratory experiments there were no detectable changes in disease resistance or immunocompetance of salmonids either fed PBCO or exposed to the SWSF of PBCO. In addition, no alteration in disease resistance was demonstrated in various species of adult flatfish maintained on oil-contaminated sediments. There is little information on the effects of petroleum hydrocarbons on disease resistance of early juvenile life stages of fish. A juvenile fish may show a marked increase in disease susceptibility following levels of oil-exposure that leave adults relatively unaffected. There has also been little research on the influence of petroleum-exposure on disease resistance of crustaceans. Furthermore, there is little information on the impact of petroleum-dispersant mixtures on disease resistance of marine organisms.

PHYSIOLOGY

There is increasing evidence that crude oil may particularly affect the early developmental stages of marine fishes. Lonning (1977) demonstrated that embryos of cod (Gadus morhua), plaice (Pleuronectes platessa), and flounder (Platichtys flesus) exposed to crude oil for even short periods (1-15 hr) developed bent notochords, severe abnormalities in the head region, and changes in melanophore distribution of emerging larvae. Particularly sensitive stages were those at cleavage and gastrulation, hatching, and again after yolk resorption. Smith and Cameron (1979) observed that newly hatched Pacific herring (Clupea harengus pallasi) larvae exposed to PBCO were unable to swim and maintain themselves in the water column; abnormalities occurring in the mouth, pectoral fins, and branchiostegal membranes were also common. Linden (1975) found that petroleum hydrocarbons disrupted lipid membranes and primordial fin formation of Baltic herring (Clupea harengus membras) larvae. Mazmanidi and Bazhashvili (1975) exposed eggs of the Black Sea flounder (Platichthys luscus) at various stages of development to the water-soluble fraction of crude oil at concentrations of 2.5 to 0.025 ppm. All concentrations greater than 0.025 ppm were found to be toxic. Eggs exposed in the gastrulation stage died immediately and most embryos exposed at more advanced stages hatched but perished soon afterwards. Surviving larvae exhibited scoliosis, reduced activity and reduced rate of yolk absorption, and abnormalities in heart rate and pigment configuration. Several studies have been reported concerning the effect of petroleum on salmon embryos and alevins (Rice et al. 1975; Kuhnold and Busch 1977/78); however, these investigations have largely been focused on acute toxicity of oil and on the uptake of specific hydrocarbons. No published information has been found detailing effects of weathered crude oil on embryonic and larval development of salmonids, flatfish, or surf smelt.

Chum salmon frequently spawn in tidal areas at the mouths of streams (Bakkala 1970; Neave 1966). Eggs are deposited in the redds and then covered with gravel as a result of upstream redd digging and stream flow. Subsequently, at least one high tide a day inundates the redds with salt and brackish water;

the length of exposure to water of high salinity depending upon redd location. After approximately 50-90 days (development rate is a function of water temperature) the eggs hatch, and the chum salmon alevins remain in the gravel for another 30-50 days before emergence and migration to salt water.

Sand sole and English sole are pleuronectid flatfish with pelagic eggs and larvae. Flatfish eggs are released on or near the bottom and after about a day, depending upon depth of spawning, the eggs rise to float near the water's surface (Alderdice and Forrester 1971) where they could be subjected to floating oil contamination. The eggs hatch after approximately 1 week and the larvae emerge relatively undeveloped.

Surf smelt are found along the Pacific coast from California to the Aleutian Islands and have a life history similar to the more widely distributed capelin (Mallotus villosus) and other osmerids. The surf smelt spawn intertidally on coarse sand-pea gravel beaches; the adhesive eggs being submerged intermittently at high tide over about 30 days until the embryos hatch as well-developed larvae. Rate of embryonic development is dependent upon both water and air temperature, and hatching is promoted by wave agitation at completion of embryogenesis.

IV. STUDY AREA

All experiments were conducted either in laboratories or in fish-holding facilities at the Northwest and Alaska Fisheries Centers (NWAFC), Seattle, and at the NWAFC's saltwater field station at Mukilteo, Washington, on representative subarctic marine and anadromous species.

V. SOURCES, METHODS, AND RATIONALE OF THE DATA COLLECTION

BEHAVIOR

The initial studies on the effect of the SWSF of CICO on salmonid predator-prey relations were conducted with chum salmon fry of Quilcene stock obtained from the Tulalip Indian salmon-rearing facility at Tulalip, Washington. They averaged 6.3 cm in fork length when tested. The predators used were 2-yr old juvenile coho salmon from the Washington State Fisheries Department hatchery at Issaquah, Washington. They were obtained as fertile eggs, hatched, and reared at the NWAFC, Montlake fishery facility to an age of 1 year and then at the Mukilteo saltwater facility to an age of 2 years and an average length of 30.0 cm.

The experimental plan was to expose test fry to the SWSF of crude oil for 7 days while holding control fry under similar conditions for an identical length of time. An equal number of test and control fry would then be introduced simultaneously into an observation tank containing hungry predators. After approximately one-half of the fry were consumed, the predation would be halted and the numbers of test and control prey remaining would be determined. The effect of exposure to the SWSF of crude oil on the ability of chum fry to avoid predation would then be determined by chi-square analysis (Coutant 1973).

One week prior to the start of an experiment, test and control fry were distinctively marked by cold-brand marking (Fujihara and Nakatani 1967) and the coho juveniles were trained to feed on chum fry. The predator coho were always starved at least 24 hr before being used in the study.

The SWSF of crude oil was produced by a flow-through apparatus similar to that described by Roubal et al. (1977). Crude oil was first mixed with seawater and the larger oil particles rising to the surface were drained off. This product was then passed through a baffle tank where the remainder of the oil particles were allowed to rise to the surface and be carried away. The SWSF exposure tanks were analyzed by gas chromatography.

was then routed to the glass exposure tanks. Water samples collected from the

The water quality (temperature, pH, and dissolved oxygen) was monitored every other day. Normally 5 test and 5 control fish were introduced to the predator tank simultaneously, but the numbers were varied to as high as 10 test and 10 control fish. Four to five predators that had not eaten for at least 24 hr were placed in the predation tank 12 hr before the tests.

CHEMISTRY

Uptake of PAH by Flatfish from Sediment and Diet

Juvenile starry flounder from the estuary of the Columbia River and English sole from Point Pulley, Washington were acclimatized to flowing unfiltered seawater at 12 ± 1°C for several weeks. Fish were not fed for three days prior to initiation of the exposure as well as during the entire week of exposure.

Eight starry flounder were placed in a small glass aquarium containing 10 ppm of radioactively labeled BP in oiled-sediment (1% PBCO). The oiled-sediment was identical to that used in the Pathology studies carried out under OCSEAP (See last Annual Report). At 24 hr after the exposure, three fish were sampled for radioactivity in liver, bile, muscle, and skin using a previously described method (Varanasi et al. 1979). The remaining five fish were placed on sediment containing neither PBCO or BP for depuration and sampled after 24 hr. One group of starry flounder was fed tritiated BP mixed in corn oil (20.5 uCi or 104 ug per fish), and tissues were analysed for radioactivity at 24 and 168 hr after feeding of BP. Another group of fish was fed tritiated naphthalene.

Bile of BP-exposed fish was treated with β-glucuronidase (Dodgeson et al. 1953) and ethyl acetate-soluble metabolites were separated by thin-layer chromatography (TLC). Bile of naphthalene-fed starry flounder was similarly treated and analysed by TLC.

Metabolism and Subsequent Binding of BP to DNA by Liver Enzymes of Flatfish

Starry flounder and English sole were injected intraperitoneally with 10 mg/kg of various PAH, such as BP, 3-methylcholanthrene (MC), or PBCO, in corn oil. There was no detectable difference in the binding of metabolically activated $[^3H]$BP to DNA when liver enzymes from untreated or corn oil-treated fish were used. Accordingly, most of the data for control fish in these studies were from untreated fish. The fish were killed 24 hr after the injection and supernatants of liver homogenates (10,000 x g) were prepared according to previously described procedures (Pedersen et al. 1976). The standard reaction mixture for *in vitro* binding of BP to DNA contained 2 mg of DNA added in 2.5 ml of 0.02 M phosphate buffer (pH 7.4), 0.75 mg NADPH added in 0.1 ml of 0.1 M EDTA (pH 7.4), and 0.2 ml of the 10,000 x g supernatant (5 mg protein). The reaction was started by adding 5 nmoles of BP in 50 ul of ethanol. The mixture was incubated in the dark for 15 min at 25°C when fish liver supernatant was used, and at 37°C when rat liver supernatant was used. The reaction mixture was then treated according to the procedure previously described in detail (Buty et al. 1976).

Benzo[a]pyrene metabolites were formed by incubating liver supernatants with $[^3H]$BP under the conditions described above, without the addition of DNA. The mixture was extracted with ethyl acetate (2 x 6 ml) as described organic phases was determined. Ethyl acetate extracts were spotted on silica gel plates and developed in benzene:ethanol (9:1, v/v). The extracts were cochromatographed with known standards of BP and its metabolites. Separation and quantification of the metabolites were carried out using both TLC (Cohen and Moore 1976; Varanasi and Gmur 1980) and high-performance liquid chromatography (HPLC) as described previously (Selkirk et al. 1974; Varanasi et al. 1980a). All operations were carried out under dim light to reduce possible photo-oxidation.

Six English sole were injected (i.p.) with 100 ul each of aromatic fraction of PBCO. The aromatic fraction was prepared by the method described previously (Pancerov 1974; Malins et al. 1978). Control fish were injected with peanut oil. After 24 hr, fish were killed and liver and bile extracts were prepared for the Ames mutagenecity test (Ames et al. 1975). Another group of fish was also injected with the aromatic fraction of PBCO or BP (10 mg/kg body wt) to induce liver enzymes and after 24 hr, S-9(9000 x g) fractions were prepared from liver homogenates. The aromatic fraction of PBCO was incubated with the S-9 fractions from English sole, and the ethyl acetate extracts from these incubations were sent out for testing for mutagenicity by the Ames test.

PATHOLOGY

Pathological Changes in Flatfish from Exposure to Oil-Contaminated Sediment

In the two experiments performed during the last year, juvenile English sole were exposed to two basic types of sediment (sandy and silty) contaminated with 1% (v/v) PBCO. The experiment employing silty sediment (Experiment One) lasted 4 mo and the other using sandy sediment (Experiment Two) was terminated after approximately 5 1/2 weeks. Particle size analyses of the sandy and silty sediment types showed that approximately 1.0 and 47.4%, respectively, were composed of silt. Mixtures of PBCO and sediment were prepared using a cement mixer. The sediment was placed in a previously described aquarium (McCain et al. 1978) at a depth of 5 cm. After rinsing the sediment overnight by allowing seawater to flow through the tank, the experimental fish were added. An equal amount of nonoil-contaminated sediment placed in a similarly designed aquarium at the same depth was used for control fish. After adding the fish to the sediment-containing aquaria, the aquaria were examined daily for dead or moribund fish, and the fish were fed to satiation with a combination of frozen euphausiids and clams.

At intervals of 2 wk to 1 mo, all of the fish were examined for externally visible abnormalities, and they were measured for weight and length. Six fish from each group were sacrificed at each examination period and tissue samples were removed for histological, hematological, morphological, and chemical analyses. For histological examination of each fish, pieces of gill, gonad, fin, skin, gastrointestinal tract, kidney, liver, and eye lens were removed and preserved in appropriate fixatives. Specimens to be examined by light microscopy were embedded in paraffin, sectioned, and stained by a variety of histochemical stains and methods. The histopathologists examining the stained specimens knew only the species, length, and sex of fish from which the specimens were taken; they did not know the type of exposure. Procedures used for electron microscopic examinations of tissues were as previously described (Hawkes 1974). The following hematological tests were performed: hemoglobin, hematocrit, and total red blood cell and leucocyte counts. Concentrations of serum albumin and proteins were also measured by standard spectrophotometric methods. Samples of muscle, skin, and liver were collected for analyses of aromatic hydrocarbons. Muscle samples from each fish were analyzed individually, and skin and liver samples from the three fish in each group were pooled. Tissue samples were frozen at -20°C immediately after they were taken and thawed just before chemical analysis. Sediment was also collected at each sampling interval. Sediment samples were taken from the top 2 cm of sediment with a coring device.

Hydrocarbon analyses of sediment, water, and fish tissue were performed by the NOAA National Analytical Facility using a modification of procedures described by Brown et al. (1979) and MacLeod et al. (1977) which involved gravimetric determination of total extractable hydrocarbons and gas-liquid chromatography (GLC) for alkanes and arenes. By subtracting the concentration of total extractable hydrocarbons in the nonoil-contaminated sediment from the concentration in the oil-contaminated sediment, the value of total extractable petroleum hydrocarbons (TEPH) in the oil-contaminated sediment was determined.

PHYSIOLOGY

Preparation of Weathered Oil

Weathered oil was prepared in a wave machine that subjected fresh PBCO or CICO to mixing with seawater by wave action, exposure to sunlight, and loss of volatile components through evaporative processes (Fig. 1). A paddle hinged at the bottom was attached to an electric motor which produced a steady wave periodicity of 48/min. At the opposite end, an artificial beach was added to dampen waves and simulate water-accommodated oil passing down through the gravel of a chum salmon spawning redd. Coarse gravel (80% 1 to 5 cm diameter, remainder fine) was spread 25 cm deep over a perforated pipe. Over this gravel beach model was placed a removable baffle which isolated the gravel from the oil during the weathering process, thus preventing oil from coming in contact with the "beach" before weathering was completed.

Six-hundred and eighty ml of fresh PBCO or CICO were layered on the water surface of the wave machine resulting in an oil film of 91 $\mu l/cm^2$ and an initial oil concentration in the water of 4,000 ppm (v/v). During the weathering process, there was a continuous flow of salt water (27-30 $^o/oo$) through the wave machine with a water replacement time of once per hour. Water overflow was removed 25 cm beneath the water's surface via an adjustable standpipe in order to maintain the oil slick. After 30-48 hr of flow-through operation and wave action, the oil was defined as weathered.1/ For experiments with chum salmon eggs and alevins,

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1/ Tentative evaluations of the concentration of petroleum hydrocarbons present in the water during exposure of eggs and larvae, were presented in the OCSEAP Quarterly Reports (RU 73) for June and September 1979. These chemical analyses are being re-evaluated and/or additional samples are being analyzed and are not presented in this Annual OCSEAP Report, but will be presented in a later report along with qualitative analyses of the weathered oil. In the experiments concerned with embryo and larvae development the term water-accommodated oil or the saltwater-soluble fraction (SWSF) denotes water removed from under an oil slick. In water samples collected there was a Tyndall effect indicating that along with the soluble petroleum hydrocarbon components there were some globular oil products dispersed in the water column.

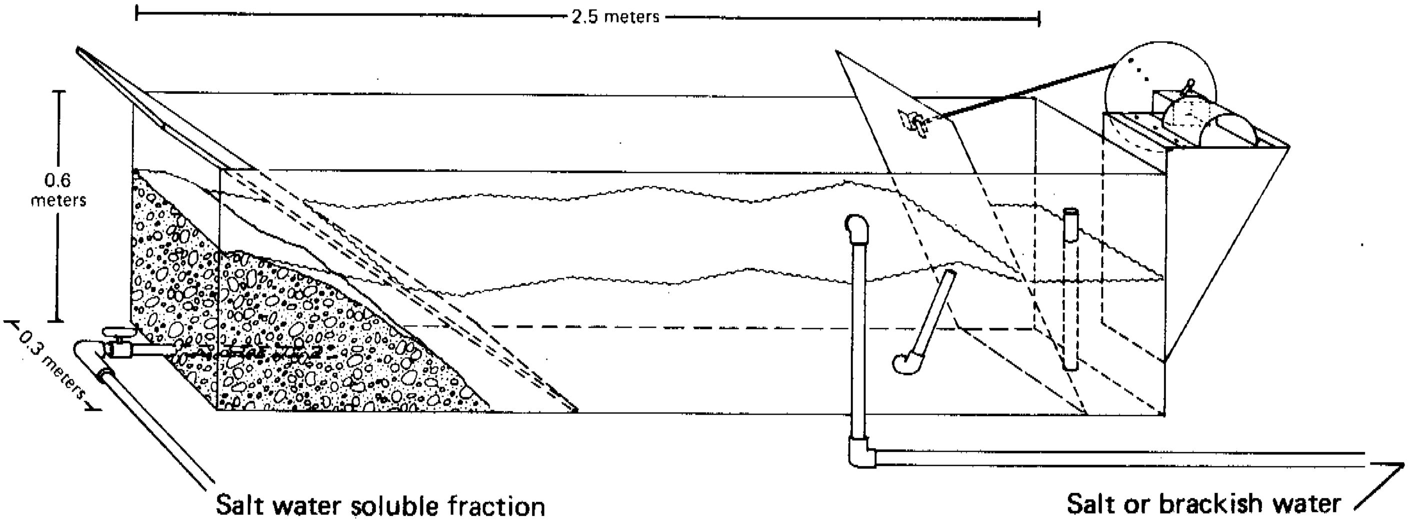

FIGURE 1. Apparatus for weathering of crude oil.

salinity of the incoming water was then reduced (to 16-24 o/oo) and the baffle removed, allowing the water-accommodated oil to come in contact with the gravel. The oil-contaminated water was then drawn off through the gravel for treatment of the eggs and alevins. Once a week the gravel and wave machine were cleaned, a change of fresh oil was added, and the process was repeated. For experiments with flatfish and surf smelt eggs, salinity was not reduced after oil weathering nor was the oil replaced during the course of each experiment.

Source of Eggs

Chum salmon eggs were obtained from the U.S. Fish and Wildlife Service National Fish Hatchery at Quilcene, Washington. Immediately after fertilization, the eggs were transported to the Mukilteo laboratory. Subsequent sampling from control groups indicated that 2.6% of the salmon eggs were not fertilized.

Spawning English sole and sand sole were obtained by trawling in Puget Sound and the eggs fertilized immediately on board the trawling vessel. Fertilization success and subsequent viability in flatfish eggs were high, approximately 90%, as indicated by cell cap formation. Flatfish and salmon eggs used in each experiment were taken from a single female to reduce variations in viability between females. Surf smelt eggs were collected from either the intertidal area of Hood Canal, Puget Sound, or from spawning females from Hood Canal. All surf smelt eggs were visually checked for a viable 6 day old embryo at the initiation of each experiment.

Exposure of Chum Salmon Eggs and Alevins

One day after fertilization, approximately 70 chum salmon eggs were placed in each of 30 x 75 cm glass cylinders having both ends covered with fine mesh teflon netting. A glass tray was divided longitudinally into eight troughs and small pea gravel was layered 2.5 cm deep on the bottom. Seven vials of eggs were placed horizontally into each trough (Fig. 2).

Eggs were exposed 3 hr/day to oil-contaminated brackish water (16-24 o/oo, and 4.5-10.2°C ambient temperature) at a flow rate of 400 ml/min per trough. For 21 hr/day the eggs received fresh dechlorinated water (5.5 to 10.5°C, ambient temperature) at the same flow rate for a water replacement of 8 times per hr. Exposure to oil-contaminated water occurred 4 days per week. On the other 3 days eggs and alevins received uncontaminated brackish water for 3 hr/day. Table 1 gives the oil exposure conditions (by group) designated for each of the 8 troughs.

Table 1. Chum salmon egg and alevin exposure to the SWSF of weathered PBCO by stage of development and duration of exposure.

Group	Developmental stage	Exposure period (days post fertilization)	Total hr exposed
1	Control	0	0
2	Midembryo	14-26	24
3	Late alevin	92-113	36
4	Early embryo	1-26	45
5	Total alevin	75-113	72
6	Late embryo	26-75	84
7	Total embryo	1-75	132
8	All stages	1-113	213

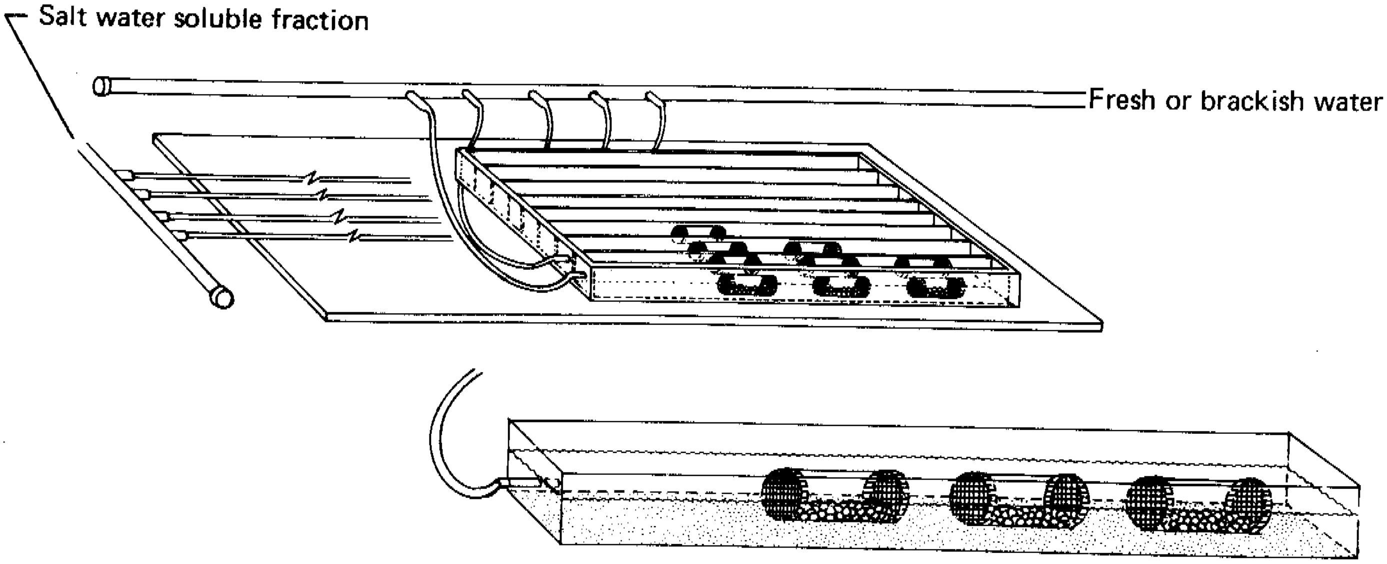

FIGURE 2. Chum salmon egg incubation apparatus with delivery of brackish SWSF of weathered PBCO from the wave generator (Fig. 1) for 3 hr/day and delivery of fresh water for 21 hr/day.

The exposure period by stage of development is also expressed diagramatically in Figure 3.

In addition to the exposure of alevins in troughs to oil, some alevins were held in inverted, brown-glass, 1-gallon jugs, with the bottoms removed for evaluation of effects of oil on alevin emergence from gravel. The jugs were filled with coarse gravel to a depth of 20 cm, and supplied with water upwelling from the bottom (neck).

Water samples for chemical analysis were taken daily, four days a week, throughout the 113-day exposure period (see footnote 1/ for statement on chemical analyses).

Exposure of Flatfish Eggs

Twenty-four hours after fertilization (early cell-cap stage) flatfish eggs were introduced into 1,000 and 2,000 ml separatory funnels containing either fresh PBCO, weathered PBCO (floating "mousse" from wave machine) layered on the water surface, or the SWSF of weathered PBCO obtained from the wave machine. During oil weathering, the saltwater temperature was 7.8 to 9°C. The funnels were attached to an air supply through the bottom and bubbled slowly, thus creating a gentle current in the funnel keeping the eggs in suspension. Funnels were submerged in a water bath with ambient flowing seawater of 10°C. The following exposures were conducted:

1. English sole eggs
    a. Control
    b. Undiluted (100%) SWSF, weathered
    c. Layered "mousse" at 4,000 ppm v/v (initial mousse: water concentration)
    d. Layered fresh PBCO at 4,000 ppm v/v (initial PBCO: water concentration)
2. Sand sole eggs
    a. Control (replicated)
    b. Layered mineral oil at 2,000 ppm v/v to test effect of an oil film (no seawater-soluble components detected by gas chromatography)
    c. Undiluted (100%) SWSF, weathered
    d. 1/2 dilution (50%) SWSF, weathered (replicated)
    e. Layered fresh PBCO at 4,000 ppm v/v
    f. Layered fresh PBCO at 2,000 ppm v/v
    g. Layered "mousse" at 4,000 ppm v/v
    h. Layered "mousse" at 2,000 ppm v/v

Water samples for chemical analysis were taken after 3 days of exposure and again after hatching (day 8). Water samples were taken by transferring the contents of the funnel, except for oil on the water surface, into a beaker. The water was then siphoned from the beaker through a screened cylinder to prevent passage of eggs and larvae. For samples taken in midincubation, the eggs were then poured back into the funnels and topped off with uncontaminated seawater. Layered oil was not renewed; thus, hydrocarbon concentrations were reduced after the first water change. The SWSF was renewed with an portion of the original SWSF which had been refrigerated in a sealed glass bottle with a teflon-lined lid.

At the end of each test, flatfish eggs and larvae were examined and categorized using the following nomenclature:

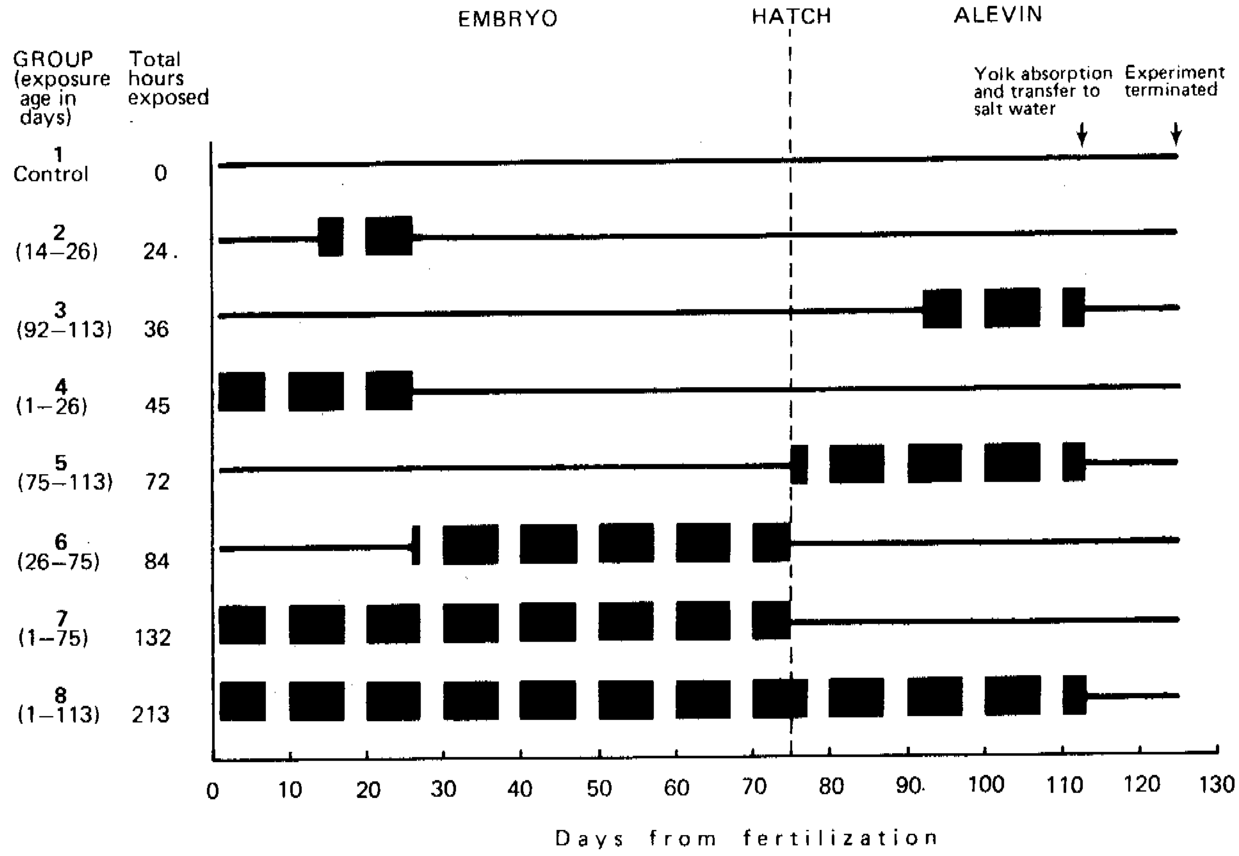

FIGURE 3. Exposure groups of chum salmon eggs showing duration and stage of exposure.

Nondeveloped eggs: Consist of two types of eggs which are indistinguishable as to the cause of nondevelopment--(1) nonviable eggs which were not sucessfully fertilized (approximately 10% in these experiments); (2) embryos which died in early cell division as a result of oil exposure or natural failure (embryo not formed).

Normal embryo: Embryo transparent, with visible heart contractions.

Abnormal or dead embryo: Opaque, often scoliosis evident, and no heart contractions.

Normal larvae: Notochord straight, finfold continuous, digestive tract complete, pigmentation complete, and larvae transparent.

Abnormal larvae: Slight curvature of the notochord and entire body, generally a lateral curvature of up to 45°.

Grossly abnormal larvae: Alive, with body curvature exceeding 45°. (some with notochord curvature of 180° and double 180° curvatures). Finfold deformed, digestive tract incomplete, pigmentation not in patches but scattered, lying motionless on bottom, opaque.

Dead larvae: No heart contraction, generally opaque, and usually contorted.

Ruptured eggs: Whole egg cases and fragments of egg envelope (chorion). Only observed in tests with sand sole and not associated with remnants of hatching.

Exposure of Surf Smelt Eggs

Experiments exposing surf smelt eggs to the SWSF of CICO were replicated once in November and once in December 1979, at ambient water temperatures of 8.8 to 11.2°C. Five-hundred eggs were placed in each of four square-sided baskets (7 x 14 x 14 cm with 500 μm mesh teflon netting on the bottom) filled with 2.5 cm of fine gravel (Figure 4). The baskets were submerged 3 hr/day throughout the incubation period in the SWSF of weathered CICO with a flow rate of 750 ml/min to each basket. The SWSF from the wave generator was introduced into a diluter and three concentrations used in exposure: (1) undiluted (100%) SWSF from the wave machine, (2) 1/2 diluted (50%) SWSF, and (3) 1/4 diluted (25%) SWSF.

Water samples for chemical analysis were collected daily from the trough containing undiluted SWSF, and every 4 days from all troughs. In addition, samples of surf smelt eggs were collected halfway through embryonic development for hydrocarbon analyses.

Samples Collected for Morpholgy

Eggs and alevins of 115 oil-exposed and 50 control chum salmon, and 170 oil-exposed and 40 control sand sole eggs and larvae were sampled for electron microscopy and fixed as previously reported (Hawkes 1974). The samples were subsequently processed for light microscopy (LM), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). Representative samples were examined with LM, SEM, and TEM, and the remainder were stored. In addition, 420 samples of surf smelt embryos and larvae from control and oil-exposed groups were collected. Twenty-six surf smelt larvae were sectioned and stained for and examined with LM, 46 examined with SEM, and 12 with TEM.

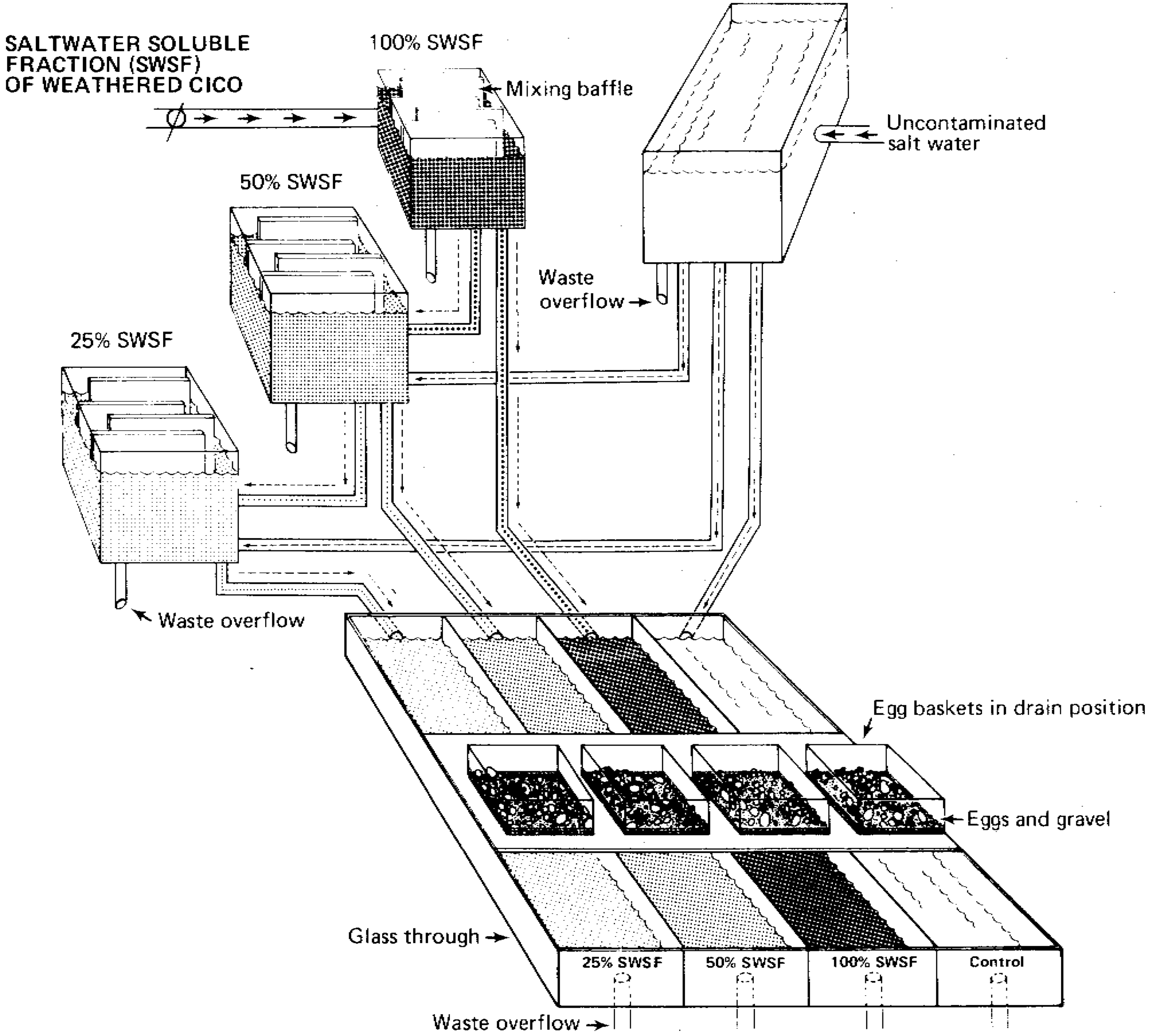

FIGURE 4. Surf smelt egg exposure apparatus with delivery of the SWSF of weathered CICO.

VI. RESULTS

BEHAVIOR

In the studies completed so far, the SWSF concentrations to which the fry were exposed averaged 0.4 ppm. After 7 days of continuous exposure to this concentration, the test fry showed signs of: (1) reduced schooling, (2) lack of feeding, and (3) lethargy. Also, mortality in the exposure tanks was considerably greater than in the control tanks: 27% compared to 4%.

Test fry exposed to the SWSF were not preyed on at a significantly different rate than the control fry. Of 109 test fish and 155 control fry introduced to the predator tank, 59 and 54 respectively, survived. Chi square analysis of the data would not allow rejection of the (null) hypothesis that there was no difference between exposed and control fry in avoiding predation.

CHEMISTRY

Uptake of PAH by Flatfish from Oiled Sediment and Diet

The data in Figure 5 show that starry flounder readily took up BP from sediment containing 1% PBCO as evidenced by the presence of considerable radioactivity in blood, liver, bile, muscle, and skin of these fish 24 hr after the initiation of exposure. When fish were subsequently placed in BP- and oil-free sediment, radioactivity in blood, liver, skin, and muscle declined; however, as much as 60% of the accumulated radioactivity was still present in the liver 24 hr after depuration.

Results in Table 2 show that at 24 hr after force-feeding of BP or naphthalene to starry flounder considerably more naphthalene (expressed as % administered dose) than BP was present in liver, skin, muscle, and bile. However, radioactivity due to naphthalene was released from liver, muscle, and skin to a much greater extent than that due to BP from 24 to 168 hr. At 168 hr, liver of BP-exposed fish contained five times as much radioactivity as did liver of naphthalene-exposed fish. From 24 to 168 hr radioactivity increased in bile of naphthalene- and BP-exposed fish. Profiles of metabolites extracted from liver, muscle, and bile of naphthalene-exposed starry flounder are given in Figure 6. Metabolites of BP were difficult to extract from liver and muscle because of their solubility in lipid. Preliminary data show that 80 and 99% of total radioactivity, respectively, in liver and bile of BP-exposed fish were due to metabolites. Since bile was seen to contain primarily metabolic products, it was chosen for analysis of types of metabolic products produced from naphthalene and BP. Our previous results (Varanasi et al. 1979) have shown that the major metabolites in bile of naphthalene-exposed starry flounder were glucuronide conjugates. Therefore, bile was hydrolyzed with β-glucuronidase to determine what types of primary metabolites (e.g., diols, phenols) were conjugated with glucuronic acid. The results in Figure 7 show that the major product from hydrolysis of biliary metabolites from naphthalene-exposed fish was 1,2-dihydro 1,2-dihydroxynaphthalene (dihydrodiol); small amounts of naphthols were also present. Hydrolysis products of biliary metabolites from BP-exposed fish separated by TLC revealed the presence of 7,8-dihydro 7,8-dihydroxy BP and a large fraction of polyhydroxy metabolite fraction (presumably tetrols formed from dihydrodiol).

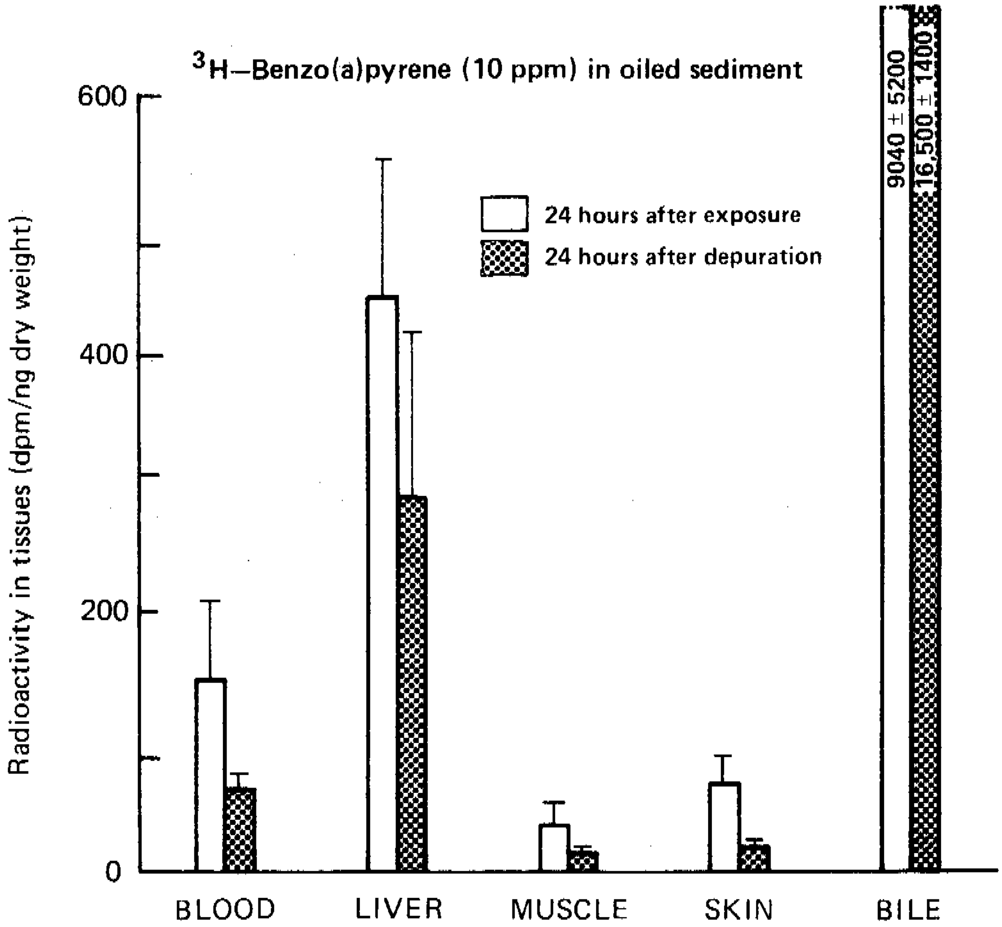

FIGURE 5. Uptake of [^{3}H]-Benzo[a]pyrene from sediment containing Prudhoe Bay crude oil (1% PBCO) by starry flounder. Values represent mean ± S.D.

TABLE 2

TOTAL RADIOACTIVITY (EXPRESSED AS % ADMINISTERED DOSE) IN STARRY FLOUNDER EXPOSED TO DIETARY AROMATIC HYDROCARBONS

Time after feeding (hr)	Liver	Skin	Muscle	Bile
	Exposure to [^{3}H] - naphthalene[1]			
24	0.7 ± 0.5	0.4 ± 0.2	1.3 ± 0.4	0.2 ± 0.2
168	0.02 ± 0.01	0.02 ± 0.01	0.09 ± 0.02	0.9 ± 0.4
	Exposure to [^{3}H] - Benzo[a]pyrene[2]			
24	0.11 ± 0.02	0.08 ± 0.01	0.33 ± 0.08	0.04 ± 0.01
168	0.09 ± 0.01	0.02 ± 0.01	0.07 ± 0.02	0.22 ± 0.04

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[1] Taken from Varanasi et al (1979); Fish were force-fed 56 μCi of naphthalene. Data are expressed as mean value ± S.E. (for 4 fish).

[2] Fish were force-fed 20.5 μCi of benzo[a]pyrene.

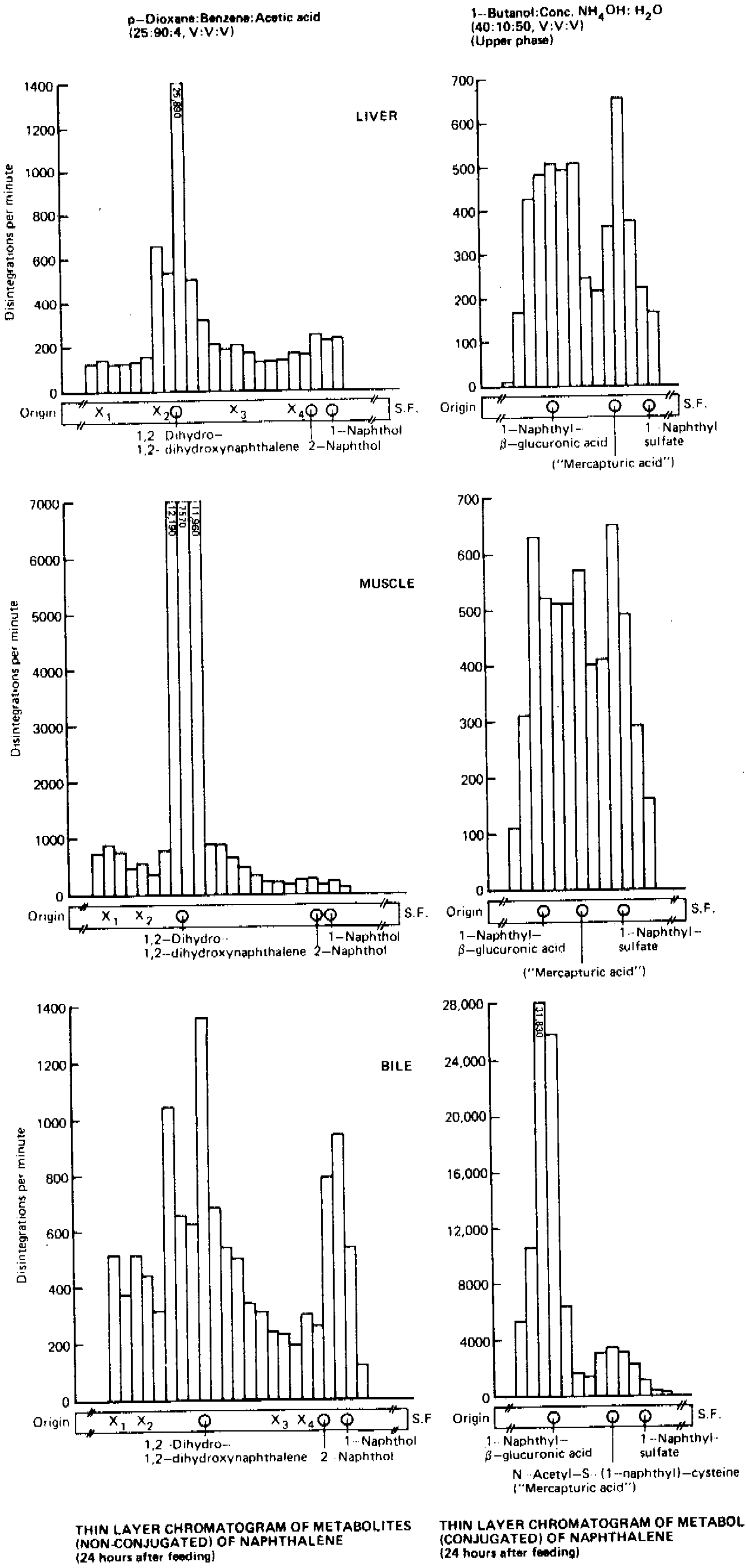

FIGURE 6. Profiles of metabolites in liver, muscle and bile of naphthalene-exposed starry flounder.

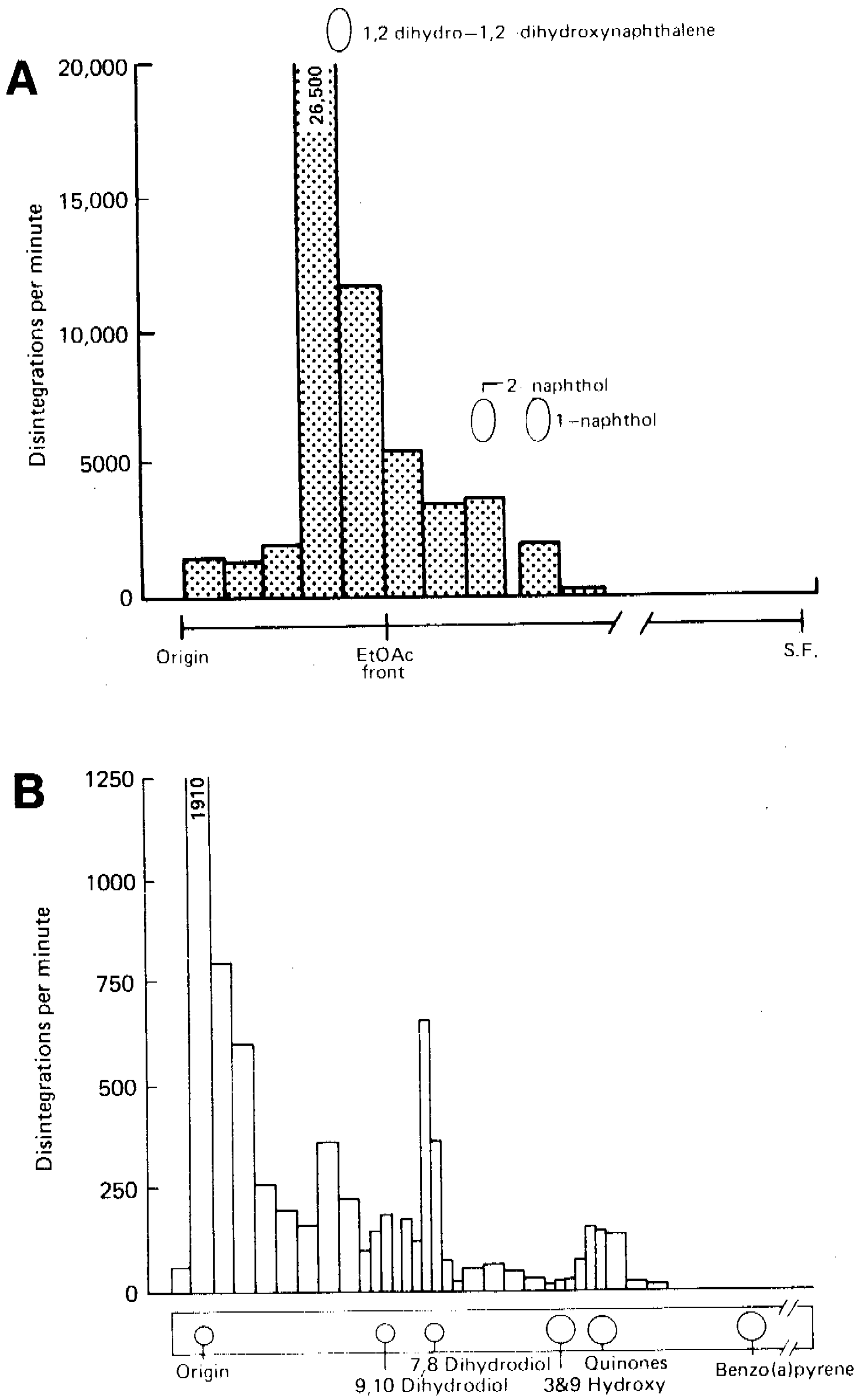

FIGURE 7. Thin-layer chromatograms of ethyl acetate extractable metabolites from bile of naphthalene (A) and benzo[a]pyrene (B) exposed starry flounder, after hydrolysis with β-glucuronidase.

Metabolism and Subsequent Binding of BP to DNA by Liver Enzymes of Flatfish

The results in Table 3 show that the binding value for BP to DNA catalysed by liver extracts for the untreated starry flounder was about 3 times greater than the corresponding value for English sole and rat. Moreover, pretreatment of English sole with PBCO resulted in an 18-fold increase in the binding value compared to the corresponding value for untreated fish; the increase in the binding in the case of PBCO-pretreated starry flounder was only 5-fold. The value for binding obtained with liver extracts from MC-pretreated starry flounder was about 10 times greater than that obtained with the untreated fish; the binding of BP to DNA was slightly greater when fish were pretreated with BP than when they were pretreated with MC.

Figure 8 depicts HPLC-ethylacetate of extractable metabolites formed by liver extracts of MC-pretreated fish species and rat. The data revealed that for both fish species 9,10-dihydro-9,10-dihydroxybenzo[a]pyrene (BP 9,10-dihydrodiol) and 7,8-dihydro-7,8-dihydroxy-benzo[a]pyrene (BP 7,8-dihydrodiol) were the major metabolites; 3-hydroxy BP was also present in considerable amounts. The metabolite profile for the MC-pretreated rat revealed the presence of a high proportion of phenols and quinones together with significant amounts of the non K-region dihydrodiols (BP 7,8-dihydrodiol and BP 9,10-dihydrodiol). It should be noted that profiles of BP metabolites obtained after incubation of liver extracts with ^{14}C-BP were similar to those obtained with ^{3}H-BP.

Results in Table 4 show that the pretreatment of starry flounder and English sole with PAH (MC, BP or PBCO) resulted in a considerable increase in BP metabolism catalyzed by the liver supernatants. Liver extracts from PAH-pretreated starry flounder and English sole produced a larger proportion of ethyl acetate-extractable metabolites than liver extracts from MC-treated rat. Ratios of the concentrations of non K-region dihydrodiols to monohydroxybenzo[a]pyrenes (3-hydroxy BP and 9-hydroxy BP) were significantly ($P<0.05$) greater in fish liver extracts than that in the rat liver extract (Table 4). Pretreatment of starry flounder and English sole with MC, BP, or PBCO resulted in marked increases in proportions of the "prediol" components (presumably triols and tetraols formed from secondary metabolism of BP via dihydrodiols and phenols) and a decrease in the proportion of BP 7,8-dihydrodiol formed by the liver extracts. For example, BP 7,8-dihydrodiol comprised 32 and 17%, respectively, of the ethyl acetate-extractable metabolites in incubations containing liver extracts from untreated and MC-pretreated starry flounder; the corresponding values for polyhydroxy compounds ("prediol") were 5 and 15%, respectively (Table 4).

PATHOLOGY

Pathological Changes in Flatfish from Exposure to Oil-Contaminated Sediment

Release and biocencentration of sediment-associated petroleum hydrocarbons

As has been reported previously, the type of sediment with which PBCO is mixed greatly influences the concentrations of petroleum hydrocarbons associated with the sediments. In experiments where the two types of sediment received 1% (v/v) PBCO, the sandy sediment (Experiment Two) lost 70% of the cumulated selected aromatic hydrocarbons (CSAH) during the first

TABLE 3

THE *IN VITRO* BINDING OF ACTIVATED BP TO DNA CATALYZED BY LIVER SUPERNATANTS FROM FISH AND RAT

Species	System[a] (supernatant)	pmole of BP equivalent/mg DNA/mg protein[b]	% of control value
Starry flounder	Control	0.15	100
	MC	1.62	1,000
	BP	1.70	1,100
	PBCO	0.74	500
	MC[c]	0.53	--[d]
English sole	Control	0.06	100
	PBCO	1.05	1,800
	MC	0.16	--[d]
Rat	Control	0.06	100
	MC	0.69	1,200

[a] Liver supernatants (10,000 x g) were obtained from either untreated (control) animals or those injected with 10 mg/kg of 3-methylcholanthrene (MC); benzo[a]pyrene (BP); or Prudhoe Bay crude oil (PBCO) when the water temperature for fish was 13°C.

[b] Liver supernatants (≈5 mg protein) from different animals were incubated in the dark with 5 nmole BP, 2 mg salmon sperm DNA and cofactors for 15 min at 25°C (for fish) and 37°C (for rat). Each value is an average of two experiments and three replicate measurements using pooled liver extracts from 5 animals. Binding values without NADPH were less than 0.001 and were subtracted from the values reported.

[c] Liver supernatants were obtained from MC-treated fish when the water temperature was 8°C.

[d] No control fish were sampled at 8°C.

[Taken from Varanasi and Gmur 1980.]

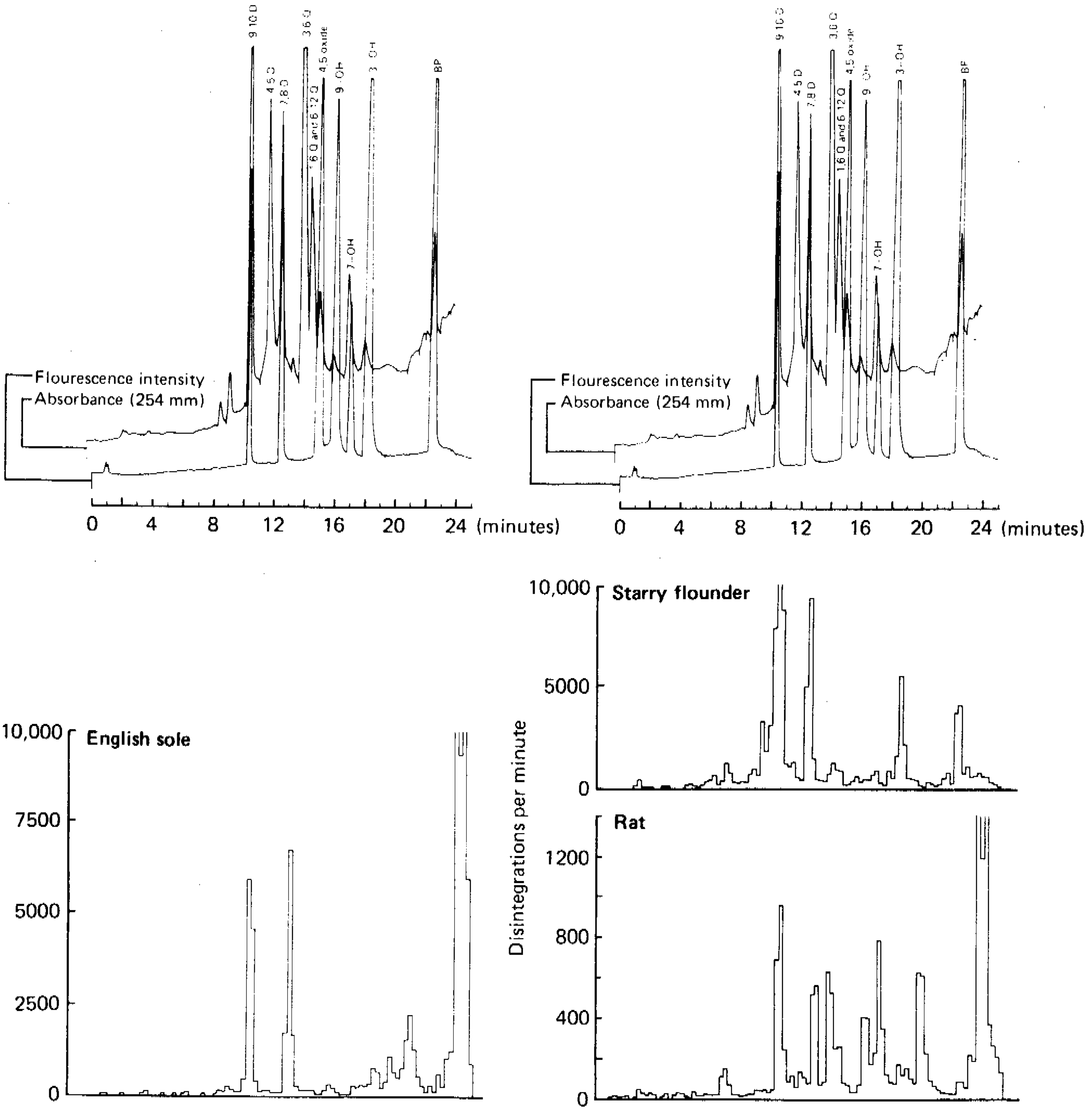

FIGURE 8. HPLC of reference BP metabolites and ethyl acetate-extractable metabolites of ^{3}H-BP produced by liver supernatants (10,000 x g) of MC-pretreated starry flounder, coho salmon, English sole, and rat. Reference compounds and metabolites were detected by both UV and fluorescence spectrometry. Metabolites formed by incubating 5 nmole ^{3}H-BP with liver supernatants (5 mg protein) of fish (at 25°) and rat at (37°) for 15 minutes were separated at fractions collected at 15-second intervals. Abbreviations are 9,10-D, BP 9,10-dihydrodiol; 4,5-D, BP 4,5-dihydrodiol; 7,8-D, BP 7,8-dihydrodiol; 3,6-Q, BP 3,6-quinone; 9,OH, 9-hydroxy BP; 7-OH, 7-hydroxy BP; 3-OH, 3-hydroxy BP; BP, benzo[a]pyrene.

TABLE 4

METABOLISM OF BENZO[a]PYRENE BY LIVER EXTRACTS FROM FISH AND RAT

	STARRY FLOUNDER			ENGLISH SOLE			RAT
	Control	MC-treated	PBCO-treated	Control	PBCO-treated	BP-treated	MC-treated
			% of total radioactivity[a]				
Unreacted BP	40	13	22	74	14	16	35
Ethyl acetate-extractable metabolites	39	52	59	22	62	62	38
Aqueous phase	21	35	19	4	24	22	27
			% of Ethyl acetate-extractable metabolites[b]				
"Prediol"[c]	5	14	11	2	18	13	11
BP 9,10-dihydrodiol	44	52	47	37	47	49	24
BP 7,8-dihydrodiol	32	17	24	36	21	22	14
BP 3,6-quinone	–[d]	4	2	2	3	3	13
3-Hydroxy BP	19	11	16	17	9	10	19
9-Hydroxy BP	–[d]	2	–[d]	5	2	2	17

[a] Incubation conditions are given in the text; 5 nmol of BP was used per each incubation. Metabolite extracts were from fish held at 13°C.

[b] Based on major components.

[c] Components (presumably triols and tetrols) eluted before BP 9,10-dihydrodiol.

[d] Less than 0.5%

[Taken in part from Varanasi et al. 1980] month, while the silty sediment (Experiment One) lost only 4% during the same period (Fig. 9). By 126 days the silty sediment had lost an additional 77%.

The composition of the aromatic hydrocarbons in the two sediment types contaminated with PBCO differed slightly. Initially the relative concentration of the minimally substituted benzenoid compounds in the silty sediment (Fig. 10) was much higher than in the sand sediment (Fig. 11). However, after 4 mo of exposure to running seawater, the concentrations of benzenoid compounds associated with the oiled silty sediment were greatly reduced.

The uptake of petroleum hydrocarbons into muscle tissues by English sole during the first 30 days of exposure to silty sediments contaminated with PBCO has been previously reported (Malins et al. 1979). The muscle tissues of fish from Experiment One of the currently reported studies were analyzed at 91 and 126 days after exposure. No aromatic hydrocarbons were detected in tissues at these times.

The muscle tissues of the English sole from Experiment Two (sandy sediment, 1% PBCO) were analyzed after 38 days of exposure. Only 1- and 2-methylnaphthalene were found at levels of 26 and 41 ng/g (dry wt), respectively. In a previous experiment in which sandy sediment was contaminated with 0.2% (v/v) PBCO, no aromatic compounds were detected in muscle tissue of English sole during this time period (McCain et al. 1978). Thus, the 5 times higher initial concentration of PBCO in the sediments used in Experiment Two was reflected in the detectable levels of the methylnaphthalenes in the muscles of oil-exposed English sole.

Biological Effects of Exposure to Oiled Sediments

After 1 mo of controlled laboratory exposures, most of the oil-exposed and control fish in both Experiments One and Two developed severe hepatocellular lipid vacuolization (HLV). All of the oil-exposed fish with severe HLV (9 of 12) also had intrahepatic sinusoidal compression and hepatocellular chromatin emargination, while only one control fish (1 of 11) had the latter two conditions. Sinusoidal compression suggests that the amount of lipid vacuolization in the hepatocytes was sufficient to cause cellular hypertrophy. Hepatocellular chromatin emargination involves the accumulation of chromatin around the nuclear membrane of a hepatocyte. This condition is considered to be one of the earliest events in cellular necrosis (Robbins and Cotran 1979). Since both this condition and sinusoidal compression were not detected in oil-exposed fish after 3 mo of exposure (Experiment One), they, like severe HLV, appear to be reversible.

In Experiment One, hematological differences were consistently observed between oil-exposed and control groups (Fig. 12). The average values for hematocrit (17.4%) and hemoglobin concentration (3.6 g/dl) for oil-exposed fish were significantly lower ($P=0.05$) than the average hematocrit (19.6%) and hemoglobin values (4.2 g/dl) in control fish.

In the previously reported experiment with English sole exposed to PBCO-contaminated sediment for 4 mo (McCain et al. 1978), more oil-exposed than control fish lost weight and became emaciated. The average coefficient of condition (ACC) values ($k=\text{weight}/\text{length}^3$) for the English sole sampled in Experiment One were not significantly different, however, between control and oil-exposed fish during the 126 days. Both groups, following a slight decline in the ACC values during the first month of exposure, had essentially constant

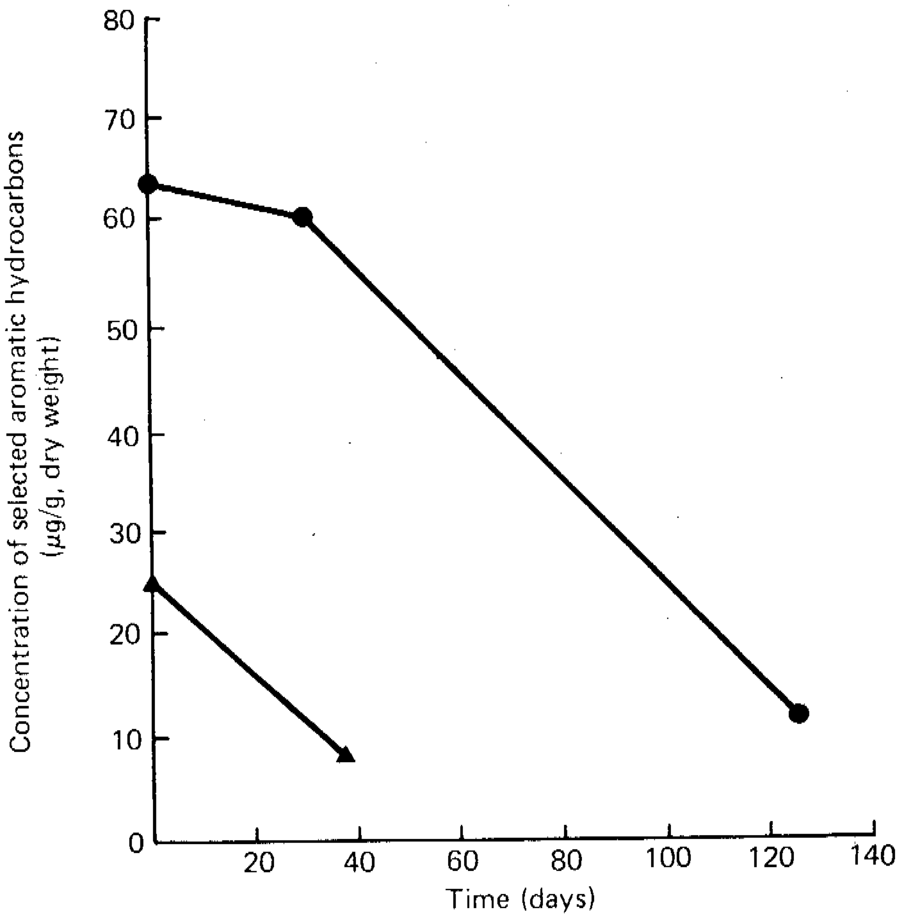

FIGURE 9. Cumulated concentrations of selected aromatic hydrocarbons in PBCO-contaminated sediments from Experiment One (silty sediment, -●-) and Experiment Two (sandy sediment, -▲-). Both experiments had initial PBCO concentrations of 1.0% (v/v).

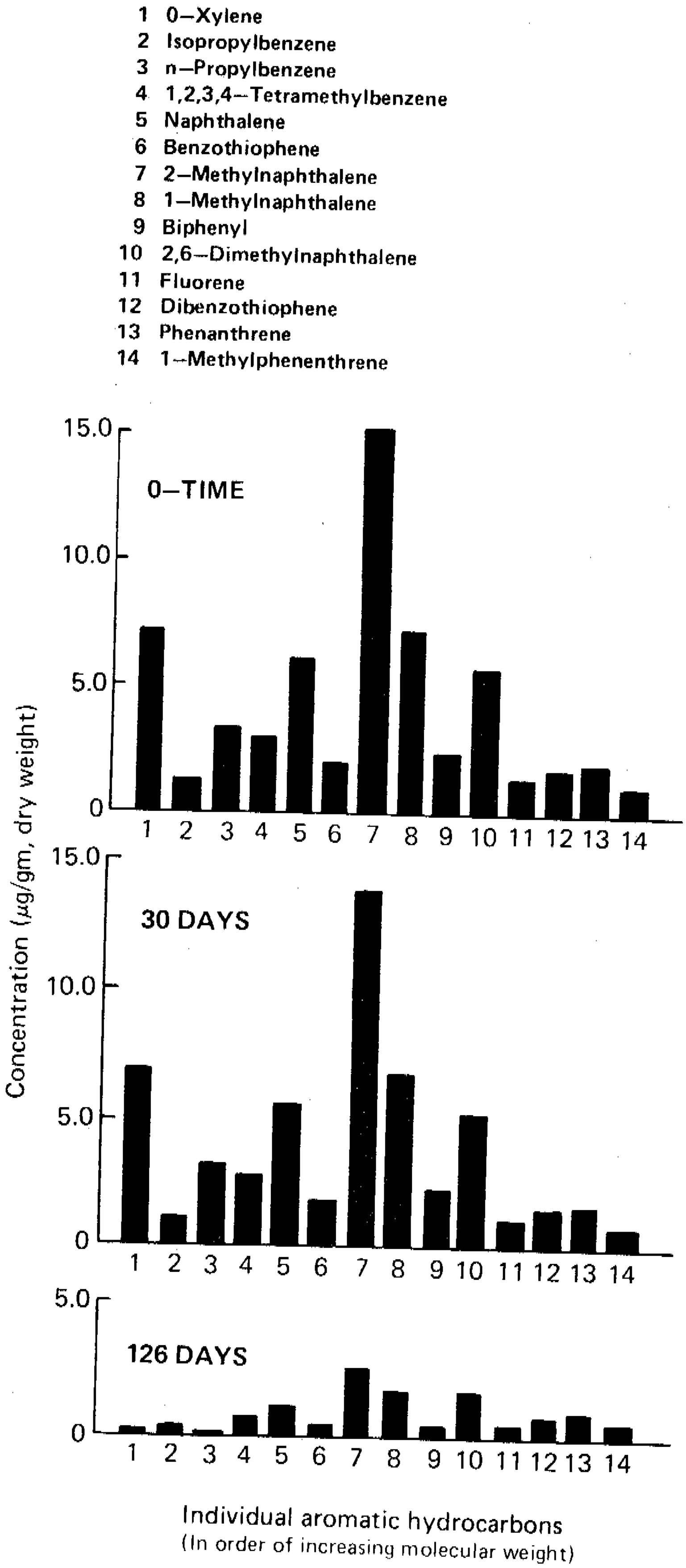

FIGURE 10. Concentrations of major aromatic hydrocarbons in PBCO-contaminated silty sediment (Experiment One) initially (0-time), and at 30 and 126 days.

1 0–Xylene
2 Isopropylbenzene
3 n–Propylbenzene
4 1,2,3,4–Tetramethylbenzene
5 Naphthalene
6 Benzothiophene
7 2–Methylnaphthalene
8 1–Methylnaphthalene
9 Biphenyl
10 2,6–Dimethylnaphthalene
11 Fluorene
12 Dibenzothiophene
13 Phenanthrene
14 1–Methylphenenthrene

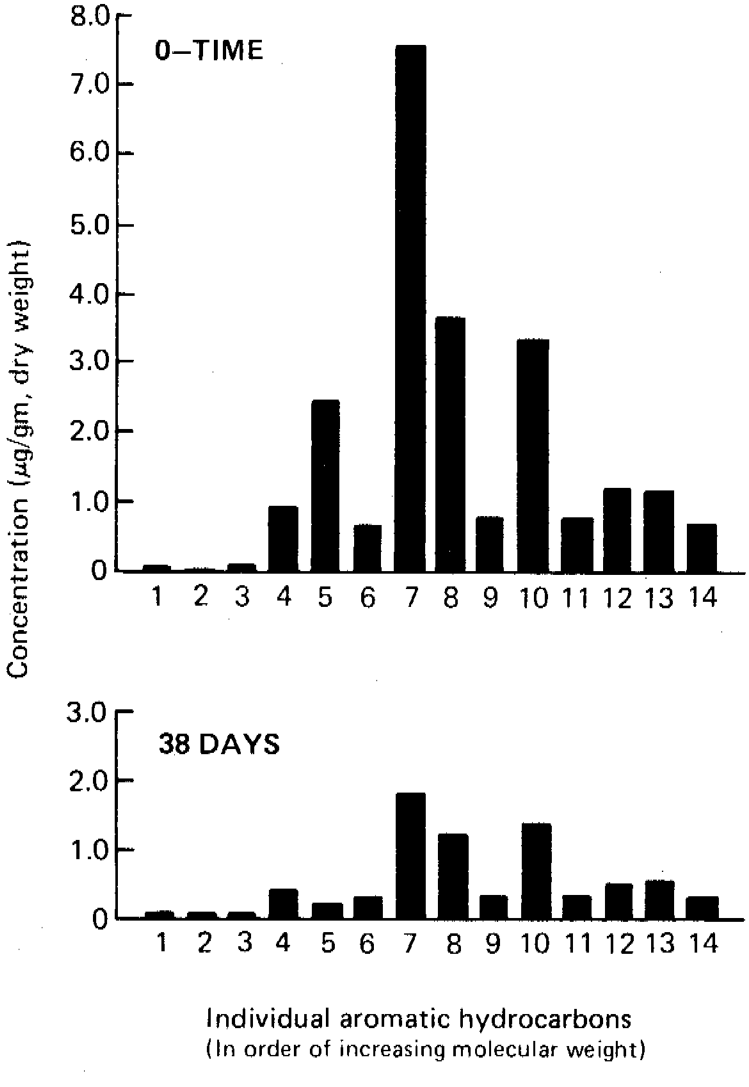

FIGURE 11. Concentrations of major aromatic hydrocarbons in PBCO-contaminated sandy sediment (Experiment Two) initially (0-time) and at 38 days.

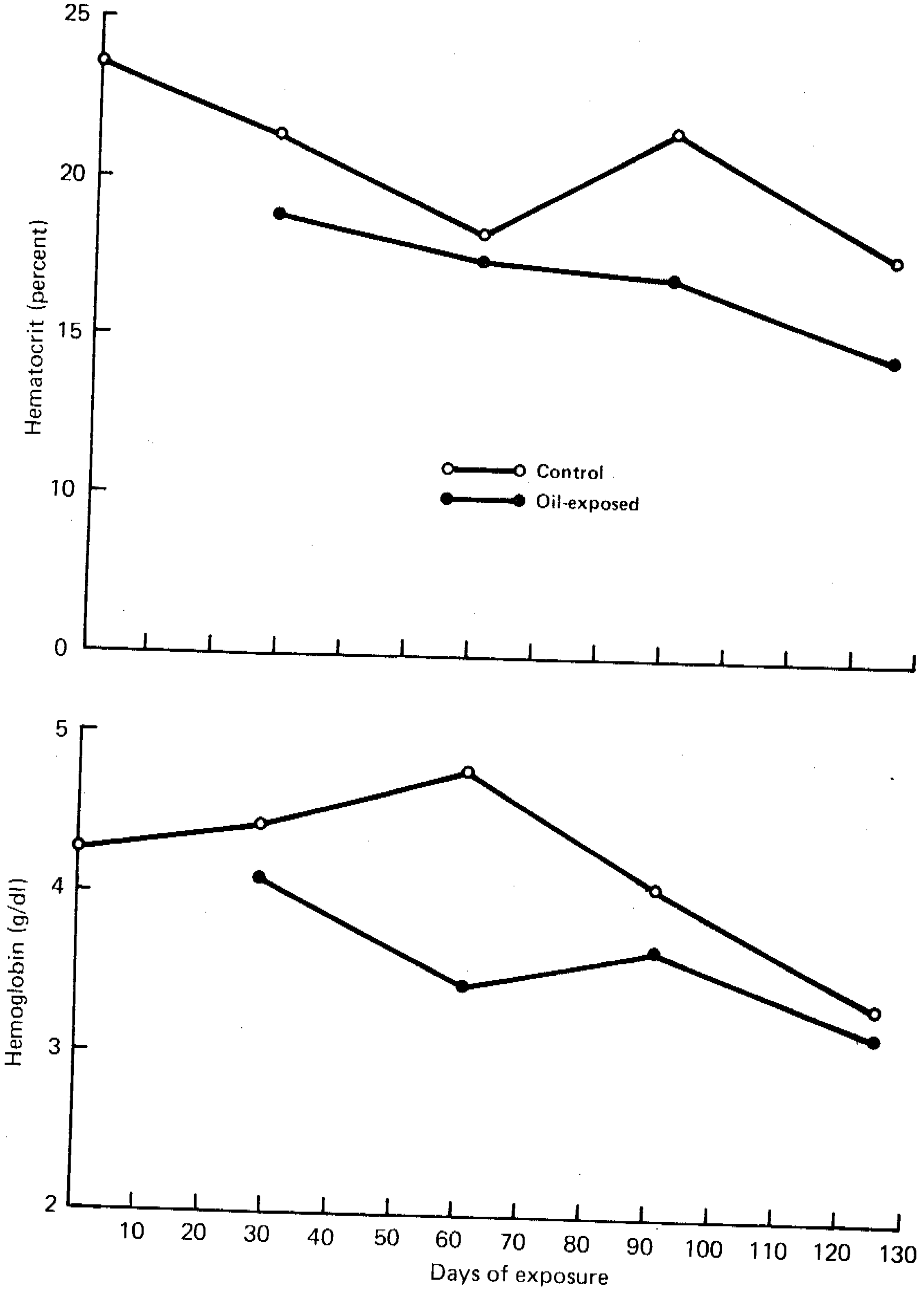

FIGURE 12. Concentrations of hemoglobin and hematocrit values in oil-exposed (-●-) and control (-o-) English sole over a 126-day period (Experiment One).

ACC values during the experiment. Also, no significant difference was observed between the ACC values of the control and oil-exposed groups in Experiment Two.

PHYSIOLOGY

Chum Salmon

Mortality of embryos in oil-treated and control groups was evaluated at two intervals during development: 26 and 75 days after fertilization. Twenty-six days after fertilization eggs treated for 24 and 45 hr showed a higher mortality than controls, but after 75 days of development, mortalities for these groups were similar. Eggs treated intermittently (132 hr total exposure, see Section V) for the full duration of embryonic development of 75 days showed a marked increase in embryo mortality over controls (P=0.01).

After hatching, all 8 groups of chum salmon were held for 50 days to observe latent mortalities. Exposure to the SWSF of weathered PBCO was continued in two groups: Group 8 which was exposed continuously after fertilization, and Group 5 consisting of alevins which had not been exposed to the SWSF as embryos. In Group 3, late alevin exposure (day 92 after hatching to day 113), there were no mortalities; the cumulative mortality for all other groups of alevins is shown in Figure 13. Generally, the longer the duration of exposure to the SWSF the lower the survival. Highest mortality occurred in Group 8, which was exposed continuously after fertilization; in this group 70% of the alevins were dead by 12 days after hatching. The second highest mortalities occurred in Group 7. These were exposed continuously as embryos, but with no oil exposure as alevins; 50% of this group died within 12 days after hatching. Only 12% of the control alevins died during this period.

Alevins were removed from each trough 12 days after hatching and examined for gross abnormalities. Three types of abnormalities were evident: malformed yolk sac, "domed" head, and "upturned" notochord.

The normal yolk sac shape is elliptical compared with the foreshortened and bulbous sac observed in some oil-exposed individuals (Figs. 14, 15). This abnormality occurred in the majority of oil-exposed groups, but was most frequent (61%) in those exposed continuously after fertilization (Table 5).

Table 5. Gross morphological abnormalities observed in chum salmon alevins 12 days after hatching (87 days post fertilization).

Group	Exposure period (days post fert.)	Hours exposed	Sample size	% abnormalities		
				Yolk sac	head	notochord
1	(Control)	0	204	0	0	0
2	(14-26)	24	15	0	9	0
4	(1-26)	45	19	16	16	0
5	(75-87)	32	10	10	33	0
6	(26-75)	84	15	0	33	0
7	(1-75)	132	6	33	33	0
8	(1-87)	164	16	61	44	11

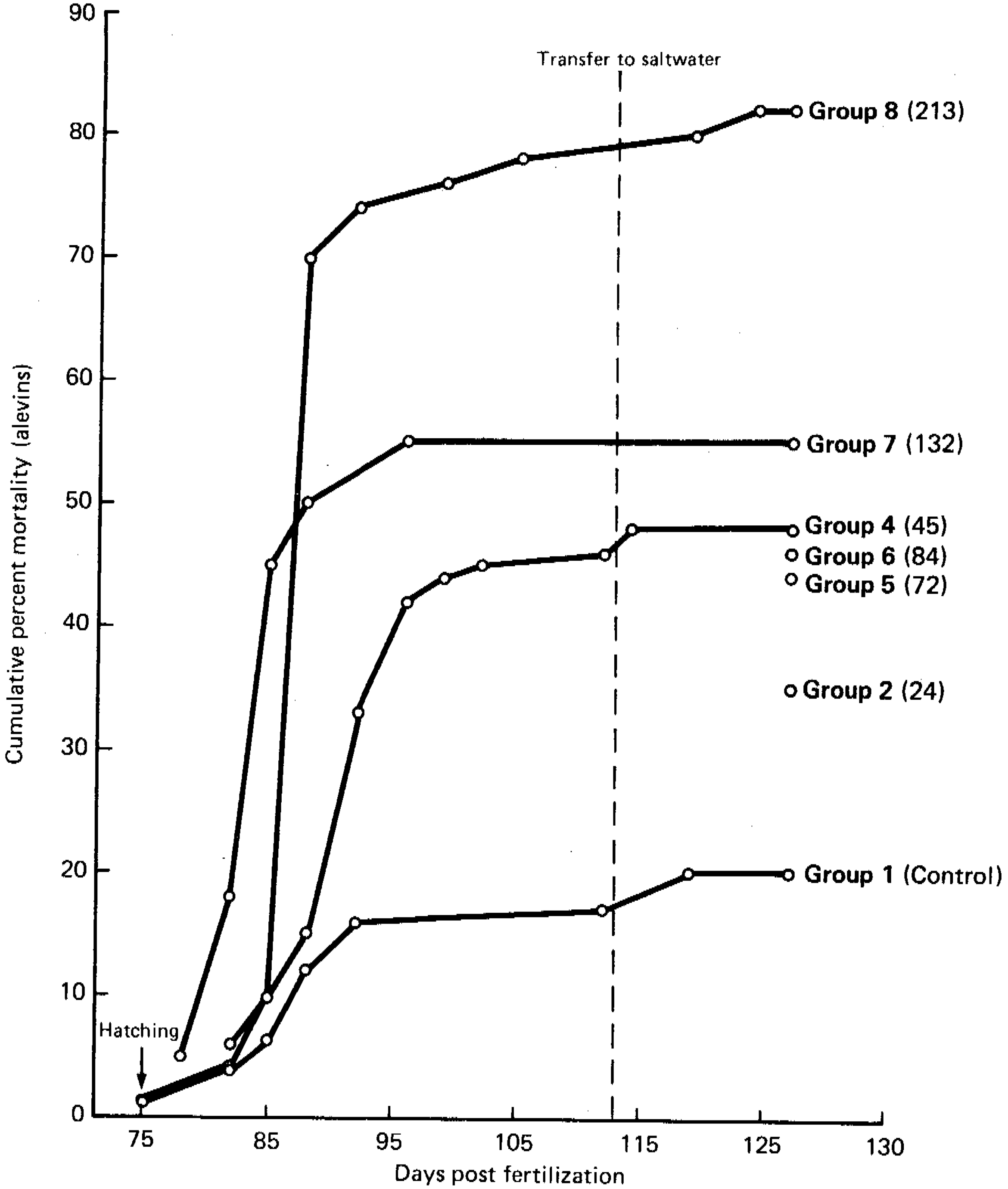

FIGURE 13. Cumulative percent mortality for alevin chum salmon exposed to the SWSF of weathered PBCO as embryos and/or alevins. Refer to Figure 3 for exposure at stage of development (groups). Total hr of exposure for each group are given in parenthesis.

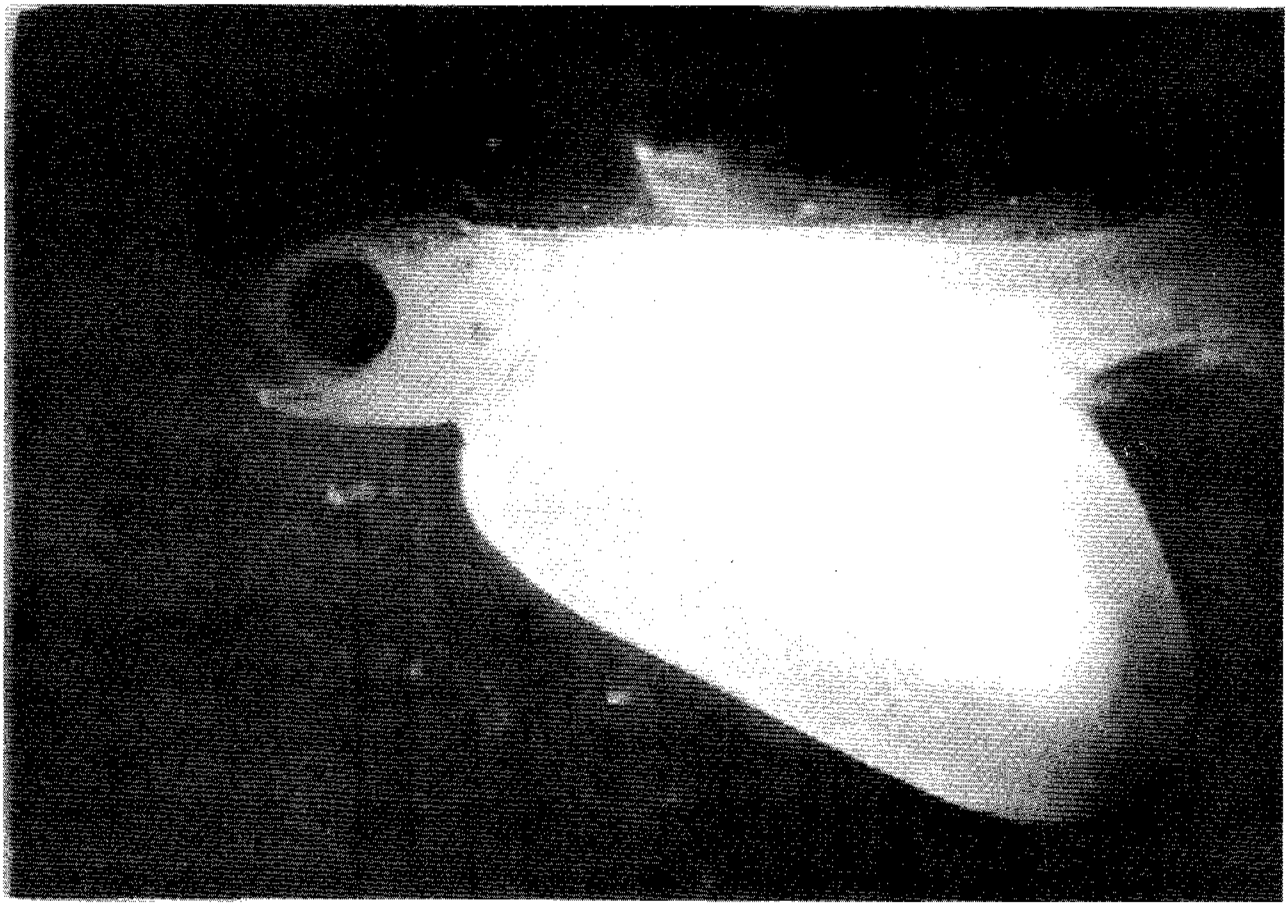

FIGURE 14. Chum salmon alevins showing normal yolk sac.

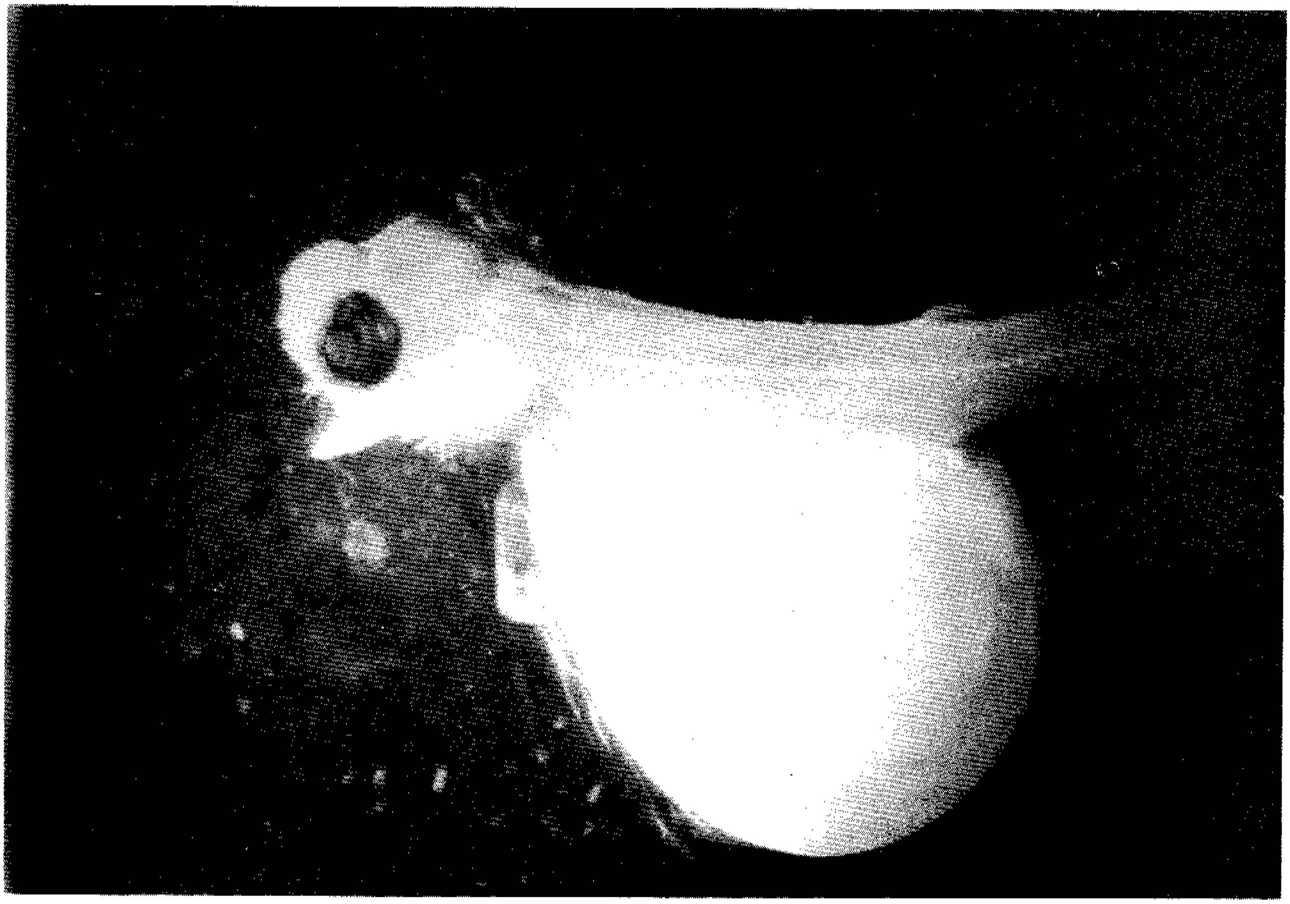

FIGURE 15. Chum salmon alevin exposed to the SWSF of weathered PBCO continuously since fertilization;with abnormal yolk sac.

Normally developing chum salmon have heads with a slight "dome" shape above the brain in newly hatched alevins (Distler 1954). Those groups exposed to oil had individuals with single- or double-"domed" heads (Fig. 16) which were much more prounounced than in Distler's illustrations and in our controls (Fig. 14). Samples of alevins with cephalic abnormalities were dissected and there was no evidence that the "dome" shape was a result of hydrocephaly. Subsequent processing of these samples and examination of stained tissue sections revealed normal appearing neurological tissue. "Upturned" scoliotic notochords occurred only in 12-day-old alevins exposed to oil continuously (164 hr); other groups did not exhibit any obvious scoliosis.

Three control and 5 oil-exposed alevins were processed for SEM with particular attention focused on the surface morphology of the skin and ciliated olfactory cells. Also, 5 alevins (3 oil exposed, 2 control) were processed for LM and TEM. Upon examination of the LM, SEM, and TEM preparations no differences were evident between the oil exposed and control alevins.

Eighteen days after hatching, exposure to the SWSF of weathered PBCO was initiated on Group 3 (Fig. 3). There were no mortalities in this oil-exposure group; however, it was observed that during the 3-hr exposure periods 50% or more of the alevins were swimming near the water surface at a 45 to 80 degree angle to the horizontal. This posturing at the surface appears typical of fry and juvenile salmon during exposure to petroleum hydrocarbons (Morrow, Gritz, and Kirton 1975; Cardwell 1973; Bean, Vanderhorst, and Wilkinson 1974). To determine if this surface behavioral response was sufficient to force alevins out of the gravel prematurely (which would subject them to displacement-drift down stream), a small-scale experiment was conducted. Twenty control alevins were placed in each of two 1-gallon jugs filled with coarse gravel and kept in subdued light.

Because salmon alevins are normally negatively phototropic, they immediately burrowed into the gravel. For the following 10 days (103-113 post-fertilization) one jug was flushed with SWSF 3 hr/day and one received uncontaminated brackish water as a control. There were no detectable differences in behavioral response between the two groups; 5 to 10% of the alevins in each jug emerged from the gravel and were lying on the gravel surface, and 10% mortality was observed in each group.

Flatfish

English Sole

Exposure of English sole eggs to fresh and weathered PBCO "mousse" layered on the water surface at a concentration of 4,000 ppm (volume oil/volume water) and to the SWSF of weathered PBCO all produced high percentages of deformed larvae or dead eggs and larvae, while in the control group 75% of the larvae were normal. Almost all (97%) of the eggs exposed to fresh PBCO layered on the water surface were killed. Weathered PBCO "mousse" layered on the surface produced about equal amounts of dead embryos and grossly abnormal larvae, and eggs exposed to the SWSF hatched, but this resulted in 75% grossly abnormal and dead larvae. These results are depicted graphically in Figure 17 (for nomenclature of categories of development, see Section V, Sources, Methods, and Rationale of Data Collection).

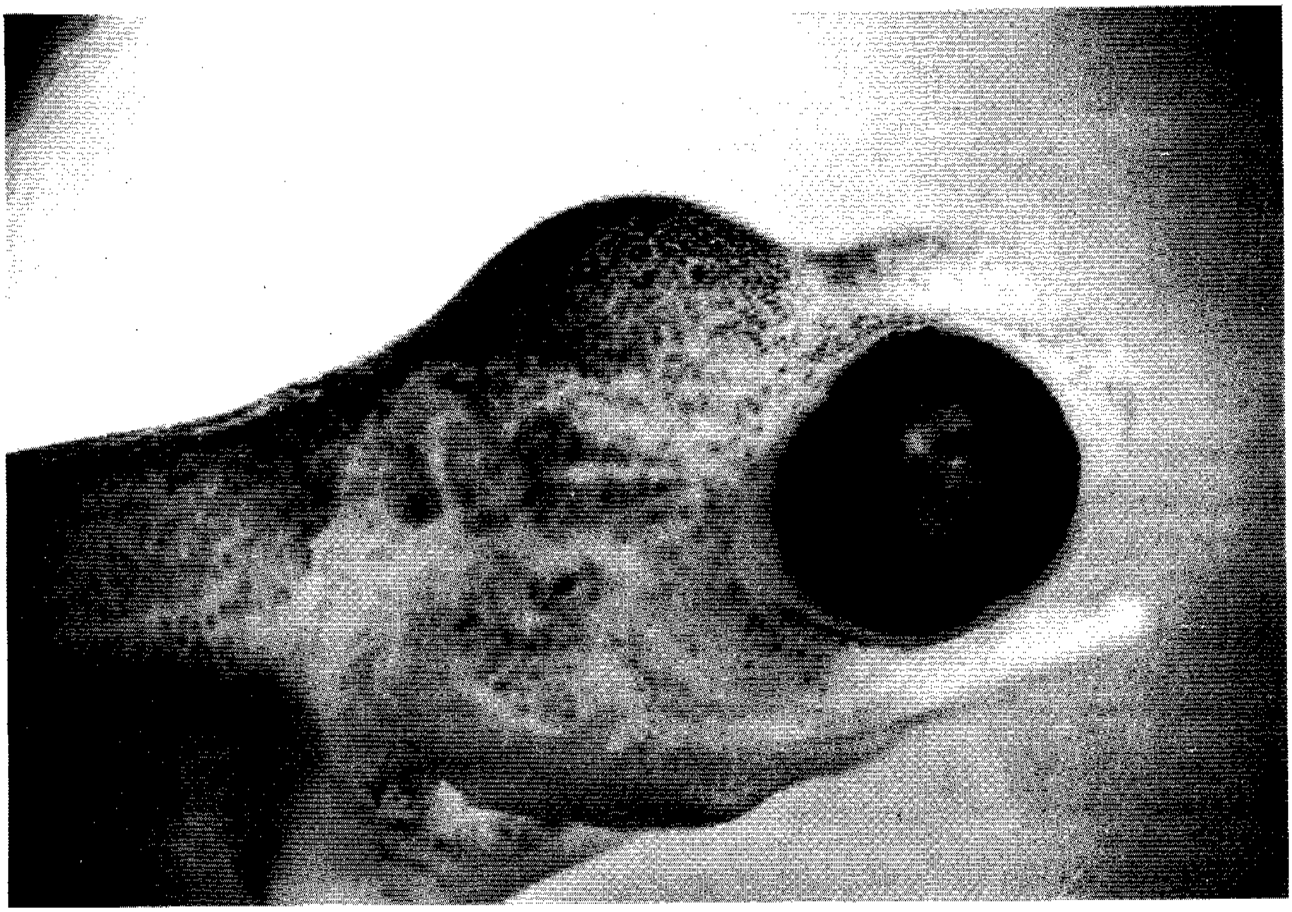

FIGURE 16. Chum salmon alevin with abnormal cephalic development.

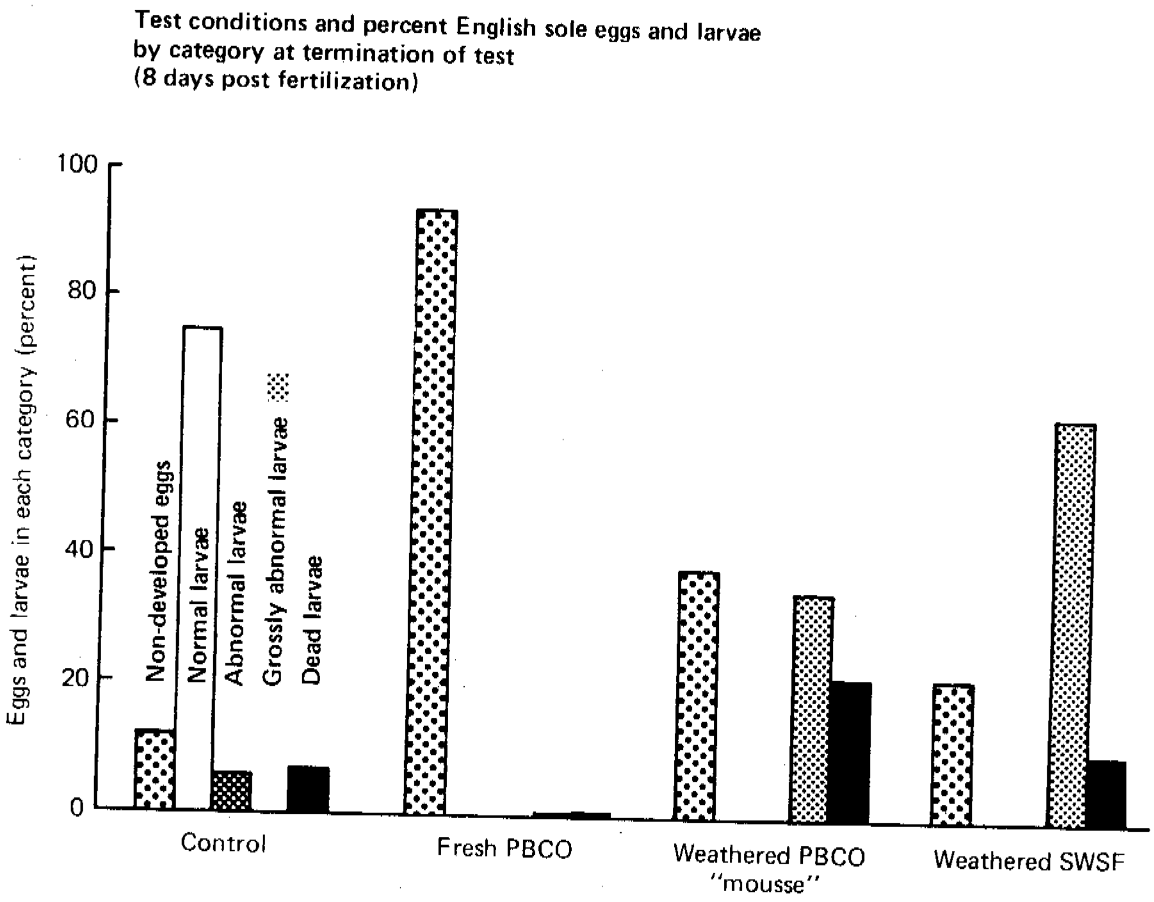

FIGURE 17. Test conditions and percent of English sole eggs and larvae by category of development at termination of test (8 days post fertilization).

Sand Sole

In the first experiments with English sole eggs the concentrations of oil used produced a high percentage of dead eggs and deformed larvae; thus, in follow-up experiments with sand sole eggs, both similar and lower concentrations of oil were employed. In an additional test, mineral oil was layered on the surface at a concentration of 2,000 ppm (v/v) to evaluate the effect of an oil film which did not produce high concentrations of GC-detected water-soluble components.

Effects of oil-exposure on eggs of sand sole are summarized in Figure 18. In all tests, counts of eggs and larvae were taken on the day of hatching; in three tests using either fresh or weathered PBCO layered on the surface, the oil apparently caused rupture of the egg membrane with resultant disintegration of the yolk and fragmentation of the chorion.

In replicate control tests an average of 89 ± 2% of the eggs hatched into normal larvae. Mineral oil had no apparent effect on development. Fresh PBCO layered on the surface at a concentration of 2,000 ppm had a devastating effect, as a result of which over 90% mortality occurred prior to development of a recognizable embryo. Weathered PBCO layered on the surface at either 4,000 or 2,000 ppm produced effects similar to that caused by fresh oil, with 67 to 88% mortality as nondeveloped eggs. The undiluted SWSF of weathered PBCO produced an entirely different effect. In this exposure, eggs developed and apparently hatched; however, two-thirds of the larvae were deformed. The most common abnormality was scoliosis in varying degrees of severity (Fig. 19). Severe secondary abnormalities were observed in some larvae: absence of yolk, shortened length, pigment scattered rather than in patches, finfold deformed, incomplete digestive tracts, and inactive larvae lying on the bottom of the containers. Exposure to the SWSF at a 50% dilution resulted in 79 ± 2% normal larvae and only 10 ± 1% deformed larvae.

SEM examination of 5 sand sole larvae exposed to the undiluted SWSF of weathered PBCO revealed 4 of 5 with severely reduced olfactory cilia (Figs. 20, 21), and 1 of 5 that appeared normal (comparable to controls). The olfactory cilia of larvae exposed to mineral oil during embryogenesis appeared normal. In fish with reduced olfactory cilia, the epidermal microridges, a feature of normal keratinocytes, were absent from the keratinocytes surrounding the olfactory epithelium. In addition, the keratinocytes of oil-exposed larvae were rounded and protruded from the skin surface, a possible indication of cellular hypertrophy.

TEM examination of sections from 8 sand sole larvae (4 exposed to undiluted SWSF, and 4 controls) revealed ultrastructural changes in the mitochondria of epidermal cells of this group of oil-exposed fish. Although the sample size was too small to definitely relate observed change to oil exposure, the abnormal mitochondria showed classic hydropic changes, a reduction in cristae and a reduction in the electron density of the matrix (Figs. 22, 23). Separation between the outer and inner mitochondrial membranes was quite pronounced and breaks in both membranes were observed. Other organelles such as the nuclei, Golgi assemblies, and microtubules were normal.

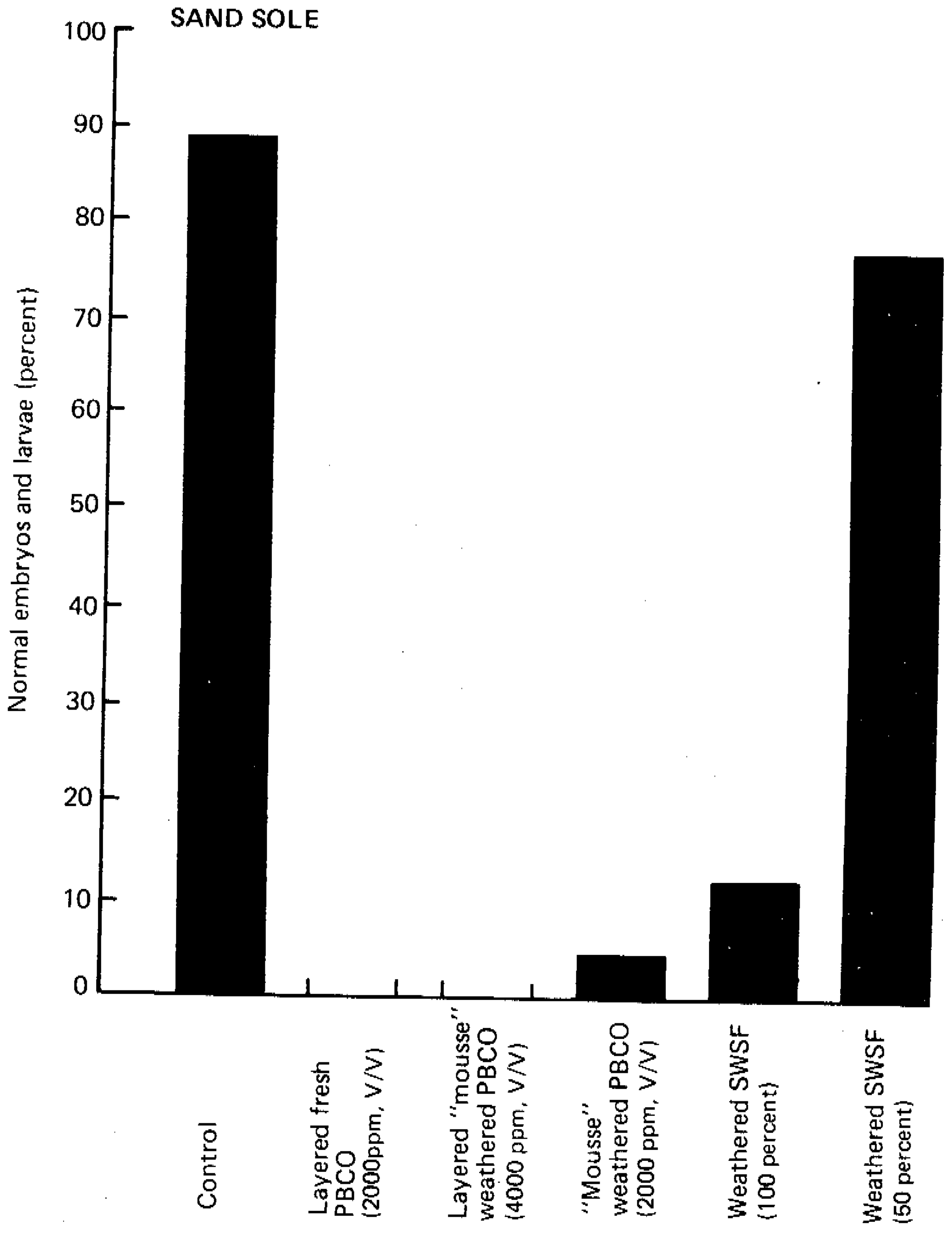

FIGURE 18. Test conditions and percent of sand sole eggs which developed into normal embryos and larvae.

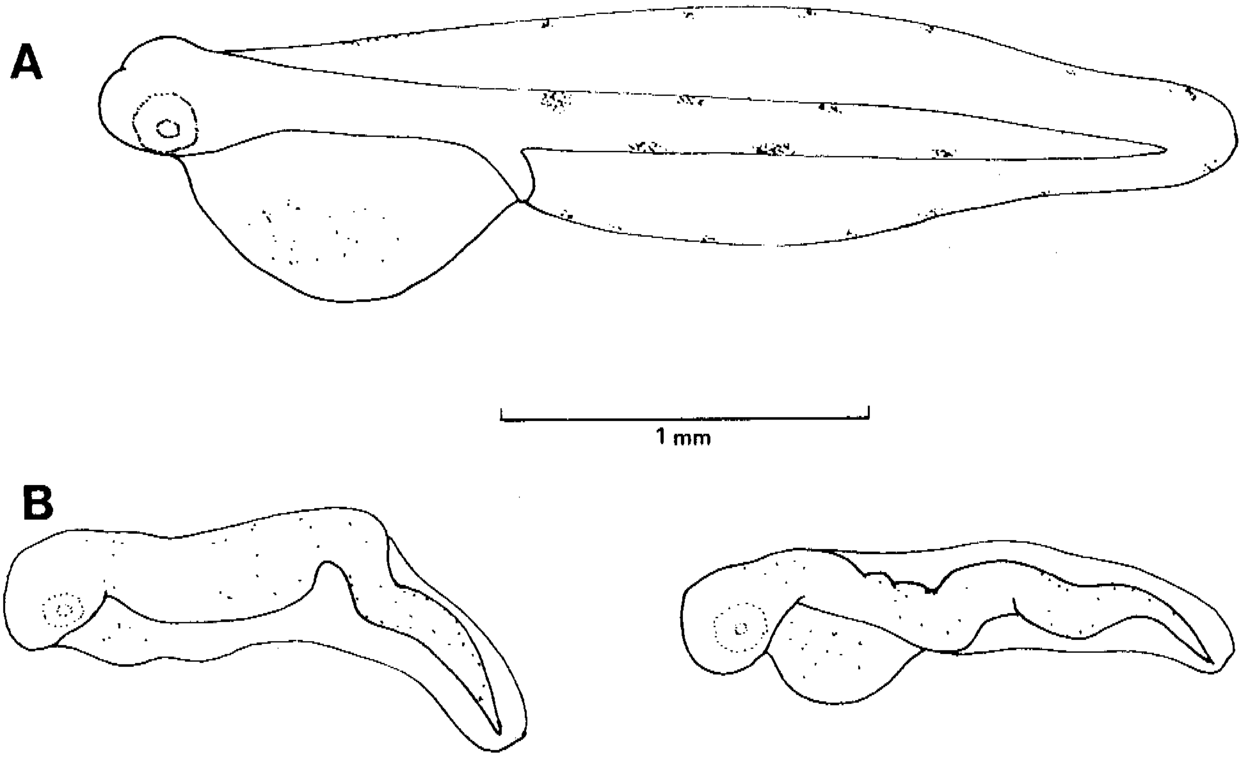

FIGURE 19. Normal sand sole larvae A, and two abnormal larvae B.

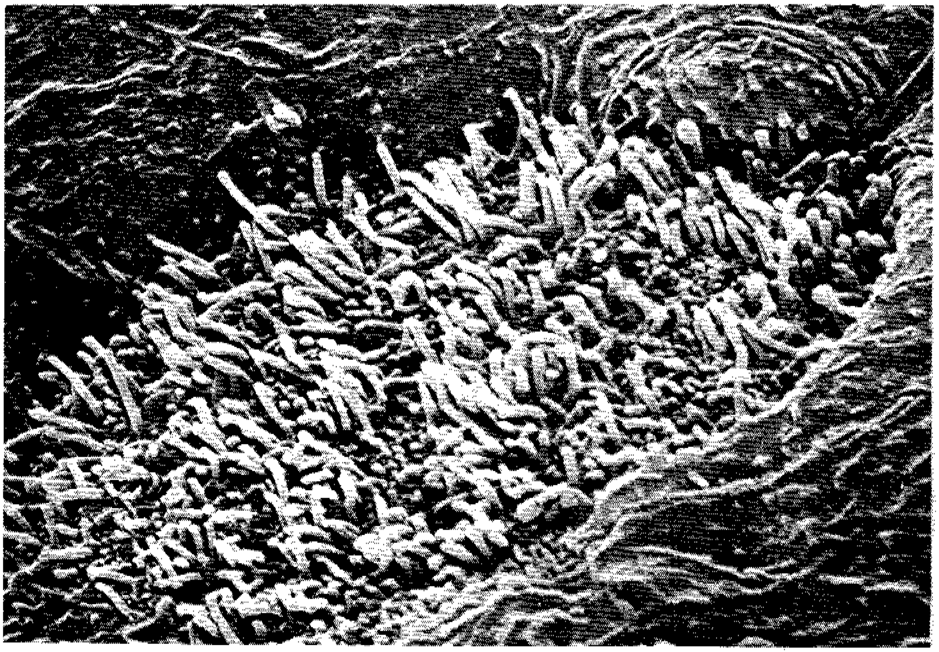

FIGURE 20. SEM of the olfactory cilia of a control sand sole (3,000 X).

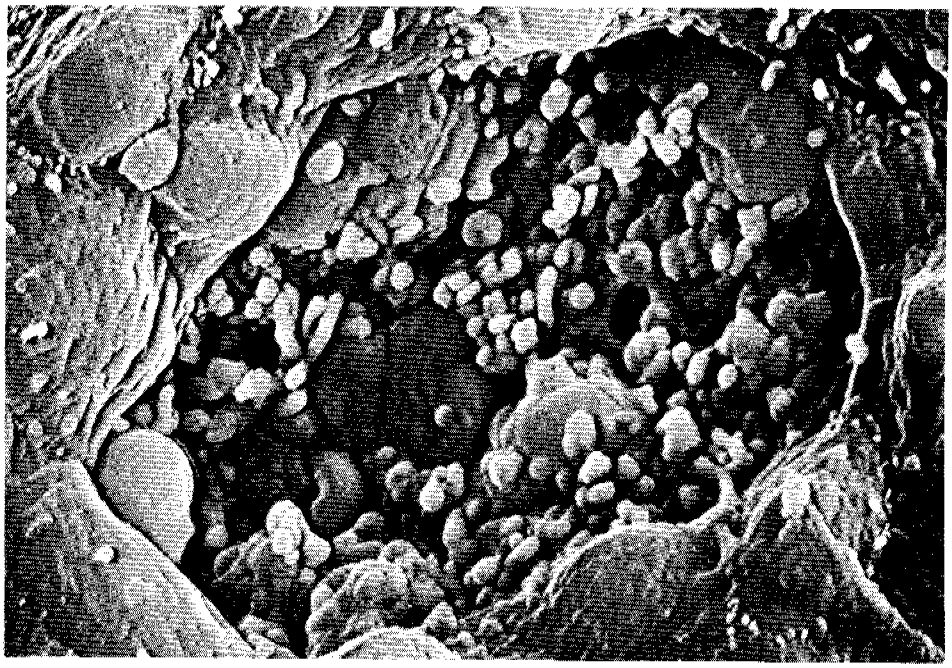

FIGURE 21. SEM of olfactory cilia from a sand sole larvae exposed to the SWSF of weathered PBCO during embryogenesis (3,000 X).

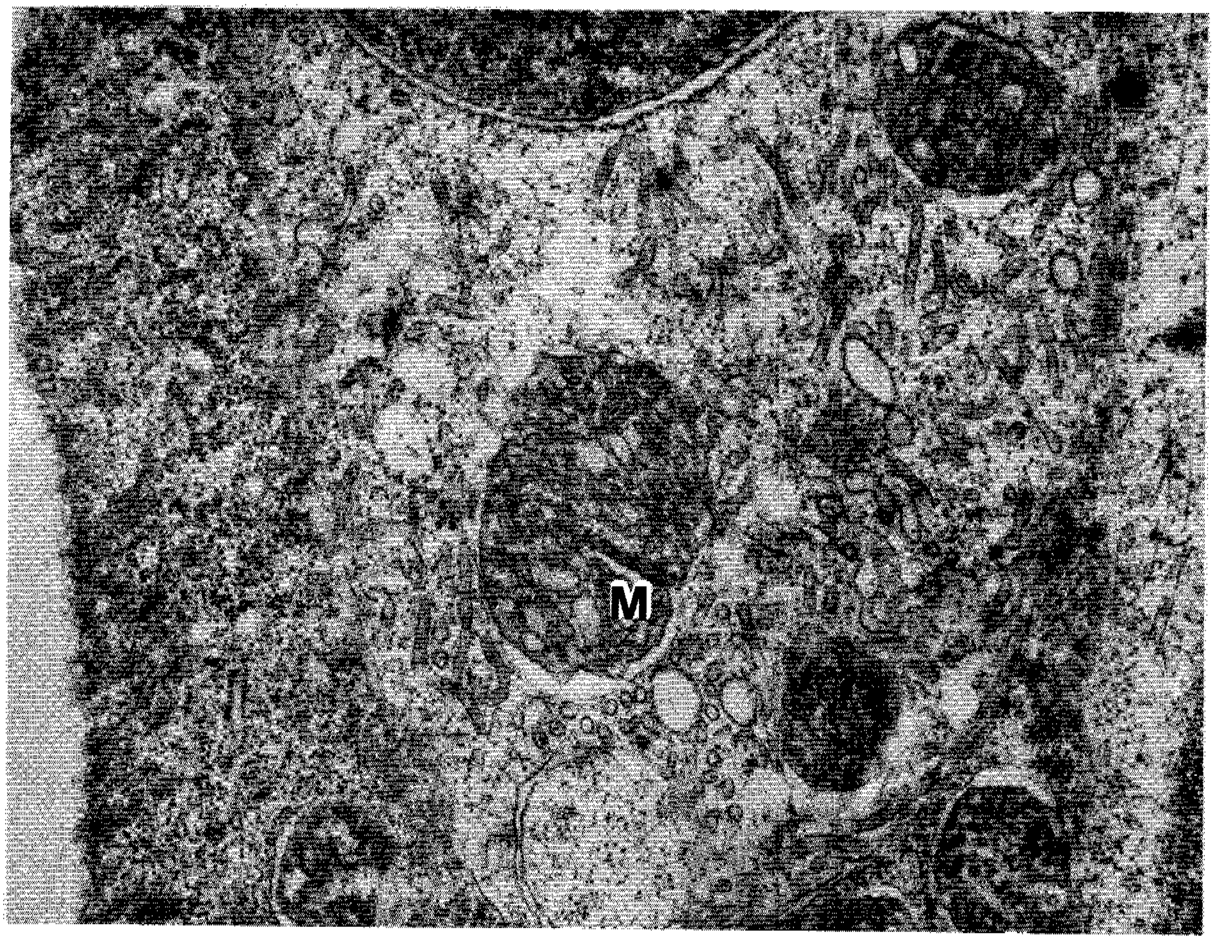

FIGURE 22. TEM of control sand sole larvae epithelium. Note the electron-dense matrix and abundance of cristae in the mitochondria (M). (34,000 X)

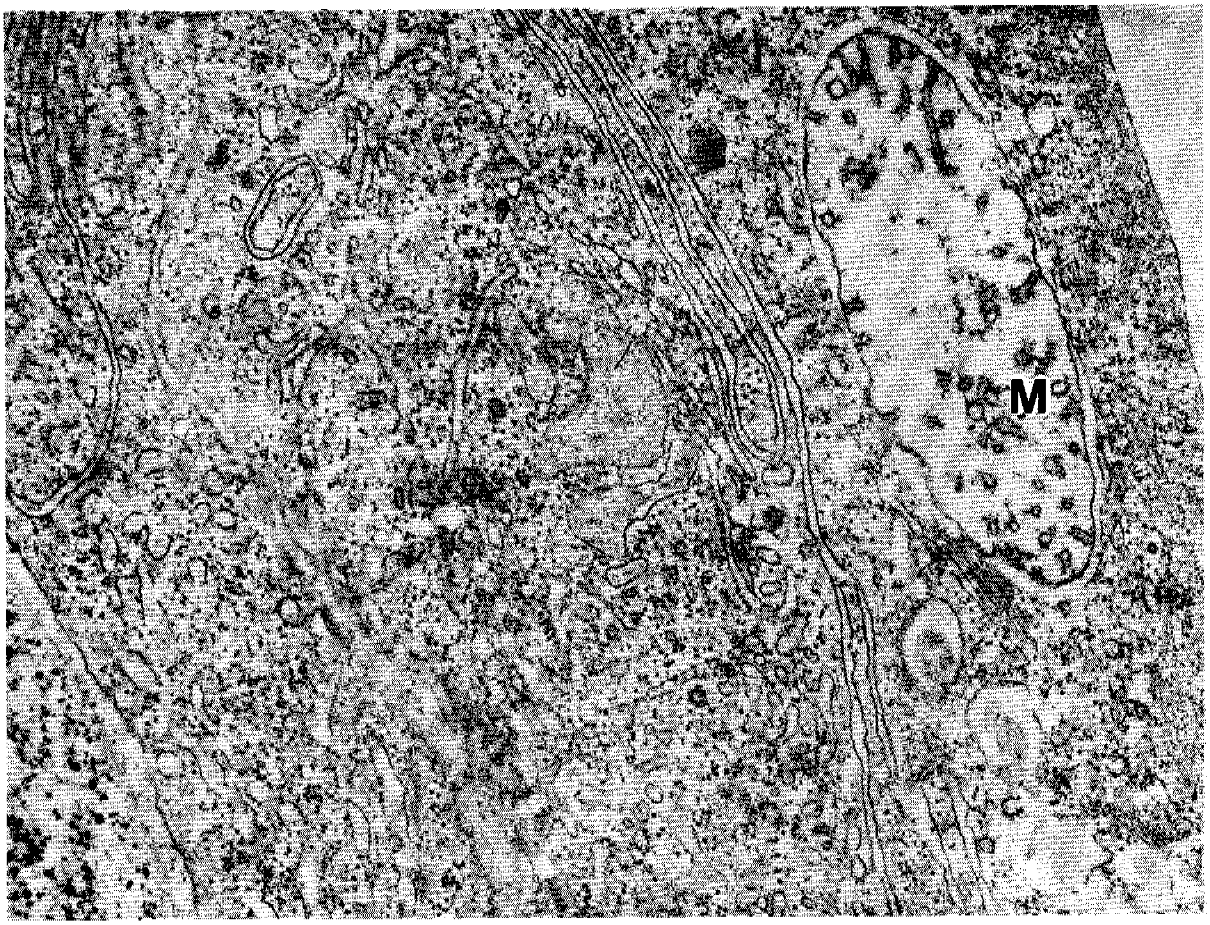

FIGURE 23. Epithelium of larvae exposed to the SWSF of weathered PBCO during embrogenesis. The mitochondria (M) are hydropic, have broken membranes, an electron-lucent matrix, and reduced cristae. (34,000 X)

Surf Smelt

The surf smelt eggs started hatching 30 days after fertilization with a distinct difference in hatching success between control groups of eggs and eggs exposed to the undiluted SWSF of weathered CICO (46% vs 5% successful hatching).

Samples of eggs were taken intermittently to measure heart rates, growth, and occurrence of abnormalities during embryogenesis and are being analyzed. Preliminary histological examination of larvae from the undiluted-SWSF exposure group revealed necrotic areas in the brain and retina.

VII. DISCUSSION

BEHAVIOR

Initial studies have been completed to examine the effect of the SWSF of CICO on the ability of chum salmon fry to avoid coho predators. These studies were primarily designed to develop needed facilities and identify technical problems. The major studies are now in progress and will continue during the spring and early summer. Small chum fry at this time of year are at the developmental stage when they are considered to be particularly vulnerable to salmonid predators.

CHEMISTRY

The results showing that starry flounder were able to take up benzo[a]-pyrene from diet and oiled sediment (1% PBCO), and that the release of metabolites of BP was much slower than naphthalene metabolites indicate that metabolites of higher molecular weight aromatic hydrocarbons will persist in tissues of fish over a longer period. It is reported (Herbes and Schwal 1979) that aromatic hydrocarbons having more than 3 rings accumulate in sediment because they are less prone to microbial degradation than hydrocarbons such as benzenes and naphthalenes. These findings together with the present results suggest that although higher molecular weight hydrocarbons, such as BP, are minor components of petroleum (MacLeod 1980), their metabolites may be bioconcentrated in tissues of benthic organisms to critical levels that promote the onset of deleterious biological effects. Our results suggest the need to assess the effects of long-term exposure of benthic organisms to this fraction of petroleum.

The results also show that both naphthalene and benzo[a]pyrene were largely converted to their dihydrodiols and conjugated derivatives by flatfish. The presence of BP-7,8 dihydrodiol in bile of BP-exposed starry flounder suggests strongly that "toxic" metabolites (e.g., diolepoxides) were produced in liver of flatfish because BP 7,8 dihydrodiol is the precursor of the ultimate carcinogen, BP 7,8-dihydrodiol 9,10 epoxide, of BP. This compound binds covalently to DNA in mammals (Sims et al. 1978). Binding of xenobiotics to DNA is the first step in events leading to genetic damage and tumor formation.

It was very difficult to isolate metabolites from liver of BP exposed fish because of the presence of lipid. However, preliminary results show that BP was extensively converted into metabolic products in liver. The ability of liver enzymes of flatfish to metabolize BP was also determined by using liver extracts. The results show that liver enzymes of pleuronectid (starry flounder and English sole) extensively converted BP into metabolites which were qualitatively similar to those produced by liver of rat and other mammals (Burke et al. 1977; Jones et al. 1978). However, the metabolites formed by fish liver extracts were characterized by the preponderance on non K-region dihydrodiols (e.g., BP 7,8-dihydrodiol and BP 9,10 dihydrodiol). It should be noted that non K-region oxygenation is believed to be very important for covalent binding of metabolites of PAH to DNA.

Much of the petroleum released into the marine environment probably will accumulate in bottom sediment, and, as a consequence, benthic fishes will be exposed to increasing concentrations of PAH. The present results showing that the magnitude of increase in the *in vitro* binding was much greater for English sole after treatment with PBCO than for starry flounder suggest that English sole was more sensitive to petroleum exposure than starry flounder. These results are in agreement with results described in Pathology that English sole was more sensitive to PBCO exposure in sediment than starry flounder.

It has been proposed that the induction of hepatic aryl hydrocarbon monooxygenases (AHM) in fish can indicate the presence of toxic chemicals in the environment (Payne 1976). Our results (Varanasi et al. 1980a) and those of others (Ahokes et al. 1979) show that the magnitude of increase in *in vitro* binding of BP to DNA on pre-exposure of fish or rat to PAH (MC or BP) was relatively greater than the increase in AHM acitivity. Covalent binding of BP to DNA may prove to be more sensitive than AHM activity as an index of pre-exposure of fish to certain toxic chemicals. Moreover, the binding value serves as a useful index for correlating metabolism with the carcinogenicity of a PAH. The carcinogenic potential of a compound to mammals is roughly correlated with the extent of covalent binding to DNA (Buty et al. 1976; Pelkonen et al. 1978). Accordingly, studies to assess the extent of covalent binding of a variety of pollutants to cellular DNA in various target tissues of marine organisms may give useful information.

The hepatic mixed function oxidases, together with conjugating enzymes, are responsible for both activation and detoxification of PAH. Therefore, treatment of animals with chemicals that alter these enzyme systems can result in either increased or decreased toxicity of the PAH. Pretreatment of flatfish with PAH (MC, BP, or PBCO) in the present study resulted in a marked decrease in the proportion of BP 7,8-dihydrodiol and a considerable increase in the proportion of "prediol" components (Table 4) indicating that BP 7,8-dihydrodiol was further metabolized by liver enzymes to 7,8,9,10-tetrahydro-7,8,9,10-tetrahydroxy BP (prediol component) which is formed via BP 7,8-dihydrodiol 9,10-epoxide (Jones et al. 1978), the postulated ultimate carcinogen of BP (Sims et al. 1974).

In conclusion, the results showing a considerable retention of metabolites of BP by flatfish together with the findings showing the ability of the liver enzymes to convert BP into mutagens and carcinogens are of concern especially in view of the possibility that concentrations of carcinogenic PAH will be increasing in the marine environment. Moreover, the results (Varanasi et al. 1979, 1980b) showing the presence of PAH and their metabolites in edible tissues (e.g., muscle) of PAH-exposed fish may be of public health interest.

PATHOLOGY

Pathological Changes in Flatfish from Exposure to Oil-Contaminated Sediment

The major differences between the sediment-exposure experiments detailed in this report and similar experiments from the two previous years were the use this year of younger experimental fish (English sole) and higher concentrations of PBCO in the sediments (1% v/v). The experimental results with both adult and juvenile English sole were quite similar. The oil-exposed fish in both age groups developed hematological changes (lowered hematocrits and hemoglobin levels), and transitory histological changes in the liver. The observed changes suggest that English sole are temporarily stressed by exposure to oil-contaminated sediments. It is reasonable to anticipate from this evidence that these fish may undergo a temporarily impaired viability during initial periods of exposure to petroleum-contaminated sediment, but that they may accomodate to it.

PHYSIOLOGY

Survival of chum salmon embryos was not decreased at hatching following exposure to slightly weathered PBCO for either the first third or the last two-thirds of their development period. However, continuous exposure to the weathered oil throughout embryonic development did significantly (P=0.01) reduce embryo survival, compared with controls. The primary effect of oil exposure during embryonic development was on alevins in the first 10 to 15 days after hatching. For embryos and alevins exposed continuously during development, only 20% of those hatching survived through yolk sac absorption; 85% of the control alevins survived during a comparable period.

Fresh PBCO and weathered PBCO "mousse" layered on the water surface generally resulted in mortality of flatfish eggs prior to development of a recognizable embryo. The SWSF of weathered PBCO had a different effect, with apparent high embryo survival, but with few normal larvae. The results of these experiments suggest that the release of oil in an area where flatfish are spawning would potentially be very detrimental to egg and larval survival.

Surf smelt eggs were exposed to the SWSF of weathered CICO for a total of 69 hr, and at the highest SWSF concentration only 5% hatched. However, for chum salmon eggs exposed to approximately the same SWSF concentration of weathered PBCO for a total of 132 hr, embryo and alevin survival was over one magnitude greater. Until chemical analysis is complete we do not know if this difference is due to variation in hydrocarbon products between the two weathered crude oils, species susceptibility, or relative duration of the embryonic stages between these two species. From fertilization to hatching, the chum salmon required 2 1/2 times longer to complete embryonic development than surf smelt. Thus, oil exposure over a similar time period in surf smelt encompasses relatively more embryonic development than eggs of species with longer incubation times.

Damage to the olfactory epithelium has been reported in adult Atlantic silversides (*Menidia menidia*) exposed to fractions of Texas-Louisiana crude oil. The saltwater-soluble fraction induced epithelial metaplasia and loss of the sensory epithelium (Gardner 1975). In the sand sole, the reduction of the ciliated cell surfaces of the olfactory epithelium that was observed in the present studies is similar, although not as severe as the loss of the ciliated epithelium reported by Gardner.

The skin structure of sand sole, as revealed by TEM, appeared normal except for hydropic mitochondria, which are commonly encountered in many types of tissues from animals subjected to various stresses. Histological examination of chum salmon alevins revealed no abnormal cell types or structural changes as were noted in the epithelium of sand sole.

VIII. CONCLUSIONS

BEHAVIOR

An initial study demonstrated that exposure to SWSF of CICO altered some characteristics of chum salmon fry behavior; there was, however, no demonstrable change in their ability to avoid predation by large coho salmon predators in this preliminary study.

CHEMISTRY

The results demonstrating slow release of benzo[a]pyrene metabolites from flatfish suggest that although BP is a minor component of petroleum (e.g., PBCO, CICO), metabolites of BP may accumulate in tissues of benthic organisms to a critical level leading to deleterious biological effects. One of such damaging effects was demonstrated to occur when BP was metabolized by flatfish liver to reactive intermediates that bind to DNA. Binding of metabolites of PAH to DNA is an important and necessary step in the chain of events leading to genetic damage and tumor formation.

PATHOLOGY

The results of 3 years of experimentation on the pathological effects of exposing flatfish to PBCO-contaminated sediments suggest that, of the flatfish species tested, English sole are the most sensitive to adverse effects of crude oil. The changes observed appear to be mostly reversible and not directly life-threatening, although they do reflect alterations that may reduce fitness, and thereby survival, of flatfish in heavily oiled environments.

PHYSIOLOGY

Exposure to fresh and/or weathered crude oil induced high levels of mortality in embryos and larvae of salmon, flatfish, and smelt.

The effect of oil exposure on chum salmon eggs showed up primarily as mortality in the alevins. Oil exposure of newly hatched alevins, not previously subjected to oil contamination during embryogenesis, resulted in mortality double that of controls. In addition, this group of alevins exhibited cephalic abnormalities and deformed yolk sacs typical of other groups of alevins which were exposed to oil only during the embryonic stage. Mortality of alevins was generally directly related to total hours of oil exposure.

Experiments with English and sand sole eggs demonstrated quite clearly that fresh PBCO and weathered "mousse" of PBCO layered on the water surface produced extremely high embryo mortalities. With sand sole eggs this method of oil exposure fragmented the egg envelope in early embryonic development; this characteristic was not examined in English sole. Exposure of both species of flatfish eggs to the SWSF of weathered PBCO resulted in dead and deformed larvae which may be related to premature hatching due to egg envelope fragmentation.

At the cellular level, no morphological effects were detected in chum salmon alevins from exposure to the SWSF of weathered PBCO, but in sand sole larvae there were several deleterious changes evident particularly in the olfactory cilia and epidermal mitochondria.

IX. NEED FOR FURTHER STUDY

Research on the effects of petroleum hydrocarbons on flatfish should deemphasize work with adults and juveniles, with the exception that possible effects of petroleum-dispersant mixtures on these life stages should be examined. Generally, biological changes in eggs and larvae of this species resulting from petroleum exposure should be given preferential consideration.

Studies conducted under this program have shown that PAH are converted into a variety of oxidized products in marine organisms. The extent of conversion is dependent on species, tissues, compounds, and mode and time of exposure. Accordingly, in the assessment of petroleum impact an immediate need exists for determining individual metabolites in tissues from environmentally exposed organisms. Thus reliable and rapid methods for the analysis of oxidized products in tissues and body fluids of marine organisms should be developed.

A complementary effort to increase our very limited understanding of the nature and extent of formation of oxidized products (photo-oxidative and microbiological) in marine environments is imperative. Studies relating to the routine analysis of these oxidized products and to their biological effects is also of vital importance in assessing the impact of petroleum products on marine life.

X. SUMMARY OF FOURTH QUARTER OPERATIONS

SHIP OR LABORATORY ACTIVITIES

Ship or Field Trip Schedule

Several trips were made by small boat or via car to various areas of Puget Sound to collect animals for testing. Research activities were conducted at the NWAFC, Seattle, and the Mukilteo facility of the NWAFC.

Scientific Party

The scientific party consists of scientists and technical personnel in several major study areas. The overall supervision of the research is carried out by Dr. Donald C. Malins, Principal Investigator, Director of the Environmental Conservation (EC) Division, NWAFC, Seattle, Wash. The scientific party also consists of the following persons from the EC Division, NWAFC:

Administrative

Gloria Sergneri, Administrative Officer

Kenneth E. Evans, Clerk-Typist

Behavior

Donovan R. Craddock, M.S., Fishery Research Biologist; in charge of studies of effect of oil pollution on predator-prey interactions.

John W. Blackwell, NOAA Corps Officer; assisting with predator-prey studies.

Chemistry (Analytical)

Donald W. Brown, M.S., Supervisory Chemist; Principal Investigator; Assistant Manager of NOAA National Analytical Facility (NAF).

Margaret M. Krahn, PhD., Research Chemist; hydrocarbon and metabolite analyses.

L. Scott Ramos, Chemist; hydrocarbon and metabolite analyses.

Victor D. Henry, Chemist; hydrocarbon and metabolite analyses.

Patty G. Prohaska, Chemist; hydrocarbon and metabolite analyses.

Donald D. Gennero, Physical Science Technician; hydrocarbon and metabolite analyses.

Chemistry (Research)

Sin-Lam Chan, PhD., Supervisory Research Chemist; Assistant Director, EC Division.

Usha Varanasi, PhD., Supervisory Research Chemist; Principal Investigator, biochemical effects of hydrocarbons and metabolites.

William T. Roubal, PhD., Research Chemist; biochemical effects of hydrocarbons and metabolites.

Robert C. Clark, Jr., M.S., Research Oceanographer; hydrocarbon and metabolite research.

Dennis Gmur, M.S., Chemist; assistant to Dr. Varanasi.

Peter S. Fraser, PhD., Research Chemist; works with Robert Clark on petroleum metabolite preparation.

Tom Hom, M.S., Chemist; assistant to Dr. Varanasi.

Kerstin M. Gleim, Chemist; assistant to Dr. Roubal.

Pathology

Harold O. Hodgins, PhD., Supervisory Fishery Research Biologist; Principal Investigator and overall supervisor of pathological, behavioral, and physiological studies.

Bruce B. McCain, PhD., Supervisory Microbiologist; Principal Investigator, in charge of work on petroleum in sediments and their effect on flatfish pathology; coinvestigator with Dr. Hodgins.

William D. Gronlund, M.S., Fishery Research Biologist; assistant to Dr. Hodgins and coinvestigator with Dr. McCain.

Donald H. Bark, M.S., Fishery Research Biologist; part-time assistant to Dr. McCain.

Mark S. Myers, M.S., Fishery Biologist; part-time assistant to Dr. McCain.

Michael H. Schiewe, M.S., Fishery Research Biologist; disease-resistance studies.

Keith K. Wong, Biological Laboratory Technician (Microbiology); assistant to Michael Schiewe.

Warren E. Ames, Fishery Research Biologist; assistant to Dr. McCain.

Physiology

Douglas D. Weber, M.S., Fishery Research Biologist; Principal Investigator, egg and larval studies.

David A. Misitano, M.S., Fishery Research Biologist; works with D. Weber on eggs and larvae.

Joyce W. Hawkes, PhD., Fishery Research Biologist; cell biology and electron microscopy.

Carla Stehr, Fishery Biologist; assistant to Dr. Hawkes.

Methods

The research is conducted primarily through laboratory studies. Except for slight modifications the methods used have been described earlier in this report or in previous OCSEAP reports.

Sample Localities/Ship or Tracklines - N/A

Data Collected or Analyzed

Behavior

Two new exposure systems were constructed for predator-prey studies--one to produce the SWSF of crude oil and the other to produce either water-accommodated oil or chemically dispersed oil.

In addition, more than 200 large coho salmon predators are being raised for testing and arrangements have been made to pick up 5,000 chum salmon fry for use as prey and transport them to our facility in mid-April, 1980.

Chemistry

The following types and number of samples have been analyzed between January 1 and April 17, 1980 for petroleum hydrocarbons:

Water	74
Sediment	24
Tissue	37

Methods for isolating metabolites of benzo[a]pyrene from liver of English sole exposed to BP in diet or in sediment are being standardized.

Currently we are measuring the total free radical burden in freeze-dried samples of liver microsomes prepared from fish taken from polluted and non-polluted regions of Puget Sound. We have shown that liver microsomes prepared from English sole taken from the Duwamish River contain significantly greater concentrations of free radicals than microsomes from fish taken from the Port Madison area, a region essentially free of industrial pollution. We are resampling the above areas in order to check the validity of our initial data.

A rapid, sensitive, and selective method for the analysis of naphthalene and its metabolic products in the bile of fish was developed. The low-fluorescent naphthalene and oxidized products were separated by reverse phase HPLC and detected by sensitive ultraviolet fluorescence spectrometry. In addition, a method for mass spectral analysis of thermally labile, conjugated metabolites of naphthalene has been developed using plasma desorption chemical ionization mass spectrometry with a modified direct insertion probe tip.

These integrated analytical methods may have application to other aromatic hydrocarbons and metabolites with some modifications in technique. Future refinement of these techniques may permit the study of petroleum organics and their metabolites in samples from polluted environments.

Pathology

Pathological Changes in Flatfish from Exposure to Oil-Contaminated Sediment

An experiment involving long-term exposure of English sole to PBCO-contaminated sediment (1.0% v/v) was initiated during 1979 using the facilities and protocols described in the accompanying Annual Report. During this quarter the 61- and 90-day samples of fish tissue and of sediment were taken for histological, hematological, and analytical chemical analyses.

a. Numbers and Types of Samples: Blood for hematology (4); Sediment samples for hydrocarbon analyses (4); Tissue samples for hydrocarbon analyses (6); Tissue samples for histological analyses (50).

b. Numbers and Types of Analyses: Hematology: Hematocrit (4); Hemoglobin (4); Total blood cell count (4); Differential white cell count (4).
Histology: Microscopic examination of histological specimens (50).
Chemical Analyses for Aromatic Hydrocarbons: Sediment samples (4); Tissue samples (6).

Effects of Petroleum on Disease Resistance

a. Numbers and Types of Samples: Adult spot shrimp for disease tests (300); Sediment samples for hydrocarbon analyses (4); Water samples for hydrocarbon analyses (4); Tissue samples for hydrocarbon analyses (6).

b. Number and Type of Analyses: LC_{50} determinations (2)--five shrimp per group and five groups per determination.

Physiology

English sole eggs and larvae were subjected to CICO under a variety of static exposure conditions; fresh and weathered CICO "mousse" layered on the water surface, the SWSF of weathered CICO, and the above in combination with a chemical oil dispersant. Water samples were collected for chemical analysis, and eggs taken for histological examination. Exposure of English sole eggs to the SWSF of weathered CICO in a flow-through system of exposure was not successful due to technical difficulties.

XI. AUXILIARY MATERIAL

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C. ORAL PRESENTATIONS

CLARK, R.C., JR. and D.C. MALINS. Presented written testimony and gave cross examination testimony on the biological effects of petroleum on marine organisms and on laboratory studies of the impact of petroleum on marine organisms, respectively, at Boston, Massachusetts, in adjudicatory hearings (30 January to 1 February 1980) on a proposed refinery site at Eastport, Maine, involving the Pittston Company. This effort required the integration of results from studies on the fate and effect of petroleum to a specific subarctic site.

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VOLUME III:

CONTAMINANT BASELINES

CONTAMINANT BASELINES

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ANNUAL REPORT

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DISTRIBUTION AND COMPOSITION OF SUSPENDED MATTER IN LOWER COOK INLET AND NORTON SOUND, ALASKA

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I.A. Lower Cook Inlet

The seasonal distributions, elemental compositions, and fluxes of suspended particulate matter in lower Cook Inlet were studied and compared with current patterns and bottom sediment distributions. In general, the suspended matter distributions appear to follow the pattern of circulation in lower Cook Inlet and Shelikof Strait. The inflowing clear saline Gulf of Alaska water, which is enriched in biogenic particles of marine origin, flows northward along the eastern coast until it reaches the region near Cape Ninilchik where it mixes with the outflowing brackish water. The outflowing turbid water, which contains terrigenous particles derived primarily from the Susitna, Matanuska, and Knik Rivers, moves seaward along the western side of the inlet past Augustine Island and Cape Douglas into Shelikof Strait where it mixes with the oceanic water and is dispersed. Comparisons of physical characteristics and sedimentation rates of suspended particles and sediments from the central basin indicate that net sedimentation of fine-grained suspended particles is minimal. However, net sedimentation is occurring primarily in Shelikof Strait and to a lesser extent in several embayments along the coast. Chemical analysis of the particulate matter reveals that: (1) fine-grained aluminosilicate minerals comprise about 80-95% of the suspended matter with biogenic material making up the rest; (2) Kachemak Bay is characterized by trace element enrichments in the organic phases of the particulate matter; (3) Kalgin Island region is characterized by trace element enrichments in the Fe-Mn oxyhydroxide phases; and (4) lower Cook Inlet and Shelikof Strait are linked by biogeochemical processes involving Mn and organic matter. These studies lead to the speculation that bioaccumulation of certain trace elements could occur in Kachemak Bay if it were to receive a sudden massive insult of these dissolved trace elements.

I.B. Norton Sound

The distributions and elemental compositions of suspended particulate matter in Norton Sound were studied and compared with current patterns and sediment distributions. The suspended matter distributions appear to follow the general pattern of cyclonic circulation in the Sound. The inflowing water picks up terrigenous aluminosilicate material from the Yukon River and transports it to the north and northwest around the inside periphery of the Sound, with some material settling to the bottom and the remaining material being transported to the northwest through the Bering Strait into the Chukchi Sea. Chemical analysis of the suspended material from Norton Sound reveals that: (1) aluminosilicate material from the Yukon River comprises about 88-92% of the suspended matter, with biogenic matter making up the rest; (2) organic matter of marine origin predominates in Norton Sound basin, whereas organic matter of terrestrial origin predominates in the Yukon River Estuary; and (3) Mn and Zn are enriched in an oxyhydroxide phase of the surface and near-bottom suspended matter in Norton Sound.

II. Introduction

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

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

Since crude oil is sparingly soluble in seawater, it tends to form emulsions when introduced into marine waters, especially under intense wave action. The emulsions have a high affinity for particles and tend to be adsorbed rapidly. Recent studies of oil spills in coastal waters containing high suspended loads have indicated rapid dispersal and removal of the oil by sorption onto particles along frontal zones (Forrester, 1971 and Klemas and Polis, 1977). These zones are regions where turbid brackish water contacts seawater. At the interface downwelling occurs in most cases, causing the inorganic material from the rivers and any associated contaminants to be carried down into the water column. Similarly, laboratory studies involving the interaction between Prudhoe Bay and Cook Inlet crude oils and river-derived inorganic suspended matter have indicated that significant amounts of oil may be accommodated by suspended material, and that the quantity of oil retained on the particles is dependent upon the isoelectric point of oil and sediment particles, particle size, temperature, and the concentration of oil relative to that of the suspended material (Baker et al., 1978; Feely et al., 1978). Since these processes play a major role in the dispersal and deposition of petroleum hydrocarbons, this report addresses the spatial and temporal variations of the distribution, chemical composition, and dispersal of suspended material in lower Cook Inlet and Shelikof Strait.

III. Current State of Knowledge

III.A. Cook Inlet

Previous studies of the distribution of suspended material in lower Cook Inlet have been limited to observations of LANDSAT satellite and aircraft photographs, augmented with sea-truth measurements in some cases. These studies have provided useful information about near-surface suspended matter dispersal patterns, particularly in the region surrounding Kalgin Island where concentration gradients have been observed to be extremely high.

Sharma et al. (1974) used density-sliced LANDSAT photographs and sea truth measurements to study suspended matter distributions in Cook Inlet during late summer of 1972 and early spring of 1973. Suspended matter concentrations ranged from 100 mg/L near The Forelands to 1-2 mg/L near the entrance to the inlet. Large temporal variations were observed which were related to tidal variations in water circulation and seasonal variations in river runoff.

Gatto (1976) studied the dispersal of sediment plumes from coastal rivers as affected by tidal currents in the inlet. Turbid plumes from the Drift, Big, McArthur, and Tuxedni Rivers on the west side of the inlet and the Kenai, Kasilof, and Ninilchik Rivers on the east side formed distinct surface layers, riding over and mixing with the saline water from the south. During flood tide, the plumes migrated northward along the coast. On ebb tide, the plumes migrated back again to the south and west. Occasionally, relict plumes were observed far offshore which indicated that at least some plumes of sediment-laden water were capable of maintaining their identity for several tidal cycles.

Burbank (1977) used LANDSAT imagery to study suspended matter dispersal patterns in Kachemak Bay. Suspended material in Kachemak Bay is derived from in situ production of organic material and from runoff from the Fox, Bradley, and Martin Rivers. Sediment plumes from inner Kachemak Bay were observed along the northwest shore of the bay. These plumes were diverted around Homer Spit and into the outer Kachemak Bay by a counterclockwise rotating gyre. In the outer bay, the plumes move to the west and north under the influence of a second counterclockwise gyre.

III.B. Norton Sound

Previous work on suspended matter in Norton Sound has been limited to studies of LANDSAT photographs and suspended matter distributions. Sharma et al. (1974) used density-sliced LANDSAT photographs and sea truth measurements to study suspended matter distributions in Norton Sound during the late summer of 1973. Suspended matter concentrations were highest near the mouth of the Yukon River (range: 2-8 mg/L) and in Norton Bay (range: 3-4 mg/L), located in the northeast corner of the Sound. The authors postulated that the general pattern of cyclonic circulation in the Sound caused suspended material to be transported to the north and northeast along the coast. The authors also noted that unusually high particulate matter concentrations (>9.0 mg/L) were observed throughout the water column in the region approximately 30 km south-southwest of Nome. They suggested that this plume could have been a detached portion of the Yukon River plume which was isolated by tidal pulsation.

Cacchione and Drake (1979) combined suspended matter surveys during September-October 1976 and July 1977 with deployments of a tripod (GEOPROBE) containing instruments designed to measure bottom currents, pressure, temperature, and light transmission and scattering to study suspended matter dispersal patterns in Norton Sound. They described the transport of suspended materials as dominated by distinctly different quiescent and storm regimes. The quiescent regime was characterized by relatively low levels of sediment transport caused by tides and mean flow to the north and northeast, which was augmented by surface waves during spring tides. The authors stated that during this period, much of the fine-grained suspended matter present over the prodelta was resuspended at shallow depths during spring tide and transported northward with the mean current. The storm regime, which occurs during the months of September through November, was characterized by strong southerly and southwesterly winds which generate waves with heights of 1-3 m and periods of 8-11 sec. The storm events cause near-bottom shear velocities which are in excess of that required for resuspension of bottom sediments and, as a result, more than 50% of the sediment transport occurs during this regime.

Although there is no background information on the chemistry of suspended matter in Norton Sound, extensive studies of trace metal partitioning in various phases of Yukon River materials were conducted by Gibbs (1973; 1977). He concluded that transition metals associated with oxyhydroxide coatings and crystalline phases comprised the major fraction (72-91%) of riverine transition metal transport to the sea. Particulate organic phases contained the next largest fraction (3-16% of the total). Metals in solution and metals sorbed to particulate materials made up the remainder (5-15% of the total).

IV. The Study Area

IV.A. Cook Inlet

Cook Inlet is a large tidal estuary in south central Alaska (Fig. 1). It lies on a northeast-southwest axis and is about 150 nautical miles long and 50

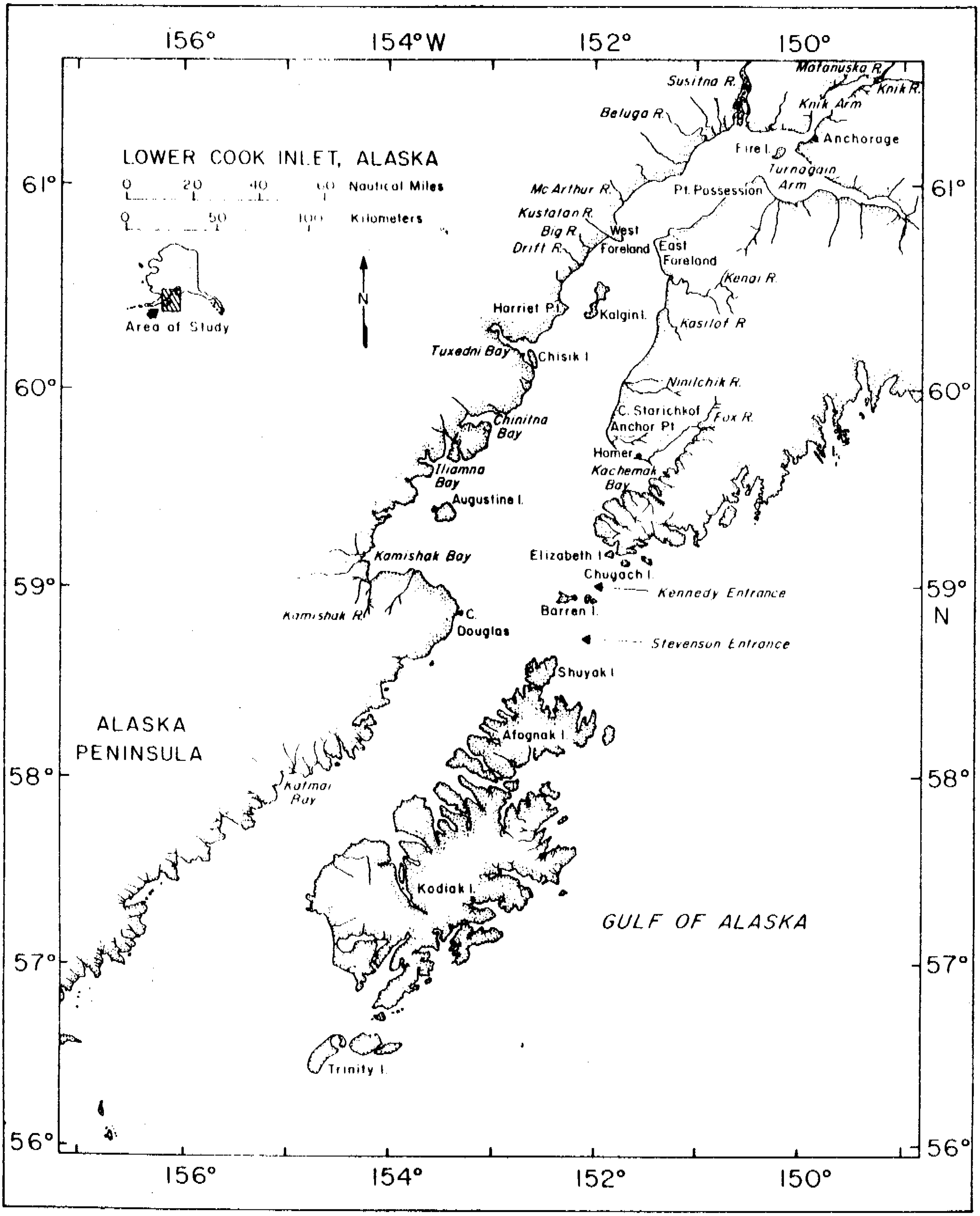

Figure 1. Physiographic setting of lower Cook Inlet, Alaska.

nautical miles wide at the mouth. Physiographically, the inlet is divided into three sections. At the head of the inlet, it separates into Knik and Turnagain Arms, which are 45 and 43 nautical miles long, respectively. Near the middle, upper Cook Inlet is separated from lower Cook Inlet by two geographic constrictions, the East and West Forelands.

The inlet receives freshwater from four major rivers: the Matanuska and Knik Rivers at the head of Knik Arm and the Susitna and Beluga Rivers to the northwest. These rivers supply about 70% to 80% of the freshwater input (Rosenberg and Hood, 1967). In addition, numerous streams containing large concentrations of glacial flour drain into the lower inlet from both sides. Included in this category are the Kenai, Kalisof, Nihilchik, and Anchor Rivers on the eastside and the McArthur, Big, Drift, and Tuxedni Rivers which discharge into the inlet from the west.

Water circulation in lower Cook Inlet has been described by several authors (Kinney et al., 1970; Wright et al., 1973; Gatto, 1976; Burbank, 1977; and Muench et al., 1978). The last reference provides the most completed description of water circulation in lower Cook Inlet. Circulation in the inlet is characterized by a net inward movement of oceanic water up the eastern shore and a net outward movement of a mixture of oceanic water and runoff water along the western shore. In the vicinity of the Forelands, the water masses are vertically mixed due to the turbulent action of tidal currents. However, lateral separation of the water masses is apparent, resulting in a shear zone between the incoming saline water on the eastside and the outgoing less saline water on the west. Coastal upwelling occurs in the vicinity of the Chugach Islands, from the region west of Elizabeth Island to Cape Starichkof.

The distribution and composition of bottom sediments in lower Cook Inlet have been studied (Sharma and Burrell, 1970; Bouma and Hampton, 1976; Hein et al., 1979). The sediments are primarily composed of medium-to-fine grain sands; however, occasionally silt and clay-sized sediments have been observed. The deposits in the northern part of the inlet are winnowed Pleistocene-early Holocene gravels, with many of the sand-sized and smaller particles being removed and redeposited to the south. In addition to the relict sands and gravels, the sediments also contain a very thin cover of fine-grained silts and clays which are modern. Hein et al. (1979) state that the clay mineral deposits in lower Cook Inlet are dominated by clay mineral suites from two distinct sources. A chlorite-rich dominates the clay mineral fraction in deposits from the region around the Barren Islands to Kachemak Bay. The Copper River appears to be the major source of this material as it discharges chlorite-rich fine grained material into the northeast Gulf of Alaska which is diverted to the west and southwest by the coastal alongshore currents (Feely et al., 1979). Apparently, some of this material reaches Kennedy Entrance and is transported into lower Cook Inlet along with the inflowing Gulf of Alaska water.

The region to the west and north of Kachemak Bay is dominated by an illite-rich suite which has the Susitna River in upper Cook Inlet as its major source. These authors further state that the distribution of clay minerals in the bottom sediments in lower Cook Inlet reflects the dispersal routes for suspended material in the overlying water. Thus, fine-grained particles from these two sources follow the genral pattern of water circulation in the inlet and form the bulk of the mud deposits in the quiet embayments along the shore and throughout Shelikof Strait.

IV.B. Norton Sound

Norton Sound is a shallow embayment located in the central region of the west coast of Alaska (Fig. 2). Relative to the Bering Sea, it is an east-west extending embayment which is about 220 km long in the east-west direction and about 150 km wide in the north-south direction. The Yukon River, which flows the southwest quadrant of the embayment, is the major source of freshwater and suspended matter to the Sound as well as to the entire eastern Bering Sea Shelf. Its annual suspended matter load of 88 x 10^6 tons ranks 18th among the major rivers of the world (Inman and Norstrom, 1971). The annual discharge curve for the Yukon River (Fig. 3) is unimodal with peak flow occurring during June and low flow conditions persisting throughout the winter months. Additional smaller freshwater inputs into the Sound occur along the coastline east of the Yukon River Delta and along the northern coast.

Water circulation in the vicinity of Norton Sound has been described by several authors (Coachman et al., 1975; Muench and Ahlnäs, 1976; Muench et al., in press). The shelf water west of Norton Sound, the Alaska Coastal water, has a net northward flow of about 1.5 x 10^6 m^3 sec^{-1}. About one-third of this flow passes between St. Lawrence Island and the mouth of Norton Sound. The intensity of the cyclonic flow appears to be affected by local winds and by freshwater runoff. The eastern half of the Sound is characterized by two vertically well-mixed layers. The upper layer contains runoff water from the coastal rivers; the lower layer contains cold, dense residual water formed during the previous winter. Both water masses follow the general pattern of cyclonic flow in the region, although much more sluggishly than surface and bottom waters further to the west.

The distribution of sediments in Norton Sound has been summarized (McManus et al., 1974; Sharma, 1974; Nelson and Creger, 1977; and McManus et al., 1977). In the central and southern regions, the sediments consist of very fine-grained sands and silts which are modern. In the northern region, silty sands predominate everywhere except for a narrow strip along the coast between Cape Nome and Cape Douglas. Here, coarse sands and gravels predominate

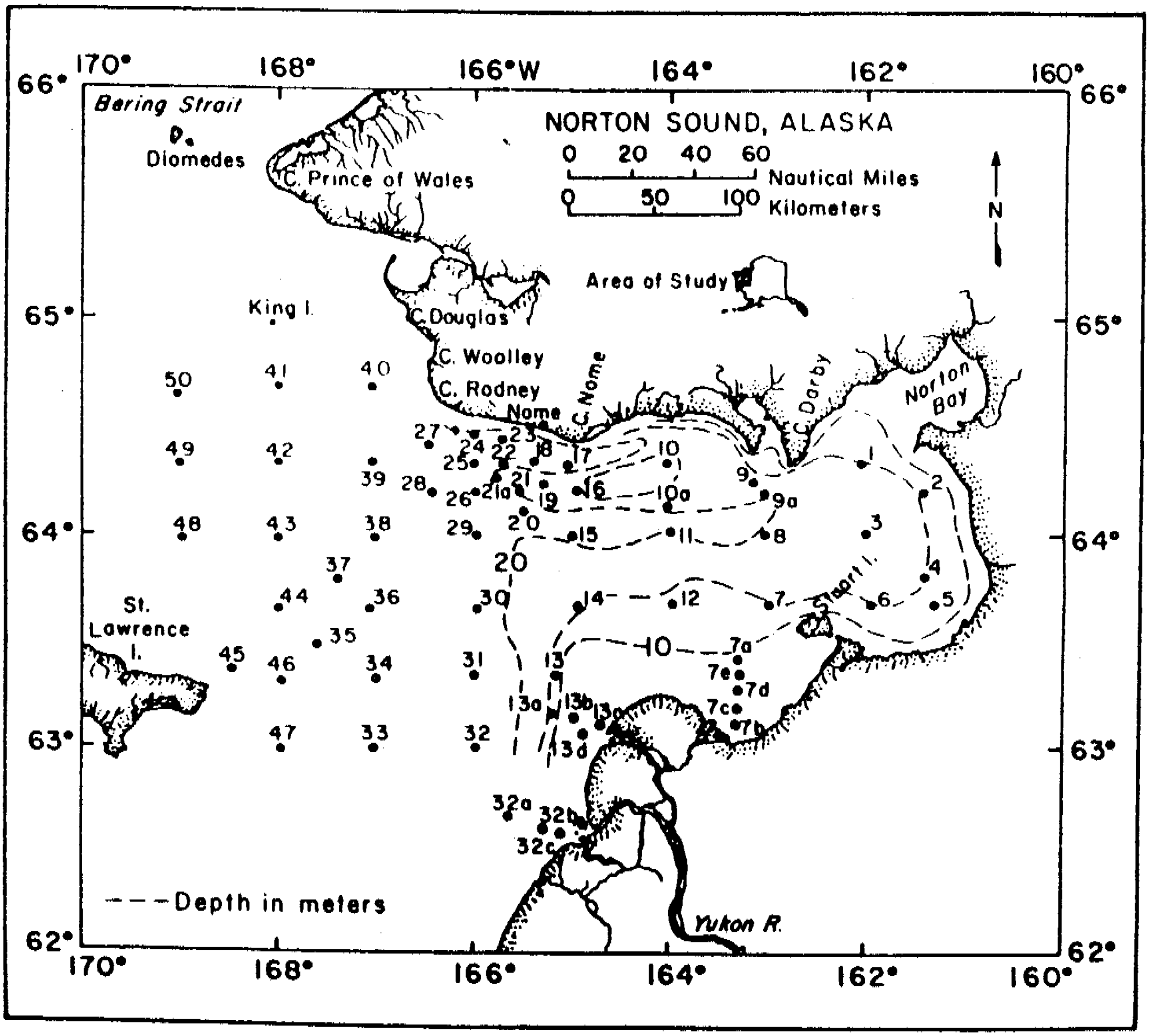

Figure 2. Locations of suspended matter stations in Norton Sound, 7-18 July, 1979.

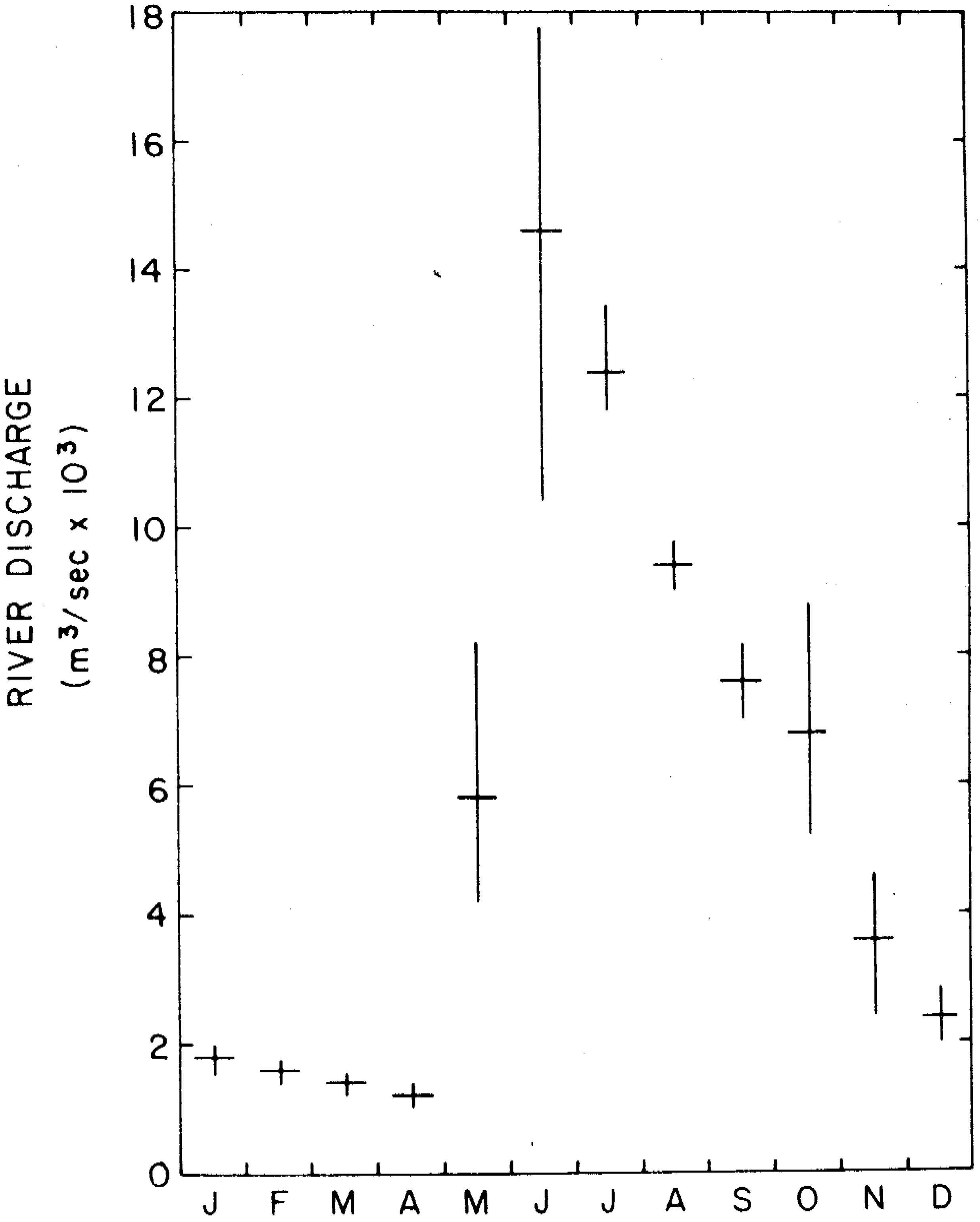

Figure 3. Monthly means and ranges for Yukon River discharge. Data compiled from USGS streamflow obtained at Pilot Station (located approximately 200 km from the river mouth) for period of record: 1975-1978.

because bottom currents have caused almost complete erosion of the fine-grained sediments. Approximately one-half to two-thirds of the sediment load of the Yukon River is deposited as a bank of sediments extending from the Yukon River Delta northward and eastward around the inside periphery of the Sound. The remaining sediment load of the Yukon River is transported to the north through Bering Strait and deposited in the Chukchi Sea.

V. Sources, Methods and Rationale of Data Collection

In order to obtain information about the seasonal variations of the distribution and composition of suspended matter, we have conducted six cruises in lower Cook Inlet (Cruise RP-4-Di-77A-IV, 4-16 April 1977; Cruise Acona-245, 28 June-12 July 1977; Cruise RP-4-Di-77C, 3-12 October 1977; Cruise RP-4-Di-78A-III, 4-17 May 1978; Cruise RP-4-Di-78B-II, 22 August-6 September 1978 and Cruise RP-4-Di-79A-II, 7-20 May 1979) during 1977-79. The field studies have been intergrated with the physical oceanography program so that concomitant information about water mass structure has been obtained. In Norton Sound a single field study was conducted in July of 1979 (Cruise RP-4-Di-79A-VI, 7-18 July 1979).

In addition to the seasonal studies, we have conducted a number of high frequency (hourly) time series studies at selected locations in the inlet. This has provided valuable information about the variability of the distribution and chemical composition of suspended matter that may be due to the influence of tidal currents and/or variations of primary productivity in surface waters and resuspension of sediments in near-bottom waters.

Another aspect of the suspended matter program was concerned with the vertical fluxes and composition of settling material in areas of contrasting sedimentation and productivity. To this end, self-closing sediment traps were deployed on three moorings along a transect line extending from Kamishak Bay to Kachemak Bay. The materials recovered by the traps were subjected to extensive gravimetric and chemical analyses, designed to determine the sedimentation rates for particulate material and the partitioning of trace elements among major solid phases.

V.A. Sampling Methods

V.A.1. Particulate Matter

Water samples were collected from preselected depths in General Oceanics 1070 10-L PVC Top-Drop Niskin bottles. Nominally these depths included: 0-2 m, 10 m, 20 m, 40 m, 60 m, 80 m, and 5 meters above the bottom. Aliquots were drawn within one-half hour after collection from each sample and vacuum filtered through preweighed 0.4 μm pore diameter Nuclepore polycarbonate filters for total suspended matter concentration determinations and multi-element particulate composition analyses. Samples were also filtered through 0.45 μm pore diameter Selas silver filters for particulate carbon and nitrogen analyses. All samples were rinsed with three 10 mL aliquots of deionized and membrane filtered water, placed in individual petri dishes with lids slightly ajar for a 24-hour desiccation period over sodium hydroxide, and then sealed and stored (silver filters frozen) for subsequent laboratory analysis.

V.A.2. Bottom Sediments

Bottom sediment samples were collected with a Shipek grab sampler, a three-inch gravity corer equipped with a plastic core liner, and a HAPS corer. Twelve gravity corer samples and all HAPS corer samples were sectioned into 1 cm segments upon collection and frozen in individual plastic bags. All remaining bottom sediment samples were immediately frozen and returned to the laboratory intact.

V.A.3. Nephelometry

The vertical distribution of suspended matter was determined with a continuously recording integrating analog nephelometer. The instrument was interfaced with the ship's CTD system using the sound velocity channel (14-16 KHz). Continuous vertical profiles of forward light scattering were obtained in analog form on a Hewlett Packard 7044 X-Y recorder.

V.A.4. Conductivity (Salinity), Temperature, and Depth

These standard hydrographic data were acquired with a Plessy Model 9040 Environmental Profiling System (CTD probe) and a Model 8400 digital data logger using 7-track, 200 B.P.I. magnetic tape. Temperature and salinity calibration data were provided by NOAA ship personnel from discrete water samples utilizing reversing thermometers and a bench salinometer, respectively. Signals from the CTD system and the nephelometer were also simultaneously interfaced with the ship's data acquisition system. This resulted in computer listings of continuous (uncorrected) data for conductivity, temperature, depth, salinity, sigma-t, and light scattering for all vertical sampling stations.

V.A.5. Sediment Trap/Vertical Particulate Flux Studies

During Cruise RP-4-MF-78A-II (19 May-4 June 1978) three moorings, each supporting one set of tandem sediment traps located 10 m above the bottom, were deployed along a transect line extending from Kamishak Bay to Kachemak Bay in lower Cook Inlet. The sediment trap capture period was set (trap closure to be activated by self-contained timers approximately 85 days after deployment) to obtain a long-term average of the particulate vertical flux mass (rate) and composition. Recovery of the sediment traps occurred in October 1978 (DISCOVERER Cruise RP-4-DI-78C-V).

V.B. Analytical Methods

V.B.1. Gravimetry

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

V.B.2. Gas Chromatography

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

V.B.3. X-ray Secondary Emission Spectrometry

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

V.B.4. Atomic Absorption Spectrophotometry

The suspended matter samples from lower Cook Inlet and Norton Sound were analyzed for Al, Fe, Mn, Cr, Cu, Ni, Zn and Pb by means of several extraction procedures. The first extraction procedure involves the use of hydrogen peroxide to release organically-bound trace metals. The second treatment utilizes 0.3 N hydrochloric acid to release trace metals which are weakly bound to inorganic phases. The third procedure involves the use of 25% acetic acid to remove amorphous Fe and Mn oxides. The details and validity of these procedures are outlined below.

V.B.4.1. H_2O_2 Treatment

Crecelius et al. (1974) have demonstrated that 30% hydrogen peroxide efficiently oxidizes particulate organic matter and thus removes certain trace metals from sediments. Landing (1978) has shown that the modification of this procedure, as described below, efficiently removes organic carbon and nitrogen from suspended matter. The release of trace metals from suspended matter during this procedure is attributed to the dissolution of organically bound trace metals.

> Procedure. Dilute 30% ULTREX (J. T. Baker) hydrogen peroxide to 10% with the addition of quartz distilled water (Q-H_2O). Combine 5 mLs of 10% H_2O_2 with 100-500 mg of sample material in a precleaned centrifuge tube equipped with a nonsealing cap. The volume and mass of extractant and sample, respectively, may vary within the above limits depending on the relative magnitude of the organic fraction in the sample. We are currently using polypropylene centrifuge tubes and caps. Heat the extractant-sediment solution in a water bath at approximately 50°C for 48 hours. During the final 24 hours of heating, vigorously sonicate the solution to assist in dispersal and breakdown of the organic matter. Centrifuge the tube contents at 2000 rpm for 1 hour. Decant the supernate into a precleaned and tared polyethylene (CPE) bottle. Rinse the residual particulate matter with one 10 mL aliquot of quartz-distilled water. Centrifuge, as above, after the rinse and combine all supernates in the polyethylene bottle. Since the centrifugation separation is not complete, filter the samples through a 0.4 μm Nuclepore filter. Determine the weight of the supernate by difference.

V.B.4.2. 0.3 N HCl Treatment

Malo (1977) has shown that leaching with hot 0.3 N HCl is the most effective method for dissolving trace metals associated with surface coatings. In this study, this method was modified by heating the sediment-0.3 N HCl mixture to 75°C instead of 100°C. The time required for completion of the reaction was determined by leaching subsamples for different lengths of time. The results of this kinetic study (Fig. 4) indicate that no additional Cu is released after the first 2 hours while Ni and Zn continue to be leached for 12 hours. Therefore, the sediment-acid mixture was heated for 24 hours to insure that the reaction was complete. A high efficiency for this reaction was confirmed by analyzing the amount of Cu and Mn released on a subsequent 0.3 N HCl leach (Table 1).

> Procedure. Dilute ULTREX (J. T. Baker) HCl to 0.3 N with Q-H_2O. Add 8 mLs of 0.3 N HCl to 100-500 mg of sample which has been treated

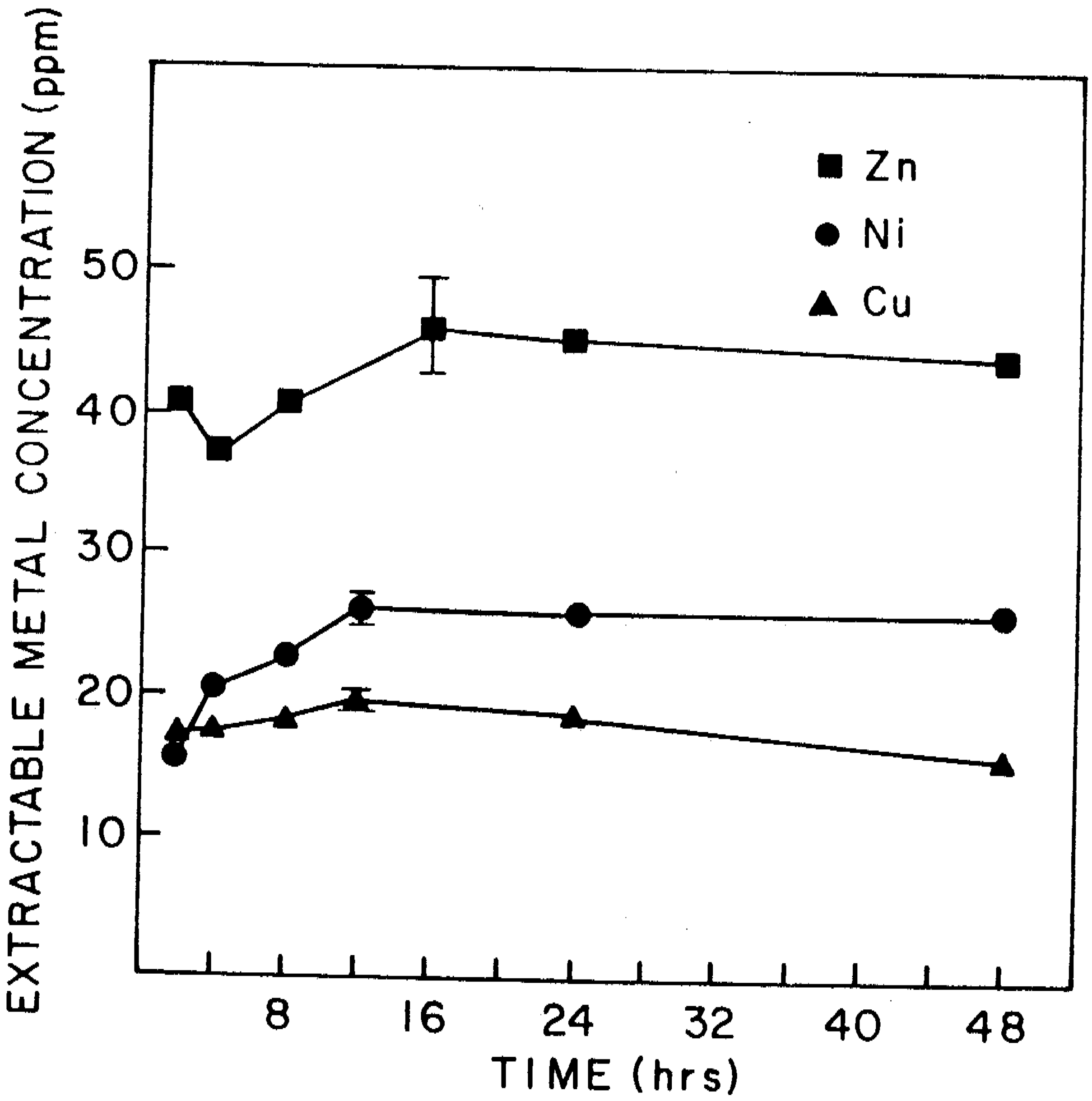

Figure 4. Extractable metal concentration versus time in contact with 0.3 N HCl for Zn, Ni, and Cu. The range of values is given for duplicate samples at 12 hrs.

with H_2O_2. Heat the mixture to 75°C for 24 hours while sonicating. Centrifuge the mixture at 2000 rpm for 1 hour. Decant the supernate into a precleaned and tared polyethylene bottle. Add 8 mLs of 0.3 N HCl to the residual sediment. Shake this mixture, then centrifuge as above and decant the supernate into the bottle. Repeat the rinsing of the residual sediment once. Filter the combined supernates through a 0.4 μm Nuclepore filter. Determine the weight of the final supernate by difference.

Table 1. Efficiency of successive 0.3 N HCl treatments

		Mn (ppm)	Cu (ppm)
First Treatment	(n=3)	911 ± 78	49.3 ± 2.5
Second Treatment	(n=3)	6.7 ± 0.3	0.7 ± 0.1

V.B.4.3. 25% Acetic Acid

The amorphous Mn and Zn in the poorly structured oxyhydroxide phase of selected suspended matter samples were determined by the method of Bolger et al. (1978). Desiccated samples were leached with 5 ml of 25% (v/v) Ultrex acetic acid at room temperature for 2 hrs. The resulting supernate was filtered through an acid-cleaned polypropylene-glass apparatus containing a 0.4 μm Nuclepore filter. The residue was rinsed with quartz-distilled water, then filtered; and the supernate was combined with the original supernate, acidified with 0.5 ml of concentrated Ultrex HCl, and stored in an acid cleaned polyethylene bottle. The Mn and Zn in this solution (Weak-acid Soluble) were analyzed by flameless atomic absorption procedures using standard addition methods. The remaining solid suspended matter (Weak-acid Insoluble) was dissolved in an Ultrex HCl - HNO_3 - HF matrix according to Eggiman and Betzer (1976) and analyzed for Mn and Zn in a similar manner.

V.B.4.4. Bulk Elemental Analysis

Elemental composition of suspended matter was determined using a modification of the method of Eggimann and Betzer (1976).

> Procedure. If the sediment is refractory, grind the dry sediment in a boron carbide mortar and pestle. Weigh out approximately 2 mg and place in a digestion bomb (Bombco, Inc.). Add 0.75 mL of 12 N HCl (ULTREX) and seal the bomb tightly and place in boiling water for 45 minutes. Cool for 45 minutes in a freezer. Add 0.25 mL of 16 N HNO_3 (ULTREX), seal, and place in boiling water for 45 minutes. Cool for 45 minutes in freezer. Add .05 mL of concentrated HF (ULTREX), seal, and place in boiling water for 90 minutes. Cool for 90 minutes. Quantitatively transfer the contents of the digestion bomb to a wide mouth bottle and rinse the bomb with Q-H_2O. Dilute the sample to 20 gm with Q-H_2O.

V.B.4.5. Atomic Absorption Spectrophotometry Analysis

Flameless atomic absorption measurements were made using a Perkin-Elmer 603 spectrophotometer equipped with an HGA-2200 furnace control, deuterium arc background corrector, AS-1 automatic sampler and a Model 54 recorder. The normal instrument parameters are listed in Table 2. Baker AAS standards are diluted in a matrix similar to the samples. The instrument was calibrated using this standard which covered the absorbance range of the samples. The total dissolution analysis for Al was done by the standard addition method.

Table 2. Summary of the analytical parameters utilized in the flameless atomic absorption determinations. Analyses conducted with a Perkin-Elmer 603 AAS, D-2 Arc Background Corrector, HGA-2200 Flameless Atomizer, AS-1 Automatic Sampler. Pyrolitically-coated tubes used for all elements. Std. Add. = Standard Additions.

Element	Wavelength (nm)	Slit (nm)	Volume (µl)	Dry Cycle Time/Temp	Ash Cycle Time/Temp	Atomize Cycle Time/Temp	Gas	Flow Units	Bkg. Cor.	Comment
Al	257	0.2	10	30/100	22/1300	5/2600	Ar	40	No	Std. Add.
Fe	347	0.2	10	30/100	22/1050	5/2600	N_2	40	No	
Mn	280	0.2	10	30/100	22/1000	5/2600	N_2	55	No	
Cr	358	0.7	10	30/100	22/1000	5/2600	Ar	45	No	
Cu	325	0.7	10	30/100	22/ 800	5/2500	Ar	35	No	
Ni	232	0.2	20	40/100	32/ 900	5/2500	Ar	35	Yes	
Pb	217	0.7	20	40/100	32/ 600	5/2500	Ar	35	Yes	
Zn	214	0.7	10	30/100	22/ 500	5/2500	Ar	40	Yes	

VI. Results and Discussion

VI.A. Lower Cook Inlet and Shelikof Strait

VI.A.I. Particulate Matter Distributions and Transport

To date we have completed six cruises in lower Cook Inlet and Shelikof Strait which have been schedules for FYs 77 thru 79. The first cruise was conducted during early spring of 1977 (4-16 April); the second, in summer of the same year (28 June-12 July); the third, in fall (3-12 October); the fourth, in spring of 1978 (4-17 May); the fifth cruise was conducted in late summer of 1978 (22 August-6 September), and the sixth cruise was conducted in the spring of 1979 (7-20 May). Horizontal surveys of the entire region were obtained on the first two cruises and vertical sections between Kachemak Bay and Kamishak Bay were obtained on the first five cruises. The station locations for the 1977 cruises are shown in Figures 5 and 6. The vertical sections for the first three cruises were obtained at stations 24 through 29. The station locations for the 1978 cruise are shown in Figures 7 and 8 and the station locations for the 1979 cruise are shown in Figure 9. Vertical sections were obtained at stations CB1 through CB8 in lower Cook Inlet and stations SS2, SS3, SS6, SS8, SS10, and SS12 in Shelikof Strait (Fig. 8).

Figures 10 through 13 show the distributions of salinity, temperature, sigma-t, and suspended matter at the surface and 5 m above the bottom for the April and July 1977 cruises in lower Cook Inlet and Shelikof Strait. As shown in Figures 10 and 12, the surface particulate matter distributions are characterized by unusually high horizontal gradients. On the eastern side particulate concentrations were relatively low, ranging from 0.5 mg/L near Cape Elizabeth to about 5.0 mg/L near Cape Ninilchik. On the western side suspended loads increased rapidly from concentrations around 5.0 mg/L in the vicinity of Kamishak Bay to concentrations greater than 100 mg/L north of Tuxedni Bay. The salinity

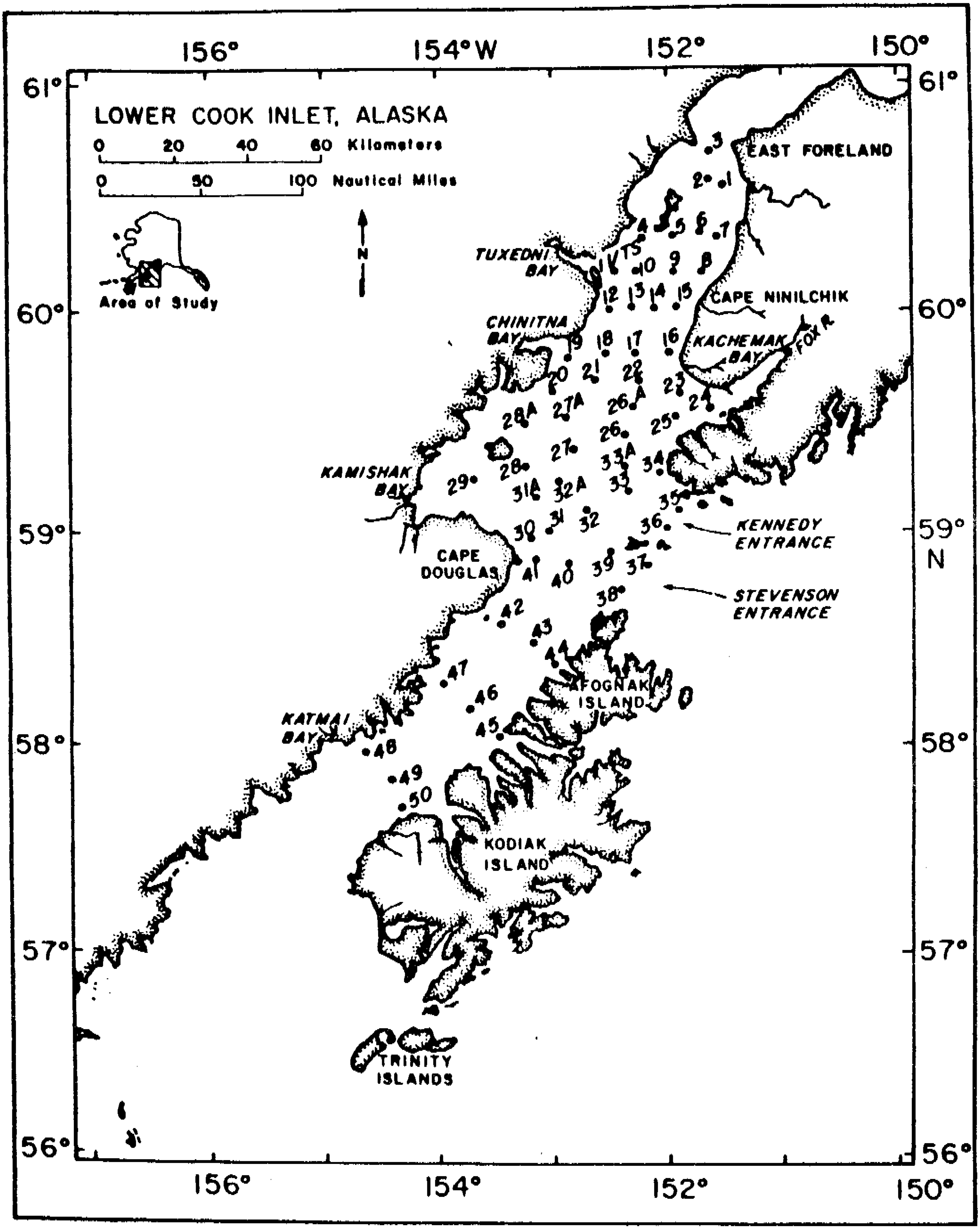

Figure 5. Locations of suspended matter stations in lower Cook Inlet and Shelikof Strait (Cruise RP-4-Di-77A-IV, 4-16 April 1977).

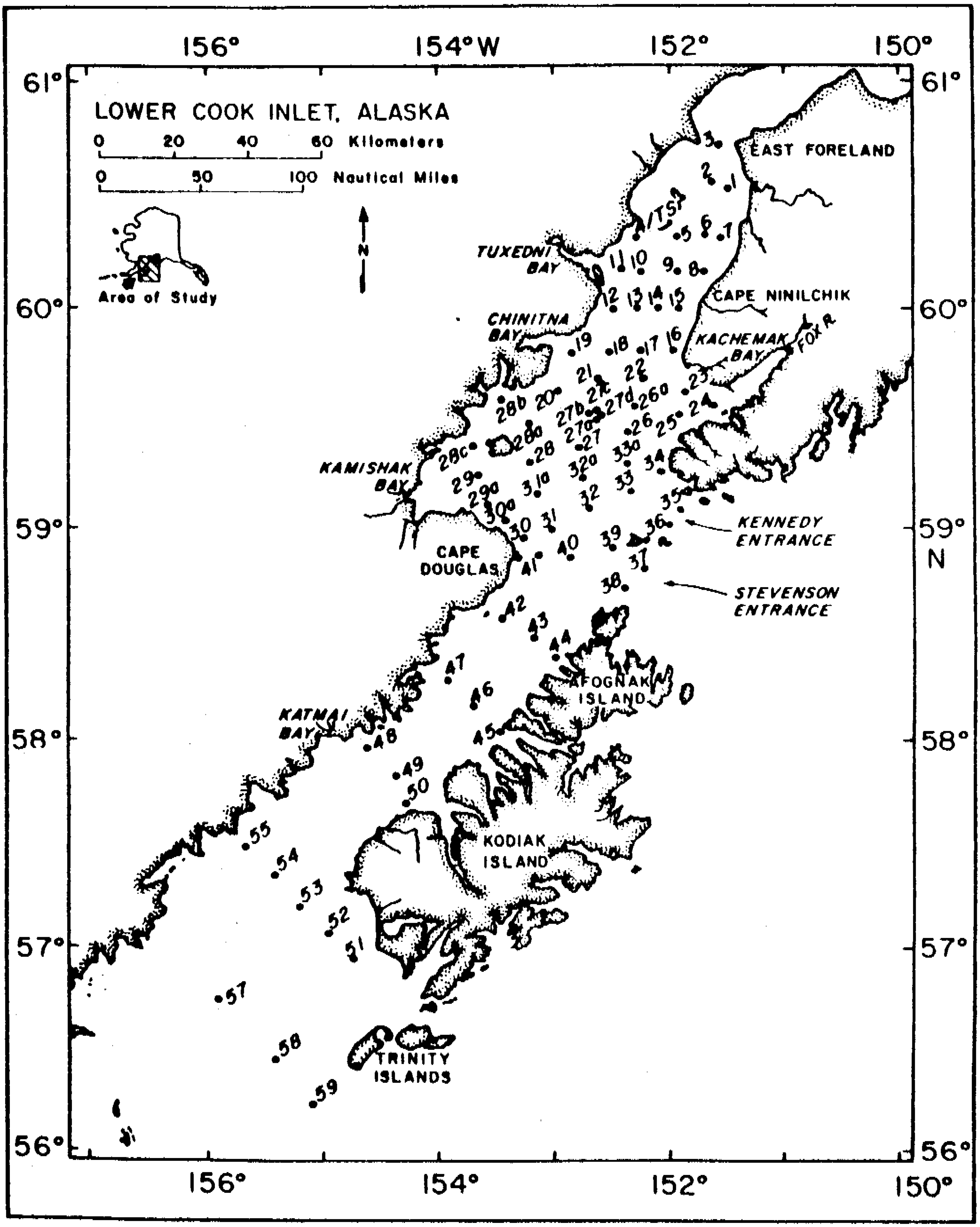

Figure 6. Locations of suspended matter stations in lower Cook Inlet and Shelikof Strait (Cruise Acona-245, 28 June - 12 July 1977).

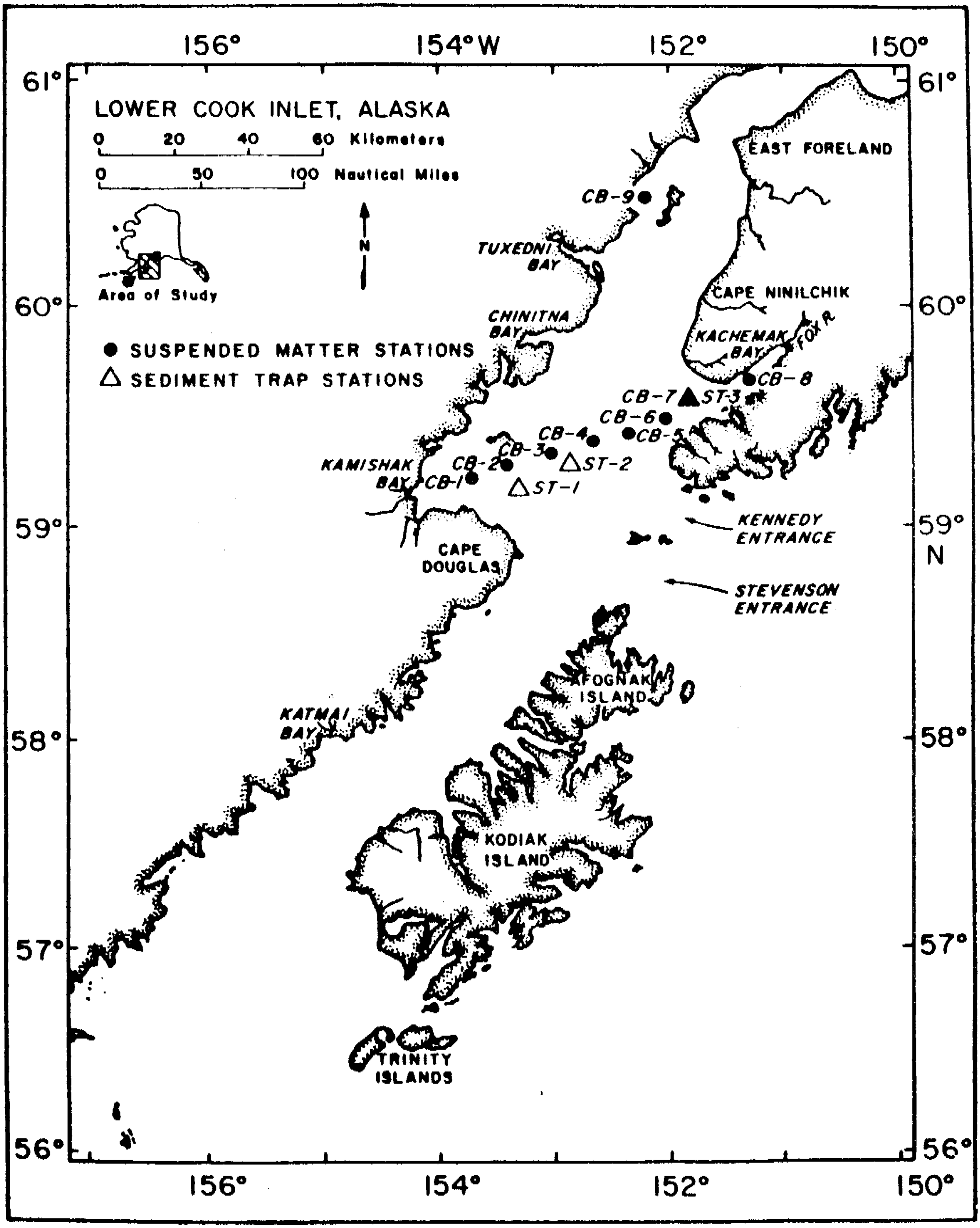

Figure 7. Locations of suspended matter and sediment trap stations in lower Cook Inlet (Cruise RP-4-Di 78A-III, 4-17 May 1978).

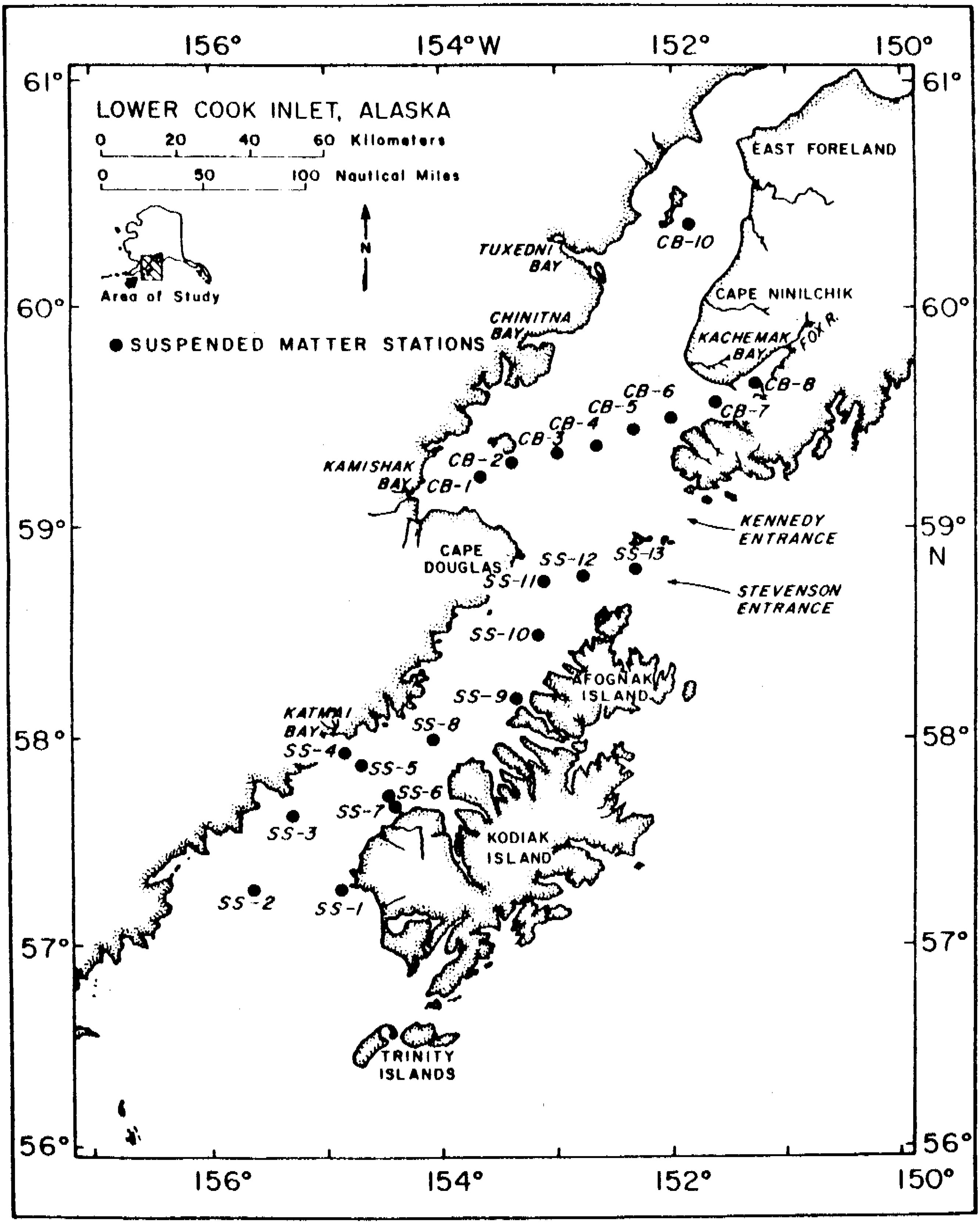

Figure 8. Locations of suspended matter stations in lower Cook Inlet and Shelikof Strait (Cruise RP-4-Di-78B-II, 22 August - 6 September 1978).

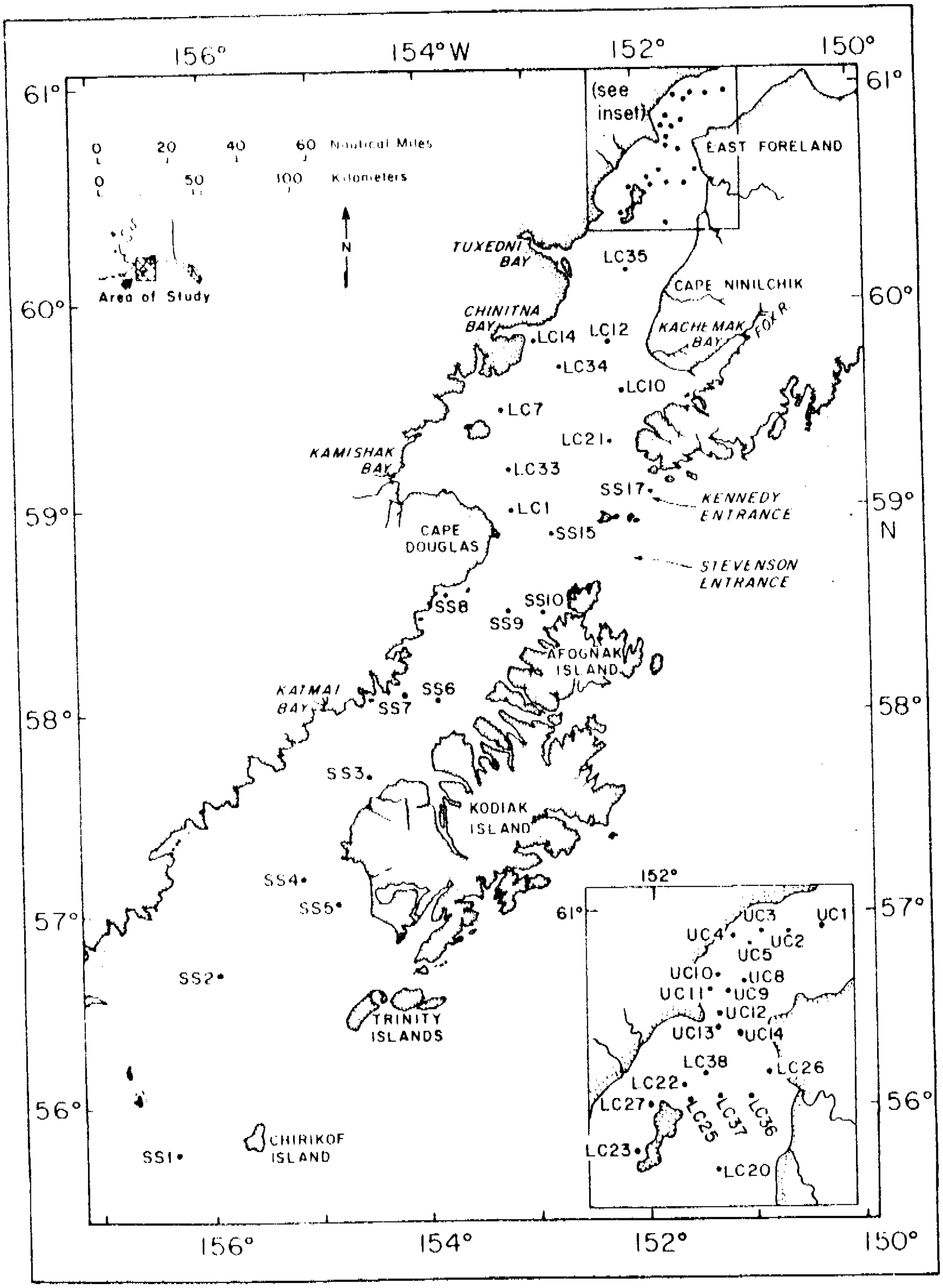

Figure 9. Locations of suspended matter stations in lower Cook Inlet and Shelikof Strait (Cruise RP-4-Di-79A-II, 7 - 20 May 1979).

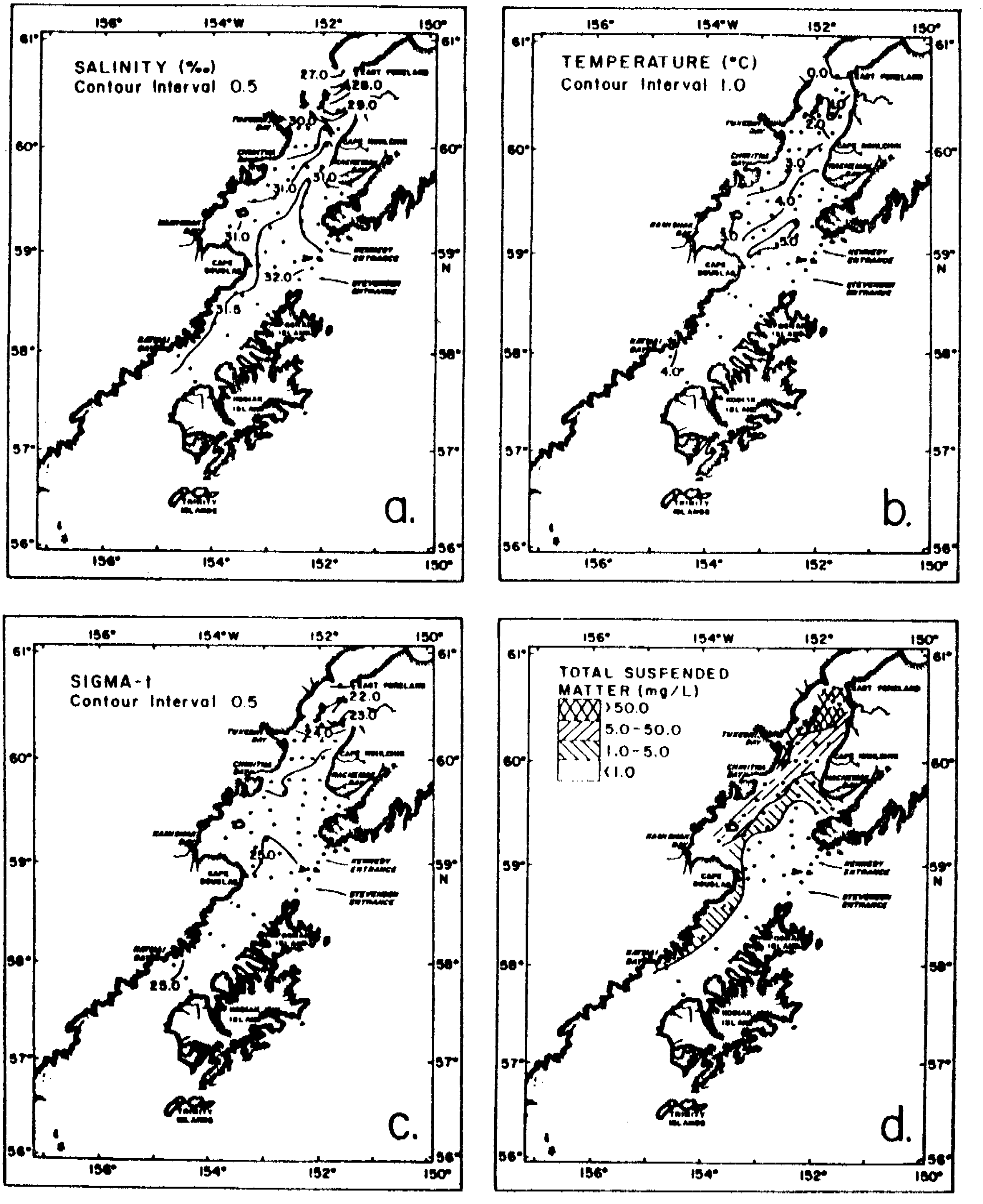

Figure 10. Distribution of: a. salinity; b. temperature; c. sigma-t; and d. total suspended matter at the surface (Cruise RP-4-Di-77A-IV, 4-16 April 1977).

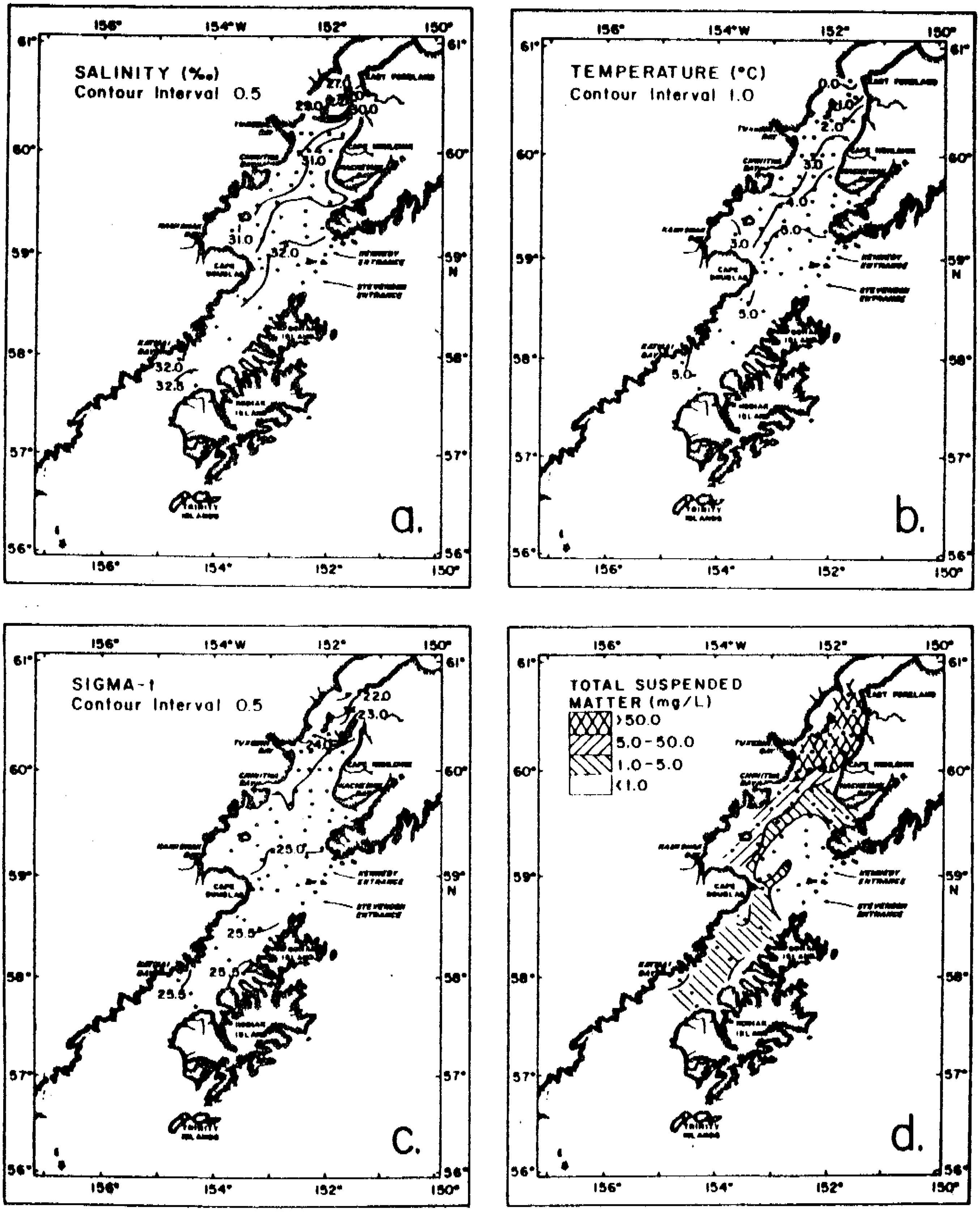

Figure 11. Distribution of: a. salinity; b. temperature; c. sigma-t; and d. total suspended matter 5 m above the bottom (Cruise RP-4-Di-77A-IV, 4-16 April 1977).

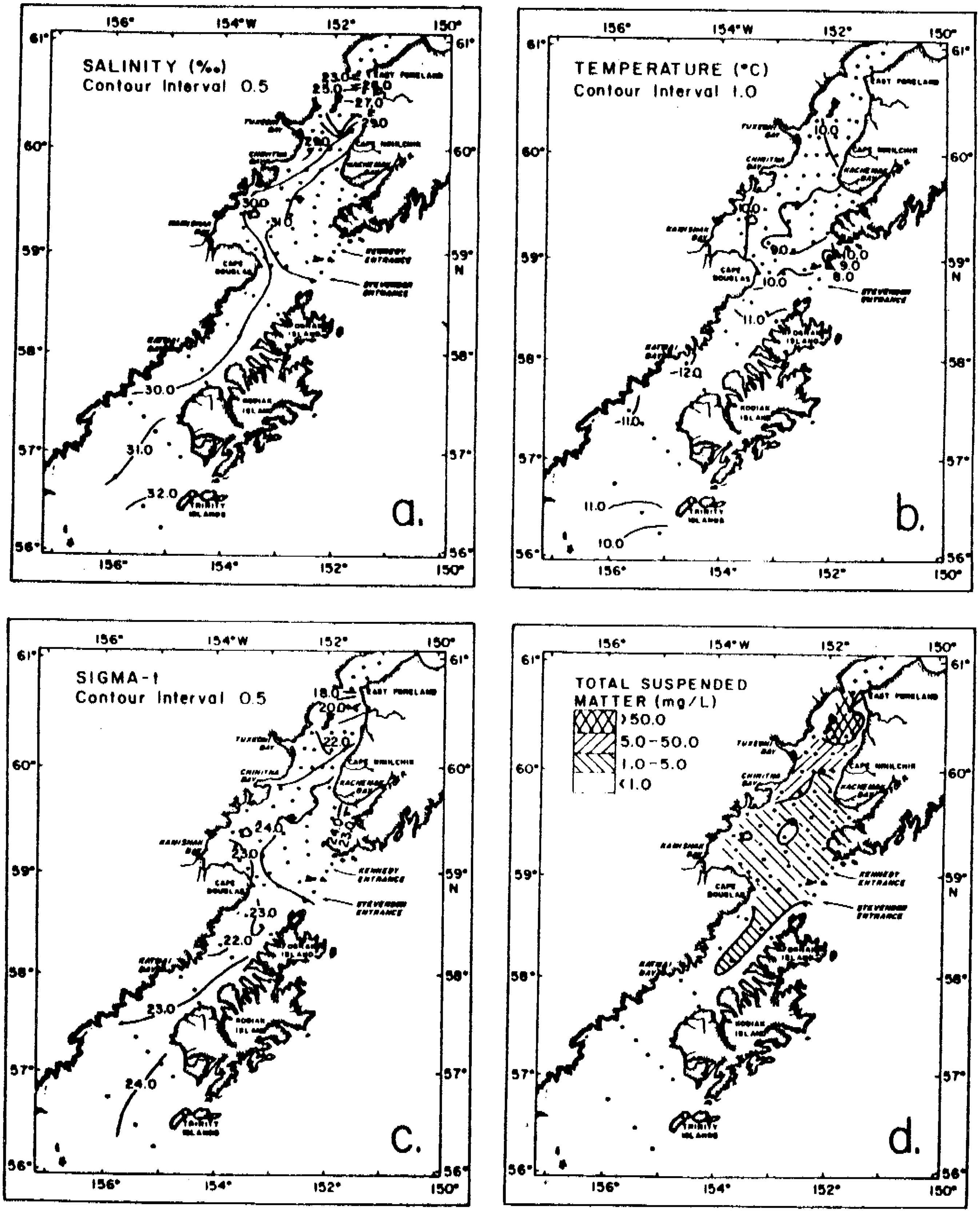

Figure 12. Distribution of: a. salinity; b. temperature; c. sigma-t; and d. total suspended matter at the surface (Cruise Acona-245, 28 June - 12 July 1977).

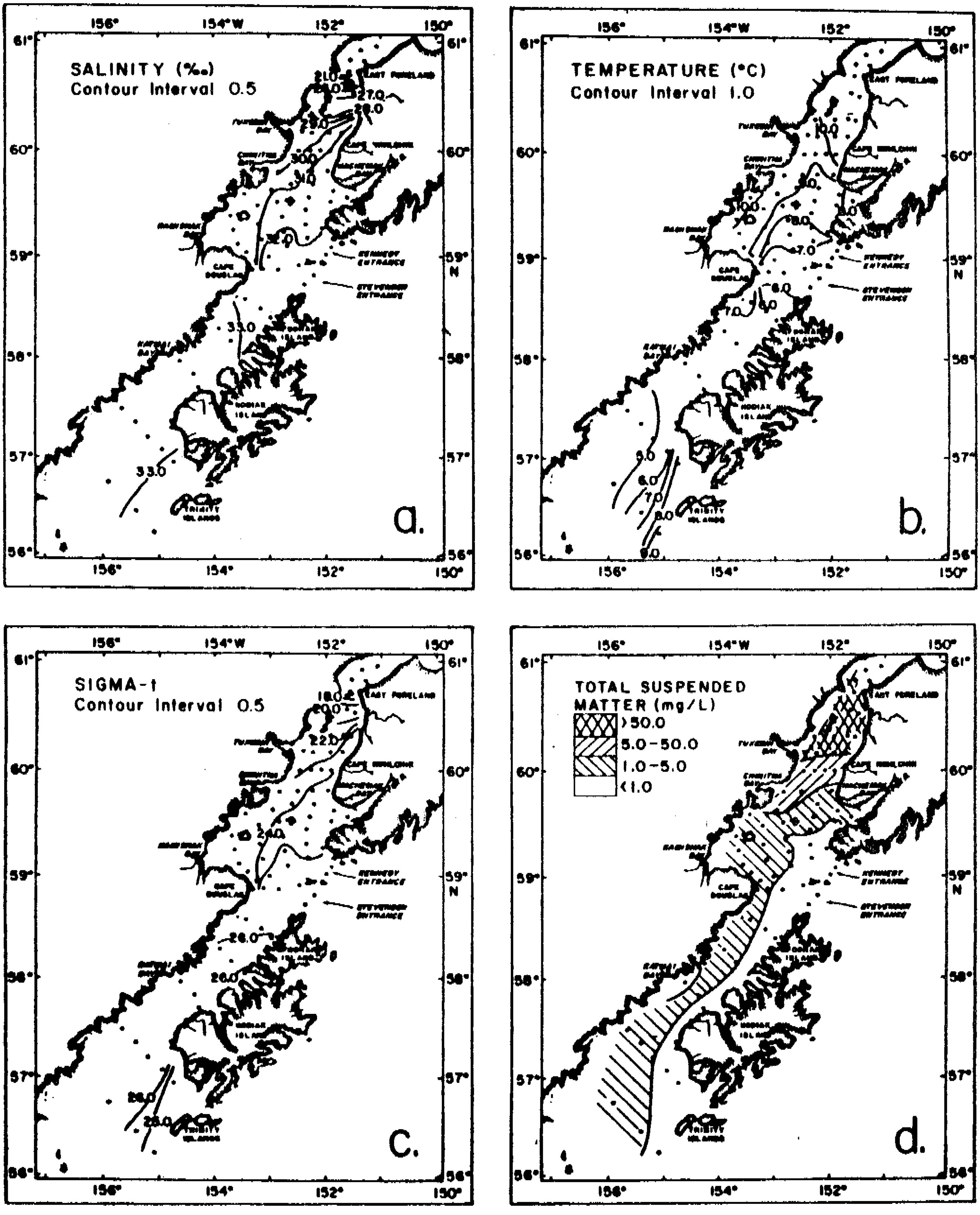

Figure 13. Distribution of: a. salinity; b. temperature; c. sigma-t; and d. total suspended matter 5 m above the bottom (Cruise Acona-245, 28 June - 12 July 1977).

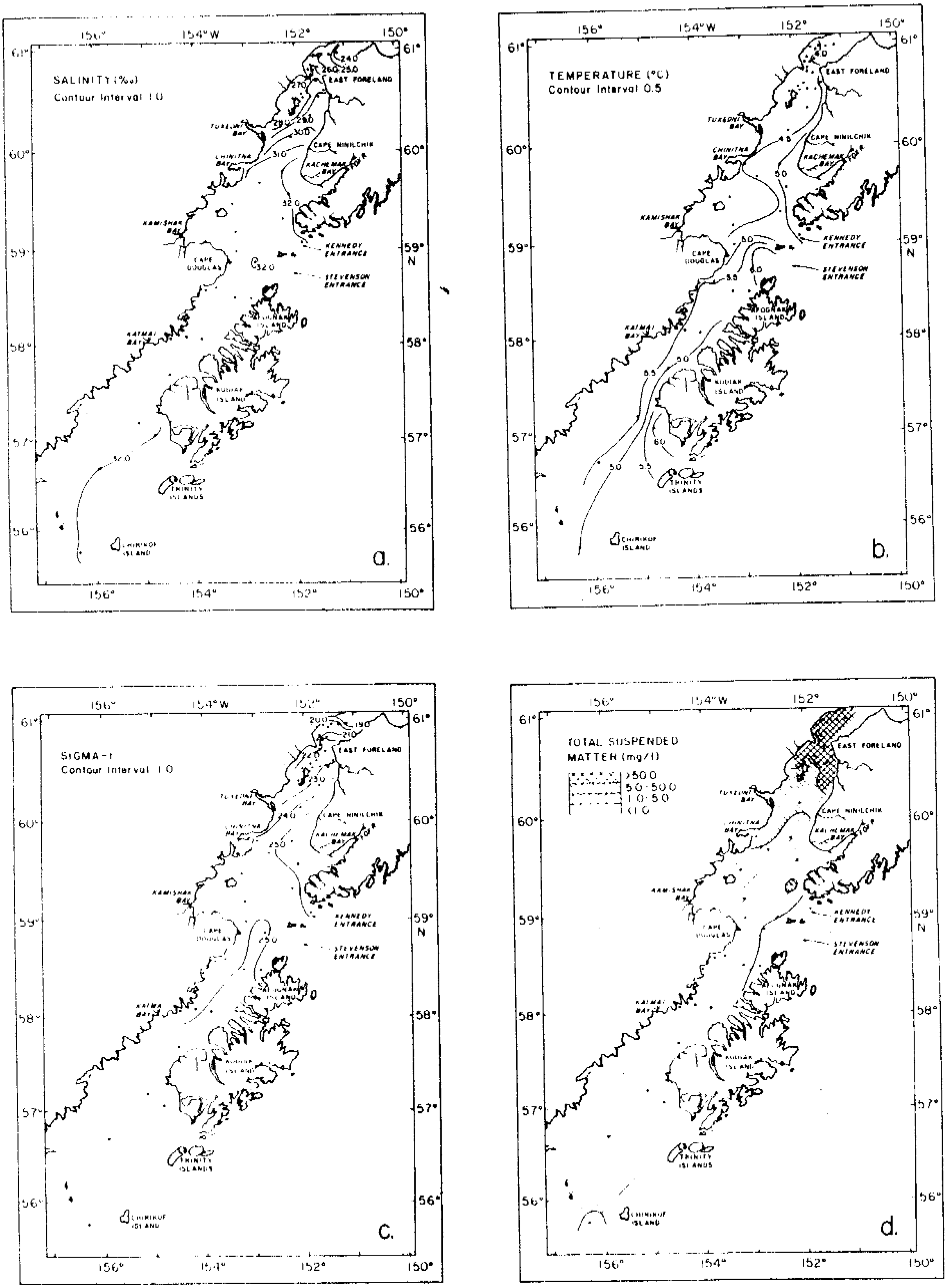

Figure 14. Distribution: a. salinity; b. temperature; c. sigma-t; and d. total suspended matter at the surface (Cruise RP-4-Di-79A-II, 7-20 May 1979).

and temperature data (Figs. 10 and 12) for these cruises show very similar horizontal distribution patterns, illustrating the predominance of the inflowing relatively clear saline Gulf of Alaska water on the eastern side and the outflowing turbid low salinity water from upper Cook Inlet on the western side. The outflowing turbid water is transported to the southwest past Augustine Island and Cape Douglas into Shelikof Strait where it continues to mix with the oceanic water and the suspended matter is dispersed. The near-bottom suspended matter distributions (Figs. 11 and 13) are very similar to the surface distributions, suggesting that cross-channel gradients in the suspended matter distributions exist throughout the water column. In apparent agreement with this, the vertical cross-sections of the distribution of suspended matter from Kachemak to Kamishak Bay (Figs. 15 through 19) show large cross-channel variations which can be utilized to identify three distinct water masses. On the west side (stations 28 and 29 for the 1977 data and stations CB1 through CB3 for the 1978 data) the water properties are low salinity (29.8-31.6^{0}/oo) and high suspended matter concentrations (0.9-8.2 mg/L). The water is virtually unstratified from top to bottom. These properties are characteristic of the outward flowing brackish water which originates from upper Cook Inlet and flows south along the western coast. This water mass contains significant amounts of terrigenous rock debris from the rivers which drain into upper Cook Inlet. The central region (stations 25 through 26 for the 1977 data and stations CB5 and CB6 for the 1978 data) contain water which is more saline (31.4-31.8^{0}/oo) and less turbid (0.4-1.4 mg/L). This water is characteristic of the inflowing Gulf of Alaska water which flows north along the east side of the inlet. In Kachemak Bay (station 24 from the 1977 data and stations CB7 and CB8 from the 1978 data), the waters are relatively warmer, less saline (27.3-31.4^{0}/oo) and more turbid (0.9-2.8 mg/L) than the water in the central region of the inlet. These waters are moderately stratified, with the freshwater from the Fox and Martin Rivers extending as far as station CB7.

The May and August-September 1978 data show some patterns which are consistent with the data from the previous year. First, the outward flowing brackish water on the western side is colder in May and warmer in August-September than the inward flowing Gulf of Alaska water. This feature is consistent with data obtained in April and July 1977 (Figs. 10 and 12) and May 1979 (Fig. 14), and appears to be related to the temperature of the inflowing river water and shows larger seasonal variations due to the larger fluctuations of temperature over the continental land masses. Furthermore, suspended matter concentrations in the Kamishak Bay region are higher in early spring than in late summer even though there is more freshwater input into Cook Inlet during late summer (Gatto, 1976). A possible explanation for this phenomenon is that early spring is usually the time when most of the ice breakup occurs in upper Cook Inlet. Resuspension and transport of previously deposited sediments may result from the ice movement. Another possibility is that if the currents are strong, there is less time for mixing and dilution of ambient suspended matter. This probably is true to some degree as the April 1977 data show higher suspended matter concentrations and lower salinities than the May 1978 data. However, this cannot be the only explanation because the July and October 1977 data show relatively low suspended matter concentrations (< 2.0 mg/L) in Kamishak Bay waters without extensive mixing with seawater (i.e., salinity $< 30^{\circ}/_{oo}$). Nevertheless, the data suggest that more riverborne suspended matter is transported out of the inlet and into Shelikof Strait during early spring than during the summer.

Above the Forelands, suspended matter concentrations range from 120 mg/L starting at about the Forelands (Fig. 14) to values greater than 1000 mg/L near the mouths of the Susitna River and Knik Arm (Sharma et al., 1974). Suspended

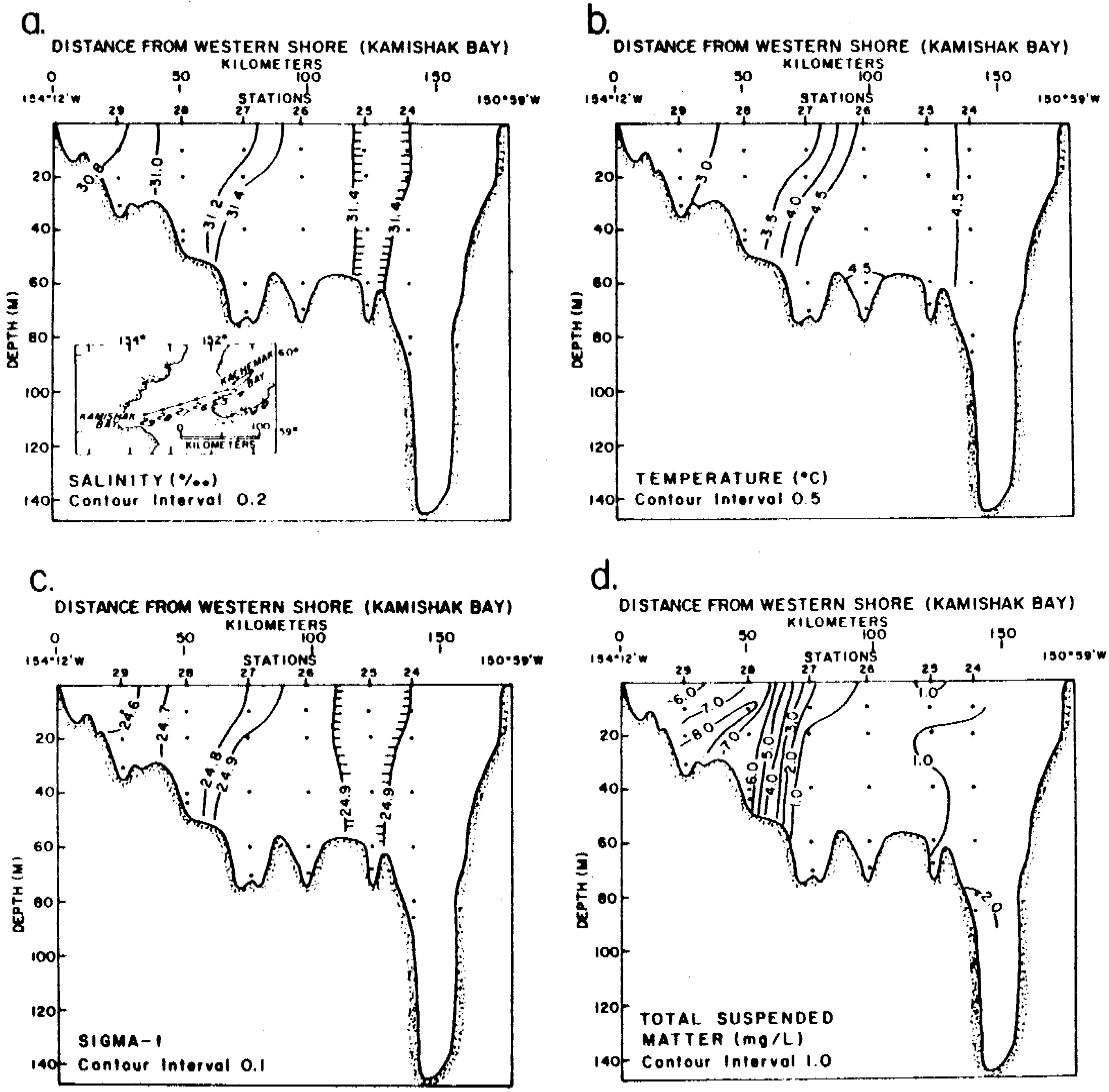

Figure 15. Vertical cross sections of the distributions of: a. salinity; b. temperature; c. sigma-t; and d. total suspended matter for stations 24 thru 29 in lower Cook Inlet (Cruise RP-4-Di-77A-IV, 4-16 April 1977).

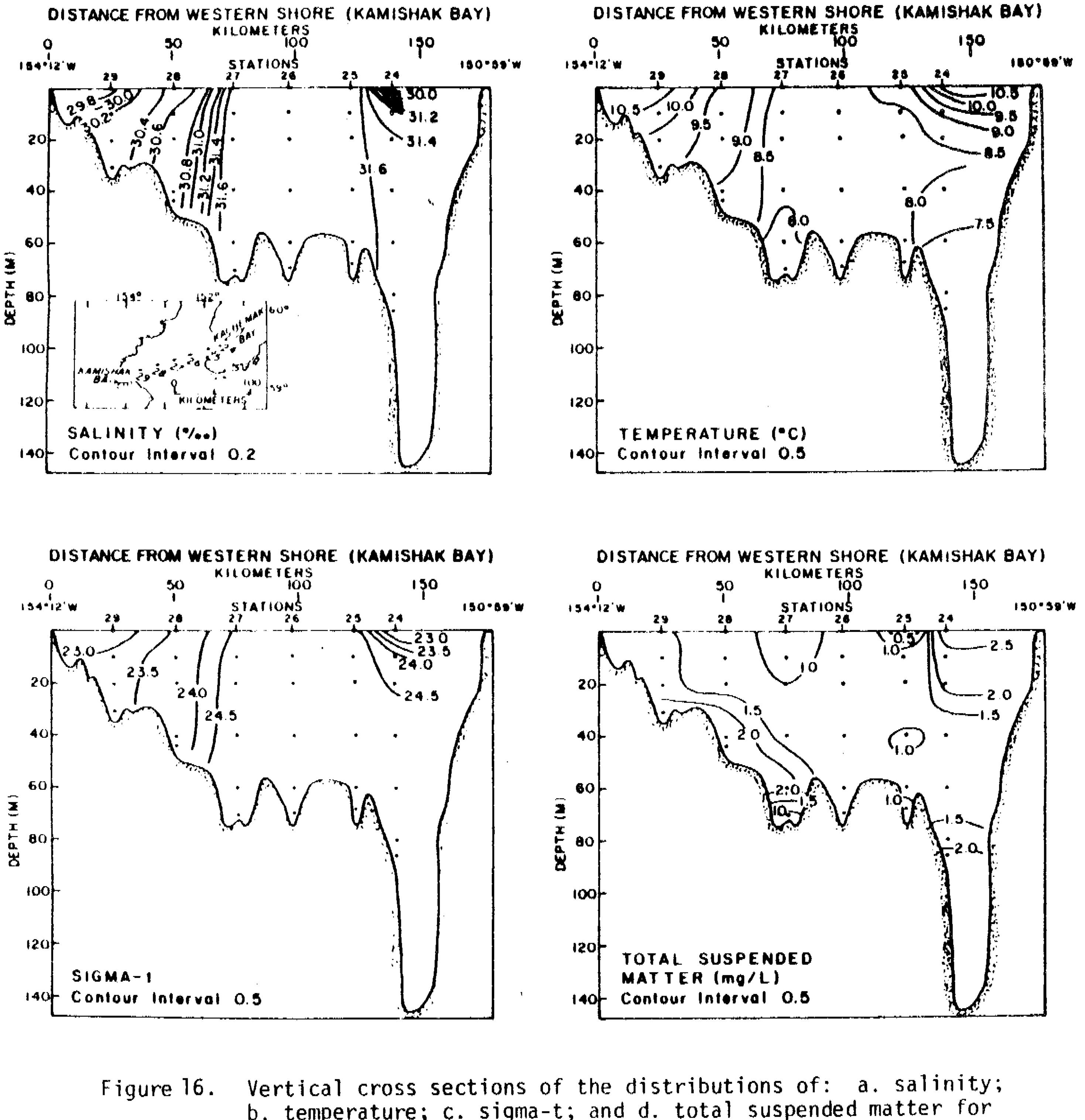

Figure 16. Vertical cross sections of the distributions of: a. salinity; b. temperature; c. sigma-t; and d. total suspended matter for stations 24 thru 29 in lower Cook Inlet (Cruise Acona-245, 28 June-12 July 1977).

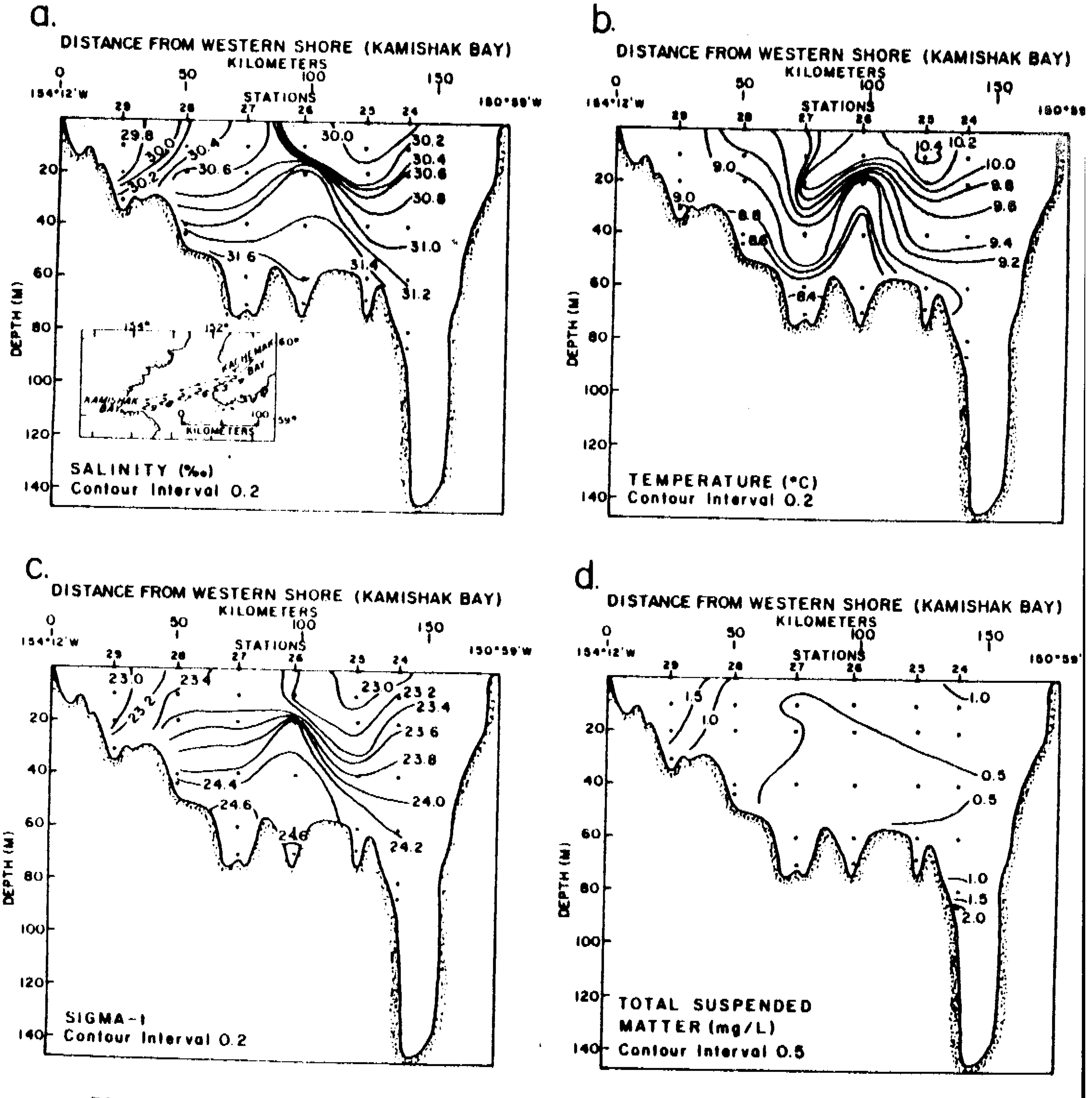

Figure 17. Vertical cross sections of the distributions of: a. salinity; b. temperature; c. sigma-t; and d. total suspended matter for stations 24 thru 29 in lower Cook Inlet (Cruise RP-4-Di-77C-II, 3-12 October 1977).

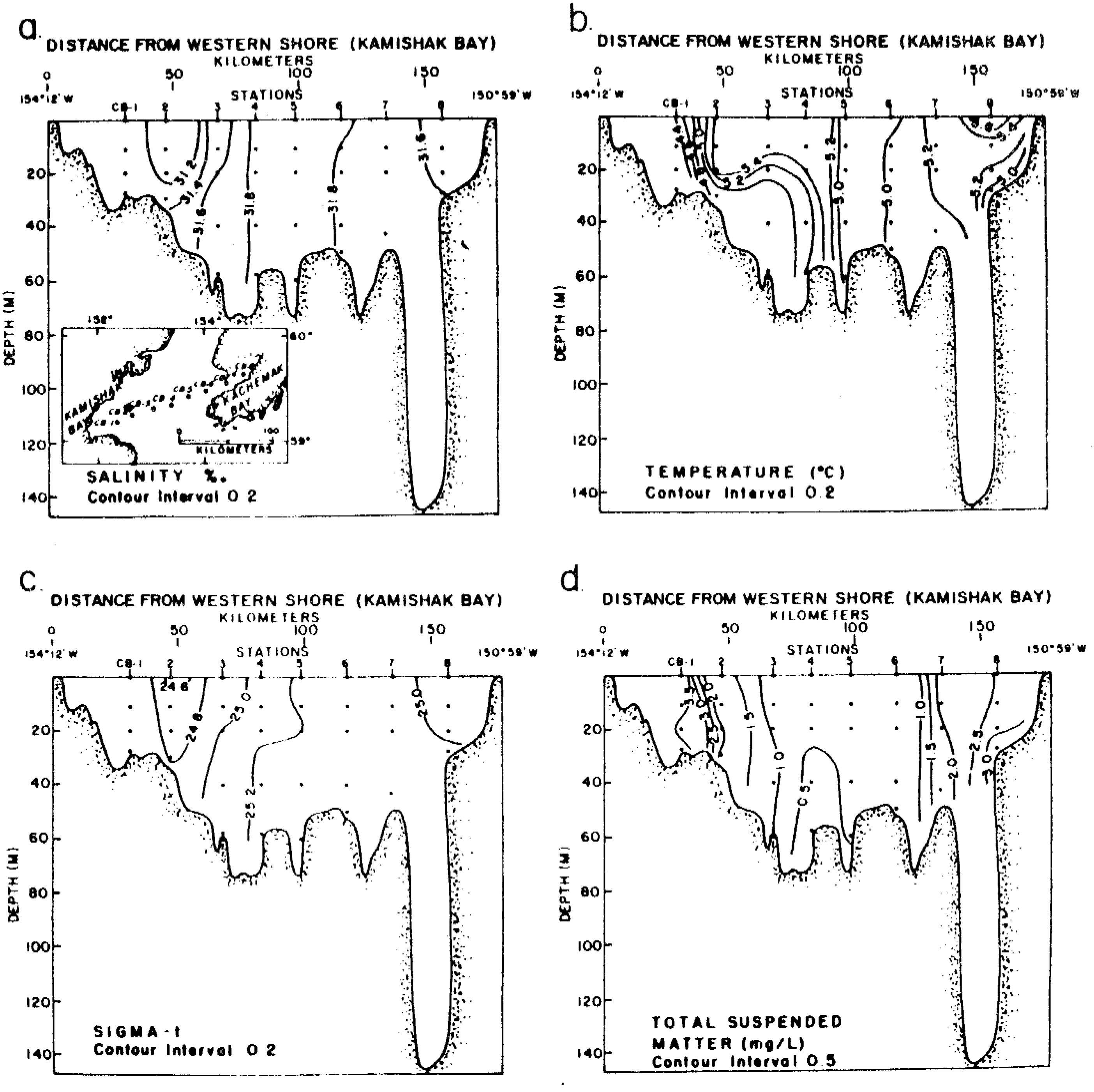

Figure 18. Vertical cross sections of the distributions of: a. salinity; b. temperature; c. sigma-t; and d. total suspended matter for stations CB-1 thru CB-8 in lower Cook Inlet (Cruise RP-4-Di-78A-III, 4-17 May 1978).

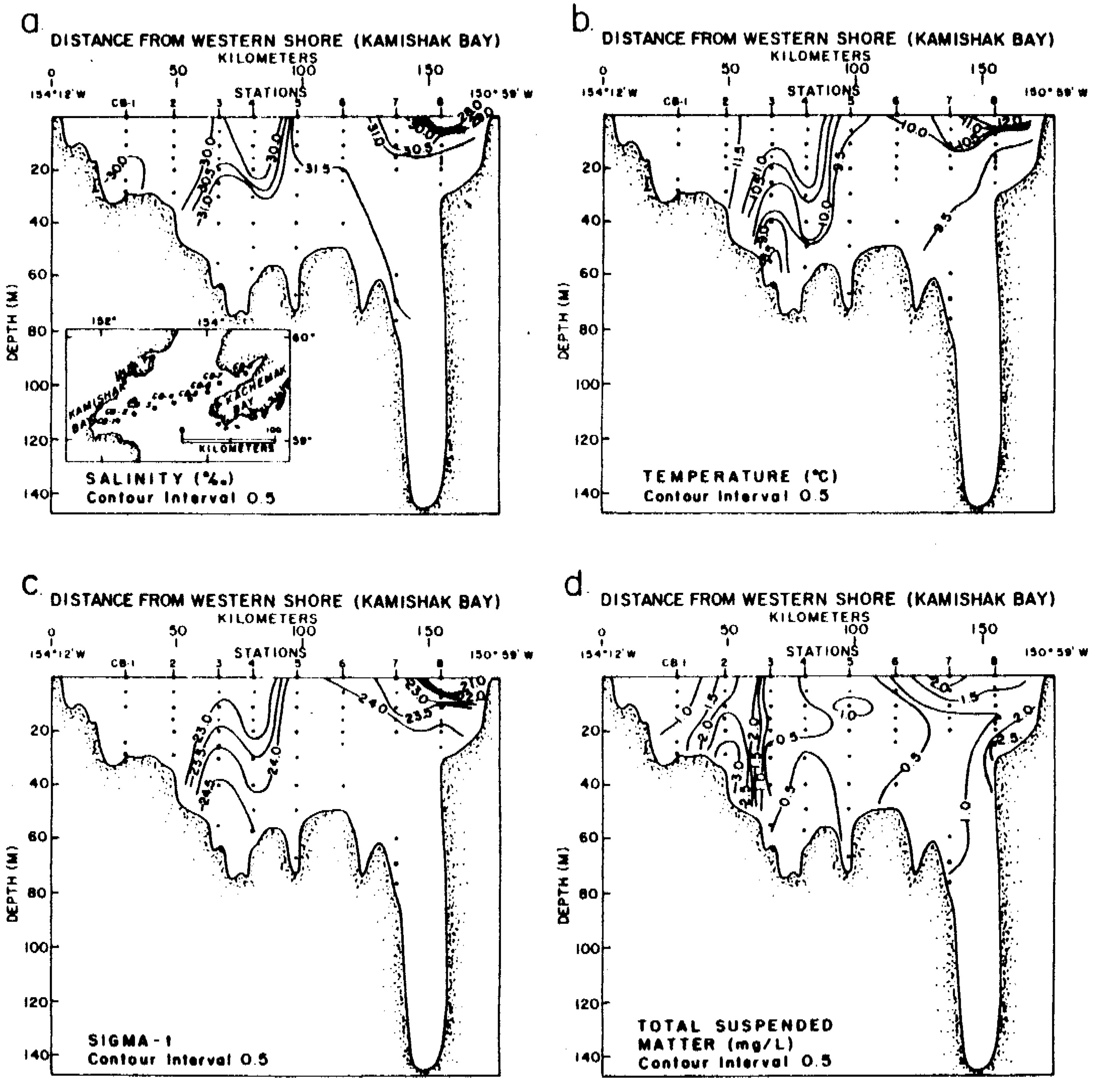

Figure 19. Vertical cross sections of the distributions of: a. salinity; b. temperature; c. sigma-t; and d. total suspended matter for stations CB-1 thru CB-8 in lower Cook Inlet (Cruise RP-4-Di-78B-II, 22 August-6 September 1978).

matter distribution in this region are totally dependent upon input from the rivers and tidal mixing. Sharma (1979) states that the amount of suspended matter varies considerably throughout the Foreland region during each tidal cycle, with significant quantities of suspended material being carried south of the Forelands during ebb tide.

Since suspended matter may play an important role in scavenging and transporting contaminants from the study region, the question of where the large amount of suspended materials that pass into lower Cook Inlet ultimately reside becomes important. The dramatic decrease in suspended loads from > 100 mg/L near the Forelands to < 1.0 mg/L near the inlet's mouth may be an indication of particulate settling. However, recent studies of major sediment types in lower Cook Inlet indicate that the sediments in the central part of the inlet consist primarily of unconsolidated coarse-grained sands deposited during the retreat of the Pleistocene glaciers (Bouma and Hampton, 1976). Another possibility is that the suspended matter gradients are the result of dilution of the brackish water by the less turbid oceanic water. Figure 20 shows a scatter plot of the relationship between total suspended matter and salinity for the surface samples from the central region of lower Cook Inlet, where the cross-channel gradients are highest. The data, which were from the April 1977 cruise, show that the suspended loads are linearly correlated with salinity, indicating that dilution is the major process controlling suspended matter concentrations in the central portion of the inlet. A scatter plot for the July 1977 data shows similar results. These results suggest that the central part of lower Cook Inlet acts like a conduit, allowing large amounts of suspended material to pass through the system with little net sedimentation. Sedimentation of suspended matter may be occurring in the numerous small embayments along the coast. Some information on the relative significance of this process is discussed in section VI-C of this report.

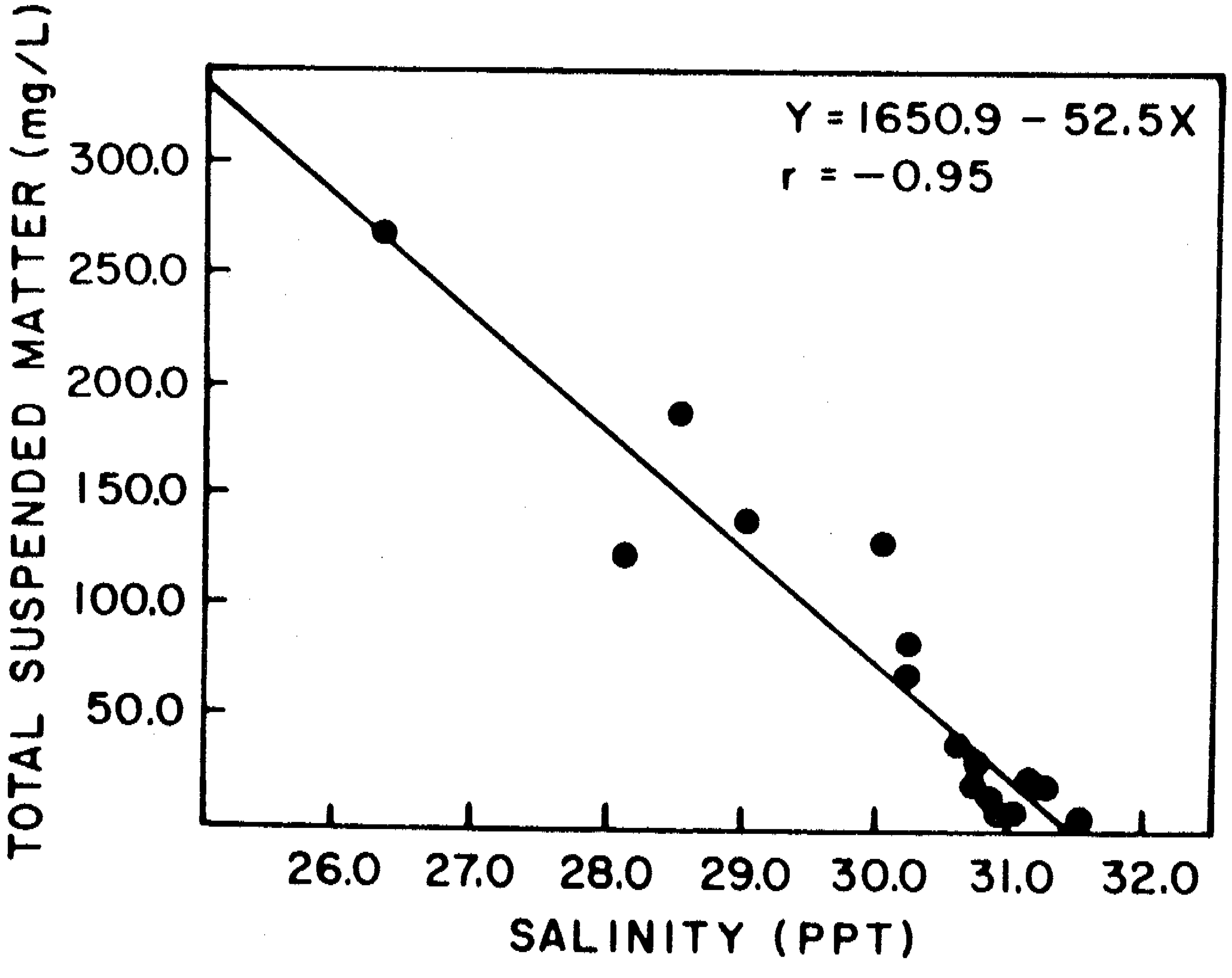

Figure 20. Scatter plot of the relationship between total suspended matter and salinity for surface samples from lower Cook Inlet (Cruise RP-4-Di-77A-IV, 4-16 April 1977).

Figures 21 and 22 show vertical cross-sections of temperature, salinity, total suspended matter, and sigma-t for stations located in Shelikof Strait. The data were obtained on the August-September cruise. Stations SS2, SS5, SS6, SS8, SS9, SS10, and SS12 represent a longitudinal cross-section along the axis of the strait. Stations SS4 through SS6 and SS11 through SS13 represent transverse cross-sections at mid-channel and at the upper mouth, respectively. The data show cross-channel gradients of temperature, salinity, and suspended matter which are consistent with the cross-channel gradients in lower Cook Inlet. This is the strongest evidence to date which suggests that riverborne suspended matter from Cook Inlet is transported into Shelikof Strait. There is also evidence for a near-bottom nepheloid layer in the strait which exists in the lower 50-60 m of the water column. Since there are no corresponding large changes in temperature and salinity which would tend to buoy up suspended material, the bottom nepheloid layer in this region is probably due to resuspension of bottom sediments. This suggests that sediments and/or contaminants probably get redistributed in the strait before final deposition occurs.

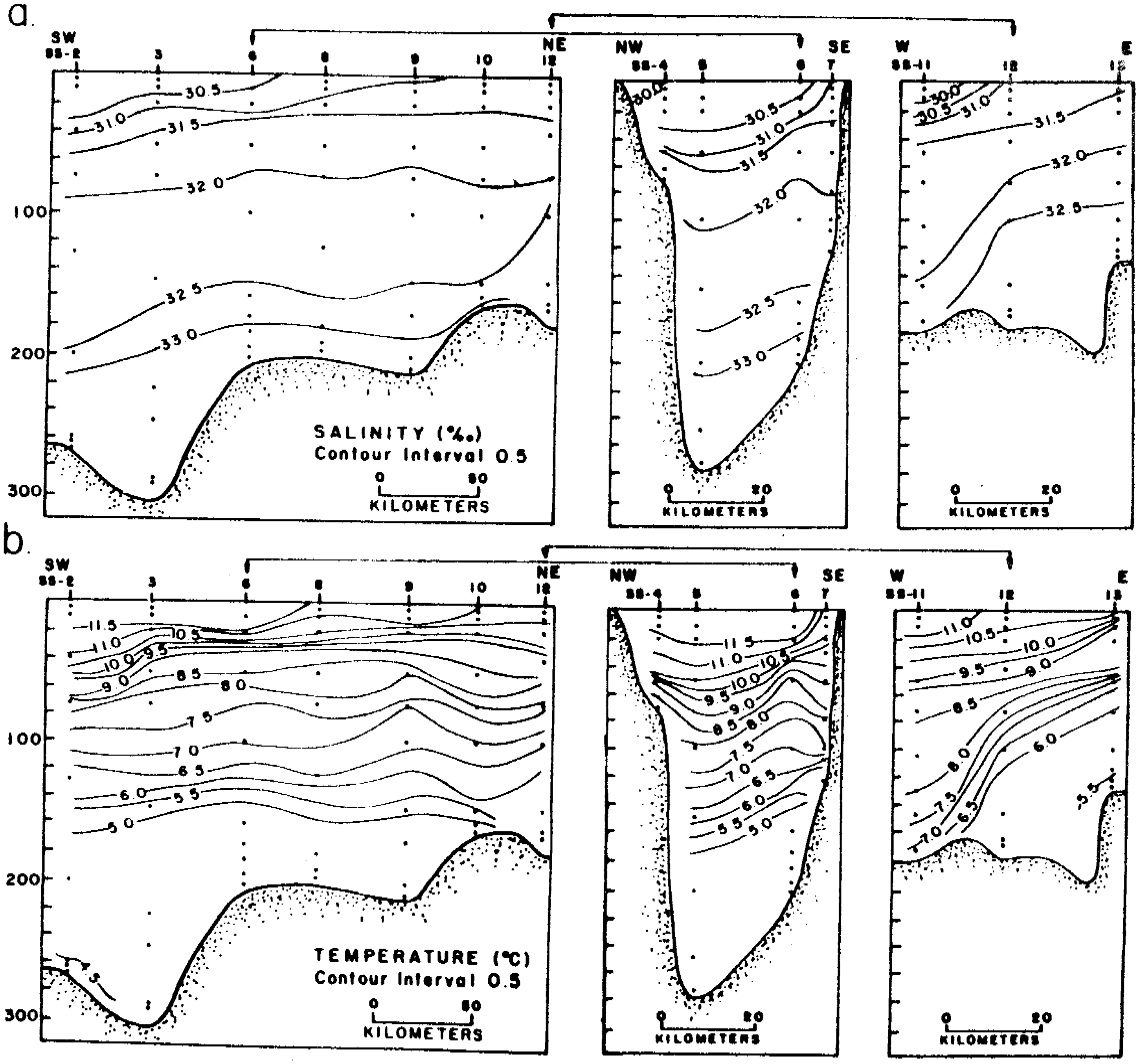

Figure 21. Vertical cross sections of the distributions of: a. salinity; and b. temperature for stations SS-2 thru SS-13 in Shelikof Strait (Cruise RP-4-Di-78B-II, 22 August-6 September 1978).

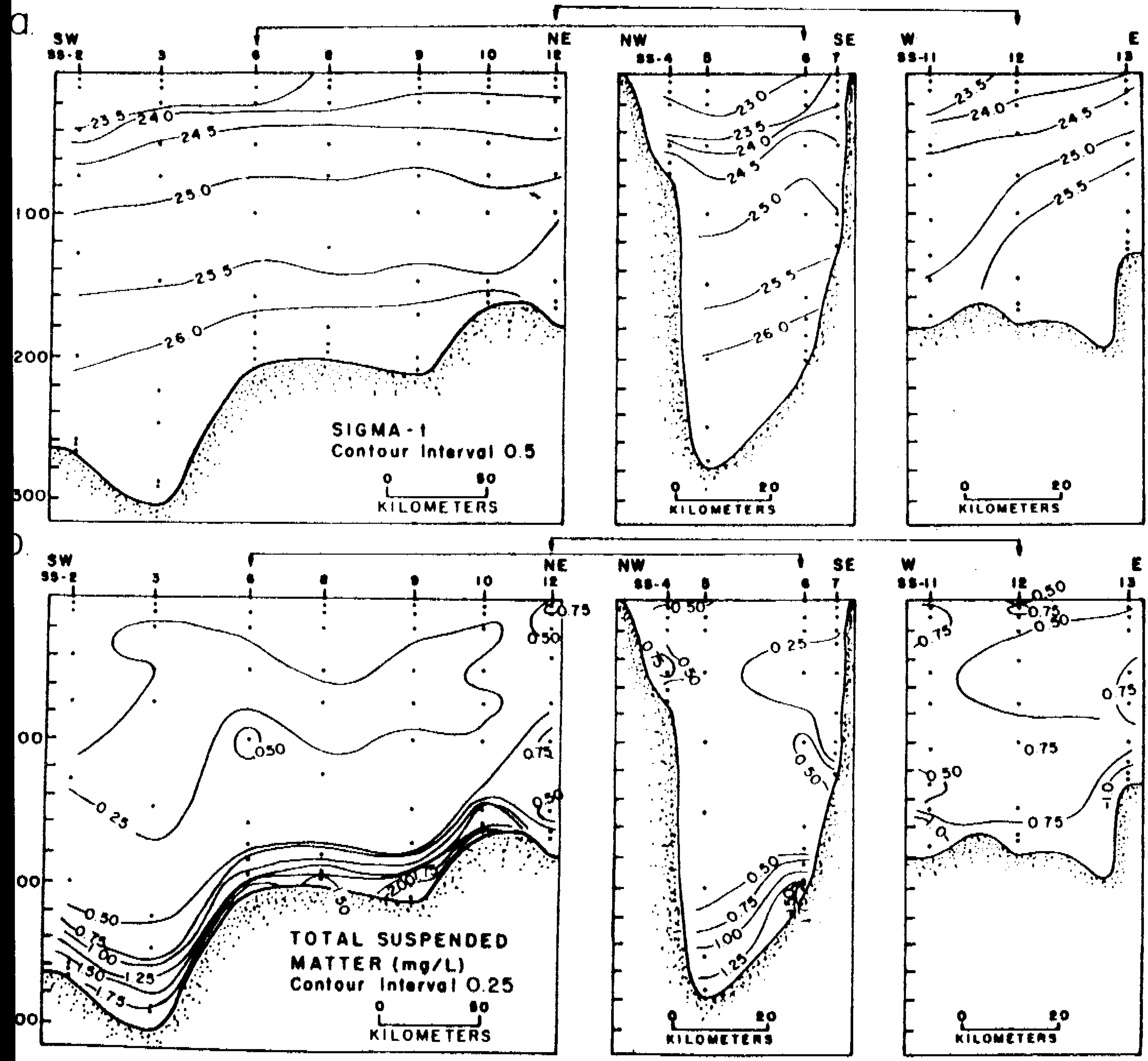

Figure 22. Vertical cross sections of the distributions of: a. sigma-t; and b. total suspended matter for stations SS-2 thru SS-13 in Shelikof Strait (Cruise RP-4-Di-78B-II, 22 August-6 September 1978).

VI.A.2. Temporal Variability of Suspended Matter

In order to obtain some information about high frequency (hourly) fluctuations of particulate concentrations in lower Cook Inlet, a number of time-series experiments were conducted at different locations during each of the five cruises. Figure 23 shows the times and locations of the individual experiments. As shown in the figure, time-series experiments were conducted at stations 4 and 11 during the April and July 1977 cruises, respectively, at stations CB-7 and CB-9 during the May 1978 cruise, and at CB-10 on the August-September 1979 cruise. Water samples were collected and filtered every two hours from the surface and 5 m above the bottom. The results of these experiments are shown in Figure 24. The high and low tides are represented in the figures by arrows. The reference points for the tidal data are indicated in the figure caption. At the stations on either side of Kalgin Island, suspended matter loads are highly variable both at the surface and near the bottom. At the surface particulate concentrations range from 10 to 180 mg/L. The highest concentrations were obtained at CB-10 on the east side of Kalgin Island. The surface maxima at CB-10 have a 6-hour period and appear to reach their peak shortly after the tidal currents have reached maximum velocity. At this location, ebbing and flooding waters converge, current velocities are high and the water column is vertically mixed, causing complex circulation patterns (Gatto, 1976). On the west side of the island, flow patterns are dominated by tidal currents, with maximum suspended matter concentrations in surface waters usually occurring during flood tide. This is probably the result of lateral movement of suspended matter plumes from Drift and Big Rivers during flood tide (Gatto, 1976).

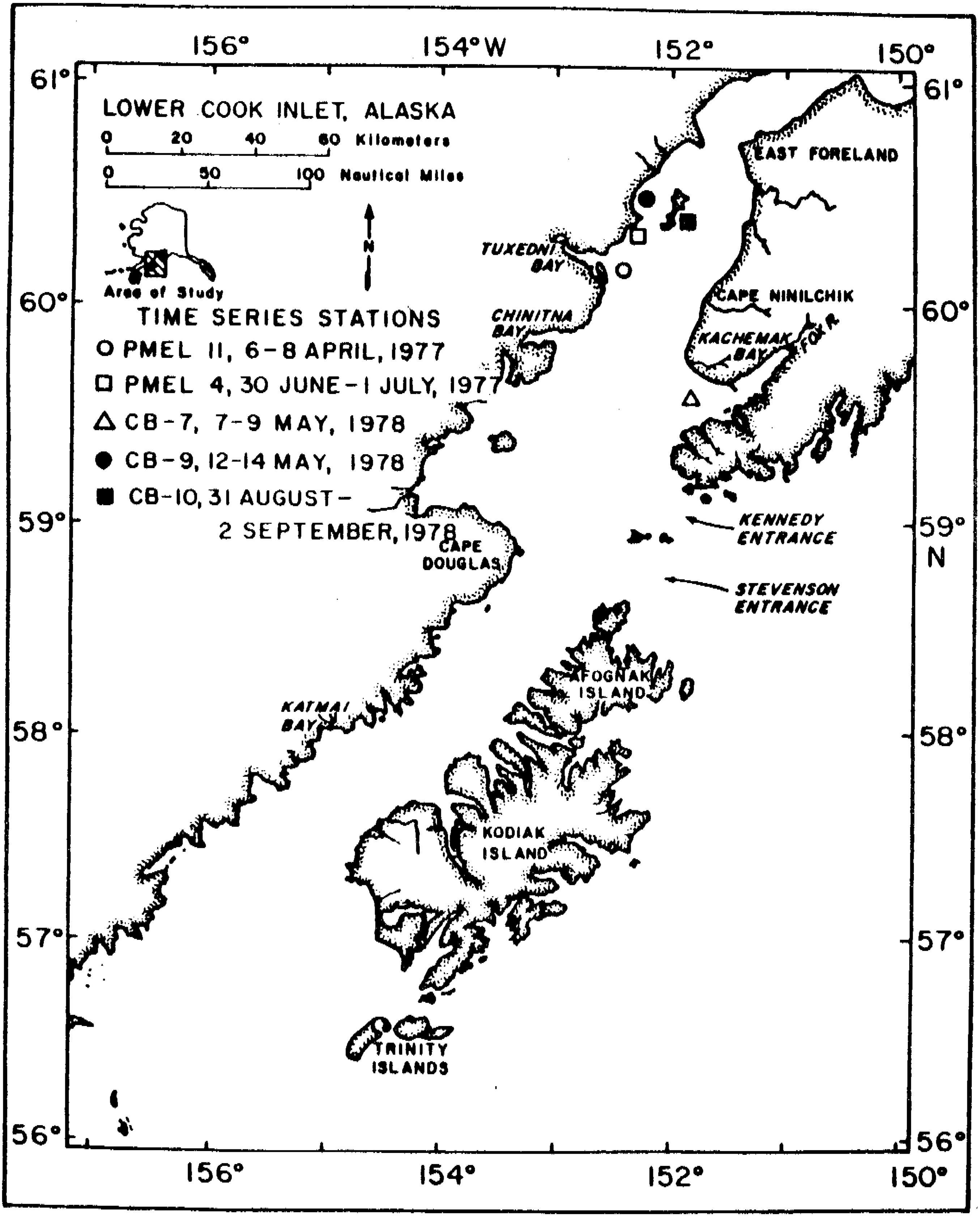

Figure 23. Locations and dates of time series experiments conducted in lower Cook Inlet.

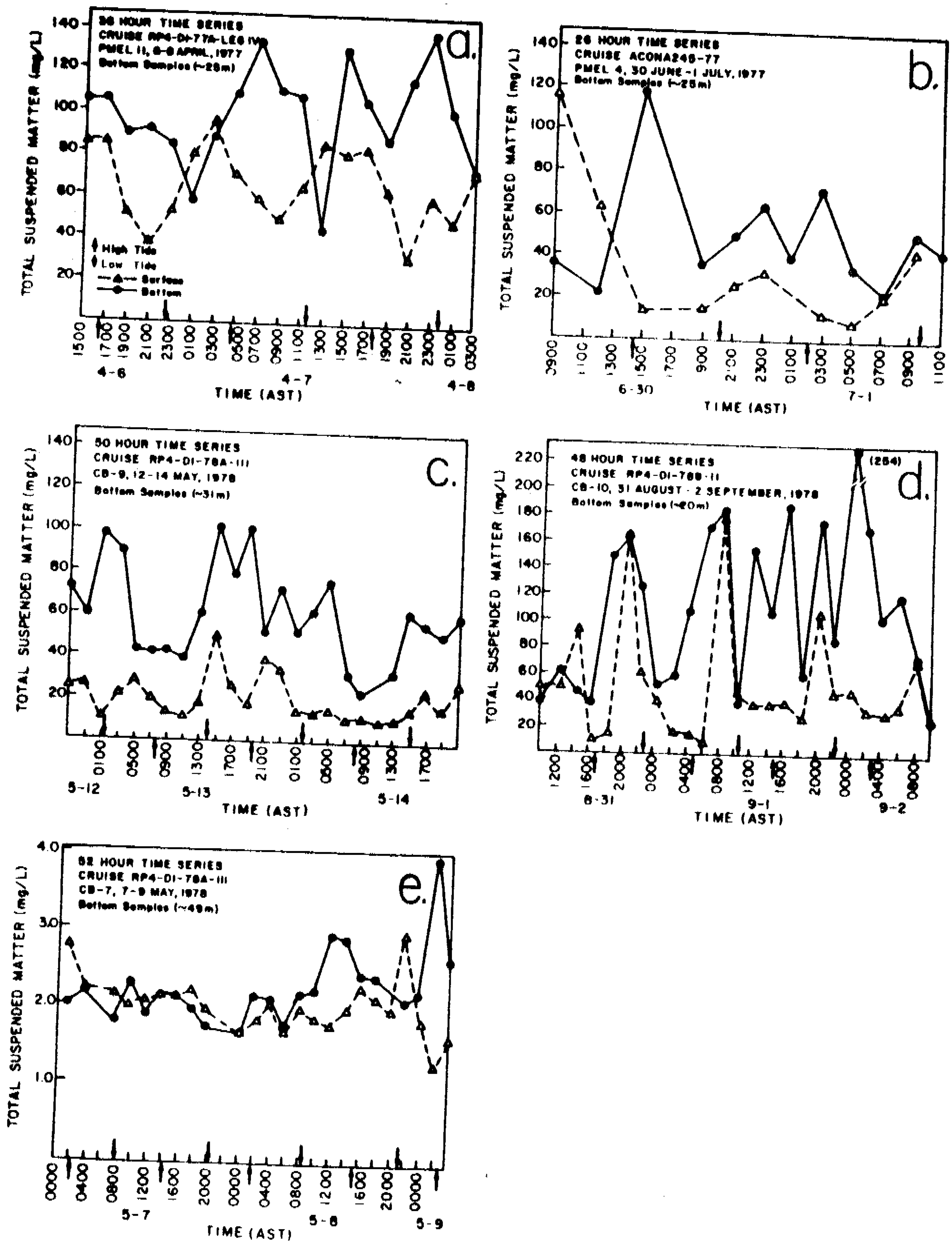

Figure 24. Temporal variability of total suspended matter at the surface and 5 m above the bottom at the time-series stations in lower Cook Inlet. The reference points for the tidal data are: a. Tuxedni Channel; b. Drift River Terminal Tide Station; c. Drift River Terminal Tide Station; d. Kenai City Pier; and e. Homer, Alaska.

The near-bottom particulate maxima do not show a consistent periodicity pattern, but peaks associated with both the ebb and flood currents are evident. Furthermore, near-bottom suspended matter concentrations generally are higher than at the surface, indicating that when the tidal currents reach maximum velocity, the bottom sediments are being resuspended.

While the time series data for the Kachemak Bay station show evidence for greatly reduced concentration fluctuations, the general trend of particulate maxima in surface waters occurring shortly after the ebb current reaches maximum velocity still exists. These data suggest that throughout the inlet tidal currents are a major cause of high frequency fluctuations of suspended matter distributions. It appears that during ebb current, the turbid brackish water from the north moves southward, elevating the ambient suspended load. In near-bottom waters this process is augmented by local resuspension of bottom sediments, if the bottom currents reach some threshold velocity. These conclusions are consistent with the general conclusions of Gatto (1976), who stated that from observations of LANDSAT images of lower Cook Inlet, it appeared that turbid plumes were more prominent in the southern and central part of the lower inlet just after the ebb current.

VI.A.3. Sedimentation Studies

During cruise RP-4-MF-78A-11 (19 May-4 June 1978), three moorings, each supporting one set of tandem sediment traps located 10 m above the bottom, were deployed along a transect line extending from Kamishak Bay to Kachemak Bay in lower Cook Inlet (Fig. 7). The purpose of the traps was to obtain long-term averages of the vertical fluxes of suspended matter in selected regions of lower Cook Inlet. The sediment trap capture period was set for closure approximately 85 days after deployment, which occurred on 27 May 1978.

Of the six sediment traps deployed, four were recovered. The two sediment traps from station ST-3 were accidentally dredged up by the fishing vessel, Columbian, and the samples were lost. In addition, one sample from the sediment traps at ST-2 was also lost due to breakage of the sodium azide diffusion cup during recovery. Table 3 summarizes the particulate matter fluxes obtained by gravimetric analysis of the material captured by the traps. Also included are the mean particulate fluxes obtained by Larrance (1978) for short-term sediment trap deployments at CB-1, CB-4, and CB-7. The long-term flux at ST-1 is about the same as the mean value obtained by Larrance for traps deployed at CB-1 (20.8 g m^{-2} day^{-1} vs. 22.0 g m^{-2} day). This suggests that the two locations are very similar in their sedimentation characterisitics and the data from the two sets of traps can be intercompared. The long-term sediment flux at ST-2 was 2.4 times greater than the mean of the sediment fluxes at CB-4 (28.5 g m^{-2} day^{-1} vs. 12.0 g m^{-2} day). While these stations were less than 15 nautical miles apart (Fig. 7), these differences are probably real because station ST-2 is within the region dominated by the outflowing brackish water and station CB-4 is in the region influenced by the inward flowing Gulf of Alaska water. Presumably, a significant fraction of the suspended matter in the outward flowing brackish water settles out in Kamishak Bay. These data are consistent with the ^{210}Pb sediment accumulation rates for the underlying sediment cores (Table 3). The good agreement between the sedimentation rate and the sediment accumulation rate for CB-1 in Kamishak Bay indicates that this region is a depositional environment for the fine-grained material that originates from upper Cook Inlet.

In order to obtain a more detailed picture of the long-term sedimentation history of fine-grained sediments in lower Cook Inlet and Shelikof Strait, sediment cores were collected during three of the cruises for ^{210}Pb geochronological studies. The locations of the gravity cores obtained are illustrated

Table 3. Comparison of sedimentation rates of suspended materials collected by sediment traps deployed on moorings approximately 10 m above the bottom at selected locations in lower Cook Inlet with average accumulation rates of the underlying sediments as determined by ^{210}Pb geochronology.

Location	Station No.	Average Sedimentation Rate of Suspended Matter ($g\ m^{-2}\ day^{-1}$)	Average Accumulation Rate of Sediments ($g\ m^{-2}\ day^{-1}$)
Kamishak Bay	CB-1*	22.0 ± 25	27.1
	ST-1	20.8 ± 7	2.2
Central Inlet	ST-2	28.5	no data
	CB-4*	12.0 ± 8	no data
Kachemak Bay	CB-7*	18.8 ± 2	10.5

*After Larrance et al. (1979).

in Fig. 25. The cores were cut into 2-cm sections and delivered to C. W. Holmes and E. A. Martin (U.S. Geological Survey, Corpus Christi, Texas) who performed the ^{210}Pb analyses. No cores were collected from the central basin of lower Cook Inlet although numerous attempts were made. The sediments there are primarily composed of relict sands and gravels (Bouma and Hampton, 1976) which did not remain intact during recovery of the gravity corer. The results of the ^{210}Pb radiometric analyses are given in Table 4. The data show that the major regions of sedimentation in decreasing order of importance are: Shelikof Strait, Kamishak Bay, and Kachemak Bay. Using the sediment distribution map of Bouma and Hampton (1976) for lower Cook Inlet, it is estimated that the areas of active sedimentation are 750 km^2 in Kamishak Bay and 60 km^2 in Kachemak Bay. Averaging the ^{210}Pb sediment accumulation rates for these two regions (i.e., 0.66 g cm^{-2} y^{-1} in Kamishak Bay and 0.38 g cm^{-2} g^{-1} in Kachemak Bay) and multiplying by the area of active sedimentation yield estimates of annual sediment accumulations of 4.9 x 10^{12}g y^{-1} and 2.3 x 10^{11} g y^{-1}, respectively, for these two regions. This represents only about 18% of the total annual input of fine-grained sediments to Cook Inlet from the rivers (estimated to be approximately 2.8 x 10^{13} g y^{-1}, Gatto, 1976; Sharma, 1979). The remaining 82% must either be deposited in upper Cook Inlet or transported in Shelikof Strait. Since the sediments of upper Cook Inlet also consist primarily of relict sands and gravels (Sharma and Burrell, 1974; Sharma et al., 1979), we believe that the major fraction of fine-grained sediments that originates in Cook Inlet is transported to Shelikof Strait where it is deposited. This conclusion is supported by ^{210}Pb data for Shelikof Strait. Using the 100 m contour as the upper limit of the region of active sedimentation in the upper third of the Strait and the 200 m contour as the upper limit of the region of active sedimentation in the lower Strait, an area of 9200 km^2 is estimated to be the region of active

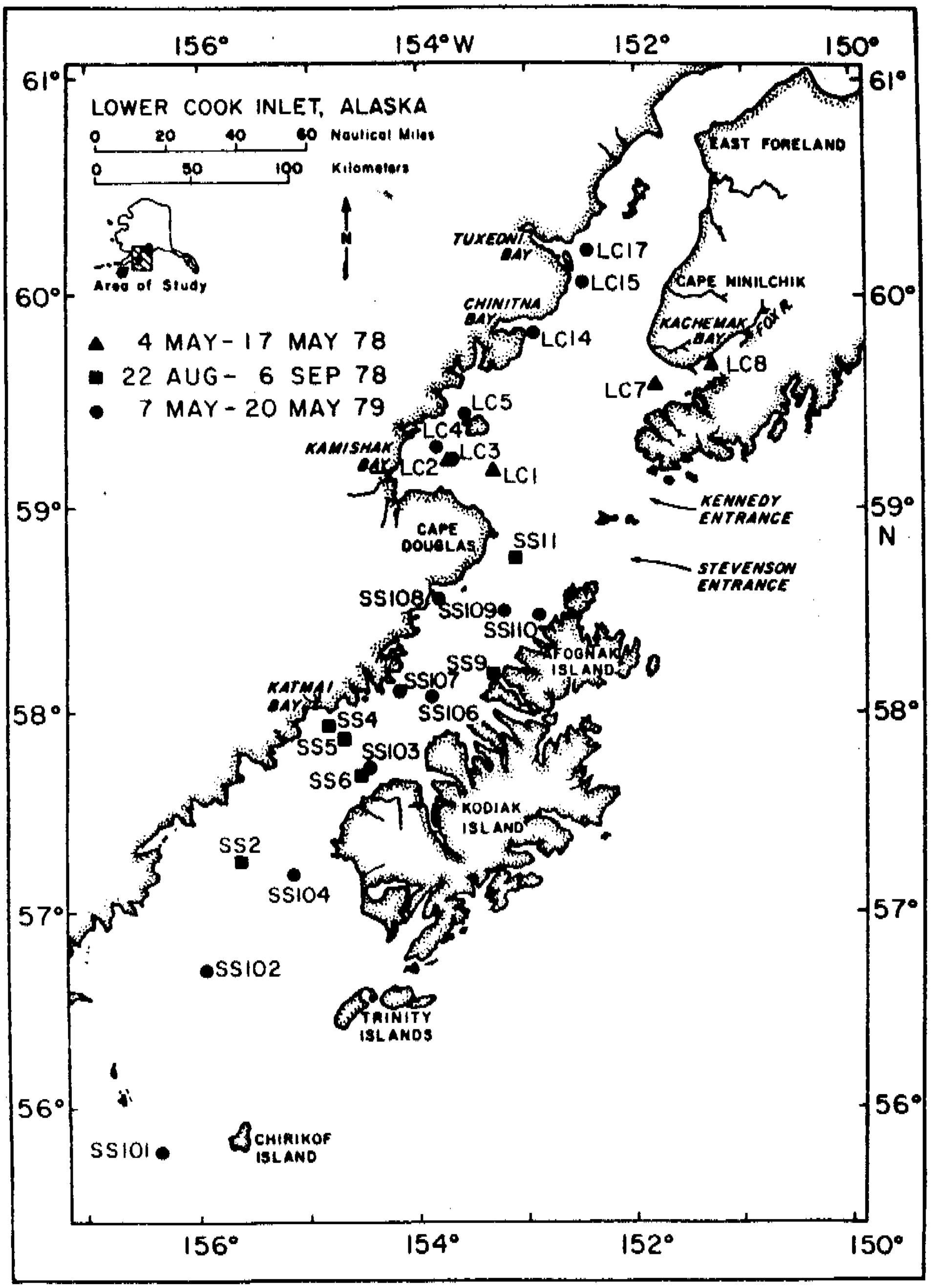

Figure 25. Locations of stations where gravity cores have been collected for the determination of excess ^{210}Pb activity.

Table 4. Sediment accumulation rates for sediment cores collected from Lower Cook Inlet and Shelikof Strait. Accumulation rates were determined by the excess ^{210}Pb method.[1]

Station No.	Position	Depth (m)	Core Acquired Month/Year	Accumulation Rate (g m^{-2} d^{-1})
SS101	55°46.8'N, 156°22.1'W	245	May 1979	DNA[2]
SS102	56°42.8'N, 155°56.7'W	292	May 1979	16.7
SS104	57°11.2'N, 155°07.8'W	225	May 1979	DNA
SS2	57°17.1'N, 155°37.0'W	278	Sept.1978	DNA
SS4	57°55.3'N, 154°48.4'W	152	Sept.1978	DNA
SS5	57°52.1'N, 154°42.9'W	273	Sept.1978	17.8
SS6	57°42.4'N, 154°29.1'W	208	Sept.1978	20.3
SS103	57°43.0'N, 154°26.7'W	208	May 1979	16.7
SS106	58°03.5'N, 153°51.7'W	194	May 1979	37.2
SS107	58°05.2'N, 154°09.2'W	285	May 1979	DNA
SS9	58°11.3'N, 153°21.1'W	210	Sept.1978	-
SS108	58°32.9'N, 153°47,2'W	51	May 1979	22.5
SS109	58°28.9'N, 153°12.9'W	168	May 1979	8.8
SS110	58°28.2'N, 152°53.6'W	192	May 1979	DNA
SS11	58°46.4'N, 153°08.3'W	186	Sept.1978	NA[3]
LC1	59°11.5'N, 153°19,2'W	38	May 1978	2,2
LC2	59°14.4'N, 153°40.9'W	33	May 1978	27.1
LC3	59°13.4'N, 153°40.7'W	35	May 1979	DNA
LC4	59°16.4'N, 153°50.6'W	24	May 1979	9.3
LC5	59°25.6'N, 153°35.5'W	26	May 1979	DNA
LC7	59°34.1'N, 151°37.1'W	79	May 1978	10.4
LC8	59°39.3'N, 151°16.7'W	30	May 1978	5.2
LC14	59°46.9'N, 152°55.5'W	27	May 1979	DNA
LC15	60°03.5'N, 152°28.4'W	30	May 1979	DNA
LC17	60°14.2'N, 152°23.6'W	48	May 1979	NA

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[1] Data prepared by C. W. Holmes and E. A. Martin, U.S.G.S., Corpus Christi, Texas

[2] DNA - data not available

[3] NA - no excess ^{210}Pb detected.

sedimentation. This region was divided into three sections and average accumulation rates were computed for each (i.e., 0.8 g cm^{-2} y^{-1} for the upper third; 0.7 g cm^{-2} g^{-1}; for the middle third; and 0.6 g cm^{-2} y^{-1} for the bottom third). Multiplying the sediment accumulation rates by the respective areas and obtaining the sum yields an estimate of the annual sediment accumulation rate of 6.2 x 10^{13} g y^{-1} for Shelkiof Strait between Cape Douglas and the Trinity Islands. This value is approximately 220% of the annual input of fine-grained sediments from the rivers discharging into Cook Inlet. This suggests that additional sources of fine-grained sediments are required to balance this accumulation rate. The recent findings of Feely and Massoth (in press) indicate that suspended sediments in Shelikof Strait consist of a mixture of clay-sized suspended material from Cook Inlet, terrigeneous sediments from the Copper River in the northeast Gulf of Alaska, and biogenic material produced in the water column. If these materials form the bulk of the fine-grained sediments in Shelikof Strait then the sedimentalogical data presented here would indicate that the sediments of Shelikof Strait are probably composed of nearly a 40:60 mixture of Cook Inlet-derived material and Cooper River-derived material.

VI.A.4. Elemental Composition of the Particulate Matter in the Water Column

The particulate matter collected during the six cruises in lower Cook Inlet have been analyzed using a variety of methods to determine how the elements are distributed in the particles. Total elemental composition of the particulate matter was determined by the x-ray fluorescence and atomic absorption techniques described in section V of this report. Trace elements associated with the easily oxidizable organic matter and iron and manganese oxyhydroxide coatings were determined on selected samples from 1978 time series stations at CB-7, CB-9, and CB-10. The results of these studies are described below.

VI.A.4.1. Total Elemental Composition of the Particulate Matter

Tables 5 through 7 compare summaries of the data on the total elemental composition of suspended matter from the Susitna, Knik, and Matanuska Rivers

Table 5. Summary of the elemental composition of particulate matter samples from the major rivers discharging into Cook Inlet. (Surface samples were obtained with a precleaned 4-L polyethylene bottle extended from a bridge 26 June 1977.)

Element	Susitna River	Matanuska River	Knik River
C (Wt.%)	1.04	0.55	0.75
N (Wt.%)	0.06	0.03	0.05
Mg (Wt.%)	4.28	3.02	4.30
Al (Wt.%)	10.39	8.57	12.90
Si (Wt.%)	36.12	28.53	36.32
K (Wt.%)	2.62	1.54	2.73
Ca (Wt.%)	2.33	2.37	1.33
Ti (Wt.%)	0.63	0.55	0.67
Cr (ppm)	172	112	182
Mn (ppm)	1308	1157	1206
Fe (Wt.%)	6.45	6.07	6.90
Ni (ppm)	94	43	70
Cu (ppm)	71	49	61
Zn (ppm)	186	106	152
Pb (ppm)	56	25	51

with summaries of the surface and near-bottom data for the April and July 1977 cruises in lower Cook Inlet. Within the statistical limits of the measurements the samples from lower Cook Inlet have very nearly the same major element composition as the samples from the rivers. This is especially true for Al, K, Ti, and Fe which have been shown to be almost exclusively associated with aluminosilicate minerals of terrestrial origin (Price and Calvert, 1973). The high concentrations of these elements in the surface and near-bottom samples from lower Cook Inlet indicate that aluminosilicate minerals are the most dominant solid phase in the particulate matter. These data indicate that approximately 80-95% of the particulate matter is aluminosilicate minerals.

Table 6. Summary of the elemental composition of particulate matter samples from lower Cook Inlet (Cruise RP-4-Di-77A-IV, 4-16 April 1977).

Element	Average of 50 surface samples	Average of 50 samples from 5 m from the bottom
C (Wt.%)	4.01 ± 4.0	2.72 ± 2.5
N (Wt.%)	0.65 ± 0.5	0.41 ± 0.4
Mg (Wt.%)	3.54 ± 0.6	3.47 ± 0.9
Al (Wt.%)	3.64 ± 1.6	8.70 ± 1.6
Si (Wt.%)	31.04 ± 3.4	30.20 ± 4.3
K (Wt.%)	2.15 ± 0.4	2.24 ± 0.4
Ca (Wt.%)	2.20 ± 0.4	2.23 ± 0.3
Ti (Wt.%)	0.55 ± 0.1	0.58 ± .07
Cr (ppm)	95 ± 15	99 ± 16
Mn (ppm)	1313 ± 113	1326 ± 159
Fe (Wt.%)	6.22 ± 1.0	6.42 ± 0.8
Ni (ppm)	61 ± 10	63 ± 10
Cu (ppm)	71 ± 15	76 ± 17
Zn (ppm)	165 ± 32	176 ± 34
Pb (ppm)	56 ± 13	56 ± 12

These results are not surprising since the Susitna, Matanuska and Knik Rivers supply about 15-20x10^6 tons of sediment annually to the inlet (Rosenberg and Hood, 1967).

Tables 6 and 7 also summarize the elemental composition of 42 samples taken 5 m above the bottom. In general, the major element concentrations of the near-bottom samples are similar to the surface samples. This is especially true for the April 1977 cruise and in the northern part of the inlet where the water column is well mixed. However, during the July 1977 cruise and in the southern part of the inlet the water column was vertically stratified (Fig. 16) and the elemental composition of the suspended matter showed distinct differences between the surface and 5 m above the bottom. For example, Figure 26 shows vertical cross-sections of particulate carbon and carbon-nitrogen ratios for the May and August-September 1978 cruises. The August-September data show higher particulate carbon concentrations at the surface than at the bottom, indicating a vertical stratification of the particulate organic matter. Similar vertical gradients are not easily discernible in the May 1978 or April 1977 data which suggests that in early spring the waters are extremely well-mixed with respect to water properties and suspended matter.

The vertical cross-sections of particulate carbon also show significant cross channel gradients in both spring and summer data, with the highest concentrations and vertical gradients occurring at stations located in Kachemak Bay. Larrance et al. (1977) state that phytoplankton productivity and standing stocks of chlorophyll a are highest in Kachemak Bay and decrease steadily to low values in the middle of the inlet. These data suggest that the observed variations of particulate carbon are directly related to production of marine organic matter in the inlet, with Kachemak Bay being the most productive. This is probably the result of a number of factors, including:

Table 7. Summary of the elemental composition of particulate matter from lower Cook Inlet and Shelikof Strait (Acona-245, 28 June-12 July 1977).

	Lower Cook Inlet		Shelikof Strait	
Element	Average of 50 Surface Samples	Average of 51 Samples from 5 m above the Bottom	Average of 17 Surface Samples	Average of 16 Samples from 5 m above the Bottom
C (Wt. %)	10.77 ± 11.0	6.18 ± 9.0	31.17 ± 11.2	8.40 ± 5.8
N (Wt. %)	1.98 ± 2.0	0.99 ± 1.4	4.89 ± 1.5	1.24 ± 0.8
Mg (Wt. %)	2.86 ± 1.41	3.59 ± 0.82	1.89 ± 0.91	4.01 ± 1.22
Al (Wt. %)	6.98 ± 4.24	8.88 ± 2.34	3.72 ± 2.46	9.49 ± 3.20
Si (Wt. %)	35.75 ± 5.56	38.09 ± 4.92	28.67 ± 10.10	44.71 ± 3.60
K (Wt. %)	1.86 ± 0.86	2.24 ± 0.45	0.89 ± 0.43	2.19 ± 0.63
Ca (Wt. %)	1.84 ± 0.63	2.33 ± 0.32	1.53 ± 0.35	2.08 ± 0.33
Ti (Wt. %)	0.46 ± 0.20	0.58 ± 0.10	0.27 ± .09	0.53 ± 0.12
Cr (ppm)	99 ± 30	115 ± 24	75 ± 36	116 ± 29
Mn (ppm)	1138 ± 574	1460 ± 362	981 ± 709	4174 ± 7642
Fe (Wt. %)	5.14 ± 2.11	6.50 ± 0.95	3.15 ± 1.14	6.39 ± 1.71
Ni (ppm)	70 ± 25	81 ± 16	59 ± 19	77 ± 13
Cu (ppm)	99 ± 33	100 ± 31	94 ± 27	112 ± 30
Zn (ppm)	352 ± 158	343 ± 194		
Pb (ppm)	65 ± 19	69 ± 13	60 ± 10	76 ± 22

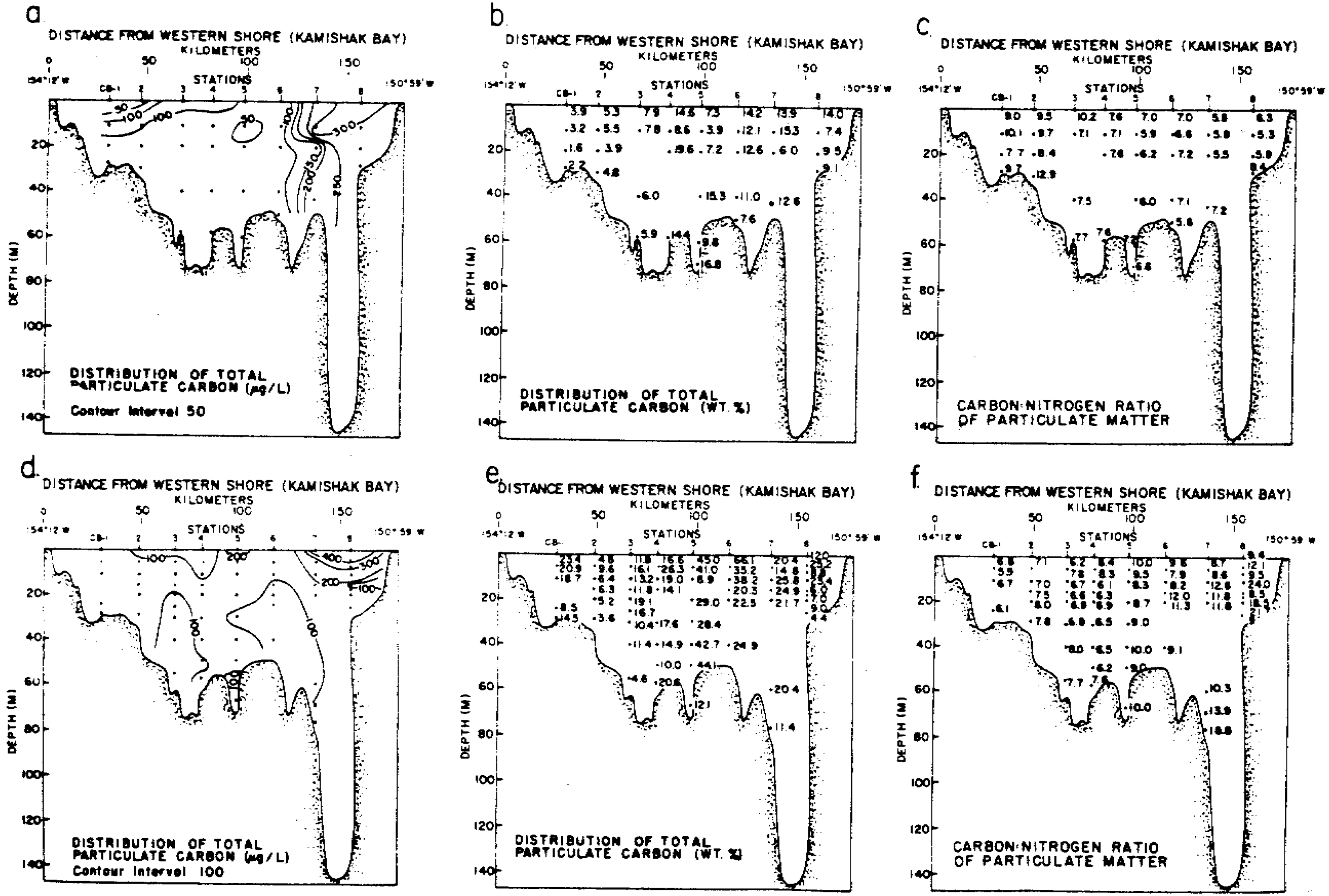

Figure 26. Vertical cross sections of the distributions of: a. particulate carbon in units of μg/L; b. particulate carbon in weight percent of the suspended matter; and c. carbon to nitrogen atom ratios for stations CB-1 thru CB-8 in lower Cook Inlet (Cruise RP-4-Di-78A-III, 4-17 May 1978). Figures 20d, 20e and 20f show the same type of data for Cruise RP-4-Di-78B-II (22 August - 6 September 1978).

(1) upwelling of nutrient-rich subsurface waters in the region northwest of the Chugach Islands (Burbank, 1977); (2) stratification and stabilization of the surface waters due to formation of two gyre systems (Burbank, 1977 and Larrance et al., 1977); and (3) deeper light penetration due to input of relatively nonturbid oceanic water from the Gulf of Alaska (this report).

Undoubtedly, some of the organic matter that is produced in the Kachemak Bay region settles to the bottom and gets buried within the sediments. However, since the net circulation is to the north and back again to the southwest into Shelikof Strait, a significant fraction of the organic matter produced in Kachemak Bay probably gets deposited in Shelikof Strait. This means that the two regions are linked by physical, chemical, and biological processes. While detailed information on chemical and biological processes in Shelikof Strait are unavailable at this time, some recent data from the August-September cruise are available which tend to support the hypothesis that the two regions are linked by chemical processes. Figure 27 shows the distributions of particulate C and particulate Mn in Shelikof Strait. The enrichment of particulate Mn in the near-bottom waters is probably due to release of reduced Mn from the sediments. This process occurs in regions of high productivity and high sedimentation (Graham et al., 1976). While data on regional productivity and sedimentation in Shelikof Strait are unavailable at this time, the data suggest that there is a positive correlation between particulate carbon and manganese in the near-bottom waters and that lower Cook Inlet is probably a major source for the organic matter. Although limited to a great extent, these data indicate that physical and chemical processes occurring in dynamic environments in lower Cook Inlet directly affect bottom water chemistry in the less dynamic environments of Shelikof Strait. If any of these processes are altered, either by natural or artificial means, the major effect might be observed in Shelikof

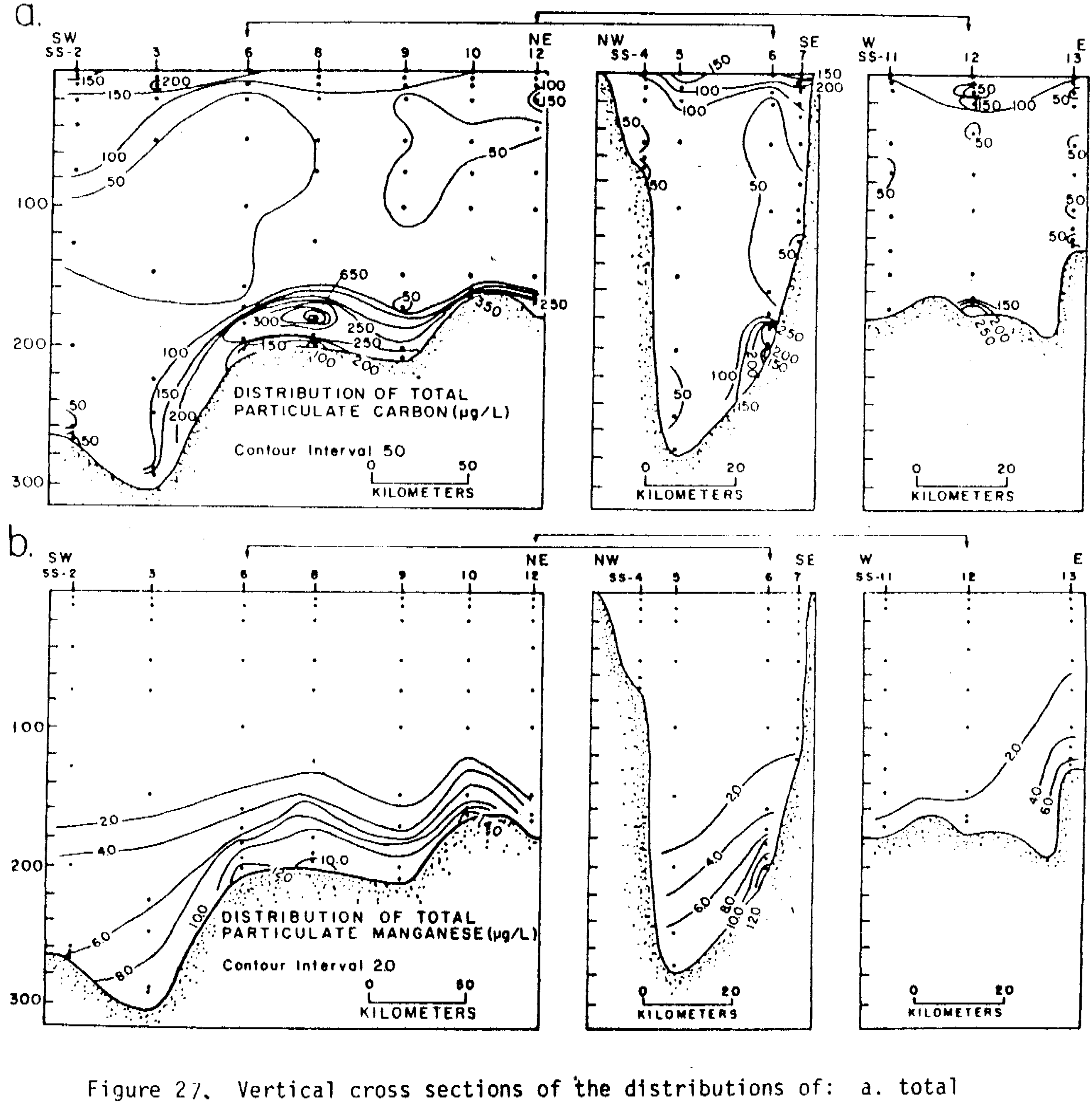

Figure 27. Vertical cross sections of the distributions of: a. total particulate carbon and b. total particulate manganese for stations SS-2 thru SS-13 in Shelikof Strait (Cruise RP-4-Di-78B-II, 22 August-6 September 1978).

Strait. If this is the case, then environmental parameters monitored in Shelikof Strait may be sensitive indicators of subtle changes occurring in the inlet.

VI.A.4.2. Extractable Elements in the Particulate Matter

During the May and August-September 1978 cruises, large volume particulate samples were collected on 142 mm Nucleopore filters for the purpose of providing information on the potential availability of trace elements to organisms. Water was collected at the surface and 5 m above the bottom every 12 hours for 4.8 hours in Kachemak Bay (CB-7) and west of Kalgin Island (CB-9) in May, and east of Kalgin Island (CB-10) in August-September (Fig. 23). In addition, a single surface sample was collected in May at CB-1 in Kamishak Bay (Fig. 9). The samples were subjected to: (1) a peroxide treatment to release organically bound trace elements; (2) a 0.3 N HCl treatment to release elements associated with Fe-Mn oxyhydroxide coatings on particles; and (3) a total element analysis of untreated samples. A full description of the procedures is provided in section V.

In contrast to the highly variable amount of particulate material in the water column at CB-9 (Fig. 24), the trace element content of this surface particulate material remained fairly constant (Fig. 28). The average total elemental composition and the partitioning between organic and oxyhydroxide phase are listed in Table 8. The major cation content of the particulate matter from CB-9 suggests that source of this material was the illite-rich suspended material of the rivers flowing into upper Cook Inlet. The small amount of trace metals present in the peroxide extractable phase reflects the concentration and character of the particulate organic matter. Due to the turbidity associated with the high suspended matter concentrations, the biological productivity in this region is low (Larrance et al., 1977), resulting in organic matter comprising only 2% of the total weight of suspended material. This organic matter has a C:N ratio of 11.3 indicative of terrestrial origin (Loder and Hood, 1972). Copper showed the highest degree of organic association with 1.7% of the total copper being present in peroxide extractable phase, followed by manganese and chromium each with 0.5%. The weak acid extraction released a major portion of the total iron and manganese demonstrating the amorphous character of these metal oxides. Many of the trace elements were enriched in this component of the suspended matter. An average of 85% and 76% of the total nickel and copper, respectively, were present in this phase, while half of the zinc and chromium were also present. The residual material, which is comprised of highly crystalline material, contained 90% of the aluminum and lead, and a lesser fraction of the other metals. As a consequence of vertical mixing in this region, the elemental compositions and phase associations of the surface and near-bottom suspended matter samples were not significantly different ($p<0.05$). The time-series data at CB-10, east of Kalgin Island in September-August, showed the same constancy in elemental compositions and phase associations (Fig. 29). There were no significant differences ($p<0.05$) between surface and near bottom samples in the fall time series. Comparison of the two time-series data in the Kalgin Island region showed no differences in elemental compositions nor phase associations. In summary, the Kalgin Island region is characterized by a highly flucuating amount of suspended matter of a constant composition. This suspended matter is composed primarily of structured aluminosilicates coated with iron-manganese oxyhydroxides. With the exception of Pb and Zn, these coatings contain the largest fraction of trace elements in the particulate matter. The small amount of organic matter present is of terrestrial origin and contains less than 2% of the total amount of trace metals present in suspension.

Water originating from the Kalgin Island region flows along the western side of lower Cook Inlet where a major portion is diverted into Kamishak Bay (Muench et al., 1978). Consistent with this observation, the major element composition of Kamishak Bay suspended material reflects the dominance of illite material similar to that found in upper Cook Inlet. (Feely and Massoth, in press). However, analysis of a single large volume surface sample from Kameshak Bay shows enrichments of Cr, Cu, Ni, Zn and Pb relative to that of Kalgin Island (Table 9). Although organic matter comprises 6% of the suspended material, the increased amount of metals in the peroxide extractable phase cannot account for the enrichments of the whole sample. Examination of the weak-acid extractable phase suggests that the additional Zn, Cu, and Pb were associated with a weakly structured phase while the additional Cr and Ni were present in a highly crystalline phase. These enrichments are probably due to either resuspension of bottom material or a source of trace metal-enriched illite material transported by local rivers flowing into Kamishak Bay.

Unlike the upper Cook Inlet region, the suspended matter concentration in Kachemak showed smaller flucuations with time and little difference with depth (Fig. 30). However, the flucuation in elemental composition and phase associations was greater than in upper Cook Inlet and there was significant difference between the composition of surface and bottom material (Fig. 30 and Table 9). The surface suspended material consisted of 35% organic matter and had a C:N ratio of 7.6, characteristic of a marine origin (Loder and Hood). The remaining material consisted of 40% biogenic SiO_2 and 20% aluminosilicates. The marine origin of this material can also be seen in their trace elemental compositions and phase associations (Table 9). The surface suspended matter was depleted in all elements relative to terrestrial aluminosilicates. The

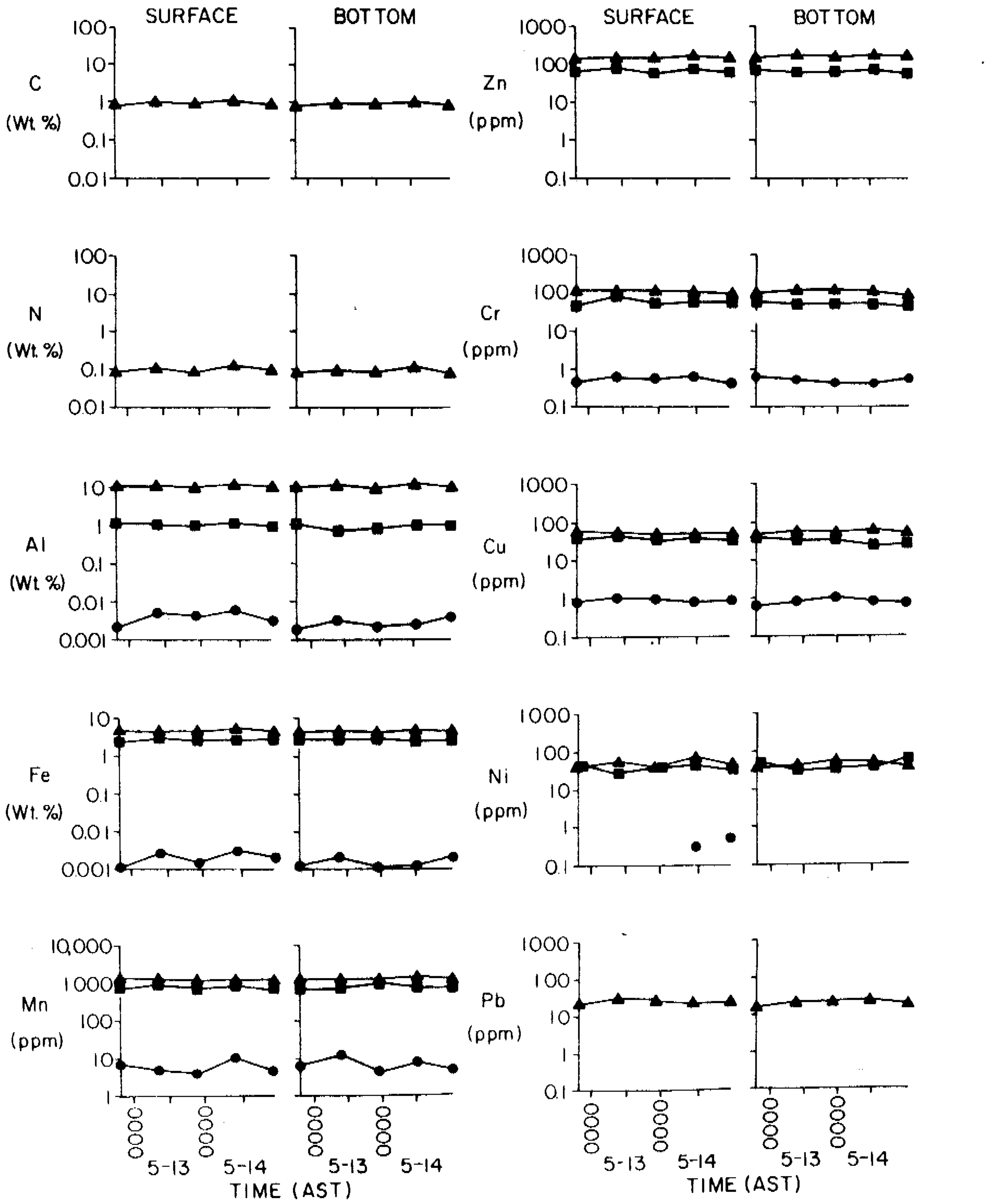

Figure 28. Temporal variations of major and trace elements in suspended matter (total concentration [▲], weak acid extractable [■], and peroxide extractable [●] from station CB-9 in lower Cook Inlet. Samples were collected 13-14 May 1978.

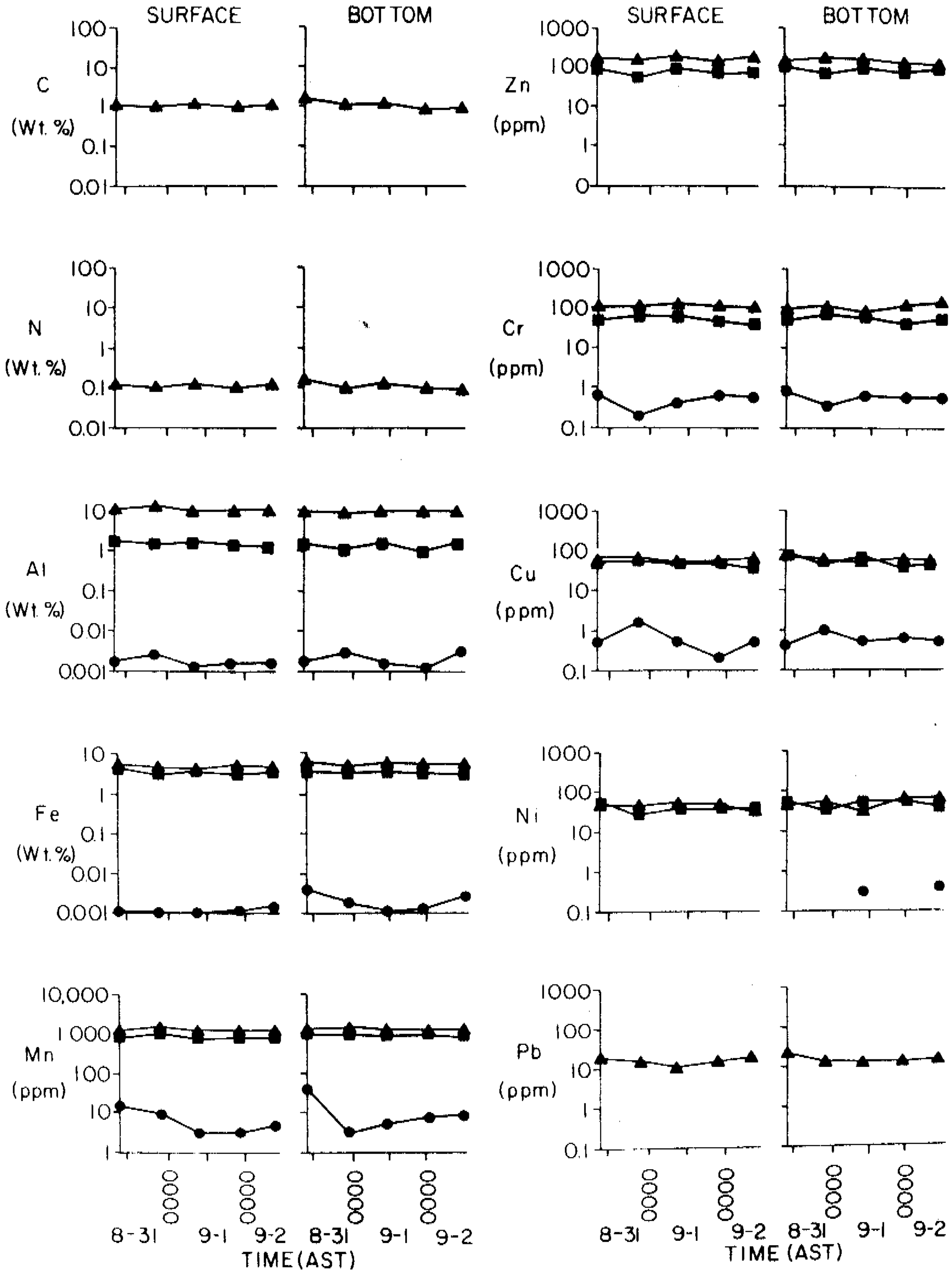

Figure 29. Temporal variations of major and trace elements in suspended matter (total concentration [▲], and peroxide extractable [●]) from station CB-10 in lower Cook Inlet. Samples were collected 31 August and 1-2 September 1978.

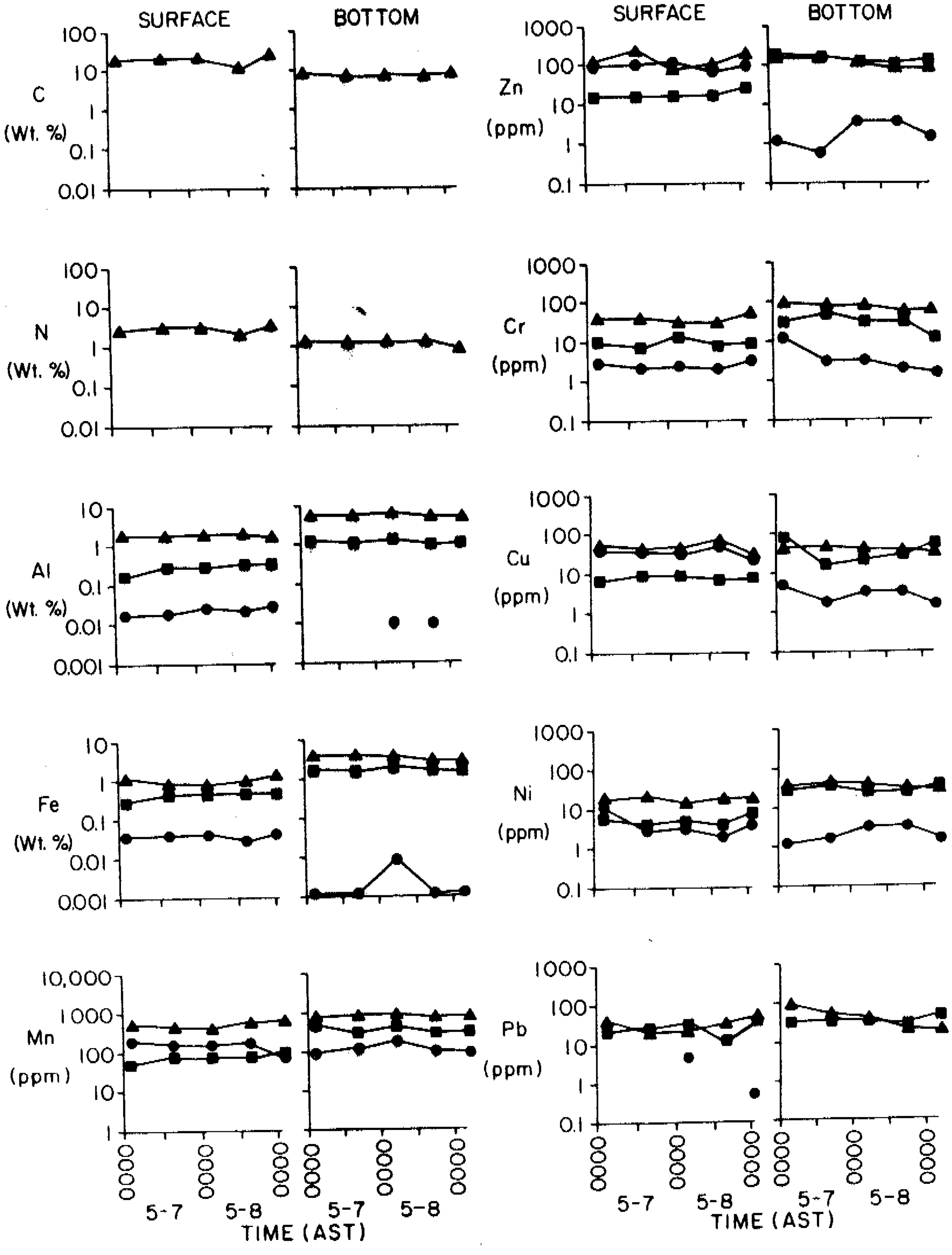

Figure 30. Temporal variations of major and trace elements in suspended matter (total concentration [▲], weak acid extractable [■], and peroxide extractable [●] from station CB-7 in lower Cook Inlet. Samples were collected 7-9 May 1978.

TABLE 8. Elemental composition and phase association of trace metals in suspended particulate matter from the Kalgin Island Region. Values are the average of samples throughout the time series. Errors are ± 1 standard deviation.

	KALGIN ISLAND REGION											
	Surface (CB-9)			Bottom (CB-9)			Surface (CB-10)			Bottom (CB-10)		
	Elemental Composition	Peroxide Extractable	Weak Acid Extractable	Elemental Composition	Peroxide Extractable	Weak Acid Extractable	Elemental Composition	Peroxide Extractable	Weak Acid Extractable	Elemental Composition	Peroxide Extractable	Weak Acid Extractable
C(wt%)	0.95 ± 0.09			0.89 ± 0.09			1.1 ± 0.1			1.1 ± 0.3		
N(wt%)	0.098 ±0.014			0.090 ±0.014			0.11 ±0.01			0.11 ±0.03		
Si(wt%)	25.8 ± 1.5			24.7 ± 1.6			25.2 ± 1.0			25.5 ± 2.4		
AL(wt%)	10.4 ± 0.7	0.0038 ±0.0014	1.04 ± 0.08	10.1 ± 1.5	0.0026 ±0.0008	0.95 ± 0.15	9.9 ± 1.0	0.0015 ±0.0002	1.32 ± 0.38	9.0 ± 0.7	0.0021 ±0.0008	1.26 ± 0.28
FE(wt%)	5.1 ± 0.5	0.0020 ±0.0010	3.2 ± 0.5	4.8 ± 0.2	0.0020 ±0.0012	3.2 ± 0.2	5.3 ± 0.5	0.0010 ±0.0002	3.3 ± 0.1	5.4 ± 0.8	0.0017 ±0.0013	3.3 ± 0.6
Mn(ppm)	1310 ± 20	6.3 ± 2.8	1000 ± 180	1300 ± 80	7.3 ± 3.2	940 ± 90	1280 ± 100	8.3 ± 5.9	1060 ± 100	1260 ± 70	6.0 ± 2.2	1030 ± 30
Zn(ppm)	158 ± 9	ND	72 ± 11	151 ± 12	ND	67 ± 7	158 ± 18	ND	86 ± 16	146 ± 18	ND	83 ± 13
Cr(ppm)	108 ± 7	0.5 ± 0.1	55 ± 12	112 ± 12	0.5 ± 0.1	51 ± 5	113 ± 7	0.5 ± 0.2	48 ± 20	110 ± 27	0.6 ± 0.2	47 ± 17
Cu(ppm)	58 ± 3	1.00 ± 0.13	43 ± 4	55 ± 6	0.80 ± 0.14	36 ± 7	60 ± 6	0.67 ± 0.50	49 ± 15	60 ± 11	0.61 ± 0.24	47 ± 7
Ni(ppm)	46 ± 10	0.25* ± 0.05	38 ± 6	48 ± 6	ND	46 ± 10	45 ± 7	ND	44 ± 9	49 ± 15	0.35* ± 0.05	49 ± 6
Pb(ppm)	23 ± 4	ND	ND	20 ± 2	ND	ND	16 ± 4	ND	ND	14 ± 4	ND	ND

ND - Not Detected (< 0.2 ppm for Ni, 0.5 ppm Zn and 1.0 ppm Pb)

* Three of five samples had nondetectable values. The mean and error are for the two samples with detectable values.

TABLE 9. Elemental composition and phase association of trace metals in suspended matter from Kamishak and Kachemak Bays. Elemental composition values for Kamishak are the averages of duplicate analysis of a single sample. Values for Kachemak Bay are the average of samples throughout the time series. Errors are ± 1 standard deviation.

	KAMISHAK BAY			KACHEMAK BAY					
	Surface (CB-1)			Surface (CB-7)			Bottom (CB-7)		
	Elemental Composition	Peroxide Extractable	Weak Acid Extractable	Elemental Composition	Peroxide Extractable	Weak Acid Extractable	Elemental Composition	Peroxide Extractable	Weak Acid Extractable
C(wt%)	3.93			19.3 ± 5.6			7.65 ± 0.5		
N(wt%)	0.50			2.9 ± 0.6			1.29 ±0.03		
Si(wt%)	18.9 ± 0.2			18.7 ± 3.7			24.6 ± 2.9		
AL(wt%)	9.3 ± 1.1	0.0035	2.1	2.2 ± 0.4	0.022 ±0.004	0.29 ± 0.26	5.2 ± 0.5	0.0009 ±0.0005	1.12 ± 0.13
Fe(wt%)	4.5 ± 0.1	0.022	3.5	1.0 ± 0.3	0.038 ±0.004	0.44 ± 0.08	3.4 ± 0.4	0.0027 ±0.0033	1.78 ± 0.19
Mn(ppm)	1110 ± 30	21	882	539 ± 86	264 ± 77	81 ± 15	887 ± 81	124 ± 39	338 ± 89
Zn(ppm)	210 ± 20	0.8	140	159 ± 72	106 ± 20	28 ± 7	162 ± 62	2.6 ± 2.0	155 ± 38
Cr(ppm)	158 ± 4	2.1	55	39 ± 12	2.5 ± 0.6	10 ± 2	83 ± 13	2.9 ± 0.6	33 ± 14
Cu(ppm)	146 ± 6	14	134	43 ± 12	35 ± 13	8 ± 1	39 ± 6	3.3 ± 1.5	42 ± 27
Ni(ppm)	60 ± 2	2.5	37	17 ± 2	5 ± 4	17 ± 2	37 ± 5	2.2 ± 1.0	34 ± 7
Pb(ppm)	66 ± 3	ND	63	32 ± 17	ND	26 ± 6	45 ± 29	ND	38 ± 8

ND - Not Detected (< 1.0 ppm for Pb)

manganese concentration of this material was 540 ppm while that of CB-9 was 1300 ppm. The greater organic matter content of the surface material resulted in increase in the amount of trace metal present in the peroxide extractable phase. In the case of Cu, Zn and Mn, a major fraction of these elements were present in the organic phase (81%, 66% and 49%, respectively). The near bottom suspended samples contained 50% aluminosilicates and only 14% organic matter. This influx of inorganic material was probably a result of resuspension of bottom sediments. As expected, the trace metal content in the weak-acid extractable phase increase relative to the surface consistent with the increased amount of oxyhydroxides associated with the aluminosilicates. The decrease in organic matter content of the near-bottom sample resulted in a smaller portion of the trace metals being present in the peroxide extractable phase.

VI.A.5. Elemental Composition of Particulate Matter Collected from Sediment Traps

After the sediment trap particulates were collected and dried for gravimetric measurement, the samples collected at ST-1, ST-2, and CB-7 were analyzed for total elemental composition and phase associations according to section V. The results of these analyses are listed in Table 10.

VI.A.5.1. Total Elemental Analysis of Sediment Trap Particulates

There are significant regional differences in the major elemental composition of the sediment trap particulates which can be related to the source suspended particulate matter. The aluminum content of the sediment trap particulates at ST-1 in Kamishak Bay was higher than that at CB-7 in Kachemak Bay. The aluminum content of the suspended particulate material also follows this relationship (Feely and Massoth, in press), indicating the dominance of aluminosilicates on the western side of lower Cook Inlet. Several trace metals

(Fe, Cr, and Ni) which are associated with aluminosilicates in the suspended particulate matter also had significantly greater concentrations in the sediment trap particulates of Kamishak Bay relative to those of Kachemak Bay.

In contrast, Kachemak Bay sediment trap samples contained three times as much organic carbon as those of Kamishak Bay, indicating a similar relationship in the organic carbon flux (0.95 g m^{-2} day^{-1} at CB-7 as compared to 0.32 g m^{-2} day^{-1} at ST-1). As a result of high primary productivity in Kachemak Bay (Larrance et al., 1977), the suspended particulate matter contained about 20% organic carbon and had a C:N ratio of 6.7 characteristic of a marine origin. The sediment trap particulates also had a C:N characteristic of a marine origin, indicating that the surface suspended matter was a major source of organic carbon to the sediment trap. The lower primary productivity in Kamishak Bay resulted in a significant portion of the organic carbon flux being terrestrial in origin as indicated by a C:N ratio midway between marine and terrestrial organic matter. Therefore, it appears that there is a definite relationship between production of organic matter in the water column and the amount and type of organic matter settling to the bottom and providing a food source for filter-feeding organisms.

VI.A.5.2. Extractable Trace Metals in Sediment Trap Particulates

The trace metal data for the sediment trap particulates showed similar associations with the oxyhydroxide phase in all three sediment trap stations. For instance, the portion of chromium present in the weak-acid extractable phase ranged from 49% - 56% of total chromium for the samples from the three stations, while 100% of the nickel was present in this phase. These trace metal associations were similar to those found in the suspended matter, emphasizing the importance of the oxyhydroxide phase in transporting metals through the water column.

The trace metal data in the peroxide extractable phase show regional differences consistent with the organic fluxes. With the exception of chromium, the trace metals present in the peroxide extractable phase follow the order: CB-7 > ST-1 > ST-2. The organic fraction of Kachemak Bay sediment trap particulates contained 5.3% and 10.9% of the total Mn and Cu, respectively, present in the whole sample. The coupling between biological accumulation of trace metals in the water column and the flux of organically bound trace metals is demonstrated by the fact that a major portion of both Cu and Mn were also present in the organic fraction of the surface suspended matter (see section VI.A.4.2). This coupling may be a major mechanism for transporting these trace metals to the benthic community.

The significance of these results is evident when one considers recent studies of the availability of sediment bound trace elements to organisms. Luoma and Bryan (1978) studied the distribution of Pb and Fe in the soft tissues of the deposit feeding bivalve Scorbicularia plana and in the underlying sediments from 20 estuaries in southern and western England and northwest France. It was found that the Pb concentrations in the bivalves directly correlated with the Pb/Fe ratio in the sediment. The authors concluded that the iron concentration in the sediments was influencing the availability of Pb to the bivalves. To be more specific, they suggested that the availability of Pb to the bivalves may be a function of the partitioning of Pb between organically bound Pb and iron oxide-bound Pb in the sediments, with the organically bound Pb being more biologically available. Similarly, Eaganhouse and others (1976; 1978) found enrichments of Hg in tissues of the intertidal mussel Mytilus californianus in sediments that contained high concentrations of organically bound Hg. Here again, the implication is that organically bound trace elements are more available to organisms than trace elements that are bound to some other phase in the sediments.

In lower Cook Inlet organically bound trace elements predominate only in Kachemak Bay where primary production is higher than any other region in the inlet. It is also the region where water circulation is the least dynamic. Therefore, it is possible to speculate that anthropogenic inputs of dissolved Cu, Ni, and Zn resulting from development activities would have a more profound impact on biological communities in Kachemak Bay than other regions in lower Cook Inlet because of their apparent incorporation into biologically available organic matter.

TABLE 10. Elemental composition and phase association of trace metals in sediment trap particulates at ST-1, ST-2 and CB-7. Values for ST-1 and ST-2 are the average of triplicate analysis of a single sample from a long-term deployment. Values for CB-7 are the average of four samples from short-term deployment. Values for CB-7 are the average of four samples from short-term deployment. Errors are ± 1 standard deviation.

	ST-1 (32m)			ST-2 (75m)			CB-7 (60m)		
	Elemental Composition	Peroxide Extractable	Weak Acid Extractable	Elemental Composition	Peroxide Extractable	Weak Acid Extractable	Elemental Composition	Peroxide Extractable	Weak Acid Extractable
C(wt%)	0.87 ± 0.02			0.84 ± 0.40			2.8 ± 0.4		
N(wt%)	0.09 ± 0.01			0.09 ± 0.05			0.35 ± 0.05		
Si(wt%)	21.8 ± 1.0			26.5 ± 1.0			22.5 ± 3.2		
Al(wt%)	9.4 ± 0.9	0.0011 ±0.0004	3.0 ± 0.3	7.8 ± 1.0	0.0004 ±0.0004	1.2 ± 0.6	6.5 ± 0.5	0.0035 ±0.0017	1.16 ± 0.10
Fe(wt%)	4.6 ± 0.2	0.0010 ±0.0004	3.22 ±0.05	3.4 ± 0.1	0.0004 ±0.0002	2.1 ± 0.3	3.8 ± 0.9	0.0022 ±0.0007	1.2 ± 0.2
Mn(ppm)	880 ± 80	3 ± 3	426 ± 27	660 ± 35	0.6 ± 0.1	265 ± 45	915 ± 170	48 ± 29	570 ± 140
Zn(ppm)	142 ± 6	ND	118 ± 5	106 ± 20	ND	74 ± 2	215 ± 120	0.6 ± 0.3	160 ± 86
Cr(ppm)	82 ± 2	0.3 ± 0.1	40 ± 2	55 ± 6	1.5 ± 0.5	31 ± 2	63 ± 8	2.4 ± 0.3	35 ± 3
Cu(ppm)	29 ± 2	0.12 ± 0.01	23 ± 2	18 ± 2	0.04 ± 0.01	13 ± 3	43 ± 3	4.7 ± 0.8	36 ± 7
Ni(ppm)	51 ± 14	ND	51 ± 1	30 ± 7	ND	30 ± 6	34 ± 2	1.3 ± 0.1	37 ± 6
Pb(ppm)	15 ± 2	ND	ND	10 ± 2	ND	ND	13 ± 6	ND	1.1 ± 0.5

ND - Not Detected (< 0.2 ppm for Ni and Zn and 1.0 ppm for Pb)

VI.B. Norton Sound

VI.B.1. Particulate Matter Distribution and Transport

Figures 31 and 32 show the distributions of salinity, temperature, sigma-t and total suspended matter at the surface and 5 m above the bottom for the July 1979 cruise in Norton Sound. As shown in Figure 31, surface particulate matter distributions were dominated by the discharge of sedimentary material from the Yukon River. Surface suspended matter concentrations were highest near the mouth of the Yukon River, where values ranging between 100 and 154 mg/L were observed. The Yukon River plume (as indicated by the 5.0-mg/L isopleth) extended to the north and northeast across the length of the Sound. Another portion of the plume with lesser suspended matter concentrations (1.0-2.7 mg/L) extended north and northwest to a point about 20 km southwest of Cape Rodney. Both portions appear to have originated from the Yukon River and their trajectories tend to follow the general pattern of cyclonic circulation in the Sound (i.e., Yukon River material enters the Sound from the southwest, is transported north and northeast around the inside perimeter of the Sound, and exits the Sound from the northwest). These data are supported by the salinity and temperature measurements which indicated movements of low-salinity (12-24^{o}/oo), relatively warm (10-11^{o}C) water to the northeast along the coast. These results are consistent with the general conclusions of Sharma et al. (1974) for suspended matter data obtained in August 1973. They are also consistent with dispersal patterns of the Yukon River Plume inferred from LANDSAT satellite photographs (Nelson et al., 1975). For example, Figure 33 shows a LANDSAT photograph of the Yukon River Plume taken on July 20, 1979. The plume, which appears lighter in the grey tones than the less turbid water, can be traced as far north as approximately 70 km from the Yukon River Delta and as far east as 50 km from Stuart Island. These features are also consistent with the data of Cacchione and Drake (1979) for surveys made during quiescent periods in September 1976 and July 1977. Thus, it would appear that the transport processes described above predominate throughout the region, at least during periods of calm weather in the summer.

The near-bottom distribution of salinity, temperature, and total suspended matter also indicated evidence for cyclonic movement of low-salinity (20-22^0/oo), warm water ($\sim$10^{0}C) to the northeast along the coast. This water mass can be traced as far north as Cape Darby. Near-bottom suspended matter concentrations were highest near the mouth of the Yukon River and in the region about 20-30 km south-southwest of Nome. The near-bottom plume just seaward of the Yukon River extended to the northeast along the coast in a manner very similar to the surface plume. The near-bottom concentrations were generally higher than surface concentrations, indicating that: (1) some fraction of the Yukon River material had settled to the near-bottom region during transit, and/or (2) a portion of the bottom sediments had been resuspended and remained in suspension.

Figures 34 and 35 show cross-sections of total suspended matter, salinity, temperature, and sigma-t for two east-west transects across the length of Norton Sound. Transect I is near the middle of the Sound and Transect II is in the northern half of the Sound, approximately 20-30 km from the coast. Both transects show very similar water mass characteristics and suspended matter distribution patterns.

On the eastern side of the Sound, both transects showed evidence for a two-layer system with the pycnocline varying in depth between 8 and 14 m (e.g., stations 3 and 8 from transect I and stations 1, 9, and 10 from transect II). Suspended matter concentrations in this region showed a steady increase from about 6-8 m to the bottom.

In the middle region (stations 15, 20, and 29 for transect I and stations 22, 25, 27, and 39 for transect II) the water column was virtually unstratified and suspended matter concentrations increased to values greater than 30 mg/L in the near-bottom waters (e.g., station 25 in transect II). These water properties suggest the presence of a tidally induced frontal zone with vertical mixing intensity sufficient for breakdown of the stability, with subsequent resuspension of sediments throughout the water column in some locations. This feature has the same characteristics as the anomalous suspended matter plume described by Sharma et al. (1974) for data obtained in August 1973 at the same location. These data support the general conclusion of Drake and Cacchione (1979): during quiescent periods in the Sound, resuspension of bottom sediments occurs as a result of increased tidal mixing during spring tide.

Further seaward, the water column was moderately stratified and suspended matter concentrations decreased to values below 0.5 mg/L in surface waters. In near-bottom waters, however, suspended matter concentrations were generally greater than 2.0 mg/L. The enriched suspended matter concentrations near the bottom were probably due to a combination of factors including advective transport of particle-laden water to the northwest from within Norton Sound (Muench et al., in press) and local resuspension of bottom sediments.

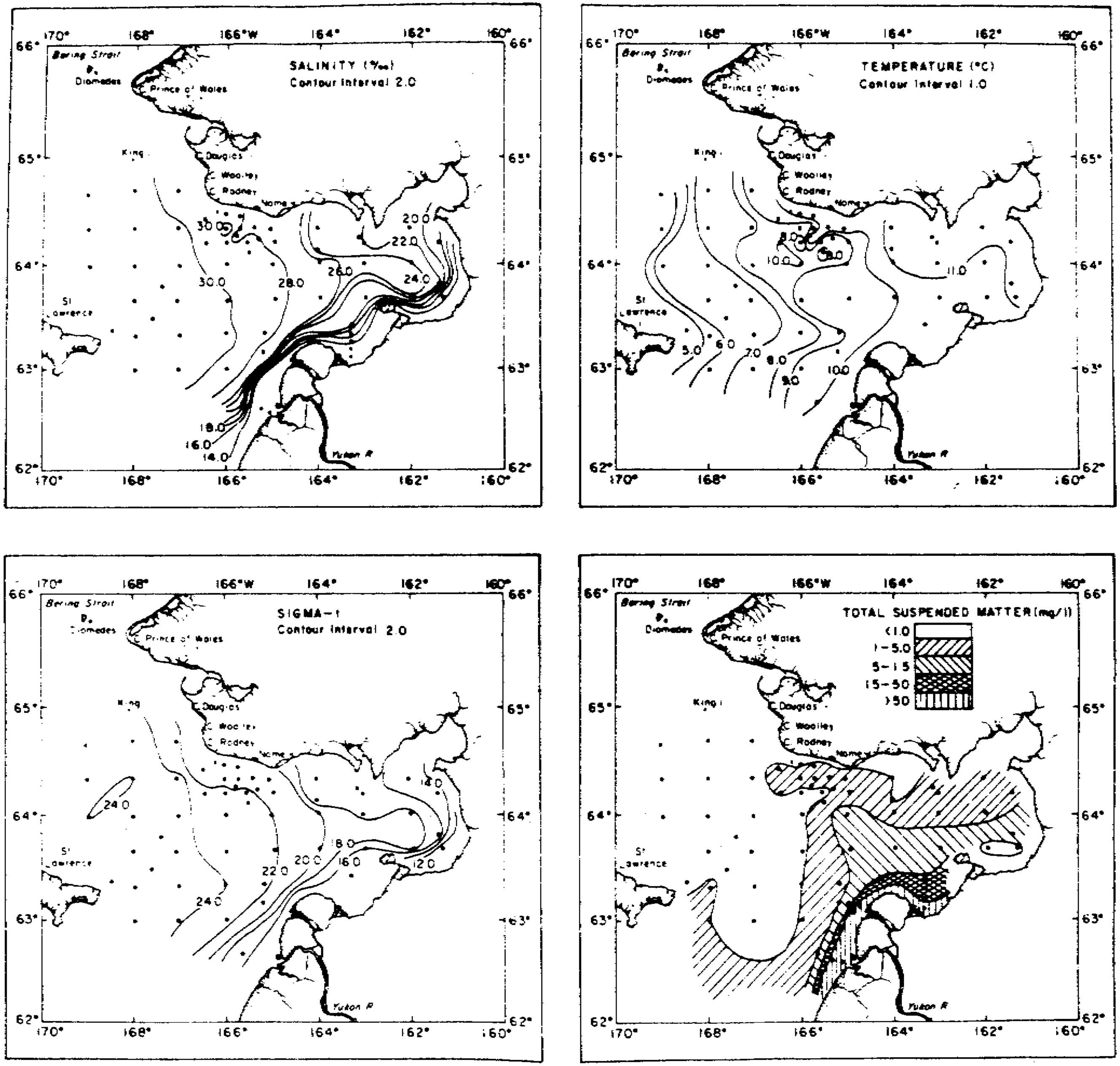

Figure 31. Distribution of: (a) salinity; (b) temperature; (c) sigma-t; and (d) total suspended matter at the surface in Norton Sound, 7-18 July, 1979.

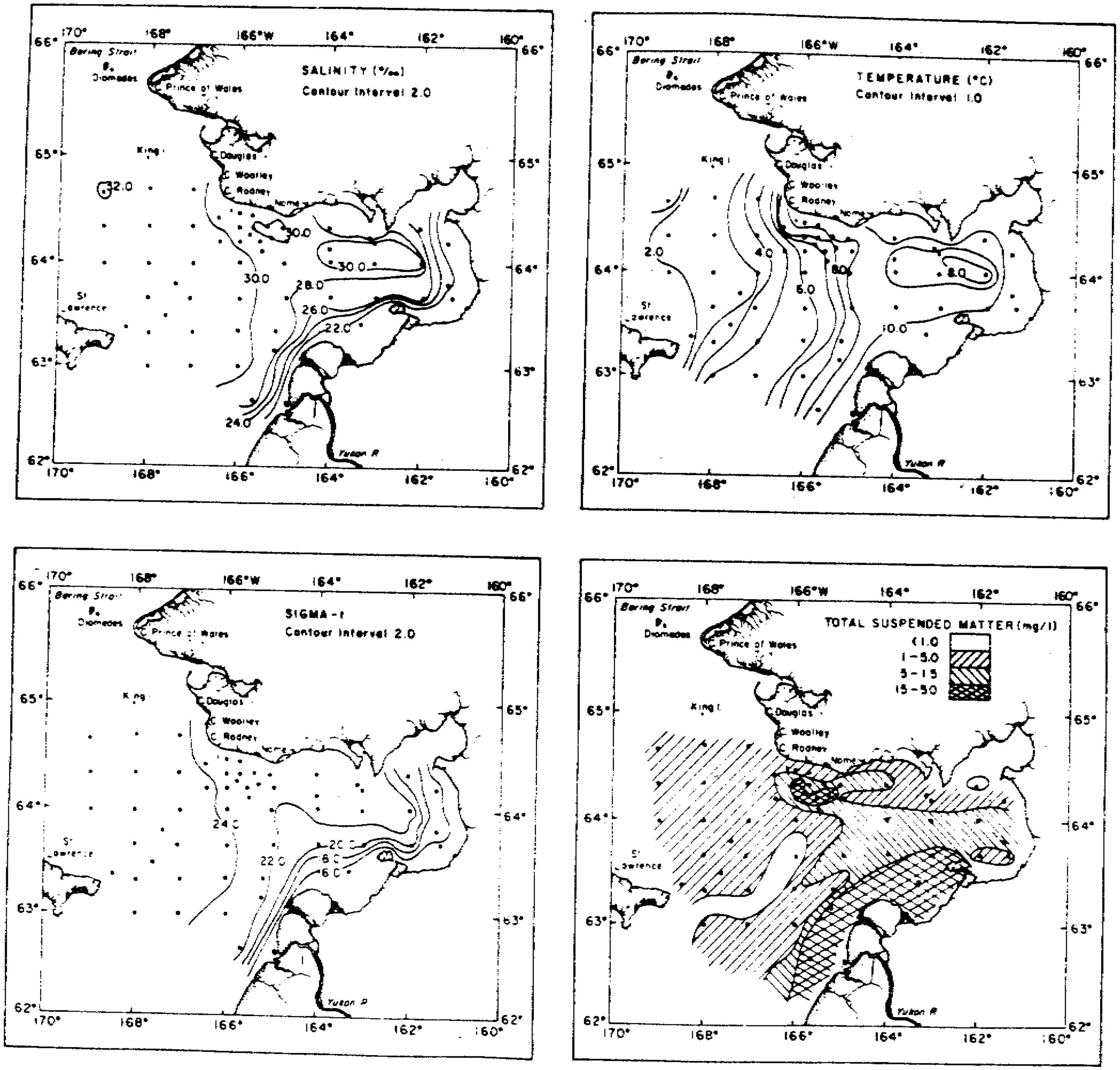

Figure 32. Distribution of: (a) salinity; (b) temperature; (c) sigma-t; and (d) total suspended matter at 5 m above the bottom in Norton Sound, 7-18 July, 1979.

Figure 33. MSS Band 5 of LANDSAT images E-21640-21360-5 and E-21640-21363-5 taken on July 20, 1979, showing evidence for suspended matter (appearing lighter in tone than the less turbid water) transport into Norton Sound.

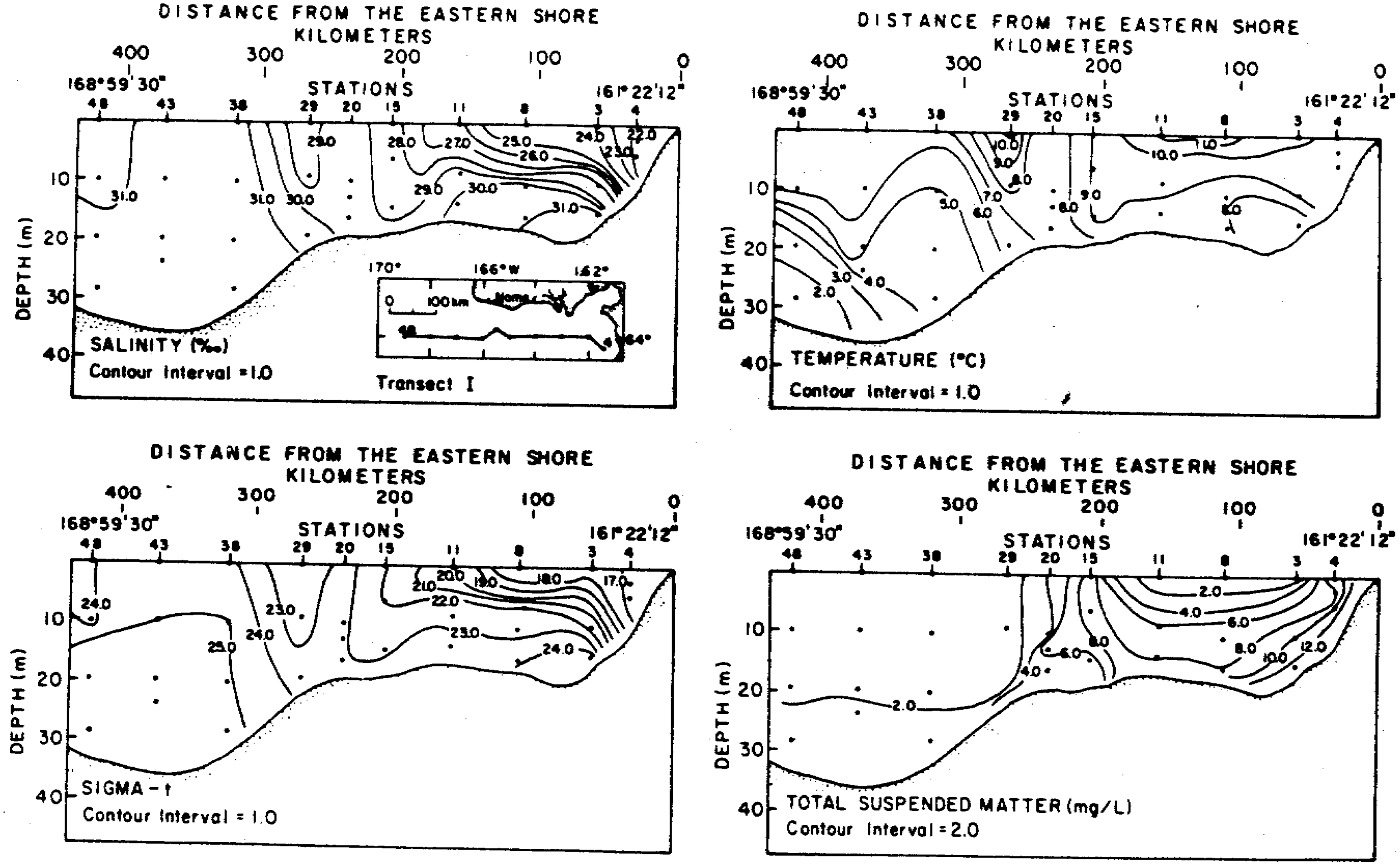

Figure 34. Vertical cross section of the distribution of: (a) salinity; (b) temperature; (c) sigma-t; and (d) total suspended matter for transect I in Norton Sound.

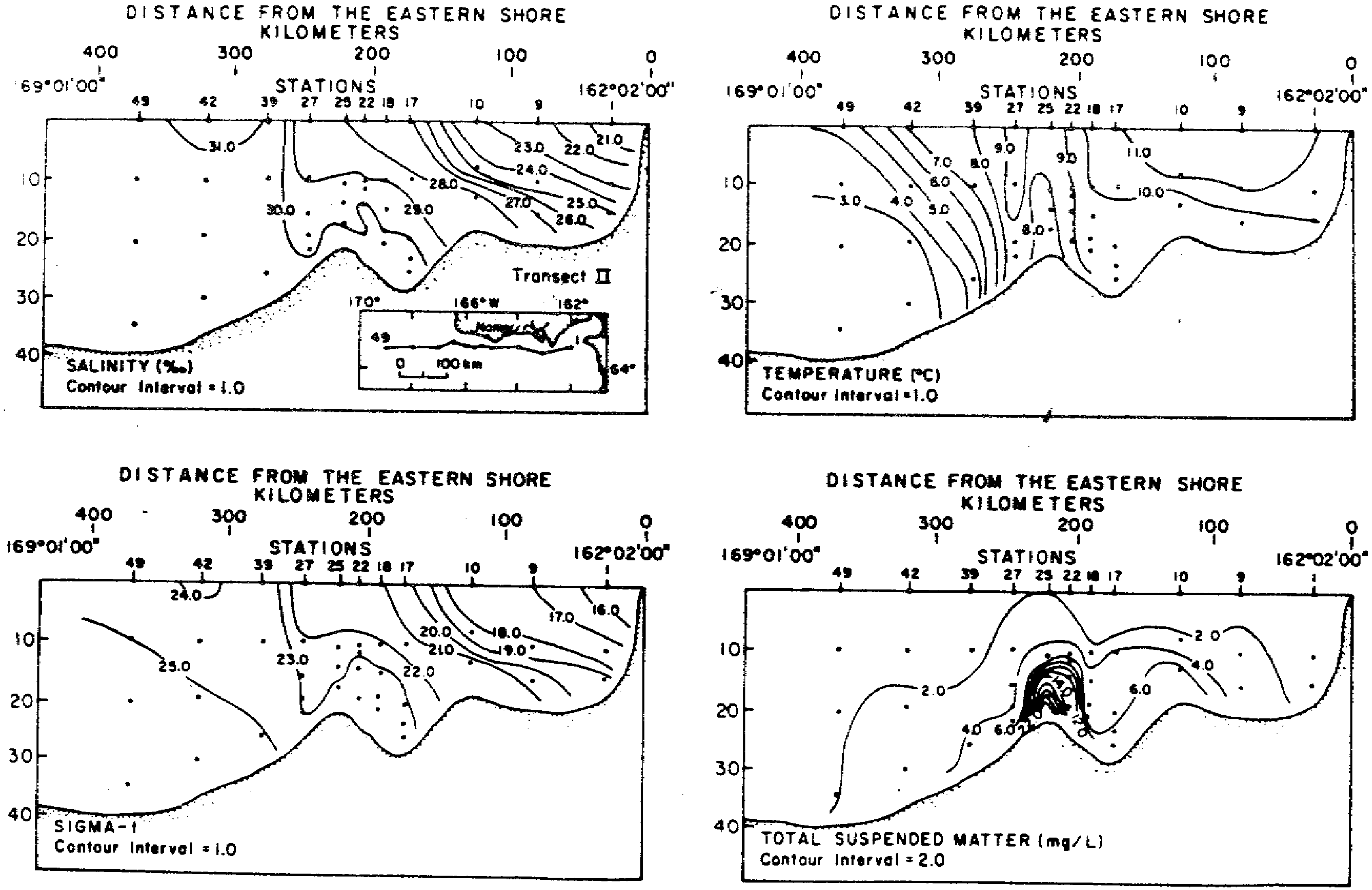

Figure 35. Vertical cross section of the distribution of: (a) salinity; (b) temperature; (c) sigma-t; and (d) total suspended matter for Transect II in Norton Sound.

VI.B.2. Particulate Elemental Composition

In order to determine regional variations of the chemical composition of suspended material in Norton Sound, the particulate samples from the July 1979 cruise were analyzed for their major and trace element content by the methods described previously. The resulting data have been separated into five regions: Yukon River estuary with salinities less than 15 parts per thousand; Yukon River estuary with salinities between 15 and 25 parts per thousand; eastern Norton Sound; central Norton Sound; and western Norton Sound-northeastern Bering Sea Shelf. The averaged chemical data, along with published data for the Yukon River, are given in Tables 11 and 12. Table 13 shows C/N and element/Al ratios for the averaged data.

The elemental concentrations and elemental ratios illustrate some compositional differences between the suspended material discharging from the Yukon River and suspended matter in the Sound. These differences can be viewed in terms of relative aluminosilicate and organic matter percentages. Since most of the aluminum in marine particulate matter is located in aluminosilicate material (Sackett and Archenius 1962), the Al concentrations in the suspended matter when multiplied by 10 can be used to estimate aluminosilicate percentages in the particulate matter. Similarly, Gordon (1970) suggested that particulate carbon may be used, when multiplied by a factor of 1.8, to estimate the amount of organic material in the suspended matter. Based on the particulate Al and particulate C concentrations, the suspended matter from the Yukon River estuary was composed of approximately 88% aluminosilicate material and 6% organic matter. In the like manner, samples from eastern and central Norton Sound contain about the same percentage of aluminosilicate material (88-92%). These results illustrate the predominance of the detrital material from the Yukon River in the central and eastern regions of the Sound. This finding is additionally supported by the chemical data for Si, K, Ca, Ti, Fe, Ni, and Cu which are at about the same concentration levels in eastern and central Norton Sound and the Yukon River estuary. Only C, N, Mn, and Zn show enrichments offshore. For C and N these enrichments are attributed to a relative increase in the concentration of marine organic matter in offshore waters, which is probably due to increased light penetration away from the zone of high turbidity. This conclusion is supported by the C/N ratios (Table 13) which show a general decrease seaward, indicating a transition from organic matter dominated by terrestrial material of marine origin with C/N ratios ranging between 6 and 9 (Loder and Hood, 1972). Mn and Zn enrichments can be attributed to a number of processes which are discussed in detail later.

In the western Norton Sound-northeastern Bering Sea Shelf region, the suspended matter was depleted in particulate Mg, Al, K, Ti, Fe and Ni and enriched in particulate C and N relative to the Yukon River estuarine samples. These depletions are attributed to a drop in the relative amount of aluminosilicate material in the suspended matter (< 52% by weight) and an increase in the proportion of marine organic matter (> 40% by weight), which is depleted in Mg, Al, K, Ti, Mn, Fe, Ni and Zn relative to aluminosilicate material (Martin and Knauer, 1973). It is important to note, however, that Mn and Zn concentrations do not decrease appreciably in the samples from this region. These findings indicate that Mn and Zn concentrations in the suspended matter are controlled by distinctly different chemical processes.

In an attempt to determine the chemical nature and source of the enriched Mn and Zn in the offshore suspended matter, selected surface and near-bottom samples were treated wtih 25% (v/v) acetic acid to separate poorly-structured oxyhydroxides from the more crystalline phases. This procedure has been shown to selectively dissolve trace elements precipitated in acid-soluble metal oxides and those adsorbed onto mineral surfaces without affecting highly oxidized ferromanganese minerals or the lattice structure of clays (Hirst and Nichols, 1958, Chester and Hughes, 1967; and Bolger et al., 1978). The results of these experiments are given in Table 14. The data show increased amounts of weak-acid-soluble Mn in the offshore samples relative to the estuarine samples, which are significant at the $p < 0.05$ level. These increases, which are computed by taking the differences between the offshore samples and estuarine samples as a ratio to the estuarine samples, range between 134% and 351% and account for all of the excess Mn in the suspended matter. Similarly, the data for Zn in the weak-acid-soluble fraction show enrichments ranging between 61% and 83% in the offshore samples which are significant at the $p < 0.20$ level. These results indicate that in the offshore waters Mn and Zn are being concentrated in the weak-acid-soluble fraction of the particulate matter, which in these samples probably consists of poorly structured oxyhydroxides of Mn.

TABLE 11. Comparison of the Elemental Composition of Suspended Material from the Yukon River with the Composition of Suspended Material Collected from the Near-Shore Regions Seaward of the Mouths of the Yukon River Distributaries (Surface Samples Collected with Precleaned Polyethylene Bottles, July 11 and 12, 1979). Standard deviations are given only for data obtained during a single sampling event wherever applicable.

Sample Description	No. of Samples	C†† Wt.% ± 1σ	N†† Wt.% ± 1σ	Mg Wt.% ± 1σ	Al Wt.% ± 1σ	Si Wt.% ± 1σ	K Wt.% ± 1σ	Ca Wt.% ± 1σ	Ti Wt.% ± 1σ	Cr ppm ±1σ	Mn ppm ±1σ	Fe Wt.% ± 1σ	Ni ppm ±1σ	Cu ppm ±1σ	Zn ppm ±1σ
Yukon River Suspended Material															
Yukon River at Klakanak*										147	1079	5.4	109	320	
Yukon River at Pilot Station**		0.24-3.8								48	788-1308	3.1-4.3		24-148	49-14
Yukon River Estuary															
Surface Samples (0-15^{0}/oo)	6	2.9 ±0.6	0.2 ±0.04	2.3 ±0.7	8.2 ±1.3	30.6 ±1.9	2.2 ±0.3	1.5 ±0.2	0.50 ±0.06	110 ±15	992 ±131	5.5 ±0.8	59 ±8	59 ±8	171 ±49
Yukon River Estuary															
Surface Samples (15-25^{0}/oo)	6	4.2 ±1.2	0.4 ±0.8	3.1 ±0.8	9.3 ±1.8	31.5 ±3.7	2.1 ±0.2	1.6 ±0.2	0.52 ±0.03	129 ±15	1299 ±192	5.81 ±0.4	60 ±5	61 ±10	193 ±30

*Data from Gibbs (1977)

**Water Resources Data (1976-1977) U.S. Geological Survey

††Weight percentages of C and N were determined using two different filter types (Selas® silver filters and Nuclepore® filters) and, therefore, are subject to a greater number of errors than the data obtained for the inorganic elements, which were obtained from a single filter type.

TABLE 12. Summary of the Elemental Composition of Suspended Material Collected from Selected Locations in Norton Soun
and northeastern Bering Sea Shelf (Samples were collected with 10-L Niskin Bottles, July 7-18, 1979).

Sample Description	No. of Samples	C†† Wt.% ± 1σ	N†† Wt.% ± 1σ	Mg Wt.% ± 1σ	Al Wt.% ± 1σ	Si Wt.% ± 1σ	K Wt.% ± 1σ	Ca Wt.% ± 1σ	Ti Wt.% ± 1σ	Cr ppm ± 1σ	Mn ppm ± 1σ	Fe Wt.% ± 1σ	Ni ppm ± 1σ	Cu ppm ± 1σ	Zr ppm ± 1σ
Eastern Norton Sound															
Surface	7	15.4 ±5.8	2.4 ±0.9	3.1 ±0.5	9.2 ±1.4	30.1 ±3.7	1.7 ±0.3	1.4 ±0.3	0.44 ±0.06	199 ±59	2346 ±845	5.3 ±0.6	52 ±8	60 ±9	201 ±41
5 m Above Bottom	7	10.1 ±6.2	1.1 ±0.8	2.9 ±0.5	9.1 ±1.3	31.0 ±2.7	2.0 ±0.2	1.4 ±0.2	0.53 ±0.08	144 ±38	2182 ±682	5.7 ±0.4	57 ±5	62 ±10	276 ±289
Central Norton Sound															
Surface	18	14.6 ±8.6	1.9 ±1.1	3.3 ±0.7	9.0 ±1.7	30.8 ±4.8	1.7 0.4	1.7 ±0.2	0.48 ±0.08	148 ±36	2672 ±1104	5.4 ±0.8	59 ±21	61 ±12	246 ±90
5 m Above Bottom	18	5.6 ±3.6	0.7 ±0.5	3.0 ±0.6	8.8 ±1.2	32.4 ±2.5	2.0 ±0.2	1.6 ±0.6	0.54 ±0.06	138 ±27	1797 ±287	5.8 ±0.6	57 ±7	58 ±6	196 ±65
Western Norton Sound-northeastern-Bering Sea Shelf															
Surface	18	25.6 ±6.8	4.0 ±0.9	0.9 ±0.7	3.2 ±1.4	20.0 ±7.9	0.5 ±0.2	1.4 ±0.4	0.23 ±0.10	100 ±93	2160 ±1392	2.3 ±0.9	29 ±17	50 ±39	194 ±111
5 m Above Bottom	18	12.3 ±6.9	1.3 ±0.4	1.9 ±0.5	5.1 ±1.2	31.8 ±3.5	0.9 ±0.3	1.2 ±0.2	0.31 ±0.07	81 ±17	1506 ±761	3.4 ±0.7	30 ±13	36 ±11	137 ±60

†† Weight percentages of C and N were determined using two different filter types (Selas® silver filters and Nuclepore® filters) and, therefore, are subject to a greater number of errors than the data obtained for the inorganic elements, which were obtained from a single filter type.

TABLE 13. Average C/N and Element/Al Ratios for Suspended Materials from the Yukon River Estuary, Norton Sound and northeastern Bering Sea Shelf.

Sample Description	C/N	C/Al	N/Al	Mg/Al	Si/Al		K/Al	Ca/Al	Ti/Al $x10^{-3}$	Cr/Al $x10^{-3}$	Mn/Al	Fe/Al $x10^{-3}$	Ni/Al $x10^{-3}$	Cu/ x10
Yukon River Estuary (0-15^0/oo)	14.5	0.35	0.02	0.28	3.73	0.27	0.18	0.06	1.34	12.1	0.66	0.72	0.72	2.08
Yukon River Estuary (15-25^0/oo)	10.5	0.45	0.04	0.33	3.39	0.23	0.17	0.06	1.38	14.0	0.62	0.64	0.66	2.07
Eastern Norton Sound														
Surface	6.4	1.71	0.27	0.34	3.34	0.19	0.16	0.05	2.21	26.1	0.59	0.58	0.66	2.23
5 m Above Bottom	9.2	1.11	0.12	0.32	3.41	0.22	0.15	0.06	1.58	24.0	0.63	0.63	0.68	3.03
Central Norton Sound														
Surface	7.7	1.62	0.21	0.37	3.42	0.19	0.19	0.05	1.64	29.7	0.60	0.65	0.67	2.73
5 m Above Bottom	8.0	0.63	0.08	0.34	3.68	0.23	0.18	0.06	1.57	20.4	0.66	0.65	0.66	2.23
Western Norton Sound-Northeastern Bering Sea Shelf														
Surface	6.4	8.0	1.30	0.28	6.35	0.16	0.44	0.07	3.12	67.5	0.72	0.91	1.56	6.06
5 m Above Bottom	9.5	2.4	0.25	0.37	6.23	0.17	0.24	0.06	1.59	29.5	0.66	0.59	0.67	2.68

TABLE 14. Partitioning of Mn and Zn between Weak-Acid Soluble (WAS) and Weak-Acid Insoluble (WAI) Fractions of Suspended Material from Norton Sound and northeastern Bering Sea (Data Presented as a Percentage of Total Suspended Matter).

Sample	No. of	WAS Mn ± 1σ	WAI Mn ± 1σ	WAS Zn ± 1σ	WAI Zn ± 1σ
Yukon River Estuary	3	0.066 ±0.017	0.052 ±0.006	0.0059 ±0.0028	0.0140 ±0.0031
Eastern Norton Sound	5	0.155 ±0.038	0.040 ±0.011	0.0095 ±0.0031	0.0099 ±0.0021
Central Norton Sound	7	0.184 ±0.085	0.054 ±0.017	0.0108 ±0.0056	0.0114 ±0.0026
Western Norton Sound	5	0.298 ±0.092	0.074 ±0.041	0.0107 ±0.0053	0.0125 ±0.0070

VII. Conclusions

VII.A. Lower Cook Inlet and Shelikof Strait

The most significant findings of the suspended matter program in lower Cook Inlet are listed below.

VII.A.1. The suspended matter distributions appear to follow the general pattern of circulation in lower Cook Inlet and Shelikof Strait. The inflowing relatively clear Gulf of Alaska water, which contains significant amounts of biogenic particles as well as aluminosilicate material from the Copper River, flows northward along the eastern coast until it reaches Cape Ninilchik, where it mixes with the outflowing turbid brackish water. The outflowing turbid water moves along the western side of the inlet past Augustine Island and Cape Douglas into Shelikof Strait where it mixes with the oceanic water and is dispersed. Comparison of suspended matter and sediment characteristics as well as regional sedimentation rates indicates that net sedimentation of suspended matter in the central basin of lower Cook Inlet is minimal. However, net sedimentation is occurring in the embayments along the coast.

VII.A.2. Chemical analyses of the suspended material from lower Cook Inlet reveal that aluminosilicate minerals from the coastal rivers comprise about 80-95% of the suspended matter, with biogenic matter making up the rest. Analysis of seasonal and regional variations of C:N ratios indicates that organic matter of marine origin predominates the eastern part of lower Cook Inlet throughout the year, whereas organic matter of terrestrial origin predominates the western part of the inlet during winter and early spring when primary production is at a minimum.

VII.A.3. Comparisons of regional average concentrations of major and trace elements in the particulate matter indicate regional differences which can be related to differences in the average composition of source material and the relative amounts of biogenic and terrigenous components.

VII.A.4. Studies of trace metal associations with particulate matter reveal that: (1) Mn, Cu, and Zn are enriched in the organic phase of suspended matter in surface waters of Kachemak Bay; and (2) the weak acid soluble phase contains about 46-99% of the total Cu, Ni, and Zn in the samples from the Kalgin Island region. These differences are attributed to differences in the sources for the particles, with primary production of biogenic particles predominant in Kachemak Bay and river discharge of terrestrial rock debris predominant in the Kalgin Island region.

VII.A.5. Studies of sediment accumulation rates in lower Cook Inlet indicate that most of the suspended material discharged from the local rivers is deposited in Shelikof Strait, <u>not</u> in Cook Inlet. This finding is important for understanding and predicting the long-term fates of contaminants associated with suspended matter.

VII.B. Norton Sound

The most significant findings of the suspended matter program in Norton Sound are listed below.

VII.B.1. The suspended matter distribution appears to follow the general pattern of cyclonic circulation in the Sound. The inflowing water picks up terrigenous aluminosilicate material from the Yukon River and transports it to the north and northwest around the inside periphery of the Sound, with one-half to two-thirds of the material being deposited as a band of sediments extending from the Yukon River Delta northward and eastward and the remaining material being transported to the northwest through Bering Strait and deposited in the Chukchi Sea.

VII.B.2. Chemical analyses of the suspended material from Norton Sound reveal that aluminosilicate material from the Yukon River comprises about 88-92% of the suspended matter, with biogenic matter making up the rest. Analysis of regional variations of C:N ratios indicates that organic matter of marine origin predominates in Norton Sound basin, whereas organic matter of terrestrial origin predominates in the Yukon River Estuary.

VII.B.3. Comparisons of regional average concentrations of major and trace elements in the particulate matter indicate regional differences which can be attributed to differences in the average composition of source material and the relative amounts of biogenic and terrigenous components.

VII.B.4. Studies of trace metal associations with particulate matter reveal that Mn and Zn are enriched in an oxyhydroxide phase of the surface and near-bottom suspended matter in Norton Sound.

VIII. Suggested Future Studies

The results of the sediment accumulation studies show that while suspended matter concentrations in lower Cook Inlet are extremely high, little net sedimentation occurs in the central basin of lower Cook Inlet. Therefore, the embayments along the coasts of lower Cook Inlet and the deep basins of Shelikof Strait may be receiving most of the fine-grained particulate materials which are discharged from the coastal rivers. Since suspended particles from Cook Inlet have been shown to be efficient scavengers of crude oil (Feely et al., 1978) and because many of the living resources indigenous to lower Cook Inlet are suspension and detrital feeders, future studies should be devoted to determining the fates of these contaminants in the embayments along the coast and in Shelikof Strait.

IX. Summary of Second Quarter Operations

IX.A. Task Objectives

The primary objectives of the particulate matter programs during the second quarter have been to complete the chemical analyses of the samples that were collected during the spring and fall cruises.

IX.B. Laboratory Activities from 1 January to 1 April 1980

During the second quarter, most of our laboratory work has been concerned with chemical and gravimetric analyses of samples from the spring and summer cruises. We have completed all of the analyses and the data are presently being compiled according to the format designed by EDS and will be submitted to the project office in the near future.

IX.C. Laboratory Procedures

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

IX.D. Sampling Protocol

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

IX.E. Data Analysis

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

IX.F. Results

The results of our laboratory activities have been reported in Sections VI and VII of this report.

XI. Publications and Presentations

Following is a list of publications and presentations that have resulted from this research unit:

Feely, R. A., G. J. Massoth, and W. M. Landing (1976). "Factors controlling the trace element composition of suspended matter from the Northeast Gulf of Alaska, "Trans. Amer. Geophys. Union, 57(12): 931.

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Annual Report

Distribution and Abundance of Low Molecular Weight Hydrocarbons and Suspended Hydrocarbons in Cook Inlet, Shelikof Strait, and Norton Sound, Alaska

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1. GENERAL SUMMARY

1.1 Objectives

The low molecular weight hydrocarbon program was initiated on the OCS of Alaska in response to the environmental guidelines set forth in the Environmental Study Plan for the Gulf of Alaska, Southeastern Bering Sea, and the Beaufort Sea (January 1975). The purpose was to establish the spatial and temporal variations (seasonal and diurnal) in the dissolved hydrocarbon fraction composed of methane, ethane, ethene, propane, propene, isobutane, and n-butane. These data were collected in order to establish baseline levels of naturally occurring hydrocarbons in the lease areas prior to exploration, development, and production of fossil fuel reserves as these components have proven to be valuable indicators of petroleum input (Sackett, 1977).

During the past two years, emphasis was shifted toward sources of LMW hydrocarbons in Cook Inlet, including both natural and anthropogenic sources. Special attention was devoted to sources of LMW aromatics in upper Cook Inlet and the fate of these compounds. Specialized studies in Cook Inlet have continued on the air-sea exchange of LMWH and in situ production of gases in both the water column and from the underlying sediments. These data provide necessary information for the identification and sources of petroleum-like hydrocarbons in the waters of Cook Inlet.

In addition to the LMW hydrocarbon tracer studies, a subprogram was initiated into the significance of particulate transport of sorbed hydrocarbons. Upper Cook Inlet represents a large source of detrital suspended matter, largely derived from the glacially-fed rivers at the northern extremity (Feely et.al., 1980). Given the large flux of particulate matter through Cook Inlet and the affinity of sediments for the hydrophobic components of petroleum (Huang and Elliott, 1977).

suspended matter transport was investigated by analyzing bottom sediments, suspended sediments, and suspended sediments collected in moored traps for the heavier fractions of petroleum. The goal of this study was to evaluate the probable significance of suspended matter for petroleum hydrocabons.

1.2 Implications to Oil and Gas Development

These studies were enacted to characterize the dissolved LMW natural hydrocarbons in Cook Inlet, Shelikof Strait, and Norton Sound, Alaska. The purpose was to establish concentration levels and temporal and spatial variability of hydrocarbon components common to petroleum or natural gas resources prior to actual production.

Examination of our data indicates that the LMWH will be excellent tracers of petroleum or natural gas input in all of the Alaskan OCS areas. Although methane occurs ubiquitously over the shelf regions of Alaska in moderate concentrations, the concentrations of the C_2-C_4 hydrocarbons are everywhere low (except upper Cook Inlet and Norton Sound), thereby increasing their effectiveness as petroleum tracers. Of course, the value of these components as tracers will depend critically on the magnitude of the input, whether it is at depth or at the surface, and the prevailing hydrographic and meteorological conditions at the point of input.

Studies to date also have revealed useful compositional parameters for distinguishing hydrocarbon sources. The most valuable of these is the ethane: ethene and propane:propene ratios. The low abundance of the aliphatic unsaturates in crude oil coupled with low production of alkanes by biological systems gives an unequivocal indicator of fossil gas and oil sources.

More recently our investigations in upper Cook Inlet have shown that dissolved LMW aromatics may be useful indicators of petroleum and refined products.

These compounds are unique to crude oil and refined products, possess modest solubilities, and apparently are not produced by marine biological systems. Because of the low ambient levels found in pristine marine environments, such as Alaska, these compounds should provide a sensitive and reliable measure of chronic spillage.

2. INTRODUCTION

2.1 General Nature of Study

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

Petroleum contains three broad classes of hydrocarbons: paraffins, naphthenes, and aromatics, but few olefinic hydrocarbons. The proportions of each varies in petroleum, depending on the geologic and geographic sources, but on the average paraffins represent about 30% of the total (NAS, 1975). In contrast, some of the gas wells in upper Cook Inlet are producing methane in excess of 98 mole percent (Kelly, 1968), the remainder of the gases being largely carbon dioxide and nitrogen.

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

The occurrence of light hydrocarbons in the water column may arise from either injected petroleum or natural biological processes. Biological systems tend to produce an abundance of the undersaturated compounds in oxic waters, whereas the oil forming process leads to the exclusive accumulation of saturated compounds. These simple observations allow one usually to distinguish the source of the hydrocarbons, based on their compositional characteristics (Cline et al., 1979). Typical diagnostic ratios include the C_1/C_2+C_3 ratio (Brooks and Sackett, 1973), the C_2/C_3 ratio (Nikonov, 1972), and the $C_{2:0}/C_{2:1}$ ratio. If sufficient methane can be recovered from the water, its isotopic composition is highly useful in distinguishing thermogenic and biogenic methane (Bernard et al., 1976).

2.2 Objectives

During the past year, studies were conducted in two site-specific areas, namely Cook Inlet and Norton Sound, Alaska. The objectives were two-fold: to further increase our knowledge of the compositional characteristics of LMW hydrocarbons associated with thermogenic sources and to evaluate the efficiency of suspended matter transport of heavy hydrocarbons. The thermogenic sources discovered in Cook Inlet and Norton Sound were used as natural laboratory settings to investigate the aforementioned processes.

2.2.1 Low Molecular Weight Hydrocarbons

The abundance and composition of dissolved LMW hydrocarbons associated with gas seeps in Cook Inlet and Norton Sound were studied to define selective compositional parameters unique to thermogenic sources. These are then contrasted to the ambient compositions derived largely from biological processes. Since the LMW aliphatics are not unique to thermogenic sources, we initiated an observational program to determine the presence of dissolved LMW aromatics that might be associated with the seeps. Compounds such as benzene and C_1-, C_2-benzenes are ubiquitious components of crude oils. Given their relatively high solubility and unique crude oil signature, it is felt that these compounds might serve as unique tracers.

2.2.2 Suspended Sediment-Oil Transport Studies

The objectives of this study were to assess the significance of suspended sediments in the transport of sorbed hydrocarbons. Assuming that the aforementioned seeps were significant sources of liquid petroleum, analyses of suspended solids and bottom sediments for HC should provide a basis for estimation of both the transport capacity and dispersion characteristics of suspended solids.

2.3 Relevance to OCSEAP

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

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

The principal goal is to provide the analytical criteria for an early warning detection of petroleum-derived hydrocarbons and to establish the feasibility of using light hydrocarbons as tracers of the dissolved or emulsified fractions of petroleum.

3. Current State of Knowledge

3.1 Cook Inlet

Observations into the distributions and abundances of the low molecular weight aliphatic hydrocarbons in numerous lease areas of Alaska have been carried out over the past three years. These studies have shown that under certain conditions the abundances of the higher homologs of methane, together with the alkane/alkene ratio, serve as a useful indicator of the presence of petroleum-derived hydrocarbons. This was shown to be the case in Norton Sound with the discovery of a submarine gas seep (Cline and Holmes, 1977).

Recent surveys of LMWH in upper Cook Inlet documented the occurrence of unusually high concentrations of ethane, propane, and butanes, not accompanied by similar increases in the low molecular weight alkenes. The source of these hydrocarbons is in Trading Bay. In a survey of dissolved LMWH conducted in 1968, elevated concentrations of methane were observed in the region between the Forelands and just to the north in Trading Bay (Kinney et al., 1970).

Unfortunately, analytical difficulties apparently precluded the analysis of the higher homologs of methane.

The sources of these gaseous hydrocarbons may include subsurface seepage from structural faults or leakage from closed wells. The earlier measurements of Kinney et al. (1970) and our own taken in May and September of 1978 suggest that the source is obviously chronic in nature. Moreover, heavier fractions of petroleum may be associated with the seep gas, since the MacArthur field produces petroleum (API 33) with the dry gas component being used to run machinery associated with the liquid extraction plant (Blasko, 1974).

The occurrence of the LMW alkanes was largely confined to the region between Trading Bay and Kalgin Island. It is assumed that strong tidally-induced vertical and horizontal mixing results in rapid dilution and volatilization of these components. The lower inlet, in contrast to the area above The Forelands, reflects a strong seasonal biological component of LMWH (Cline, 1977). Lower Cook Inlet, in particular the region near Kamishak and Kachemak Bays, reveals elevated concentrations of ethene and propene during summer, which is presumably related to primary productivity, either directly or indirectly, or perhaps to photochemical reactions (Wilson et al., 1970). Our work has shown that under normal conditions the ethane/ethene ratio rarely exceeds 0.5 in most shelf areas and is more nearly 0.1-0.2 for lower Cook Inlet during summer. There is a concomitant rise in the concentration of ethane that accompanies increases in ethene, but the $C_{2:0}/C_{2:1}$ ratio rarely exceeds 0.5. How these two C_2 aliphatics are related is not clearly understood, but the ratio has direct bearing on the utility of the LMW aliphatics for the detection and discrimination of petroleum-induced hydrocarbons, whether it be in Cook Inlet or elsewhere in Alaskan shelf waters.

This year's study focused on the occurrence of LMW aromatics (e.g., benzene, C_1-benzenes, etc.) in Trading Bay, since their occurrence would provide the highest order of distinguishability for the presence of petroleum hydrocarbons. Preliminary data taken in May 1978 indicated a significant accumulation of LMW aromatics north of the Forelands, particularly within Trading Bay, where excess concentrations of ethane and propane also were observed. Although not quantified, the identified aromatic compounds were benzene, toluene, and xylenes. Compounds of lower boiling point than benzene were also observed, presumably pentanes, hexanes, and cycloparaffins.

3.2 Norton Sound

The first survey of LMW aliphatic hydrocarbons in Norton Sound was conducted in September 1976 (Cline, 1977). That survey identified a bottom source of thermogenic hydrocarbons south of Nome (Cline and Holmes, 1977), which subsequently was investigated in detail by scientists at USGS (e.g. Kvenvolden et al., 1979). Prior to these measurements, no other observations of LMW hydrocarbons had been made in Norton Sound.

The salient feature in the hydrocarbon chemistry of this embayment was the bottom gas seep. Its subsurface plume (e.g. ethane) could be traced for over one hundred kilometers along the axis of flow. Other significant features included a strong bottom source of methane in the southeastern corner of Norton Sound and a surface plume of methane emanating from Safety Lagoon east of Nome. Concentrations of the higher homologs of methane were typical for high latitude Alaskan shelf waters.

Distributions of LMW hydrocarbons are largely dictated by sources (e.g. seep, Yukon River, organic rich sediments, etc.) and circulation processes. The outer sound is influenced by the coastal current, which entrains some Yukon River water as it moves north through the Bering Strait. Transport of dissolved hydrocarbons within the inner sound appears to be largely diffusive, but some weak advective transport may be operative (Muench et al., 1980).

3.3 Shelikof Strait

Prior to the OCSEA Program, no observations were available on the distributions and abundance of LMW hydrocarbons in Shelikof Strait. Whereas no specific surveys were conducted in this region, some measurements were conducted in concert with other research activities. The results of these measurements will be described below.

4. Study Areas

4.1 Cook Inlet

Cook Inlet is a relatively shallow, elongated embayment extending approximately 300 km in a north-south direction. The lower inlet is delineated by the Forelands in the north and by Stevenson and Kennedy Entrances on the south. Mean depth of the lower inlet is approximately 60 m (Muench et al., 1978). Significant geographic features within the inlet include Kamishak Bay and Kachemak Bay, Augustine Island, an active volcano, and Kalgin Island located just south of the Forelands.

Water from the Gulf of Alaska enters Cook Inlet primarily through Kennedy Entrance, traverses the lower inlet cyclonically, generally following the bathymetric contours, and returns to the Gulf via Shelikof Strait (Muench et al., 1978). Freshwater, introduced primarily during summer from the upper inlet, passes just to the east of Kalgin Island and flows down the western side of the inlet in general agreement with the physics of estuarine flow. During the southward movement, salinity steadily increases in the outflowing water due to lateral entrainment and mixing (Muench et al., 1978). Because of intense tidal mixing, vertical stratification is limited to the lower inlet, primarily during the summer season. Additional information concerning hydrography and circulation processes can be found in the work of Muench et al. (1978).

In May 1979, a single cruise to Cook Inlet was conducted. The sampling grids occupied in lower and upper Cook Inlet are shown in Figures 4-1 and 4-2. A single time series station was occupied along the east side (20 m isobath) of Kalgin Island.

Over the past two years, surficial bottom sediments were collected from lower Cook Inlet and Shelikof Strait as sample splits from box cores. For comparative purposes, suspended matter and sediment trap samples also were collected in lower Cook Inlet. The location of these sampling sites are shown in Figure 4-3.

4.2 Shelikof Strait

Shelikof Strait is a northeast-southwest trending channel between Kodiak Island and the Alaska Peninsula. Maximum depths in the north are 200 m, increasing to more than 300 m at the southern end (Schumacher et al., 1978). Surface circulation is primarily to the southwest at speeds up to 70 cm sec^{-1} with water entering from the Gulf of Alaska through Stevenson Entrance and from Cook Inlet.

Sampling of dissolved hydrocarbons was conducted in April 1977 and again in June - July 1977. The grid occupied during the latter cruise is shown in Figure 4-4. Only a portion of this sampling grid was occupied on the earlier occasion because of time constraints. Both data sets will be discussed below.

4.3 Norton Sound

Norton Sound is a shallow embayment located in the northern Bering Sea. It is bounded on the north by Seward Peninsula and on the west by St. Lawrence Island. The major freshwater source is the Yukon River that discharges into the southern portion of the region.

During the summer months, Norton Sound is characterized by low salinity ($< 20^{0}/oo$) surface water along the shore perimeter. Salinity increases offshore, reaching values of $32^{0}/oo$ near St. Lawrence Island. The outer portion of Norton Sound is dominated by the coastal stream that flows north through the Bering Strait. Inside the basin, the mean current velocities are apparently weak, resulting in waters that are dominated by tidal mixing. A weak cyclonic circulation may exist along the perimeter.

The cruise track occupied in July 1979 is reflected in Figure 4-5. The section lines (I and II) show the location of zonal water properties to be discussed below.

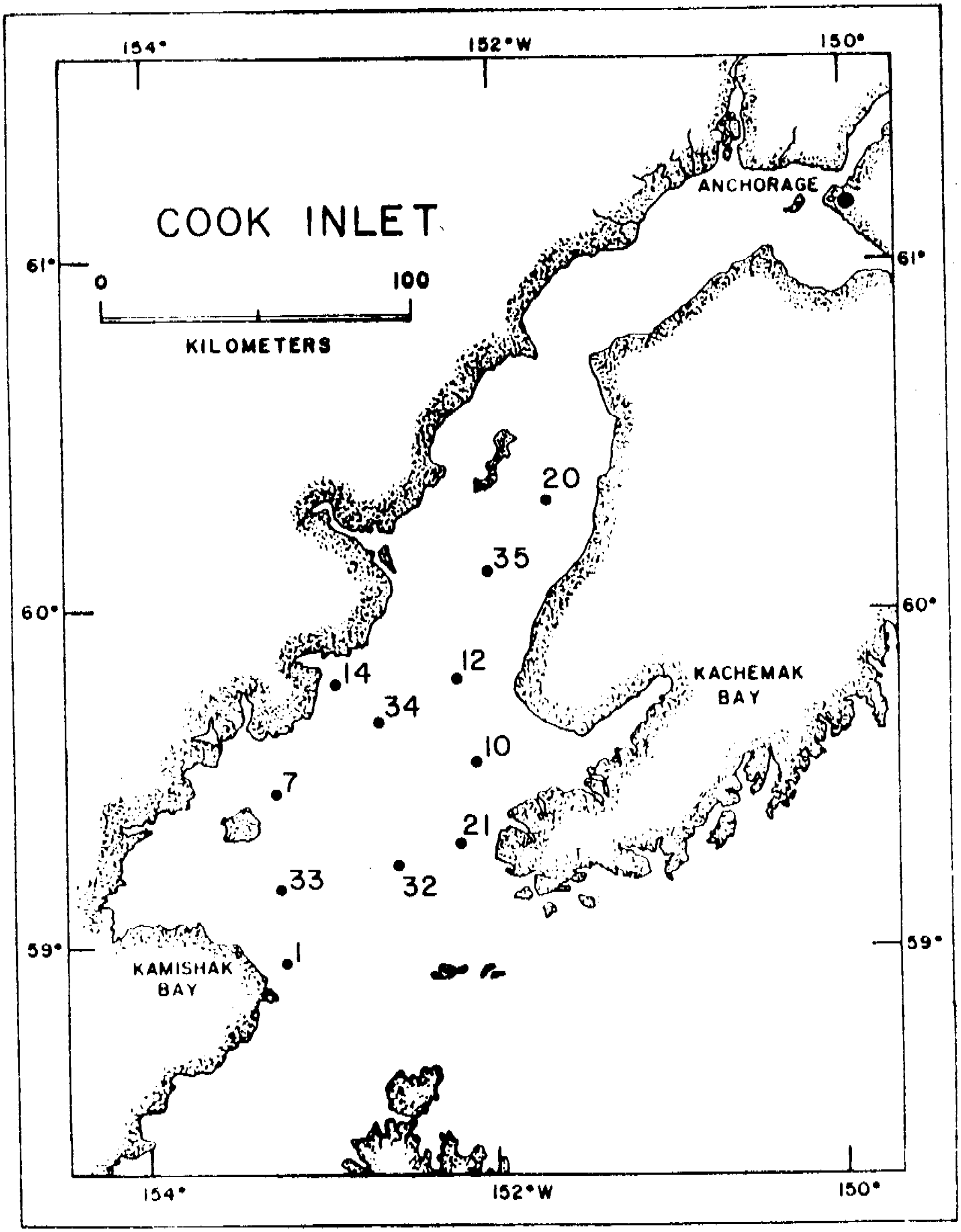

Figure 4-1. Station locations in lower Cook Inlet in May, 1979.

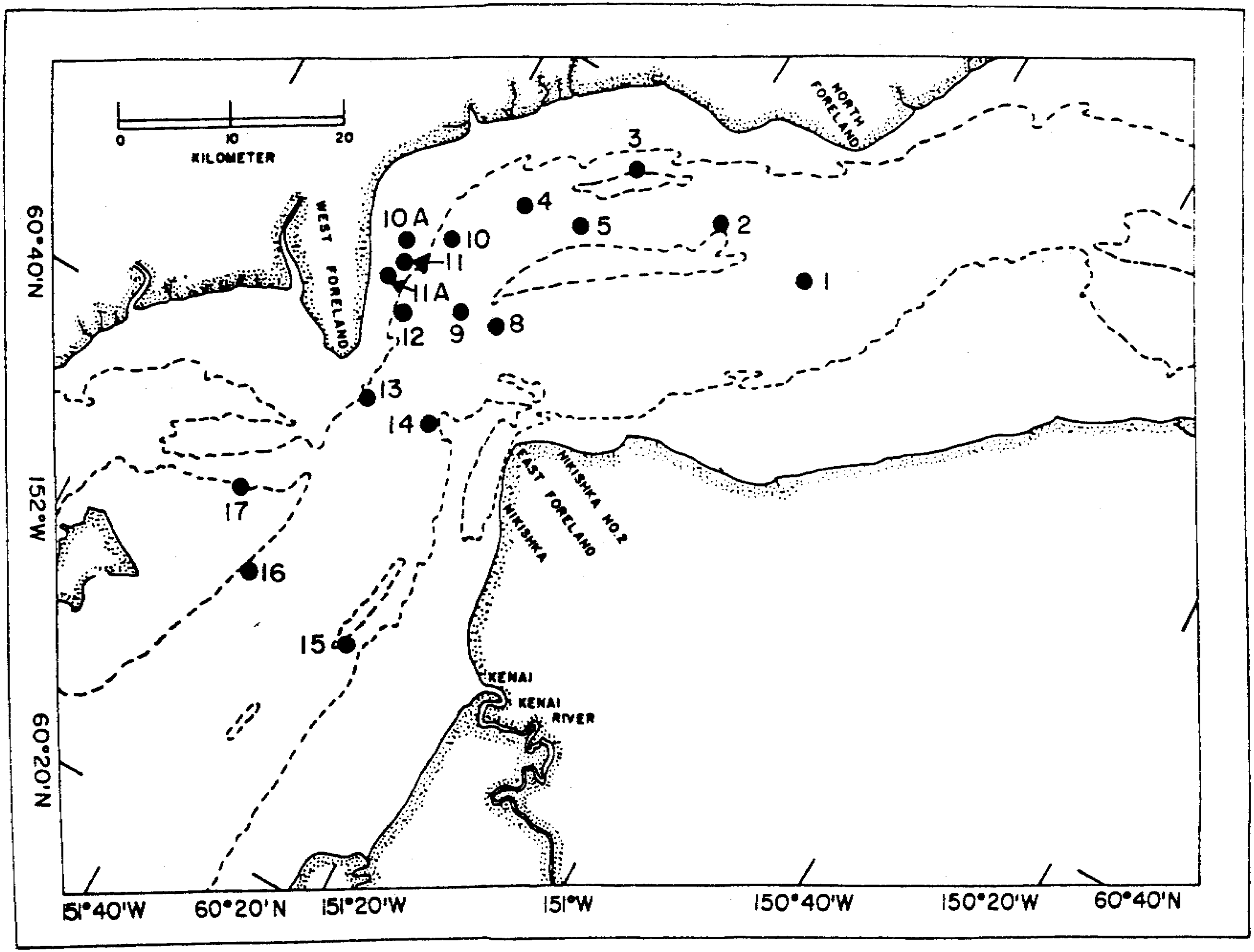

Figure 4-2. Station locations in upper Cook Inlet in May, 1979.

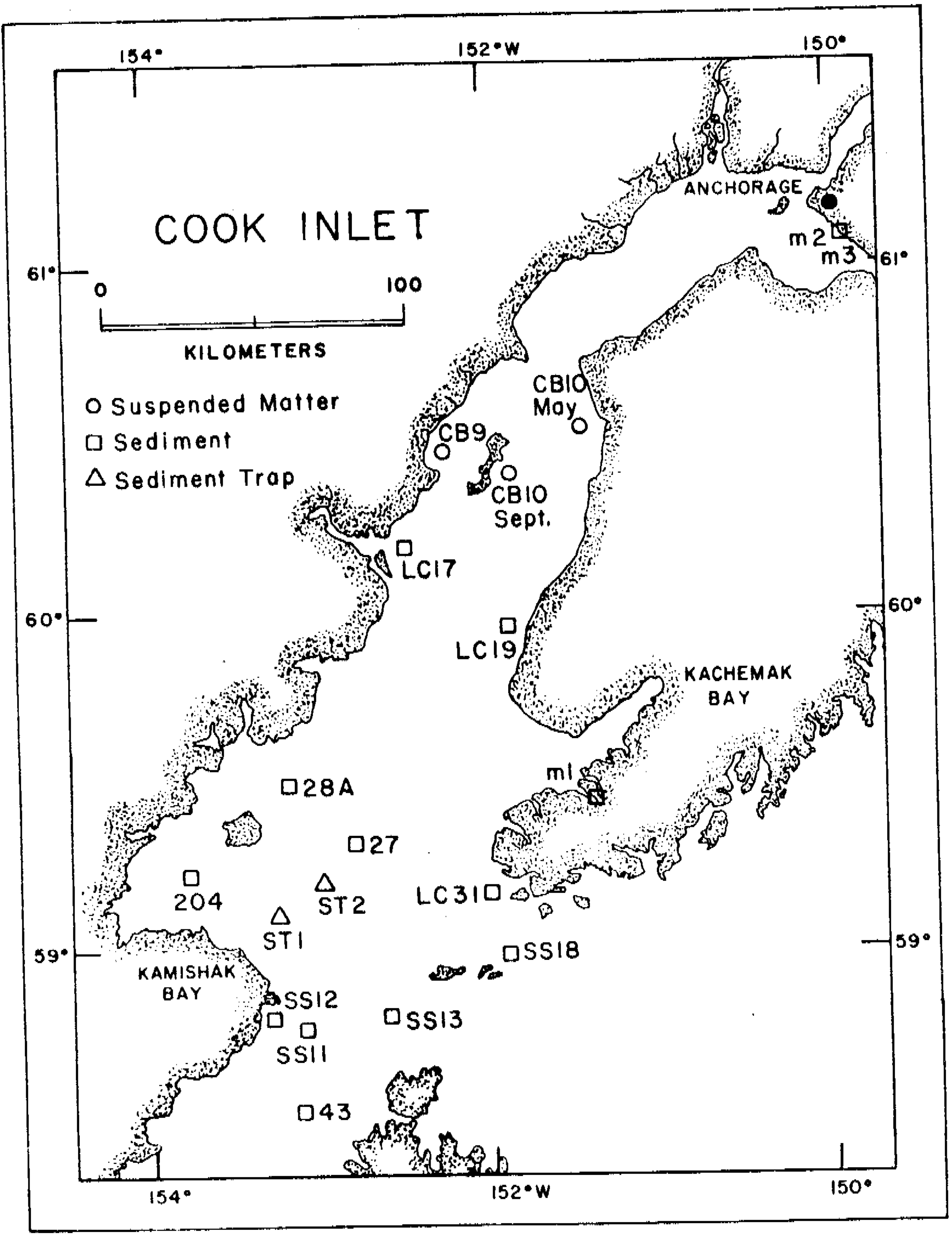

Figure 4-3. Sampling locations of bottom sediments, marsh sediments, and suspended matter in Cook Inlet and upper Shelikof Strait. Locations marked m1, m2, and m3 are the marsh samples. Suspended matter samples were taken at stations CB-9 and CB-10 (May and September). All other stations were sampled for bottom sediments.

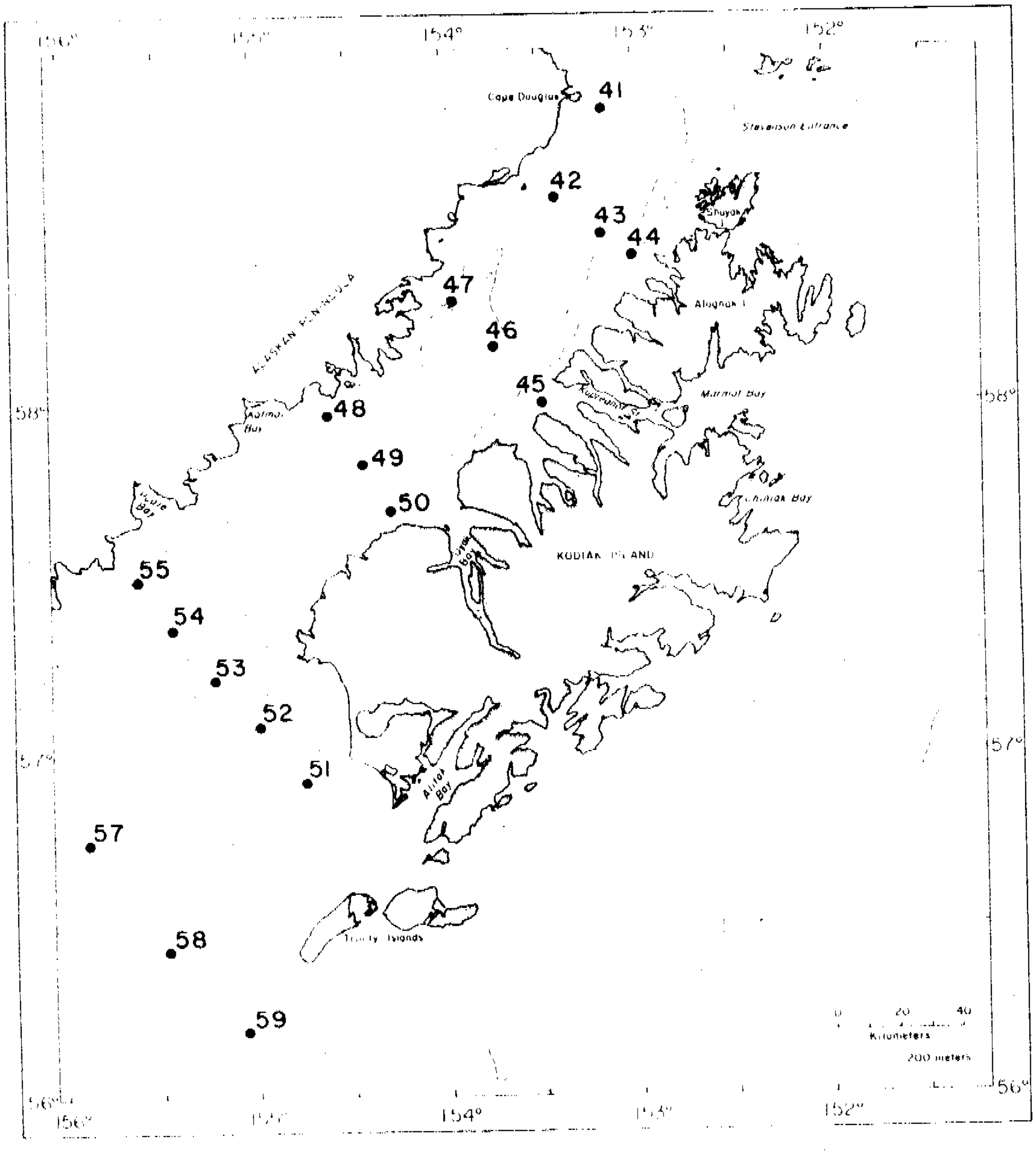

Figure 4-4. Location of stations in Shelikof Strait. Stations 41-46 were occupied in April, 1977; all were occupied in June-July, 1977.

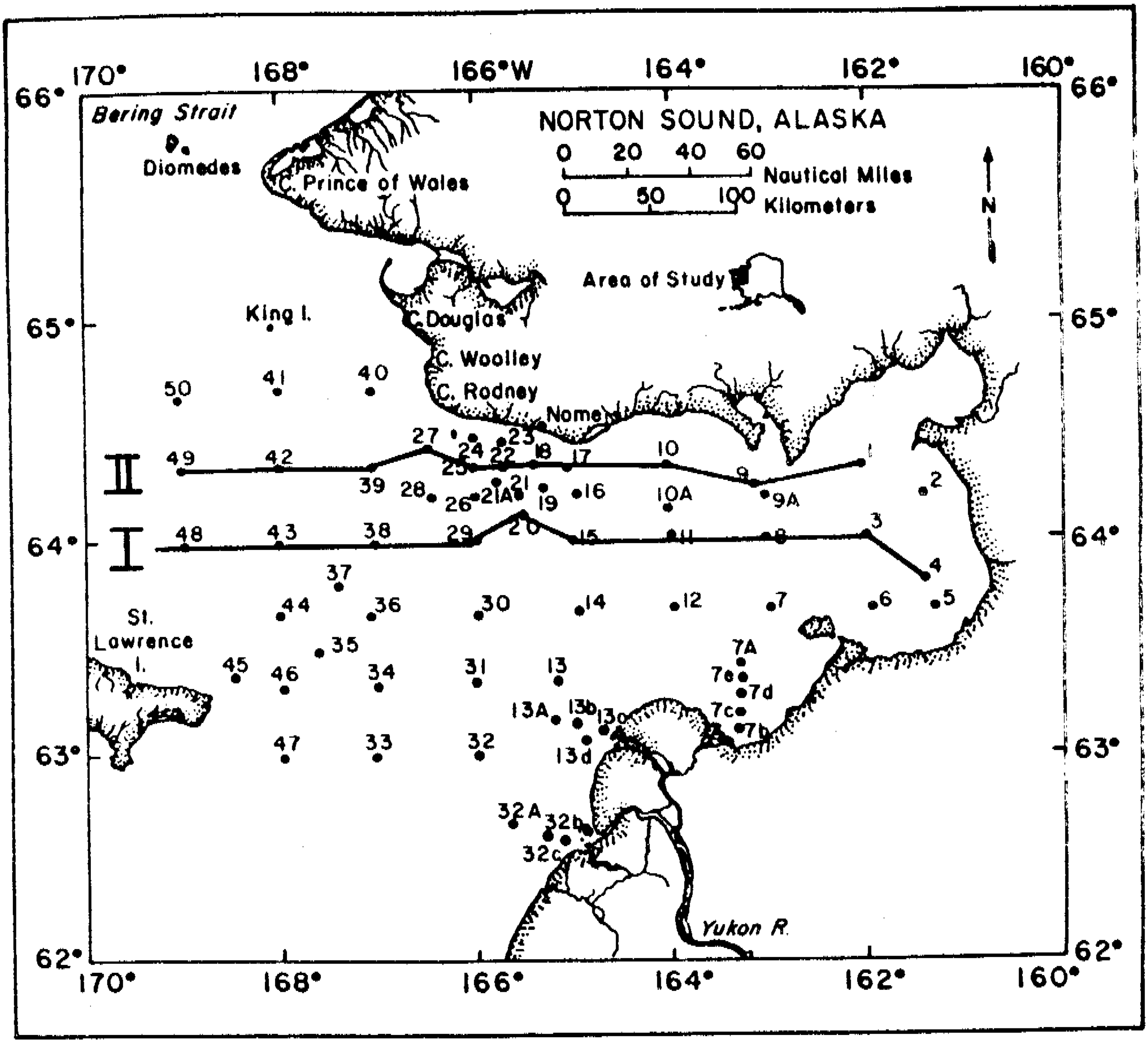

Figure 4-5. Location of stations in Norton Sound in July, 1979. The location of zonal transects (I and II) are also indicated.

5. Methodology

5.1 Low Molecular Weight Aliphatics

LMWHs were stripped from a 1 liter volume of seawater using a modified procedure recommended by Swinnerton and Linnenbom (1967).

Briefly, the hydrocarbon gases are quantitatively removed from solution in a stream of helium and concentrated on an activated alumina trap held at -196°C. The trap is then warmed to 100°C and the gases backflushed into the gas chromatograph. Preconcentration of the components is accomplished in approximately 10 min.

Chromatography of the components was effected on a column of activated alumina (6' x 3/16"), 60-80 mesh, temperature programmed from 100°C to 170°C at 8°/min. Retention times of the unsaturated hydrocarbons were controlled by the water content of the solid support. Chromatography of LMWH components through C_4 was accomplished in approximately 6 minutes. Detection of the component hydrocarbons as they emerge from the column was made with a flame ionization detector.

Calibration of detector response was accomplished using a Certified Matheson hydrocarbon standard that is injected through the system at regular intervals. One of the hydrocarbon mixtures used was previously standardized by NBS and found to be in conformance with stated accuracy specifications.

Water was recovered from standard depths using either 5- or 10ℓ Niskin^R bottles. Within 15 min., the water was transferred to 1ℓ g.s. bottles, pickled with approximately 100 mg of NaN_3. Usually 1 liter of water was allowed to overflow for rinsing. The samples were stored in the dark at deck temperatures (e.g. 0-10°C).

5.2 Low Molecular Weight Aromatics

5.2.1 Collection of Water Samples

Seawater was obtained for analysis in several different ways. Routine sampling was made using 5 liter Niskin GO-FLO ^{R} bottles, which were precleaned as described below. To assess contamination levels, water samples also were taken periodically from the ship's biological pumping system, which was allowed to run continuously to reduce contamination and from a hand-held surface bottle sampler, which allowed a clean, 500 ml bottle to be lowered through the air-sea interface.

The GO-FLO ^{R} samplers were carefully cleaned in a strong detergent, rinsed with copious quantities of ambient seawater from the North Pacific, and finally soaked in clean seawater (changed every several hours) for a minimum of 24 hours. Samplers were attached to a clean, stainless steel line spooled on a small hand winch. The winch was mounted forward of the ship's bridge on the starboard side to reduce contamination from the ship's stack gases and surface discharges.

Two seawater pumping systems on the R/V DISCOVERER were tried during the Cook Inlet cruise. The first was the biological pumping system, which collects water from approximately 6 m depth near the bow. Both this system and the normal seachest pump, which is located amidship, were flushed for several days before use.

The glass bottles used in the collection of surface samples (down to 1 m) were cleaned in a strong detergent, rinsed thoroughly, and oven dried before tightly sealing with Teflon ^{R} lined screw caps. These bottles were attached to a modified lake sampler in which the bottle could be lowered through the interface closed to prevent contamination from the surface layer. All water samples were stored at 3°C in the dark with 0.5 g NaN_3 to reduce biological effects.

5.2.2 Removal of LMW Aromatics from Seawater

Water samples (approximately 500 ml) were transferred to a modified gas dispersion bottle, heated to 40°C in a water bath and stripped for 30 minutes with prepurified Helium. Flow rate was set at 100 ml/min. Hydrocarbons, air gases, and water vapor were carried through a water cooled condensor, to reduce the concentration of water, and finally through a Tenax ^{R} trap (1/4" o.d. x 3") to remove the aromatic compounds. Prior to sample collection, the Tenax ^{R} was purged with He for several hours at 275°C to remove adsorbed contaminants. Tenax ^{R} was found to retain nuisance levels of water, thus drying with He at 100 ml/min for 15 min was necessary to remove the water interference. At the conclusion of the drying step, the Tenax ^{R} traps were placed in a Bendix Flasher (Applied Science, Inc.), where the sorbed aromatic compounds were thermally eluted onto a glass-lined metal trap held at -196°C. Subsequent to the sample transfer, the trap was heated and the contents transferred to the glass capillary column as described below.

5.2.3 Analysis of LMW Organics

During a previous Cook Inlet cruise, the Bendix Flasher was attached directly above the gas lined injector of the GC-MS system (HP 5992A). However, because of poor hydrocarbon elution efficiencies from Tenax ^{R} at low flow rates (4 ml/min), we decided to place in series with the Bendix Flasher a small cold finger (1.6 mm o.d. x 12 cm glass-lined stainless steel U-tube) cooled to -196°C with LN_2. The larger diameter cold finger allowed the hydrocarbons to be purged from the Tenax ^{R} at higher flow rates (30 ml/min) and condensed into a small plug near the injector. A heat gun was used to transfer the hydrocarbons from the cold finger to the head of a 30 m wall coated (SE-54) open tubular glass capillary column held at -50°C. The oven was then quickly heated to an initial temperature of 0°C and programmed from there at 2°/min to a final temperature of 100°C. The column was baked out at 250°C between samples.

Mass spectral data were collected and synthesized using two separate software packages. The first program provided a total ion scan from 45 to 350 AMU at each peak. The second program (Selected Ion Monitoring) allowed 20 preselected ions to be monitored for area response. This program was used for quantitation of the selected LMW aromatic compounds such as benzene, toluene, ethylbenzene, and xylenes.

5.2.4 Standardization Procedures

Five μl aliquots of individual aliphatic, cycloalkane, and aromatic hydrocarbons were vaporized in a heated 3000 ml flask to produce a gaseous HC standard of approximately 1.4 ng/μl for each component. This standard, which could be injected directly into the g.c. - m.s., was used to assess g.c. operating conditions and detector sensitivity (m.s.).

Aqueous standards were prepared by mixing known amounts of pure solvents in methanol, which were diluted in purged distilled water and used as secondary standards (EPA, 1977). Stripping efficiencies were assessed by comparing the response of the g.c. - m.s. to each of the above standards. Aqueous standards were used to determine area response factors for individual compound quantitation.

5.3 Hydrocarbon Analysis of Suspended Matter and Sediment

5.3.1 Collection

Each suspended matter station was occupied for 18 to 24 hours, during which seawater was continuously pumped from approximately 5 m with a Peabody Barnes ^{R} submersible water pump. The water was passed through an intake maniford, 100 μm prefilter, and a Sorvall Model ^{R} SS-3 high speed centrifuge. Sedimentation was accomplished with the centrifuge operating at approximately 30,000 gravitational units and the supernatant being exhausted at the rate of 400-500 ml/min. The collected suspended matter was immediately frozen and returned to the laboratory for analysis.

Sediment samples were collected with a modified aluminum Van Veen grab sampler. The depth interval sampled was approximately 0-4 cm. Sediment samples were frozen immediately after collection in glass, solvent-rinsed, jars.

5.3.2 Analysis of High Molecular Weight Hydrocarbons

Frozen sediment and suspended matter samples ($-60^{\circ}C$) were thawed overnight in a refrigerator and transferred to pre-extracted, preweighed cellulose thimbles (25 x 80 mm Whatman single thickness), Soxhlet extracted 48 hours in methanol: dichloromethane (1:2) of known weight. The wet sample was Soxhlet extracted for 48 hours with 100 ml of methanol: dichloromethane (1:2). The solvent was changed after 24 hours. After extraction the sample and thimble were oven dried and reweighed to determine the dry weight of the sample extracted. Recovery standards were added to the extract. Reagent and procedural blanks were carried through the entire analysis with each batch of samples.

The total extract (200 ml) was rinsed twice in a separatory funnel with 100 ml of distilled deionized water to separate the water and methanol from the dichloromethane. The total organic extract was then eluted through a clean-up column with dichloromethane. The 10 mm i.d. column contained 25 cm of silica gel (20 ml dry, 100-200 mesh, grade 923, activated at $150^{\circ}C$ overnight), and 1 cm of activated Cu powder (rinsed with 12 N HCl, H_2O, CH_3COCH_3, and CH_2Cl_2). The clean-up column was designed to remove elemental sulfur, residual water, and the majority of the pigments from the organic extract.

The extract volume was then reduced to 15 ml on a water bath at $60^{\circ}C$, transferred to a Kontes ^{R} tube, and reduced to 1 ml. After partitioning into 1 ml of hexane, the sample extract was fractionated by silica gel column chromatography (20 cm of activated silica gel in a 1 cm i.d. column). Saturated hydrocarbons were eluted with 1.5 column volumes of petroleum ether. Unsaturated hydrocarbons were eluted with 2 column volumes of dichloromethane. The fractions were reduced to 1 ml in Kontes ^{R} tubes, transferred to vials and reduced to 0.1 ml under a stream of nitrogen. A 0.01 ml aliquot of each fraction was weighed on a Cahn 4100 microbalance prior to gas chromatography for gravimetric determination of the total extract.

Saturated hydrocarbons were analyzed with a Hewlett Packard model 5730A gas chromatograph coupled to a Hewlett Packard 3385 integrator. Component separation was accomplished on a 30 m SP-2100 wall-coated open-tubular glass capillary column temperature programed from $70^{o}C$ to $270^{o}C$ at 4^{o}/min. Selected samples were also analyzed with a Hewlett Packard model 5992B gas chromatograph-mass spectrometer equipped with a SP-2100 glass capillary column. Unsaturated hydrocarbons were analyzed with the above instrumentation on a SE-54 glass capillary column.

5.3.3 Recovery and Precision

The entire analytical procedure was examined by testing hydrocarbon recovery of spiked samples and reproducibility of replicate samples. A standard mixture of hydrocarbons ($n\text{-}C_{11}$ through $n\text{-}C_{32}$) was added to pre-extracted sediment and carried through the extraction/analysis procedure. Recoveries ranged from 60-90% for $n\text{-}C_{12}$ - $n\text{-}C_{15}$ and 90-95% for $n\text{-}C_{16}$ - $n\text{-}C_{32}$.

Sediment from station 204 in Cook Inlet was carefully homogenized and extracted in triplicate. The precision of the gravimetric weighings was 15% (relative standard error). Weights of individual hydrocarbons per gram dry weight of sediment varied by an average of 3%. A similar experiment carried out on homogenized suspended matter from a station near Kalgin Island showed individual hydrocarbons varying by an average of 8.5%.

6. Results and Discussion

6.1 Cook Inlet

The geographical subregions of Cook Inlet are hydrographically and biologically distinct. For this reason, discussion of the various hydrocarbon distributions in the two regions will be separated.

6.1.1 LMW Aliphatics - UCI

As has been our custom in past years, high density sampling of the waters in Trading Bay was undertaken again this year. Trading Bay is the location of several offshore gas and oil fields.

The surface distribution of methane is reflected in Figure 6-1. The highest concentrations were observed in Trading Bay (up to 4000 nl/l) near the McArthur River. The locus of the gas source is within 1 km of a well. The second source of methane is to the south near the West Foreland and also may be associated with closed-in wells. In general, methane concentrations (surface and near-bottom) were in excess of 2000 nl/l throughout Trading Bay and reflect the highest levels measured to date in Cook Inlet or elsewhere on the Alaskan OCS.

The surface distributions of ethane and propane are shown in Figures 6-2 and 6-3. The highest concentrations of dissolved ethane were found near the West Foreland, as before. In the past, the maximum concentrations of dissolved ethane approached 10 nl/l, approximately 50% of that observed during the May cruise. It appears that sampling closer to shore on this particular occasion intercepted higher concentrations of the saturated alkanes.

The structure of the plume shows an efflux of hydrocarbon-rich water down the west side of the inlet, whereas water deficient in hydrocarbons moves

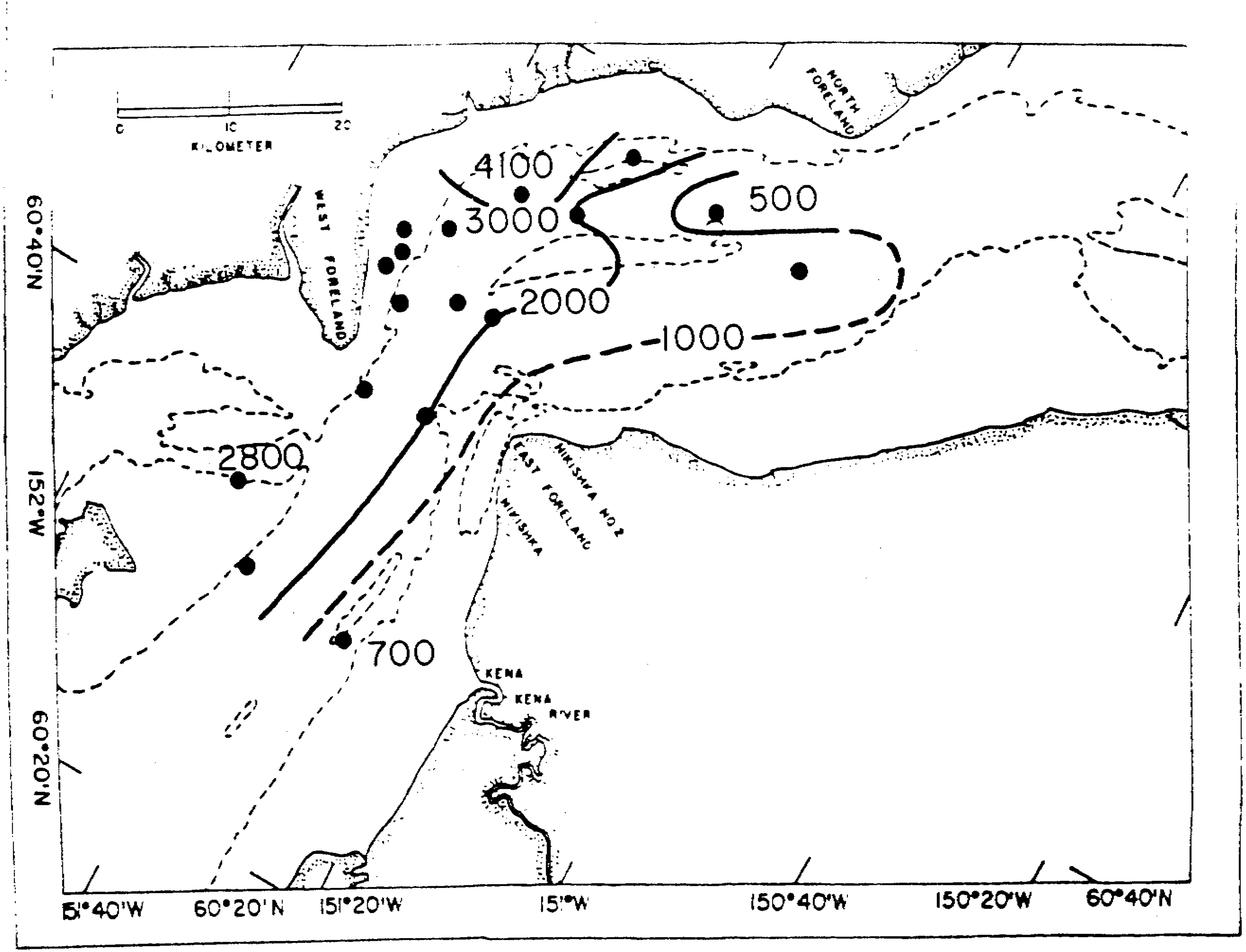

Figure 6-1. Surface distribution of dissolved methane in upper Cook Inlet in May, 1979. Concentrations are given in nl/l (STP).

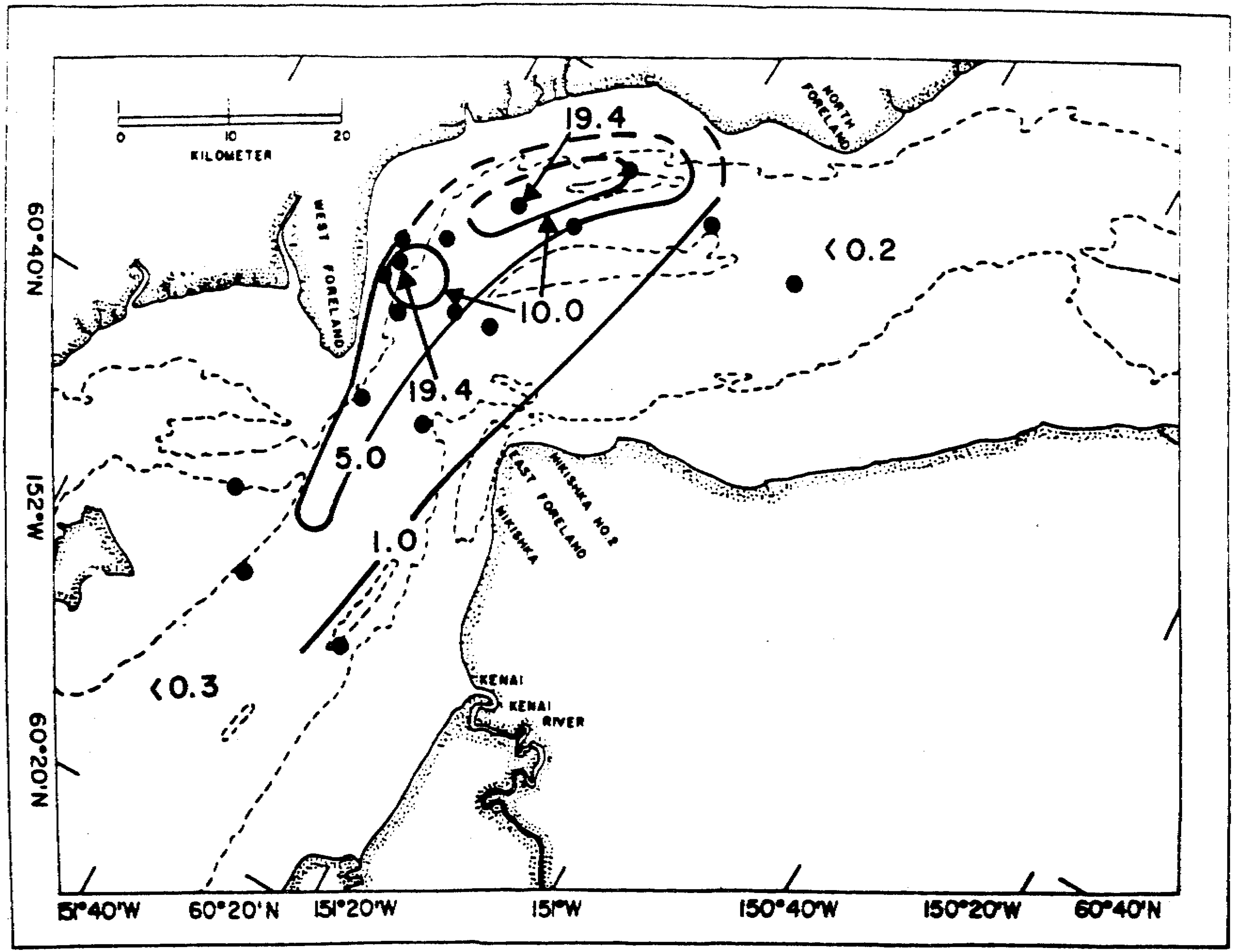

Figure 6-2. Surface distribution of dissolved ethane in upper Cook Inlet in May, 1979. Concentrations are given in nl/l (STP).

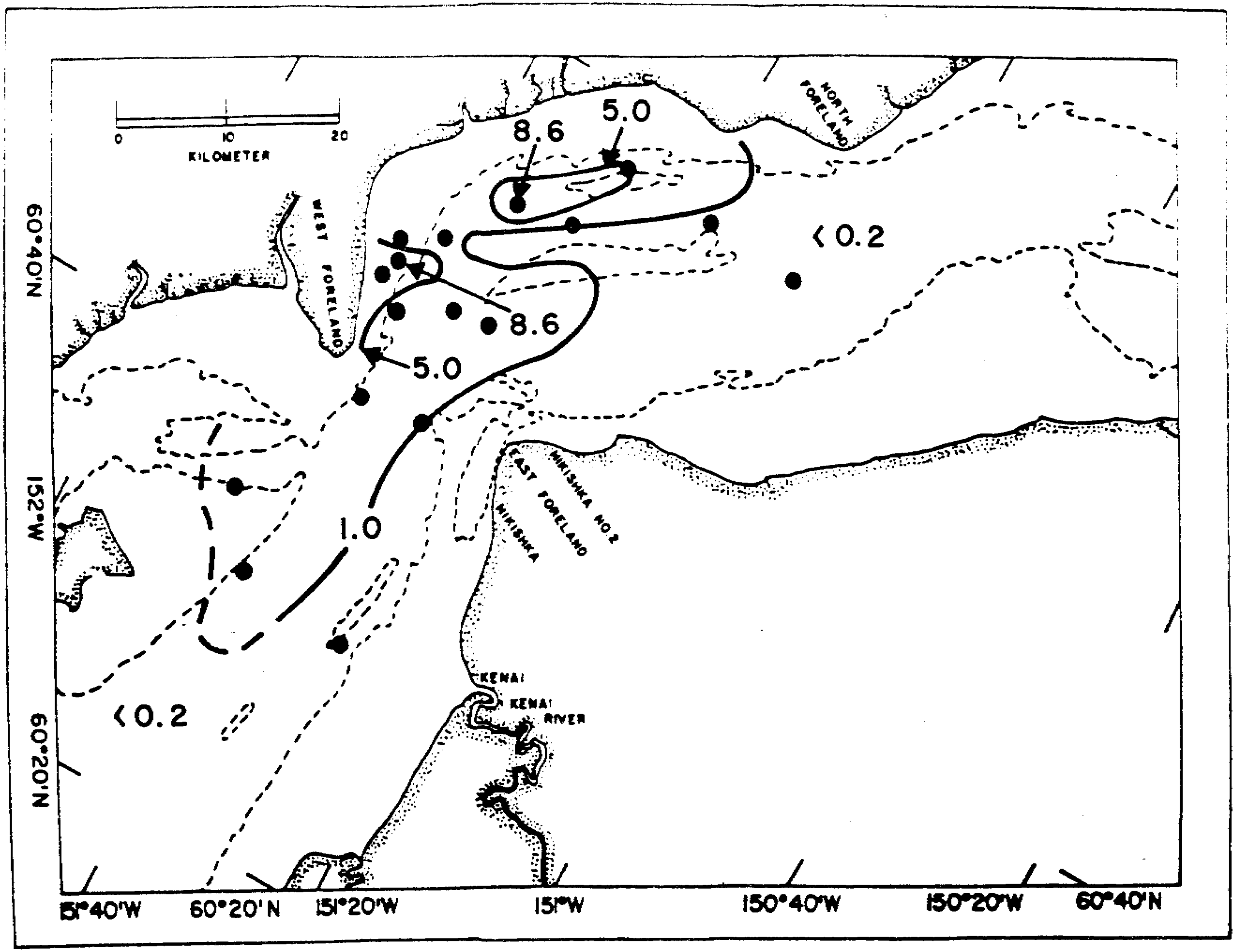

Figure 6-3. Surface distribution of dissolved propane in upper Cook Inlet in May, 1979. Concentrations are given in nl/l (STP).

up the eastern side. Notwithstanding the presence of two or more gas vents, the bifurcated plume is probably the result of unequal tidal velocities and flow trajectories.

The highest surface concentrations of propane were observed at stations 11A and 4 (see Figure 4-2), the same locations where maximum ethane concentrations were seen. The general feature of the hydrocarbon plume is preserved. The highest concentrations of propane were 8.6 nl/l, decreasing to approximately 0.2 nl/l above and below Trading Bay (Fig. 6-3). Table 6-1 summarizes the aliphat concentrations and diagnostic ratios observed at stations 4 and 11A.

Table 6-1. Concentrations of alkane hydrocarbons and diagnostic ratios at stations 4 and 11A in Trading Bay (see Figure 4-2).

Station	CH_4	C_2H_6	C_3H_8	C_3/C_1	C_1/C_2+C_3
			nl/L (STP)		
4	4080	19.4	3.6	0.002	145
11A	2380	19.0	8.6	0.003	86

As reflected in Table 6-1, the C_1/C_2+C_3 ratio is near 100 at stations close to the seep locus. Under normal circumstances where biogenic hydrocarbon assemblages prevail, the ratio would be expected to be in excess of 500. If natural gases associated with petroleums are the source, the ratio decreases to values below 20. The values shown here suggest an admixture of both thermogenic and biogenic hydrocarbons. One additional complication is that some of the gas fields in upper Cook Inlet produce an exceptional "dry gas", that is to say, methane is present at concentrations in excess of 98 mole percent. If this is the dominant source of gas, then the C_1/C_2+C_3 ratio shown in Table 6-1 is lower than one would expect. More than likely, the hydrocarbon composition is due to three distinct sources, two of which are gas seeps of different compositions, the third being normal biogenic methane commonly found in shallow marine coastal environments. We suspect the biological component is small in upper Cook Inlet because of the reduced production of marine carbon and the high energy of the environment. The local strength of the source and its temporal stability both suggest a deep-seated source of significant magnitude.

Observations taken during this cruise confirm our previous findings, namely that the gas seep appears to emanate from one or two major sources, which are located near shore.

6.1.2 LMW Aromatics - UCI

Observations were conducted in Shelikof Strait, lower Cook Inlet and upper Cook Inlet, with emphasis on the region of Trading Bay. This is the principal site of offshore oil and gas production in upper Cook Inlet and was chosen for intensive study on the basis of elevated concentrations of low molecular weight hydrocarbons.

Figure 6-4 shows the distribution of benzene in the surface waters of upper Cook Inlet. The distribution is similar to that observed for the alkanes, but because of increased noise, additional artistic license was taken in the contouring. The highest concentrations of benzene were found near the West Foreland, approximately 60 ng/l. Typical background levels of benzene in lower Cook Inlet were 10-20 ng/l. In a general way, toluene and the C_2-benzenes were observed to co-vary, although the statistical basis is not as firm as one would like (Table 6-2). A more complete discussion of the significance of ambient levels of aromatics will be developed in the next section on Shelikof Strait.

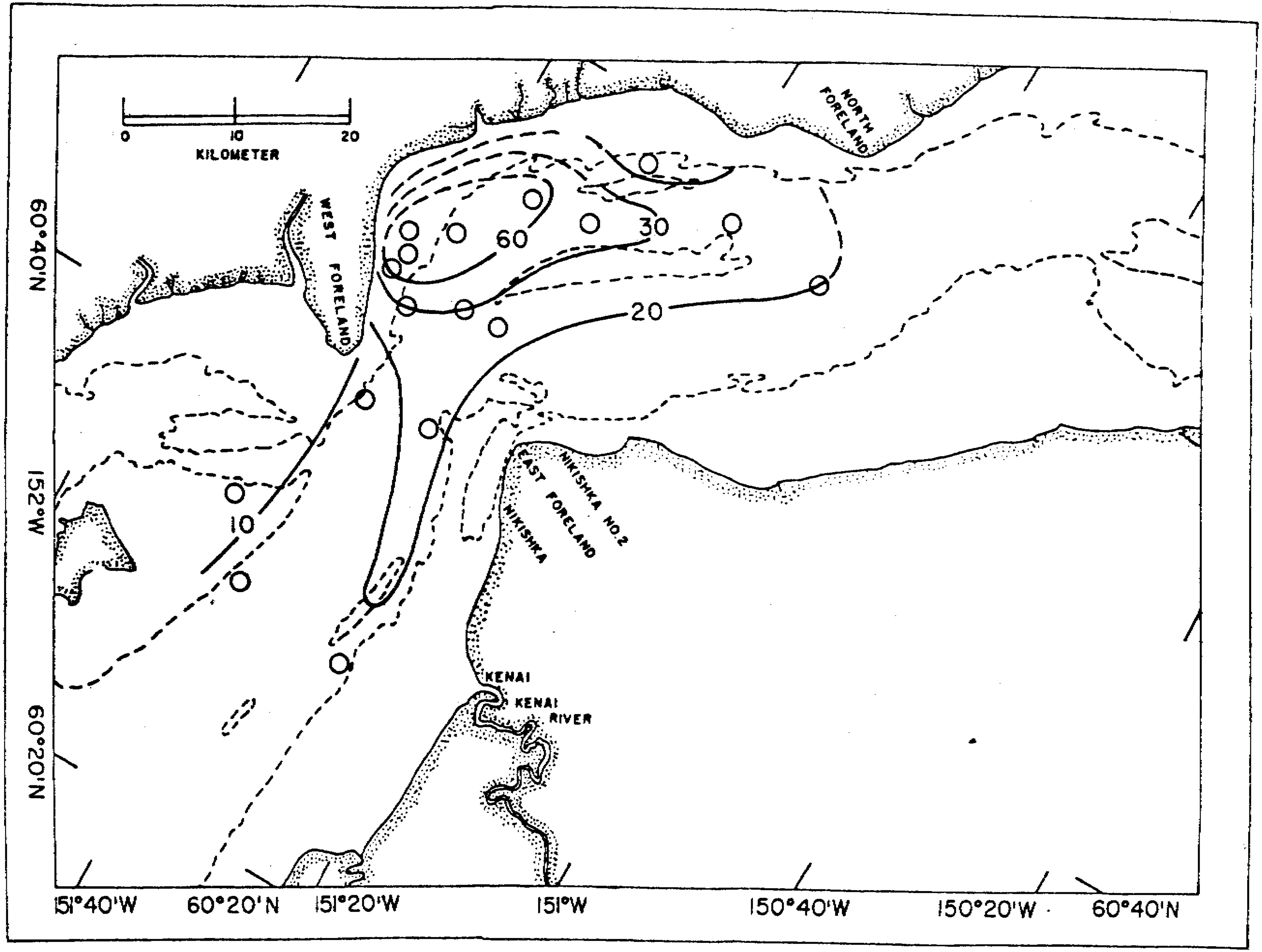

Figure 6-4. Surface distribution of dissolved benzene in upper Cook Inlet in May, 1979. The benzene concentration at station 11A, near the West Foreland, was only 22 ng/l and was ignored for the purpose of contouring. The reason for the anomalously low concentration at this station is not known.

Table 6-2. Summary of aromatic hydrocarbon concentrations by station number in upper Cook Inlet.

Station No.	Benzene	Toluene	C_2-Benzenes
		ng/liter	
UC-1	19	52	18
UC-2	32	45	13
UC-3	14	55	13
UC-4	60	194	35
UC-5	32	55	13
UC-8	43	58	13
UC-9	30	113	62
UC-10	-	48	35
UC-10A	57	110	26
UC-11	22	39	31
UC-11A	60	281	53
UC-12A	30	84	57
UC-13	11	78	-
UC-14	24	36	71
UC-15*	24	32	31
UC-16*	8	13	18
UC-17*	11	36	18

* These stations are south of the Forelands, see Figure 4-1.

Based on these few data, our conclusion is that the aromatic signature in the gas seep is not large, suggesting that only small amounts of volatile aromatics are actually present in the seep gas. Chromatographic measurements made by Sauer et al. (1978), show that benzene and toluene concentrations, determined at three offshore stations (30, 38, 39) in the Gulf of Mexico, are roughly 14 ng/l and 11 ng/l respectively. These values are similar to our surface values in lower Cook Inlet, although we would expect Alaskan waters to be more pristine. It is highly likely that aromatic hydrocarbons are present in one of the gas seeps, but contamination problems associated with the ship's atmosphere must be overcome before their significance can be accurately assessed.

6.1.3 LMW Aliphatics - LCI

The efflux of methane from upper Cook Inlet is displayed in Figure 6-5. Concentrations in excess of 2000 nl/l were found south of Kalgin Island in sharp contrast to normal conditions. As usual, the highest concentrations were found along the western shore, whereas low methane-high salinity water was observed to move north along the eastern shore. Water entering through Kennedy Entrance contains approximately 150 nl/l of dissolved methane, a typical concentration for the shelf waters of the Gulf of Alaska.

Surface concentrations of ethane are shown in Figure 6-6. Analogous to methane, elevated concentrations of ethane were found south of Kalgin Island (C_2H_6 > 0.9 nl/l). Throughout the remainder of the inlet, concentrations were less than 1 nl/l. In the vicinity of Kalgin Island, strong lateral concentration gradients were observed, reflecting the estuarine flow pattern characteristic of the inlet.

Surface concentrations of ethene ranged from 1.8 nl/l in the southern portion of the inlet to approximately 0.2 nl/l in upper Cook Inlet. These

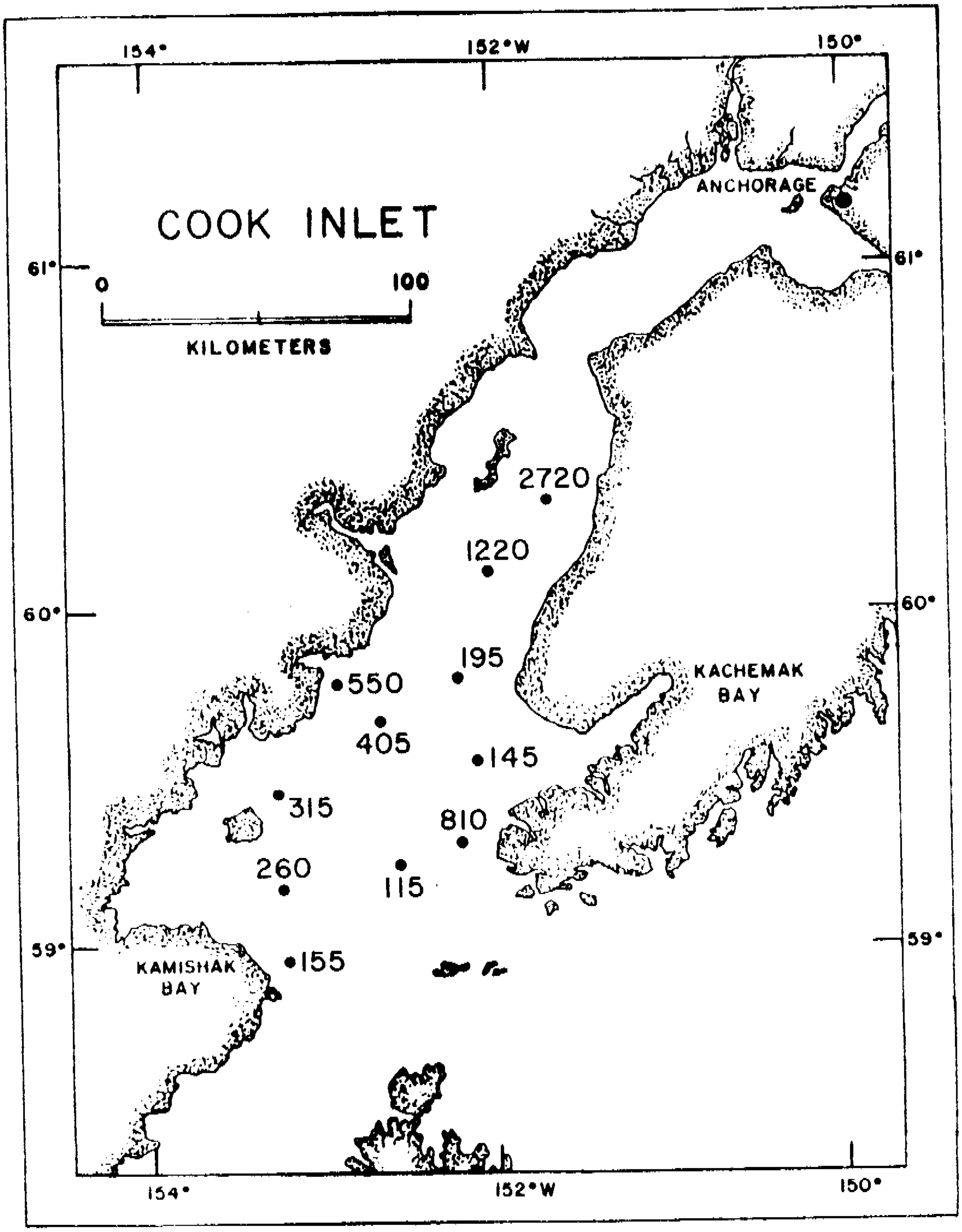

Figure 6-5. Surface distribution of dissolved methane in lower Cook Inlet in May, 1979. Concentrations are given in nl/l (STP).

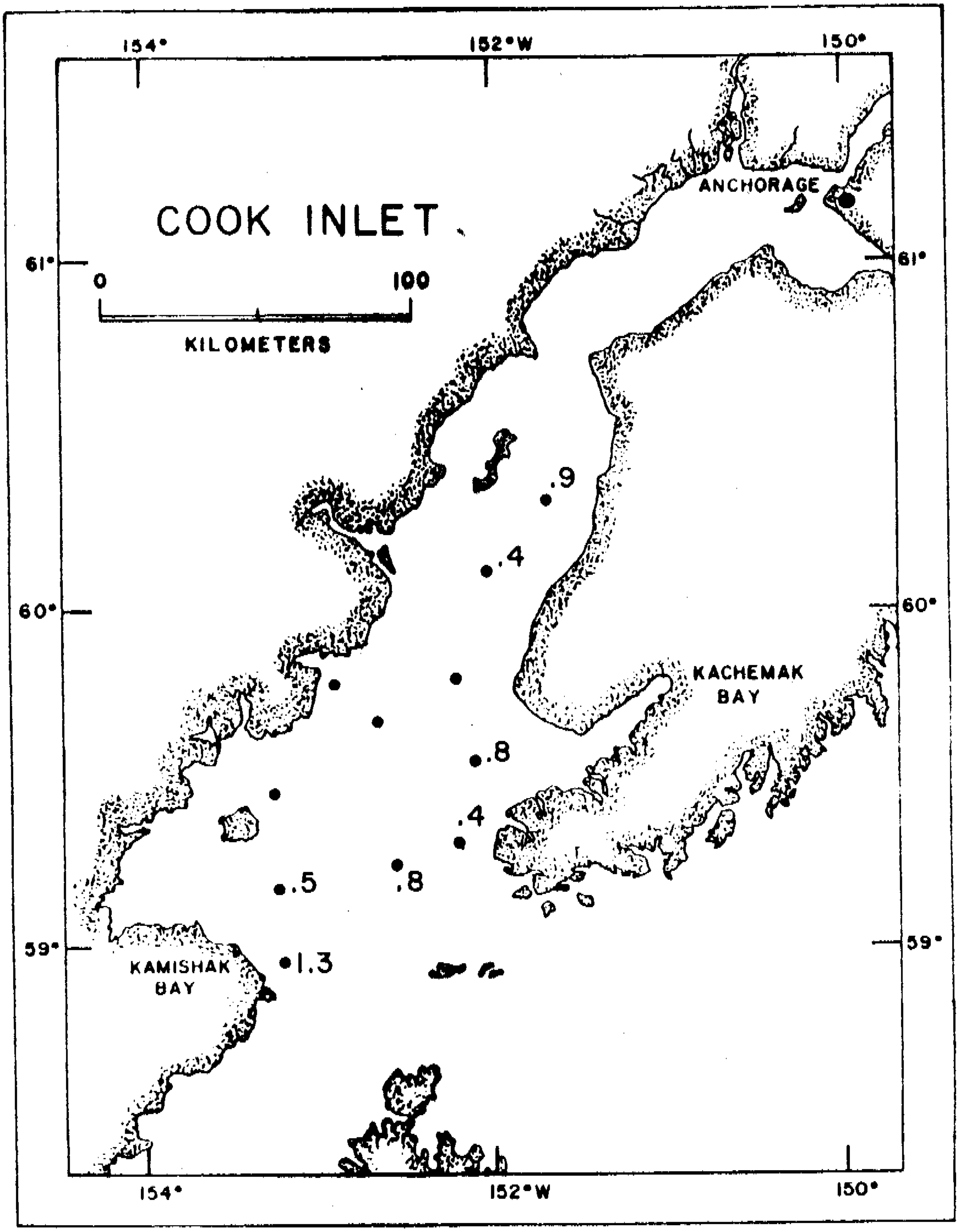

Figure 6-6. Surface distribution of dissolved ethane in lower Cook Inlet in May, 1979. Concentrations are given in nl/l (STP).

differences are ascribable to increased turbidity and/or reduced biological activity in the upper inlet.

Propane concentrations averaged 0.2 nl/l in the lower inlet in contrast to concentrations in excess of 4 nl/l in upper Cook Inlet. Propene was near zero concentration levels in upper Cook Inlet, averaging 0.3 nl/l in lower Cook Inlet. Butanes were below the detection limit of 0.05 nl/l.

6.1.4 LMW Aromatics - LCI

Two surface measurements were made for benzene, toluene, ethylbenzene, and xylenes. They will be discussed together with the data from Shelikof Strait in the next section.

6.1.5 Particulate Hydrocarbons

Suspended matter, surficial sediment, and sediment trap samples were analyzed in order to assess the significance of suspended matter on the transport of saturated hydrocarbons in Cook Inlet. Individual hydrocarbon concentrations are listed in Table 6-3. The compositional characteristics of these saturated hydrocarbons are presented in Table 6-4.

6.1.5.1 Suspended Hydrocarbons. The hydrocarbon composition of Cook Inlet suspended matter was similar at all three stations sampled. A representative chromatogram (CB-10, Figure 6-7) shows a strong predominance of odd carbon numbered aliphatic hydrocarbons indicative of a terrigenous source. The ratio of the sum of N-C_{13} to n-C_{20} divided by the sum of n-C_{21} to n-C_{32} is .20 (Table 6-4). Literature values compiled by Gearing et al. (1976) show vascular plants demonstrating a characteristic ratio of 0-.5. The September sample from CB-10 also shows higher values of n-C_{15} and n-C_{17}, implying an increased marine plankton input during this period.

TABLE 6-3. Saturated hydrocarbon concentrations (ng/g dry wt.) in Cook Inlet and Shelikof Strait sediment and suspended matter samples.

Station	Date	n-C_{12}	n-C_{13}	n-C_{14}	n-C_{15}	n-C_{16}	n-C_{17}	Pristane	n-C_{18}	Phytane	n-C_{19}	n-C_{20}
Suspended Matter												
CB-9	5/78	12	16	19	43	27	34	30	24	8	26	28
CB-10	5/78	11	15	18	34	27	33	34	28	9	32	28
CB-10	9/78	15	17	20	106	32	41	42	35	12	31	33
Bottom Sediments												
SS-18	5/79	12	13	12	22	14	18	35	15	6	17	14
SS-13	5/79	10	11	12	22	12	16	38	12	4	16	13
SS-12	5/79	5	6	7	11	10	13	14	10	3	14	11
SS-11	5/79	8	7	8	14	10	14	28	11	4	14	14
43	4/77	20	22	21	31	18	21	47	21	7	28	24
LC-31	5/79	1	2	2	4	3	4	6	3	1	4	3
LC-19	5/79	1	1	1	1	2	3	2	3	1	9	5
LC-17	5/79	10	8	9	19	12	19	22	12	4	22	19
27	4/77	3	3	4	6	6	7	6	7	1	10	6
28A	4/77	4	5	5	10	7	10	10	8	2	13	9
204	9/78	8	10	10	21	14	18	22	14	-	21	17
M1	9/78	-	6	7	63	13	35	24	12	5	20	14
M2	9/78	6	8	9	54	14	29	19	15	-	29	16
M3	9/78	7	16	9	27	16	21	21	16	-	23	31
Sediment Trap Material												
ST-1	10/78	18	22	21	62	33	49	1875	63	42	184	167
ST-2	10/78	32	39	43	232	64	78	365	56	33	83	82

TABLE 6-3. Saturated hydrocarbon concentrations (ng/g dry wt.) in Cook Inlet and Shelikof Strait sediment and suspended matter samples.

Station	Date	n-C_{21}	n-C_{22}	n-C_{23}	n-C_{24}	n-C_{25}	n-C_{26}	n-C_{27}	n-C_{28}	n-C_{29}	n-C_{30}	n-C_{31}	n-C_{32}
Suspended Matter													
CB-9	5/78	49	41	89	42	128	41	256	46	187	27	164	22
CB-10	5/78	58	46	116	57	180	59	340	71	270	73	255	75
CB-10	9/78	67	56	129	62	200	68	370	72	262	44	243	40
Surficial Sediment													
SS-18	5/79	14	13	14	12	14	12	23	12	24	8	23	7
SS-13	5/79	16	14	18	14	21	14	35	14	37	11	31	11
SS-12	5/79	14	12	21	12	31	11	97	10	63	8	50	6
SS-11	5/79	22	19	41	23	77	25	161	22	119	20	100	15
43	4/77	38	32	47	32	60	31	108	30	86	18	73	10
LC-31	5/79	4	3	4	3	5	3	8	3	9	2	8	2
LC-19	5/79	12	9	29	14	47	14	90	18	120	13	100	10
LC-17	5/79	50	31	88	37	149	35	284	40	205	35	163	30
27	4/77	12	12	19	9	29	8	42	15	69	24	74	15
28A	4/77	19	16	40	20	65	20	145	23	120	20	80	9
204	9/78	34	25	66	27	109	28	257	21	169	23	157	19
M1	9/78	75	28	140	41	460	74	1100	250	1800	170	400	140
M2	9/78	54	32	120	37	219	41	381	39	390	35	308	23
M3	9/78	61	47	113	41	180	46	402	57	277	30	218	22
Sediment Trap													
ST-1	10/78	140	72	136	65	300	74	390	51	261	69	243	58
ST-2	10/78	95	70	150	90	217	102	326	118	347	145	322	128

TABLE 6-4. Compositional characteristics of Cook Inlet and Shelikof Strait saturated hydrocarbons

Station	Date	Total Saturated Hydrocarbons(µg/g)	Pristane n-C_{17}	Phytane n-C_{18}	Pristane Phytane	Σ_{13}^{31} odd Σ_{14}^{32} even	Σ_{13}^{20} Σ_{21}^{32}	CP1 14-20	CP2 20-32
				Suspended Matter					
CB-9	5/78	7.0	.88	.33	3.8	3.1	.20	1.39	3.93
CB-10	5/78	6.1	1.03	.32	3.8	2.8	.13	1.27	3.42
CB-10	9/78	6.6	1.02	.34	3.5	3.2	.20	1.91	3.75
				Surficial Sediment					
SS-18	5/79	7.0	1.94	.40	5.8	1.5	.71	1.35	1.66
SS-13	5/79	3.0	2.38	.33	9.5	1.8	.48	1.48	2.00
SS-12	5/79	5.7	1.08	.30	4.7	3.3	.24	1.32	4.50
SS-11	5/79	8.4	2.00	.36	7.0	3.4	.14	1.32	4.21
43	4/77	3.8	2.24	.33	6.7	2.2	.32	1.30	2.58
LC-31	5/79	0.9	1.50	.33	6.0	1.9	.46	1.42	2.31
LC-19	5/79	3.8	.67	.33	2.0	4.6	.05	1.73	5.28
LC-17	5/79	6.6	1.16	.33	5.5	3.9	.10	1.61	4.64
27	4/77	-	.86	.14	6.0	2.6	.15	1.28	3.13
28A	4/77	4.0	1.00	.25	5.0	3.7	.12	1.51	4.34
204	9/78	7.1	1.22	-	-	4.4	.13	1.46	5.58
M1	9/78	-	.68	.35	4.8	5.5	.04	3.36	6.27
M2	9/78	5.7	.66	-	-	6.1	.10	2.72	7.24
M3	9/78	-	1.00	-	-	4.2	.11	1.43	5.06
				Sediment Trap					
ST-1	10/78	35	38.3	.67	44.6	2.7	.32	1.82	3.36
ST-2	10/78	34	4.7	.59	11.1	2.1	.32	2.17	2.31

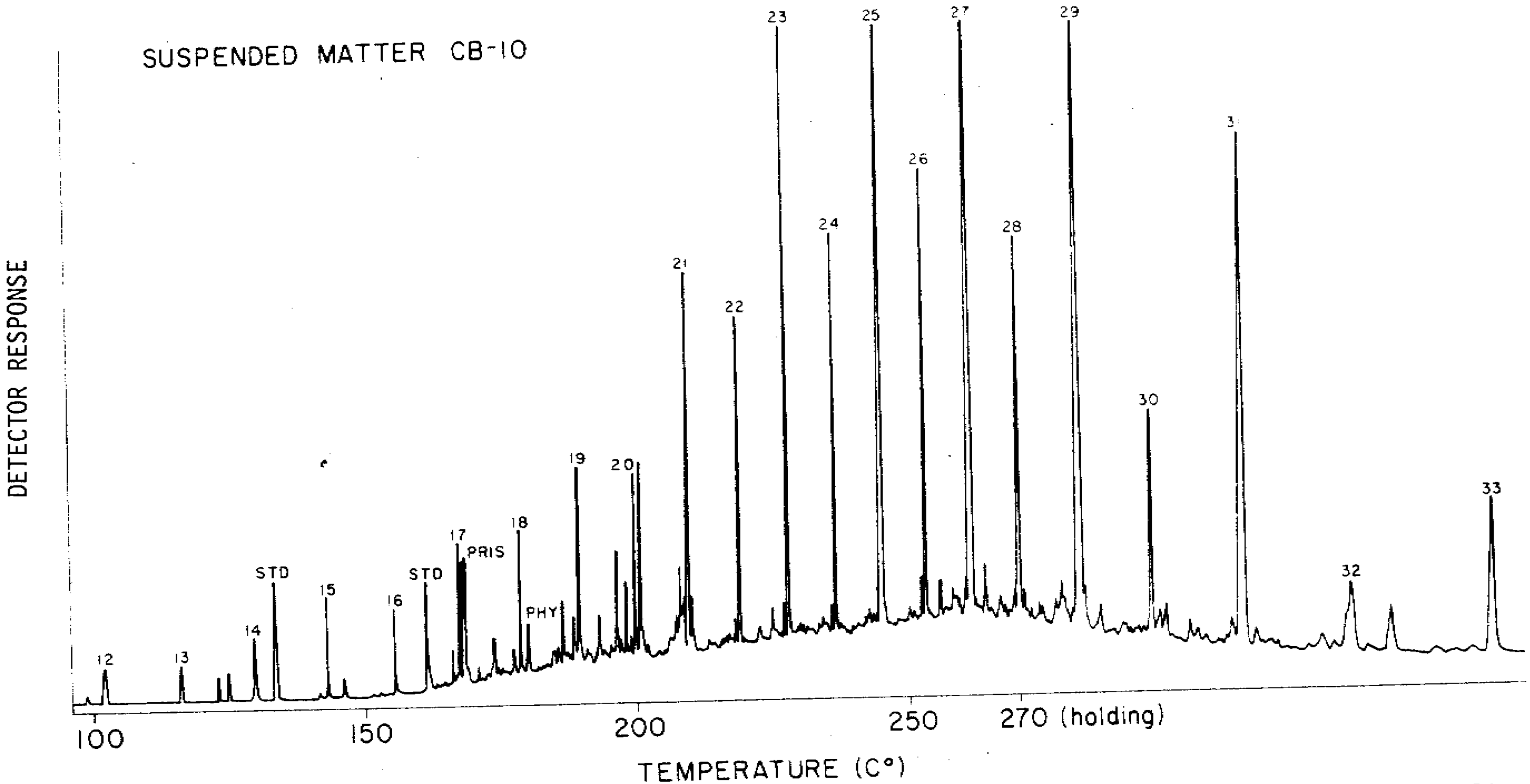

Figure 6-7. Gas chromatogram of the saturate fraction extracted from suspended matter taken at CB-10 in September, 1978. This station was located near the east side of Kalgin Island.

Suspended matter was also collected in sediment traps deployed by Dr. Feely (RU#152) in the summer of 1978. Both sediment traps, deployed for 86 days, were located 10 m from the bottom at stations ST-1 and ST-2 in lower Cook Inlet (Figure 4-3). Aliquots from each trap were analyzed for saturated hydrocarbon. A broad unresolved complex and a high phytane/n-C_{18} ratio (Table 6-4) suggest that some contamination or microbial activity may have altered the sample. It is of interest to note, however, that the alkane hydrocarbon pattern and abundances closely resemble the suspended matter collected by centrifugation at the north end of Cook Inlet (CB-9 and CB-10). The exceptions are the increased levels of marine planktonic hydrocarbons, expecially pristane, which is extremely high (1875 ng/g) at ST-1. These data suggest a large contribution from marine plankton and in particular fecal material, not unlike that observed in material recovered from sediment traps in Dabob Bay, Washington (Prahl and Carpenter, 1979).

6.1.5.2 Bottom Sediments. Surficial sediment samples from Cook Inlet were analyzed for saturated hydrocarbons for comparison with our suspended matter samples. A representative chromatogram (station LC-17, Figure 6-8) shows the dominance of terrestially derived odd-carbon-numbered n-alkanes. Sediment samples from stations 204 and 28A (Figure 4-3) show a similar pattern with comparable abundances. The sandy sediment from Station 27, more centrally located in Cook Inlet, contained significantly lower concentrations of hydrocarbons, as would be expected. Surficial sediment from station LC-19 on the east side of the Inlet also contained low hydrocarbon concentrations. The Chomatographic pattern of the sediment extract from station 31 in the southeast corner of the Inlet resembled that of SS-13 (Figure 6-9) although the concentrations were much lower. The hydrocarbon patterns and abundances in Cook Inlet

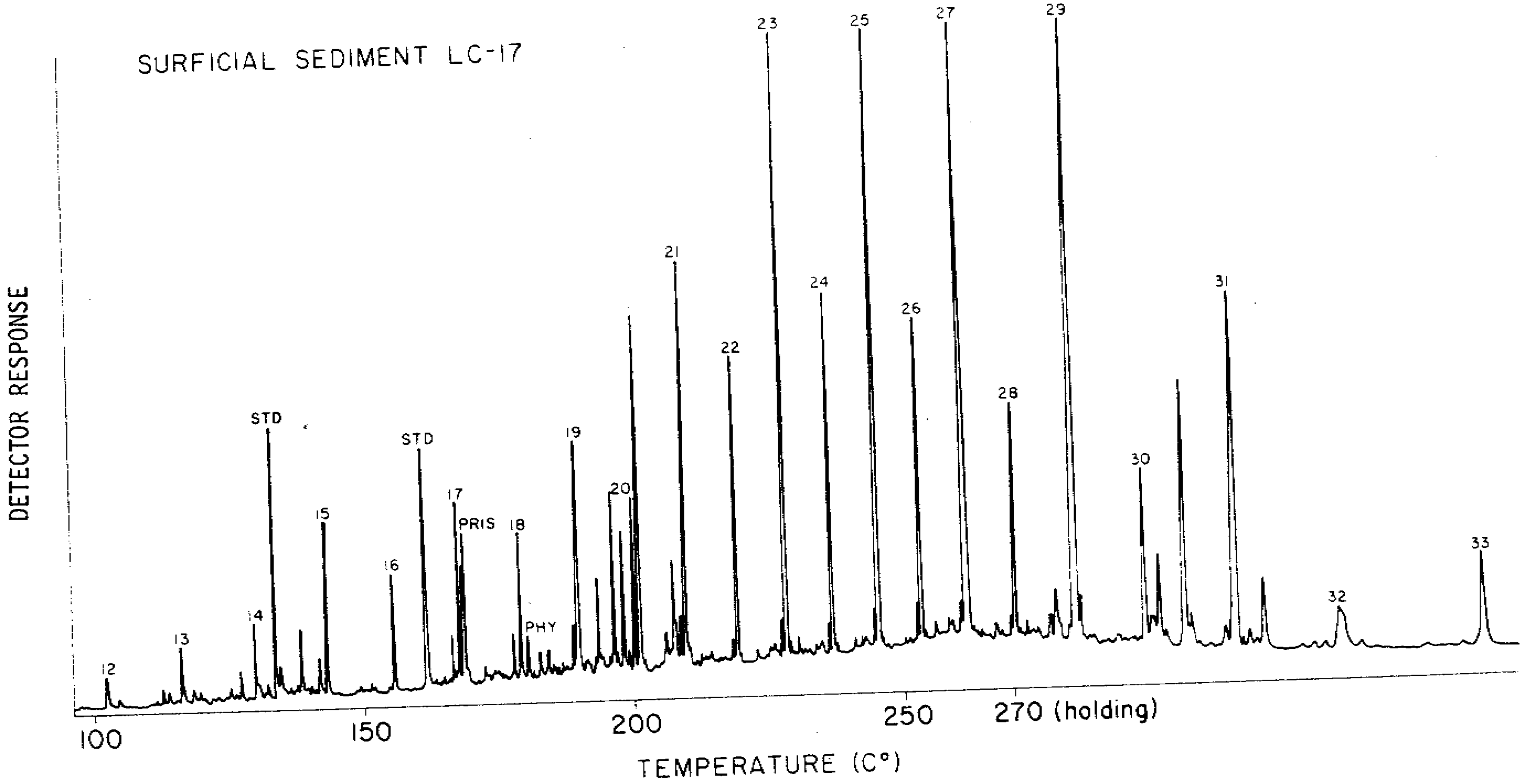

Figure 6-8. Gas chromatogram of the fraction extracted from bottom sediments at station LC-17 in lower Cook Inlet. Sample was taken with a Van Veen-Box Core.

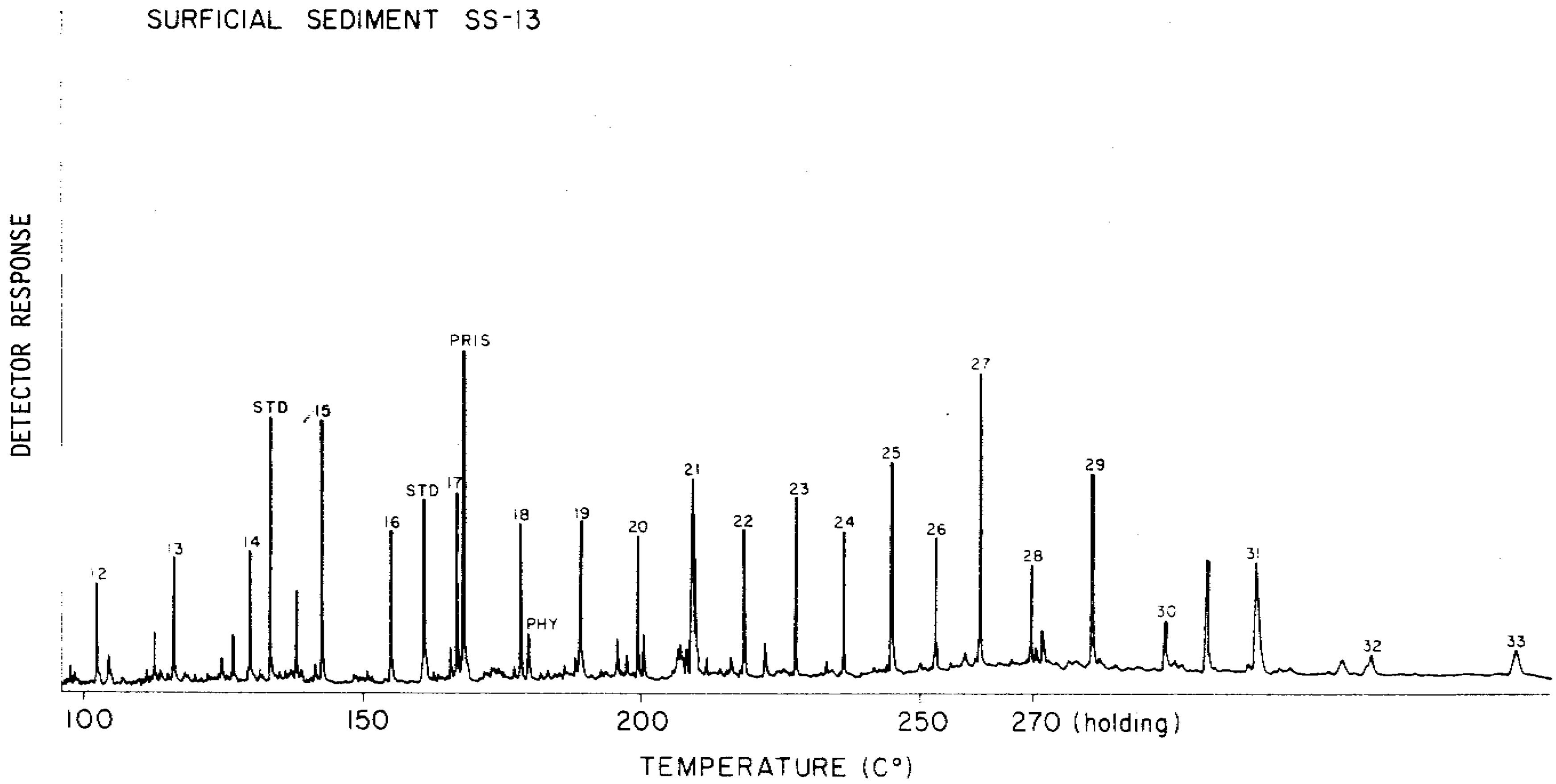

Figure 6-9. Gas chromatogram of the saturate fraction extracted from bottom sediments at station SS-13 in Shelikof Strait. Sample was taken with a Van Veen-Box Core.

suspended matter, therefore, closely compare compositionally with the sediments on the west side of the Inlet, but not with a sample taken near Kennedy Entrance. This is probably due to the marine influence along the eastern boundary. We would expect that both the suspended matter and surficial bottom sediments near Kachemak Bay would be strongly influenced by marine-derived hydrocarbons.

Sediment from two marshes and one mudflat were also analyzed for saturated hydrocarbons. The Marsh (M2) and mudflat (M3) samples from Potters Marsh on Turnagain Arm and Poot Bay (M1) (Figure 4-3) were quite similar in their hydrocarbon composition, showing a high abundance of terrestially-derived odd carbon n-alkanes. The exception was the higher concentration of n-C_{15} in the marsh sample. Normal pentadecane is often the dominant hydrocarbon of marine benthic algae (Clark and Blumer, 1967). It also was present in higher concentrations (63 ng/g) in the China Poot Bay marsh sample (M1). The odd-carbon number high molecular weight saturated hydrocarbons were again in the predominant alkanes of this sample.

6.1.6 Transport of Saturated Heavy Hydrocarbons

Suspended matter samples, collected both by centrifugation and by sediment traps, were extracted and analyzed for saturated hydrocarbons. The chromatographic patterns and hydrocarbon abundances closely resemble the sediment samples analyzed from the western side of Cook Inlet and Shelikof Strait. Characteristic features of these hydrocarbon extracts are the dominance of the terrestrially-derived odd-carbon plant waxes (n-C_{25}, n-C_{27}, n-C_{29}, n-C_{31}) and the absence of an unresolved complex mixture, usually observed in sediment contaminated with petroleum or refined products. As expected, sediment samples from near Kennedy Entrance (LC-31, SS-13, SS-18) show a diminished terrestrial input relative to the typical marine hydrocarbons. In the context of the general circulation pattern, these distributions support the conclusion that suspended matter is an important mechanism by which hydrocarbons may be transported from Cook Inlet. However, some fraction of these sediments and their associated hydrocarbons are being deposited in selected low-energy environments along the western side of Cook Inlet (e.g. Kamishak Bay) and in Shelikof Strait (Feely et al., 1980).

6.2 Shelikof Strait

Shelikof Strait, as a potential lease area, was not formally included in previous surveys of the Alaskan OCS. However, by virtue of our presence in Shelikof Strait during other program objectives, water samples were analyzed for LMW aliphatics and aromatics and bottom sediments for heavy hydrocarbons. All water column measurements were made in Anril and again in June-July of 1977. Sample splits of box cores (Kaplan, Ru #480) for HC analyses were taken at selected stations in Shelikof Strait in April 1977 and again in May 1979.

6.2.1 LMW Aliphatics

In April 1977, six stations were occupied at the north end of Shelikof Strait between Cape Douglas and Afognak Island. With the exception of a single surface sample near Cape Douglas, concentrations of methane at the surface and near the bottom ranged from 106 to 214 nl/l. The mean surface concentration was 109 nl/l; at depth the average was 155 nl/l. Concentrations of ethene ranged from 0.5 nl/l near Cape Douglas to 0.9 nl/l near Afognak Island. Both ethane and propane were largely invariant with depth, averaging 0.33 ± 0.11 nl/l and 0.15 ± 0.03 nl/l respectively. As usual, the butanes were below the detection level.

In June-July 1977, a total of 17 stations in Shelikof Strait were sampled. Locations of the stations are shown in Figure 4-4.

The surface distribution of methane is shown in Figure 6-10. Concentrations of methane are generally lower near the southern end of Kodiak Island

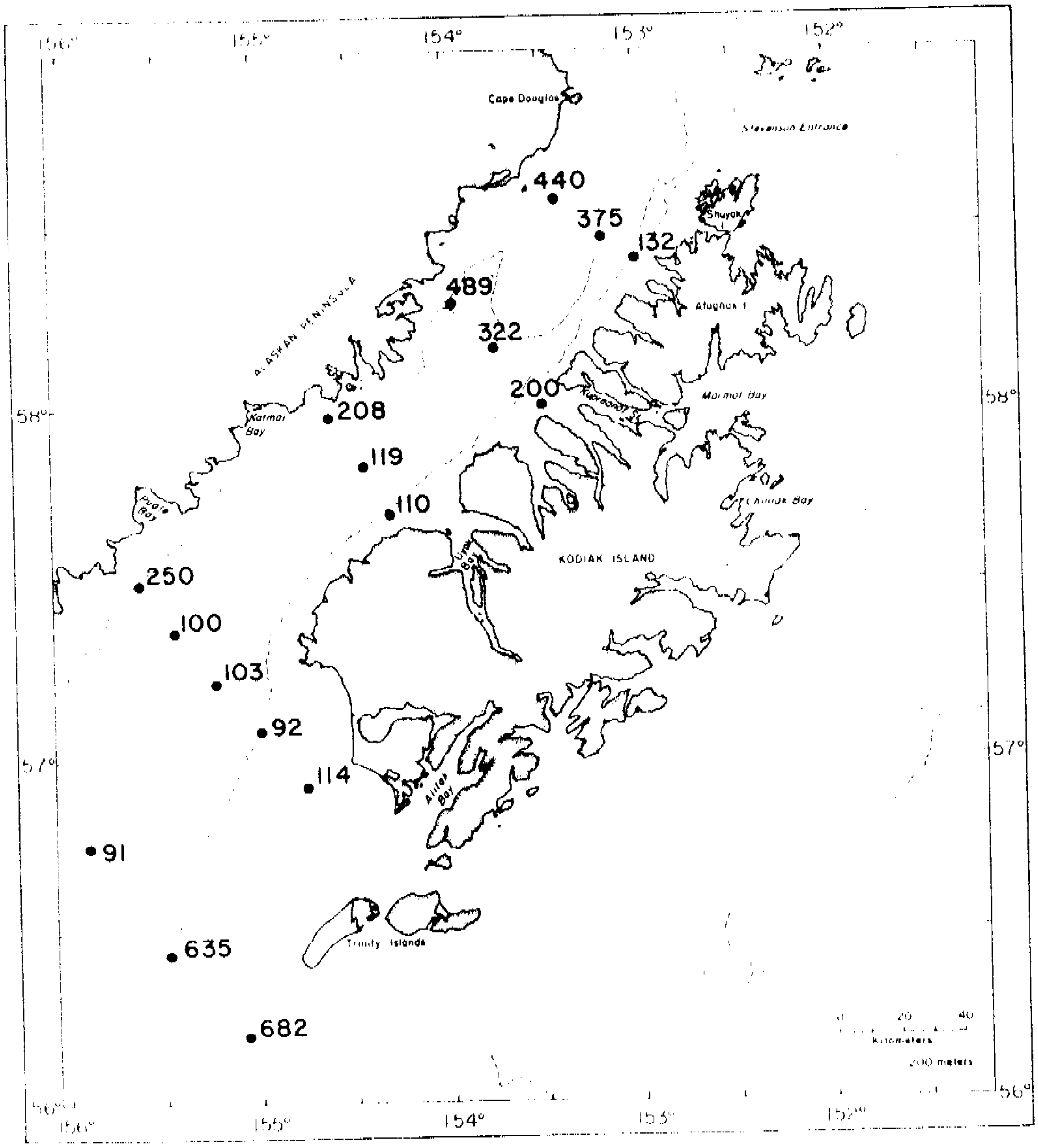

Figure 6-10. Surface distribution of dissolved methane in Shelikof Strait in June-July, 1977. Concentrations are given in nl/l (STP).

(approx. 100 nl/l), increasing to over 600 nl/l near the Trinity Islands. High surface concentrations (>400 nl/l) were found along the northern shelf of the Alaska Peninsula. Surface concentrations of methane throughout most of Shelikof Strait range from 100 to 500 nl/l, representing the spatial variability normally associated with biological activity over shelf waters.

Methane concentrations within 5 m of the bottom were, of course, elevated, either as the result of benthic activity or near bottom microbial activity (Figure 6-11). Ignoring a single sample near Cape Douglas and one near Afognak Island, the average near-bottom methane concentration was 524 nl/l (± 128 1σ). These values are rather high relative to other Alaskan OCS areas surveyed and may be the result of increased organic loading.

Surface ethene concentrations are shown in Figure 6-12. Values range from 2.3 nl/l near Cape Douglas to a high of 4.3 nl/l near the Trinity Islands. This parameter is biological and/or photochemical in origin and probably reflects the spatial and temporal variability of plankton communities. The mean value was 3.4 nl/l (± 0.6 nl/l 1σ).

Ethane and propane, unlike their unsaturated homologs, were invariant with depth. The average ethane and propane concentrations were 0.58 ± 0.20 nl/l and 0.40 ± 0.12 nl/l, respectively, over the entire area. These are typical concentrations found in the Alaskan OCS during this time of year.

A summary of the average surface concentrations of the C_1-C_4 hydrocarbons is shown in Table 6-5.

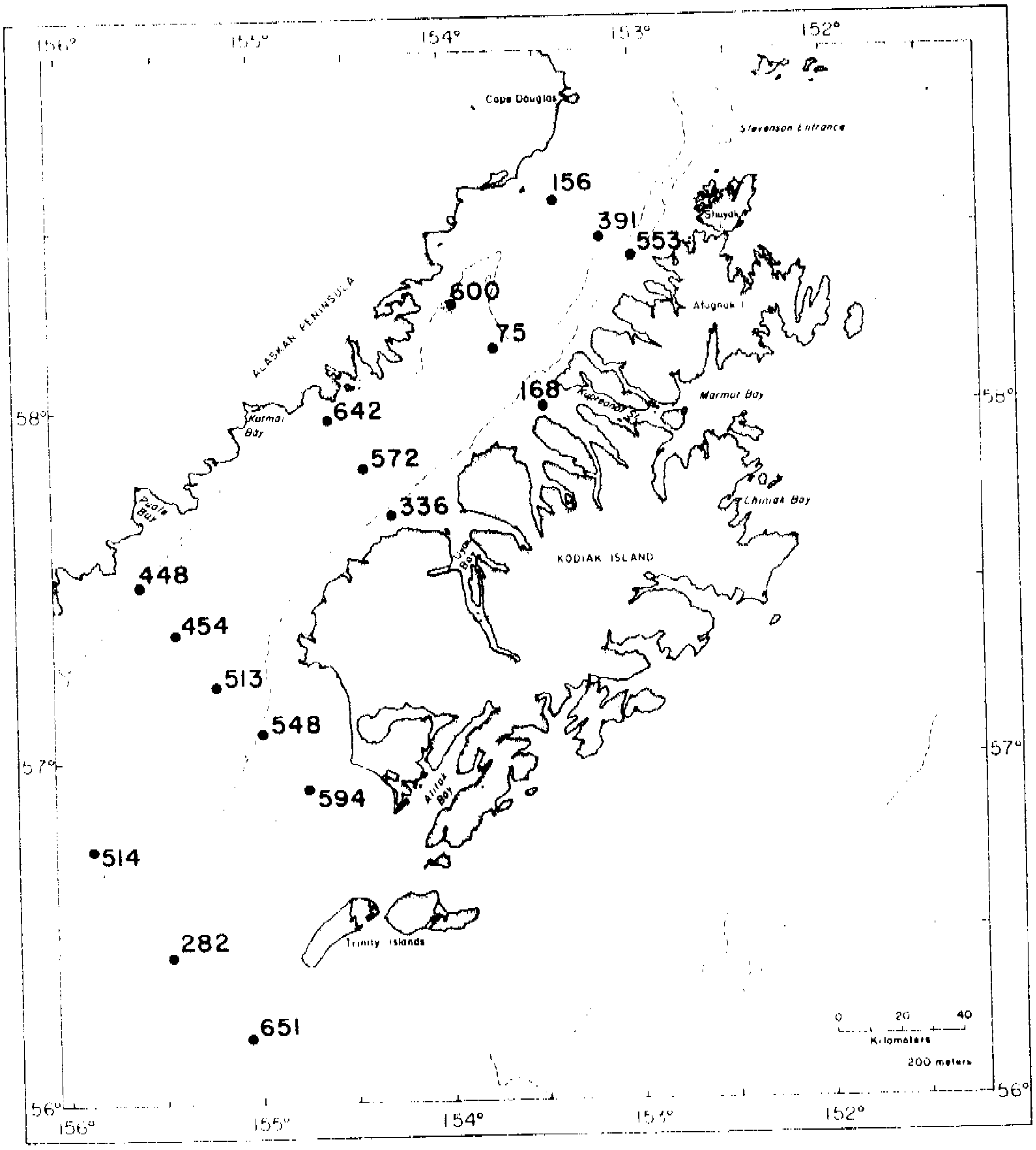

Figure 6-11. Distribution of dissolved methane within 5m of the bottom in June-July, 1977. Concentrations are given in nl/l (STP).

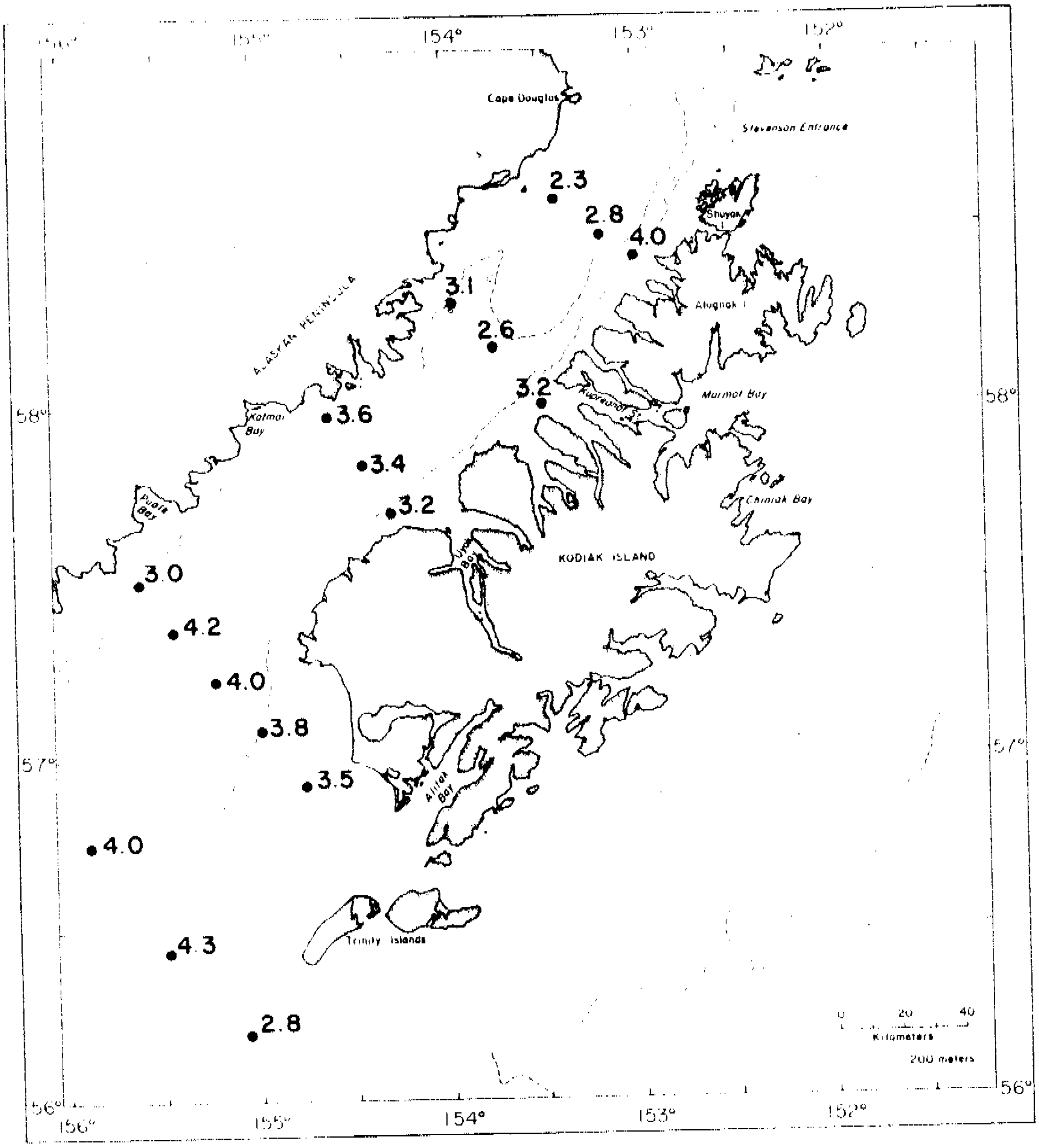

Figure 6-12. Surface distribution of dissolved ethene in Shelikof Strait in June-July, 1977. Concentrations are given in nl/l (STP).

Table 6-5. Summary of the average surface concentrations of LMW hydrocarbons in the months of April and July, 1977.

Component	April nl/l	July
methane	135	290
ethane	0.3	0.6
ethene	0.6	2.0
propane	0.2	0.4
propene	0.3	0.7
ethane/ethene	0.6	0.3

In general, the concentrations of all hydrocarbons doubled between the two sampling intervals, reflecting a biological input. The decrease in the ethane/ethene ratio is due to the increased production of ethene in the surface waters and the increased stability of the water column that isolates the relatively ethane-rich bottom water from exchanging with the surface.

Finally, we discuss the classical tracers of thermogenic gas. The ethane/ethene ratio was invariant at 0.3 to 0.5, clearly indicative of hydrocarbons of biogenic origin. Likewise, the C_1/C_2+C_3 ratio, at all stations and depths, was in excess of 100. No anomalous concentrations of the C_{2+} hydrocarbons were found.

6.2.2 LMW Aromatics

As a part of the general program to investigate the occurrence and abundance of LMW aromatics in Cook Inlet (Trading Bay), samples were taken in the North Pacific Ocean along a transect between Seattle and Adak, Alaska, and in Shelikof Strait, prior to our survey in Cook Inlet. The analytical system consisted of a Hewlett-Packard Model 5992 gas chromatograph-mass spectrometer, which was used in both a qualitative and quantitative mode. The gas chromatograph was fitted with a glass capillary column, allowing high resolution of both petroleum related and natural organic compounds. The utility of the technique is depicted in the selected ion chromatogram shown in Figure 6-13 of a seawater sample taken in Shelikof Strait.

The mass spectrometer enabled us to identify several laboratory contaminants (B, C, D, F) as well as two natural products (A, G). The mass spectrometer can also be used quantitatively to integrate the areas under the peaks and then compare these areas to the response of standards. The precision of the analytical method based on three analyses of a standard added to the stripping apparatus is ±10% (one standard deviation expressed as a percentage of the mean). The precision of the entire experimental procedure based on three samples collected at station UC-3 in upper Cook Inlet is ±35%. The limit of detection (signal/noise = 2) is 3 ng/L.

The concentrations of LMW aromatics in Shelikof Strait are summarized in Table 6-6, together with similar analyses from surface waters of the North Pacific. A discussion of the distributions in Cook Inlet was discussed in the previous section. Given the uncertainties in the data, Shelikof Strait surface waters are similar to those of lower Cook Inlet (LCI). As pointed out earlier, upper Cook Inlet appears anomalous with respect to all aromatics surveyed. Also, benzene concentrations in the North Pacific appear low (Table 6-6), but this average is based on only two analyses and may not be representative. Although there are few data with which to compare our results, particularly from pristine areas such as Alaska, our concentrations of aromatics are close to those obtained by Sauer et al. (1978) from the Gulf Coast. If anything, we would expect our observations to be lower than theirs.

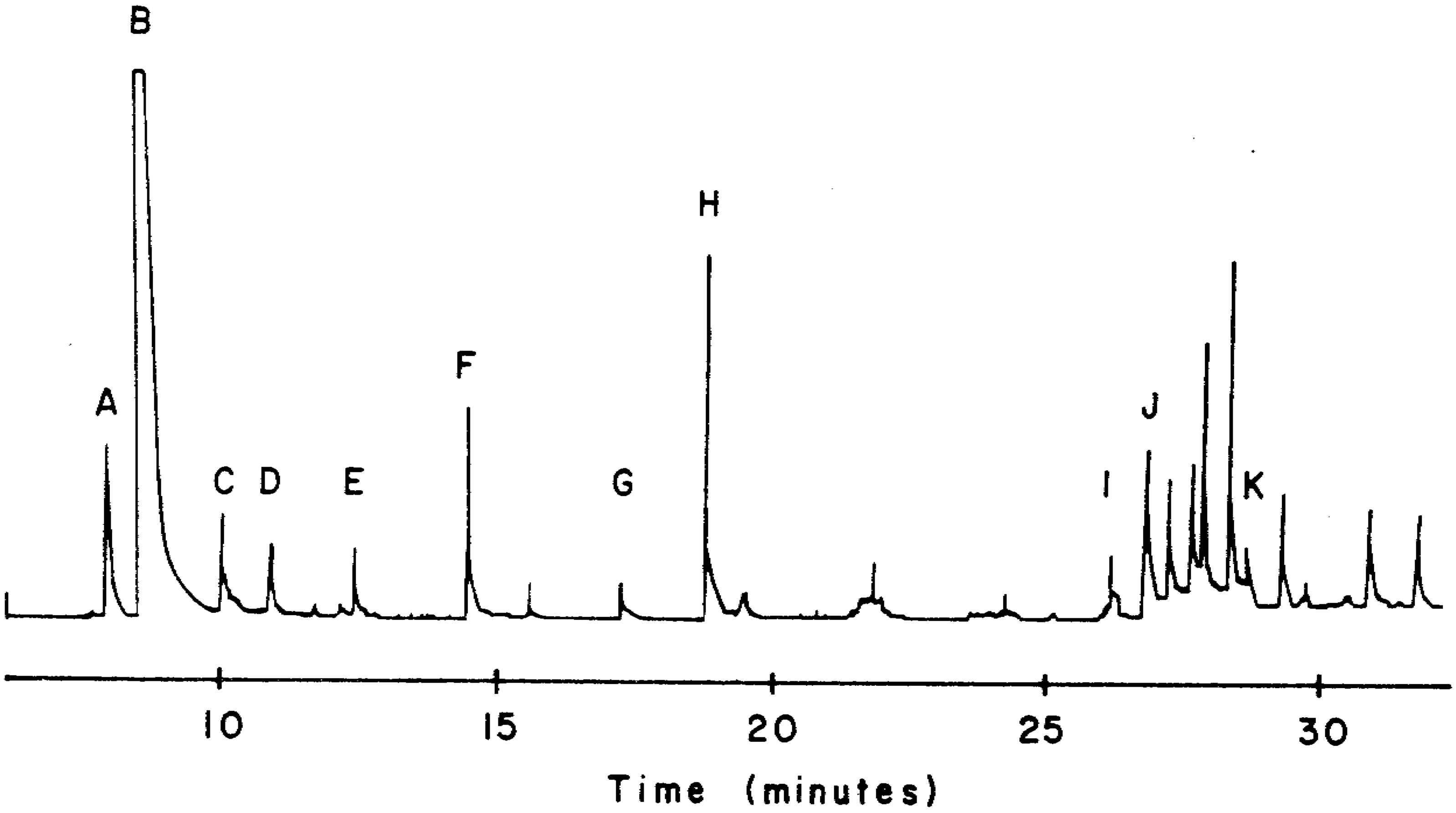

Figure 6-13. Ion chromatogram of a surface sample taken in Shelikof Strait and analyzed for LMW aromatic compounds. A: dimethylsulfide, B: dichloromethane, C: hexane, D: trichloromethane, E: benzene, F: trichloroethylene, G: dimethydisulfide, H: toluene, I: ethyl-benzene, J: m- and p-xylene, K: xylene.

Table 6-6. Summary of the average concentrations of LMW aromatics in surface waters from the North Pacific, Shelikof Strait, lower Cook Inlet and upper Cook Inlet. The C_2-benzenes include ethylbenzene, and xylenes.

Location	No. Samples	Benzene	Toluene	C_2-Benzenes
			ng/liter	
N. Pacific	2	3	21	48
Shelikof Strait	17	16 ± 4	38 ± 14	11 ± 4
LCI	2	18	26	12
UCI	17	30 ± 17	78 ± 67	32 ± 19

6.2.3 Sedimentary Hydrocarbons

Surficial bottom sediments were subsampled from box cores taken in Shelikof Strait to assess depositional sites of suspended matter derived from Cook Inlet. The sampling sites (stations SS-11, 12, 13, 18) are all located toward the north end of Shelikof Strait (see Figure 4-3). Concentrations of the saturated hydrocarbons taken from the aforementioned stations are reflected in Table 6-3. Characteristically, the sediments are "clean", showing a mix of terrestrially-derived and marine biogenic hydrocarbons and no unresolved complex mixture usually associated with petroleum contamination (Farrington and Tripp, 1977). A chromatogram of the saturate fraction is shown in Figure 6-9. Other compositional characteristics reveal that the Shelikof Strait sediments are diminished in the terrestrial plant waxes compared to suspended matter samples taken in Cook Inlet. This observation is presumably due to dilution with marine organic matter and detrital sediments. The concentrations of the typical planktonic hydrocarbons, n-C_{15} and n-C_{17}, are lower than those found in the suspended matter samples from LCI, but they are higher than those found in some bottom samples taken in lower Cook Inlet. In agreement with the sources, samples SS-11 and SS-12 showed relatively higher concentrations of the terrestrially-derived plant waxes, which were highly enriched in the suspended matter samples taken from near Kalgin Island (see Table 6-3).

Station 43, located south of the previous stations (Figure 4-3), shows the characteristic pattern of odd carbon terrestrial plant waxes and a slightly enriched level of the plankton hydrocarbons. The implication is that terrestrially-derived hydrocarbons from Cook Inlet are being admixed with locally-derived marine hydrocarbons. However, contributions from diffuse sources on Kodiak Island and the Alaska Peninsula cannot be ruled out without developing a complete mass budget. Circulation (Muench et al., 1978) and suspended matter transport (Feely et al., 1980) suggest that particulate hydrocarbons are being transported south from Cook Inlet into the less turbulent waters of lower Shelikof Strait.

6.3 Norton Sound

6.3.1 Hydrography

The surface distribution of salinity and temperature is shown in Figures 6-14 and 6-15. Offshore coastal water is identified approximately by surface salinity greater than $30^{0}/oo$ and surface temperatures less than $7.5^{0}C$. At the eastern extremity, salinities as low as $19^{0}/oo$ were observed along with warm temperatures ($T > 11^{0}C$). Most of the fresh water appears confined to the coastal regime, where numerous diverse sources of freshwater exist. Shape of the isohaline contours would suggest a weak cyclonic circulation nearshore.

The vertical distribution of density is reflected in two zonal sections (Figures 6-16 and 6-17). Distribution of mass along section I (Figure 6-16) shows a moderate degree of stratification within the inner sound, with a

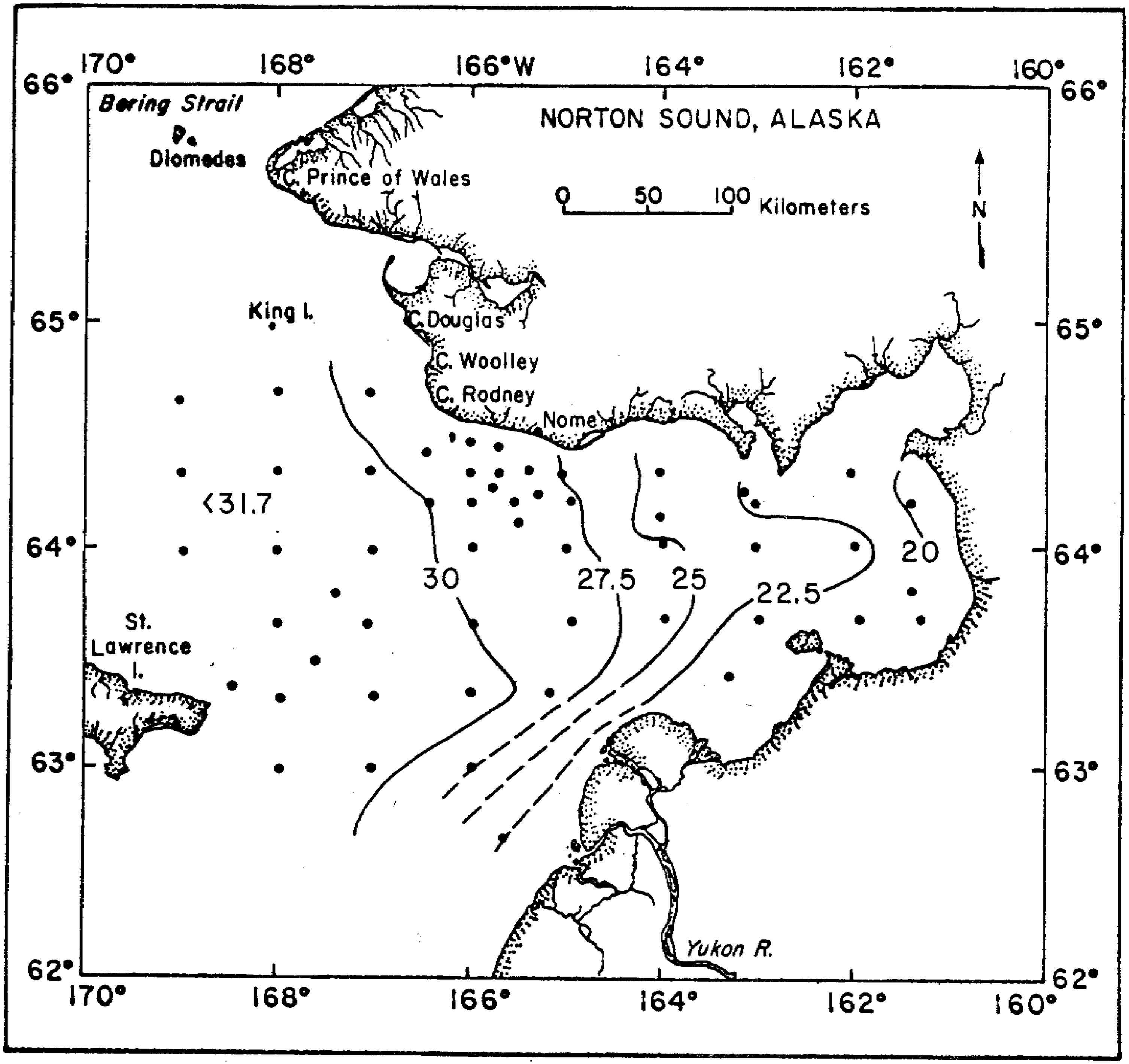

Figure 6-14. Surface distribution of salinity ($^{0}/oo$) in Norton Sound in July, 1979.

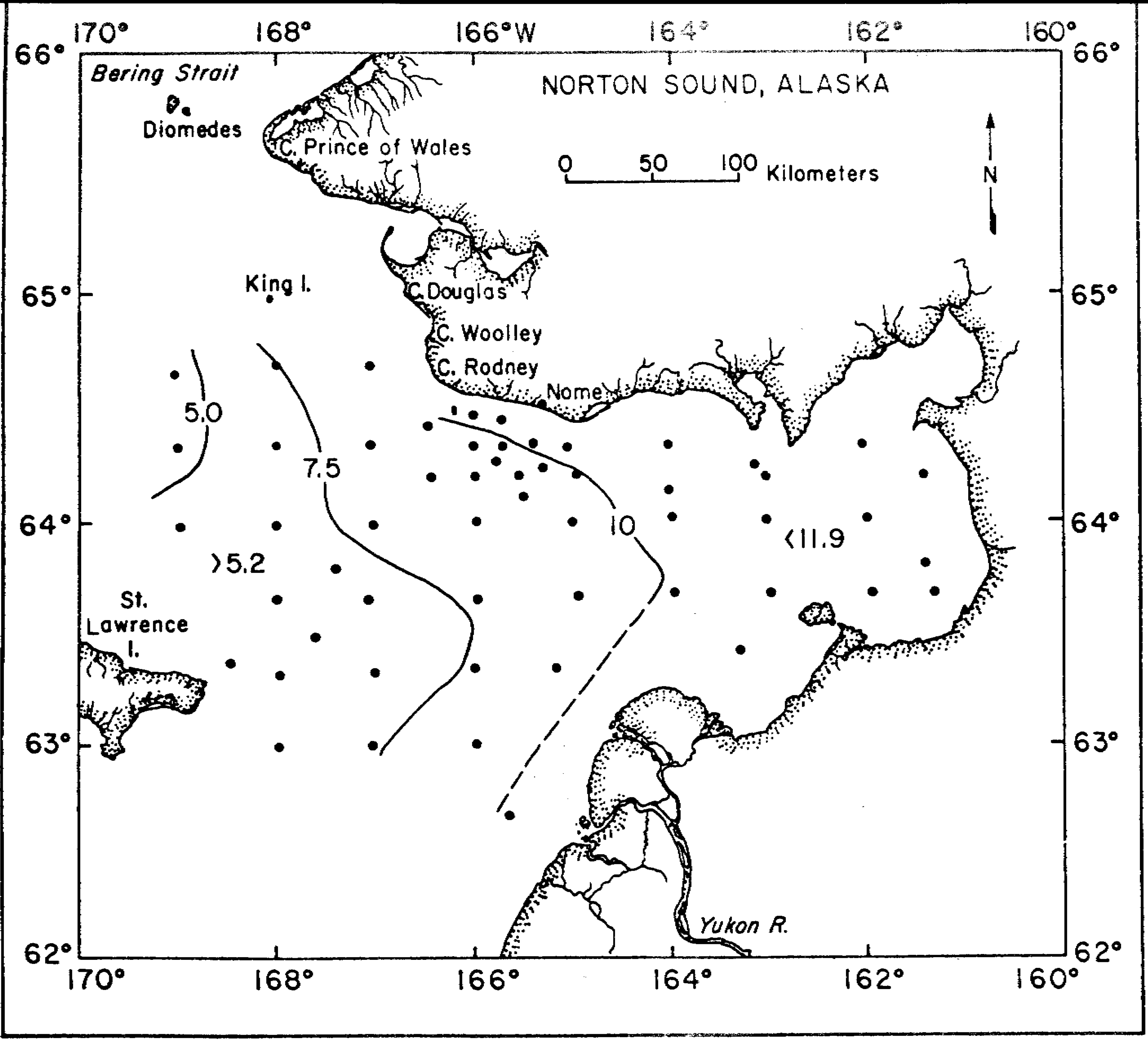

Figure 6-15. Surface distribution of temperature (^{O}C) in Norton Sound in July, 1979.

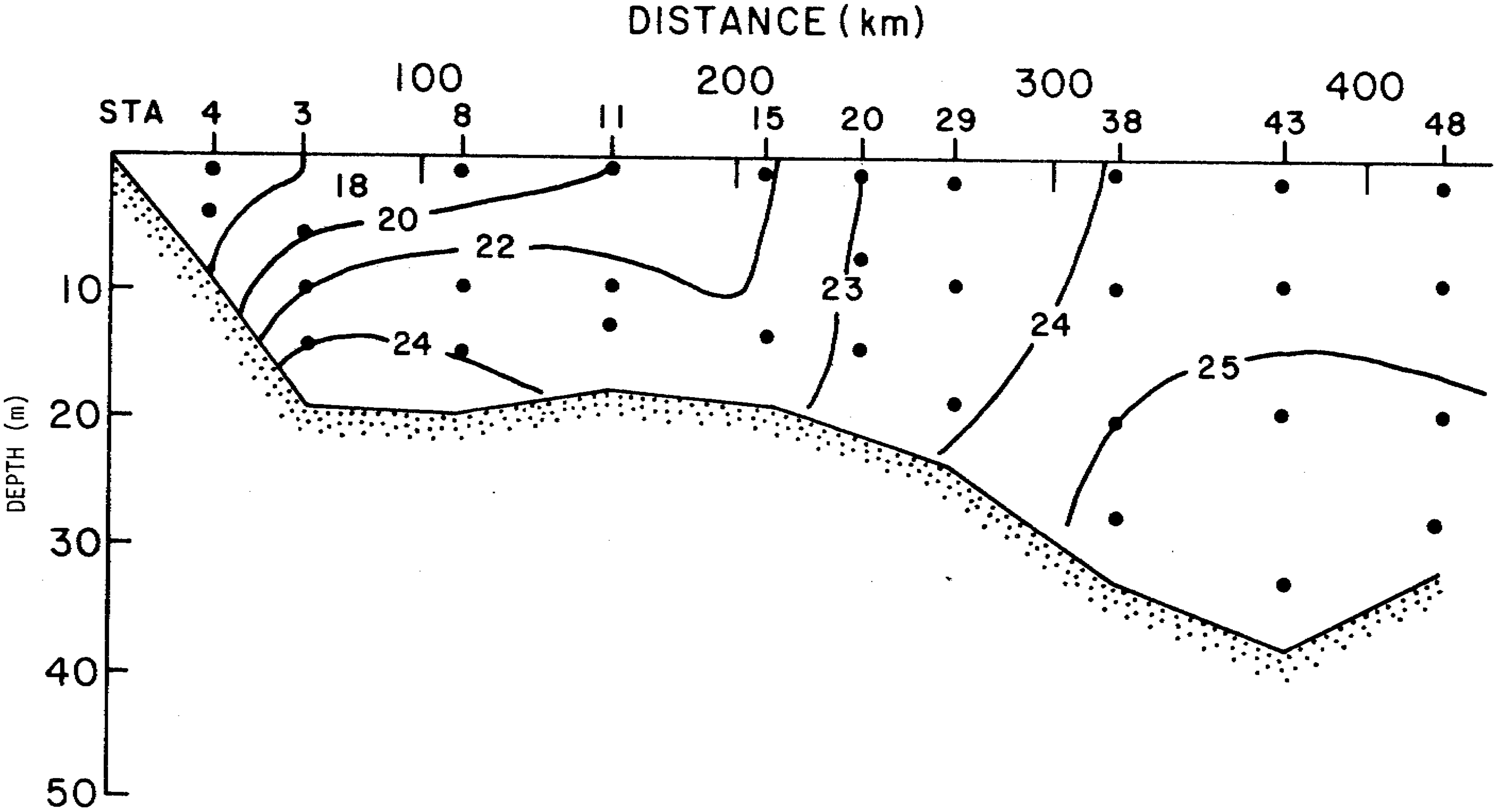

Figure 6-16. Zonal distribution of density (σ_t) along section I (see Figure 4-5) in Norton Sound.

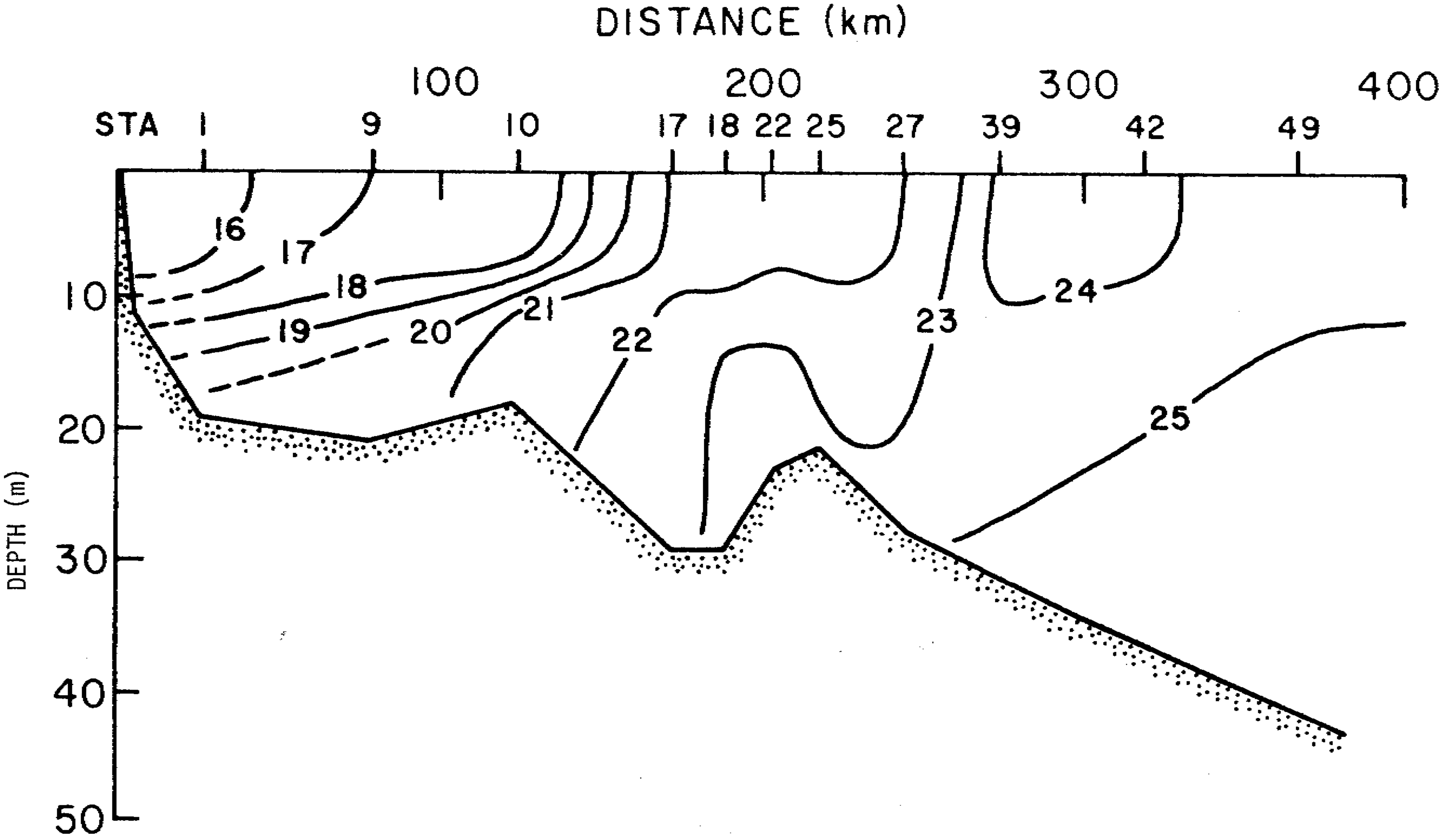

Figure 6-17. Zonal distribution of density along section II (see Figure 4-5) in Norton Sound.

complete breakdown of stratification between stations 15 to 38. Offshore, stratification is only weakly developed. The breakdown of the salinity-induced pycnocline is due to a frontal-like feature along the 20 m isobath.

Section II passes north of section I and crosses near the locus of the seep. Again, we see a disintegration of the density structure near stations 18 through 25, close to the probable location of the seep. Near the location of the seep, there appears a doming of the isopycnals, which may result from current shear associated with the front or the possible injection of brine waters associated with the seep. Unfortunately, the salinity and temperature gradients across the front were so large as to confuse any salinity or thermal structure that might be the result of the seep.

The apparent frontal structure in the region of the seep was further elucidated by time series measurements taken at station N21B. Here, the near bottom (14-16 m) density (σ_t) changed from 22.95 to 23.13 over a period of 36 hours. The increase in density was largely due to temperature which monotonically decreased during the period. Again stratification, largely induced by bouyancy, was well developed between stations 1 and 17.

In summary, hydrographic conditions during July suggest a strong interaction between the warm water of the inner sound with the cold, high salinity water found offshore. This interaction occurred along or near the 20 m isobath, nearly coincident with the location of the Alaskan Coastal water (Coachman et al., 1975).

6.3.2 LMW Aliphatics

The horizontal distribution of methane at the surface and 10 m is shown in Figures 6-18 and 6-19. As was observed in September 1976, a strong source of methane was again identified in the southeastern corner of Norton Sound. This area is characterized by organic rich fine-grained sediments, which

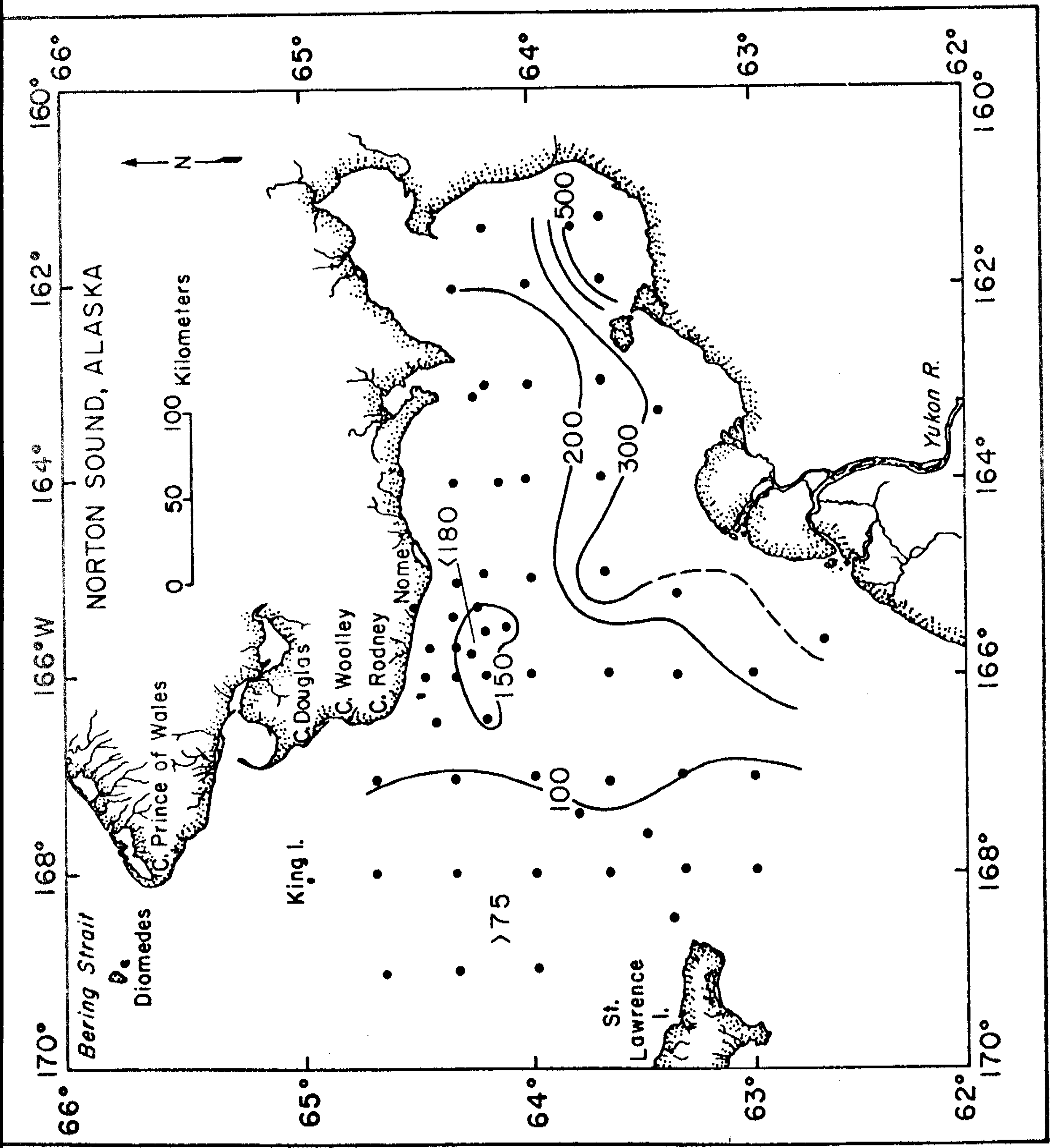

Figure 6-18. Surface distribution of dissolved methane in Norton Sound in July, 1979. Concentrations are given in nl/l (STP).

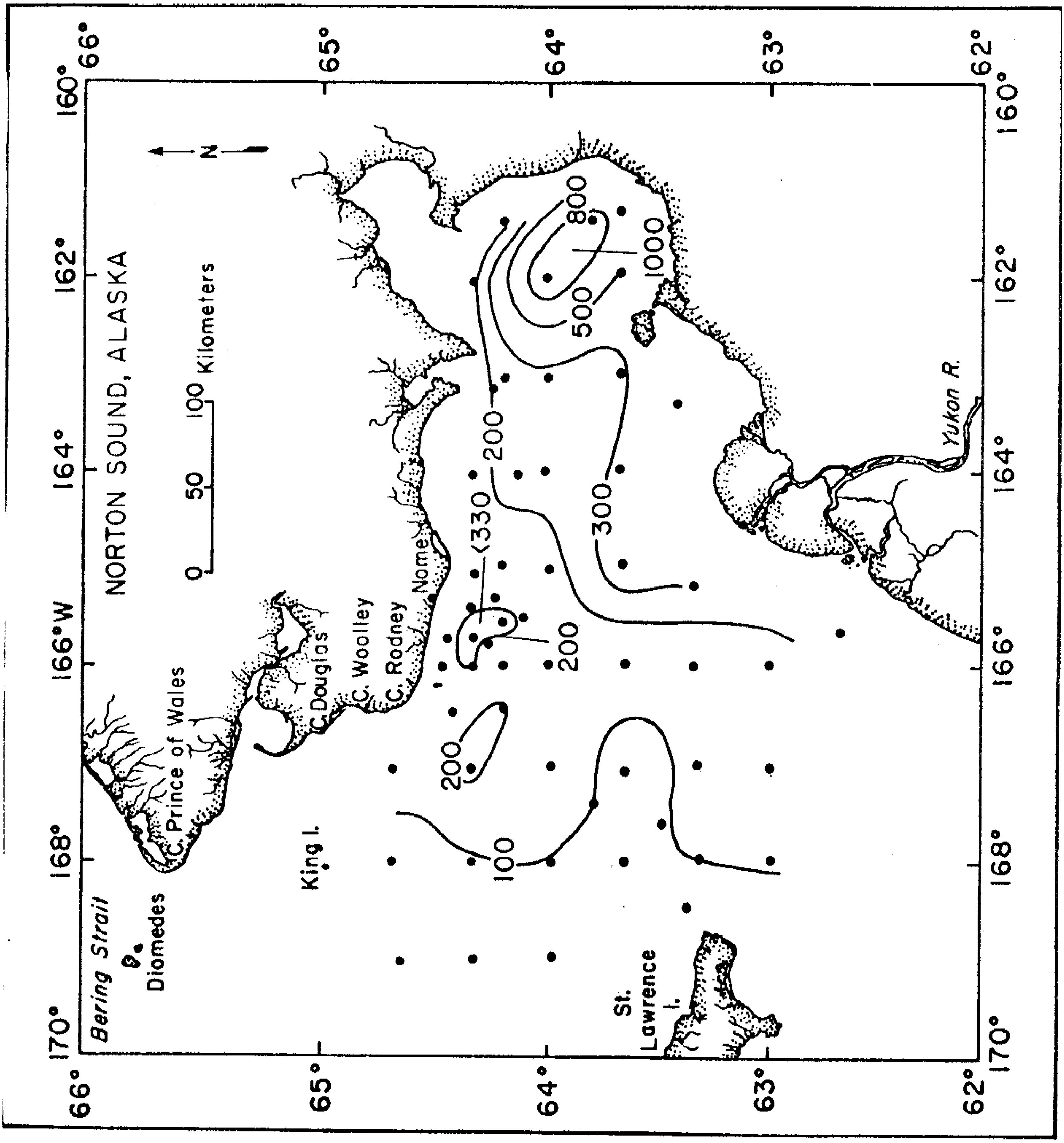

Figure 6-19. Concentration of dissolved methane within 5m of the bottom in Norton Sound in July, 1979. Concentrations are given in nl/l (STP).

apparently support significant methane production. In contrast to conditions in September of 1976, stratification near shore was minimal (see Figure 6-17), allowing methane to outcrop at the surface. The highest concentration of methane was 1020 nl/l at station 3. Since the concentration decreased near the bottom, we assume that the source actually exists inshore. Diffusion of methane to the west is evident in Figure 6-19.

Also apparent in Figures 6-18 and 6-19 is the significant source of methane associated with the Yukon River. The highest concentration of methane (< 2000 nl/l) was found in association with the low salinity water near the Yukon Delta. Although the isolines of concentration suggest the plume extends northwest (Figure 6-18), the salinity distribution reveals that low salinity water is largely confined to the immediate coast (Figure 6-14). Relatively high concentration of methane in the surface waters at station 14 was the result of strong vertical mixing from below (see Figure 6-19) and does not necessarily reflect the actual trajectory of the Yukon River plume.

Distribution of methane near the seep also is shown in Figures 6-18 and 6-19. In contrast to conditions obtained in September 1976, methane, arising from the seep, was observed in the surface layers. The distinction from ambient levels is marginal and is shown by the 150 nl/l contour. Again, a breakdown in vertical stratification allowed methane to outcrop at the surface. Concentrations at 10 m (Figure 6-19) reached 330 nl/l (STP), approximately a factor of two higher than the surrounding waters.

A summary of the sources of methane is shown in Figure 6-20. Section II shows the bottom methane source emanating from the southeastern corner as well as the vertical plume structure near station 22. In all likelihood, excess concentrations of saturated hydrocarbons near the seep are caused by

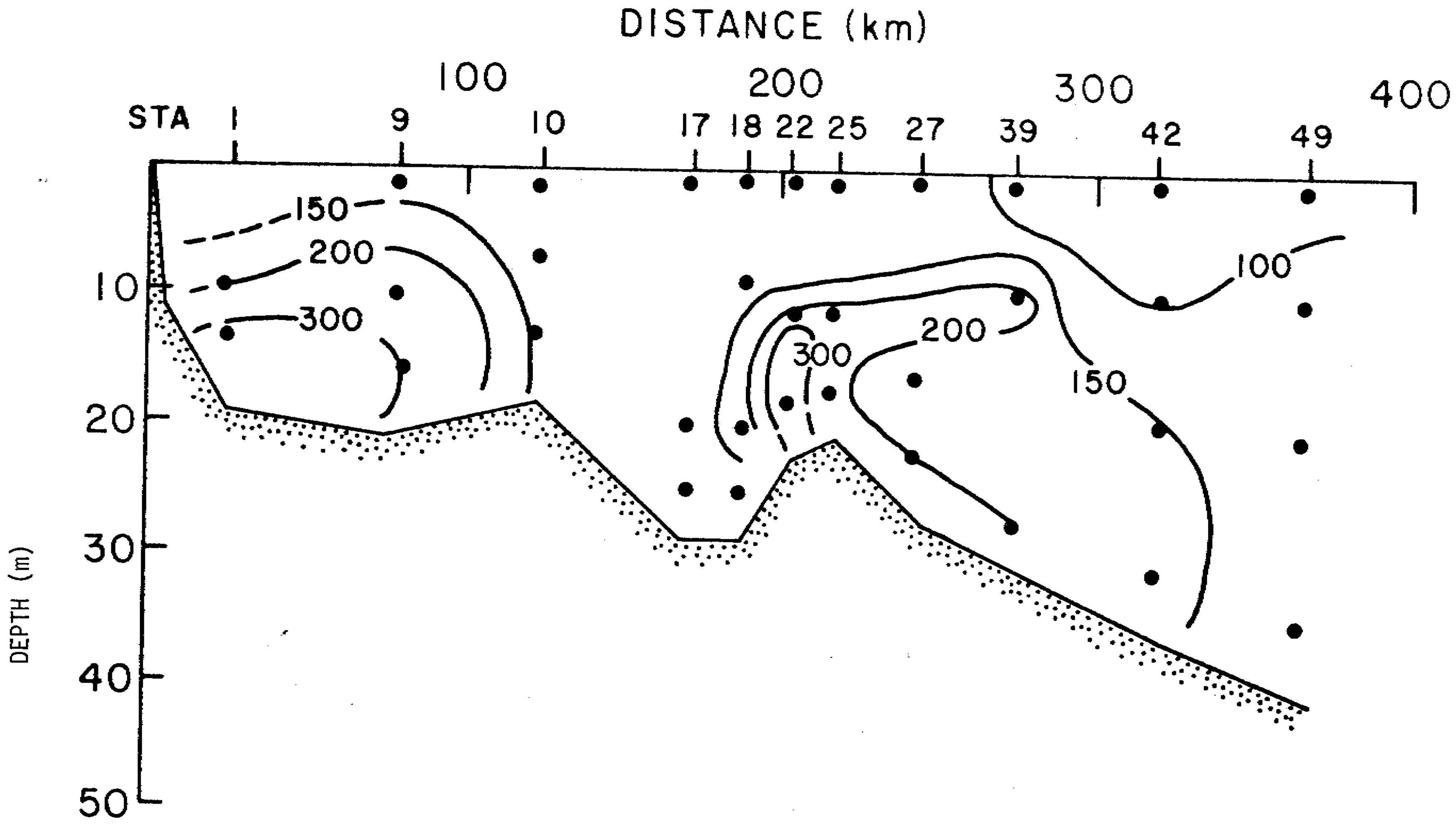

Figure 6-20. Distribution of dissolved methane along section II (see Figure 4-5) in Norton Sound. Concentrations are given in nl/l (STP).

venting gas. Subsequent measurements by Kvenvolden et al. (1979) have shown that the bulk of the gas is probably carbon dioxide, with only trace amounts of aliphatic hydrocarbons. Because the methane plume is located near a small topographic high, in a region characterized by strong vertical mixing, we can not rule out resuspension or erosion of methane-rich muds from the bottom. However, the production rate of methane and other hydrocarbons in surficial sediments would have to be inordinately high to result in the observed plumes.

In September 1976, the seep was clearly identifiable on the basis of the ethane and propane distributions. This year, as evidenced in Figure 6-21, the ethane signature was much reduced. The highest concentration of ethane observed was 4 nl/L (10 m depth) at a site a few kilometers west and north of the previously defined seep locus. Although the ethane signature was reduced, compared to the observations in 1976, the low background levels of ethane (0.1-0.3 nl/l STP) allowed the ethane plume to be defined over an area of 2500 km^2.

Slightly higher concentrations of ethane were observed offshore (0.5 to 0.8 nl/l STP) compared to the inner sound and correlated with higher concentrations of ethene. Presumably, this circumstance was related to biological processes in the colder, more productive offshore waters.

Regions of active biological activity are usually characterized by high levels of dissolved ethene. Surface distribution of ethene is shown in Figure 6-22. The Alaskan Coastal Water is characterized by concentrations of ethene ranging between 2 and 4 nl/l. In the region of the seep, the surface concentrations average 1.5 nl/l. Somewhat higher values were observed in the vicinity of Norton Bay ($\sim$ 2 nl/l).

During the recovery of suspended matter at station N21B (seep) and at a control station (N17A) located northeast of the seep, water samples were analyzed every four hours for LMW hydrocarbons. The ethane/ethene ratio

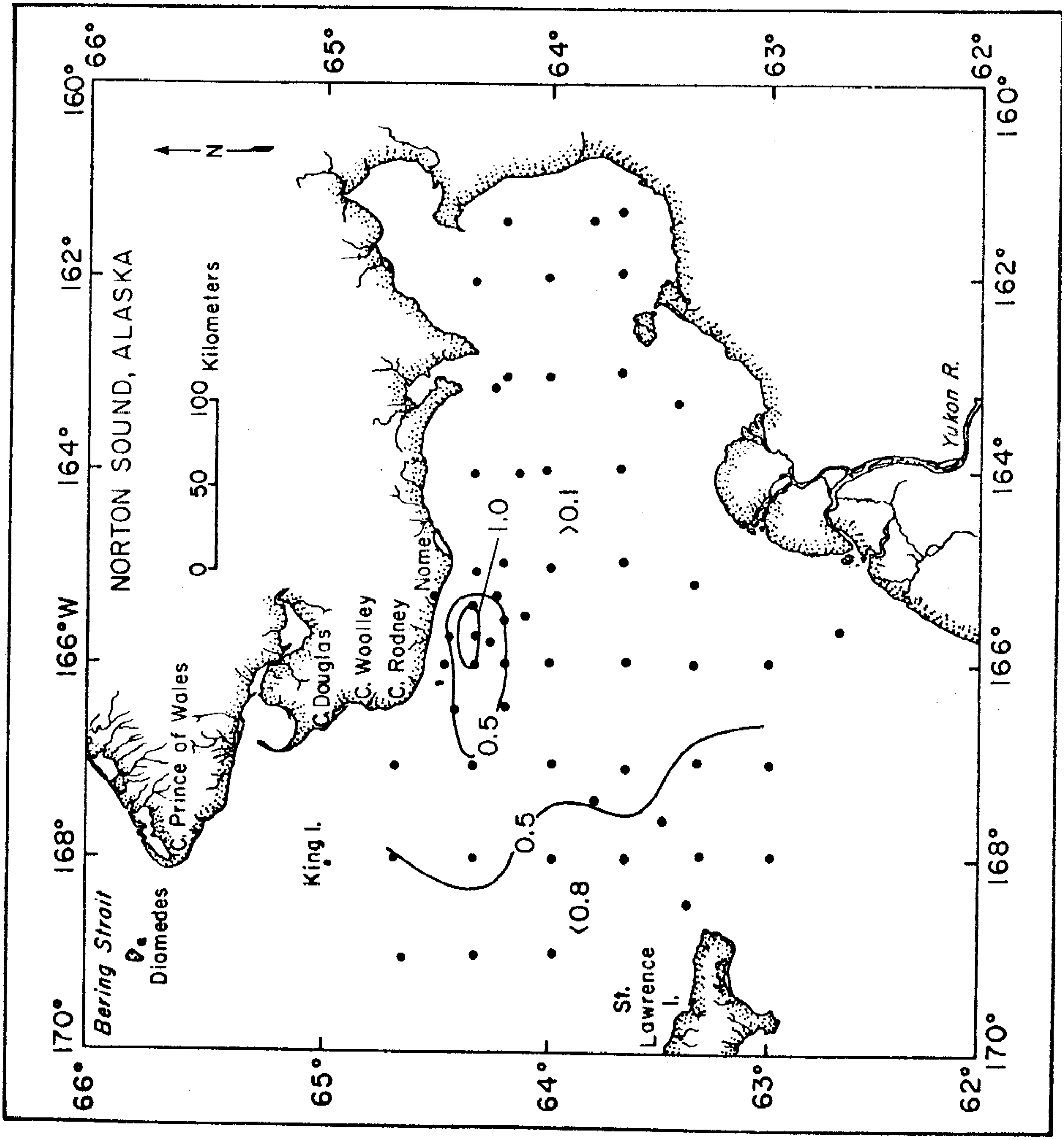

Figure 6-21. Surface distribution of dissolved ethane in Norton Sound in July, 1979. Concentrations are given in nl/l (STP).

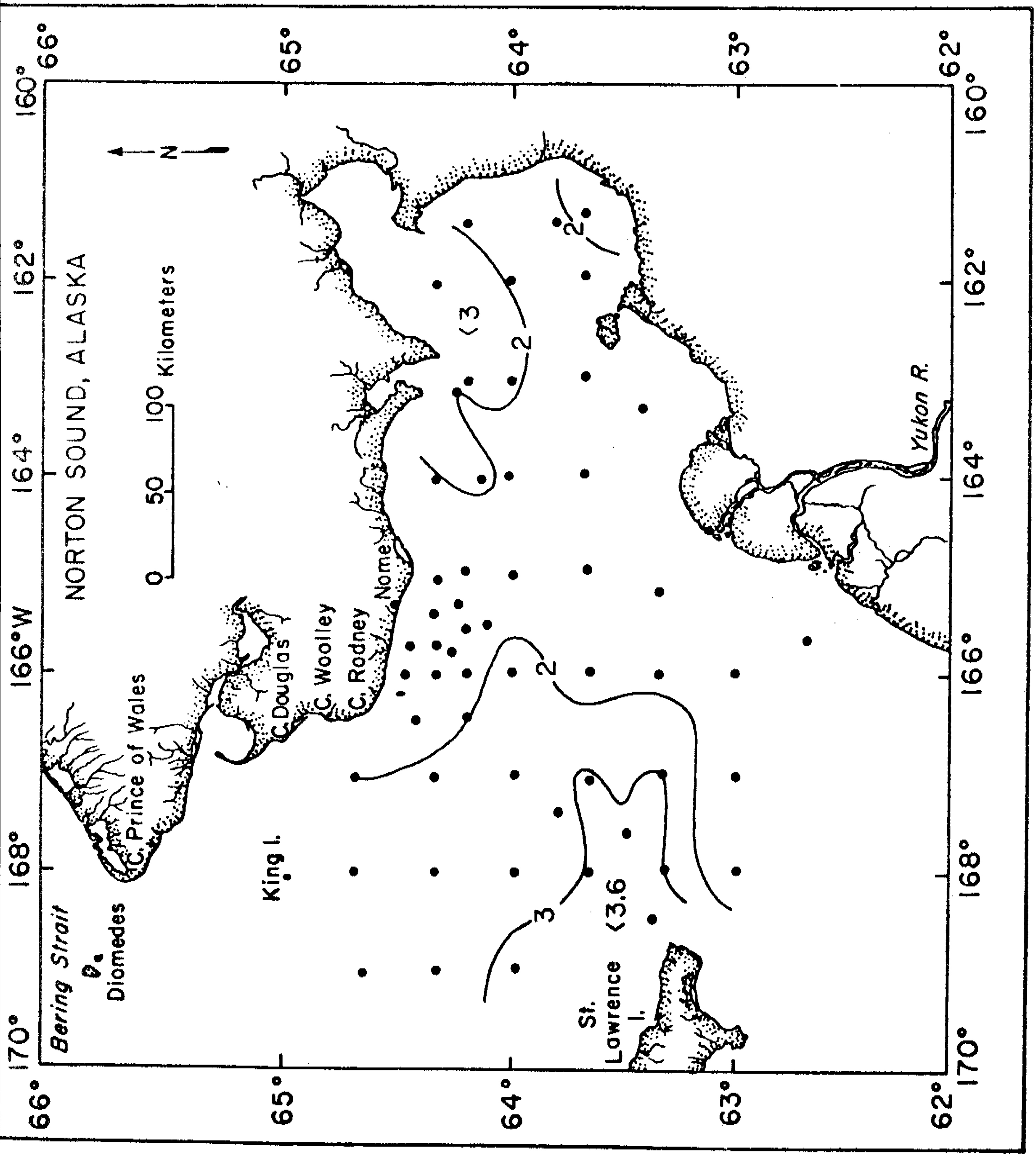

Figure 6-22. Surface distribution of dissolved ethene in Norton Sound in July, 1979. Concentrations are given in nl/l (STP).

($C_{2:0}/C_{2:1}$) at these two stations is shown in Figure 6-23 A, B. At station N21B, the ethane/ethene ratio varied from 0.2 to 2.4. Values of this ratio in excess of 0.5 suggest either a thermogenic source of ethane, or biogenic hydrocarbons from anoxic sediments. The control station (Figure 6-23B) generally reflected lower ratios, but appeared to be contaminated from waters near the seep.

Compared to observations in and near the seep in September 1976, ethane and propane were found at significantly lower concentrations this year. We postulate two mechanisms leading to a reduced signature. Increased mixing in and near the seep together with a reduced injection rate of hydrocarbons resulted in a poorly developed hydrocarbon plume. Moreover, during our attempt to identify the locus of the seep, numerous small patches and lenses of hydrocarbon-rich water were identified. This suggests that the seep was episodically active or that complex circulation over the seep prevailed during the observational period.

In summary, it appears that the activity of the seep was minimal and probably episodic. Strong vertical mixing near the seep locus further attenuated the hydrocarbon signature.

6.3.3 Low Molecular Weight Aromatics

During the cruise, eleven stations were sampled in the region of the seep and compared to six control stations located east and west of the seep. Concentrations of benzene, toluene, ethylbenzene, and xylenes were everywhere less than 10 ng/l. Hence, it was not possible to identify the location of the gas seep on the basis of dissolved LMW aromatic compounds. This is in agreement with our previous statement that the seep was minimally active.

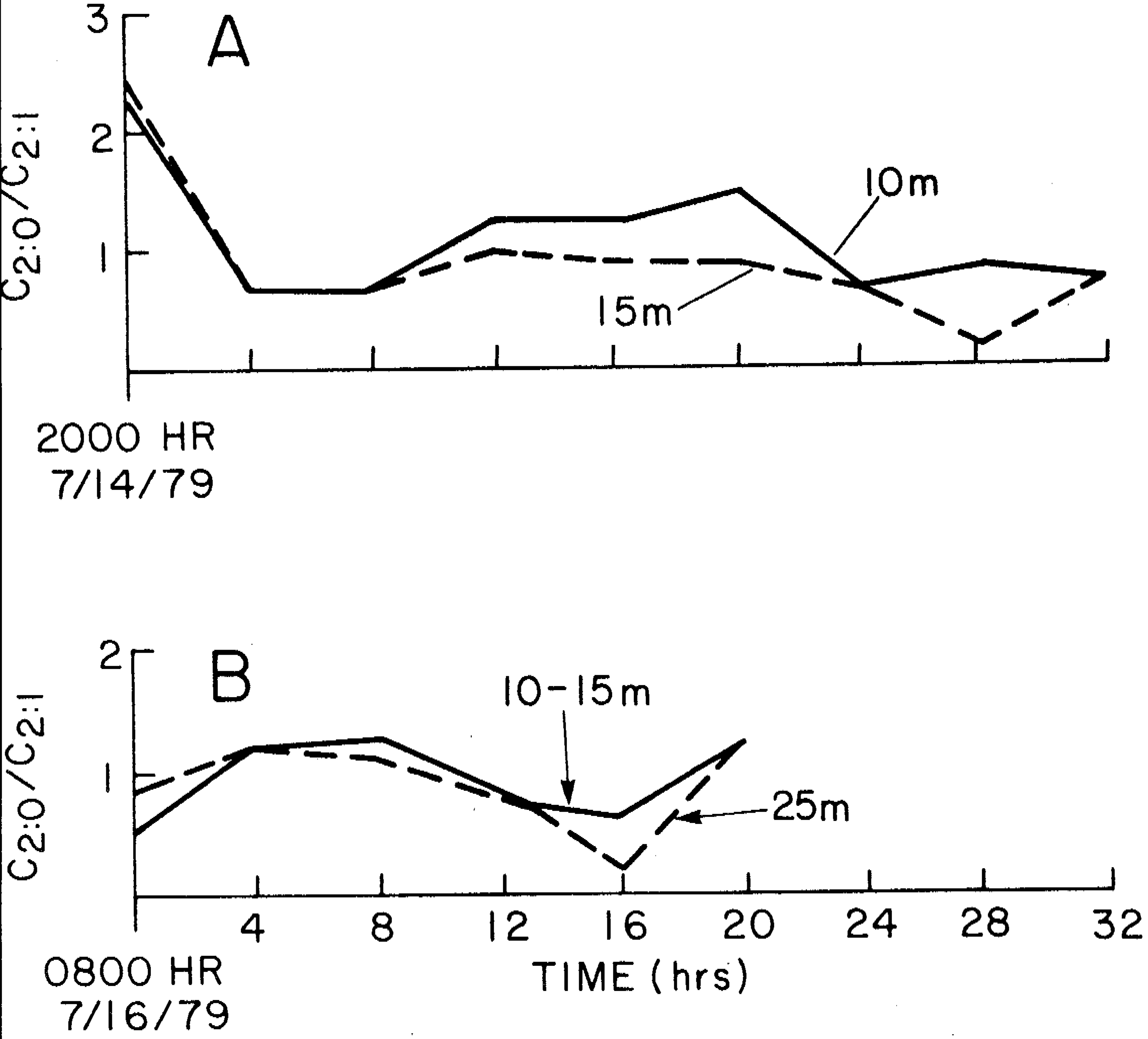

Figure 6-23. Diurnal changes in the ethane/ethene ratio at station N21B (A) located near the seep and at a control station N17 (B) located north and east of the seep locus.

6.3.4 Suspended Petroleum Hydrocarbons

During this cruise, two stations were sampled (N17A and N21B) for suspended hydrocarbons. Deploying a pump and continuous flow centrifuge suspended matter was collected for periods of 20 hours (N17A) and 32 hours (N21B). These samples have been analyzed for their alkane components, but because of small sediment recoveries, the results are inconclusive. The suspended sediments appear to be devoid of petroleum-like hydrocarbons, but they will be reanalyzed before the final report. Also distressing is the fact that the control station (N17A) was too close to the seep to be reliably designated as a control site. This conclusion was derived from the aforementioned ethane data.

7. SUMMARY

7.1 Cook Inlet

Observations of LMW dissolved hydrocarbons in upper Cook Inlet confirmed our previous measurements. That is, a source of both LMW aliphates and aromatic compounds is present in the region of Trading Bay. Elevated levels of methane, ethane, and propane were observed including significant levels of benzene, toluene and C_2-benzenes. Analysis of previous data taken in upper Cook Inlet suggests that at least two seeps are present, one which is predominantly a "dry" gas, the other having significant concentrations of the higher homologs. Since both gas compositions are currently being produced in the region, these observations are not altogether surprising. Whether the gases are originating from natural seeps or from previously drilled test wells is not clear at this time. The shallowness of the reserves in Trading Bay (T. McCulloh, USGS) and to the west (onshore) support a natural source rather than faulty technology.

The production of both gas and oil in upper Cook Inlet led to the speculation that the heavier fractions of petroleum may be leaking from the system and be associated with the large flux of sediments emanating from the rivers of upper Cook Inlet. Analysis of the saturate HC fraction extracted from suspended matter collected near Kalgin Island shows a dominant assemblage of terrestrially-derived plant waxes. No alkanes common to crude oil were present in significant concentrations, although the aromatic fraction has not been analyzed. The presence of polyolefins and methylesters precludes the identification of petroleum components. These fractions will be processed and reexamined for aromatic hydrocarbons.

7.2 Shelikof Strait

Concentrations of LMW hydrocarbons in Shelikof Strait were typical of those found in other shelf regions of Alaska. High concentrations of methane were observed locally in near-bottom waters, reflecting local benthic sources and circulation dynamics. The biological hydrocarbons, ethene and propene, were found at elevated levels near the Trinity Islands, suggesting a phytoplankton bloom during the observational period. Using the diagnostic ratios, C_1/C_2+C_3 and $C_{2:0}/C_{2:1}$, no significant thermogenic source of gaseous hydrocarbons exists.

As a part of our study to evaluate the transport of suspended hydrocarbons from Cook Inlet, we examined bottom sediments for the heavy petroleum hydrocarbons. Our samples, which were taken from the same Van Veen-Box Core as those taken by Kaplan (RU #480), showed the familiar pattern of terrestrially-derived plant waxes mixed with hydrocarbons of marine origin. Again, there was no evidence of petroleum hydrocarbons. Our results will be compared to those of Kaplan (RU #480) in the final report.

7.3 Norton Sound

The objective of last year's visit was to collect more information on the previously defined gas seep, relative to its composition and plume trajectory. High density sampling near the seep showed that the hydrocarbon concentrations had decreased significantly from the observations conducted two years prior. During the search, small parcels of water enriched slightly in alkanes were found in the vicinity, but no well-defined plume structure was evident. Measurement of LMW aromatics near the seep and in other locations around Norton Sound and the Bering Sea revealed no enrichment as the result of the seep. Preliminary analysis of suspended matter for heavy hydrocarbons showed no evidence for petroleum hydrocarbons, which agrees with the previous measurements taken by Kaplan (RU #480). Our general conclusion is that the seep was minimally active in July 1979. Preliminary evidence suggests that the effluent from the seep is restricted to the LMW aliphatics. Because of compositional ratios and concentration levels, the major component of the seep is not methane, but probably is carbon dioxide based on pore water analysis of dissolved gases.

8. FUTURE RESEARCH

As a consequence of our studies in upper Cook Inlet, one or more major gas seeps were identified. Measurements over the past three years indicate that these seeps are more or less continuous in time, and thus represent features which can be reliably studied.

Having found a source of thermogenic hydrocarbons, systematic studies can be developed to study the dispersion and fate of these compounds in a turbulent estuary such as Cook Inlet. The goal of such a program would be to understand the mixing and air-sea exchange of LMW hydrocarbons originating from a point source with the aim of defining useful trajectory scales. This would be accomplished with a high density sampling field program to collect hydrocarbon concentrations as a function of time.

Interpretation would be provided through the application of a tidal box model modified to include air-sea exchange. The output of such a model is the trajectory scale over which hydrocarbons can be used as tracers. The long range goal of this study would be to develop a monitoring strategy for the use of LMW hydrocarbons as tracers of injected petroleum.

9. BUDGET STATUS (Est.)

Budget Items	Allocated	Expended	Balance
Salaries	$54,890	$27,445	$27,445
Major Equipment	0	0	0
Expendables	3,921	2,350	1,571
Travel	1,680	0	1,680
Shipping	0	0	0
Publications	3,500	1,500	2,000
Contracts	3,500	1,000	2,500
	$67,491	$32,295	$35,196

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HYDROCARBONS: NATURAL DISTRIBUTION AND DYNAMICS ON THE ALASKAN OUTER CONTINENTAL SHELF

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I. SUMMARY

The objective of the work reported here has been to characterize the ambient concentrations of non-volatile hydrocarbons in the marine environment of Cook Inlet, Alaska and to provide information about processes which control those concentrations. This report integrates results obtained in the last twelve months with work performed in Cook Inlet during the previous three years to provide an overview of all of the information about the kinds and amounts of hydrocarbons in Cook Inlet which this project has produced.

We have found that hydrocarbon concentrations in central Cook Inlet are extremely low. This turbid, high energy environment is also biologically quite unproductive. Lower Cook Inlet (roughly south of Tuxedni Bay) has hydrocarbon arrays in water, biota and sediment more typical of southcentral Alaskan marine environments. These hydrocarbons are primarily derived from contemporary biosynthesis. In the vicinity of Homer, fossil hydrocarbons derived from coal are also present. Experimental work indicates that in Cook Inlet association with suspended sediments is not an important pathway for the dispersion of petroleum hydrocarbons dissolved in water.

II. INTRODUCTION

As indicated by this report's title, the general goal of this study has been to investigate the natural distribution and dynamics of hydrocarbons on Alaska's outer continental shelf. These parameters have also been investigated in nearshore and intertidal environments since these inevitably effect and are affected by conditions further offshore. The work reported here is concerned with one geographical area: lower Cook Inlet; where we have determined concentrations of non-volatile hydrocarbons in seawater, biota and sediments. This report not only presents results obtained during the last year but also interprets those findings in light of previous years' results.

The hydrocarbon determinations made this year in Cook Inlet fall into three discrete data sets: water samples, pelagic biota (largely zooplankton) and benthic biota (largely intertidal). The water and plankton samples were investigated to determine whether any petroleum residue from the petroleum production operations of upper Cook Inlet were detectable and to obtain background information about ambient hydrocarbon concentrations. The benthic biota were collected to provide information about ambient hydrocarbon compositions in central Cook Inlet. This was needed to round out previously obtained results for the southern part of the Inlet.

The first value of this work as it relates to the environmental management of outer continental shelf oil development is providing an indication of ambient hydrocarbon concentrations prior to development. In this context these data provide a point of comparison for results that may be obtained at a later date. However, such use of this information, while potentially important, is essentially passive, documenting changes after they occur. These data can also be used in a more active way: the current distribution of hydrocarbons can provide insights to the processes that control those distributions. Inferred knowledge of this kind can be used to predict the behavior of hydrocarbons that might be added to the systems in the process of oil development. Although such predictions inherently contain an element of uncertainty, they provide a rational basis for the development of environmental management policy that seeks to avoid and mitigate hydrocarbon pollution problems.

III. METHODS

A. Water

Surface water samples were collected in upper Cook Inlet from the bow of a small boat using weighted 1 gallon bottles. Aboard ship, 4 ℓ volumes of water were filtered through Gelman type A glass filters which had been previously cleaned at 500° for 24 hours. The filters from each sample were frozen for laboratory analysis. The filtered water was twice extracted with 50 ml of methylene chloride for 3 minutes. Extracts of each sample were pooled and returned to the laboratory for analysis.

In the laboratory water extracts were dried over sodium sulfate and concentrated to 1 ml. Extracts were concentrated to 0.2 ml and analysed by gas chromatography.

Filters of suspended sediment and phytoplankton from Cook Inlet water samples were thawed, counted, and cut into 1 mm strips. The cut filters were placed in clean 50 ml centrifuge tubes. Twenty ml of aqueous 4 N NaOH and 10 ml hexane were added to each tube. Random samples and two blanks of clean filters, NaOH solutions and hexane were constructed and internally spiked with chrysene and docosane standards.

The tubes were topped with teflon-lined caps and refluxed 2 hours in a 90°C H_2O bath. After cooling, the samples were extracted 3 times with 15 ml of hexane following 15 minute centrifugations at 2,000 rpm. The extracts were dried over Na_2SO_4 overnight, and then were concentrated to 1 ml.

Column chromatography was performed using silica gel deactivated with 5-8% water. Two column configurations were used. For environmental samples which yielded less than 15 mg extractable lipids 5 g of silica was packed in a 9 mm column. For larger extracts 10 g of silica was packed in an 11 mm column. Two fractions were eluted. For the smaller column, the first fraction was 10 ml of hexane and the second was 15 ml of 20% dichloromethane in hexane. Elution volumes were doubled for the larger column system. These elution volumes are approximate; each batch of silica gel was calibrated by elution of an aliphatic and aromatic standard. Elution volumes and/or percent water used to deactivate the silica were then adjusted.

Gas chromatography was performed on a Hewlett Packard 5710A instrument using 50 m x 0.7 mm support coated open tubular columns coated with OV-101. Carrier gas was helium flowing at 10 ml/minute with an addition 30 ml/minute of helium as makeup gas at the flame ionization detector. The column was temperature programmed from 70° to 270° at 8°/minute while the injector and detector were held at 300°.

Quantification was accomplished with Hewlett Packard 3380 or 3385 digital integrators using internal and external quantitative standards and adjusting reported results for percent recovery. Quantification of unresolved complex mixtures was by digital integrator or planimetry. Peak identifications were based on the use of external standards and gas chromatography-mass spectrometry.

B. Plankton

Plankton collections were made at 12 hour intervals using a 230 μm net. At station CB-7 in outer Kachemak Bay (59°39.4'N, 151°45.9'W) sufficient material was obtained by a single vertical tow. However, at station CB-9 near Drift River (60°28.2'N, 152°12.2'W) 3 hour horizontal tows were required because of the shallower water depth and lower biological productivity. For the horizontal tows the ship was anchored and tidal currents were allowed to fish the nets. All collections were begun at high slack water. The mixed plankton samples were transferred along with a minimal amount of water to glass vials and frozen.

For analysis, a plankton sample was thawed and transferred to a 10 ml glass centrifuge tube with a Teflon lined cap. At this time an aliquot was taken for dry weight determination. To the centrifuge tube was added 3.0 ml of 10 N aqueous KOH and 3.0 ml of hexane. The tube was then capped and placed in a 90° water bath for 3 hours and then in an ice bath to cool. When the tube and its contents had cooled the hexane phase was removed by syringe. The remaining aqueous phase was extracted three times with 3.0 ml portions of hexane. The combined hexane extracts were dried over Na_2SO_4 and concentrated to 1 ml with a rotary evaporator and then to 0.5 ml with a stream of N_2. Silica gel cleanup and hydrocarbon determination by gas chromatography were carried out as described above.

C. Benthic Biota

Samples were removed from shell or test as necessary. Large pieces of tissue were cut into 1 cm^2 pieces. One sample of *Collisella scutum* was rinsed four times with clean H_2O. Samples were all spiked with docosane and chrysene standards after weighing. Large samples (> 25 g wet weight) were saponified for 24 hours in 150 ml strong base and 100 ml hexane; small samples (< 25 g wet weight) were saponified 24 hours in 60 ml strong base and 60 ml hexane. The base used in saponification was 4 N KOH for all samples except the limpets, where 2 N of KOH was used. Samples were extracted 3 times with hexane using 100 ml for large and 60 ml for small samples. Samples were washed with 60 ml saturated salt solution and dried overnight in Na_2SO_4.

Column chromatography cleanup and hydrocarbon determination by gas chromatography were carried out as described above.

IV. RESULTS

A. Water

The 17 stations at which water was collected in May 1979 are shown in Table I. The results of particulate matter analyses are shown in Table II while those for the filtered water are presented in Table III. In all samples analysed, hydrocarbons were not detectable. For the filtered water samples, the limit of detection is approximately 0.01 μg/ℓ and for the particulate matter the limit is approximately 0.01 μg/ℓ (water weight basis). Thus all stations were found to have hydrocarbon concentrations below these values.

B. Plankton

The results of 12 analyses of plankton collected at two time series stations in May 1978 are shown in Table IV. No hydrocarbon other than pristane was found in any sample. The limit of detection for these samples was approximately 0.5 μg/g.

TABLE I

SAMPLE LOCATION FOR WATER COLUMN INVESTIGATION STATION LOCATIONS, COOK INLET - MAY 1979

Station	Latitude (°N)	Longitude (°W)
Upper Cook Inlet		
UC1	60°57.2'	151°08.5'
UC2	60°56.8'	151°18.3'
UC3	60°56.7'	151°26.9'
UC4	60°53.6'	151°25.0'
UC5	60°54.6'	151°28.3'
UC8	60°38.3'	151°32.1'
UC9	60°48.1'	151°30.8'
UC10	60°50.6'	151°40.8'
UC10A	60°48.9'	151°43.0'
UC11	60°47.6'	151°42.3'
UC11A	60°47.3'	151°43.0'
UC12	60°45.8'	151°40.3'
UC12A	60°46.3'	151°40.0'
UC13	60°42.1'	151°40.0'
UC14	60°52.3'	151°32.8'
Lower Cook Inlet		
LC15	60°32.3'	151°30.5'
LC16	60°32.8'	151°40.2'

TABLE II

HYDROCARBONS IN SUSPENDED MATTER FROM COOK INLET
μg/ℓ (Water Weight Basis)

Station	Hydrocarbons	
	Saturated	Unsaturated
Upper Cook Inlet		
UC1	ND*	ND
UC2	ND	ND
UC3	ND	ND
UC4	ND	ND
UC5	ND	ND
UC8	ND	ND
UC9	ND	ND
UC10	ND	ND
UC10A	ND	ND
UC11	ND	ND
UC11A	ND	ND
UC12	ND	ND
UC12A	ND	ND
UC13	ND	ND
UC14	ND	ND
Lower Cook Inlet		
LC15	ND	ND
LC16	ND	ND

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*ND = not detectable.

TABLE III

HYDROCARBONS IN COOK INLET FILTERED SEAWATER (μg/ℓ)

Station	Date	Volume extracted	Depth	Hydrocarbons
UC1	5/14/79	4 ℓ	surface	ND*
UC2	5/14/79	4 ℓ	surface	ND
UC3	5/14/79	4 ℓ	surface	ND
UC4	5/17/79	4 ℓ	surface	ND
UC5	5/17/79	4 ℓ	surface	ND
UC8	5/14/79	4 ℓ	surface	ND
UC9	5/17/79	4 ℓ	surface	ND
UC10	5/17/79	4 ℓ	surface	ND
UC10A	5/17/79	4 ℓ	surface	ND
UC11	5/17/79	4 ℓ	surface	ND
UC11A	5/17/79	4 ℓ	surface	ND
UC12	5/14/79	4 ℓ	surface	ND
UC12A	5/17/79	4 ℓ	surface	ND
UC13	5/17/79	4 ℓ	surface	ND
UC14	5/17/79	4 ℓ	surface	ND
LC15	5/15/79	4 ℓ	surface	ND
LC16	5/15/79	4 ℓ	surface	ND

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*ND = not detectable.

TABLE IV

HYDROCARBONS IN PLANKTON FROM COOK INLET TIME SERIES STATIONS
(μg/g Dry Weight Basis)

Station	Dry Weight (% of Wet Weight)	Pristane
CB-7-0	4.5	28, 50*
CB-7-12	4.4	ND, ND*
CB-7-24	4.4	ND
CB-7-36	4.9	18
CB-7-48	5.1	0.9
CB-9-0	7.0	30
CB-9-12	9.5	23
CB-9-24	8.6	1.5
CB-9-36	7.6	23
CB-9-48	9.7	42

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*duplicate analyses; ND = not detectable.

C. Benthic Biota

The dates and locations of collection of the 29 benthic biota samples are shown in Table V. All are intertidal organisms except number 7, *Cancer magister*, and even this specimen was a single individual found stranded in the intertidal zone. The results of hydrocarbon determinations for these organisms are presented in Tables VI and VII. The limit of detection for these samples is 0.01 μg/g. All results are expressed on a wet tissue weight basis.

V. DISCUSSION

This section is divided into two parts: first a discussion which specifically addresses the results reported in the previous section, then a general discussion of all this project's work in Cook Inlet.

A. Discussion of Results Presented Here

The stations occupied for samples of particulate matter and filtered seawater were in the vicinity of operating offshore oil production platforms in upper Cook Inlet. They were chosen to determine the impact of the discharge of co-produced water on the hydrocarbon concentrations of the water and suspended sediment. In all cases the concentrations were below the limit of detection (0.01 μg/ℓ). The high degree of tidal mixing which is characteristic of Cook Inlet probably accounts in large part for our inability to detect hydrocarbons in water. Rosenberg *et al.* (1969) performed a dye study which measured dilution from a point source due to mixing at a nearshore point in central Cook Inlet. On an incoming tide they observed a dilution factor of 10 in a horizontal distance of 20 m due to tidal mixing. If one assumes that this dilution factor is typical of central Cook Inlet and extrapolates to a distance of 1 km, a dilution factor of 10^{50}/km is predicted. This very large dilution factor indicates that any hydrocarbons discharged in upper or central Cook Inlet (where tidal currents are strong) will be diluted to below detectable concentrations in very short distances (< 1 km).

The plankton analyses from time series stations were part of a group of time series observations the remainder of which were reported in our 1979 Annual Report. Sample collection at station CB-9 near Drift River in central Cook Inlet was difficult. We had planned to collect plankton by vertical

TABLE V

SAMPLING LOCATIONS AND DATES FOR COOK INLET BENTHIC BIOTA

Sample Number	Species	Date	Location	Position	
				Latitude (N)	Longitude (W)
1	*Alaria* sp.	18 May 79	Tuxedni Bay	60°13.1'	151°37.0'
2	*Collisella pelta*	13 May 79	Homer Spit	59°36.0'	151°24.5'
3	*Collisella pelta*	18 May 79	Chisik Island	60°10.5'	151°35.7'
4	*Collisella pelta*	18 May 79	Tuxedni Bay	60°13.1'	151°37.0'
5	*Collisella persona*	2 May 78	Homer Spit	59°36.0'	151°24.5'
6	*Collisella scutum*	2 May 78	Homer Spit	59°36.0'	151°24.5'
7	*Cancer magister*	15 May 79	Kalgin Island	60°21.7'	151°57.7'
8	*Enteromorpha linza*	18 May 79	Tuxedni Bay	60°13.1'	151°37.0'
9	*Fucus distichus*	18 May 79	Chisik Island	60°10.5'	151°35.7'
10	*Fucus distichus*	18 May 79	Tuxedni Bay	60°13.1'	151°37.0'
11	*Fucus distichus*	13 May 79	Homer Spit	59°36.0'	151°24.5'
12	*Fusitriton oregonensis*	5 May 78	Anchor Point	59°46.2'	151°52.4'
13	*Laminaria saccharina*	18 May 79	Chisik Island	60°10.5'	151°35.7'
14	*Laminaria saccharina*	18 May 79	Tuxedni Bay	60°13.1'	151°37.0'
15	*Leptasterias* sp.	5 May 77	Anchor Point	59°46.2'	151°52.2'
16	*Littorina sitkana*	23 June 77	Kasitsna Bay	59°28.8'	151°34.3'
17	*Macoma balthica*	12 May 79	Kasilof Bay	60°23.2'	151°18.0'
18	*Macoma balthica*	18 May 79	Tuxedni Bay	60°13.1'	151°37.0'
19	*Mytilus edulis*	7 May 79	Diamond Gulch	59°40.3'	151°42.3'
20	*Mytilus edulis*	6 May 78	Homer	59°38.0'	151°30.7'
21	*Mytilus edulis*	18 May 79	Tuxedni Bay	60°13.1'	151°37.0'
22	*Neptunea lyrata*	18 May 79	Tuxedni Bay	60°13.1'	151°37.0'
23	*Nucella lima*	18 May 79	Tuxedni Bay	60°13.1'	151°37.0'
24	*Nucella lima*	18 May 79	Chisik Island	60°10.5'	151°35.7'
25	*Nucella lamellosa*	5 May 78	Anchor Point	59°46.2'	151°52.2'
26	*Palmeria palmata*	18 May 79	Chisik Island	60°10.5'	151°35.7'
27	*Siliqua patula*	15 May 79	Kalgin Island	60°21.7'	151°57.7'
28	*Strongylocentrotus droebachiensis*	6 May 77	Homer	59°38.0'	151°30.7'
29	*Ulva* sp.	18 May 79	Tuxedni Bay	60°13.1'	151°37.0'

TABLE VI

COOK INLET BENTHIC BIOTA SATURATED HYDROCARBONS
µg/g Wet Weight

Species	14*	15	16	17	Pr	18	Ph	19	20	21	22	23	25	27	29	UCM	TOTA SATURA
Alaria sp.		15		0.16													15
Collisella pelta		1.0	1.9	1.5	6.4	1.2	3.3	2.0	0.74							350	350
Collisella pelta		0.33		0.19													0.52
Collisella pelta				0.47													0.47
Collisella persona			23	10	33	39	40	52	110	150						240	390
Collisella scutum				0.40	4.8	0.69	2.6	1.1	0.51							340	360
Collisella scutum				0.27	2.8	0.74	1.6	0.80	0.42							230	240
Cancer magister																	ND
Enteromorpha linza		0.62		1.1													1.7
Fucus distichus		20	0.08	0.23													20
Fucus distichus		13	0.06	0.19													14
Fucus distichus	3.4	22	29	30	45	25	20	30	11	6.7	3.9					950	1200
Fusitriton oregonensis																	0.03
Laminaria saccharina		8.2															8.2
Laminaria saccharina		4.4		0.21													4.6
Leptasterias sp.																	ND
Littorina sitkana		t															t
Macoma balthica		t	t	0.08	0.20											19	19
Macoma balthica					0.18												0.1
Mytilus edulis		0.03	0.02	0.05	0.05				t	t							0.1

TABLE VI (continued)

COOK INLET BENTHIC BIOTA SATURATED HYDROCARBONS
µg/g Wet Weight

Species	14*	15	16	17	Pr	18	Ph	19	20	21	22	23	25	27	29	UCM	TOTAL SATURAT
Mytilus edulis		0.02	0.01	0.01	t	0.01			t								0.05
Mytilus edulis				0.10													0.10
Neptunia lyrata																	ND
Nucella lima																	ND
Nucella lima																	ND
Nucella lamellosa																	ND
Palmeria palmata		10	0.25	49													59
Siliqua patula																	ND
Strongylocentrotus droebaciensis		0.18		0.07	0.15							0.02	0.03	0.06	0.05		0.76
Ulva sp.		0.73		1.2													1.9

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* 14, etc. = carbon length; Pr = pristane; Ph = phytane; UCM = unresolved complex mixture; ND = not detectable.

TABLE VII

LOWER COOK INLET BENTHIC BIOTA SAMPLES
UNSATURATED HYDROCARBONS - µg/g Wet Weight

Species	15:1*	17:1	17:2	18:1	19:1	21:5	21:6	Sq.	UCM	TOTAL
Alaria sp.						0.75	4.4	0.44		5.7
Collisella pelta								1.6	129	130
Collisella pelta	0.41	0.12	0.07			2.2	1.7	2.2		12
Collisella pelta	0.26					1.7	0.52	1.4		5.8
Collisella persona							0.80	0.97	101	120
Collisella scutum							t	2.5		7.4
Collisella scutum								1.5		2.9
Cancer magister										ND
Enteromorpha linza		32	30			1.3		1.8		66
Fucus distichus						86		23		110
Fucus distichus						73		34		110
Fucus distichus						9.3	19	43	640	710
Fusitriton oregonensis								0.60		1.6
Laminaria saccharina							4.9	0.80		5.7
Laminaria saccharina							2.4	1.1		3.6
Leptasterias sp.										0.15
Littorina sitkana								0.07		0.22
Macoma balthica						1.5		2.1		13
Macoma balthica						0.19		0.14		3.1
Mytilus edulis							0.60	0.70		4.8
Mytilus edulis							0.79	0.97		2.5
Mytilus edulis							3.6	1.3		5.3
Neptunia lyrata								0.14		0.85
Nucella lima										0.47
Nucella lima						1.5				1.5

TABLE VII (continued)

LOWER COOK INLET BENTHIC BIOTA SAMPLES
UNSATURATED HYDROCARBONS - μg/g Wet Weight

Species	15:1*	17:1	17:2	18:1	19:1	21:5	21:6	Sq.	UCM	TOTAL
Nucella lamellosa								0.06		0.23
Palmeria palmata						0.57		1.2		2.5
Siliqua patula										ND
Strongylocentrotus droebachiensis							4.7	160		210
Ulva sp.		93	1.8	0.59	0.31		0.80	1.6		100

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* 15:1, etc. = carbon length and unsaturation; Sq. = squalene; UCM = unresolved complex mixture; ND = not detectable.

tow and had done so at CB-7. However, because of the shallow water depth and low plankton abundance associated with high suspended sediment load, vertical tows provided insufficient plankton at CB-9. Therefore, it was decided to make 3-hour collections while the ship was at anchor. Plankton were swept into the net by the tidal current. However, larger, more mobile zooplankton may have been able to avoid the net. The samples collected in this way were distinctly green, indicating a substantial portion of phytoplankton. The small size of samples collected (< 0.2 g dry weight) is in large part responsible for the higher than usual limit of sensitivity. Our finding that pristane was the only hydrocarbon present is in keeping with the finding of others that this compound is often dominant in zooplankton. The reason for the variation in pristane concentration is unclear; it is not a function of the day-night cycle.

The organisms investigated (Tables VI and VII) can be divided into three groups based on the presence or absence of fossil hydrocarbons. Limpets (*Collisella pelta, C. persona* and *C. scutum*) and rockweed (*Fucus distichus*) collected within the small boat harbor on Homer Spit showed evidence of contamination by fuel oil: normal hydrocarbons in the range tetradecane to docosane without strong odd carbon chain length dominance, pristane and phytane, and unresolved complex mixtures. Animals collected in the Homer-Diamond Gulch area contained diterpenoids indicative of detrital coal in that area. Mussels (*Mytilus edulis*) from Diamond Gulch contained simonellite, 0.88 μg/g; iosene, 0.04 μg/g; and fichtelite, 0.02 μg/g. Mussels from Homer contained a trace of iosene (0.02 μg/g). Urchins (*Strongylocentrotus droebachiensis*) from Homer contained fichtelite (0.03 μg/g) and iosene (0.05 μg/g). The remainder of the organisms examined (22 specimens) contained only biogenic hydrocarbons. This last group included not only materials collected at Anchor Point and Kasitsna Bay (both in the Kachemak Bay area) but also four locations in central Cook Inlet: Kasilof Bay, Kalgin Island, Chisik Island and Tuxedni Bay. All of the plant and animal materials from these locations showed kinds and amounts of hydrocarbons consistent with modern biosynthetic origin. The absence of petrogenic hydrocarbons in the biota of Chisik Island and Tuxedni Bay is notable since this area on the western side of central Cook Inlet is the closest protected (and therefore containing abundant intertidal biota) area to present oil production activities of Drift River and upper Cook Inlet.

B. General Discussion of Cook Inlet Hydrocarbon Determinations

Annual Reports of this project submitted in 1977, 1978 and 1979 have contained information about the distribution and dynamics of hydrocarbons in Cook Inlet. In the following discussion, which reviews those results, those reports will be cited in an abbreviated form. Thus (77) will be used to indicate that information is presented in the 1977 Annual Report of RU 275.

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 the time series measurements discussed for plankton above and as a reconnaissance of the petroleum production area of upper Cook Inlet. Of the 29 samples analysed, 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 analysed. 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.

We have investigated the ability of suspended sediments of the type found in Cook Inlet to sorb and transport to the bottom petroleum hydrocarbons (78) (Malinky and Shaw, 1979). Using a model which systematically tended to overestimate the importance of hydrocarbon-sediment interaction, we estimated that a point source of petroleum hydrocarbons equivalent to the treated ballast water discharged by the trans-Alaska pipeline terminal at Valdez would in Cook Inlet result in a hydrocarbon-on-suspended-sediment concentration of 240 μg/kg (dry sediment weight basis). At least from a mass balance standpoint, this process is not important for chronic, low level hydrocarbon inputs.

Biota

Over the past three years (78, 79, this report) 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 dominated 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 droebaciensis* 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 compositions 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, this report). 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.

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VII. PROGRESS SUMMARY FOR THE QUARTER
1 JANUARY 1980 THROUGH 31 MARCH 1980

I. Field Activities

None during this quarter.

II. Laboratory Activities

Analysis of environmental materials from Cook Inlet has been completed for this Annual Report. Laboratory work has now shifted to samples from other lease areas including the Beaufort Sea and Gulf of Alaska.

III. Results

See Sections IV and V of this report.

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Characterization of Organic Matter in Sediments From Cook Inlet and Norton Sound

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I. SUMMARY

Sediments were collected from the lease areas of Cook Inlet and Norton Sound and analyzed for total carbon, organic carbon, aliphatic and aromatic hydrocarbon contents. The objectives of the investigation are: 1) to establish concentration levels and spaticl variability of hydrocarbon components prior to actual production of oil in the area, 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 each of the areas in case of an oil spill. The baseline studies indicate that the sediment in these areas is generally unpolluted except two stations in Cook Inlet around Kalgin Island. The *n*-alkanes are characteristic of a mixture of marine and terrestrial inputs. The distribution of polycyclic aromatic hydrocarbons is complex and indicates pyrolytic origin (natural and/or anthropogenic). The two stations in Cook Inlet show weathered petroleum distribution of *n*-alkanes, which could be derived from petroleum production and transport in Upper Cook Inlet.

II. Introduction

A. General nature and scope of study

Major objective of this investigation is to determine the baseline hydrocarbon concentrations and their distributions in the surface sediments of the Alaskan seas. An assessment of the hydrocarbon concentrations in surficial sediments is important in providing a background from which subsequent changes in the environment caused by petroleum exploration and offshore oil drilling can be monitored. The determination of sources and fates of hydrocarbon in the surface sediments in this marine environment could help in obtaining a predictive understanding of petroleum pollution, if any, in the area.

B. Specific objectives

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

1. To establish baseline hydrocarbon levels in the Lower Cook Inlet and Norton Sound areas 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 the surficial sediments; whether biogenic or anthropogenic.
4. To understand the probable pathways of hydrocarbon transport in the event of oil spill in the areas.

C. Relevance to problems of petroleum development

Oil production and transport had started in the Upper Cook Inlet and sales have occurred already in the Lower Cook Inlet. Lower Cook Inlet is scheduled for its second sale (#60) in March of 1981. Shelikof Strait will also be included in this sale. Lower Cook Inlet and Shelikof Strait are known for high biological productivity and are important for commerical and sport fisheries. The renewable resources in this area are of considerable value and therefore a baseline study of hydrocarbons is important to assess any environmental impact of hydrocarbon pollution on the ecosystem, resulting from oil exploration.

The Norton Basin in the northeastern Bering Sea is scheduled for a September 1982 sale. Information on the present level of hydrocarbon in this area is required for the assessment of any chronic pollution arising from offshore drilling for oil and gas.

III. Current state of knowledge

Studies on the Alaskan Seas reported in open literature are relatively scant to date. Thermogenic gas seep containing predominantly carbon dioxide and relatively abundant petroleum hydrocarbons (two-to-four-carbon alkanes) in the gas phase and water column, respectively, has been found in the area approximately 40 km south of Nome in Norton Basin (Kvenvolden _et al_., 1979; Cline and Holmes, 1977). Studies undertaken by our group on organic constituents of sediments from Norton Sound and Cook Inlet are probably the most extensive investigations of hydrocarbons in this area as far as we know (Brenner _et al_., 1978; Kaplan _et al_., 1979; Venkatesan _et al_., 1980a).

IV. Study area and cruises

A set of 23 samples was collected during the cruise of R/V SEA SOUNDER in June, 1976 from Kachemak Bay and the central part of Lower Cook Inlet. The second set of 9 samples was collected by Ms. J.W. Wiggs of the University of Alaska (RV 275) during the November, 1977 cruise of the NOAA ship SURVEYOR. Approximately 35 samples were collected in the spring and summer of 1978 from the western part of Lower Cook Inlet by

David Meredith and David Winter during the cruises of the R/V DISCOVERER, to determine whether the organic material originating in the Upper Cook Inlet is being deposited near Kamishak Bay, or transported and dispersed beyond Shelikof Strait. Mr. Dave Meredith participated in the May, 1979 cruise of the R/V DISCOVERER, Leg 2 in the Cook Inlet area to collect samples in the remaining stations. A detailed description of the Van Veem Grab Sampler can be found in the September 1976 quarterly report (RU #480). A 45' charter boat (MISS VICKI ANN), was used to collect samples at locations at water depths of less than 10 fathoms, around Kalgin Island and the western foreland of Cook Inlet. In these areas, surface sediments (bulk) were collected with a Shipek Grab Sampler, instead of the usual Van Veem Grab Sampler. Sediment samples from stations 16A and B were collected with a mud-snapping device.

Samples from Norton Sound were collected by Mark Sandstrom during Leg 2 of the R/V SEA SOUNDER cruise in October, 1976. The sample grid was extended to the western part of Norton Sound in July, 1977 to sample the sediments south of Nome, Alaska, containing the potential seep. In addition, a few samples were collected by K. Kvenvolden (USGS) from vibracores and box cores near the seep area to be analyzed by our group. Mr. Dave Meredith collected about 20 sediment samples and 2 core samples from Norton Sound area in the cruise of the R.V. DISCOVERER (July, 1980).

The station locations and the cruise area are shown in Figures 1 and 4. For station locations of the 1976, 1977 Cook Inlet samples, refer to Annual Report, April 1978 (RU #480).

V. Methods

Details of methodology followed for elemental and hydrocarbon analyses are presented elsewhere (Venkatesan et al., 1980a). The lipid extracts from sediments were fractionated into aliphatic and aromatic hydrocarbons on a silica gel column and gas chromatography was performed on a Hewlett-Packard 5840A Model with a Grob Injector and a glass capillary column, wall-coated with OV-101 (J&W; 30m x .25mm). GC/MS analyses of selected fractions were carried out with a Finnigan Model 4000 Quadrupole mass spectrometer directly interfaced with a Finnigan Model 9610 gas chromatograph, equipped with SE 54 (J&W) column. The mass spectrometric data was acquired and processed using a Finnigan INCOS Model 2300 data system.

VI. Results

Total organic carbon, the lipid contents, typical gas chromatograms of aliphatic and aromatic fractions of Cook Inlet and Norton Sound sediments and relative distribution histograms of di- and triterpenoids of a few stations are represented in Figures 1 to 10.

Total hydrocarbon content from gravimetric data, the alkane distributions from gas chromatography (only 1979 Cook Inlet and Norton Sound samples; for alkane distribution data of 1976-1978 samples, refer to Annual Reports, April 1978 and 1979, RU #480) and the characteristic parameters from gravimetric and gas chromatographic analyses are given in Tables from 1 to 17.

The levels of major PAH compounds from representative stations in the study areas are presented in Table 18.

Pertinent analytical results of samples studied in the previous years also have been included to compare the trend in the hydrocarbon distributions within the area. Thus, an effort has been made in this report to synthesize the data obtained so far in Cook Inlet and Norton Sound.

VII. Discussion

a. Cook Inlet

Organic Carbon.

The total organic carbon contents (Figure 2) vary from 0.06 to 1.30% with the 1979 spring samples, most of which are in the northern region, having carbon content below 0.6%. The Kachemak Bay stations have carbon content > 1.0%. This is expected from the inflow of terrigenous silt into the Bay. In general, stations farther from Kachemak and Kamishak Bays have relatively less organic carbon content (Tables 1,2,4,6 and 8). The values are typical of unpolluted, relatively coarse marine sediments.

Hydrocarbons

Alkanes: The total n-alkanes of the 1979 spring samples range generally from < 0.006 to 0.46 μg/g with an average of 0.17 μg/g, which is six times lower than the average of Kachemak Bay stations (Tables 1 and 2), sampled in 1977 (Annual Report 1978, RU #480). Station 17 is the exception, which has the highest hydrocarbon and n-alkane content (1 to 47 μg/g) in this suite of 1979 samples (Tables 8 and 9). Stations 22, 23 and 27 have very low lipid content and aliphatic and aromatic hydrocarbons, comparable to stations 215 and 217 collected in the summer of 1978 (Table 6). The former three stations are around Kalgin Island and close to station 265, sampled in the spring of 1978, which was found to be the richest in lipids and hydrocarbon content of all the stations in the north and central regions of the study area (Table 4). The differences in the hydrocarbon distributions in stations 22, 23, 27 and 265 are probably real, because replicate samples collected in a few stations had similar gravimetric and gas chromatographic data. Stations 43 and 37 in Kachemak Bay have the highest lipid, hydrocarbon and _n_-alkane content in the entire Cook Inlet area studied.

The analyses of samples from stations 204, 212, 234 and 390 in both spring and summer (1978) gave similar gravimetric and gas chromatographic results, indicating there might be no apparent seasonal trend in the hydrocarbon input to the sediments (Kaplan _et al._, 1979). Yet, the concentration of suspended matter was found to be higher in spring (Feely _et al._, 1978) than in summer of 1977.

The analyses of samples collected from 1976-1979 in the Cook Inlet region indicate the following: The hydrocarbon and _n_-alkane contents are highest in and around Kachemak Bay (Annual Report, 1978) and lowest in the central and upper parts (except stations 265 and 255) of Lower Cook Inlet. Stations near Shelikof Strait are next to Kachemak Bay in the order of abundance, whereas the Western part (Kamishak Bay) is moderately enriched with lipids. In general, the resolved _n_-alkanes follow the same trend. This distribution could be a result of net circulation pattern of the water and suspended matter, which is to the north along the eastern side of the inlet, and back again to the southwest into Shelikof Strait. This could result in the deposition of considerable organic matter produced in Kachemak and Kamishak Bays into Sheilkof Strait, which is consistent with our observations. Presumably, a significant fraction of the suspended matter containing hydrocarbons is buried in the sediments of the bays where they cannot be resuspended, which may explain why the bay sediments, especially in the narrow Kachemak region, are relatively rich in organic matter, in spite of the strong tidal currents.

The representative gas chromatograms are depicted in Figures 7 and 9. The n-alkanes range from C_{15} to C_{34}, with a maximum at n-C_{27} for most of the samples. A few samples maximize at n-C_{29}. Most of the gas chromatograms have flat baselines and lack the unresolved envelope, characteristic of oil pollution. In most of the samples, the odd/even ratio ranges from 1.5 to 7.4 (Tables 3, 5, 7 and 10). Generally, the stations along Kachemak and Kamishak Bays have odd/even ratios greater than 3, indicating larger terrigenous input compared to those in the central part of the inlet. The terrigenous input could get diluted with the inflowing Gulf of Alaska water in the central part. Terrigenous silt and anthropogenic contaminants if any, could be transported southwest along the Kamishak Bay from Upper Cook Inlet under the influence of tidal currents and coriolis forces (Feely et al., 1978). Stations 265 and 27, north of Kalgin Island (Figures 7 and 9), contain an n-alkane suite, overlapping a large unresolved complex mixture, with an odd/even ratio close to unity (1.06; 1.20), suggesting the input of weathered petroleum, although in station 27, the hydrocarbon content is much lower (Tables 5 and 10). This material could originate from petroleum production and transport in upper Cook Inlet. Yet, station 255, southeast of Kalgin Island collected in the same cruise, or stations 22, 23 and 25 around Kalgin Island, collected after one year, did not show any petrogenic input. This may indicate a localized source of hydrocarbon generation, or it could be related to seasonal variation of water circulation and particulate transport, although samples collected at the same station during different seasons from the other sites had similar hydrocarbon distribution.

Station 31 has the lowest odd/even ratio (0.87). However, the very low concentration of aliphatic hydrocarbons which approaches almost the limit of detection levels resulted in the low accuracy of this data.

Caution should therefore be taken in assigning any interpretations. Further, the gas chromatographic profile implies that this station is unpolluted.

Pristane and phytane range from 0.1 to 37 μg/g with pristane/phytane ratios from 1 to 12 (Tables 3, 5, 7 and 10). The only sample which has anomalous ratio is station 24 (44). In two of the stations, 388 and 398, around Afognak Island, the alkane of highest concentration is pristane. This was also observed in station 24 sampled in 1976 (Annual Report, 1978, RU#480). However, the nearby stations, UC200 and 13, collected in 1978 and 1979 do not show anomalously high levels of pristane. This may be due to a localized benthic community, a potential source of pristane.

A moderate level of unresolved complex mixture in the region between $\underline{n}$-C_{19} and $\underline{n}$-C_{25} is observed in stations UC100, 200, 300, 378 and 394, as shown for station 398 in Figure 7. Correspondingly, their odd/even ratios are also in the lower range (1.5 to 3.5), compared to other stations in the study area. Some of these samples were chosen for GC/MS analyses which could confirm the presence or absence of petroleum pollution in the area.

Alkenes: Gas chromatographic-mass spectrometric analysis revealed that most of the stations (except 265) contain normal and branched alkenes of molecular formula $C_{17}H_{34}$, $C_{18}H_{36}$, $C_{19}H_{38}$ and $C_{20}H_{40}$ in moderate amounts. These are most likely the same biogenic alkenes reported from many other marine environments (Farrington and Tripp, 1977). Pristene and phytene were also detected in many of the stations. In general, stations in the central part of Cook Inlet contain relatively more alkenes than those in Kamishak and Kachemak Bays.

Di- and triterpenoids: Diterpanes ranging from C_{19} to C_{26} have been identified by GC/MS. These are probably derived from resinous higher plants (Simoneit, 1977) C_{19} and C_{20} diterpanes are quite predominant in most of the samples and it is as abundant as n-C_{19} in stations 204 and 30. In station 217, they are the most abundant alkanes, preceded only by n-C_{29}, which is the most predominant component of the aliphatic fraction. Diterpenes are also relatively abundant. UC200 is the only sample which has a minor amount of diterpenoids (Figure 10).

The triterpenoids consist of 17β(H)hop-22(29)-ene (diploptene), hop-17(21)ene, 17β(H)-22,29,30 trisnorhopane and 17α and 17β(H)-hopane and the series of extended 17β(H)-hopanes ranging from C_{31} to C_{33}, with minor amounts of the 17α(H)-hopanes (Appendix). The stations which have one or more predominant 17α hopanes are 30 (C-31, Figure 10) and 265 (C-27 to C-35). In all the other stations, the most abundant triterpenoid is diploptene and the next most abundant homolog is C-27 (17ββ).

In general, the Alaskan sediments contain predominantly C_{27}, C_{30} and C_{31} ββ triterpanes. Several C_{30} triterpenes, other than diploptene, with one double bond, have also been detected. A $C_{30}H_{50}$ triterpene with base peak of 69 and a molecular ion of 410 a.m.u. (not a hopene) is present in most of the stations and is also as abundant as n-C_{30}. The reason for its occurrence is not understood. The presence of predominantly 17β(H) stereomers and of the di- and triterpenes which are present in living organisms indicates a recent biogenic origin for these compounds.

Minor amounts of a C_{28} triterpenoid were detected in four of the samples analyzed (17, 30, 200 and 204), which is not a bisnorhopane. It is most likely the same one as previously detected in Cook Inlet and Walvis Bay (Simoneit and Kaplan 1980) whose structure is not known.

Station 265 consists predominantly of 17α analogs from C_{27} to C_{35} (Fig. 10). The two diastereomers at position 22 are present as a homologous series in almost a 1:1 ratio, as in Southern California Bight samples which are contaminated with oil (Venkatesan *et al.*, 1980b). Thus, the triterpenoidal distribution is consistent with the *n*-alkane profile and indicates weathered petroleum pollution in station 265. Station 27, north of station 265, which has a similar gas chromatographic profile is also probably contaminated with petroleum from the same source.

A low level petroleum contamination was indicated in stations UC100, 200, 300 and 378, 394 and 398 around Shelikof Strait by the gas chromatographic profiles. However, GC/MS analyses of two of these samples (UC200, 394) do not show the presence of petroleum input. Unlike in station 265 (Figure 10) or any of the Southern California Bight samples, 17α analogs in these two stations are not the predominant homologs, although they are present in relatively greater abundance, compared to the other Alaskan sediments. The two diastereomers at position 22 were detected in only one or two of the homologs (C_{30} and/or C_{31}) in these two stations and their ratio is not close to unity.

Polycyclic aromatic hydrocarbons: Aromatic fractions (about 9 samples) were analyzed by GC/MS. The resolved PAH compounds range from .07 to 1.8μg/g sediment in these samples and are much less than those found in Beaufort Sea sediments (Kaplan *et al.*, 1979). Concentrations of selected PAH compounds from a few stations are presented in Table 18.

The concentrations are only approximate since they were computed based on the response factors of the individual components in an external standard mixture (supplied by NOAA) and not by coinjection. However, their order of magnitude of the concentrations should be reliable for comparative study. The peak identifications were from GC/MS analysis. Generally, naphthalene, phenanthrene, fluorene, fluoranthene, pyrene, chrysene, their alkyl-substituted homologs, biphenyl and considerable amount of binaphthyl are found in these samples. Benzo(e)pyrene is ubiquitous, although present only in traces. The parent PAH compounds are more abundant than their alkyl homologs. The C_3-substituted homologs are much less in abundance than the C_2 homologs and alkyl chain lengths with $> C_4$ are relatively rare in these sediments. This type of distribution suggests pyrolytic source (natural and/or anthropogenic) rather than input from crude oil (Coleman et al., 1973; Youngblood and Blumer, 1975). Long distance transport from anthropogenic sources through atmospheric fallout could be an important source of the pyrolytic arenes (Lunde and Bjorseth, 1977; Rahn et al., 1977; Laflamme and Hites, 1978). The samples which had a moderate amount of unresolved hump (398, UC200, UC300) also show similar distribution patterns, indicating that oil pollution may be absent in the area. The source of binaphthyl is unknown. A trace amount of p,p'-DDE and PCB were detected in station UC300, the reason for which is not known at present.

Perylene is found in the samples from trace to 50 ng/g. Like any other aliphatic or aromatic compound, perylene is also found at higher concentrations in Kachemak Bay (CB8-51 ng/g), Shelikof Strait (388, UC300, Table 18) than around Kamishak Bay or central part of Cook Inlet (203, 233). The origin of perylene in these sediments is not yet known. GC/Ms analysis of sediments from deep cores at different stations would give more information about the origin and precursors of perylene. Coronene and 1,12 benzoperylene have also been detected in these samples.

Retene and simonellite (Appendix) are present at levels below 18 ng/g in all the stations, the former being more abundant then the latter. These diterpenoid molecular markers are derived from terrigenous resinous plants (Simoneit, 1977). Cadalene, a sesquiterpenoid residue found in minor amounts in these sediments, can be of mixed marine and terrigenous origin. This compound has also been identified in petroleum (Bendoraitis, 1974) and in shales and siltstones from the North Atlantic Ocean (Simoneit and Mazurek, 1979a,b).

b. Norton Sound

Organic Carbon

Total organic carbon content (Tables 11, 13 and 15) ranges from 0.12 to 1.30% and is similar to Cook Inlet, Beaufort Sea and other uncontaminated marine sediments. The 1979 summer samples (Table 15) have carbon content below 0.9%. Sediments in the open ocean have a slightly lower carbon content in general than those nearshore. Apparently, the organic carbon content in this region is generally related to the distance from the presumed terrigenous source, the Yukon River.

Hydrocarbons

Alkanes: Stations 1,5 and 7 (collected in 1979) and 49, 131 and 137 (collected in 1976), which are nearshore in the Sound, have the highest lipid and hydrocarbon contents and *n*-alkanes (Tables 11, 13, 15 and 16). The lipid and *n*-alkane contents gradually decrease along the northeast to southwest transect from stations 1, 131 in the Bay through 121, 125 to stations 33A and 47A in the open ocean. The southwest stations 154, 156 and 13, which are near the mouth of the Yukon River, are richer in organic content and n-alkanes. These may have been derived from terrigenous silt resuspended from the Yukon prodelta which extends across the mouth of the Sound. Further south, around stations 162 and 29A and west, offshore in stations 39 to 44, 33A and 47A, the terrigenous detritus is diluted by open ocean sedimentation. The northern region of Norton Sound seems to be poorer in lipid content and also n-alkanes (stations 40, 70, 88 and 105), possibly because there are no major sediment sources, i.e., rivers, near the area and the longshore current movement and sediment transport are directed north toward the Bering Strait.

Examples of gas chromatograms of hexane fractions from a few stations are presented in Figures 8 and 9. The odd carbon n-alkanes from C_{23} to C_{31} are predominant with a maximum at n-C_{27}, indicating land plants to be the major contributors of hydrocarbons. Hydrocarbons from marine plankton in the Norton Sound region is very low compared to the stations outside the Bay. Almost all the gas chromatograms of alkanes exhibit a flat base line, suggesting a "clean" environment. The odd/even ratio varies from 2.80 to 11.20 in the area, characteristic of predominant terrigenous input, masking the marine biogenic lipid contribution (Tables 12, 14 and 17).

Pristane and phytane are found in trace amounts in a few stations. The minor quantities detected suggest that zooplankton species rich in pristane may be impoverished in this area.

Several samples from stations 47, 172, 174 (1976), 14 to 17 (1977), and 18 and 22 (1979), collected near the location where seepage was suspected, show alkane distribution patterns which are not characteristic of petroleum. The gas chromatograms of their aliphatic fractions have flat baseline and consist of biogenic n-alkanes derived from terrestrial and marine sources. Station 17 was chosen for GC/MS analysis to confirm the absence of petroleum input.

Alkenes: Several stations were found to contain alkenes such as $C_{17}H_{34}$, $C_{18}H_{36}$ and a cyclic alkene, $C_{25}H_{46}$. Pristene and phytene are also found in significant amounts. In general, stations from offshore contain more alkenes than those nearshore, indicating that these alkenes could be of marine origin.

Di- and triterpenoids: Diterpanes are present in minor amounts and range from C_{19} to C_{23} (Fig. 10). Diterpenes are also relatively less abundant and range from C_{21} to C_{26} except in a few stations like 17 where they are more dominant than diterpanes. These are most probably of biogenic origin.

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) as the most predominant component (Figure 10, Appendix). The other predominant homologs are the C_{27} triterpenoid, 17β(H)-22,29,30-trisnorhopane, the C_{30} homolog, 17β(H),21β(H)-hopane and the C_{31} homolog. The series of extended 17β(H)-hopanes ranging from C_{31} to C_{33}, with only minor amounts of the 17α(H)-hopanes is present. Several C_{30} triterpenes, with a double bond, in addition to diploptene have also been detected. A $C_{30}H_{50}$ triterpane with a base peak 69 and a molecular ion 410 a.m.u. (not a hopene) is found in most of the stations and is also as abundant as n-C_{30}. The reason for its occurrence is not understood. The 17α isomers are much less in abundance compared to Cook Inlet stations. The presence of minor quantities of 17α(H) stereomers and only one C-22 diastereomer (in hopanes > C_{31}) suggest the absence of input from petroleum components (Dastillung and Albrecht, 1976; Simoneit and Kaplan, 1980; Venkatesan et al., 1980b). The C_{28} triterpenoid present in small amounts in Cook Inlet samples is absent in these Norton Sound stations. The triterpenoidal distribution in stations 17, 25, 43, 131 and 169 has been discussed previously by Venkatesan et al. (1980a). It was shown that station 17, believed to be near a suspected petroleum seep, is not contaminated with petroleum based on the gas chromatographic analysis and the triterpenoidal distribution.

Polycyclic aromatic hydrocarbons: The resolved polycyclic aromatic hydrocarbons (PAH) are < 1.0μg/g sediment in these stations and much less than those found in Beaufort Sea sediments (Kaplan et al., 1979). Concentrations of selected PAH compounds are presented in Table 18. Generally, biphenyl, naphthalenes, phenanthrene, fluorene, fluoranthene, pyrene, chrysene, their alkyl substituted homologs and binaphthyl have been detected by GC/MS analyses. Benzo(e)pyrene has also been found in all the samples. In general, the parent PAH compounds are more abundant than their alkyl homologs in the surficial sediments, indicating pyrolytic sources rather than input from crude oil shales (Coleman et al., 1973; Youngblood and Blumer, 1975). On the contrary, phenanthrene, dimethyl phenanthrene, fluoranthene and benzo(e)pyrene have been found to increase generally with depth, when a core sample up to 90 cm from station 5 was analyzed for PAH as part of another detailed investigation (to be published). The three compounds except dimethylephenanthrene are believed to be mainly combustion (anthropogenic or natural) products. Pyrolysis produces a wide range of PAH, which are more frequently unsubstituted. The dimethylphenanthrenes present at concentrations comparable to phenanthrene itself at depths could be of diagenetic origin. Dehydrogenation of steroids, which are relatively abundant in Recent sediments, has been suggested to generate phenanthrenes possibly by microbial degradation (Wakeham _et al_., 1980). The observation that fluoranthene and benzo(e)pyrene contents increase with depth strongly support the natural pyrolytic source for these compounds, probably from forest fires, in the preanthropogenic period, in addition to phenanthrene also being derived from diagenetic pathways. Therefore, the surficial sediments in Alaska could receive their PAH compounds from all the three sources, namely anthropogenic and natural combustion and diagenetic alteration of steroids.

In most of the samples, perylene is 10-20 times greater than phenanthrene, which occurs commonly in marine sediments. Perylene is relatively more abundant (i.e., 10 ng/g in station 131; 34 ng/g in station 5) in nearshore sediments than in offshore sediments (i.e., traces in stations 35, 166 and 49). Perylene could be generated _in situ_ by transformation of some terrestrial precursor compounds (Bergmann _et al_., 1964). 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 (Annual Report, April 1979, RU #480). Kodiak Shelf is noted for its high biological productivity where marine hydrocarbons predominate over terrestrial hydrocarbon components. Thus, our data indicate that it is most likely the terrigenous precursor which contributes to the generation of perylene in Alsaka, rather than a marine precursor as suggested by Wakeham _et al_. (1979) from their study of perylene in two Namibian 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 (nearshore, where terrestrial input is considerable) from 0-2 to 90 cm at 5-10cm 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 the shape of this 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 Navarin Basin or Kodiak Shelf (terrigenous source minimal) would be helpful in confirming whether perylene in Alaskan Sediments is derived from a terrestrial or marine origin.

Coronene and 1,12 benzoperylene have also been detected in these samples.

Retene and simonellite (Appendix) are present at levels below 9 ng/g in all the stations, the former being more abundant than the latter. These diterpenoids are molecular markers derived from terrigenous resinous plants (Simoneit, 1977). Cadalene, a sesquiterpenoid residue found in minor amounts in these sediments can be of mixed marine and terrigenous origin.

VIII. Conclusions

Cook Inlet

The alkanes in sediments of the study area generally show a bimodal distribution of biogenic origin, typical of a mixture of marine and terrestrial hydrocarbons. An odd-carbon predominance of n-alkanes characteristic of terrigenous plants is evident in most stations, suggesting the influx of major river waters in the area.

A few stations around Shelikof Strait and Barren Islands show a moderate level of unresolved complex mixture, which could result from petroleum leakage through surface faults around the Barren Islands and off Cape Douglas. The GC/MS data of these samples rule out the presence of oil input and confirm the biogenic origin of the hydrocarbons. Exceptions are stations 265 and 27 north of Kalgin Island, which show a typical weathered petroleum distribution of n-alkanes. The triterpenoidal residue (265) 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.

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. Perylene, 1,12 benzoperylene and coronene, whose origin is still debatable have been detected in all sediment extracts. No significant trend in the concentration of perylene with distance from the presumed terrigenous sources is observed.

Norton Sound

The alkanes in these sediments are of biogenic origin, consisting of a mixed input from marine and terrestrial environment. The terrigenous input is apparently diluted with marine contribution gradually from the nearshore to the open ocean. Sediments from the Yukon prodelta are the richest in hydrocarbons. The northern part of Norton Sound seems to be impoverished in hydrocarbons, possibly because there are no major rivers contributing to terrigenous silt.

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

Polycyclic aromatic hydrocarbons in Norton Sound surficial sediments show pyrolytic origin. A core analyzed from station 5 up 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 in this core 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 either.

IX. Needs for Further Study

Two samples north of Kalgin Island show oil pollution which could be from drilling operations in the Upper Cook Inlet. Frequent and periodic sampling and analyses of sediments is required in the immediate vicinity of these drilling sites (i.e., Upper Cook Inlet); this will help in monitoring more acute environmental changes resulting from the drilling activities and the concomittant increased marine traffic. Sampling from north to central parts of Cook Inlet at regular time intervals could give an insight as to how far the oil drilling operations impart pollution in the marine environment.

Any area which is to be leased for oil drilling should be sampled and analyzed for hydrocarbon content to provide a background level before oil exploration.

X. Fourth Quarter (January-March, 1980)

Summary of Operations

Laboratory Activity: GC/MS analyses of selected samples from Cook Inlet and Norton Sound (1979 cruises) have been completed. The results have been incorporated in this report.

A milestone chart is enclosed.

XI. REFERENCES

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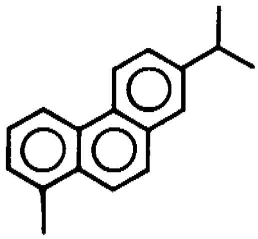
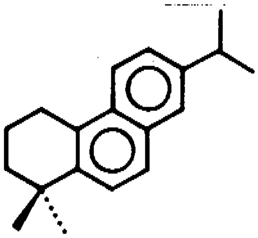
Appendix: Structures cited in the text.



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



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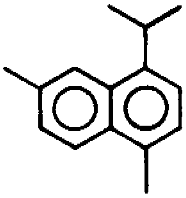
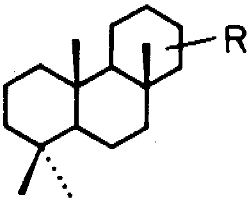
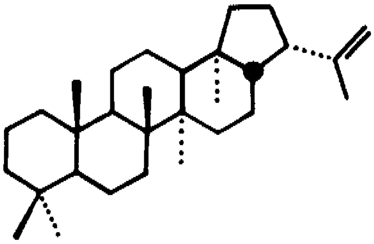


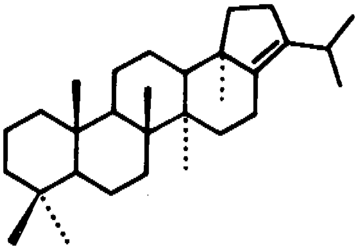
III. cadalene, $C_{15}H_{18}$



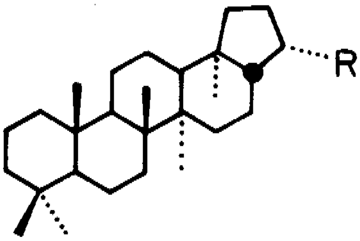
IV. extended diterpanes $R=C_2H_5-C_{12}H_{25}$



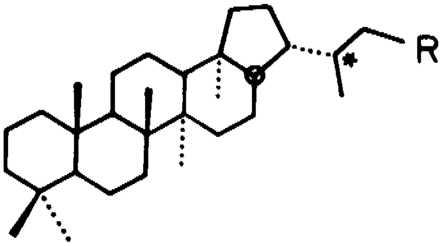
V. diploptene, $C_{30}H_{50}$



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



VII. 17β(H), 21β(H)-hopanes $R=H, C_2H_5, C_3H_7$



VIII. extended 17α(H), 21β(H)-hopanes $R=CH_3-C_5H_{11}$

Table 1. Gravimetric Data for Cook Inlet Sediment Samples (1976 Cruises) (1)

Station	Lat (N)	Long (W)	Depth (m)	Rating(2)	Total Carbon %	Organic Carbon %	Weight(3) (gr)	Non Saponi-(4) fiable Fr. (µg/g)	Aliphatic Fr. (µg/g)	Aromatic Fr. (µg/g)
8(5)	59°11.38'	153°44.10'	36	2	1.57	0.47	-	-	-	-
14	59°30.6'	152°46.6'	61	4	0.20	0.09	133.23	3.00	0.435	0.480
15(5)	59°31.8'	152°54.0'	45	4	0.26	0.19	-	-	-	-
16	59°23.2'	153°06.0'	48	4	0.44	0.15	152.03	18.62	0.868	0.842
17(5)	59°20.7'	152°53.5'	74	4	0.46	0.29	167.37	-	-	-
18	59°11.90'	152°43.00'	122	3	0.91	0.65	166.33	22.43	0.661	0.992
19	58°56.25'	152°23.36'	75	4	0.44	0.26	157.83	28.51	0.792	0.919
23	58°55.70'	152°34.30'	170	2	0.39	0.17	140.26	22.96	0.563	1.176
24	58°58.49'	152°31.11'	147	4	0.73	0.43	111.45	179.36	2.306	4.845
26	59°08.1'	152°22.1'	119	4	0.82	0.37	151.15	6.42	0.390	0.476
27	59°26.30'	152°20.70'	74	3	0.69	0.14	155.19	1.74	0.509	0.180
28	59°21.35'	152°25.90'	78	2	0.83	0.15	149.33	5.93	0.904	0.603
29	59°14.98'	152°28.15'	89	3	3.08	0.65	142.29	23.83	1.546	1.441
30	59°16.65'	152°21.70'	91	3	2.12	0.35	165.10	2.51	0.121	0.363
33	59°26.35'	152°12.44'	50	4	3.32	0.47	152.27	13.40	0.348	0.585
34	59°36.5'	151°52.0'	28	3	1.23	0.86	144.97	71.74	5.553	3.704
37	59°45.9'	152°13.8'	56	1	1.44	0.37	-	-	-	-
39	59°40.75'	151°57.15'	35	1	1.23	0.92	-	-	-	-
41	59°36.25'	151°56.00'	30	3	1.44	0.69	146.07	6.57	0.815	0.808
42	59°36.20'	151°45.6'	30	2	2.60	0.92	165.41	60.58	1.814	3.265
43	59°36.63'	151°22.07'	52	4	2.68	1.47	131.02	254.54	16.104	23.813
44	59°36.25'	152°29.90'	65	4	0.93	0.15	-	-	-	-
48	60°00.0'	152°24.6'	45	2	2.24	0.52	95.84	75.23	4.539	2.494

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(1) All samples except 37, 39 and 44 are 0-2cm. Samples 37, 39 and 44 are bulk samples and were not extracted; (2) Quality of sample recovery based on a subjective scale of 5 (excellent) to 1 (poor); (3) Extracted (salt-free) dry sediment; (4) No elemental sulfur was detected in this group of samples; (5) Samples 8, 15 and 17 were analyzed after freeze-drying and were found to be contaminated.

Table 2. Gravimetric Data for Cook Inlet Sediment Samples (1977 Cruise)

Station	Lat (N)	Long (W)	Depth (m)	Total Carbon %	Organic Carbon %	Weight(1) (gr)	Non Saponifiable Fr.(2) (μg/g)	Aliphatic Fr. (μg/g)	Aromatic Fr. (μg/g)
27	59°15.0'	153°29.0'	38	1.13	0.40	125.35	45.31	3.191	1.835
37	59°41.2'	151°12.8'	33	1.38	0.36	100.62	160.11	8.149	6.621
40A	59°33.9'	151°44.5'	82	1.03	0.66	127.74	45.87	2.583	2.583
40B	59°34.1'	151°43.5'	82	0.97	0.78	137.52	71.77	3.345	4.799
41	59°32.9'	151°53.4'	46	1.03	0.31	142.75	30.47	1.471	1.681
62A	59°50.4'	152°56.5'	16	0.87	0.44	116.45	79.43	5.582	3.349
207	58°59.9'	152°52.8'	165	0.72	0.53	131.34	55.43	2.969	4.188
227A(3)	59°33.6'	151°36.5'	88	1.51	1.30	78.05	159.51	7.687	16.784
227B(3)	59°33.6'	151°36.5'	88	1.39	1.07	88.52	148.78	7.795	9.602

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(1) Extracted (salt free) dry sediment.
(2) No elemental sulfur was detected in this group of samples.
(3) Two samples from exactly the same location.

Table 3. Characteristic Parameters for Cook Inlet Hydrocarbons (1976 and 1977 Cruises)

Station No.	Non Saponifiable fr. / org. carbon ($\times 10^{4}$)	Alkanes / org. carbon ($\times 10^{4}$)	Pristane / $n\text{-}C_{17}$	Phytane / $n\text{-}C_{18}$	Pristane / Phytane	Odd / Even
14	15.0	2.2	0.8	0.3	2.4	1.5
16	124.1	5.8	1.0	0.2	3.7	>2.8
18	34.5	1.0	2.9	0.2	11.0	2.4
19	109.7	3.1	1.9	0.2	9.4	1.5
23	135.1	3.3	2.3	0.3	7.1	1.7
24	417.1	5.4	14.7	0.3	44.5	2.0
26	17.4	1.1	1.2	0.3	3.7	1.6
27	12.4	3.6	0.8	0.2	3.0	1.3
28	39.5	6.0	4.6	0.3	7.1	1.4
29	36.7	2.4	6.4	0.2	17.6	1.8
30	7.2	0.4	1.6	0.3	2.9	1.6
33	28.5	0.7	1.8	0.2	7.1	1.3
34	83.4	6.5	0.8	0.2	4.0	>3.3
41	9.5	1.2	0.8	0.2	3.9	4.1
42	65.9	2.0	1.3	0.2	4.8	>2.7
43	173.2	11.0	2.3	0.4	6.0	>2.9
48	144.7	8.7	0.9	0.2	4.2	3.2
27'	113.3	8.0	0.7	0.2	4.6	>3.3
37'	444.8	22.6	1.7	0.3	10.1	>4.3
40A	69.5	3.9	1.1	0.2	5.0	>3.4
40B	92.0	4.3	1.1	0.2	6.1	3.6
41'	98.3	4.8	0.9	0.2	5.3	3.0
62A	180.5	12.7	0.7	0.2	3.9	2.7
207	104.6	5.6	1.6	0.2	6.8	2.3
227A	122.7	5.9	0.9	0.3	4.6	>3.1
227B	139.1	7.3	1.0	0.3	4.7	3.9

Table 4. Cook Inlet Sediment Samples (1978 - Spring Cruise)

Station* No.	Latitude (N)	Longitude (W)	Depth (m)	Total Carbon (%)	Org. Carbon (%)	Nonsapon. Fr. (ppm)	Aliphatic Fr. (ppm)	Aromatic Fr. (ppm)
201	59°12.5'	153°52.6'	22	0.61	0.94	39.09	4.49	3.24
203	59°05.8'	153°29.5'	38	0.55	0.80	13.81	1.24	1.05
204	59°13.7'	153°39.4'	34	0.45	0.69	44.51	2.12	1.91
211	59°26.1'	153°37.5'	19	0.33	1.26	20.41	1.27	1.26
212	59°32.6'	153°20.9'	26	0.42	0.69	20.09	1.58	1.42
213	59°29.9'	153°14.0	33	0.59	0.65	16.06	1.14	1.27
214	59°17.9'	153°13.2'	53	0.45	0.54	25.83	1.41	1.35
233	59°48.9'	152°55.6'	14	0.41	0.58	32.24	2.27	2.06
233R	59°48.9'	152°55.6'	14	-	-	32.67	2.70	2.45
234	59°38.2'	152°56.4'	38	0.35	0.93	13.86	0.99	0.61
245	60°07.8'	152°16.7'	46	0.42	0.63	11.01	1.17	1.01
247	59°58.3'	152°34.1'	20	0.20	0.41	7.97	1.02	0.87
255	60°18.8'	151°37.0'	42	0.25	0.78	57.07	1.45	14.10
265	60°34.7'	151°49.5'	16	0.15	0.35	95.09	28.81	8.74
370	58°17.0'	154°02.6'	112	0.71	0.91	51.76	3.09	3.66
380	58°38.4'	153°26.0'	57	0.63	0.83	24.85	2.91	1.72
390	58°53.5'	153°11.0'	170	0.47	0.61	27.77	2.13	2.56
394	58°51.3'	153°08.2'	171	0.72	1.11	42.59	2.06	3.83

* All samples are 0-2 cm; R = replicate

Table 15. Characteristic Parameters for Cook Inlet Hydrocarbons (Spring, 1978)

Station	Nonsap. fr. / Org. C (x 10^4)	Alkanes / Org.C (x10^4)	Pr. / n-C_{17}	Phy. / n-C_{18}	Pr. / Phy.	Odd / Even
201	64.08	1.74	0.98	0.39	3.34	5.15
203	25.11	0.44	1.07	0.24	2.66	5.66
204	98.91	1.02	0.97	0.27	3.01	4.06
211	61.85	1.45	1.22	0.37	3.34	4.36
212	47.83	0.50	1.34	0.26	2.56	3.74
213	27.22	0.40	0.95	0.28	2.86	4.93
214	57.40	0.62	0.97	0.20	3.66	3.67
233	78.63	1.17	1.17	0.21	4.96	3.93
233R	--	--	1.06	0.22	3.48	3.39
234	39.60	0.09	0.87	0.20	4.09	2.09
245	26.21	0.29	1.25	0.22	2.50	3.99
247	39.85	0.55	2.52	0.57	2.79	2.47
255	228.28	0.48	1.33	0.32	4.87	3.02
265	633.93	3.60	0.55	0.46	0.77	1.06
370	72.90	2.07	1.29	0.33	4.28	4.03
380	39.44	0.38	1.45	0.28	4.99	5.65
390	59.09	0.64	1.85	0.33	4.87	3.48
394	59.15	0.92	1.76	0.34	4.88	2.03

R = replicate

Table 6. Cook Inlet Sediment Samples (1978 - Summer Cruise)

Station No.*	Latitude (N)	Longitude (W)	Depth (m)	Total C (%)	Org. C (%)	Nonsapon. Fr. (µg/g)	Aliphatic Fr. (µg/g)	Aromatic Fr. (µg/g)
204	59°13.8'	153°39.7'	33	0.67	0.82	25.12	1.42	1.48
205	59°06.7'	152°40.4'	138	0.42	1.23	38.88	1.14	1.06
206	59°09.5'	153°06.5'	90	0.38	0.60	26.65	0.88	1.86
212	59°32.0'	153°21.0'	24	0.61	1.10	23.99	2.14	1.54
215	59°22.4'	152°48.3'	78	0.49	0.51	7.73	0.48	0.63
217	59°21.7'	152°22.8'	71	0.25	0.34	16.51	0.44	0.42
234	59°38.3'	152°55.7'	39	0.30	1.02	34.09	1.94	0.96
378	58°01.9'	153°28.2'	92	--	--	38.10	1.26	2.61
384	58°30.5'	153°14.5'	176	0.73	0.89	48.39	2.00	3.66
388	58°27.4'	152°56.1'	214	1.16	1.57	108.60	5.81	9.97
390	58°53.6'	153°10.8'	165	0.57	0.80	32.15	1.97	1.89
398	58°49.3'	152°12.0'	--	0.44	6.22	84.04	0.07	2.48
UC100	59°01.2'	152°28.8'	150	0.31	1.02	21.67	0.99	0.75
UC200	59°01.0'	153°32.4'	150	0.38	1.56	33.03	1.24	1.35
UC300	58°28.3'	153°45.6'	101	0.69	1.02	94.82	4.55	5.16
CB8	59°39.4'	151°16.6'	--	0.93	1.53	117.95	13.08	7.24
CB8R	59°39.4'	151°16.6'	--	--	--	90.05	9.43	7.68

* All samples are 0-2 cm.

R = replicate

TABLE 7. Characteristic Parameters for Cook Inlet Hydrocarbons (Summer, 1978)

Station	Nonsap. / O.C (x 10^4)	n-Alkanes / O.C. (x 10^4)	Pristane / n-C_{17}	Phytane / n-C_{18}	Pristane / Phytane	Odd / Even
204	37.49	0.39	0.96	0.82	1.10	4.78
205	92.57	0.34	1.64	0.37	3.02	2.36
206	70.13	0.27	3.09	0.27	6.67*	3.25
212	39.33	0.59	0.94	0.28	3.19	4.60
215	15.78	0.13	1.38	0.35*	2.0*	2.67
217	66.04	0.12	4.55	0.25	12.71	2.34
234	113.63	1.02	0.16	0.21	0.86	1.23
378	--	--	2.24	0.37	5.19	3.47
384	66.29	0.35	2.19	0.30	6.66	1.50
388	93.62	0.30	3.45	0.34	10.09	1.91
390	56.40	0.57	1.92	0.36	5.39	3.67
398	191.00	0.19	2.56	0.32	8.08	1.52
UC100	69.90	0.17	1.30	0.28	2.58	1.89
UC200	86.92	0.27	3.19	0.32	8.28	1.88
UC300	137.42	1.61	1.87	0.31	5.30	2.88
CBI 8	126.83	1.48	1.20	2.10	1.58	4.59
CBII 8R	96.83	1.79	1.32	0.52	2.04	4.81

* Approximate values based on measured peak heights.

R = replicate

Table 8. Cook Inlet Sediment Samples (1979 - Spring Cruise)

Station[1] No.	Latitude (N)	Longitude (W)	Depth (m)	Rating[2]	Organic C (%)	Nonsaponifiable[3] fr. (μg/g)	Aliphatic fr. (μg/g)	Aromatic fr. (μg/g)
11	58°46.3'	153°9.8'	190	5	0.44	29.96	2.01	1.34
12	58°48.5'	153°16.3'	28	1	0.12	22.43	1.36	2.13
13	58°47.4'	152°41.5'	200	3	0.37	14.67	1.11	5.65
16A	∿ 60°12.0'	∿ 152°35.0'	--	--	--	67.74	1.52	0.66
16B	∿ 60°13.0'	∿ 152°45.0'	--	--	--	38.46	3.51	4.19
17	60°12.4'	152°54.0'	45	4	0.58	35.48	3.66	4.20
18	58°58.8'	151°53.2'	180	4	0.33	26.65	0.43	3.04
19	59°57.9'	151°54.0'	30	5	0.23	15.25	0.53	1.08
22	60°23.2'	152°05.7'	35	--	--	6.71	1.99	0.28
23	60°30.8'	152°00.0'	35	--	0.12	1.16	0.54	0.87
25	60°30.2'	151°48.8'	10	--	0.41	6.50	0.96	0.73
27	60°41.5'	151°44.4'	20	--	0.06	3.83	0.80	0.27
30	59°21.8'	152°02.8'	56	2	--	34.68	0.92	1.01
31	59°10.8'	151'58.6'	106	3	0.15	27.22	0.48	0.48

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[1] Samples are 0-2cm

[2] Quality of sample recovery based on a subjective scale of 5 (excellent) to 1 (poor)

[3] No elemental sulfur detected.

Table 9. Aliphatic Hydrocarbon Concentrations (ng/g) in Cook Inlet Sediment Samples (1979-Spring Cruise)

Station*	n-C_{15}	n-C_{16}	n-C_{17}	Pristane	n-C_{18}	Phytane	n-C_{19}	n-C_{20}	n-C_{21}	n-C_{22}	n-C_{23}
11	n.d.	0.8	1.8	3.8	2.4	0.6	3.7	9.8	21.1	5.1	12.0
12	1.1	2.0	4.5	3.9	4.1	1.0	6.5	7.8	11.5	8.2	24.0
13	n.d.	n.d.	0.8	1.9	n.d.	n.d.	2.9	3.1	6.0	3.4	4.5
16A	n.d.	n.d.	0.6	0.8	0.6	0.4	0.6	0.8	1.8	1.0	2.6
16B	1.1	1.4	2.8	3.2	2.6	n.d.	3.4	3.6	15.2	7.3	21.7
17	8.5	10.0	32.5	24.0	20.3	6.8	33.4	29.2	57.0	40.8	137.7
18	n.d.	n.d.	n.d.	0.2	0.5	n.d.	1.1	1.9	2.4	2.4	3.6
19	n.d.	n.d.	n.d.	n.d.	0.4	n.d.	1.2	10.7	40.6	2.9	10.5
22*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
23*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
25	n.d.	0.4	1.3	1.0	1.4	0.4	3.5	2.6	2.7	4.7	16.6
27	0.3	0.5	0.9	0.5	0.9	0.5	0.7	0.8	0.7	0.7	1.0
30	n.d.	0.7	1.2	1.5	1.1	0.3	1.7	5.0	12.1	2.0	5.1
31	n.d.	n.d.	0.3	0.6	0.3	n.d.	0.3	2.5	0.3	0.3	0.5

Station*	n-C_{24}	n-C_{25}	n-C_{26}	n-C_{27}	n-C_{28}	n-C_{29}	n-C_{30}	n-C_{31}	n-C_{32}	n-C_{33}	n-C_{34}
11	5.3	21.2	5.8	48.2	5.6	38.2	3.7	26.4	2.6	8.2	0.6
12	10.7	43.6	11.4	132.8	10.0	66.6	6.0	51.3	1.3	16.5	2.1
13	3.8	5.9	4.1	10.6	4.4	13.7	4.6	18.0	4.0	5.2	1.4
16A	1.7	8.4	1.7	32.1	1.4	5.2	n.d.	2.0	n.d.	n.d.	n.d.
16B	10.3	52.0	13.8	139.8	12.7	79.4	6.8	53.7	5.1	20.1	2.1
17	65.6	186.1	46.2	319.1	36.2	201.4	37.6	133.6	15.3	52.1	4.5
18	2.9	3.5	2.3	4.2	2.2	4.0	0.9	2.9	0.7	1.2	n.d.
19	5.3	17.5	5.6	33.0	5.2	42.4	11.5	28.2	8.8	9.3	2.8
22*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
23*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
25	8.4	27.8	7.0	53.0	5.5	33.8	6.0	19.7	1.9	6.2	1.2
27	0.7	0.6	0.5	0.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
30	2.6	6.6	2.8	11.4	2.4	13.2	1.2	11.0	2.3	2.9	n.d.
31	0.3	0.6	1.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detected

* Concentrations at these stations all too low to be detected.

Table10. Characteristic Parameters for Cook Inlet Sediment Samples (1979-Spring Cruise)

Station	Non-saponifiable fr. / Organic Carbon (x10^4)	Alkanes / Org. C. (x10^4)	Pristane / n-C_{17}	Phytane / n-C_{18}	Pristane / Phytane	Odd / Even
11	68.09	0.66	2.09	0.29	6.53	4.32
12	186.92	4.56	0.88	0.24	3.50	5.62
13	39.65	0.38	2.28	n.d.	n.d.	2.35
16A	--	--	1.41	0.67	2.00	7.42
16B	--	--	1.12	n.d.	n.d.	5.92
17	61.17	3.96	1.16	0.34	3.53	3.77
18	80.76	0.14	n.d.	n.d.	n.d.	1.66
19	66.30	1.49	n.d.	n.d.	n.d.	4.96
22	--	--	n.d.	n.d.	n.d.	n.d.
23	9.67	n.d.	n.d.	n.d.	n.d.	n.d.
25	15.85	0.67	0.92	0.29	2.50	4.19
27	63.83	0.20	0.54	0.56	0.93	1.20
30	--	--	1.24	0.25	5.31	3.24
31	181.47	0.08	2.02	n.d.	n.d.	0.87

n.d. = not detected

Table 11. Norton Sound Sediment Samples (1976 Cruises).

Station[1]	Lat (N)	Long (W)	Depth (m)	Rating[2]	Total Carbon %	Organic Carbon %	Weight[3] (gr)	Non Saponifiable Fr.[4] (μg/g)	Aliphatic Fr. (μg/g)	Aromatic Fr. (μg/g)
47	64°25'	165°29.90'	15	3	1.02	0.93	104.42	77.95	9.644	7.470
49	63°27.77'	163°52.57'	10	3	1.40	1.12	84.74	199.91	24.782	4.130
70	65°6.13'	167°40.40'	31	4	0.37	0.31	153.58	8.47	2.207	6.186
88B	65°46.01'	168°05.51'	9	1	0.84	0.53	70.58	119.58	3.953	5.682
105	64°49.00'	166°44.00'	15	2	1.29	0.93	124.13	18.05	1.845	0.886
121	63°52.99'	163°01.34'	20	0	1.37	1.18	-	-	-	-
125	64°00.12'	162°24.60'	18	3	0.98	0.55	127.95	51.97	0.141	2.438
131	64°23.60'	161°49.27'	17	4	0.96	0.44	97.07	135.47	9.035	2.988
137	63°40.89'	161°13.29'	14	3	-	-	72.61	221.32	17.766	4.531
147	63°47.00'	163°41.50'	17	2	0.87	0.33	111.23	104.38	6.779	2.293
152	64°05.00'	164°26.50'	22	2	0.50	0.35	-	-	-	-
154	63°45.08'	164°37.43'	18	2	1.25	0.99	86.08	209.69	16.264	4.182
156	63°28.39'	165°19.28'	17	3	1.40	1.30	97.63	104.89	7.119	5.511
157S	63°18.11'	165°03.26'	8	1	1.16	0.82	-	-	-	-
160S	62°54.50'	165°08.15'	10	1	2.40	0.70	-	-	-	-
162	63°02.80'	165°53.99'	21	3	1.26	0.92	120.88	45.09	2.316	2.316
166S	63°14.62'	167°02.21'	26	1	1.54	1.16	161.30	39.99	1.097	0.756
168S	63°26.25'	166°29.64'	28	1	1.33	1.10	150.44	57.03	3.191	2.180
169S	63°34.79'	166°05.53'	27	1	1.09	0.33	137.47	117.12	2.619	4.001
170S	63°41.72'	165°45.81'	25	2	0.87	0.52	128.86	62.86	4.439	2.208
172S	64°00.10'	165°29.25'	20	1	1.36	0.87	115.55	80.14	10.904	3.773
174S	64°21.15'	165°00.40'	36	2	1.48	0.82	160.13	53.21	3.872	2.005

1. Samples are 0-2 cm except B- Bulk and S- Surface.
2. Quality of sample recovery based on a subjective scale of 5 (excellent) to 1 (poor).
3. Extracted (salt free) dry sediment.
4. No elemental sulfur was detected in this group of samples.

Table 12. Characteristic Parameters for Norton Sound Hydrocarbons (1976)

Station	$\frac{\text{Non. Sap. Fr.}}{\text{Org. C}}$ (x 10^4)	$\frac{\text{n-alkanes}}{\text{Org. C}}$ (x 10^4)	$\frac{\text{Pristane}}{\text{n-C}_{17}}$	$\frac{\text{Phytane}}{\text{n-C}_{18}}$	$\frac{\text{Pristane}}{\text{Phytane}}$	$\frac{\text{Odd}}{\text{Even}}$
47	83.82	3.74	0.38*	0.20*	2.00*	5.38
49	178.49	5.08	0.30*	0.14*	1.50*	6.06
70	27.32	0.03	2.66	0.25	8.00	1.65
88	225.62	1.30	2.03	3.80	2.14	4.11
105	19.41	0.08	n.d.	n.d.	n.d.	11.21
125	94.49	1.25	0.40	0.19	2.00	4.02
131	307.89	16.32	n.d.	n.d.	n.d.	2.80
137	--	--	0.64*	0.18*	3.00*	4.07
147	316.30	6.79	0.60*	0.36*	1.80*	2.85
154	211.81	5.51	0.64*	0.17*	3.60*	5.69
156	80.69	3.89	0.50*	0.19*	2.67*	5.57
162	107.36	0.49	0.50	0.23*	2.00*	4.75
166	34.47	0.14	0.67	0.23*	4.00*	5.16
168	51.85	1.35	0.58*	0.17*	3.50*	5.26
169	354.91	2.89	0.58	0.23	3.60	4.47
170	120.88	4.95	0.46*	n.d.	n.d.	5.80
172	92.11	3.33	n.d.	n.d.	n.d.	4.70
174	64.89	2.19	2.00*	2.20*	6.00*	4.50

* Approximate values based on measured peak heights

Table 13 Norton Sound Sediment Samples (1977 Cruises).

Station[1]	Latitude (N)	Longitude (W)	Depth (m)	Rating[2]	Total C(%)	Org. C (%)	Weight[3] (gr)	Non-Saponi-[4] fiable Fr. (μg/g)	Aliphatic Fraction (μg/g)	Aromatic Fraction (μg/g)
34 0-2cm	64°52.30'	167°39.65'	32	3	0.35	0.12	160.71	4.72	0.809	0.678
35 0-2cm	65°14.90'	167°45.70'	52	3	0.67	0.59	121.01	100.74	2.248	1.132
39 surf.	64°07.09'	171°18.00'	34	2	1.54	0.38	174.11	7.98	0.643	0.247
41 surf.	64°02.75'	171°36.10'	27	2	0.91	0.44	171.15	50.83	2.466	0.847
42 surf.	63°58.40'	169°22.65'	39	3	1.76	0.32	114.48	114.26	4.444	1.922
43 0-2cm	63°57.85'	167°48.03'	35	4	0.63	0.60	156.38	23.42	1.010	1.714
44 0-2cm	63'45.40'	167°00.50'	31	4	0.66	0.52	128.89	34.06	2.072	0.900
48 surf.	62°58.20'	165°16.25'	10	2	9.08	4.23	95.38	83.16	5.829	5.012
14 IK 0-3cm	64°14.80'	165°25.50'	18	-	1.12	0.28	86.41	67.93	5.360	1.296
17 SV 0-3cm	64°05.10'	165°28.62'	19	-	1.09	0.86	121.21	68.48	14.066	2.228
17 0-3cm	64°05.10'	165°28.62'	19	-	0.31	0.24	99.74	49.43	5.494	2.667
17 IK160cm	64°05.10'	165°28.62'	19	-	0.64	0.50	111.12	17.19	3.150	0.855

[1] Samples 14-17 belong to a different program

[2] Quality of sample recovery based on a subjective scale of 5 (excellent) to 1 (poor).

[3] Extracted (salt free) dry sediment.

[4] Small amounts of elemental sulfur were detected in samples: 39, 41, 42, 44 and 14 IK.

Table 14. Characteristic Parameters for Norton Sound Hydrocarbons (1977 Cruise)

Station	$\frac{\text{Non-Saponifiable Fr.}}{\text{Organic Carbon}}$ (x 10^4)	$\frac{\text{Alkanes}}{\text{Org. Carbon}}$ (x10^4)	$\frac{\text{Pristane}}{\text{n-C}_{17}}$	$\frac{\text{Phytane}}{\text{n-C}_{18}}$	$\frac{\text{Pristane}}{\text{Phytane}}$	$\frac{\text{Odd}}{\text{Even}}$
34 (0-2 cm)	39.3	0.75	1.38	0.14*	2.0*	4.55
35 (0-2 cm)	170.7	0.87	1.67	0.22*	7.0*	5.15
39 (Surf)	2.1	0.24	1.44	0.33*	2.5*	5.35
41 (Surf)	115.5	0.53	1.0*	0.25*	4.0*	4.78
42 (Surf)	357.1	2.60	1.82	0.25*	5.5*	4.78
43 (0-2 cm)	39.0	0.64	1.06	0.16*	6.5*	4.22
44 (0-2 cm)	65.5	0.48	1.44	0.13*	6.0*	3.21
48 (Surf)	19.6	0.38	1.38	0.17*	5.0*	6.37
14 IK (0-3 cm)	242.6	4.37	0.55	0.23*	3.1*	5.26
17 (0-3 cm)	79.6	2.04	2.03	0.19*	1.3*	5.12
17 SV (0-3 cm)	206.0	6.40	0.5*	0.17*	2.0*	5.67
17 IK (160 cm)	34.4	1.91	0.5*	0.17*	4.0*	5.34

* Approximate values based on measured peak heights.

Table 15. Norton Sound Sediment Samples (1979 Cruise)

Station[*] No.	Latitude (N)	Longitude (W)	Depth (m)	Total C (%)	Org. C (%)	Nonsaponifiable fr. (µg/g)	Aliphatic fr. (µg/g)	Aromatic f (µg/g
1	64°19.2'	162°00.5'	17	1.20	0.72	83.43	4.68	3.31
1[†]	64°19.2'	162°00.5'	17	--	--	94.80	17.59	3.84
5	63°39.9'	161°17.8'	13	1.63	0.74	168.45	17.83	8.76
5[§]	63°39.9'	161°17.8'	13	--	--	134.91	20.06	4.13
7	63°40.3'	162°59.8'	17	1.28	0.57	161.79	9.66	6.08
8	64°00.3'	163°04.0'	20	0.69	0.46	29.20	1.56	1.49
13	63°20.2'	165°12.4'	15	0.65	0.38	55.61	4.51	5.14
15	63°59.6'	164°58.5'	18	0.73	0.48	57.82	3.96	1.79
18	64°19.9'	165°23.2'	25	0.62	0.48	65.10	3.15	1.53
20	64°06.6'	165°30.4'	18	0.64	0.40	41.96	5.40	1.52
21	64°12.1'	165°30.5'	18	0.72	0.47	126.35	9.08	5.14
22	64°19.8'	165°42.7'	21	1.34	0.86	119.28	8.87	5.54
25	64°20.2'	166°00.8'	22	1.14	0.66	62.47	5.19	1.95
29A	63°50.3'	165°41.7'	20	0.61	0.41	36.34	2.77	0.96
29B	63°46.1'	166°07.5'	27	0.96	0.54	89.90	3.93	lost
33A	62°25.4'	166°40.2'	20	--	--	16.27	1.68	0.87
36	63°40.0'	167°02.8'	29	--	--	78.57	8.67	1.73
40	64°40.2'	167°03.6'	26	0.20	0.17	6.56	2.25	0.11
47A	62°26.0'	168°48.6'	--	--	--	25.23	1.37	1.14
49	64°20.1'	169°00.3'	40	--	--	32.46	2.45	3.04
50	64°39.4'	169°00.3'	44	0.33	0.28	46.38	1.67	1.92

* All samples are surface sediments except: † = 15-25cm; § = 82-90 cm

Table 16. Aliphatic Hydrocarbon Concentrations (ng/g) in 1979
Norton Sound Sediment Samples

Station*	$\underline{n}$-C$_{15}$	$\underline{n}$-$_{16}$	$\underline{n}$-C$_{17}$	Pristane	$\underline{n}$-C$_{18}$	Phytane	$\underline{n}$-C$_{19}$	$\underline{n}$-C$_{20}$	$\underline{n}$-C$_{21}$	$\underline{n}$-C$_{22}$	$\underline{n}$-C$_{23}$
1	3.2	3.3	9.3	7.6	8.7	1.6	25.4	30.7	116.0	96.3	289.0
1 †	n.d.	n.d.	3.6	5.4	5.6	n.d.	21.2	33.8	125.2	119.1	322.5
5	4.7	4.7	12.7	13.4	14.4	n.d.	43.1	59.8	199.4	185.9	504.5
5 §	9.6	7.6	16.6	14.1	19.8	5.0	55.3	81.2	242.1	234.4	569.4
7	n.d.	2.4	11.1	10.5	13.1	n.d.	38.8	49.4	163.6	138.7	369.2
8	0.8	0.9	2.5	1.2	2.8	0.7	7.8	8.9	26.0	20.9	50.2
13	n.d.	n.d.	4.3	2.6	6.5	1.6	21.0	31.7	101.9	34.6	218.0
15	n.d.	n.d.	4.1	2.0	4.9	0.8	14.3	19.8	70.4	63.3	166.4
18	n.d.	n.d.	4.1	1.8	5.2	1.0	15.7	20.3	68.6	62.9	175.9
20	n.d.	n.d.	5.1	2.3	5.2	n.d.	15.0	19.9	65.9	57.1	148.7
21	n.d.	1.8	6.3	3.9	7.2	n.d.	22.3	28.9	100.5	83.0	230.8
22	5.9	5.5	12.7	5.3	12.3	2.2	33.1	42.1	157.4	133.4	346.5
25	n.d.	n.d.	5.7	2.7	6.1	n.d.	16.2	20.3	66.4	57.8	150.6
29A	n.d.	n.d.	4.1	1.5	4.4	1.0	13.3	16.0	50.4	44.0	120.1
29B	2.0	1.3	3.5	1.1	3.4	n.d.	10.7	13.2	46.9	47.4	128.9
33A	n.d.	n.d.	1.3	0.7	1.7	n.d.	4.0	5.0	13.2	10.9	26.6
36	n.d.	n.d.	2.1	n.d.	2.7	n.d.	12.6	14.4	52.7	44.3	132.6
40	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.7	1.2	3.0	3.3	7.2
47A	0.7	0.5	1.3	0.8	1.3	n.d.	4.0	4.7	21.6	12.2	35.3
49	1.0	1.0	2.6	5.9	2.4	0.7	7.1	8.0	23.0	22.5	57.0
50	1.1	0.5	0.8	0.6	1.0	n.d.	2.4	3.0	9.0	8.4	22.7

* All samples are surface sediments except: † = 15-25 cm; § = 82-90 cm.

n.d. = not detected.

Table 16. Aliphatic Hydrocarbon Concentrations (ng/g) in 1979 Norton Sound Sediment Samples (continued)

Station*	*n*-C$_{24}$	*n*-C$_{25}$	*n*-C$_{26}$	*n*-C$_{27}$	*n*-C$_{28}$	*n*-C$_{29}$	*n*-C$_{30}$	*n*-C$_{31}$	*n*-C$_{32}$	*n*-C$_{33}$	*n*-C$_{34}$	Total *n*-Alkanes
1	124.1	332.5	154.9	875.4	98.7	536.2	252.5	422.5	22.7	121.4	5.7	3540.3
1 †	143.7	535.1	169.3	889.3	112.8	579.2	507.0	522.7	30.4	152.3	5.8	4293.2
5	215.2	795.8	233.8	1154.0	153.8	814.6	186.2	673.3	42.7	198.5	7.9	5526.7
5 §	239.9	935.7	295.5	1238.6	170.9	766.1	145.8	822.8	44.6	237.0	10.3	6412.4
7	154.9	570.2	172.3	892.1	116.7	634.7	193.1	570.2	33.7	168.8	7.5	4318.9
8	23.2	73.1	22.6	105.5	15.7	76.5	33.8	82.7	5.7	28.1	1.4	594.7
13	85.0	242.4	60.5	415.7	41.0	325.5	65.1	278.8	14.9	85.3	2.5	2084.8
15	69.6	195.9	55.8	322.4	36.9	249.6	68.7	206.0	11.5	60.3	2.1	1627.7
18	80.4	280.6	84.8	492.6	59.4	348.2	64.4	299.9	46.8	91.0	6.3	2217.0
20	60.2	171.9	49.7	287.2	33.3	232.2	52.5	210.7	8.9	67.9	11.9	1503.2
21	89.3	435.6	115.0	694.7	71.4	400.1	107.1	346.1	11.8	88.6	13.6	2853.9
22	136.6	363.2	97.6	493.4	58.1	363.0	141.5	311.9	18.6	94.5	3.5	2833.2
25	61.0	177.3	60.2	295.8	35.6	240.9	51.5	232.0	11.3	76.0	2.8	1567.5
29A	49.3	180.8	55.6	301.4	38.2	211.9	32.2	184.2	10.9	57.6	2.5	1384.1
29B	69.3	218.6	77.6	287.9	42.0	178.7	23.2	136.5	8.7	35.7	1.9	1344.0
33A	11.7	39.5	11.5	60.6	7.5	40.6	4.6	34.6	1.2	9.3	2.1	236.0
36	54.6	251.6	71.9	416.4	48.9	263.6	100.8	210.7	7.9	50.7	n.d.	1743.7
40	n.d.	10.2	3.5	14.2	2.2	10.3	n.d.	8.4	n.d.	n.d.	n.d.	64.2
47A	16.0	58.5	18.2	91.6	13.0	68.9	11.2	60.5	3.8	17.9	0.9	444.1
49	27.8	73.9	23.1	125.4	17.4	97.8	9.2	86.2	4.5	22.3	0.8	614.9
50	9.8	27.5	9.3	44.3	6.8	33.7	3.5	32.6	1.5	9.3	0.5	253.3

* All samples are surface sediments except: † = 15-25cm; § 82-90cm.

n.d. = not detected

Table 17. Characteristic Parameters for 1979 Norton Sound Sediment Samples

Station No.*	Non-Saponifiable fr. / Organic Carbon ($\times 10^4$)	n-Alkanes / Org. Carbon ($\times 10^4$)	Pristane / n-C$_{17}$	Phytane / n-C$_{18}$	Pristane / Phytane	Odd / Even
1	115.88	4.92	0.37	0.18	0.75	3.37
1†	--	--	1.49	--	--	2.76
5	227.64	7.74	1.06	--	--	3.91
5§	--	--	0.88	0.25	2.82	3.89
7	283.84	7.58	0.95	--	--	3.80
8	63.48	12.93	0.48	0.25	1.71	3.27
13	146.34	5.48	0.59	0.24	1.65	4.32
15	120.46	3.39	0.50	0.17	2.47	3.81
18	135.63	4.62	0.44	0.19	1.86	4.04
20	104.90	3.76	0.44	--	--	4.03
21	268.83	6.07	0.62	--	--	4.40
22	138.70	3.29	0.42	0.18	2.44	3.35
25	94.65	2.38	0.41	--	--	4.12
29A	88.63	3.38	0.37	0.23	1.50	4.33
29B	166.48	2.49	0.31	--	--	3.56
33A	--	--	0.54	--	--	4.09
36	--	--	--	--	--	3.97
40	38.59	0.38	--	--	--	5.27
47A	--	--	0.62	--	--	4.29
49	--	--	2.27	0.28	8.88	4.18
50	427.36	0.90	0.75	--	--	3.87

* All samples are surface sediments except: † = 15-25 cm; § = 82-90 cm

Table 18. Polycyclic Aromatic Hydrocarbons in Sediment Samples Analyzed by GC/MS (ng/g)

	Cook Inlet						Norton Sound		
	203	233I	234	388	UC300	17	5	5 (82-90 cm)	25
O-Xylene	--	--	--	--	--	--	--	--	0.2
Isopropylbenzene	--	--	--	--	--	--	--	--	--
n-Propylbenzene	--	--	--	--	--	--	--	--	--
Indan	--	--	--	--	--	--	--	--	--
1,2,3,4-Tetramethylbenzene	--	--	--	--	--	--	--	--	--
Naphthalene	T	T	T	--	T*	T	T	T	T
2-Methylnaphthalene	T	T	0.7	T	T	2.2	--	--	T
1-Methylnaphthalene	T	T	T	T	T	0.6	--	--	T
Biphenyl	--	--	0.7	--	T	T	--	--	T
Dimethylnaphthalenes	T	T	2.7	27.4	3.4	4.1	T	0.6	0.1
Trimethylnaphthalenes	1.6	T	2.7	24.5	9.4	8.7	T	--	0.3
Fluorene	1.8	0.7	T	5.3	3.0*	T	T	6.2	0.1
Dibenzothiophene	--	--	--	--	--	--	T	T	--
Phenanthrene	10.4	2.3	4.1	63.8	14.5	14.7	0.7	8.0	0.4
Anthracene	--	--	--	--	--	--	--	--	--
Methylphenanthrenes	11.9	6.0	9.7	124.0*	55.4*	16.4	2.0	9.4	0.8
Fluoranthene	5.5	--	T	10.4	T	T	T	T	T
Pyrene	3.9	1.2	T	5.7	3.0	4.6	3.1†	0.7	0.2
Benz[a]anthracene	--	--	T	T	T	--	--	--	--
Chrysene	3.1	1.9	1.3	6.9	T*	T	--	4.7*	1.0
Benz[e]pyrene	T	T	0.6	5.2	T	T	T	T	T
Benz[a]pyrene	--	--	T	T	--	--	--	T	--
Perylene	3.9	3.1	1.9	8.2	14.8	8.4	33.5	71.1	9.4
Simonellite	4.9	3.9	1.2	4.7*	22.7	--	3.1†	T	T
Cadalene	2.2	0.3	T	5.5	2.6	5.8	T	2.0	T
Retene	7.6	3.6	1.1	18.6*	5.8	17.4	6.1	8.6	1.4

T = trace
* = Coelutes with unknown compound
† = Coelutes with simonellite

FIGURE LEGENDS

Figure 1: Sample locations in Cook Inlet. ● 1978 spring samples; △ 1978 summer samples; ⬟ 1979 spring samples.

Figure 2: Total organic carbon content (%) in Cook Inlet samples. For explanation of symbols, refer to Figure 1.

Figure 3: Nonsaponifiable fraction (μg/g) in Cook Inlet samples. For explanation of symbols, refer to Figure 1.

Figure 4: Sample locations in Norton Sound. ● 1976 samples; + 1977 samples; △ 1979 samples.

Figure 5: Total organic carbon content (%) in Norton Sound samples. For explanation of symbols, refer to Figure 4.

Figure 6: Nonsaponifiable fraction (μg/g) in Norton Sound samples. For explanation of symbols, refer to Figure 4.

Figure 7: Gas chromatographic traces of hexane fractions from Cook Inlet sediments.

Figure 8: Gas chromatographic traces of hexane and benzene fractions from Norton Sound sediments.

Figure 9: Gas chromatographic traces of hexane fractions from 1979 Cook Inlet and Norton Sound sediments.

Figure 10: Relative distribution histograms of di- and triterpenoids based upon m/z 191 mass chromatograms. CI = Cook Inlet; NS = Norton Sound; 17α,21α (diastereomers at position 22 indicated by continuous and dotted lines ┬┬┬), .-.-.- 17β,-21β; -....- 17β,21α; — — — mono-enes.

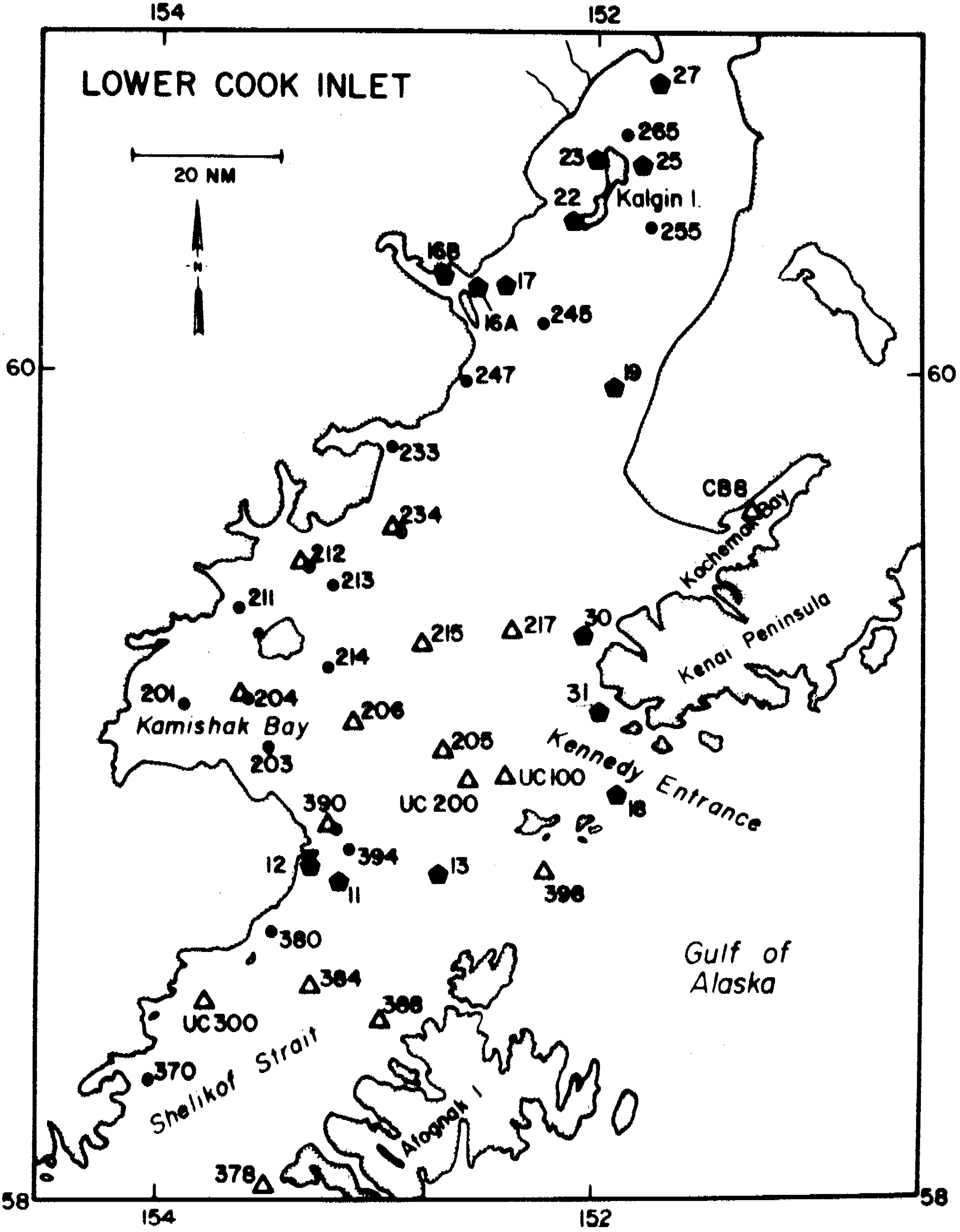

LOWER COOK INLET
20 NM
N
154
152
60
58
27
265
23
25
22
Kalgin I.
255
16B
17
16A
245
247
19
233
CB8
Kachemak Bay
234
212
213
211
Kenai Peninsula
217
30
215
214
201
204
31
206
Kamishak Bay
205
Kennedy Entrance
203
UC100
UC 200
18
390
394
12
11
13
398
380
Gulf of Alaska
384
UC300
386
370
Shelikof Strait
Afognak I.
378

Figure 1

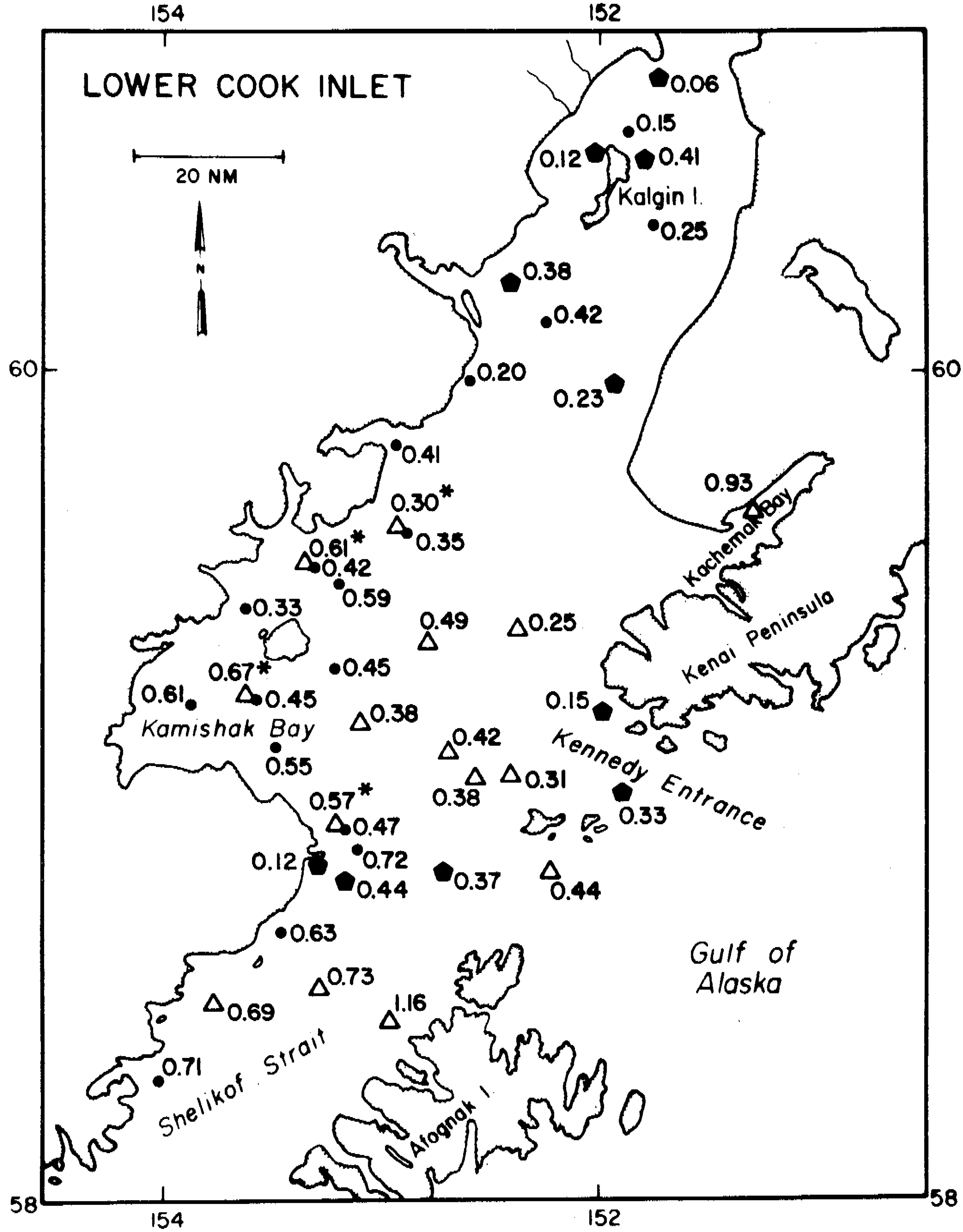

LOWER COOK INLET
20 NM
N
154
152
60
58
Kalgin I.
Kamishak Bay
Kachemak Bay
Kenai Peninsula
Kennedy Entrance
Gulf of Alaska
Shelikof Strait
Afognak I.
0.06
0.15
0.12
0.41
0.25
0.38
0.42
0.20
0.23
0.41
0.93
0.30*
0.35
0.61*
0.42
0.59
0.33
0.49
0.25
0.67*
0.45
0.61
0.45
0.38
0.15
0.55
0.42
0.38
0.31
0.33
0.57*
0.47
0.72
0.12
0.44
0.37
0.44
0.63
0.73
0.69
1.16
0.71

Figure 2

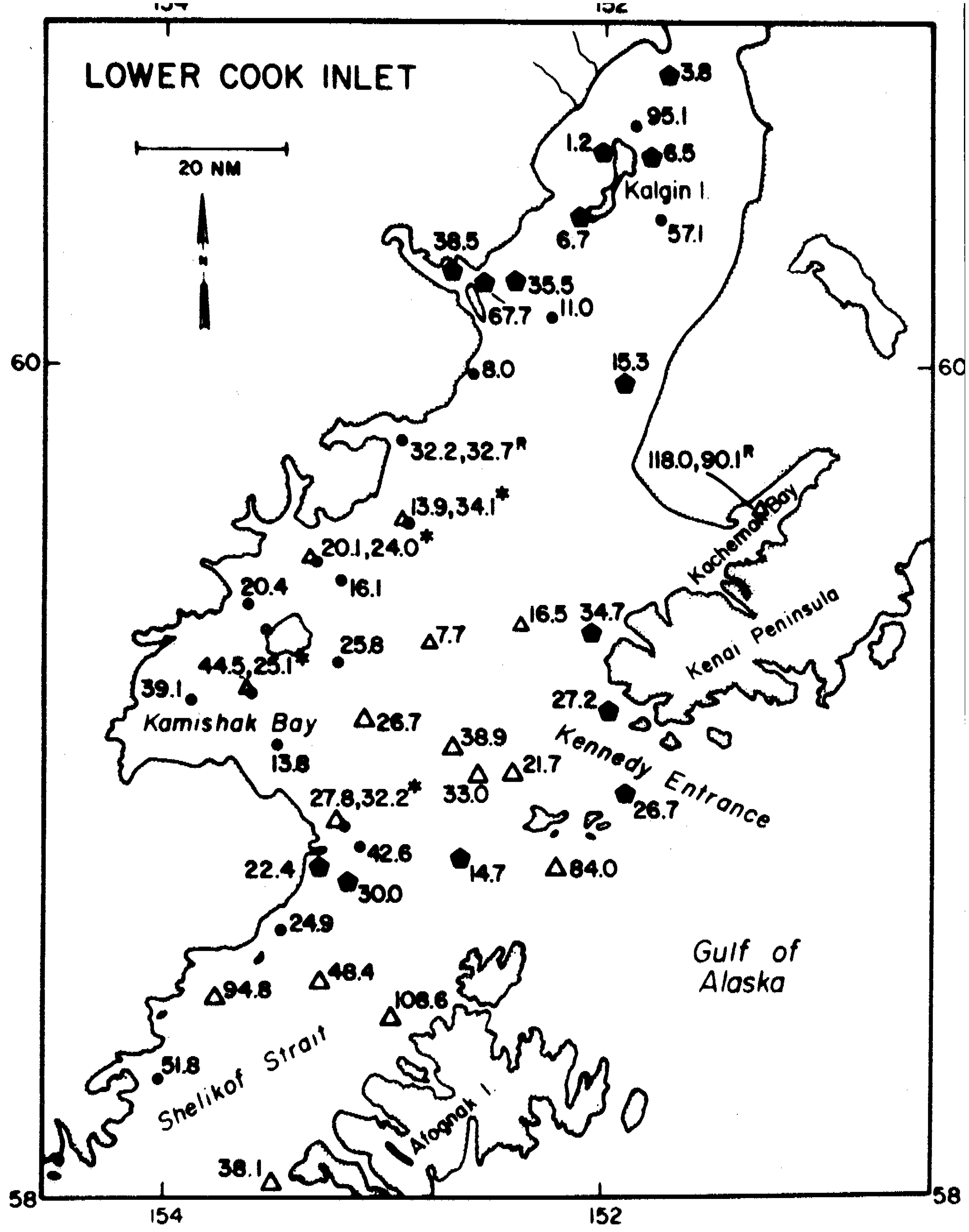

LOWER COOK INLET
20 NM
N
Kalgin I.
Kamishak Bay
Kachemak Bay
Kenai Peninsula
Kennedy Entrance
Gulf of Alaska
Shelikof Strait
Afognak I.
154
152
60
58
3.8
95.1
1.2
6.5
6.7
57.1
38.5
35.5
67.7
11.0
8.0
15.3
32.2,32.7R
118.0,90.1R
13.9,34.1*
20.1,24.0*
16.1
20.4
16.5
34.7
7.7
25.8
44.5,25.1*
39.1
27.2
26.7
38.9
13.8
21.7
33.0
27.8,32.2*
26.7
42.6
22.4
14.7
84.0
30.0
24.9
48.4
94.8
108.6
51.8
38.1

Figure 3

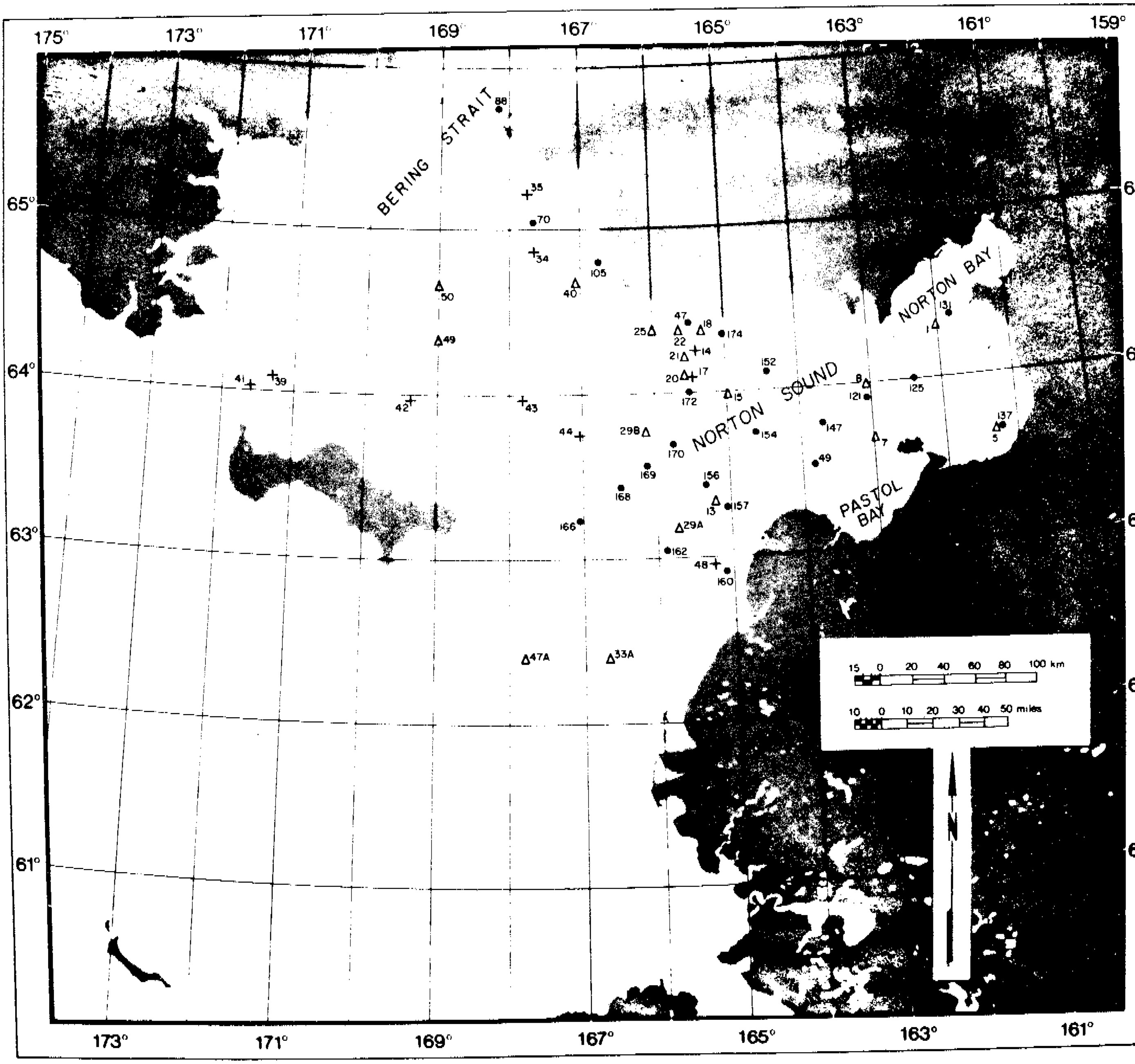

175°
173°
171°
169°
167°
165°
163°
161°
159°
65°
64°
63°
62°
61°
BERING STRAIT
NORTON SOUND
NORTON BAY
PASTOL BAY
88
35
70
34
105
50
40
49
47
18
25
22
174
21
14
20
17
152
8
125
131
1
172
15
121
41
39
42
43
44
29B
170
154
147
7
137
5
49
169
156
168
13
157
166
29A
162
48
160
47A
33A
15 0 20 40 60 80 100 km
10 0 10 20 30 40 50 miles
N
173°
171°
169°
167°
165°
163°
161°

Figure 4

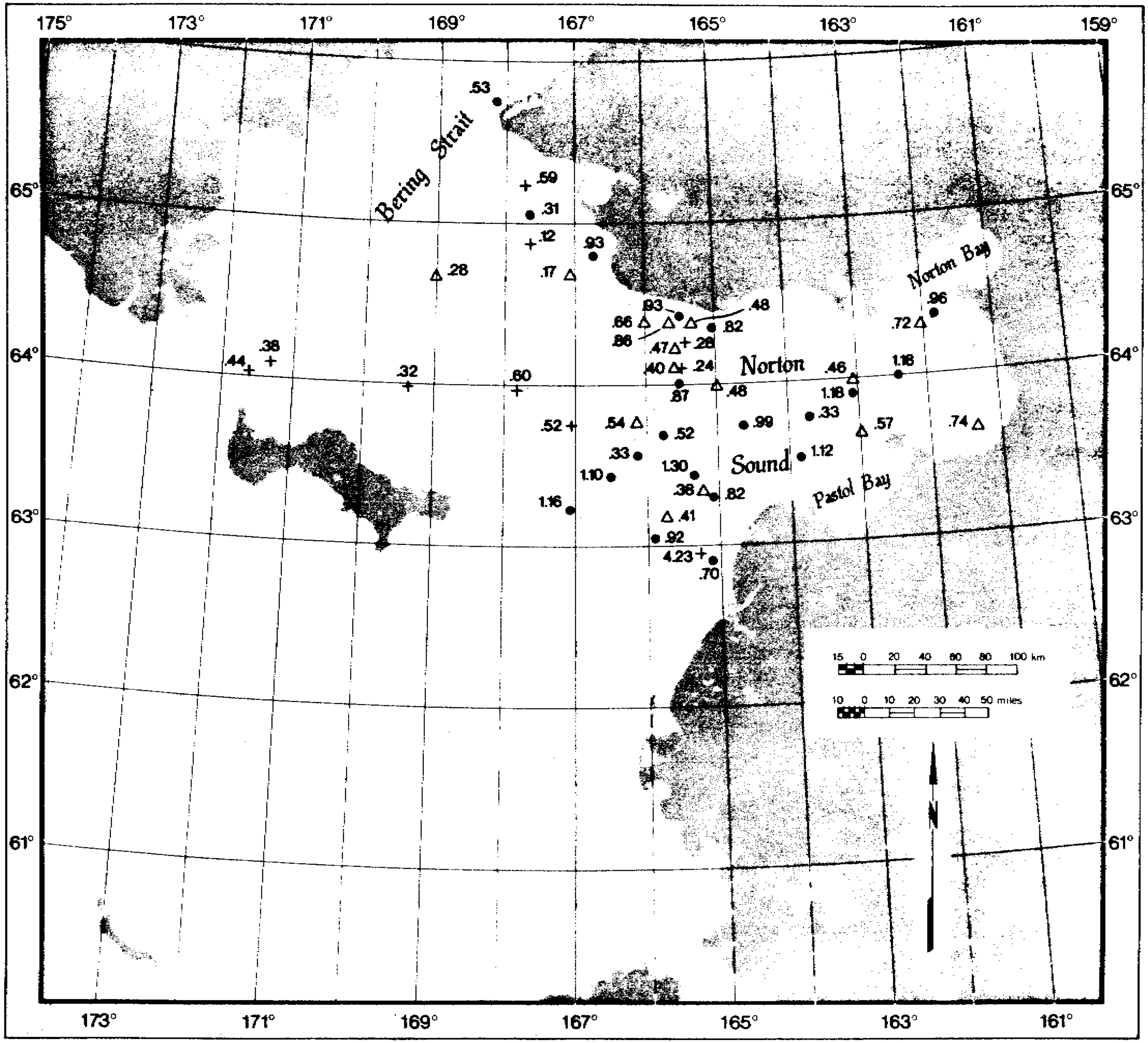

175°
173°
171°
169°
167°
165°
163°
161°
159°
65°
64°
63°
62°
61°
Bering Strait
Norton Bay
Norton
Sound
Pastol Bay
.53
.59
.31
.12
.93
.28
.17
.93
.48
.66
.82
.72
.96
.86
.47
.28
.38
.44
.32
.60
.40
.24
.48
.46
1.16
.87
1.18
.54
.52
.52
.99
.33
.57
.74
.33
1.12
1.10
1.30
.36
.82
1.16
.41
.92
4.23
.70
15 0 20 40 60 80 100 km
10 0 10 20 30 40 50 miles

Figure 5

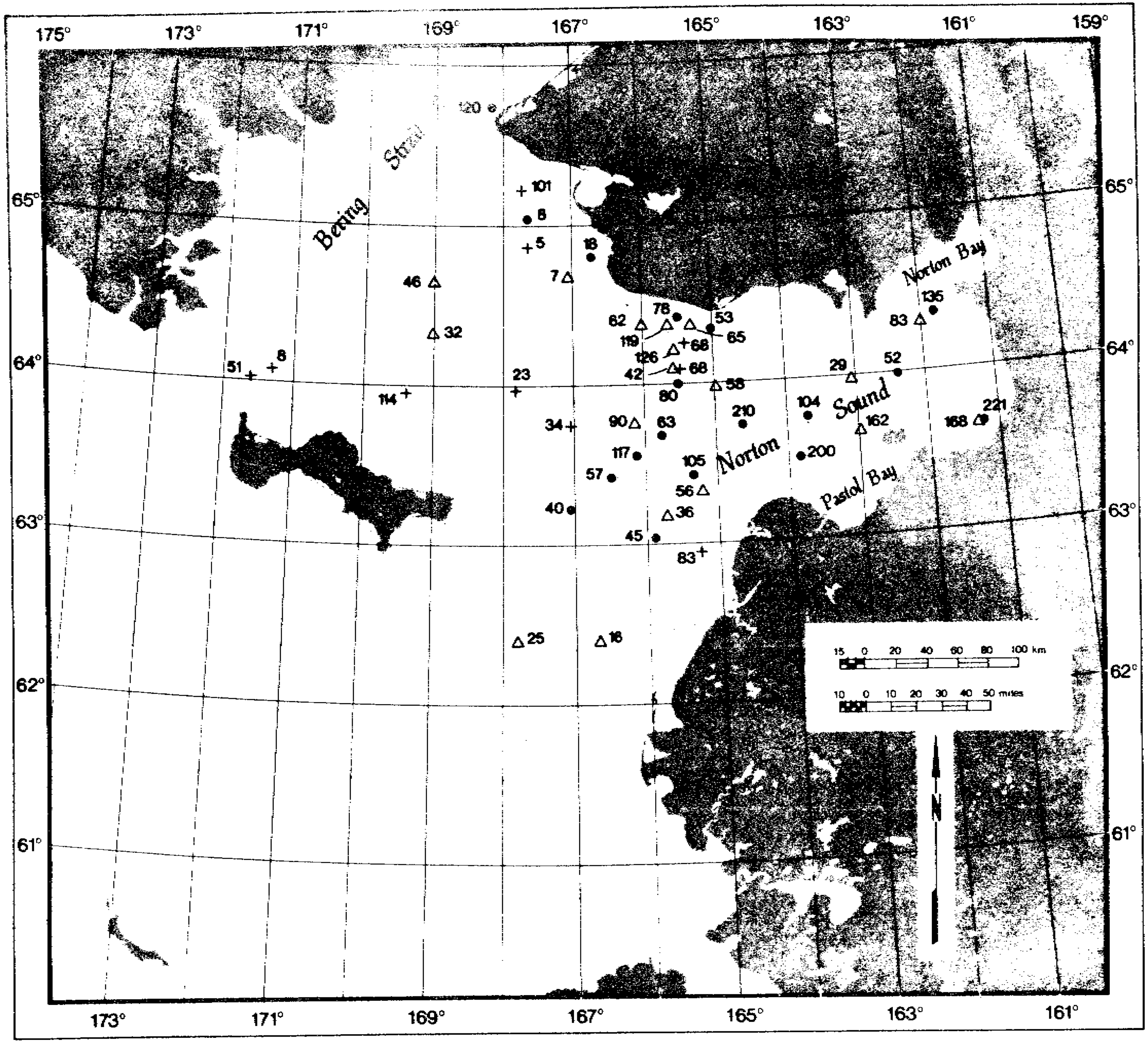

175°
173°
171°
169°
167°
165°
163°
161°
159°
65°
64°
63°
62°
61°
Bering Strait
Norton Sound
Norton Bay
Pastol Bay
120
101
8
5
18
7
46
32
62
78
53
65
119
68
126
42
68
80
58
29
52
83
135
51
8
114
23
34
90
63
210
104
162
168
221
117
105
200
57
56
40
36
45
83
25
16
15 0 20 40 60 80 100 km
10 0 10 20 30 40 50 miles
N

Figure 6

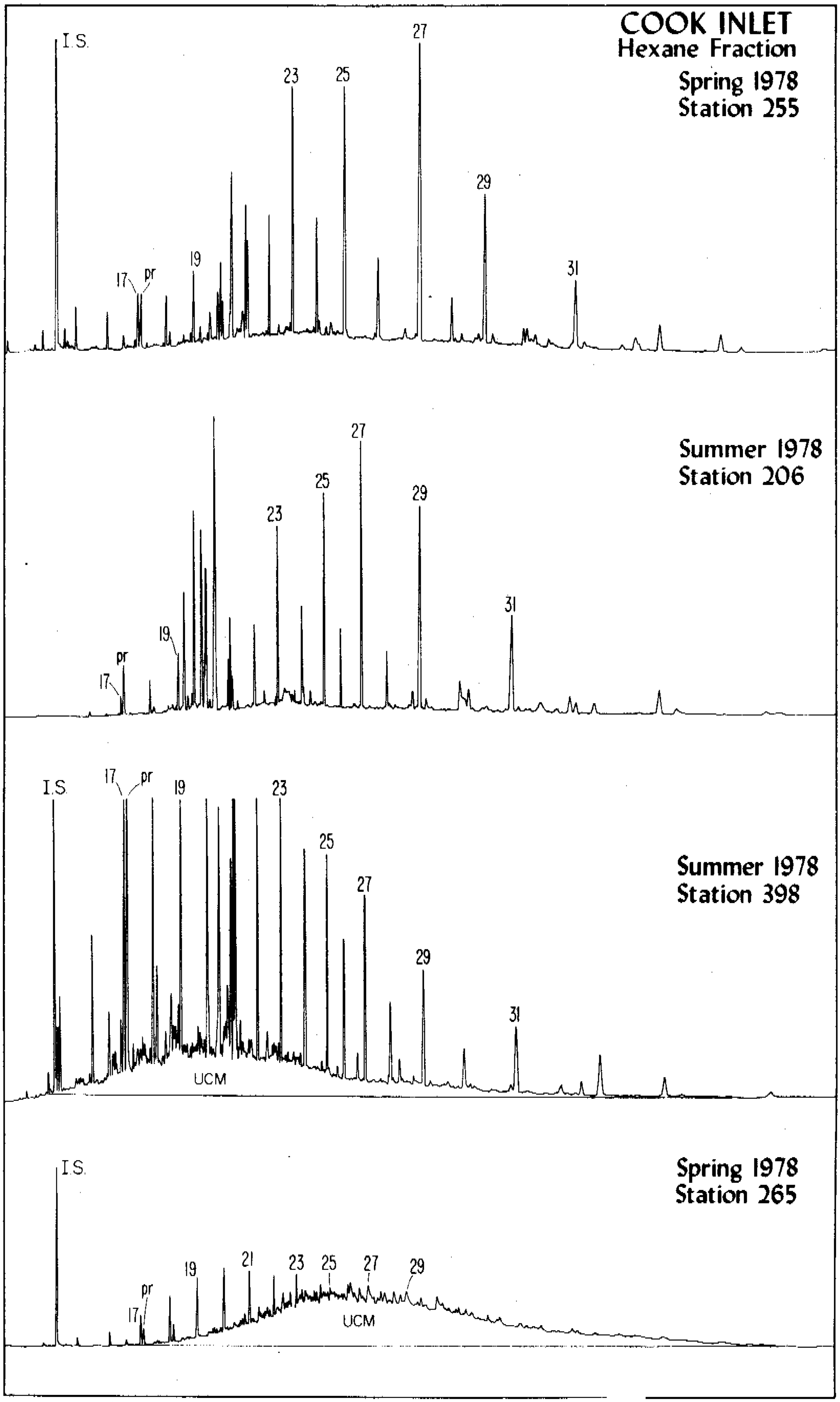
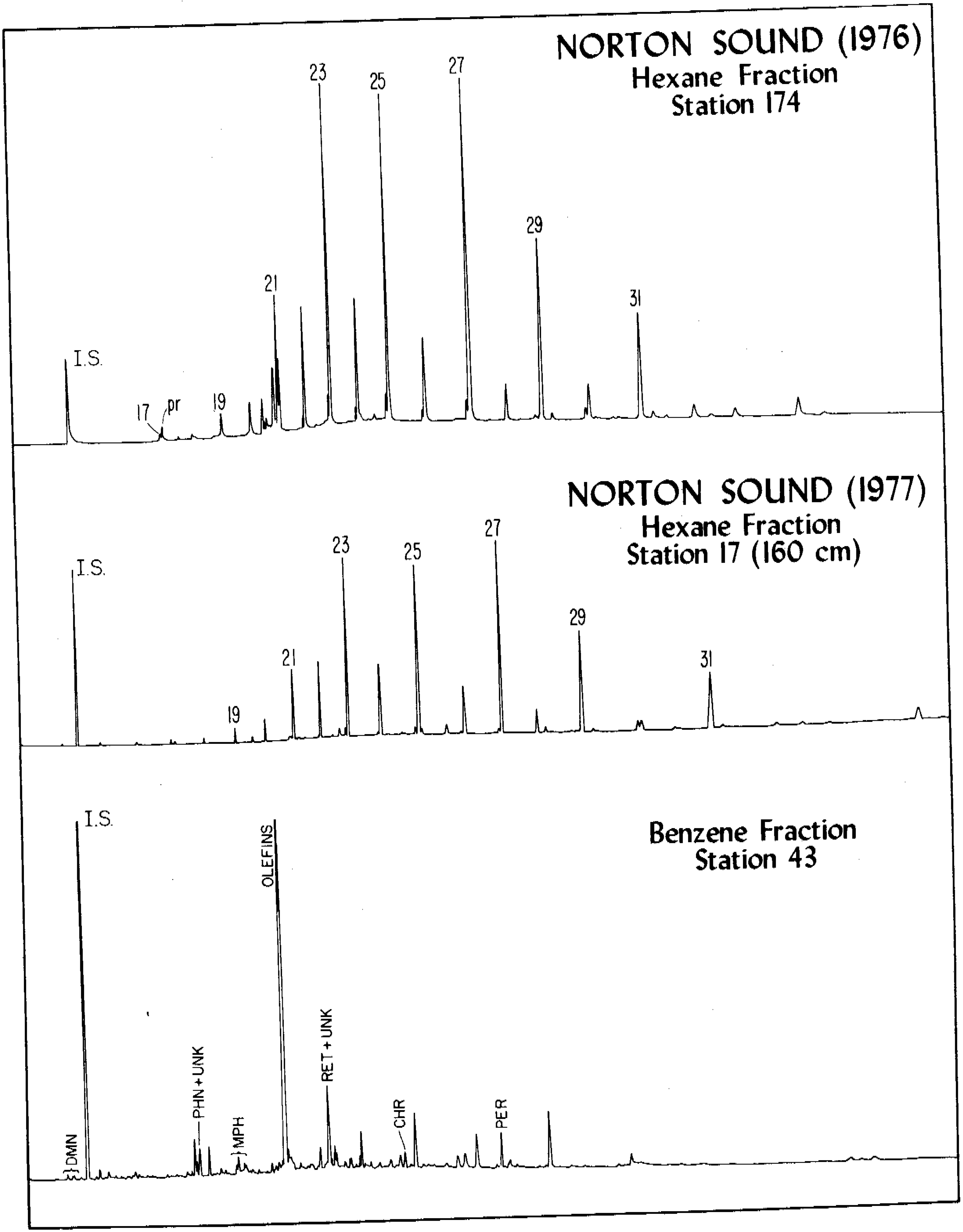

COOK INLET
Hexane Fraction
Spring 1978
Station 255
I.S.
17
pr
19
23
25
27
29
31
Summer 1978
Station 206
17
pr
19
23
25
27
29
31
Summer 1978
Station 398
I.S.
17
pr
19
23
25
27
29
31
UCM
Spring 1978
Station 265
I.S.
17
pr
19
21
23
25
27
29
UCM

Figure 7



NORTON SOUND (1976)
Hexane Fraction
Station 174

NORTON SOUND (1977)
Hexane Fraction
Station 17 (160 cm)

Benzene Fraction
Station 43

Figure 8

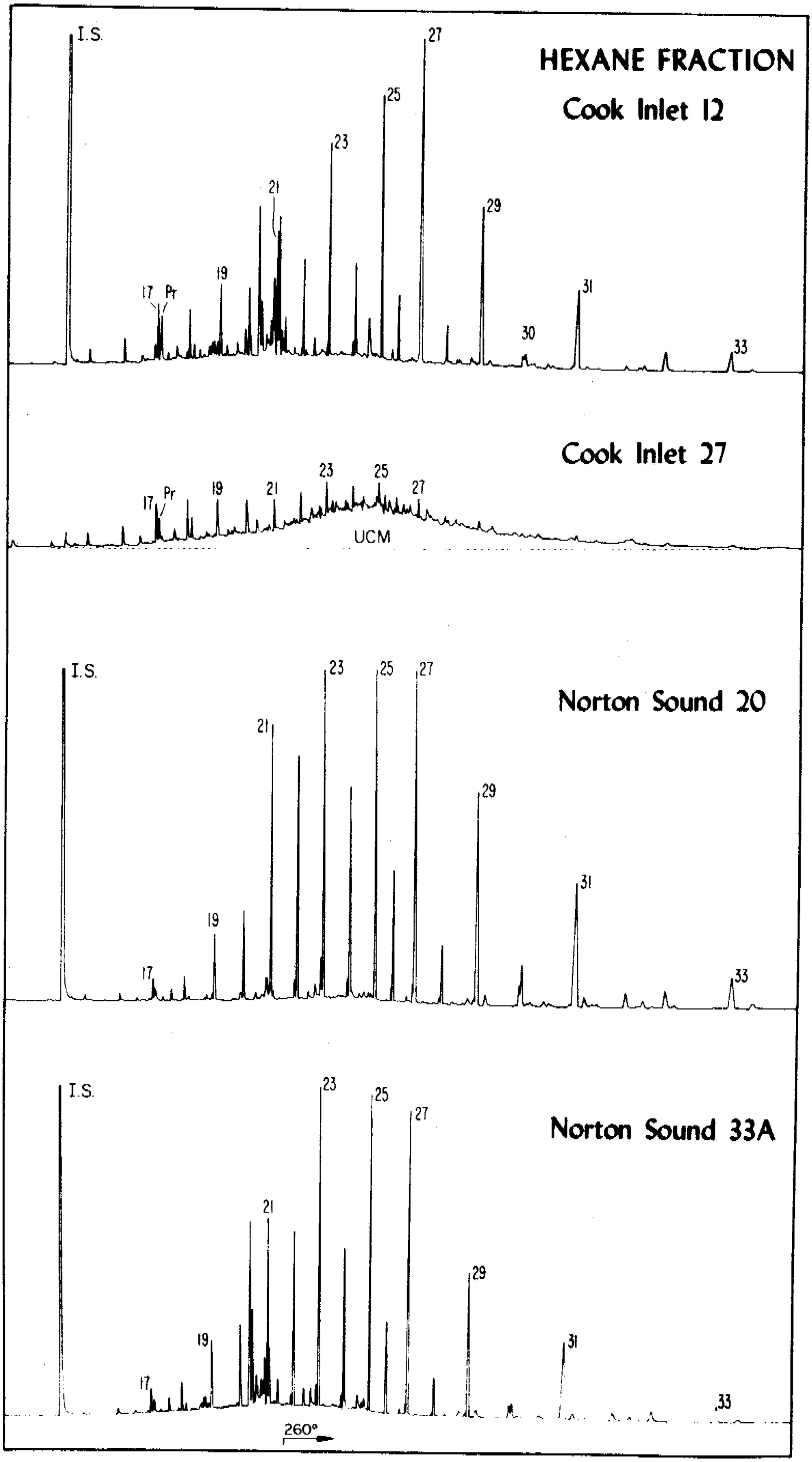

HEXANE FRACTION
Cook Inlet 12
I.S.
27
25
23
21
29
19
17
Pr
30
31
33
Cook Inlet 27
23
25
17
Pr
19
21
27
UCM
Norton Sound 20
I.S.
23
25
27
21
29
31
19
17
33
Norton Sound 33A
I.S.
23
25
27
21
29
19
31
17
33
260°

Figure 9

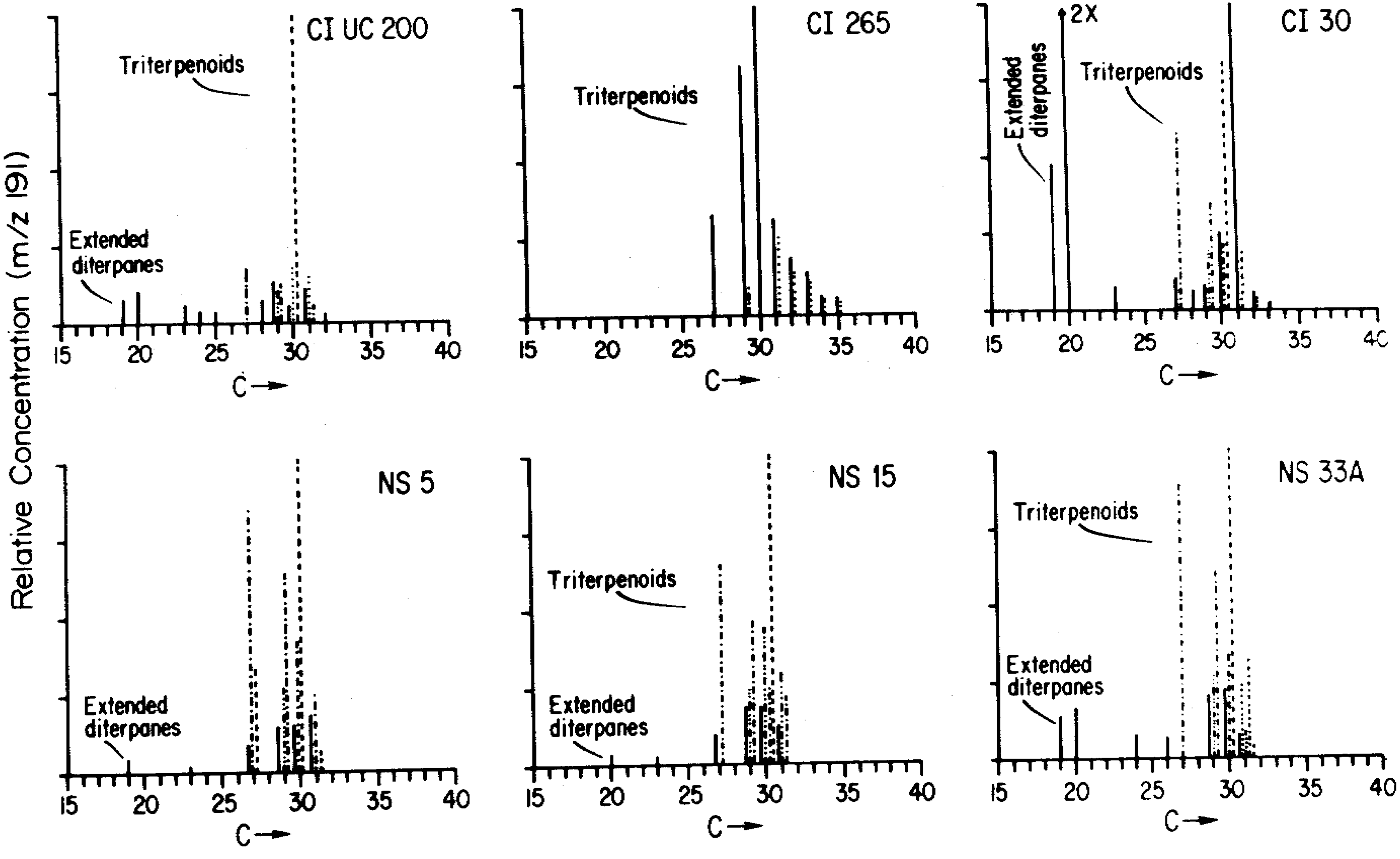

Relative Concentration (m/z 191)
CI UC 200
Triterpenoids
Extended diterpanes
CI 265
Triterpenoids
CI 30
2X
Extended diterpanes
Triterpenoids
NS 5
Extended diterpanes
NS 15
Triterpenoids
Extended diterpanes
NS 33A
Triterpenoids
Extended diterpanes
15
20
25
30
35
40
C→

Figure 10

MILESTONE CHART

0 - Planned Completion Date
X - Actual Completion Date
(to be used for updates)

RU # 480 PI: I.R. Kaplan and M.I. Venkatesan

Major Milestones: Reporting, data management and other significant contractual requirements; periods of field work; workshops; etc.

	1979												1980		
MAJOR MILESTONES	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D
Field Sampling								0	0						
Sample Analysis (1979 Cruise)	<—	X	—	—	—	—>									
Data Processing (1979 Cruise)				X											
Data Submission in Coding Sheets and keypunched cards for (1976-1978 samples)				X											
Quarterly Reports	X			X						0			0		
Annual Report							0	X							