NOAA Technical Memorandum ERL PMEL-26

PROCESSES AFFECTING THE DISTRIBUTION OF LOW-MOLECULAR-WEIGHT ALIPHATIC HYDROCARBONS IN COOK INLET, ALASKA

C. N. Katz
J. D. Cline

Pacific Marine Environmental Laboratory
Seattle, Washington
April 1981

UNITED STATES DEPARTMENT OF COMMERCE
Malcolm Baldrige, Secretary

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
James P. Walsh, Acting Administrator

Environmental Research Laboratories
Joseph O. Fletcher, Acting Director

NOTICE

The Environmental Research Laboratories do not approve, recommend, nor endorse any proprietary product or proprietary material mentioned in this publication. No reference shall be made to the Environmental Research Laboratories or to this publication furnished by the Environmental Research Laboratories in any advertising or sales promotion which would indicate or imply that the Environmental Research Laboratories approve, recommend, or endorse any proprietary product or proprietary material mentioned herein, or which has as its purpose an intent to cause directly or indirectly the advertised product to be used or purchased because of this Environmental Research Laboratories publication.

CONTENTS

FIGURES

TABLES

Table #

PROCESSES AFFECTING THE DISTRIBUTION OF LOW-MOLECULAR-WEIGHT ALIPHATIC HYDROCARBONS IN COOK INLET, ALASKA

C. N. Katz
J. D. Cline

ABSTRACT

Measurements of low-molecular-weight (LMW) aliphatic hydrocarbons, C_1 to C_4, were made in Cook Inlet, Alaska, on five cruises between 1977 and 1979. The distributions of these compounds were variable in both space and time. Concentration levels and composition of these gases in the lower Inlet appeared to be typical of those found in other coastal marine environments. The upper Inlet, however, had significantly elevated concentrations of methane and the C_2+ paraffins. On the basis of the contrasting hydrographic conditions of the two regions and the differing compositional characteristics of the hydrocarbon assemblages, the source of hydrocarbons was qualitatively determined to be predominantly biogenic in the lower Inlet and thermogenic in the upper Inlet. Hydrocarbon analyses made in concert with biological measurements in the lower Inlet suggested that the major source of methane was from the sediments, whereas the C_2+ hydrocarbons were produced in the water column. The conclusions of these field studies were supported by in vitro experiments. A methane budget calculated on the basis of a two-box model of the Inlet showed air-sea exchange and tidal mixing to be the major sinks of hydrocarbons in the Inlet. The budget quantitatively supported the evidence of a thermogenic source of hydrocarbons in the upper Inlet. This source may be the result of submarine seepage or leakage from existing wells.

1. INTRODUCTION

LMW aliphatics were measured on a seasonal basis in Cook Inlet, Alaska, over a 3-yr period as a part of the Outer Continental Shelf Environmental Assessment Program (OCSEAP) sponsored by the Bureau of Land Management (BLM), and administered by the National Oceanic and Atmospheric Administration (NOAA). Five cruises were conducted during April and July 1977, May and September 1978, and May 1979; 798 samples were analyzed. This total includes 73 samples analyzed in conjunction with a biological sampling program ("Chemistry-Biology Studies") carried out concurrently by Pacific Marine Environmental Laboratory (PMEL) in order to correlate biological activity with hydrocarbon levels. A summary of the hydrocarbon sampling is shown in table 1.

TABLE 1

Summary of the LMW aliphatic sampling and analyses performed in this study.

Cruise	Dates	No. Stations	No. Time Series (hours duration)	Chem-Bio Studies No. Sta/Sam	NMLH* No. Sam	Total No. Samples
CI1	05 Apr-22 Apr 1977	35	1 (30)	-	-	77
CI2	28 Jun-16 Jul 1977	62	2 (12,16)	-	-	235
CI3	04 May-17 May 1978	58	3 (48, 48, 30)	3/26	**	200
CI4	28 Aug-06 Sep 1978	35	1 (48)	5/47	**	165
CI5	07 May-20 May 1979	29	-	-	51	121

* Natural Modification of Light Hydrocarbons experiment.
** Preliminary measurements made.

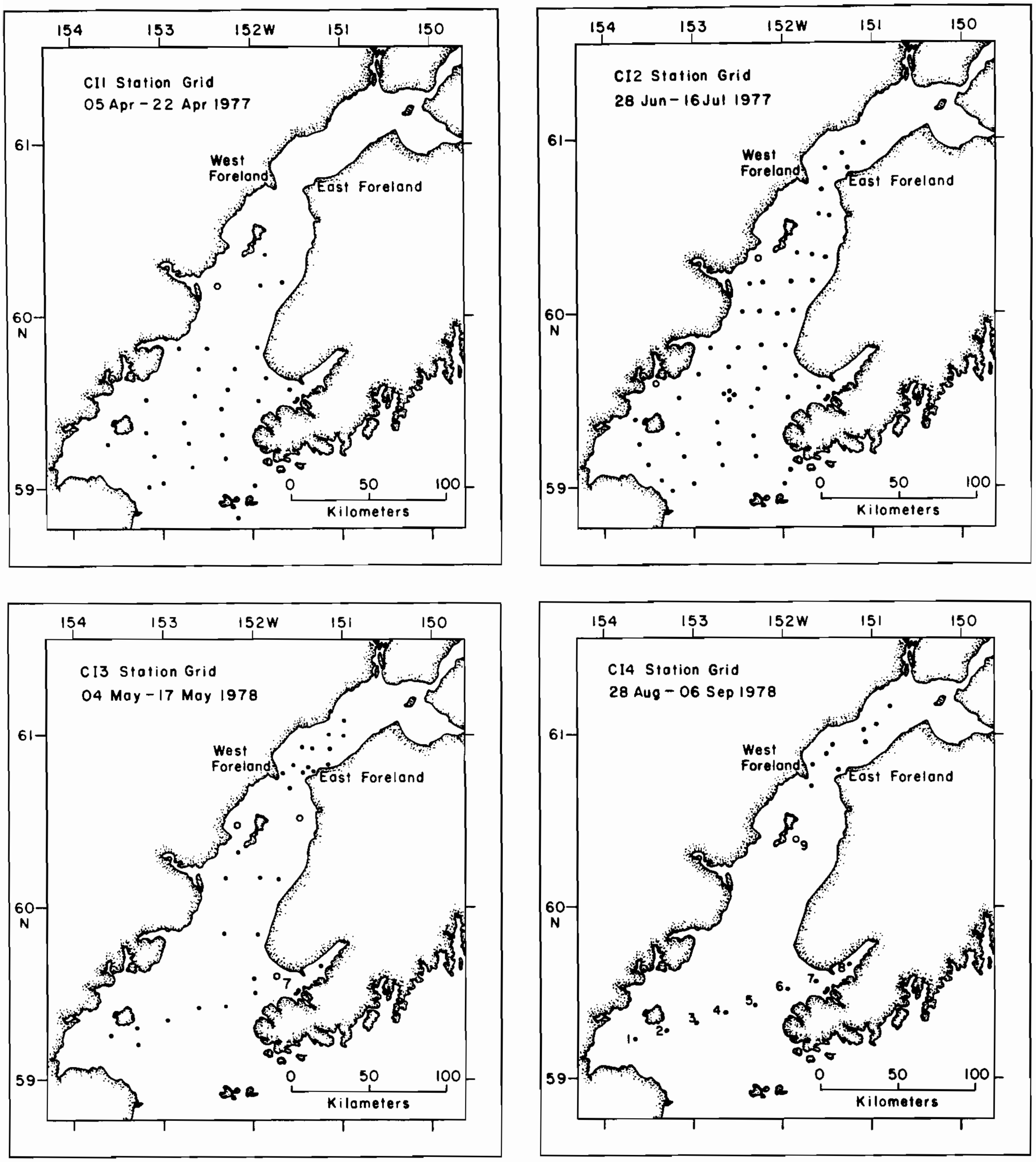
A Natural Modification of Light Hydrocarbons experiment was conducted as part of this study to determine the oxidation rate of methane in Cook Inlet waters. The experiment was expanded to include measurements of the C_2+ hydrocarbons in order to gain insight into the natural processes affecting these compounds. The 51 samples analyzed in this experiment are included in the total of 798. The experimental design is described in section 2.3.

Station grids employed for each cruise, which were for the most part determined by program requirements and logistics, are presented in figures 1 through 5. Station numbers are shown only for those stations discussed in the text. Vertical profiles taken at each station usually included surface, intermediate, and bottom-minus-5-m samples, although the number of samples taken depended on the depth of the water column. Seven time series stations (designated by O) were occupied during the five cruises. The stations were occupied for 12 to 48 hours with sampling intervals of 4 or 6 hours.

1.1 Light Hydrocarbons in the Marine Environment

The ability to distinguish among the various sources of hydrocarbons, which are ubiquitous in the marine environment, is dependent upon the ability to identify the physical, chemical, and biological processes influencing their distribution. This report examines processes influencing the distribution of the LMW aliphatic hydrocarbons, C_1 through C_4, in the estuarine environment of Cook Inlet, Alaska. In this study the magnitudes and relative importance of these processes will be estimated. Characterization of the sources of these hydrocarbons on the basis of compositional parameters in the marine environment will also be made.

LMW aliphatic hydrocarbons, methane, ethane, ethene, propane, propene, and iso- and n-butane are among the most easily measured hydrocarbons found in seawater. These dissolved gases (boiling points range from -164 to -0.5°C) are only slightly soluble in water, 20-60 parts per million by weight (ppmw) (McAuliffe, 1963), and thus are easily purged from seawater by gas stripping. The ease with which they are measured and their relative abundance in oil and natural gas have made these light hydrocarbons useful tracers of petroleum in the marine environment.



Figures 1-4. Station grid for LMW aliphatic hydrocarbon sampling in 1) April 1977; 2) July 1977; 3) May 1978; 4) September 1978. Time series stations are designated by 0.

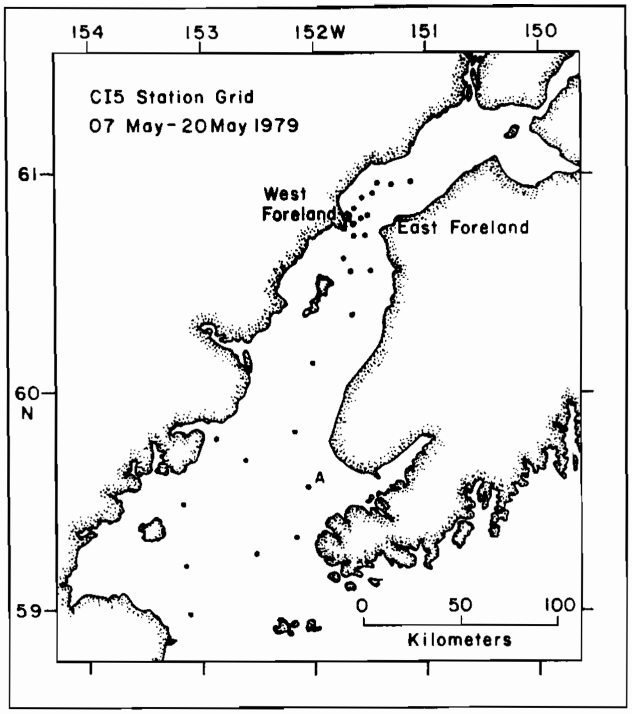


Figure 5. Station grid for LMW aliphatic hydrocarbon sampling in May 1979. Water was obtained for the Natural Modification of Light Hydrocarbons experiment at station A.

Measurements of LMW aliphatics have been conducted in various marine environments throughout the world. The most extensive measurements of the C_1 to C_4 hydrocarbons have been made in the Gulf of Mexico and the outer continental shelf of Alaska. Areal and seasonal data were obtained in the Gulf of Alaska, Bering Sea, Chukchi Sea (Cline et al., 1978) and Beaufort Sea (MacDonald, 1976). Similar data have been obtained in the Gulf of Mexico by a number of investigators at Texas A & M University (Frank et al., 1970; Brooks and Sackett, 1973 and 1977; Brooks et al., 1975; Brooks, 1976; Bernard et al., 1976 and 1978). Surface transects of the North and South Pacific, North Atlantic, Greenland, and Norwegian Seas have been made by Swinnerton and Lamontagne (1974) and by Lamontagne et al. (1974). Other areas studied include Puget Sound, Washington (Baker et al., 1978), the Persian Gulf and Gulf of Oman (Ross and Stoffers, 1978) and the anoxic waters of the Cariaco Trench (Linnenbom and Swinnerton, 1968) and Black Sea (Hunt, 1974).

Table 2 is an abridged summary of the average hydrocarbon concentrations found in the previously mentioned areas. The most abundant gaseous hydrocarbon in seawater is methane. Average concentrations in oxygenated waters range from approximately 40 to 950 nl l^{-1}. In contrast, methane concentrations reach over 100,000 nl l^{-1} in anoxic wa-

TABLE 2

Selected summary of the average and ranges of LMW aliphatic hydrocarbon concentrations measured in various marine environments.

Region	Methane	Ethane	Ethene	Propane	Propene	C_1/C_2+C_3	$C_{2:0}/C_{2:1}$	n	Reference
Tropical N. Pacific	47(41-69)	0.2(0.1-0.3)	5.9(2.2-11)	0.2(0.1-0.6)	1.6(0.6-3.6)	118	<0.1	88	Swinnerton and Lamontagne, 1974
South Pacific	54(40-68)	0.4(0.1-2.0)	3.8(2.0-9.5)	0.3(0.1-1.3)	1.8(0.9-3.4)	77	0.1	97	"
Beaufort Sea	210(15-1151)	0.8(0.4-1.6)	1.2(1.2-15)	0.3(T-0.9)	1.0(0.1-8.7)	191	0.7	87	MacDonald, 1976
Chukchi Sea	243(87-2851)	0.8(0.1-3.1)	1.8(0.6-5.9)	0.4(0.1-2.3)	0.4(T-0.8)	202	0.4	178	Cline et al., 1978
Bering Sea	217(48-2222)	0.9(0.1-8.3)	2.3(0.2-6.4)	0.4(T-2.9)	0.8(T-9.5)	167	0.4	696	"
Gulf of Alaska	212(12-2075)	0.4(0.1-13)	0.9(0.1-3.4)	0.2(T-5.9)	0.4(T-1.7)	353	0.4	939	"
Puget Sound	419(59-3600)	0.6(0.3-2.8)	3.5(0.6-21)	0.6(0.2-1.8)	1.3(0.2-4.6)	349	0.2	269	Baker et al., 1978
North Atlantic	103(34-1300)	0.6(T-1.5)	6.5(0.7-30)	0.3(T-2.8)	1.6(0.4-11)	114	0.1	97	Swinnerton and Lamontagne, 1974
Norwegian and Greenland Seas	70(58-103)	1.4(1.0-1.9)	3.0(1.7-5.0)	0.9(0.4-1.4)	1.1(0.6-1.9)	30	0.5	95	"
Caribbean Sea	44(32-62)	0.2(T-0.4)	6.1(2.2-12)	0.2(T-1.0)	1.5(0.2-5.8)	110	<0.1	40	"
Gulf of Mexico	954(37-8200)	43(T-650)	8.6(1.7-35)	46(T-820)	1.3(0.1-16)	11	5	27	"
Black Sea below $O_2=0$	123,000	308	T	3.4	T	395	-	1	Hunt, 1974
Cariaco Trench below $O_2=0$	125,000	37	T	3.9	T	3056	-	2	Linnenbom and Swinnerton, 1968

Note: Concentrations are in nanoliters per liter. 'T' indicates values less than 0.1 nl l^{-1}. Butane concentrations are below detection except in isolated areas of the Gulf of Mexico, Norton Sound, (Bering Sea) and in anoxic waters.

ters. In general, near-shore areas have higher concentrations of methane than open-ocean areas, largely because of differences in biological activity. The relatively high concentrations of methane observed in the Gulf of Mexico were attributed to input from petroleum operations and submarine seepage of natural gas (Brooks and Sackett, 1977).

Ethene is generally the next most abundant hydrocarbon component. However, it is significantly lower in concentration than the C_2 and C_3 saturates in the Gulf of Mexico and in the anoxic waters of the Black Sea and Cariaco Trench. Typical concentrations of ethene range from approximately 1 to 9 nl l^{-1} with higher concentrations generally found at lower latitudes. Anoxic waters are characterized by reduced concentrations of ethene that are apparently due to a reduced redox potential. Ethane, which is typically 0.2 to 1 nl l^{-1} in most marine environments, attains average concentrations of 40 nl l^{-1} in the Gulf of Mexico, presumably as a consequence of input from offshore petroleum production activities. Ethane concentrations greater than 300 nl l^{-1} in the anoxic waters of the Black Sea presumably are the result of the reducing conditions.

Propene is typically greater in concentration than propane except in the Gulf of Mexico and anoxic waters. Propene generally ranges from 0.4 to 2 nl l^{-1}, while propane ranges from approximately 0.2 to 1 nl l^{-1}. Propane values in the Gulf of Mexico average 46 nl l^{-1}, whereas those in anoxic waters average approximately 4 nl l^{-1}.

Both iso- and n-butane are generally present at concentrations below 0.1 nl l^{-1}. In isolated areas of the Gulf of Mexico, Norton Sound (Alaska) (Cline and Holmes, 1977), and anoxic waters, however, concentrations of butanes significantly above this level have been measured.

Seasonal data from the shelf regions of the Gulf of Alaska indicate that light hydrocarbon concentrations generally increase from spring to summer (Cline et al., 1978). Methane, ethene, and propene appear to increase in response to the onset of higher light levels and general warming of the surface waters in summer. As biological activity is stimulated at these times, it is likely that the increases in hydrocarbons are biologically mediated. Ethane, propane, and the butanes show a reduced or nondetectable seasonal variation in high-latitude waters (Cline et al., 1978). Seasonal data from low-latitude regions are expected to show less variation.

Open-ocean vertical distributions of light hydrocarbons typically exhibit mid-depth maxima of methane, ethene, and propene that have been attributed to in situ production (Scranton and Brewer, 1977; Brooks and Sackett, 1977). Below the maxima, concentrations of methane generally decrease to below surface saturation values while ethene and propene similarly fall off to trace concentrations. This decrease with depth is generally attributed to biological utilization of these compounds. Ethane and propane, which are usually lower in concentration, remain more uniform with depth. The vertical structure of hydrocarbons in the shallower shelf regions of Alaska, although variable with location, generally shows increases in methane, ethene, and propene toward the bottom (Cline and Feely, 1976; Cline et al., 1978).

There have been relatively few studies of the distribution of the C_1 to C_4 aliphatics in sediments. Bernard et al. (1978) measured light hydrocarbons in the sediments of the Texas continental shelf. They found, in general, that hydrocarbon concentrations in the sediments decreased offshore, although the typical concentrations still remained 1 to 2 orders of magnitude higher than those found in the overlying water column. Methane, the most abundant of the gaseous hydrocarbons, tended to show a maximum in the top 30-40 cm, presumably as a consequence of methanogenesis. Ethene and propene were more abundant than their saturated homologs throughout the sediment column. This trend is similar to that found in oxic sediments analyzed in the Gulf of Alaska (Cline and Young, 1977; Cline and Holmes, 1978). In contrast, ethene and propene were seldom observed in the anoxic sediments of the Persian Gulf and Gulf of Oman (Ross and Stoffers, 1978). However, ethane and propane in these sediments were found in abundance.

LMW aliphatics found in seawater may arise from both biogenic and thermogenic sources. Methane is known to be produced as a consequence of bacterial decomposition of organic matter in anoxic sediments (Martens and Berner, 1974; Barnes and Goldberg, 1976) and waters (Atkinson and Richards, 1967). Methane also is apparently produced by plankton and/or by bacteria associated with plankton (Scranton, 1977;

Oremland, 1979). Ethane and propane have been shown to be produced microbiologically under reducing conditions in the laboratory (Davis and Squires, 1954), and their general presence in the marine environment has been attributed to these processes (Hunt, 1974; Swinnerton and Lamontagne, 1974; Bernard et al., 1978).

Ethene and propene have been shown to be produced photochemically in seawater enriched with dissolved organic carbon (Wilson et al., 1970). In other laboratory experiments, ethene was produced nonenzymatically in the presence of light and a variety of precursors such as methionine and other amino acids (Yang et al., 1967; Ku and Leopold, 1970) as well as by bacteria (Yang, 1974; Smith and Cook, 1974; Primrose, 1976) and marine algae (Watanabe and Kondo, 1976). Significant correlations ($r > 0.7$) of ethene and propene with biological parameters, such as cell abundance and chlorophyll a concentration (Swinnerton et al., 1977), indicate that some of these processes are likely to occur in marine waters.

Methane, ethane, propane, and the butanes are all present to some extent in natural gas and petroleum (Moore and Shrewsbury, 1966; Clark and Brown, 1977). Because of the conditions under which crude oil forms (i.e., relatively high temperatures, pressures, and reducing conditions) olefins are absent in petroleum but may occur to some extent in refined products (Clark and Brown, 1977).

LMW aliphatics produced thermogenically (i.e., those formed through thermal cracking) may be injected into the marine environment in two ways. Natural submarine seepage of gas and oil is one mode of injection in which oil and/or gas seeps up through faults and vents in the sediment column. Offshore oil exploration has commonly included measurement of the LMW aliphatics as a means of detecting these seep areas (Bernard et al., 1977; Sackett, 1977). The second mode of injection, which is more visible, is the injection of these compounds during the offshore exploration (well drilling), production, and transportation of oil and gas. This is particularly true when the gases associated with crude oil are vented underwater, as in the Gulf of Mexico (Brooks et al., 1975). The gases also can occur in significant concentrations in the water column as a result of well blowouts (Brooks et al., 1978).

Compositional characteristics of the dissolved hydrocarbon gases have been used as a basis for distinguishing between thermogenic and biogenic sources. Generally, a relatively high abundance of the C_2+ paraffinic hydrocarbons is indicative of thermogenic sources (Brooks and Sackett, 1973; Cline and Holmes, 1977; Cline and Holmes, 1978). However, this criterion does not hold for all conditions, since the saturated compounds are relatively abundant in anoxic environments (Linnenbom and Swinnerton, 1968; Hunt, 1974).

Frank et al. (1970) first proposed using the methane-to-ethane-plus-propane ($C_1/(C_2 + C_3)$) ratio as an indicator of source type in the marine environment. They argued that this ratio would have values in the thousands when the gases arose from biological processes and that values less than 20 would be expected from gases produced thermogenically. This argument, however, was based on the compositional characteristics of oil and gas well data from Texas and Louisiana fields (Moore and Shrewsbury, 1966) which might differ compositionally from other producing reservoirs; thus, use of this parameter is limited.

Bernard et al. (1977) discussed the limitation of using the $C_1/(C_2 + C_3)$ ratio as a sole descriptor of hydrocarbon sources and chose to incorporate the $\delta^{13}C$ composition of methane as well. Utilization of the carbon isotopic composition allows characterization of the sources on the basis of a two-end member (biogenic and thermogenic) mixing model. The relative abundance of gases from each source can then be determined by observing where the measured gases fall in relation to a mixing curve. However, the methane concentrations encountered in seawater are generally too low to be analyzed for isotopic composition.

Cline and Holmes (1978) proposed utilizing the $C_1/(C_2 + C_3)$ ratio in conjunction with the ethane/ethene ($C_{2:0}/C_{2:1}$) ratio as a means of differentiating biogenic from thermogenic sources. Typical values of $C_{2:0}/C_{2:1}$ are less than 1.0 in oxygenated waters and are presumed to be reflective of biologically derived hydrocarbons (see table 2). Areas affected by the input of thermogenically derived hydrocarbons, such as the Gulf of Mexico and Norton Sound, Alaska (Cline and Holmes, 1977), have $C_{2:0}/C_{2:1}$ ratios significantly greater than 1.0, as do anoxic waters (table 2). In order to distinguish the hydrocarbons produced biogenically in anoxic environments from those formed by thermal cracking, the $C_1/(C_2 + C_3)$ ratio has been used. Whereas the thermogenically produced gases tend toward low values of $C_1/(C_2 + C_3)$, those produced anaerobically tend toward high ratios (table 2). As in the other methods of characterizing sources of light hydrocarbons, the $C_1/(C_2 + C_3)$ ratio must be used with caution, because of the variable composition of crude oils and natural gases.

As will be detailed in the next section, Cook Inlet is a region of two contrasting hydrographic regimes. The lower portion of the Inlet is a biologically productive area influenced markedly by coastal water derived from the Gulf of Alaska. The upper portion of the Inlet is biologically impoverished and is the site of offshore oil and natural gas production. Thus, Cook Inlet appears to be well suited to the study of the sources of light hydrocarbons and the processes affecting their distributions.

1.2 Study Area

1.2.1 Physiography

Cook Inlet is a partially mixed tidal estuary on the south-central coast of Alaska (fig. 6). The Inlet, which is within a structural trough bounded by major fault zones on the north, east, and west (Gatto, 1976), is bordered by the Aleutian and Alaska mountain ranges on the northwest, the Talkeetna Mountains on the northeast and the Chugach and Kenai Mountains on the southwest. The local geologic history is characterized by extensive tectonism, deposition, and glaciation (Gatto, 1976).

The Inlet trends northeast-southwest, is approximately 330 km long, 180 km wide at its widest, and has an area of approximately 2 x 10^4 km^2. The average depth is 42 m. In general, depth increases from north to south and attains a maximum of 180 m at the entrance where the Inlet opens to the Gulf of Alaska to the east and Shelikof Strait to the west. The Inlet is marked by many embayments, the largest of which are Kamishak Bay on the west and Kachemak Bay on the east. Tidal marsh areas that total approximately 250 km^2 are largely confined to these regions. The two largest of the many islands located within the Inlet are Augustine Island, an active volcanic island in Kamishak Bay, and Kalgin Island in the north-central portion.

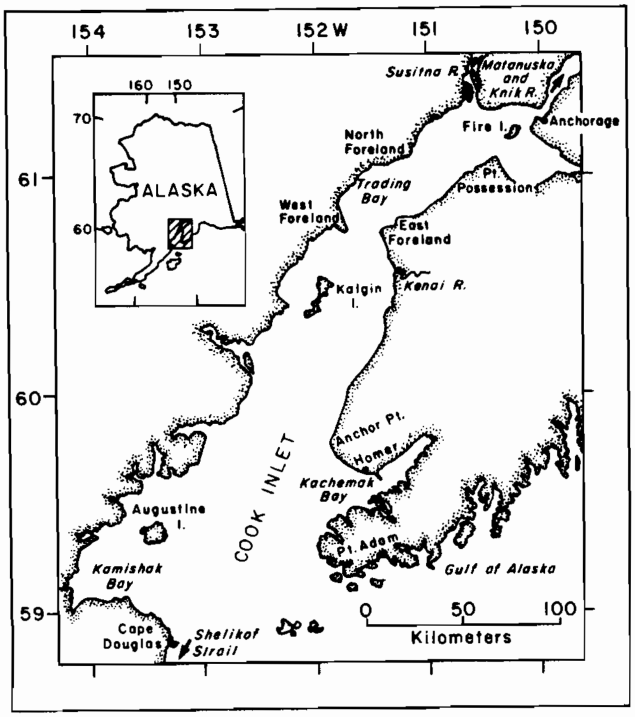


Figure 6. Physiographic setting of Cook Inlet, Alaska.

The East and West Forelands geographically divide the Inlet into two hydrographic regions. The region north of the Forelands is designated here as upper Cook Inlet; the area south of the Forelands is designated as lower Cook Inlet.

1.2.2 Climate

Meteorological conditions in Cook Inlet are seasonally quite variable. Winter weather is dominated by the Aleutian low which brings north-northeasterly winds, relatively low temperatures, and relatively high precipitation (Brower et al., 1977; Muench et al., 1978). As the effects of the Pacific high become dominant in summer, winds become southwesterly, temperatures increase and precipitation decreases (Evans et al., 1972). Meridional gradients in temperature and precipitation over the Inlet reverse from winter to summer (Brower et al., 1977).

Monthly mean wind speeds in 1977 remained relatively moderate and invariant throughout the year at 11.5 ± 1.3 km h^{-1}, although speeds greater than 90 km h^{-1} were recorded (Brower et al., 1977). Monthly mean air temperatures for 1977 ranged from a high of 12.7° C in July to a low of -10.5° C in January (Brower et al., 1977), although extremes of -44 and 29° C have been previously recorded (Evans et al., 1972). In general, air temperatures tend to decrease to the north in winter, leading to extensive ice formation in the mudflat areas of the upper Inlet (Muench et al., 1978). The average annual precipitation of approximately 53 cm is mainly in the form of snow (Evans et al., 1972).

1.2.3 Hydrography

Detailed circulation of Cook Inlet is relatively unknown. A generalized mean circulation pattern adapted from Knull and Williamson (1969), Burbank (1977), Muench et al. (1978), and Feely and Massoth (1981) is shown in figure 7. Except for Kachemak Bay, the Inlet is in general vertically well mixed and horizontally inhomogeneous in late spring and summer. Large-scale turbulence caused by dissipation of tidal energy results in a vertically well-mixed water column. The large size of the Inlet leads to a lateral separation of flows; hence, the general characteristics of the mean circulation are a net inward flow of saline oceanic water along the eastern shore and a net outward flow of relatively low-salinity water along the western shore (Burbank, 1974; Gatto, 1976; Muench et al., 1978).

Cyclonic cross-channel flow at the entrance dominates the nontidal circulation of the lower portion of the Inlet and leads to upwelling of nutrient-rich Gulf water in the central portion of the lower Inlet (Muench et al., 1978). Anticyclonic gyres have been observed in the upper Inlet (Burbank, 1974; Cline et al., 1979) and in Kachemak Bay (Knull and Williamson, 1969; Muench et al., 1978), although these features may be seasonal. In Kachemak Bay this circulation pattern leads to an increase in residence time of water (Knull and Williamson, 1969; Burbank, 1977). The gyral circulation enhances primary production by upwelling nutrient-rich water and by decreasing the washout of phytoplankton populations (Larrance and Chester, 1981).

The distribution of water properties is dominated by semidiurnal tidal currents superposed on the mean circulation (Hein et al., 1979; Cline et al., 1979; Feely and Massoth, 1981). The tides of Cook Inlet are progressive in nature, so there is an increase in their amplitude and speed to the north. Currents can be greater than 300 cm s^{-1} through the Forelands, although the mean maximum is about half this value (Evans et al., 1972). The tidal range averages about 6 m, but

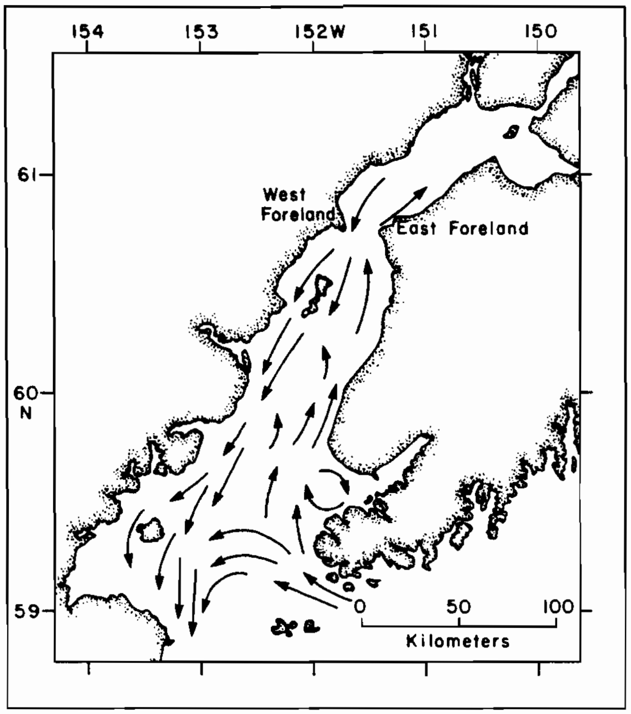


Figure 7. Generalized mean summer circulation in Cook Inlet. Composite is adapted from Knull and Williamson (1969), Burbank (1977), Muench et al. (1978), and Feely and Massoth (1981).

increases from approximately 5 m in southern Kachemak Bay to approximately 12 m at Anchorage (Brower et al., 1977).

The distribution of salinity is in agreement with the mean circulation pattern. High-salinity water resides in the southeastern portion of the Inlet, whereas fresher water is found to the northwest (fig. 8). Salinity increases from approximately 8 °/oo in the upper portion of the Inlet to 27 °/oo at the Forelands and to approximately 32 °/oo at the entrance (Kinney et al., 1970). In general, there is no vertical variation in salinity (Kinney et al., 1970; Muench et al., 1978; Cline et al., 1979).

Seasonal variations in salinity are the result of fluctuations in the amount of freshwater input. River discharge becomes significant in May and peaks in July (fig. 11), leading to a general salinity decrease from spring to fall. According to Muench et al. (1978), there is also a decrease in the salinity of incoming Gulf of Alaska water during this same period.

The surface distribution of temperature shows a marked seasonal variation. Temperatures increase to the south in spring and to the north in summer, as shown in figures 9 and 10. Spring temperatures at the surface ranged from 1.3° to 5.4° C in April 1977, and then in-

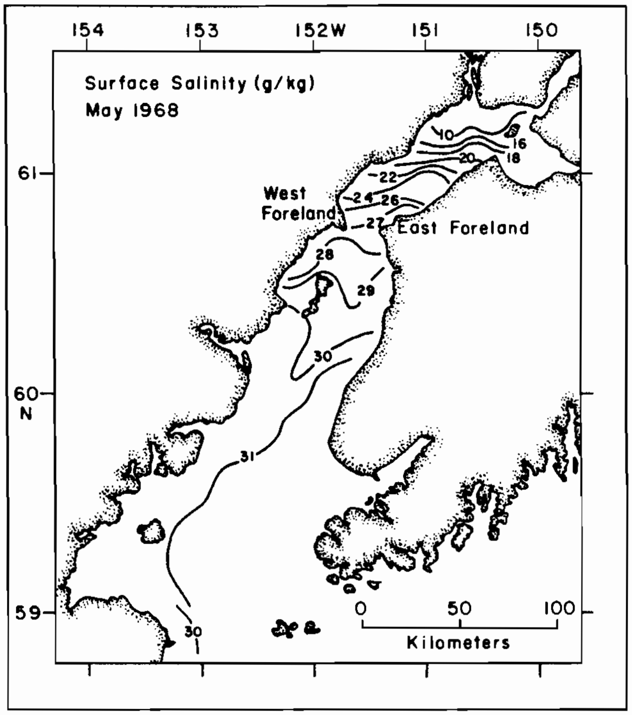
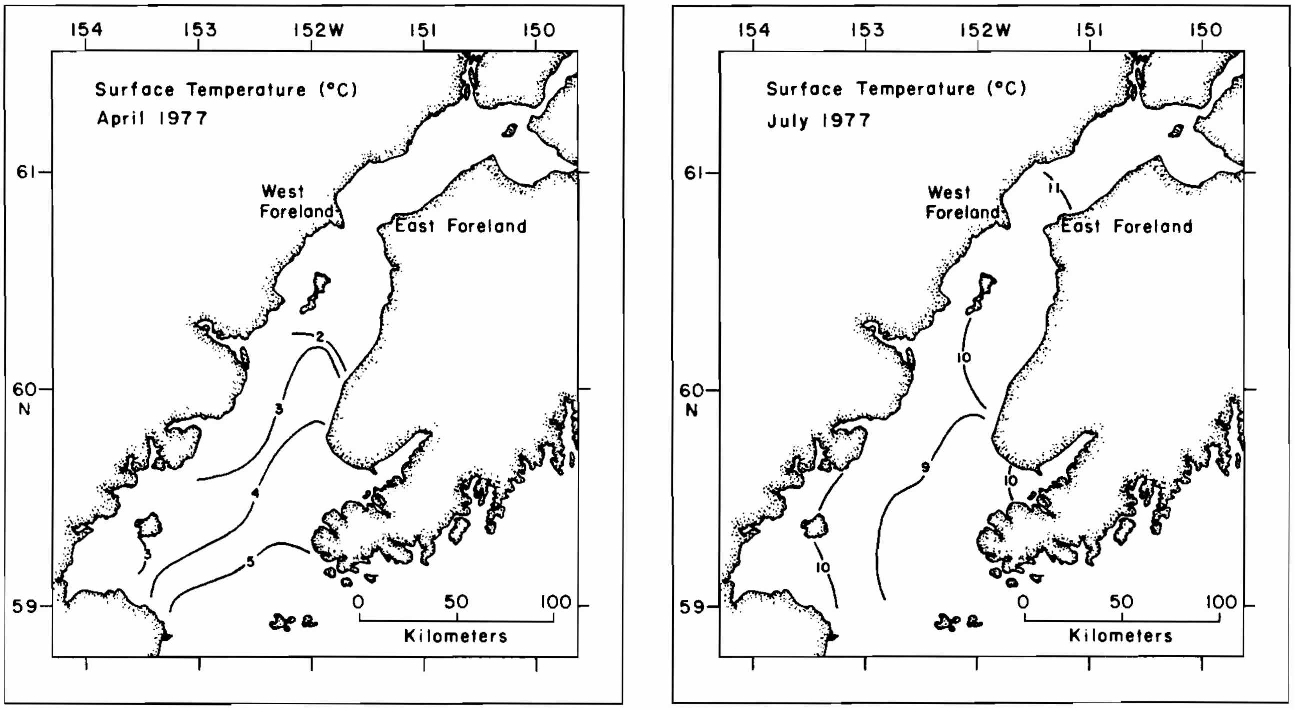


Figure 8. Surface distribution of surface salinity in May 1968. After Kinney et al. (1970).



Figures 9 and 10. Surface distribution of temperature in 9) April 1977; and 10) July 1977.

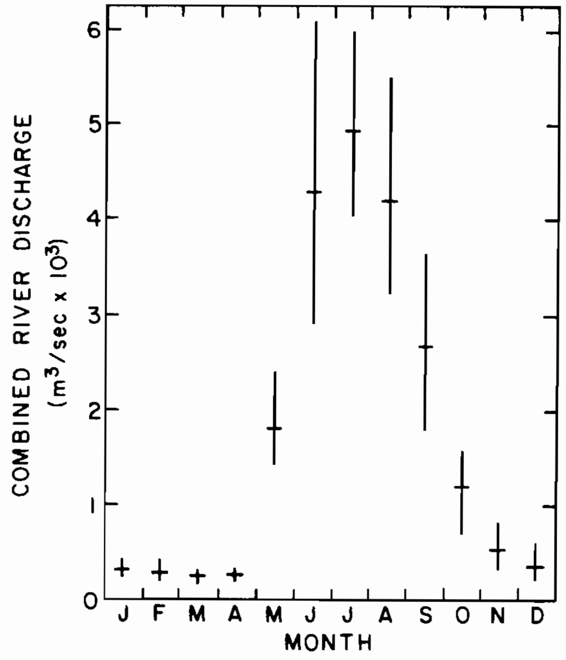


Figure 11. Combined monthly means and ranges for gaged major rivers discharging into Cook Inlet. Data were compiled from USGS streamflow records for the following rivers and periods: Susitna River at Susitna, 1975-1978; Knik River near Palmer, 1961-1973; and Kenai River at Soldotna, 1965-1978. Data and graph are from Feely and Massoth (1981).

creased to between 6.7° and 11.2° C in July of the same year. The temperature increase is due to the increase in solar insolation over that time period. The reversal in gradient is apparently due to more effective heating of the shallower waters in the upper Inlet. Slight vertical structure in temperature occurs in localized areas such as Kachemak Bay during summer (Cline et al., 1979).

1.2.4 Freshwater and Particulate Matter Input

The major source (> 70%) of fresh water to the Inlet is provided by the Susitna, Knik, and Matanuska Rivers (Gatto, 1976). These rivers, which originate in glaciers, enter Cook Inlet at its northern end. The major freshwater input below the Forelands is from the Kenai River. River discharge is relatively low from November through April, increases abruptly in May, and peaks in July (fig. 11). The combined monthly mean discharge (see fig. 11 for the years covered) peaks at approximately 5 x 10^3 m^3 s^{-1} and provides an annual freshwater input of approximately 2 x 10^{10} m^3.

The Susitna, Knik, and Matanuska rivers provide 75%-90% of the particulate matter to the Inlet (Gatto, 1976; Feely and Massoth, 1981). The glacial sediment load of these rivers is commonly as high as 2 x 10^3 mg l^{-1} during summer (Gatto, 1976). Along with resuspension, these rivers provide most of the suspended matter to the upper Inlet (Feely and Massoth, 1981). Total suspended matter concentrations in the upper Inlet average 2×10^{2} mg l^{-1}, whereas the lower Inlet has concentrations on the order of 2 mg l^{-1}, as shown in figure 12 (Sharma et al., 1974; Feely and Massoth, 1981). The decrease in concentration of suspended matter to the south and east is in general agreement with the estuarine dynamics.

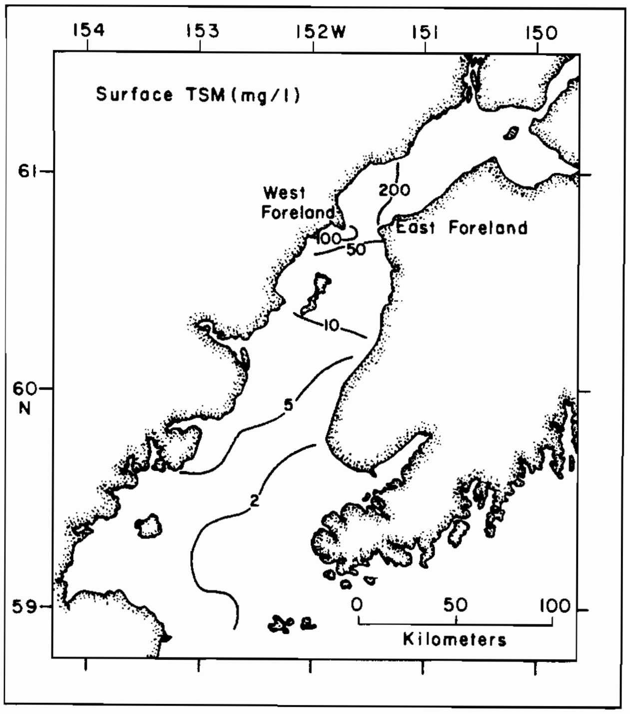


Figure 12. Surface distribution of total suspended matter concentration. Adapted from Sharma et al. (1974) and Feely and Massoth (1981).

1.2.5 Sediments

The distribution of bottom sediments in Cook Inlet is shown in figure 13. The data were compiled from preliminary data taken from Sharma and Burrell (1970), Hampton and Bouma (1976), and USDI (1976). In general, sediment texture reflects the energy of the depositional environment. Bottom sediments are primarily composed of medium- to fine-grained relect sands (Hein et al., 1979). Because of tidal scouring, the central Inlet has an abundance of pebbles, gravels, and boulders. The relatively quiescent embayments in the southern Inlet, such as Kachemak and Kamishak Bays, contain a preponderance of silt and clays (Feely and Massoth, 1981). The clays are primarily composed of illite and chlorite (Hein et al., 1979).

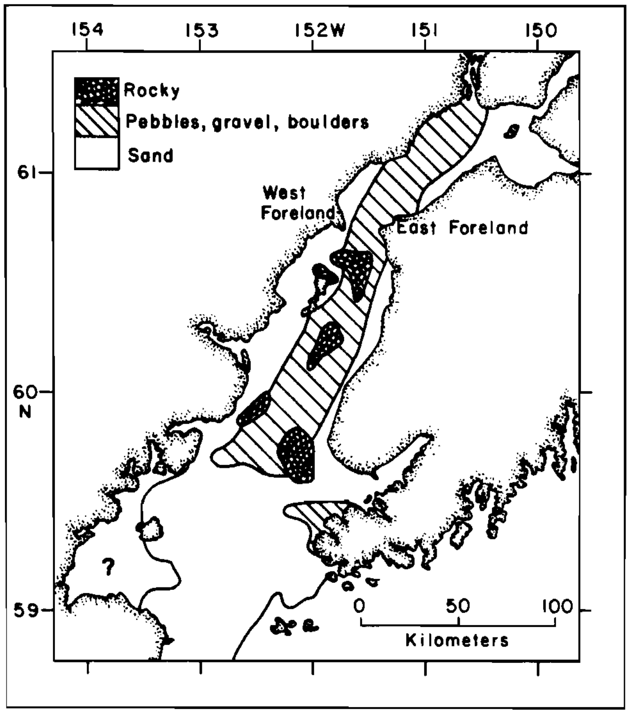


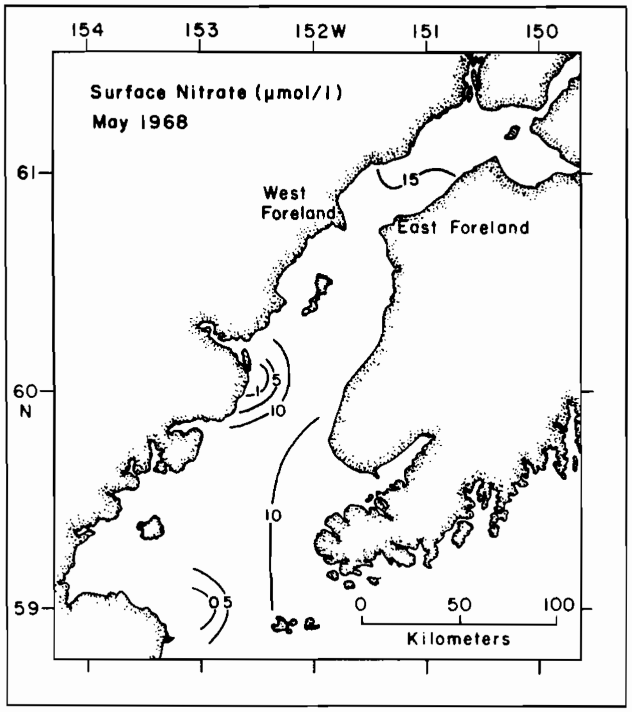
Figure 13. Bottom sediment distribution in Cook Inlet. Compiled from preliminary data from Sharma and Burrell (1970), Hampton and Bouma (1976), and USDI (1976).

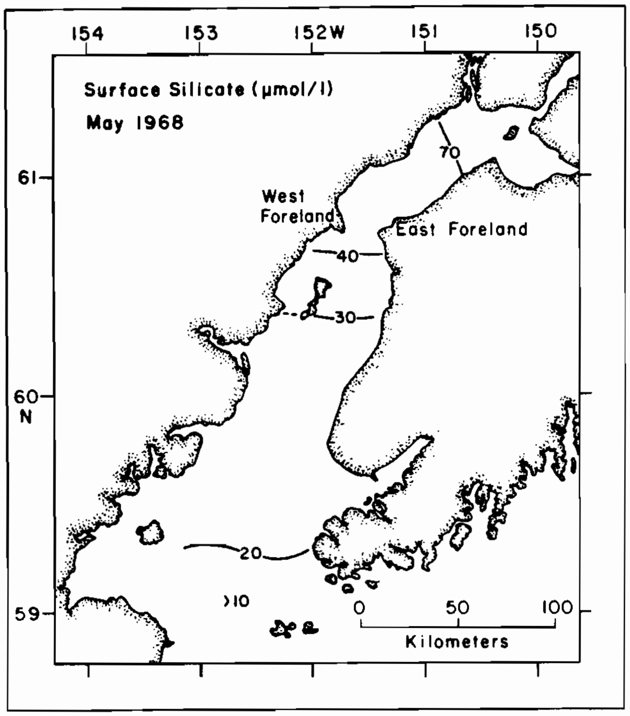
1.2.6 Dissolved Oxygen and Nutrients

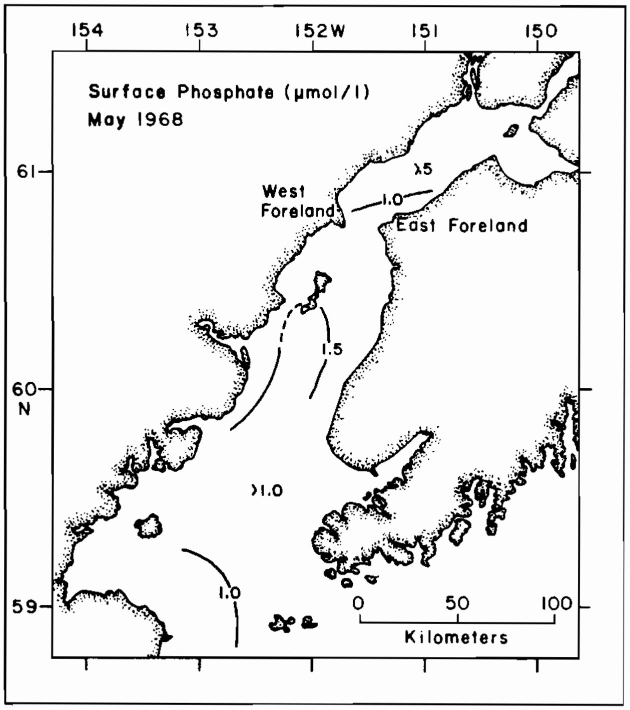
The concentration of dissolved oxygen is always equal to or greater than its saturation value with respect to the atmosphere (Kinney et al., 1970). Concentrations range from approximately 7 to 11 ml l^{-1}, with the highest concentrations typically found in Kachemak Bay. Supersaturation appears to be the result of in situ biological production (Kinney et al., 1970).

Typically, the concentrations of the nutrients nitrate and silicate increase to the north (figs. 14 and 15). In contrast, the concentration of phosphate increases to the south (fig. 16). Concentration ranges in May 1968 were 0-24 µmol l^{-1} for nitrate, 9-90 µmol l^{-1} for silicate, and 0.3-2.3 µmol l^{-1} for phosphate (Kinney et al., 1970).

The seasonal variation in nitrate and silicate concentrations, caused by localized biological uptake, is shown in figure 17. These observations, taken from Larrance and Chester (1981), were made in 1978 along a line of stations between Kamishak and Kachemak Bays similar to that shown in figure 4. March concentrations were rather uniform and relatively high across the Inlet. As summer progressed, concentrations in the bays dropped by a factor of 4 (16 to 4 µmol l^{-1} NO_3 and 32 to 8 µmol l^{-1} SiO_2). Seasonal variations in nutrients in other portions of the Inlet are not known.







Figures 14-16. Surface distribution of 14) nitrate; 15) silicate; and 16) phosphate concentration in May 1968. After Kinney et al. (1970).

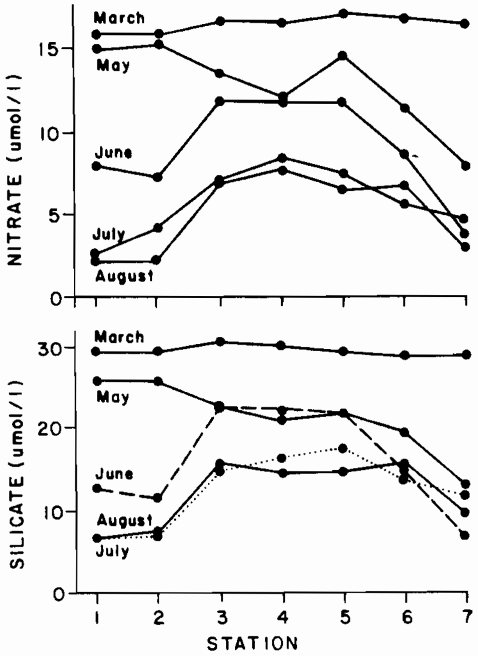


Figure 17. Nitrate and silicate concentrations for a line of stations traversing lower Cook Inlet in 1978 (Larrance and Chester, 1981). Concentrations are averaged over a 25-m water column. See figure 4 for approximate station locations.

1.2.7 Primary Productivity

Lower Cook Inlet is a biologically productive area. Data from transects made between Kamishak and Kachemak Bays, similar to the 1978 station grid shown in figure 4, show that relatively high, varying levels of primary production exist across the Inlet from May to August (Larrance and Chester, 1981). Production rates, integrated down to the 1% light depth, reach as high as 8 g C m^{-2} d^{-1} (Larrance, 1976; Larrance and Chester, 1981). These levels are sustained throughout the May to August period only in Kachemak Bay. The presumption that the primary production during winter is low is based on the relatively low (0.03-0.4 g C m^{-2} d^{-1}) rates measured across the Inlet in March 1978 (Larrance and Chester, 1981). Diatoms and microflagellates are the dominant primary producers. The high primary production supports large populations of crab, shrimp, and fish, which form the basis of a commercial fisheries industry.

Upper Cook Inlet, in contrast to the lower Inlet, is assumed to have low primary productivity throughout the year. High suspended-matter concentrations in the upper Inlet reduce the depth of the photic zone to 1 m or less (Murphy et al., 1972; Larrance, 1976). The reduced critical depth, relatively small surface area and relatively high flushing rate of the upper Inlet would all contribute to a low total production. However, no production data are available for the upper Inlet.

1.2.8 Natural Gas and Petroleum Development

The Cook Inlet Basin is underlain by natural gas and oil deposits, which are currently being exploited. Offshore oil production in Cook Inlet began in 1965 and as of 1972 accounted for 99% of all the oil produced in Alaska (Evans et al., 1972). Estimates of potential reserves for the entire basin as of 1972 were 1.2×10^{12} l of oil and 4.1×10^{14} l of gas (Evans et al., 1972). Estimates for lower Cook Inlet alone were 4.1×10^{11} l and 9.3×10^{13} l (USDI, 1976). Present offshore production is confined to 15 platforms (approximately 200 wells) in upper Cook Inlet. The most concentrated production occurs in the MacArthur River and Trading Bay Oil Fields in Trading Bay (fig. 18). The proposed development in lower Cook Inlet would add 23 platforms, 604 wells (440 producing), and 322 km of submarine pipeline (USDI, 1976). The estimated peak annual production and transport of crude oil and gas (liquefied) from lower Cook Inlet development is 5.4×10^{10} l and 4.8×10^{12} l respectively. Thus, the proposed development in lower Cook Inlet will almost double the 1971 offshore production of natural gas of 2.5×10^{12} l and increase the 1971 crude oil production of 1.0×10^{10} l by more than a factor of 5.

2. METHODS

2.1 Sampling

Water column samples were collected using standard 5- or 10-l Niskin® bottles mounted with a Plessey Environmental Systems Model 9040 CTD on a General Oceanics Rosette sampler. The bottles were rinsed by raising and lowering them routinely from 20 to 10 m.

Once on deck, water was transferred to clean 1-l glass-stoppered bottles in such a way that air bubbles were not trapped. Approximately 200 mg of sodium azide (NaN_3) were added to each bottle before it was stoppered, shaken to disperse the NaN_3, and stored in the dark at approximately 5° C. The NaN_3 was added to inhibit biological activity in the sample.

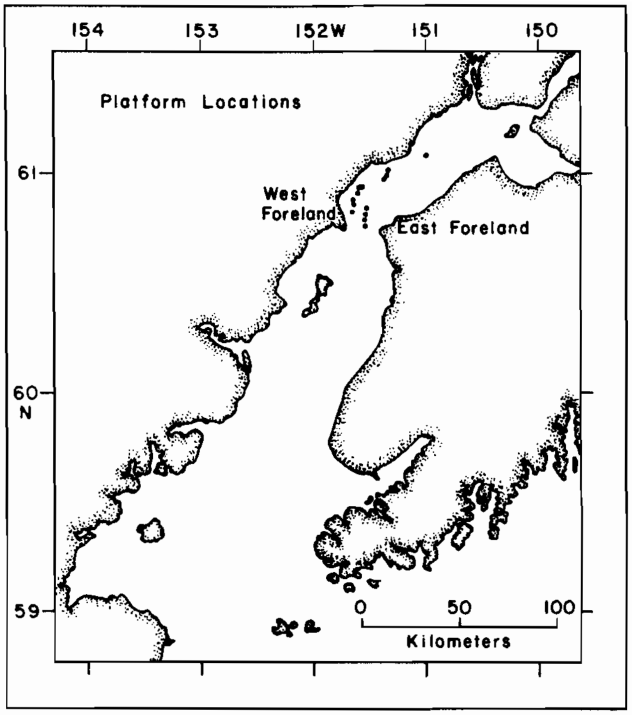


Figure 18. Locations of offshore oil and natural gas production platforms in Cook Inlet based on hydrographic Chart 16660.

Although storage time varied throughout the five cruises, samples were never stored for more than a few days. It was shown that storage in the dark for periods of a few days resulted in no significant changes in hydrocarbon composition (see results of the Natural Modification of Light Hydrocarbons experiment).

2.2 Low-Molecular-Weight Aliphatics

2.2.1 Preconcentration Techniques

Analysis of LMW aliphatics, using a procedure adopted from that proposed by Swinnerton and Linnenbom (1967), was accomplished routinely in both the field and laboratory. Briefly, the method involves removal of the gases from seawater by helium stripping, concentration by cryogenic trapping on an absorbent followed by thermal elution into a gas chromatograph where the gases are chromatographed and quantified. A diagram of the extractor is shown in figure 19.

The gas stripping method involves transferring the water sample from a 1-l glass-stoppered bottle into a calibrated fritted glass "stripper" by overpressurizing with ultrapure helium. The sample is then purged with ultrapure helium at 150 ml min^{-1} for 10 minutes. The gases removed from solution pass through Ascarite®, Anhydrone®, and

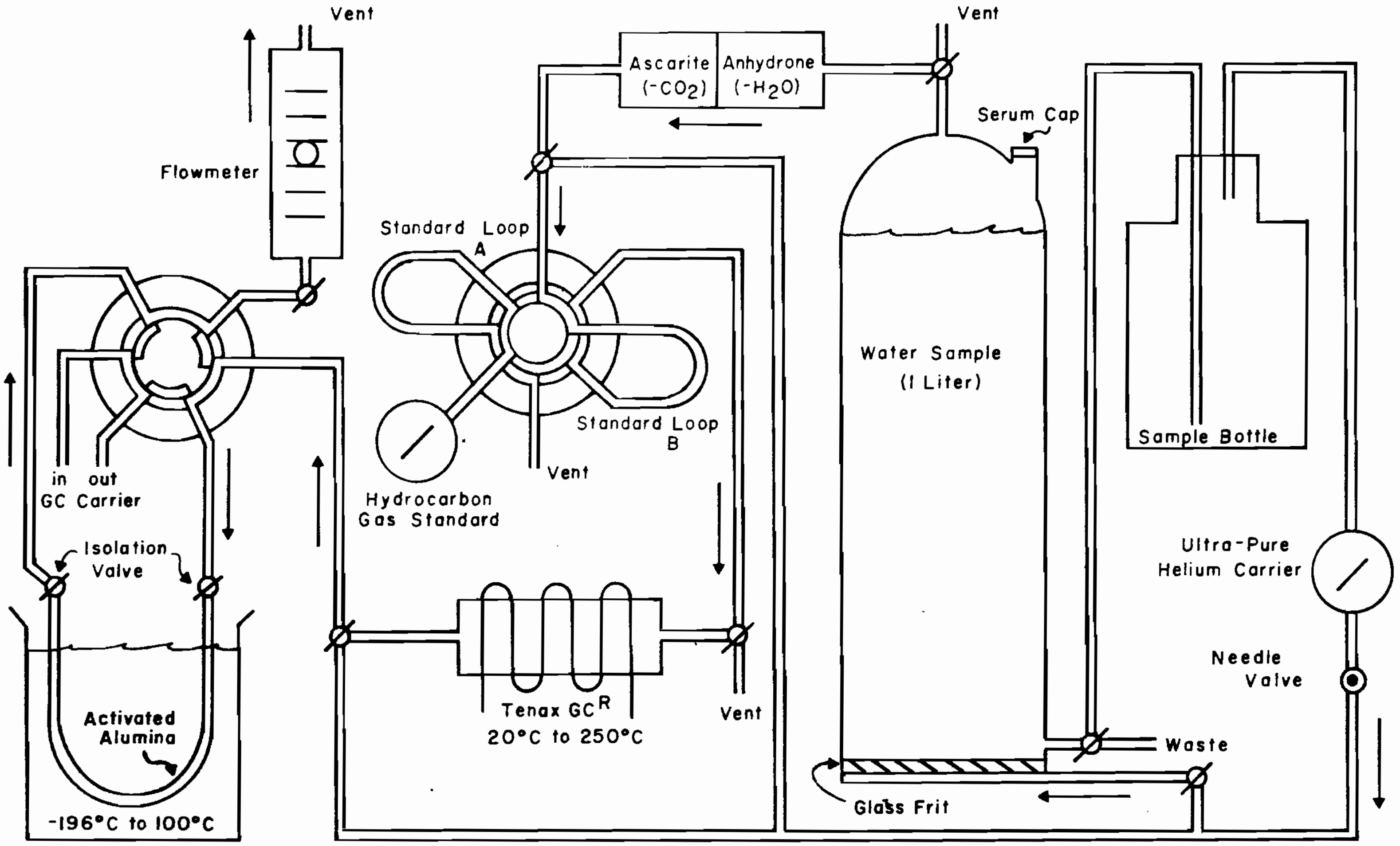


Figure 19. Diagram of the stripping procedure for LMW aliphatic hydrocarbon analysis. The arrows represent the gas flow direction during stripping.

Tenax G.C.® traps to remove carbon dioxide, water vapor, and heavier hydrocarbons, respectively. The LMW hydrocarbons are subsequently concentrated on an Activated Alumina® trap (6 cm x 0.48 cm o.d.) at -196° C. The trap is then warmed to 100° C, and the gases are backflushed directly to the gas chromatographic column.

Quantitative removal of the gases from solution was determined during each cruise by restripping samples and analyzing for the residual material left in solution. In almost all cases the restrip was found to contain insignificant amounts of hydrocarbons.

Standards and blanks were run continuously during each cruise. Built into the "stripper board" are a series of stainless-steel cylinders that contain various mixtures of the C_1 to C_4 hydrocarbon gases of known concentration. The standard gases are expanded into one of the two standard loops at ambient pressures and temperatures, and then valved into the main gas flow to be collected on the Activated Alumina® trap at -196° C.

At room temperature, Tenax G.C.® retains C_5+ hydrocarbons that are extracted from the sample. To minimize contamination, the trap was routinely heated to 250° C and backflushed with ultrapure helium for approximately 10 minutes.

2.2.2 Gas Chromatography

Separation and detection of components were carried out on a Hewlett-Packard 5710A gas chromatograph equipped with a flame ionization detector (FID). Separation was originally effected on a Porapak Q®, 60- to 80-mesh column (1.2 m x 0.48 cm), in series with an Activated Alumina® column (0.3 m x 0.48 cm) impregnated with silver nitrate (1% by weight). This column configuration (charge transfer complexing) allowed resolution of the alkenes from their corresponding alkanes (e.g., ethene from ethane). However, because of its relatively low decomposition temperature (250° C) and relatively high-bleed characteristics at lower temperatures, the Porapak Q® column was replaced with an Activated Alumina® column prior to 1978 fieldwork.

A highly Activated Alumina® (Applied Science Laboratories, Inc.), 60- to 80-mesh column (1.8 m x 0.48 cm) is now used for separation of the components. This column, with its relatively good thermal stability and low-bleed properties, has excellent resolution and good baseline characteristics. Because of the column's high activation, the alkenes are effectively chromatographed from their corresponding alkanes, but they are also partially destroyed by oxidation. This oxidation leads to a reduced response for both the standards and samples and thus is not important in quantitation.

Activation of the column was performed in two steps. In the first step the column was heated to 250° C while maintaining a carrier flow rate of 50 ml min^{-1}. This not only activates the column but also removes any contaminants that may be present. In the second step, 10 to 50 μl of distilled water were injected onto the column, which was then conditioned at 200° C for approximately 1 hour. This step selectively deactivates the alumina by hydrating many of the alumina hydration sites. This selective activation procedure was performed throughout the cruises as needed to maintain ideal alkane-alkene separation.

Elution order of the trapped gases is air gases (O_2 and N_2 in water samples only), methane, ethane, ethene, propane, propene, isobutane, and n-butane (fig. 20). Retention time of the butanes is on the order of 8 minutes with a helium flow rate of 50 ml min^{-1}. The column was temperature-programmed in the following manner: 2-minute hold at 100° C followed by an 8° C min^{-1} temperature rate increase to 170° C.

The components are detected by means of a hydrogen-air FID. As a component moves through the detector, it is ionized by the flame and produces a current in proportion to the amount of material in the carrier stream. The voltage changes are reproduced graphically and digitized by a Hewlett-Packard 3380A integrator. The digitized area under each peak is proportional to the moles of component. Assuming the ideal gas law, area is also proportional to the component volume. The linearity of the detector response was checked and found to be excellent--in the range of 0-2200 nl of methane (fig. 21), which encompasses nearly all of the range in values observed in Cook Inlet.

Components were identified and quantitated by comparing retention times and relative responses of standard hydrocarbon gas mixtures with those of the sample. The volume of standard component analyzed was calculated by multiplying the concentration, parts per million by volume (ppmv), of the component in the mixture by the total volume of gas injected through the standard loop (ml). The volume of gas in the

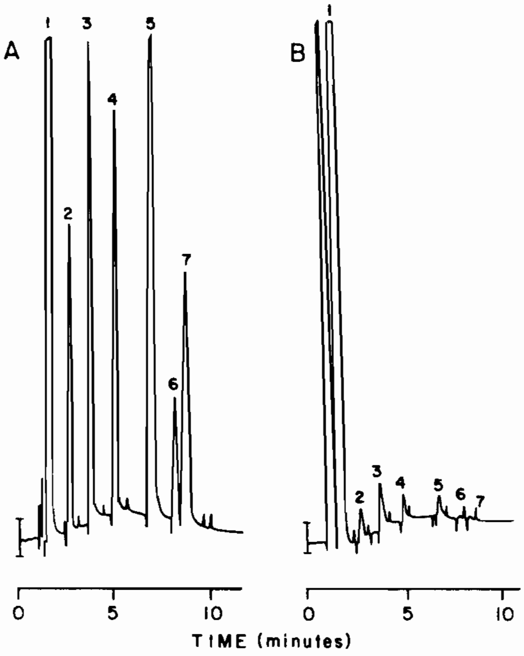


Figure 20. Chromatograms of A) standard LMW aliphatic hydrocarbon mixture and B) water sample. Elution order is: air gases (oxygen, nitrogen in water samples only): 1) methane; 2) ethane; 3) ethene; 4) propane; 5) propene; 6) iso-butane 7) n-butane.

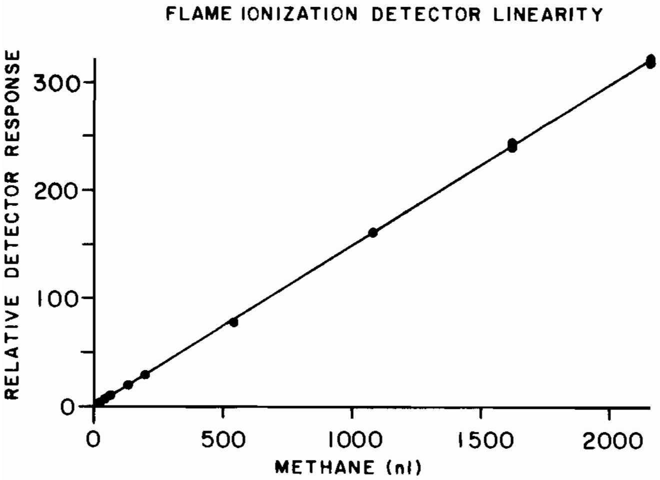


Figure 21. Flame ionization detector response as a function of methane volume (nl). All 40 data points are plotted. Regression correlation coefficient R^2 = 0.99988.

sample was determined by comparing responses of the known gas volume with those of the sample. The dissolved-gas concentration in nl l^{-1} STP was then calculated assuming the ideal gas law and correcting for temperature, pressure, and sample volume. All gas concentrations reported are STP unless otherwise indicated.

Standard hydrocarbon mixtures prepared in helium by Matheson Gas Products are reported to ± 10% (relative standard deviation) accuracy. Standard A was also calibrated by the National Bureau of Standards (NBS) and found to be in only partial agreement with the Matheson analysis within precision errors (table 3). Because the NBS analysis is more precise (< 8% error), the NBS concentrations for Standard A were used to calibrate the other two standards. This calibration assumed that the responses of ethene, propene, and iso-butane equaled those of ethane, propane, and n-butane, respectively. This was found to be true within the error of precision when using the Porapak Q® column at the time of this calibration. The component concentrations of the other two standards computed in this way generally agreed within 10% of the Matheson analysis.

The calibrated standard loop volumes were 1.051 ml and 0.112 ml. The large loop was calibrated gravimetrically using water. The small loop volume was determined by comparing the average (all components) response/volume ratio for the large loop with the response of the small loop. The valve dead volume was obtained from Carle Instruments, Inc., and added to the loop volume to obtain the total standard injection volume.

As shown in table 3, the accuracy of measurement based on the National Bureau of Standards and Matheson intercalibration is on the order of 10%. Table 4 shows the analytical precision, which for all components is less than 4% (relative standard deviation). The total sampling and analytical precision is less than 8% for all components, as shown in table 5. The detection limit of this method based on a signal-to-noise ratio of 2:1 is 0.10 nl l^{-1} for components other than methane. The detection limit for methane is near 1 nl l^{-1} because of baseline noise and a lower component response (only one carbon atom).

TABLE 3

Standard hydrocarbon gas mixtures used in this study.

Component	Standard A		Standard B	Standard C
	NBS	Matheson		
Methane	21.8 ± 0.8	21	97.4	538.5
Ethane	1.3 ± 0.1	1	4.9	5.9
Ethene	-	-	2.0	11.7
Propane	1.25 ± 0.02	2	4.7	5.9
Propene	-	-	1.8	11.5
iso-Butane	-	-	5.2	2.4
n-Butane	1.1 ± 0.02	1	1.9	5.7

Note: Concentrations are in ppmv. All standards were prepared by Matheson Gas Products. Standard A, calibrated by the National Bureau of Standards, was used to calibrate the other gas mixtures.

2.3 Natural Modification of Light Hydrocarbons Experimental Design

Seawater was pumped at 30 l min^{-1} from 15-m depth at station A just outside Kachemak Bay (fig. 5) into a prerinsed (seawater) carbuoy and left to overflow several volumes. The water was then drawn into 60 presterilized (18 minutes at 130° C @ 16 psi H_2O) 1-l glass-stoppered bottles. Twelve samples were poisoned immediately with approximately 200 mg NaN_3 ("killed" bottles).

Forty-five bottles, including those to which the NaN_3 had been added, were allowed to incubate aboard ship in natural light over an eighteen-day period while eleven bottles were incubated in the dark. Four samples were analyzed immediately for the concentration of aliphatics.

Temperature in the bottles incubated in the light was maintained at approximately 4° to 9° C by placing the bottles in Plexiglas® incubators that had surface seawater continuously flowing through them. Temperature was maintained in the same range in the "dark" bottles by placing them in a refrigerator. The original sample temperature and salinity were 5.01° C and 32.04 °/oo, respectively.

TABLE 4

Analytical precision based on replicate analyses of standard hydrocarbon mixture C.

Component	Volume (nl)	Run 1	Run 2	Run 3 (response)	Run 4	$\bar{X}$	$\sigma/\bar{X}$ %
Methane	565.8	790626	787232	782520	781815	785548	0.5
Ethane	6.2	16545	16519	16378	16333	16444	0.6
Ethene	12.3	31832	31783	31722	31745	31770	0.1
Propane	6.2	25125	25137	24887	24910	25015	0.5
Propene	12.1	27543	28767	29352	30046	28927	3.7
Iso-Butane	2.5	11927	12487	12214	12225	12213	1.9
n-Butane	6.0	31221	33079	32273	31910	32121	2.4

Note: Component volumes (nl) are calculated by multiplying the component concentration in the standard mixture (ppmv) by the total amount of gas injected through the standard loop (ml).

TABLE 5

Total sampling and analysis precision of samples taken at a station in Shelikof Strait southeast of Cook Inlet at a depth of 20 m.

Component	Run 1	Run 2	Run 3	$\bar{X}$	$\sigma/\bar{X}$ %
Methane	325.4	330.2	327.8	327.8	.1
Ethane	.73	.72	.71	.72	1.4
Ethene	2.71	2.74	2.71	2.72	.1
Propane	.55	.57	.55	.56	2.1
Propene	.69	.70	.79	.73	8.0
Iso-Butane	T	T	T	-	-
n-Butane	T	T	T	-	-

Note: Concentrations are in nl l^{-1}. "T" indicates a value below the detection limit of 0.10 nl l^{-1}.

Table 6 lists the timing, number, and types of analyses performed in this experiment. Light levels were measured using a quantum sensor (Lambda Instruments model LI-192S) sensitive to the photosynthetically active region of 400-700 nm (visible light spectrum) and integrator model LI510 (also by Lambda Instruments). The light level reading was taken immediately after removing the "light" or "killed" bottles from the light. Analysis for hydrocarbon content was made within 1 hour after these samples were removed from the light.

Dissolved oxygen was measured using a modification of the Winkler method described in Strickland and Parsons (1972). Nutrient samples were taken from the already gas-stripped samples and frozen until analyzed by autoanalyzer using methods described in Strickland and Parsons (1972). "Killed" samples could not be analyzed for nutrients because of the NaN_3 interferences.

It was noted after 14 days that substantial growth of plankton had occurred in the "light" bottles. After gas stripping, 150-ml subsamples were taken and kept at 5° C in the dark until filtration was possible. Back in the laboratory these samples were filtered through

TABLE 6

Natural modification of light hydrocarbons experimental design.

Elapsed Time (days)	Aliphatic Hydrocarbons "Light"	"Dark"	"Killed"	O_2	Nutrients	SEM
0	4	-	-	1	7	-
1	4	-	-	-	4	-
2	3	3	3	2	6	-
4	4	-	-	-	4	-
6	3	3	3	2	6	-
11	4	-	-	-	4	-
14	3	2	3	2	5	6
18	4	3	2	-	7	7

Note: Experiment was run 12-30 May 1979. Values are the number of samples analyzed. Two of the sixty samples were lost in handling.

0.4-μm Nuclepore® filters (47 mm) and prepared with gold for scanning electron microscopy (SEM). These filters were photographed using a Super Mini SEM-II® (International Scientific Instruments, Inc.) to assess the qualitative differences among the "light," "dark," and "killed" bottle growth.

3. RESULTS

3.1 Areal and Temporal Distributions

3.1.1 Methane

The distribution of dissolved methane in lower Cook Inlet was characterized by localized sources. Spring and summer distributions at the surface and within 5 m of the bottom (figs. 22 to 25) showed localized sources of methane in both Kachemak and Kamishak bays and along the eastern shore, north of Anchor Point (see fig. 6). In general, these sources appeared more pronounced in late summer and at depth. Methane in the central portion of the lower Inlet remained relatively low in concentration and vertically homogeneous throughout the year.

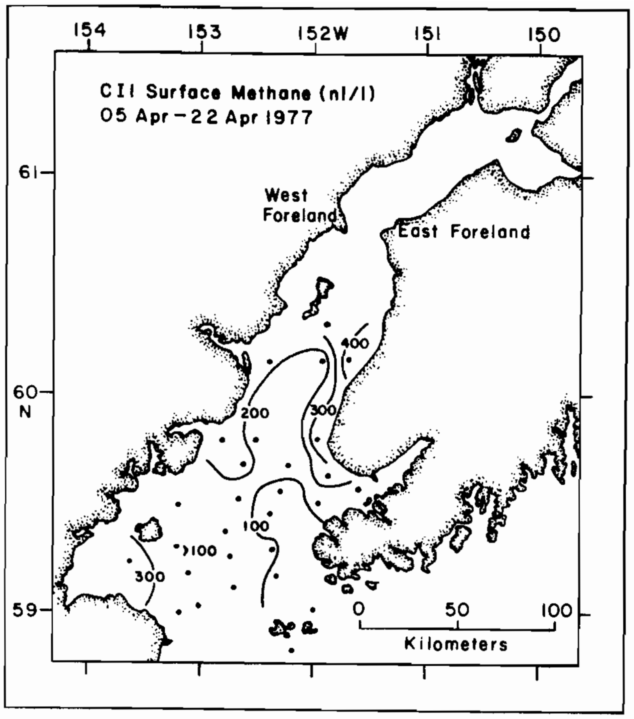


Figure 22. Distribution of dissolved methane at the surface in April 1977.

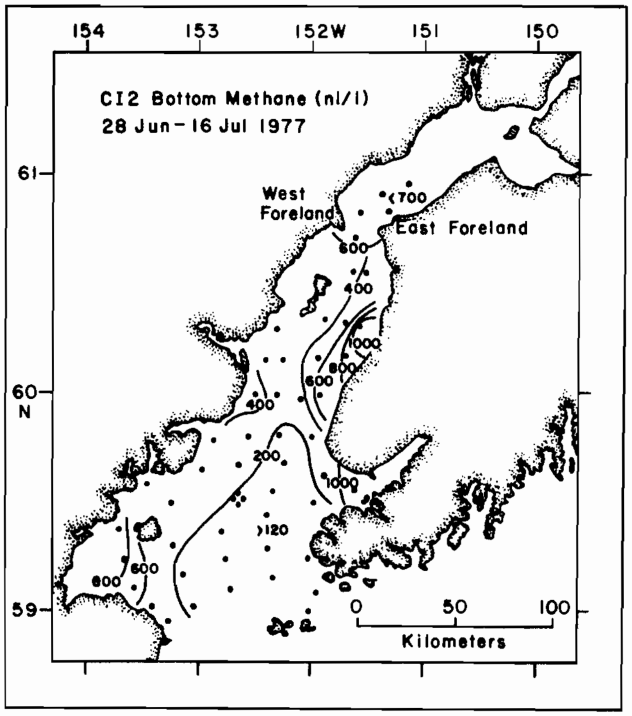


Figure 23. Distribution of dissolved methane within 5m of the bottom in April 1977.

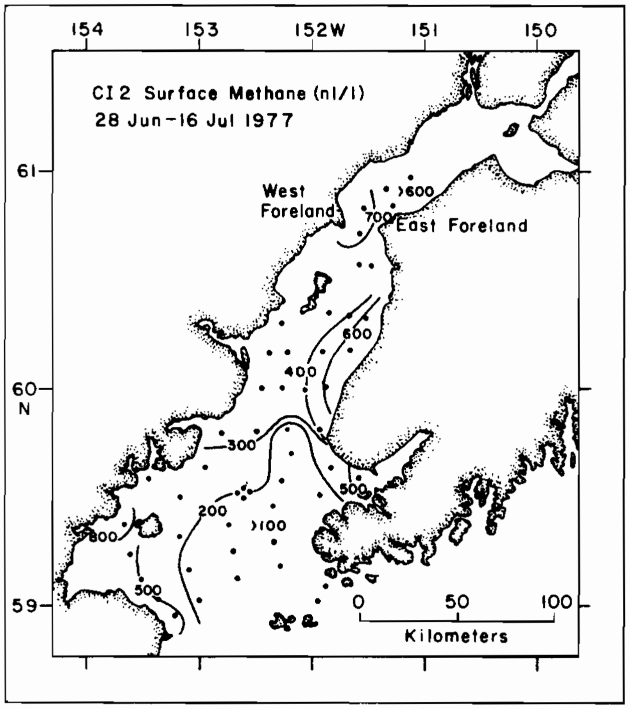


Figure 24. Distribution of dissolved methane at the surface in July 1977.

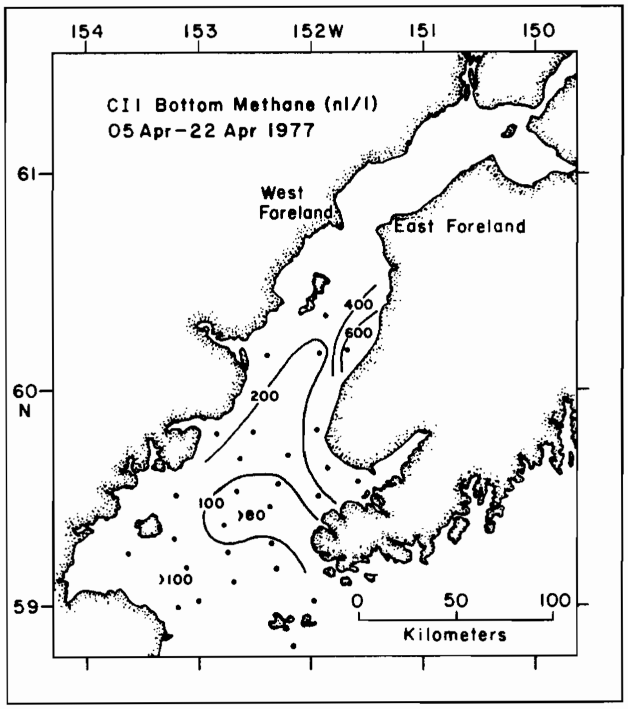


Figure 25. Distribution of dissolved methane within 5 m of the bottom in July 1977.

The increase in methane concentration to the north was in agreement with the localized sources and mean flow regime. Gulf of Alaska water, which is relatively low in methane (< 200 nl l^{-1}), flows in along the eastern shore and is spread laterally by the cross-channel flow. The core of this flow was seen particularly well in a vertical cross section of methane in September 1978 (fig. 26). As this water flows northward, its methane content is increased because of mixing with local sources.

The distribution of methane in upper Cook Inlet indicated a source of relatively high methane within Trading Bay (fig. 27). This source appeared to be less intense and more diffuse in late summer and early fall, although this may have been an artifact of the sampling grids employed. In all cases, however, concentrations of methane decreased away from Trading Bay to levels similar to those found below the Forelands.

For all cruises, locations, and depths, dissolved methane concentrations varied by almost three orders of magnitude. Concentrations ranged from 55 to 4100 nl l^{-1} and averaged 460 ± 535 nl l^{-1}. The mean concentration in upper Cook Inlet of 1090 ± 900 nl l^{-1} was approximately three times greater than the mean value in the lower Inlet of 375 ± 395 nl l^{-1}. These means are significantly different at the 99% confidence level. The highest concentrations were observed in Trading Bay. The next highest concentrations were found in Kachemak Bay, and the lowest concentrations were found in the central part of the lower Inlet, as expected.

Dissolved methane was usually supersaturated with respect to its partial pressure in the atmosphere. Equilibrium saturation concentrations based on the Bunsen solubility coefficients given by Yamamoto et al. (1976) and an atmospheric methane concentration of 1.4 ppmv (Ehhalt, 1974) would be approximately 50 nl l^{-1}.

Dissolved methane in lower Cook Inlet increased from spring to fall. The time-space mean methane concentration in the lower Inlet for April 1977 (180 ± 110 nl l^{-1}) was compared with that from July 1977 (330 ± 210 nl l^{-1}), as were the time-space means from May 1978 (350 ± 215 nl l^{-1}) and September 1978 (475 ± 490 nl l^{-1}). In both years, methane concentrations increased significantly at the 99% confidence level from spring to summer-fall.

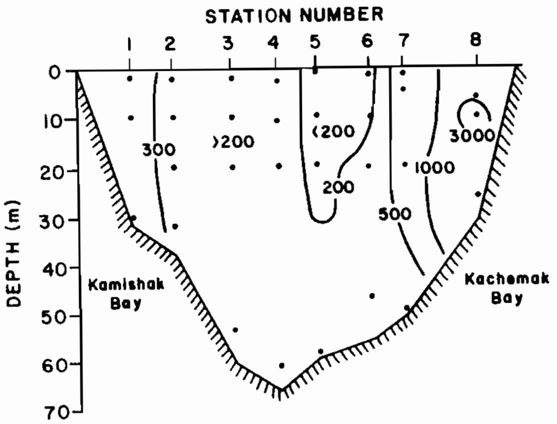


Figure 26. Vertical cross section of dissolved methane (nl l^{-1}) for a line of stations traversing lower Cook Inlet in September 1978. See figure 4 for station locations.

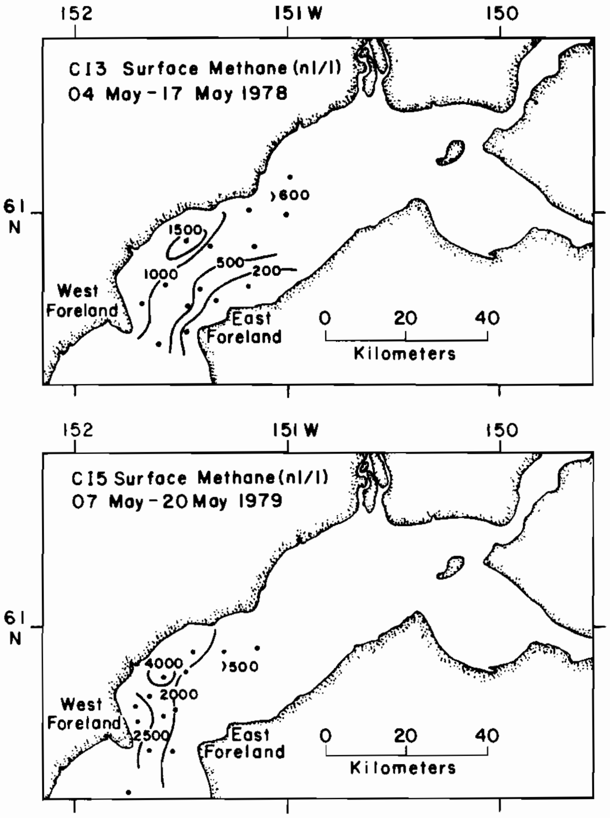


Figure 27. Distribution of dissolved methane at the surface in upper Cook Inlet in A) May 1978 and B) May 1979.

The concentration of dissolved methane in upper Cook Inlet, in contrast to the lower Inlet, showed less seasonal variability. No seasonal data are available for the upper Inlet in 1977. However, comparison of the time-space mean methane concentration in May 1978 (695 ± 405 nl l^{-1}) with that in September 1978 (455 ± 105 nl l^{-1}) yields no significant (99% confidence level) decrease from spring to fall.

Short-term changes in methane concentration showed a strong semidiurnal fluctuation. Time series stations 7, in outer Kachemak Bay (fig. 3), and 9, east of Kalgin Island (fig. 4), are examples of locations exhibiting this strong fluctuation (figs. 28A and 28B). Both stations were located near sources of dissolved methane and showed the effects of the alternating pulse of relatively methane-rich water during tidal excursions.

The semidiurnal signal in methane was approximately 90° out of phase with respect to the tides at station 7 (fig. 28A). Methane in the surface water appeared to be decoupled from the bottom water, which may have been the result of the gyral circulation superposed on the tidal cycle. The regular increase in methane concentration to greater than 400 and 500 nl l^{-1} during ebb flow and the decrease to as low as 200 nl l^{-1} during flood were in agreement with the source of methane-rich, relatively low-salinity water in inner Kachemak Bay and a source of methane-poor, relatively high-salinity water derived from the Gulf of Alaska (fig. 29A). The variation in concentration, as measured by the relative standard deviation (time averaged) for station 7, was 28% at the surface and 15% at depth (44 m). It must be noted, however, that microbiological sampling during this time series showed possible contamination from the ship's holding tanks at the beginning of the record, which would affect the absolute concentration levels measured.

The semidiurnal signal in methane at station 9 was in phase with the tidal signal (fig. 28B). The concentration of methane increased to more than 400 nl l^{-1} during flood and decreased to almost 200 nl l^{-1} during ebb. The methane variation as measured by the relative standard deviation (time averaged) for station 9, was 14% and 18%, for the surface and at depth (19 m) respectively.

Salinity data at this station also showed a fluctuation that was in phase with the tides at depth (fig. 29B). However, the surface

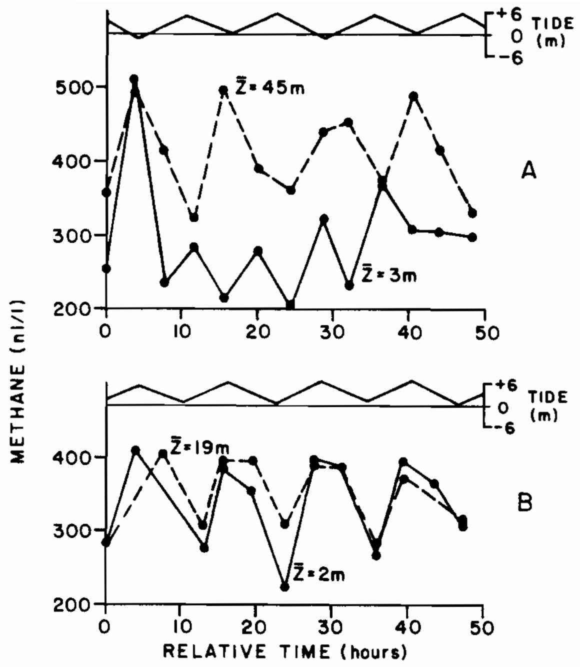


Figure 28. Fluctuations in dissolved methane at time series stations. A) Station 7 in Kachemak Bay (May 1978). B) Station 9 east of Kalgin Island (September 1978). See figures 3 and 4 for station locations.

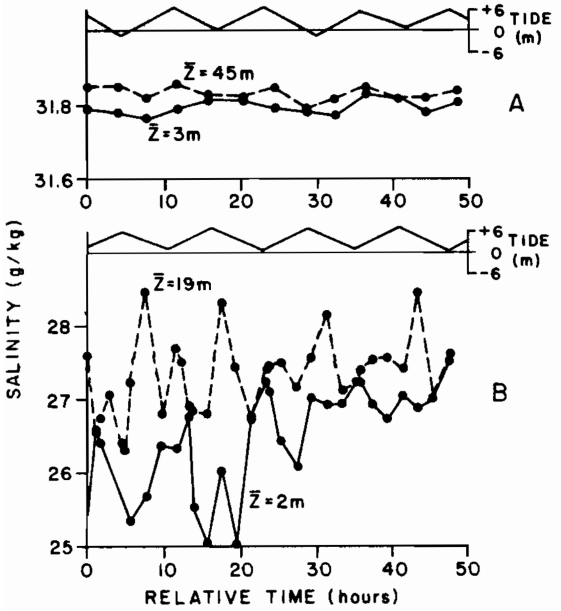


Figure 29. Fluctuations in salinity at time series stations. A) Station 7 in Kachemak Bay (May 1978). B) Station 9 east of Kalgin Island (September 1978). See figures 3 and 4 for station locations.

salinity was out of phase with the tides, suggesting that the influx of salt at depth was balanced by an efflux of fresh water at the surface. During ebb, sufficient mixing homogenized the water column such that at low water, salinity as well as methane were the same, or nearly so, at the surface and at the bottom. This shows the high degree of mixing that occurred over relatively short time scales as a result of the tidal pumping. The sparse areal coverage during this particular cruise, coupled with the fact that there was no significant linear relationship between methane and salinity, precludes delineating the methane source end members.

3.1.2 Ethane

The distribution of ethane in lower Cook Inlet was rather uniform throughout the year (figs. 30 and 31). Because of strong vertical mixing, the water column was generally homogeneous with respect to ethane. As spring progressed into summer, a slight concentration gradient developed to the west which appeared to outline the bifurcation in the mean flow regime (fig. 31). Slightly elevated concentrations of ethane usually occurred within Kachemak Bay and along the eastern shore north of Anchor Point.

Ethane concentrations in the lower Inlet were generally low. Concentrations rarely exceeded 1.0 $nl\ l^{-1}$ and exceeded 2.0 $nl\ l^{-1}$ only at two stations located just north of Kalgin Island measured in May 1979. High values at these stations represented a flux of ethane from the upper Inlet. Including even these values, the average concentration of ethane for all cruises, locations, and depths in the lower Inlet was $0.6 \pm 0.4\ nl\ l^{-1}$. The range in concentrations was from less than 0.1 (detection limit) to 4.2 $nl\ l^{-1}$. On the basis of the Bunsen solubility coefficient and the range in atmospheric concentrations of ethane given by Harrison et al. (1981), the maximum equilibrium concentration of ethane is less than 0.3 $nl\ l^{-1}$. Thus, ethane appeared to be typically supersaturated with respect to its equilibrium concentration.

The distribution and concentrations of ethane in upper Cook Inlet were in contrast to those found in the lower Inlet. At least two major sources were present in Trading Bay during May 1979 (fig. 32B). Both sources were not always observed (figs. 31 and 32A; cf. 32B), though this may have been the result of the nonsynoptic nature of the sampling

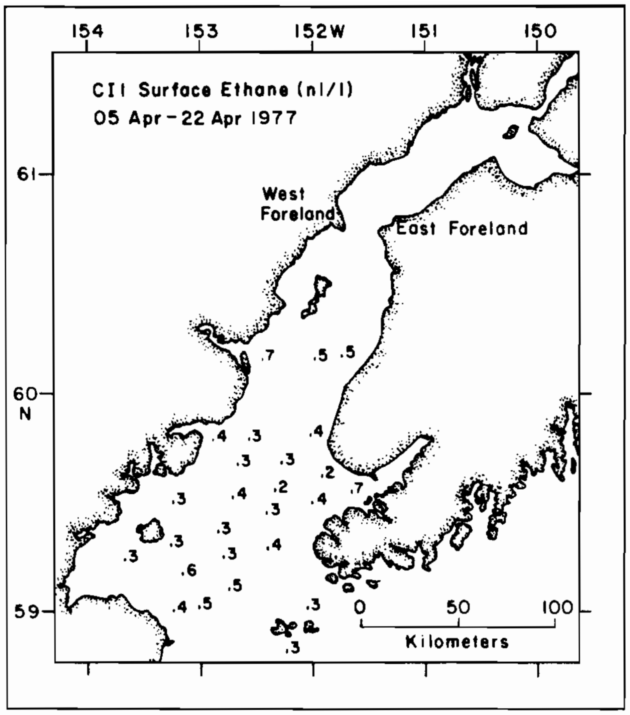


Figure 30. Distribution of dissolved ethane at the surface in April 1977.

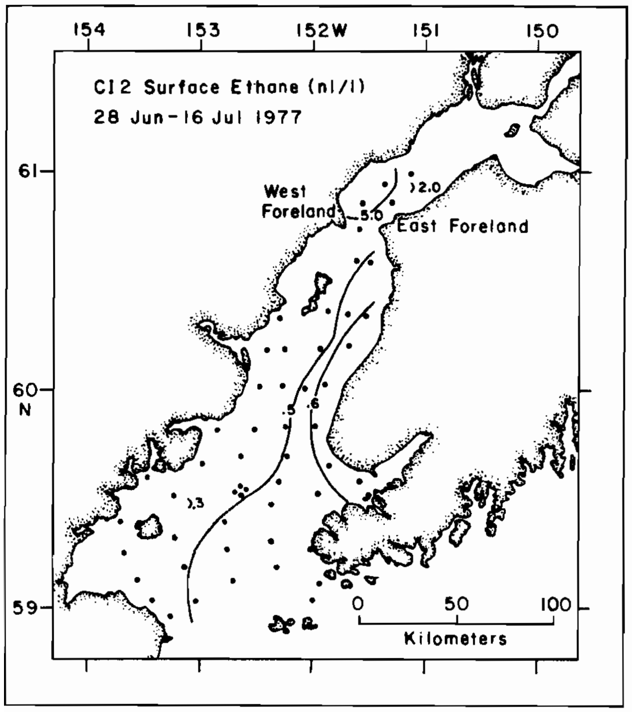


Figure 31. Distribution of dissolved ethane at the surface in July 1977.

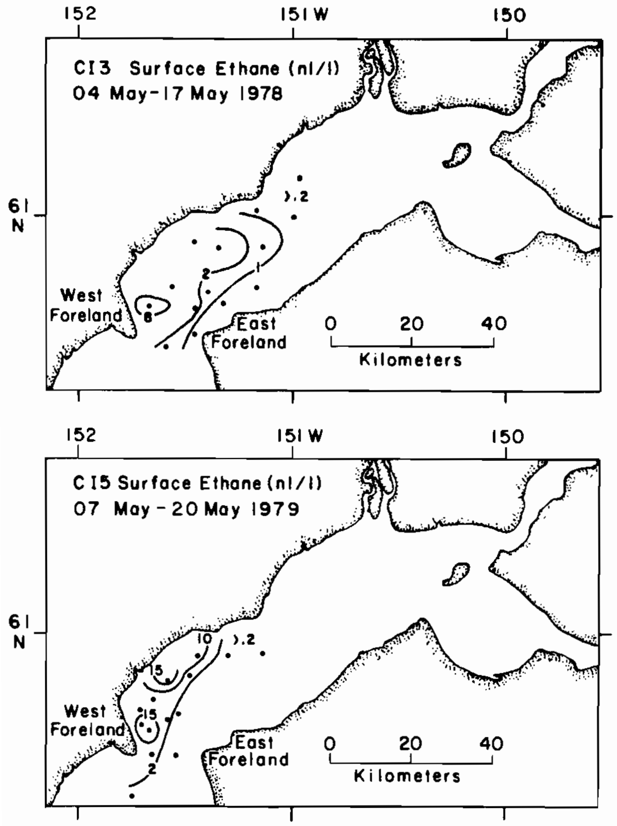


Figure 32. Distribution of dissolved ethane at the surface in upper Cook Inlet in A) May 1978 and B) May 1979.

grids or because of an episodic nature of the sources. Concentrations of ethane decreased significantly to the north and east from Trading Bay where they attained some of the lowest values in the Inlet. The concentration range for all cruises, locations, and depths in the upper Inlet spanned two orders of magnitude from 0.2 to 21.4 nl l^{-1} and averaged 4.1 ± 4.4 nl l^{-1}, which is a factor of 7 greater than the mean for the lower Inlet.

There was no predictable seasonal variation in ethane when averages were made for either the upper or lower Inlet. Although the time-space mean ethane concentration increased significantly (99% confidence level) in the lower Inlet from April 1977 (0.4 ± 0.2 nl l^{-1}) to July 1977 (0.5 ± 0.2 nl l^{-1}), no significant change was observed for May to September 1978. In the upper Inlet, no significant change was observed during either time period.

Short-term variation in the concentration of ethane was similar to that of methane, in which a semidiurnal tidal signature was seen quite clearly. Time series data for station 7 in Kachemak Bay and station 9

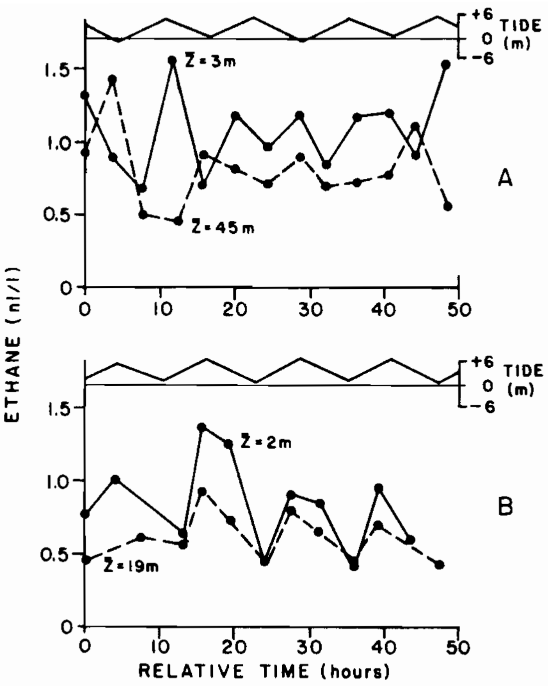


Figure 33. Fluctuations in dissolved ethane at time series stations. A) Station 7 in Kachemak Bay (May 1978). B) Station 9 east of Kalgin Island (September 1978). See figures 3 and 4 for station locations.

east of Kalgin Island (figs. 3 and 4) showed a clear semidiurnal fluctuation in the concentration of ethane (figs. 33A and 33B). However, variation of ethane in the surface water of Kachemak Bay, like methane, appeared temporally random, which may have been a result of the effects of the complex circulation and stratification within the bay. Variations in ethane for both stations, as measured by a relative standard deviation (time averaged), were between 30% and 40% for both surface and bottom waters.

The fluctuation of ethane at station 9 appeared to be in phase with the tidal cycle. The observed increase to approximately 1.4 nl l^{-1} at the surface, concomitant with flood tide, was in apparent contradiction to the source of ethane in upper Cook Inlet. However, this discrepancy is resolved by observing that ethane showed a significant (95% confidence level) negative correlation with salinity (r = -0.74) during this time series. The association of low-salinity water with high-ethane content was in agreement with the general distribution pattern of ethane. The increase of ethane and decrease in salinity at the surface during flood was apparently a consequence of the saline water intrusion at depth. Ethane levels, similar to those of methane and salinity, showed a vertical homogeneity during low water, indicating the high degree of mixing occurring in this region.

3.1.3 Ethene

There is a dramatic seasonal change in the distribution and concentration of ethene in lower Cook Inlet. Concentrations in the spring were quite uniform throughout the lower Inlet and were relatively low (all > 1.0 nl l^{-1}), as shown in figure 34. In contrast, summer and fall distributions were characterized by increased concentrations (up to 6.9 nl l^{-1}) and by localized sources in Kachemak Bay and along the eastern shore (fig. 35). The time-space mean ethene concentration increased in the lower Inlet from April to July 1977 from 0.5 ± 0.1 to 2.2 ± 0.8 nl l^{-1}. From May to September 1978 ethene increased from 1.2 ± 0.7 to 2.4 ± 1.1 nl l^{-1}. Both increases are significant at the 99% confidence level.

The distribution of ethene in upper Cook Inlet was uniform throughout the year. Concentrations in the upper Inlet were relatively low, never exceeding 1.7 nl l^{-1} and averaging 0.4 ± 0.2 nl l^{-1} for all samples analyzed. Concentrations of ethene also increased significantly (99% confidence level) from May to September 1978 (0.3 ± 0.2 to 0.5 ± 0.2 nl l^{-1}).

The previously mentioned, tidally induced fluctuations were also observed for ethene. A semidiurnal signal in dissolved ethene was observed at time series stations both 7 and 9 (figs. 36A and 36B). At station 7 the ethene signal was again out of phase with the tides and consequently was in agreement with the source of ethene, low-salinity water (fig. 29A) within Kachemak Bay. At station 9 the ethene signal was in phase with the tides at depth, but again appeared more random at the surface. Salinity, which was positively correlated with ethene ($r = 0.73$), was in agreement with source distributions.

3.1.4 Propane

The distribution and concentration of dissolved propane were similar to those of ethane. The distribution of propane in lower Cook Inlet remained relatively uniform throughout the year, although a

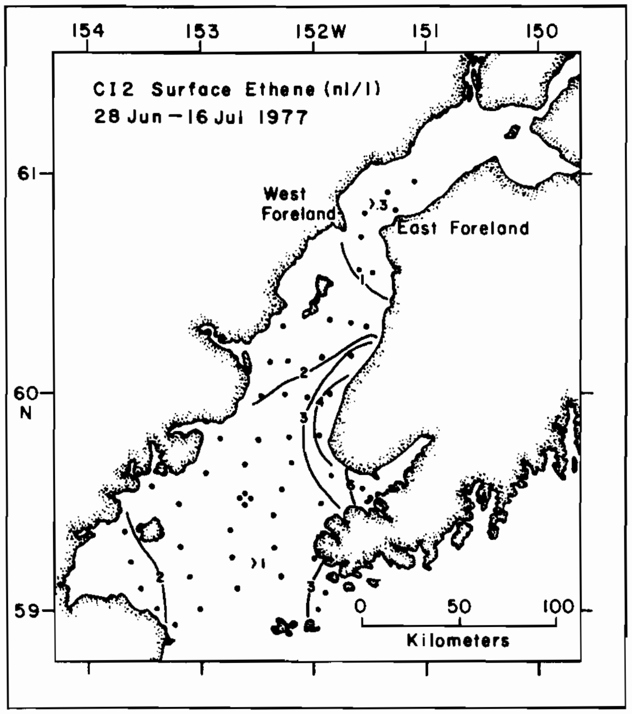


Figure 34. Distribution of dissolved ethene at the surface in April 1977.

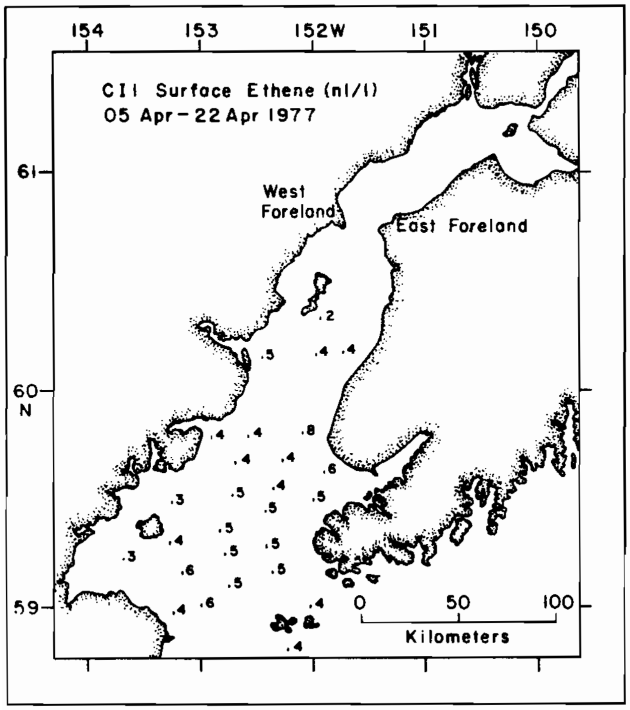


Figure 35. Distribution of dissolved ethene at the surface in July 1977.

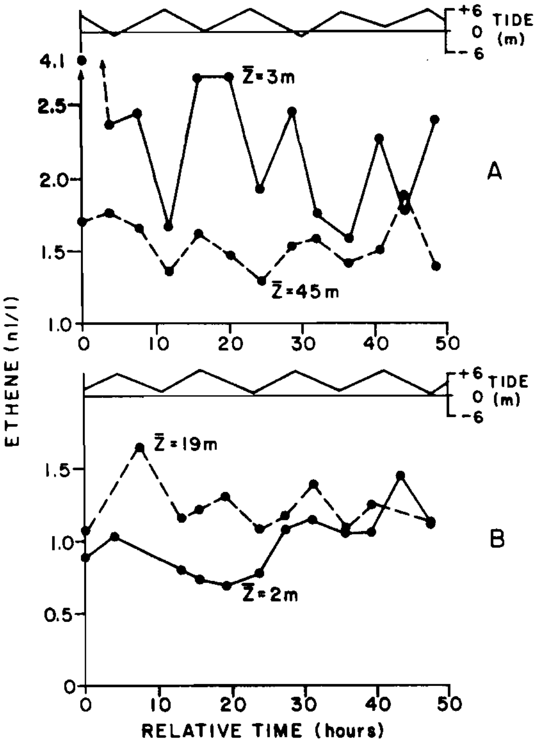


Figure 36. Fluctuations in dissolved ethene at time series stations. A) Station 7 in Kachemak Bay (May 1978). B) Station 9 east of Kalgin Island (September 1978). See figures 3 and 4 for station locations.

slight concentration gradient developed to the west in late summer (figs. 37 and 38). The mean concentration of propane for all cruises, locations and depths in the lower Inlet was 0.3 ± 0.2 nl l^{-1}. Extreme values approached 2.0 nl l^{-1}.

The distribution and concentrations of propane in upper Cook Inlet were distinctly different from those in the lower Inlet. Concentrations in the upper Inlet ranged from less than 0.1 (detection limit) to 11.2 nl l^{-1} and averaged 2.1 ± 2.4 nl l^{-1}. Analogous to methane and ethane, propane had elevated concentrations in Trading Bay. Two major sources within Trading Bay were again apparent (figs. 39A and 39B), as previously noted for methane and ethane.

Dissolved propane increased in concentration in the lower Inlet from spring to fall. Time-space mean concentrations for April and July 1977 were 0.2 ± 0.1 and 0.3 ± 0.1 nl l^{-1}, respectively. For May and September 1978 the means were 0.2 ± 0.1 and 0.4 ± 0.2 nl l^{-1}, respectively. The seasonal increases in both years are significant at the 99% confidence level.

Propane concentrations in upper Cook Inlet did not change significantly in time. Data from the May and September 1978 cruises indicated

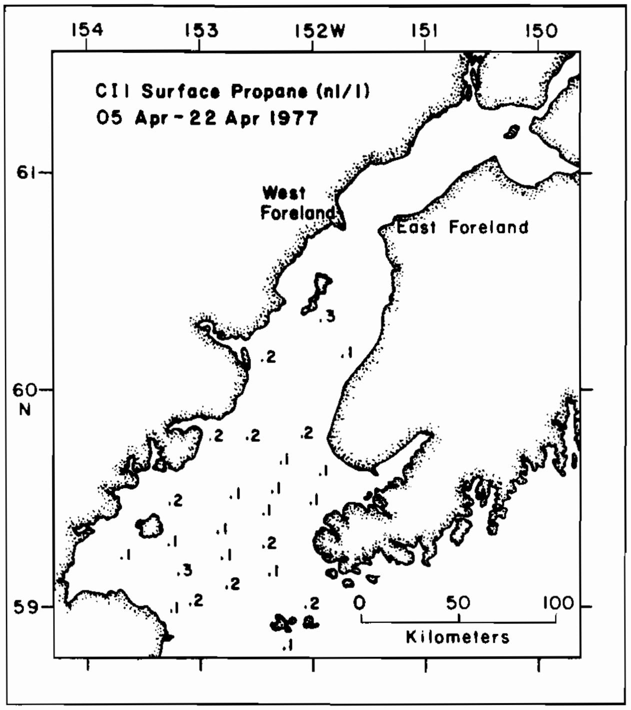


Figure 37. Distribution of dissolved propane at the surface in April 1977.

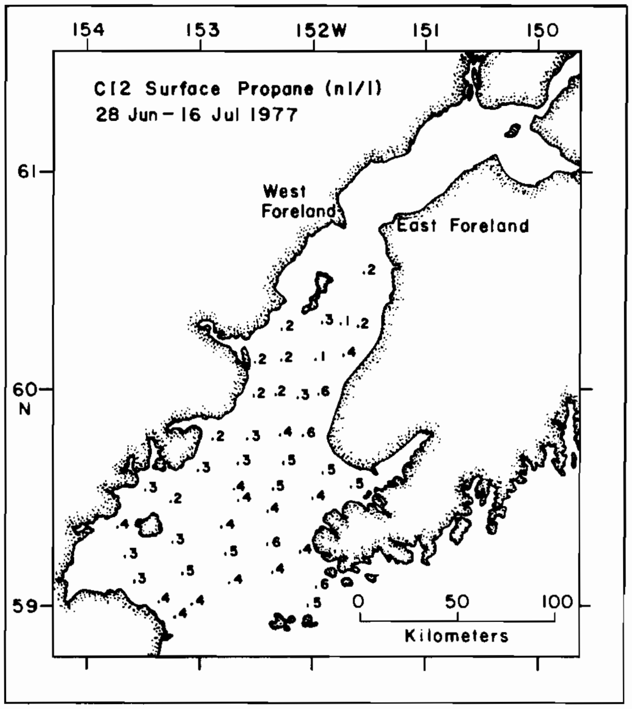


Figure 38. Distribution of dissolved propane at the surface in July 1977.

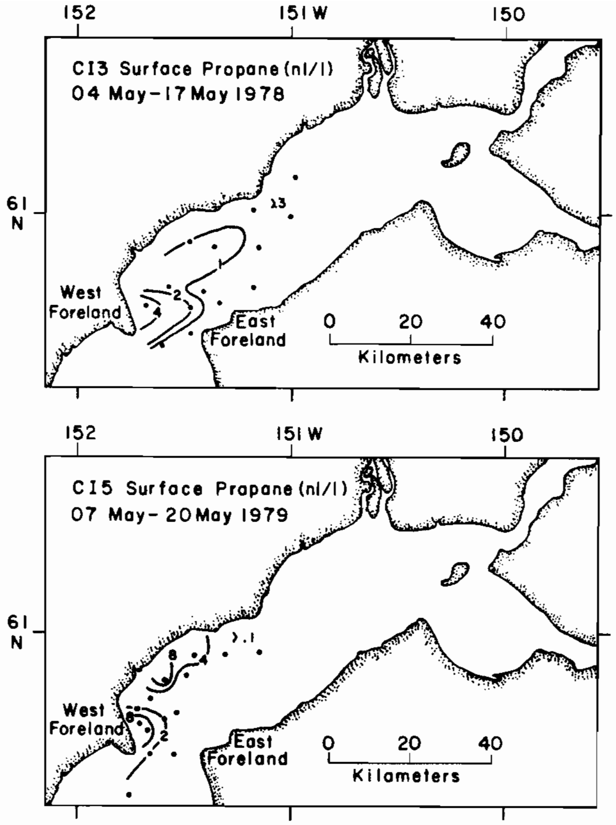


Figure 39. Distribution of dissolved propane at the surface in upper Cook Inlet in A) May 1978 and B) May 1979.

there were no significant changes in propane concentration. The time-space mean concentration in May 1978 was 1.1 ± 1.1 nl l^{-1}; for September 1978 the mean was 1.3 ± 1.1 nl l^{-1}.

Short-term fluctuations in propane were similar to those already presented for the C_1 and C_2 aliphatics. The semidiurnal signal in propane was still evident, although somewhat reduced in intensity.

3.1.5 Propene

The distribution of dissolved propene was similar to that of ethene. Most of lower Cook Inlet showed uniform concentrations of propene throughout the year, although sources in Kachemak Bay and along the eastern shore became evident in summer (figs. 40 and 41). Upper Cook Inlet was homogeneous with respect to propene throughout the year. Concentrations of propene for all cruises, locations, and depths ranged from less than 0.1 to 2.5 nl l^{-1}. The highest concentrations were found in Kachemak Bay.

Propene increased from spring to fall in the lower Inlet but showed no significant changes in the upper Inlet over the same time period. The April and July 1977 data showed a significant (99% confi-

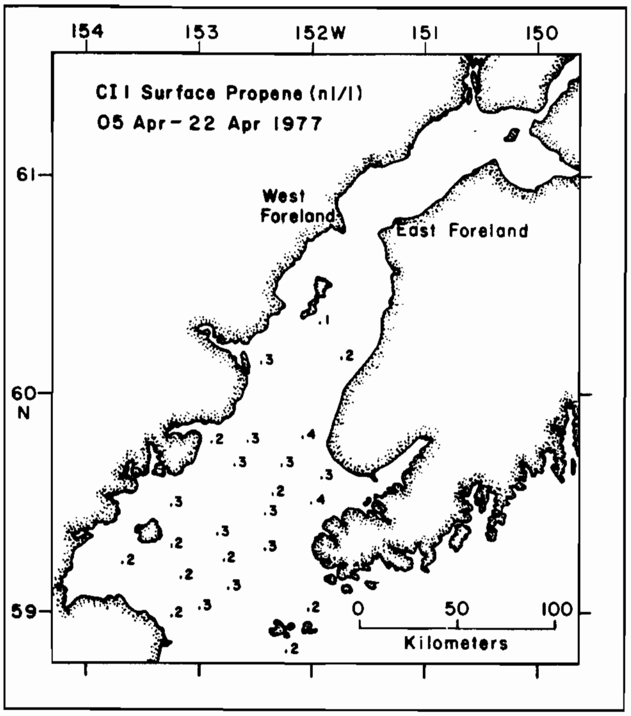


Figure 40. Distribution of dissolved propene at the surface in April 1977.

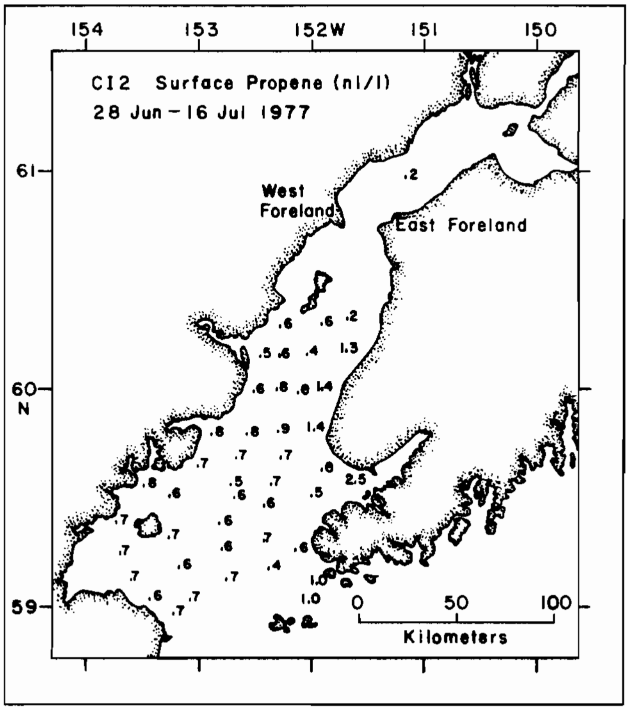


Figure 41. Distribution of dissolved propene at the surface in July 1977.

dence level) increase in the time-space means in the lower Inlet from 0.2 ± 0.1 to 0.6 ± 0.3 nl l^{-1}. The increase in concentration from May to September 1978 of 0.5 ± 0.2 to 0.7 ± 0.4 nl l^{-1} is also significant at the 99% confidence level. Short-term fluctuations in propene were not readily observed because of the low concentrations found.

3.1.6 Butanes

The distribution and concentrations of iso- and n-butane were similar. Concentrations in the lower Inlet were low, usually below the detection limit of 0.1 nl l^{-1}. Concentrations in the upper Inlet, however, were significantly above the detection limit, commonly between 0.5 and 1.0 nl l^{-1}. The maximum concentrations measured in the upper Inlet (Trading Bay) were 1.8 nl l^{-1} for iso-butane and 2.8 nl l^{-1} for n-butane. In general, n-butane concentrations exceeded those of iso-butane. No seasonal or short-term variations were detected.

3.2 Natural Modification of Light Hydrocarbons

The results of the Natural Modification of Light Hydrocarbons experiment are tabulated in appendix B. The hydrocarbon data are expressed in nl l^{-1}; the nutrient data are expressed in μmol l^{-1}. Light levels and oxygen values are reported in relative units.

Figure 42 shows the time change of methane concentration in the "light," "dark," and "killed" bottles. Methane concentration did not significantly change in the light over the 18-day period. However, both the "killed" bottles (incubated in the light) and "dark" bottles showed a decrease in methane concentration over the 18 days from approximately 145 nl l^{-1} to approximately 140 nl l^{-1}. The decrease, based on a least squares linear regression and significant at the 99% confidence interval, was -0.32 nl l^{-1} d^{-1} for both the "killed" and "dark" bottles. The R^2 values were 0.66 and 0.51 for the "dark" and "killed" regressions, respectively.

The time rate of change of ethane during the course of the experiment is shown in figure 43. The changes in propane were similar to those of ethane. There were no changes in ethane or propane concentrations over the 18 days in the dark. In contrast, both hydrocarbons showed marked increases in concentration in both the "light" and "killed" bottles. The maximum concentrations of ethane (~6 nl l^{-1}) and

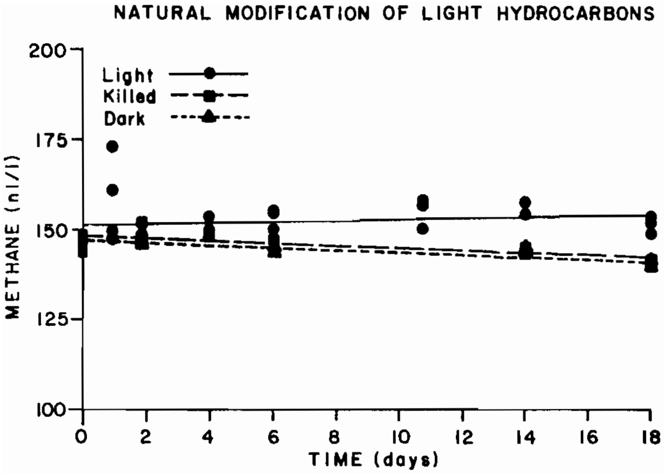


Figure 42. Time changes of methane in the "light," "killed," and "dark" bottles during the Natural Modification of Light Hydrocarbons experiment. The lines represent a least squares curvilinear fit to the data.

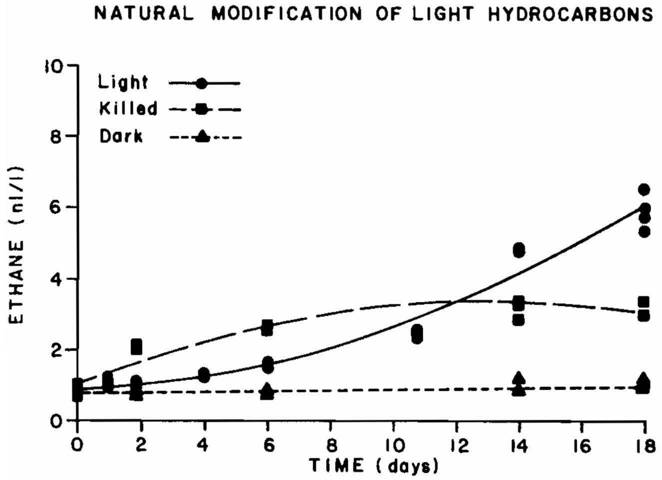


Figure 43. Time changes of ethane in the "light," "killed," and "dark" bottles during the Natural Modification of Light Hydrocarbons Experiment. The lines represent a least squares curvilinear fit to the data.

propane (~3 nl l^{-1}) were measured in the "light" bottles on day 18. These values exceeded the initial concentrations by a factor of 7 for both gases. Concentrations of both hydrocarbons in the "killed" bottles initially exceeded those measured in the "light" bottles and remained higher until day 14. At that point gas production in the "killed" bottles appeared to have leveled off, whereas increases in the "light" bottles continued.

For ethane the best fit lines based on a least squares curvilinear regression are

$$(C_{2:0})_L = 0.014t^2 + 0.035t + 0.92 \ (R^2 = 0.97)$$

and

$$(C_{2:0})_K = 0.013t^2 + 0.35t + 1.1 \ (R^2 = 0.91),$$

where

$(C_{2:0})_L$ = Ethane "light" Bottles
$(C_{2:0})_K$ = Ethane "killed" Bottles
t = time in days.

The regression coefficients are significant at the 99% confidence level.

For propane the best fit lines are

$$(C_{3:0})_L = 0.0053t^2 + 0.050t + 0.48 \ (R^2 = 0.93)$$

and

$$(C_{3:0})_K = 0.078t + 0.76 \ (R^2 = 0.81).$$

Although the propane ("killed") data showed curvature, the second-order regression coefficient is not significantly different from zero at the 99% confidence interval.

Ethene and propene concentrations showed similar modification patterns to those already described for ethane and propane. The magnitude of the change in the "light" and "killed" bottles, however, was much greater for the unsaturates. The concentration increase of ethene in the "light" bottles was from approximately 1.4 to 26 nl l^{-1}, nearly a twentyfold increase (fig. 44). Increases in the "killed" bottles were slightly smaller. The increase for propene was more than thirtyfold, increasing from approximately 0.52 to 16 nl l^{-1} in both the "light" and "killed" groups. Again the maximum values measured were observed in the "light" bottles on day 18.

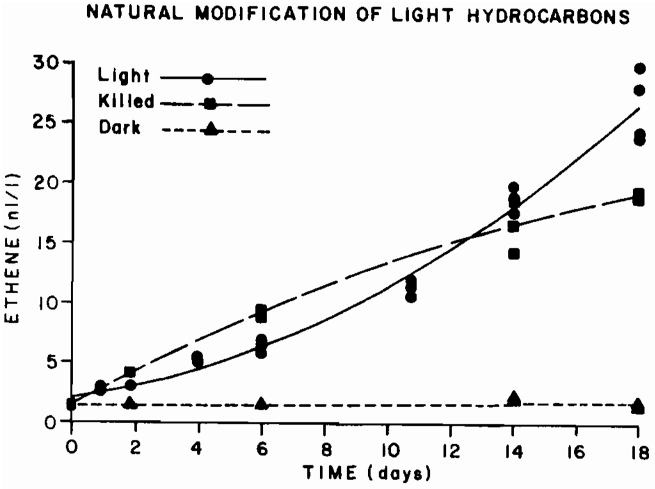


Figure 44. Time changes of ethene in the "light," "killed," and "dark" bottles during the Natural Modification of Light Hydrocarbons Experiment. The lines represent a least squares curvilinear fit to the data.

The best fit lines to the ethene data, based on a least squares curvilinear regression, are

$$(C_{2:1})_L = 0.053t^2 + 0.41t + 2.0 \ (R^2 = 0.98)$$

and

$$(C_{2:1})_K = -0.027t^2 + 1.5t + 1.5 \ (R^2 = 0.98).$$

For propene,

$$(C_{3:1})_K = 0.034t^2 + 0.25 + 1.2 \ (R^2 = 0.95),$$

and

$$(C_{3:1})_K = 1.1t + 0.67 \ (R^2 = 0.97).$$

Concentrations of ethene and propene in the "dark" bottles showed slight but significant increases in time. For ethene the concentration increase was 0.019 nl l^{-1} d^{-1}; for propene the increase was 0.014 nl l^{-1} d^{-1}. The R^2 values for the regression lines are 0.50 and 0.81 for ethene and propene, respectively. Given initial concentrations of 1 nl l^{-1} and an analysis precision of ± 10%, these increases would not be observable over the short-term (~5 days) storage of samples. However, storage for longer periods may present a problem.

No changes occurred for iso-butane in any of the bottles. Changes in n-butane concentrations showed a similar trend as for ethane and propane. No change in n-butane concentration occurred in the dark. Increases in the "light" bottles, however, were from 0.2 to 0.6 nl l^{-1}. Increases in the "killed" bottles were from 0.2 to 0.5 nl l^{-1}. The best fit line in the "light" group still showed curvature where

$$(n\ C_4)_L = 0.0014t^2 - 0.0079t + 0.23\ (R^2 = 0.76).$$

For the "killed" group,

$$(n\ C_4)_K = 0.015t + 0.22\ (R^2 = 0.79).$$

Changes in the concentration of nutrients during the experiment in both the "light" and "dark" bottles were variable. Nitrate concentrations did not change in the dark and decreased from approximately 7 μmol l^{-1} to 0 after only 4 days in the light. Silicate concentrations, which increased slightly in the dark, decreased from approximately 12 μmol l^{-1} at the beginning of the experiment to approximately 2 μmol l^{-1} by day 10 in the light. Although the phosphate data were scattered, concentrations in the light showed a similar trend in which initial concentrations of approximately 1.8 μmol l^{-1} decreased and leveled off by day 6 at 0.4 μmol l^{-1}. "Dark" bottle concentrations of phosphate decreased through a minimum at 6 days and increased again to approximately the initial levels measured. Nitrite concentrations did not change in the dark but decreased in the light. Ammonia concentrations increased substantially in the dark from approximately 1.5 μmol l^{-1} to more than 5 μmol l^{-1} at the end of the experiment. "Light" bottle ammonia levels (based on best fit line to data) decreased through a minimum of approximately 0.4 μmol l^{-1} at day 10 and increased again to initial concentration levels by day 18. Dissolved oxygen values measured during the experiment are relative, although it is estimated that initial concentrations were near saturation. The initial oxygen concentration was given a value of 1.0. Oxygen increased in the "light" bottles through day 6 and appeared to level off at a value of 1.7, a 70% increase. The one measurement made in the "killed" bottle on day 2 was relatively lower than the amount measured in the "light" bottle at the same time.

A qualitative assessment of the phytoplankton growth was made on samples taken on days 14 and 18 using SEM photography. The "light" bottles exhibited a substantial growth of diatoms during the experiment when compared with growth in the "dark" bottles. A visual comparison of the micrographs of the "killed" samples with those of the "dark" samples showed no discernible difference in cell abundance. There also was no discernible change in cell abundance from day 14 to day 18 in any of the bottle sets. Bacterial growth was undetermined.

4. DISCUSSION

4.1 Hydrocarbon Sources

The ranges in concentration and relative magnitude of the LMW aliphatic hydrocarbons in lower Cook Inlet (table 7) are typical of those found in other coastal marine environments (table 1). In general the hydrocarbon distributions are both spatially and seasonally variable. Localized sources of hydrocarbons, particularly Kachemak Bay, show a pronounced seasonal variation of methane, ethene, and propene. The increases in hydrocarbon levels are concomitant with increases in solar insolation, water temperature, and biological activity. This is suggestive of a causal relationship between hydrocarbon levels and biological processes.

In contrast to the lower Inlet, the distribution of hydrocarbons in upper Cook Inlet is characterized by a point source, or sources, within Trading Bay that appears to show little seasonality. The averages and ranges in methane, ethane, and propane concentrations measured over the three years of the study are the highest measured anywhere over the Alaskan shelf. The average methane concentration is also the highest reported in any marine environment, with the exception of the anoxic waters of the Cariaco Trench and the Black Sea, although higher values recently have been measured in Puget Sound (J. Cline, PMEL, personal communication). Measurable amounts of the butanes were observed only in the upper Inlet. The anomalously elevated concentrations of methane and the C_2+ paraffins, low seasonal signature, and limited biological activity in the upper Inlet, all indicate that the hydrocarbons most likely do not arise from recent biologically mediated processes. The fact that the point source of these hydrocarbons lies within an area of active production of natural gas and oil leads one to suspect that these anomalous distributions are thermogenic.

TABLE 7

Summary of LMW aliphatic hydrocarbon concentrations measured during this study.

	Lower Cook Inlet	Upper Cook Inlet
Methane	375(55 - 3072)	1089(138 - 4085)
Ethane	0.6 (T - 4.2)	4.1(0.2 - 21)
Ethene	1.7 (T - 6.9)	0.4(0.1 - 1.7)
Propane	0.3 (T - 2.0)	2.1 (T - 11)
Propene	0.6 (T - 2.4)	0.1 (T - 0.7)
C_1/C_2+C_3	417	176
$C_{2:0}/C_{2:1}$	0.4	10
n	593	81

Note: Values are the means and ranges of all the hydrocarbon measurements made in Cook Inlet. The butanes were typically below the detection limit of 0.1 nl l^{-1}, although significant levels were measured within Trading Bay. The hydrocarbon concentration units are nl l^{-1}.

As discussed earlier, the compositional parameters $C_1/(C_2+C_3)$ and $C_{2:0}/C_{2:1}$ may, with limitations, be used to distinguish between biogenic and thermogenic sources. $C_1/(C_2+C_3)$ values > 100 and $C_{2:0}/C_{2:1}$ values < 1 are indicative of biologically derived hydrocarbons, while ratios < 20 and > 1, respectively, are suggestive of thermogenic sources. The average values of $C_1/(C_2+C_3)$ and $C_{2:0}/C_{2:1}$ for lower Cook Inlet are 417 and 0.4, respectively. For the upper Inlet, the ratios are 176 and 10, respectively. As expected, the lower Inlet is characterized by a hydrocarbon composition arising from biological processes. For the upper Inlet, compositional parameters appear to be less diagnostic when the aforementioned criteria are used. Although the upper Inlet hydrocarbon composition resembles that found in anoxic environments, two lines of evidence suggest that the source is, in fact, thermogenic.

Natural gas produced commercially in Cook Inlet is almost exclusively (> 98%) methane and contains only trace amounts of the higher hydrocarbons (Blasko, 1974). Gas associated with crude oil production (casinghead gas), which is mainly used to maintain pressure during drilling operations, is also typically > 95% methane. Thus, it is obvious, even when we correct for differential solubilities, that these gas compositions would have a $C_1/(C_2+C_3)$ value in excess of the typical thermogenic cutoff level (< 20). Therefore, the values of the observed compositional parameters are in agreement with those expected from a hydrocarbon source of this type.

According to Nikonov (1972), the higher homologs of methane are genetically related in natural gas and oil deposits and can be used to indicate the type of natural gas source. His analysis of more than 3500 gas and oil deposits in the Soviet Union and the United States shows a systematic decrease in C_2/C_3 values, from 5 for dry gas deposits to 2 for gases of oil deposits. The relationship between ethane and propane in upper Cook Inlet, as shown in figure 45, is

$$C_2 = 1.84\ C_3 + 0.46 \quad (R^2 = 0.95).$$

This linear relationship is similar in slope to that reported by Cline and Holmes (1977) in the vicinity of a gas seep in Norton Sound, Alaska. In contrast, these gases were found to be poorly correlated in other areas of the Alaskan shelf, including the lower Inlet. Interestingly, a C_2/C_3 ratio of 1.8 would place this hydrocarbon assemblage well within the range for gases arising from gas and oil deposits (Nikonov, 1972) independent of their mode of injection (e.g., bubbles, oil seepage). However, this ratio can be altered by chemical and/or biological fractionation during migration through the sediments.

It can be concluded from the above discussion that the LMW hydrocarbon assemblages of the upper and lower Inlet are derived from different sources. Although the dominant source of hydrocarbons in the upper Inlet appears to be thermogenic, it is unknown whether this input is the result of submarine seepage or due to leakage from preexisting wells. The seepage of gas from more than one point source is likely. As oil and gas production in the upper Inlet occurs over a variety of sedimentary horizons, the sources of these gases may indeed be different. The major input of the dissolved hydrocarbon gases to the lower Inlet seems to be from biological sources although chemical processes (particularly photochemical) cannot be discounted. This relationship

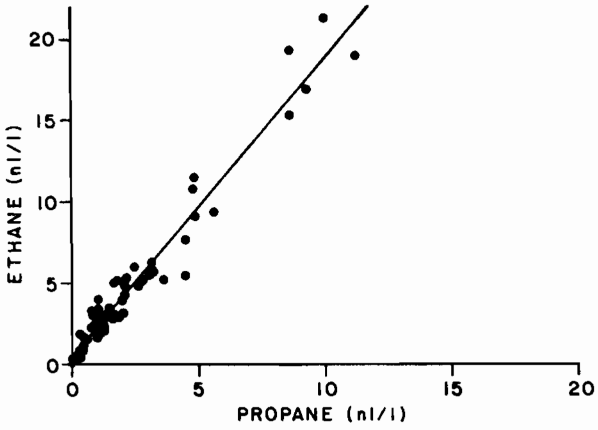


Figure 45. Relationship between ethane and propane for all samples taken in upper Cook Inlet. The relationship based on a least squares linear regression is $C_{2:0} = 1.84 \cdot C_{3:0} + 0.46$ ($R^2 = 0.95$). This association is unique to the upper Inlet and is thought to be diagnostic of a thermogenic source of hydrocarbon gases associated with petroleum.

between hydrocarbon concentrations and biological activity was further investigated during the Chemistry-Biology Studies.

During the summer of 1978, biological studies were conducted in lower Cook Inlet by PMEL. As a part of those studies, measurements of primary production, chlorophyll a, pheophorbide a, light levels, and nutrients were made monthly at stations 1 through 8, which traverse the lower Inlet from Kamishak to Kachemak Bay (fig. 4). In conjunction with these biological measurements, 73 samples were collected during May and September (CI3 and CI4) at stations 1, 4, and 7, and analyzed for their dissolved hydrocarbon gas content. The results of the chemical and biological analyses were placed into correlation matrices for interpretation. Arbitrarily, correlations with $r \geqq 0.7$ (significant at the 95% confidence level) were used in the interpretation.

When all of the data were combined into one correlation matrix, no significant correlations were observed. This is probably the result of the high degree of mixing that occurred over the space and time scales of the measurements. However, when individual stations were analyzed, some general trends were apparent (table 8). Most notably, the correlations observed with methane were, in general, opposite in sign to those seen with the higher homologs. Methane showed significantly negative correlations with primary production and chlorophyll a, and significantly positive correlations with all of the nutrients, sigma-t, and depth. There were no correlations of any of the parameters with ethane. There was also a general lack of correlation of any of the hydrocarbons with light levels or pheophorbide a. Interestingly, the negative correlations of methane with both chlorophyll a and production are opposite to those observed by Swinnerton et al. (1977) in the Gulf of Mexico.

These general trends indicate that the major source of methane is probably different from that of the C_2+ hydrocarbons. It appears that methane is not produced significantly in the water column by the primary producers. As pheophorbide a levels are indicative of grazing pressures by zooplankton in Cook Inlet (Larrance and Chester, 1981), the lack of a correlation with methane indicates that methane production is also not likely to be associated with the zooplankton. The evidence clearly points to a methane source near the bottom, probably within the fine-grained sediments of the embayments. In contrast, the source (or sources) of the higher hydrocarbons appears to be within the upper water column where nutrient assimilation, primary production, and chlorophyll a concentrations are elevated.

These results are in reasonably good agreement with the observations made during the Natural Modification of Light Hydrocarbons experiment. There appeared to be no net in situ production of methane during that experiment. If, however, the measured decrease over time in the "dark" bottles was also occurring in the light, the lack of change in methane concentration in the light implies that a production term was balancing the loss term (0.3 $nl\ l^{-1}\ d^{-1}$). Because this loss term was probably a result of bottle leakage, a slight in situ production may have actually occurred. It is not known, however, if the observed decreases in the dark were actually caused by the presence of viable bacteria rather than leakage.

A sediment production of methane in the hydrocarbon source areas is reasonable in light of the relatively high organic matter flux to

TABLE 8

Results of the chemistry-biology studies in terms of significant correlations of light hydrocarbons with biological parameters for individual station vertical profiles.

	Depth						Methane						Ethene						Propane						Propene					
Profile	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
Light	-	-	-	-		-				-																		+		+
Production	-	-	-	-		-	-		-	-							-					+			+			+		+
Chlorophyll a	-		-	-		-	-		-		-		+											+	+					+
Pheophorbide a						-				+							-							+					-	-
Nitrate	+	+		+	+	+	+	+		+			-	-			-					-	-		-	-		-	-	-
Nitrite	+	+			+	+		+						-			-								-	-			-	-
Ammonia	+	+	+	+	+	+	+	+	+	+			-	-											-	-		-		-
Phosphate	+			+	+	+	+	+		+			-	-			-					-		-	-	-		-	-	-
Silicate	+	+	+	+	+	+	+	+	+				-	-		-	-							-	-	-			-	-
Depth							+		+				-	-		-	-					-		-	-	-		-	-	-
Sigma - t	+	+	+	+	+	+	+	+	+	+			-	-			-					-		-	-	-		-	-	

Note: Plus and minus signs indicate a significant positive or negative correlation respectively. No significant correlations were observed for ethane. The butanes were generally below the detection limit of 0.1 nl l^{-1}. Vertical profiles were taken at the following stations (fig. 17) and dates in 1978: 1 - Station 7 (Bloom evident), 9 May; 2 - Station 1, 16 August; 3 - Station 1, 18 August; 4 - Station 4, 15 August; 5 - Station 7, 15 August; 6 - Station 7, 16 August.

the sediments in these locations (Larrance and Chester, 1981). The sediments of Kachemak and Kamishak Bay are relatively rich in recently deposited, fine-grained sediments containing approximately 1% organic matter (Larrance and Chester, 1981) and are expected to harbor a relatively rich benthic community. Although it is not known whether the sediments in Kachemak Bay become anoxic near the sediment surface, reducing conditions have been observed below 10 cm in Kamishak Bay sediments (R. Feely, PMEL, personal communication). Because of the large seasonal signal seen in the methane distribution, it is unlikely that the production occurs very deep in the sediment. Actually, the seasonal flux of organic matter to the sediments suggests that the methane may have its source within the thin veneer of freshly deposited material. An organic-rich ooze at the sediment surface, however, has not yet been observed.

The in situ source of C_2+ hydrocarbons suggested by the Chemistry-Biology Studies is also in agreement with the results of the natural modification experiment. Although the production rates observed during the experiment were undoubtedly accelerated by the experimental conditions, these compounds were produced in significant quantities in the "light" and "killed" bottles. Slight or no production in the "dark" bottles suggests that these compounds are produced in significant amounts only in the illuminated water column. This suggests, in agreement with Wilson et al. (1970), that the source of the C_2+ compounds may be photochemical rather than biological. The uncertainty of the presence of viable bacteria and the inability to measure nutrients in the "killed" bottles preclude a definitive argument for a strictly photochemical mechanism for the production of the C_2+ aliphatics.

The shapes of the time-concentration curves for the "light" and "killed" bottles do suggest, although not conclusively, a coupling between a biological and photochemical source of the higher hydrocarbons. Unlike the "killed" bottles, which showed initial rapid increase and subsequent leveling off of hydrocarbon concentrations, the "light" bottles showed a gradual concentration increase which continued through the entire 18 days (e.g., fig. 43). These results would have been expected if the mechanism involved a photochemical production of the hydrocarbons from an organic precursor exuded by the organisms. In the "killed" bottles the precursor is expected to be released immediately and to undergo reaction until the material is completely reacted. In the "light" bottles the material is expected to be exuded in a continuous fashion, the amount increasing in time with increases in population. Although the precursor cannot be determined from this study, the formation of ethene from methionine and its peptides (Ku and Leopold, 1970; Yang et al., 1967) suggests a possible starting material that is present in sufficient quantities in seawater (Clark et al., 1972).

4.2 Methane Budget

4.2.1 Introduction to Budget

In this section, a methane budget is developed using a simple two-box model of the Inlet. The purpose in calculating a budget is to gain an understanding of the magnitudes of the processes influencing the distribution of methane and other light hydrocarbons. In particular, it is expected that a budget will provide insight into the relative importance of the sources of light hydrocarbons in the Inlet. Also, by calculating a budget, it will be possible to determine what model parameters need to be better known in order to improve the model.

As has been clearly demonstrated, Cook Inlet is composed of two distinctly different hydrographic regimes. These two areas have also been shown to differ significantly in their dissolved hydrocarbon chemistry. For this reason, the Inlet can be modeled by two boxes, one representing the upper and one representing the lower Inlet (fig. 46). Because of the limited extent of the areal coverage in the upper Inlet and lack of circulation data, the northern boundary of this box has been chosen to be a line extending between the North Foreland and Point Possession (fig. 6). The natural dividing line between the boxes is at the Forelands. The southern boundary of the lower Inlet is at the entrance, and can be represented by a line extending from Cape Douglas to Point Adam on the Kenai Peninsula.

As was shown in the Natural Modification of Light Hydrocarbons experiment, none of the hydrocarbons is lost significantly through chemical or biochemical reactions. The only significant losses of hydrocarbons from the Inlet are therefore due to physical processes such as air-sea exchange and tidal mixing. Figure 46 shows the trans-

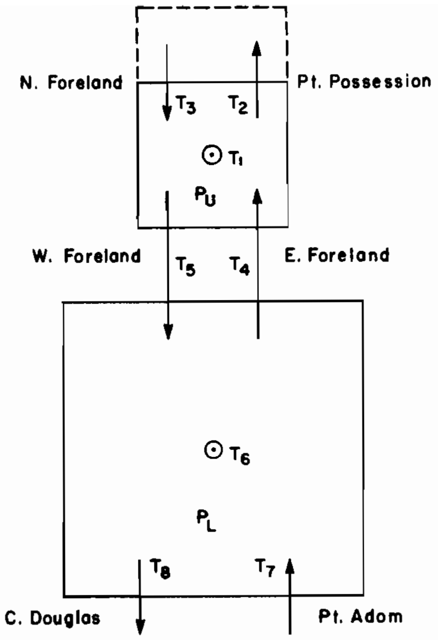


Figure 46. Two-box model of Cook Inlet used in calculating a methane budget. T_1 and T_6 are the air-sea transports out of the upper and lower Inlets, respectively. The remainder of the transport across the model boundaries is computed strictly on the basis of the tidal current flow regime. P_U and P_L are the hydrocarbon production terms which, under steady-state conditions, are equal in magnitude to the net loss of hydrocarbons from the upper and lower Inlet boxes, respectively.

ports considered in the model. Assuming steady state (i.e., inputs = outputs), the net methane lost from each box by physical removal is equivalent to the amount of methane produced within each box by either biogenic or thermogenic sources. The model equation for the upper Inlet is

$$P_U + T_3 + T_4 = T_1 + T_2 + T_5.$$

or, rearranged,

$$P_U = T_1 + (T_2 - T_3) + (T_5 - T_4), \qquad (1)$$

where P_U = upper Inlet methane production,

T_1 = air-sea transport out of the upper Inlet,

$(T_2 - T_3)$ = net tidal transport across the Pt. Possession - N. Foreland boundary,

$(T_5 - T_4)$ = net tidal transport across the Forelands.

Similarly, for the lower Inlet,

$$P_L = T_6 + (T_4 - T_5) + (T_8 - T_7), \qquad (2)$$

where P_L = lower Inlet methane production,
T_6 = air-sea transport out of the lower Inlet,
$(T_4 - T_5)$ = net tidal transport across the Forelands,
$(T_8 - T_7)$ = net tidal transport across the entrance.

Transports due strictly to mean flow and eddy diffusion, as will be shown later, are negligible terms in the budget.

In order to remove the seasonality seen in the methane distribution, and to obtain the best possible estimates of the source term, both the range and the typical values of each of the model parameters are used whenever possible. As no hydrocarbon data are available outside the 6-month period from April to September, the transports are computed on a half-year basis. The methane budget is summarized in table 9. The areas and volumes used in the computations can be found in appendix A.

4.2.2 Air-Sea Transport

Gas exchange across the air-sea interface is most commonly modeled by the stagnant film boundary layer model (Liss, 1973; Liss and Slater, 1974; Broecker and Peng, 1974; Emerson, 1975). The model assumes that gas transfer occurs by molecular diffusion through hypothetical stagnant film layers present at the interface, one each within the liquid and gas phases. For sparingly soluble gases, such as the hydrocarbon gases, transfer through the gas phase is much faster than through the liquid phase (Liss, 1973). Thus, the limiting step to transfer between air and water is molecular diffusion through a stagnant water film. The gas phase above this film and liquid phase below are both assumed to be well mixed and thus uniform in composition. The top of the stagnant film is assumed to have a gas concentration at equilibrium with the overlying gas phase. Similarly, the bottom of the film has a concentration equivalent to the concentration measured within the bulk water just below this layer. The flux of gas across the interface (F_i) can then be computed using Fick's 2nd law:

$$F_i = (D/Z)(C_i - C_{eq}),$$

where

D = molecular diffusion coefficient of the gas in the liquid phase,

Z = stagnant film thickness,

C_i = average concentration of gas measured in the mixed surface layer,

C_{eq} = equilibrium concentration of gas with respect to the atmosphere.

The air-sea transport can then be computed by multiplying the flux by the area of exchange (A):

$$T_i = (D/Z)(C_i - C_{eq})A. \quad (3)$$

Kanwisher (1963) and Emerson (1975) have shown that the stagnant film boundary layer thickness is inversely proportional to the square of the wind speed for winds greater than approximately 2 m s^{-1}. Therefore, a knowledge of the wind speed is necessary in order to calculate the exchange. The mean wind speed measured during the occupation of the station grids in 1978 was 8 m s^{-1}. These measurements were made at approximately 10 m above the sea surface. Using data presented by Emerson (1975), this wind speed can be extrapolated (for comparison purposes) to give an effective wind speed of 5 m s^{-1} at 10 cm above the sea surface. A film thickness based on this wind speed is $Z = 10^{-2}$ cm.

On the basis of the atmospheric methane concentration data of Ehhalt (1974) and the methane solubility data of Yamamoto et al. (1976), $C_{eq} \sim 50$ nl l^{-1} in the waters of Cook Inlet. The molecular diffusion coefficient for methane in distilled water at 4° C is $D = 8.5 \times 10^{-6}$ cm^2 s^{-1} (Witherspoon and Bonoli, 1969).

To obtain a box concentration for the upper Inlet (C_U), methane concentrations observed in the upper Inlet were integrated, rather than averaged, over the whole area of the box for each cruise. This was necessary because of the high density sampling within Trading Bay. Concentrations at all depths were used in the integration. The integrated concentrations measured over four cruises ranged from 455 to 1930 nl l^{-1}. The average for three of the four cruises was 600 nl l^{-1}, which is assumed to be the typical concentration value for the upper Inlet box (C_U).

For the lower Inlet box, methane concentrations measured in the top 10 m from all stations were averaged for each cruise. The average methane concentration for five cruises in the lower Inlet (C_L) was 370 nl l^{-1}; the range in concentrations was 175 to 905 nl l^{-1}.

The sea-to-air transport of methane for each box can now be computed using equation (3). For the upper Inlet, the transport is

$$T_1 = 0.8 \times 10^8 \text{g CH}_4\ ½y^{-1}; \qquad \text{range} = 0.6 - 3 \times 10^8 \text{g CH}_4\ ½y^{-1}.$$

The sea-to-air transport of methane in the lower Inlet is

$$T_6 = 5 \times 10^8 \text{g CH}_4\ ½y^{-1}; \qquad \text{range} = 2 - 14 \times 10^8 \text{g CH}_4\ ½y^{-1}.$$

The relatively higher wind speeds that occur during winter would tend to enhance the exchange by reducing the film thickness (Z). The upper Inlet, however, is partially ice covered most of this time, and the effects of the stronger winds would be nullified. For the lower Inlet, the enhanced exchange due to the increased winds would partially compensate for the reduced surface methane concentrations expected at this time of the year. Calculating an air-sea transport for the upper Inlet from concentrations averaged over both the "seep" and "non-seep" areas, rather than by integrating over the total area, would increase the value for T_1 calculated here by approximately 60%.

4.2.3 Tidal Transport

The mass of hydrocarbon transported across a boundary during a tidal excursion is

$$M_i = C_i V_t,$$

where

C_i = integrated or mean hydrocarbon concentration within (or outside) a box

V_t = tidal prism volume.

A net mass exchange between boxes over a full tidal cycle with period t is

$$M_i - M_j = C_i V_t - C_j V_t.$$

Thus, the net tidally induced transport across a boundary can be computed by

$$(T_i - T_j) = (C_i - C_j)V_t/t. \qquad (4)$$

Implicitly included in this transport term is the assumption that complete mixing occurs during each tidal cycle. This is a reasonable assumption in light of the observations made during the time series at station 9, where data showed that during low water, the water column became homogeneous with respect to salinity (fig. 29B) and hydrocarbons (figs. 28B and 33B), indicating a high degree of vertical mixing.

Tidal exchange through the Forelands, $(T_5 - T_4)$, is considered first. An average tidal current through the Forelands, calculated by taking the root mean square (rms) of the M_2 harmonic constants for the north and east components, is approximately 130 cm s^{-1} (Patchen et al., 1981). Integrating this current over a 6-hour tidal excursion (t/2) (perhaps a slight overestimation) and multiplying by the Forelands cross-sectional area gives a tidal prism volume of $V_t = 1.4 \times 10^{16} cm^3$, approximately one-half the volume of the upper box. Methane concentrations computed for the lower box (C_L) are based on the mean concentrations measured for all stations and depths during each cruise. Values for the upper Inlet box (C_U) are again based on the integrated methane concentrations measured each cruise in the upper Inlet. The range in methane concentration differences $(C_U - C_L)$ was 0 to 1175 nl l^{-1}. The difference, based on data from three of the four cruises, was nominally 225 nl l^{-1}. It should be noted that the lower limit in concentration difference of zero is an artifact of the integration techniques employed. Substitution of these values into equation (4) yields a net tidal transport of methane across the Forelands of

$(T_5 - T_4) = 8 \times 10^8$g CH_4 ½y^{-1}; range = 0 - 43 x 10^8g CH_4 ½y^{-1}.

If the source of methane in Trading Bay is due to a relatively continuous seepage of natural gas, then a concentration gradient across the Forelands should be developed throughout winter. The tidal pumping mechanism would therefore continue to transport significant amounts of methane out of the upper Inlet at that time of the year.

The tidally induced transport across the North Foreland-Point Possession boundary $(T_2 - T_3)$ is computed in a similar fashion. It is assumed that the tidal prism volume through this boundary is the same as that computed through the Forelands (equivalent to a mean current speed of approximately 70 cm s^{-1} across the boundary). The concentrations calculated for the upper Inlet box (C_U) are again based on the integrated methane concentrations measured on each cruise. The concentrations used for the waters north of the boundary (C_{UU}) are derived from the few hydrocarbon data available above the boundary. The range in concentration differences (C_U - C_{UU}) was 0 to 65 nl l^{-1} with an average value of 30 nl l^{-1}. Equation (4) gives the net tidally induced transport of methane across this boundary as

$(T_2 - T_3) = 1 \times 10^8$g CH_4 ½y^{-1};   range = 0 - 2 x 10^8 g CH_4 ½y^{-1}.

In this case, the lower limit of zero-concentration difference between the boxes, although more realistic, is a result of the paucity of data north of the boundary.

Tidal currents through the entrance to Cook Inlet are somewhat reduced from those found in the upper Inlet. This is particularly true along the western portion of the entrance (Muench et al., 1978). An average tidal current speed through the entrance, calculated by taking the root mean square (rms) of the M_2 harmonic constants for the north and east components is approximately 35 cm s^{-1} (Patchen et al., 1981). Integration of this current speed over the 6-hour (t/2) duration of a tidal excursion yields a tidal prism volume of $V_t = 2.3 \times 10^{16}$ cm^3, approximately 2% of the volume of the lower Inlet. Methane concentrations in this part of the Gulf of Alaska (C_G) range between 100 and 200 nl l^{-1}. Mean concentrations in the lower Inlet box (C_L) ranged from 180 to 750 nl l^{-1} and averaged 375 nl l^{-1}. The transport of methane across the entrance based on the concentration difference (C_L - C_G) and the tidal volume exchange:

$(T_8 - T_7) = 13 \times 10^8$g CH_4 ½y^{-1};   range = 5 - 33 x 10^8g CH_4 ½y^{-1}.

Observations made in early spring (fig. 22) suggest that concentration differences between the lower Inlet and the Gulf of Alaska will be relatively lower in winter. Thus, the tidal transport of methane out of the lower Inlet in winter will be reduced.

4.2.4 Mean Flow and Diffusive Transport

A mean flow transport of dissolved hydrocarbons can be computed on the basis of the nontidal, mean flow regime. The transport is computed following

$$T_i = C_b(v_m)_i A,$$

where

C_b = dissolved hydrocarbon concentration at the boundary
$(v_m)_i$ = nontidal, mean current velocity across boundary
A = boundary cross-sectional area.

Because of the paucity of data, the best estimate of the mean flow in the Inlet can be derived from the rate of freshwater input. 1977 and 1978 data indicate that the integrated freshwater input from the Susitna and Knik Rivers was 2.4×10^{9} cm^{3} s^{-1}. The mean current velocities across the three boundaries from north to south are thus 0.3, 0.5, and 0.1 cm s^{-1}, respectively. These current velocities are at least two orders of magnitude less than the tidal current velocities observed across these boundaries. Thus, the transport of hydrocarbons by mean flow appears to be an insignificant part of the hydrocarbon budget.

Limited mean-flow data obtained from current meter measurements indicate that a mean flow across the entrance, as a result of the Kenai current, might be on the order of 0.3 Sverdrups (J. Schumacher, PMEL, personal communication). Given a methane concentration increase at the boundary of up to 100 nl l^{-1} in the outflowing water (western one-third of entrance) relative to the inflowing water (eastern two-thirds of entrance), a methane transport out of the lower Inlet could be as high as 3×10^{8} g CH_4 ½y^{-1}. This term could add up to 30% to the lower Inlet budget and hence the lower Inlet's total production. However, the limited nature of the mean current data and the lack of an observable hydrocarbon concentration gradient at the entrance throughout the summer precludes using these numbers in the budget calculations.

In response to a concentration gradient, hydrocarbons can be transported across the model boundaries by eddy diffusion. The transport is proportional to the concentration gradient ($\Delta C/\Delta X$) across the boundary. The constant of proportionality in this case is K_H, the coefficient of horizontal eddy diffusivity. The transport can then be written as

$$T_i = -K_H(\Delta C/\Delta X)A.$$

K_H is dependent on the space (or time) scale of diffusion (l) which is related by $K_H = 0.0103 l^{1.15}$ when K_H and l are expressed in terms of centimeters squared per second and centimeters, respectively (Okubo, 1971). Although the mixing scale is somewhat arbitrary, an appropriate scale length would be certainly less than twice the distance traversed during a tidal excursion, i.e., < 50 km. This results in a $K_H \leqq 5 \times 10^{5}$ cm^{2} s^{-1}. The methane concentration differences already computed across the boundaries for the tidal transport are used to obtain the maximum transport across any of the model boundaries due strictly to horizontal eddy diffusivity is

$$T_i \leq 0.08 \times 10^8 \text{g } CH_4 \text{ ½y}^{-1}.$$

This value, which represents a maximum, is an order of magnitude less than the other transport terms computed thus far and consequently will be ignored in the model.

4.3 Budget Summary

The methane budget is summarized in table 9. It is clear that the most important physical process affecting the distribution of methane, as well as the other hydrocarbons, is tidal pumping. This result was expected because of the Inlet's high tidal energy.

The net loss of methane calculated for the upper Inlet is 10×10^8 g CH_4 ½y^{-1} with a range of $1 - 48 \times 10^8$ g CH_4 ½y^{-1}. If steady state is assumed, the total production within the upper Inlet is equivalent to the amount lost by physical removal (equation (1)). Hence, the upper Inlet production is

$$P_U = 10 \times 10^8 \text{ g } CH_4 \text{ ½y}^{-1} \quad \text{range} = 1 - 48 \times 10^8 \text{ g } CH_4 \text{ ½y}^{-1}.$$

When the production is normalized to a unit area, the production rate is 0.8 g CH_4 m^{-2} ½y^{-1} with a range of 0.08 to 3 g CH_4 m^{-2} ½y^{-1}.

The net loss of methane calculated for the lower Inlet, following equation (2), is 10×10^8 g CH_4 ½y^{-1} with a range of -36 to 47×10^8 g CH_4 ½y^{-1}. Normalizing the total production to unit area yields a production rate of 0.06 g CH_4 m^{-2} ½y^{-1} with a range of -0.2 to 0.3 g CH_4 m^{-2} ½y^{-1}.

Methane production rates calculated for lower Cook Inlet show a rather close agreement with production rates determined in sediments. Oremland (1975) measured methane production rates in vivo in both reducing and nonreducing tropical marine sediments. The initial microbial methane production rates measured ranged from 0.02 g CH_4 m^{-2} ½y^{1} in nonreducing sediments to 0.2 g CH_4 m^{-2} ½y^{-1} in reducing sediments. The lower production rate can account for approximately 30% of the total methane produced in the lower Inlet. It is unlikely that all of the sediments in the lower Inlet are reducing. If, however, as a first approximation it is assumed that the area of reducing sediments

TABLE 9

Summary of the methane budget calculated for a two-box model of the Inlet.

Upper Cook Inlet			Lower Cook Inlet		
Net Transport	Mean	Range	Net Transport	Mean	Range
T_1	0.8	0.6 - 3	T_6	5	2 - 14
(T_2-T_3)	1	0 - 2	(T_4-T_5)	-8	-(43 - 0)
(T_5-T_4)	8	0 - 43	(T_7-T_8)	13	5 - 33
Net	10	1 - 48	Net	10	(-36) - 47

$P_U = T_1 + (T_2 - T_3) + (T_5 - T_4)$

$P_U = 10 \times 10^8 g\ CH_4\ ½y^{-1}$

$P_L = T_6 + (T_4 - T_5) + (T_8 - T_7)$

$P_L = 10 \times 10^8 g\ CH_4\ ½y^{-1}$

Note: The transport terms are discussed in the text. The net loss of methane from each box is equivalent to the amount produced within each box, which is based on the assumption of steady state. The mean and ranges are expressed in 10^8 g CH_4 ½y ^{1}.

is equivalent to the area of the lower Inlet less than 18 m in water depth (10 fm), the methane produced in these sediments would account for approximately 80% of the budget, assuming Oremland's values.

Preliminary pore water methane concentration data obtained in the shelf area of the Gulf of Alaska indicate that a typical concentration gradient between the surface sediment and the overlying water column is 6 x 10^{-13} g cm^{-4}. A flux of methane strictly by molecular diffusion is clearly too small to be of significance to the budget. If, however, one chooses to use a constant coefficient of vertical eddy diffusivity of 1 cm^2 s^{-1} (Sarmiento et al., 1976) over the bottom 5- to 10-m interval (a conservatively low value considering the high degree of mixing), a flux of 0.09 g m^{-2} ½y^{-1} is calculated. This value is in reasonably good agreement with the methane production rate calculated for the lower Inlet (0.06 g m^{-2} ½y^{-1}) and falls within the range of values given by Oremland (1975). Although the sedimentary environments compared are different, a benthic microbial source of methane in lower Cook Inlet appears to be a reasonable mechanism to explain the budget values. The magnitude of this source would not, however, be sufficient to account for the major production of methane in upper Cook Inlet.

In situ production of methane within the oxygenated water column has been postulated as a mechanism for the existence of subsurface methane maxima in the ocean (Scranton and Brewer, 1977; Brooks and Sackett, 1977). In cultures of a marine diatom and a coccolithophorid, Scranton (1977) measured methane production rates of 2-3 x 10^{-10} nmol $cell^{-1}$ h^{-1}. Based on typical cell concentrations of 10^5 cells l^{-1} in the lower Inlet (Larrance and Chester, 1981), the maximum yield of methane by this mechanism is less than 0.2% of the budget total. In copepod-dominated plankton samples taken from the oxygenated waters of San Fransisco Bay, Oremland (1979) determined that the maximum formation of methane by the zooplankton and associated bacteria during the 20-day incubation was 56 nl l^{-1} (3 nl l^{-1} d^{-1}). This rate, which was considered unrealistically high because of the incubation conditions, would account for approximately 30% of the methane budget in the lower Inlet. Although this mechanism may be a source of methane in Cook Inlet, it does not appear to be the major source. This is in agreement with the qualitative assessments made earlier on the basis of the

Chemistry-Biology Studies and Natural Modification of Light Hydrocarbons experiment.

It appears that methane in lower Cook Inlet can be explained as a consequence of biological production within the sediments and, to a lesser extent, in the overlying water column. If it is assumed that the generation of methane in the lower Inlet is strictly due to biological processes, and that these processes occur mainly within the more restricted embayments and near-shore areas of the lower Inlet (< 18 m), then the most probable biological methane production rate for the Inlet is calculated as $0.3\ g\ CH_4\ m^{-2}\ \frac{1}{2}y^{-1}$. If this biological production rate occurred throughout the Inlet, it would account for only 40% of the methane produced in the upper Inlet. The excess methane in the upper Inlet must therefore be a result of an increased biological production, or is the result of natural gas seepage.

It would be difficult to explain why the upper Inlet would have an increased biological methane production rate. The sandy sediment texture of the upper Inlet is not conducive to methanogenesis. The rate of diffusion from the coarse sediments would, however, be higher. There is a relatively lower amount of marine-derived organic carbon to drive the system in the upper Inlet, although the input of terrigenously derived organic carbon, in absolute amounts, is quite high. This organic matter is expected to be of a more refractory nature, although this has not been determined.

Perhaps the major argument against an increased biological source of methane is the nature of the source itself. The source is highly localized within Trading Bay and shows no well-defined seasonality. The compositional characteristics of the suite of LMW hydrocarbons measured and the fact that the upper Inlet is currently a natural-gas- and oil-producing area lead us to conclude that the increased concentrations of methane found within Trading Bay and the increased production rates calculated for the upper Inlet are the result of natural gas seepage. Although the source of the hydrocarbons cannot be unequivocally defined, both the qualitative and quantitative assessments of their distributions strongly suggest that the hydrocarbons are thermogenic.

As a point of reference, the annual offshore gas production in Cook Inlet in both 1977 and 1978 was 1.8×10^{12} l y^{-1}, which includes both casinghead gas (gas associated with crude oil production) and dry gas (Alaska Oil and Gas Conservation Commission, 1978). The seep (or seeps) production in upper Cook Inlet, based on the amount of methane unaccounted for by biological production, is 5×10^8g CH_4 ½y^{-1} or ~7×10^8 l CH_4 ½y^{-1}. Natural gas commercially produced in Cook Inlet is almost exclusively (> 98%) methane (Blasko, 1974); a comparison of the two rates indicates that the seep produces approximately 0.08% of the total amount of methane currently being exploited.

If methane entering the water column is the result of gas seepage in the form of bubbles, it is expected that only a small fraction of the methane would dissolve during the relatively short transit time of the bubble, the amount of dissolution being dependent on the depth of the water column (< 30m) and bubble size (Schink et al., 1971). Thus, the actual seep production could be significantly greater than that calculated on the basis of dissolved measurements. If only 5% of the methane emanating from the seep dissolves (a conservative guess at best), then the seep (or seeps) could be producing as much as 1% of the total amount of natural gas currently produced commercially.

Although the methane budget presented here is based on several assumptions, we have attemped to make conservative estimates. Considering the range in values for production, simplicity of the model and model assumptions, the potential size of the seepage of natural gas is probably, at best, accurate to within an order of magnitude. However, the seepage still may represent a significant source of natural gas that has not yet been discovered or is perhaps the result of leakage from shut-in or exploratory wells already present within Trading Bay. Because of the sensitivity of the budget to transport through the Forelands, only a more detailed survey of the dissolved hydrocarbons and the circulation coupling the upper and lower Inlet will allow better estimates to be made.

4.4 Concluding Remarks

Cook Inlet has been shown to be a unique study area for the assessment of processes influencing the distribution of LMW hydrocarbons. The differing hydrographic regions of the upper and lower Inlet allowed the sources of these compounds to be defined on the basis of compositional parameters. It is obvious that these diagnostic tools can be used effectively only when the proper ancillary measurements are made. In context of the oceanographic conditions, these compounds appear to be useful tracers of hydrocarbon injection over reasonably large space scales.

Although the light hydrocarbons are not toxic, the presence of a thermogenic source indicates that the more toxic components of crude oil may also be found in these waters. Preliminary measurements of the LMW aromatics--benzene, toluene, and C_2-benzenes--which have their source in crude oils, showed values in the upper Inlet that were significantly above the ambient levels measured in Shelikof Strait. The potential injection of these toxic compounds into creek Inlet waters warrants further investigation of their distributions.

It is apparent that the coupling of the upper and lower Inlet is of the utmost importance in determining the magnitude of the hydrocarbon sources. This would require a more detailed knowledge of the time-dependent velocity field of the Inlet. Given a more complete data base of concentrations and current velocities, more sophisticated models can be used to quantify the magnitude of the source more accurately.

In terms of the biological sources of hydrocarbons, it can be seen that hydrocarbon flux measurements from the sediments need to be made for better determination of the biological production rate. Ideally, in vivo flux measurements should be made, since pore water analysis of these gases has presented many difficulties. The advantage of bell-jar type experiments would ensure measurement of production occurring at the sediment-water interface.

5. ACKNOWLEDGMENTS

We would like to thank the many people within the Geochemistry Group of NOAA/PMEL who have provided support for this project. We would also like to thank George Anderson for providing the Plexiglas® incubation boxes used in the Natural Modification of Light Hydrocarbons experiment. Finally, we thank the Captains and crew of the NOAA Ship Discoverer for their assistance in the field program.

This study was supported by the Bureau of Land Management through an interagency agreement with the National Oceanic and Atomospheric Administration under which a multiyear program responding to needs of petroleum development of the Alaskan continental shelf is managed by the Outer Continental Shelf Environmental Assessment Program Office.

6. REFERENCES

Alaska Oil and Gas Conservation Commission (1978): 1978 statistical report. Anchorage, Alaska. 262 pp.

Atkinson, L.P., and F. A. Richards (1967): The occurrence and distribution of methane in the marine environment. Deep-Sea Res. 14: 673-684.

Baker, E. T., J. D. Cline, R. A. Feely, and J. Quan (1978): Seasonal distribution, trajectory studies, and sorption characteristics of suspended particulate matter in the northern Puget Sound region. National Oceanic and Atmospheric Administration, Pacific Marine Environmental Laboratory. Interagency Energy/Environment R & D Program Report No. EPA-600/7-126. 140 pp.

Barnes, R. O., and E. D. Goldberg (1976): Methane production and consumption in anoxic marine sediments. Geology 4:297-300.

Bernard, B. B., J. M. Brooks, and W. M. Sackett (1976); Natural gas seepage in the Gulf of Mexico. Earth Planet. Sci. Lett. 31:48-54.

Bernard, B. B., J. M. Brooks, and W. M. Sackett (1977): A geochemical model for characterization of hydrocarbon gas sources in marine sediments, pp. 435-437. In paper OTC 2934 presented at the 9th Annual Offshore Technology Conference, Houston, May 1977.

Bernard, B. B., J. M. Brooks, and W. M. Sackett (1978): Light hydrocarbons in recent Texas continental shelf and slope sediments. J. Geophys. Res. 83:4053-4061.

Blasko, D. P. (1974): Natural gas fields -- Cook Inlet Basin, Alaska. U. S. Department of Interior, Bureau Mines Open File Rep. 24 pp.

Broecker, W. S., and T. H. Peng (1974): Gas exchange rates between air and sea. Tellus 26:21-35.

Brooks, J. M., and W. M. Sackett (1973): Sources, sinks, and concentrations of light hydrocarbons in the Gulf of Mexico. J. Geophys. Res. 78:5248-5258.

Brooks, J. M., J. R. Gormly, and W. M. Sackett (1975): Input of low-molecular-weight hydrocarbons from petroleum operations into the Gulf of Mexico, 26, pp. In paper presented at the Conference on Prevention and Control of Oil Spills, San Francisco, California, April 1975.

Brooks, J. M. (1975): The flux of light hydrocarbons into the Gulf of Mexico via runoff, pp. 185-200. In H. L. Windom and R. A. Duce [eds.], Marine Pollutant Transfer, Lexington Books, Lexington, Mass.

Brooks, J. M., and W. M. Sackett (1977): Significance of low molecular weight hydrocarbons in marine waters, pp. 455-468. In Proceedings of the 7th International Meeting on Organic Geochemistry, 1977.

Brooks, J. M., B. B. Bernard, T. C. Sauer, and H. Abdul-Reheim (1978): Environmental aspects of a well blowout in the Gulf of Mexico. Environ. Sci. Technol. 12:695-703.

Brower, W. A., Jr., H. F. Diaz, A. S. Prechtel, H. W. Searby, and J. L. Wise (1977): Climatic atlas of the outer continental shelf waters and coastal regions of Alaska, v. 1. Arctic Environmental Information and Data Center--University of Alaska, Anchorage, Alaska. 439 pp.

Burbank, D. C. (1977): Circulation studies in Kachemak Bay and lower Cook Inlet. In L. L. Trasky, L. B. Flagg, and D. C. Burbank [eds.], Environmental studies of Kachemak Bay and lower Cook Inlet, Alaska. Department of Fish and Game, Anchorage, Alaska. 207 pp.

Burbank, D. C. (1974): Suspended sediment transport and deposition in Alaskan coastal waters. M. S. thesis, Univ. Alaska, Fairbanks. 222 pp.

Clark, M. E., G. A. Jackson, and W. J. North (1972): Dissolved free amino acids in southern California coastal waters. Limnol. Oceanogr. 17:749-758.

Clark, R. C. Jr., and D. W. Brown (1977): Petroleum: properties and analyses in biotic and abiotic systems, pp. 1-89. In D. C. Malins [ed.], Effects of petroleum on arctic and subarctic marine environments and organisms, v. 1. Academic, New York.

Cline, J. D., and R. A. Feely (1976): Distribution of light hydrocarbons, C_1-C_4, in the northeast Gulf of Alaska and the southeastern Bering shelf. pp. 443-543. In Environmental assessment of the Alaskan continental shelf: Principal investigators' reports for the year ending March 1976, v. 9, U. S. Department of Commerce, National Oceanic and Atmospheric Administration.

Cline, J. D., and M. L. Holmes (1977): Submarine seepage of natural gas in Norton Sound, Alaska. Science 198:1149-1153.

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

Cline, J. D., and M. Holmes (1978): Anomalous gaseous hydrocarbons in Norton Sound: Biogenic or thermogenic?, pp. 81-86. In paper OTC 3052 presented at the 10th Annual Offshore Technology Conference, Houston, May 1978.

Cline, J. D., R. Feely, and A. Young (1978): Identification of natural and anthropogenic petroleum sources in the Alaskan shelf areas utilizing low molecular weight hydrocarbons, pp. 73-198. In Environmental assessment of the Alaskan continental shelf: Annual reports of principal investigators for the year ending March 1978, v. 3, U.S. Dept. of Commerce, National Oceanic and Atmospheric Administration.

Cline, J. D., C. N. Katz, and A. Young (1979): Distribution and abundances of low molecular weight hydrocarbons and suspended hydrocarbons in Cook Inlet, Alaska, pp. 264-325. In Environmental assessment of the Alaskan continental shelf: Principal investigators' reports for the year ending March 1979, v. 5. U. S. Department of Commerce, National Oceanic and Atmospheric Administration.

Davis, J. B., and R. M. Squires (1954): Detection of microbially produced gaseous hydrocarbons other than methane. Science 119: 381-382.

Ehhalt, D. H. (1974): The atmospheric cycle of methane. Tellus 26: 58-70.

Emerson, S. (1975): Gas exchange rates in small Canadian Shield lakes. Limno. Oceanogr. 20:754-761.

Evans, C. D., E. Buck, R. Buffler, G. Fisk, R. Forbes, and W. Parder (1972): The Cook Inlet environment: A background study of available knowledge. University of Alaska Resource and Science Service Center, Alaska Sea Grant Program, Anchorage, Alaska.

Feely, R. A., and G. J. Massoth (1981): Sources, composition, and transport of suspended particulate matter in lower Cook Inlet and northwestern Shelikof Strait, Alaska, U. S. Geological Survey Professional Paper (in press).

Frank, D. J., W. Sackett, R. Hall, and A. Fredericks (1970): Methane, ethane, and propane concentrations in Gulf of Mexico. Am. Assoc. Petroleum Geologists Bull. 54:1933-1938.

Gatto, L. W. (1976): Baseline data on the oceanography of Cook Inlet, Alaska. Rep. 76-25, U. S. Army Cold Regions Research and Engineering Laboratory, Hanover, N.H. 84 pp.

Hampton, M. A., and M. A. Bouma (1976): Shallow faulting, bottom instability and movements of sediments in lower Cook Inlet and western Gulf of Alaska, pp. 392-440. In Environmental assessment of the Alaskan continental shelf: Principal investigators' reports October-December 1976, v. 4. U. S. Department of Commerce, National Oceanic and Atmospheric Administration.

Harrison, H., J. E. Johnson, and J. D. Cline (1981): Light hydrocarbons in the atmospheric boundary layer over the north Pacific. Submitted to J. Geophys. Res.

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

Hunt, J. M. (1974): Hydrocarbon geochemistry of Black Sea, pp. 499-504. In E. T. Degens and D. A. Ross [eds.], The Black Sea--geology, chemistry, and biology. Am. Assoc. Petroleum Geologists Memoir 20.

Kanwisher, J. (1963): Effect of wind on CO_2 exchange across the sea surface. J. Geophys. Res. 68:589-591.

Kinney, P. J., J. Groves, and D. K. Button (1970): Cook Inlet environmental data. R/V Acona cruise 065-May 21-28, 1968. Inst. Mar. Sci., Univ. Alaska, College, Alaska, Rep. No. R-70-2. 120 pp.

Knull, J. R., and R. Williamson (1969): Oceanographic survey of Kachemak Bay, Alaska. U. S. Department of the Interior, Bureau of Commercial Fisheries Manuscript Rep. No. 60. 54 pp.

Ku, H. S., and A. C. Leopold (1970): Ethylene formation from peptides of methionine. Biochem. Biophys. Res. Commun. 41:1155-1160.

Lamontagne, R. A., J. W. Swinnerton, and V. J. Linnenbom (1974): C_1-C_4 hydrocarbons in the North and South Pacific. Tellus 26:71-77.

Larrance, J. D. (1976): Phytoplankton and primary productivity in the northeast Gulf of Alaska, pp. 760-772. In Environmental assessment of the Alaskan continental shelf: Principal investigators' reports April-June 1976, v. 1. U. S. Department of Commerce, National Oceanic and Atmospheric Administration.

Larrance, J. D., and A. J. Chester (1981): Source, composition, and flux of organic detritus in lower Cook Inlet. In Environmental assessment of the Alaskan continental shelf: Final reports of principal investigators. U. S. Department of Commmerce, National Oceanic and Atmospheric Administration. 50 pp. (in press).

Linnenbom, V. J., and J. W. Swinnerton (1968): Distribution of low molecular weight hydrocarbons and excess molecular nitrogen in the Cariaco Trench, pp. 125-130. In Symp. on Investigation and Resources of the Caribbean Sea and Adjacent Regions, FAO Fish. Rep. 71.1.

Liss, P. S. (1973): Processes of gas exchange across an air-water interface. Deep-Sea Res. 20:221-238.

Liss, P. S., and P. G. Slater (1974): Flux of gases across the air-sea interface. Nature 247:181-184.

MacDonald, R. W. (1976): Distribution of low-molecular-weight hydrocarbons in southern Beaufort Sea. Environ. Sci. Technol. 10:1241-1246.

Martens, C. S., and R. A. Berner (1974): Methane production in the interstitial waters of sulfate-depleted marine sediments. Science 185:1167-1169.

McAuliffe, C. (1963): Solubility in water of C_1-C_9 hydrocarbons. Nature 200:1092-1093.

Moore, B. J., and R. D. Shrewsbury (1966): Analysis of natural gases of the United States. Inform. Circ. 8302, U. S. Bureau of Mines, Pittsburgh, Pa.

Muench, R. D., H. O. Mofjeld, and R. L. Charnell (1978): Oceanographic conditions in lower Cook Inlet: Spring and summer 1973. J. Geophys. Res. 83:5090-5098.

Murphy, R. S., R. F. Carlson, D. Nyguist, and R. Britch (1972): Effect of waste discharges on a silt-laden estuary. A case study of Cook Inlet, Alaska. Inst. Water Resources, Univ. Alaska, College, Alaska. Rep. No. IWR 26, 42 pp.

Nikonov, V. F. (1972): Distribution of methane homologs in gas and oil fields. Doklady Akad. Nauk, SSSR. 206:234-236.

Okubo, A. (1971): Oceanic diffusion diagrams. Deep-Sea Res. 18:789-802.

Oremland, R. S. (1975): Methane production in shallow-water, tropical marine sediments. Appl. Microbiol. 30:602-608.

Oremland, R. S. (1979): Methanogenic activity in plankton samples and fish intestines: A mechanism for in situ methanogenesis in oceanic surface waters. Limnol. Oceanogr. 24:1136-1141.

Patchen, R. C., J. T. Bruce, and M. J. Conolly (1981): Cook Inlet survey report. U. S. Department of Commerce, National Oceanic and Atmospheric Administration, National Ocean Survey/Oceanographic Survey Rep. (in press).

Primrose, S. B. (1976): Ethylene-forming bacteria from soil and water. J. Gen. Microbiol. 97:343-346.

Ross, D. A., and P. Stoffers (1978): Report C: General data on bottom sediments including concentrations of various elements and hydrocarbons in the Persian Gulf and Gulf of Oman. Woods Hole Oceanog. Inst. Tech. Rep. No. WHOI-78-39. pp. 45-74.

Sackett, J. M. (1977): Use of hydrocarbon sniffing in offshore exploration. J. Geochem. Explor. 7:243-254.

Sarmiento, J. L., H. W. Feely, W. S. Moore, A. E. Bainbridge, and W. S. Broecker (1976): The relationship between vertical eddy diffusion and buoyancy gradient in the deep sea. Earth Planet. Sci. Lett. 32:357-370.

Schink, D. R., N. L. Guinasso, Jr., J. J. Sigalove, and N. E. Cima (1971): Hydrocarbons under the sea: A new survey technique. Paper presented at the 3rd Offshore Technology Conference of the Am. Inst. Mining, Metallurgical and Petrol. Eng. 11 pp.

Scranton, M. I. (1977): The marine geochemistry of methane. Ph.D. thesis, Woods Hole Oceanogr. Inst./Massachusetts Inst. Technol. 241 pp.

Scranton, M. I., and P. G. Brewer (1977): Occurrence of methane in the near-surface waters of the western subtropical North-Atlantic. Deep-Sea Res. 24:127-138.

Sharma, G. D., and D. C. Burrell (1970): Sedimentary environment and sediments of Cook Inlet, Alaska. Am. Assoc. Petroleum Geologists, 54:647-654.

Sharma, G. D., F. F. Wright, J. J. Burns, and D. C. Burbank (1974): Sea surface circulation, sediment transport, and marine mammal distribution, Alaska continental shelf. Final report of ERTS Project 110-H. University of Alaska, Fairbanks.

Smith, A. M., and R. J. Cook (1974): Implications of ethylene production by bacteria for biological balance of soil. Nature 252:703-705.

Strickland, J. D., and T. R. Parsons (1972): A practical handbook of seawater analysis, Second edition. Bull. Fish. Bd. Can. 310 pp.

Swinnerton, J. W., and V. J. Linnenbom (1967): Determination of the C_1 to C_4 hydrocarbons in seawater by gas chromatography. J. Gas Chromatogr. 5:570-573.

Swinnerton, J. W., and R. A. Lamontagne (1974): Oceanic distribution of low-molecular-weight hydrocarbons. Environ. Sci. Technol. 8:657-663.

Swinnerton, J. W., R. A. Lamontagne, and J. S. Bunt (1977): Field study of carbon monoxide and light hydrocarbon production related to natural biological processes. Naval Res. Lab. Rep. No. 8099. 9 pp.

U.S.D.I. (U.S. Dept. of the Interior). 1976. Lower Cook Inlet, final environmental impact statement. Proposed 1976 Outer Continental Shelf Oil and Gas Lease Sale lower Cook Inlet. Bureau of Land Management, 3 Vols.

Watanabe, T., and N. Kondo (1976): Ethylene evolution in marine algae and a proteinaceous inhibitor of ethylene biosynthesis from red algae. Plant Cell Physiol. 17:1159-1166.

Wilson, D. F., J. W. Swinnerton, and R. A. Lamontagne (1970): Production of carbon monoxide and gaseous hydrocarbons in seawater: Relation to dissolved organic carbon. Science 168:1577-1579.

Witherspoon, P. A., and L. Bonoli (1969): Correlation of diffusion coefficients for paraffin, aromatic, and cycloparaffin hydrocarbons in water. Industrial Eng. Chem. Funds. 8:589-591.

Yamamoto, S., J. B. Alcauskas, and T. E. Crozier (1976): Solubility of methane in distilled water and seawater. J. Chem. Eng. Data 21: 78-80.

Yang, S. F., H. S. Ku, and H. K. Pratt (1967): Photochemical production of ethylene from methionine and its analogues in the presence of flavin mononucleotide. J. Biol. Chem. 242:5274-5280.

Yang, S. F. (1974): The biochemistry of ethylene: Biogenesis and metabolism, pp. 131-164. In V. C. Runeckles, E. Sorheimer, and D. C. Walton [eds.], The chemistry and biochemistry of plant hormones, Academic, New York.

APPENDIX A

Table A-1. Cook Inlet areas and volumes based on hydrographic charts 16640 and 16660.

Subdivision*	Area $\times 10^9$ m^2	Mean Depth m	Volume $\times 10^{11}$ m^3
Lower Cook Inlet	16.7	47	7.8
Upper Cook Inlet (Total)	3.32	15	0.50
Upper Cook Inlet (Box)	1.52	21	0.32
Total Inlet	20.0	42	8.3
Lower Inlet < 18m (10fm)	4×10^9 m^2		
Upper Inlet (Total) < 18m	2		
Upper Inlet (Box) < 18m	1		
Total Inlet < 18m	6		
Entrance Cross Section	31×10^5 m^2		
Forelands Cross Section	5.1×10^5 m^2		
N. Foreland - Pt. Possession Cross Section	9.4×10^5 m^2		

* Subdivisions of the Inlet are discussed in Chapter 4 under Hydrocarbon Budgets.

APPENDIX B

Table B-1. Results of Natural Modification of Light Hydrocarbons experiment for the "light" bottles.

Time	Light	Methane	Ethane	Ethene	Propane	Propene	iso-Butane	n-Butane	O_2	PO_4	SiO_2	NO_3	NO_2	NH_3
(days)					(nl l^{-1})							(μmol l^{-1})		
0	0	149.3	0.8	1.4	0.4	0.5	0.1	0.2	1.0	1.8	12.5	7.3	0.3	1.5
		147.6	1.1	1.5	0.5	0.6	0.1	0.2						
		145.7	0.9	1.5	-	-	-	-						
		143.6	0.7	1.3	0.4	0.5	0.1	0.1						
0.9	299	160.9	1.1	3.0	0.7	1.7	0.2	0.3		1.6	11.6	5.8	0.4	1.7
		173.2	1.3	2.9	0.7	1.9	0.1	0.3		1.6	11.9	5.9	0.4	1.6
		149.6	-	-	0.6	1.6	0.1	0.2		1.5	11.7	6.0	0.4	1.2
		147.5	1.0	2.7	0.5	1.5	0.1	0.2		1.6	11.8	5.8	0.4	1.5
1.8	471	151.8	-	-	-	2.1	0.2	0.3	1.2	1.6	10.4	3.7	0.4	1.0
		151.3	1.2	3.1	0.7	2.1	0.1	0.3		1.6	9.5	3.3	0.3	0.9
		149.5	0.9	3.2	0.6	1.9	-	0.4		1.5	9.8	3.5	0.4	2.2
4.0	853	153.9	1.2	5.4	0.7	2.7	0.2	0.2		1.2	4.5	0.1	0.3	1.6
		148.2	1.3	-	0.7	2.7	-	0.2		1.2	6.4	0.8	0.3	0.9
		148.6	1.4	5.2	0.8	-	0.2	0.2		0.4	6.2	0.4	0	0.1
		150.0	1.4	5.1	0.8	2.9	0.1	0.2		0.5	5.4	0.1	0.1	0.4
6.0	1481	155.5	1.7	7.0	1.0	4.7	0.3	0.3	1.7	0.9	4.1	0.2	0.2	2.0
		154.9	1.5	5.8	0.8	-	0.1	0.2		0.4	2.9	0	0.1	0.4
		150.3	1.5	6.5	0.9	4.5	0.2	0.2		0.4	3.2	0	0.1	0.5
10.8	3922	158.3	2.6	11.4	1.3	-	0.1	0.2		0.3	1.6	0	0.1	0.5
		150.3	2.4	-	1.4	6.1	0.1	0.3		0.3	1.5	0	0.1	0.4
		157.0	2.5	10.6	1.3	6.9	0.1	0.3		0.3	2.2	0	0.1	0.4
		-	-	12.0	1.6	7.3	0.1	0.4		0.4	2.3	0	0.1	0.5
14.0	5506	154.1	4.9	17.7	2.4	10.0	-	0.4	1.7	0.3	1.3	0	0.1	0.4
		157.9	4.8	18.9	2.7	11.9	0.2	0.4		0.3	1.0	0	0.0	0.2
		154.5	5.8	19.9	3.0	12.9	0.2	0.4		0.2	1.1	0	0.1	0.5
18.0	7183	153.9	5.4	24.4	2.7	14.1	-	0.5		1.1	1.6	0.2	0.3	1.5
		153.9	6.0	28.1	2.9	16.3	0.2	0.5		0.3	1.6	0.1	0.1	0.5
		152.0	6.6	29.9	3.4	21.2	-	0.6		1.0	2.9	0.1	0.2	1.7
		149.2	5.8	24.0	2.9	14.6	-	0.6		1.1	1.6	0.1	0.3	2.5

Table B-2. Results of Natural Modification of Light Hydrocarbons experiment for the "killed" bottles.

Time (days)	Light	Methane	Ethane	Ethene	Propane	Propene	iso-Butane	n-Butane
				(nl l^{-1})				
0	0	149.3	0.8	1.4	0.4	0.5	0.1	0.2
		147.6	1.1	1.5	0.5	0.6	0.1	0.2
		145.7	0.9	1.5	-	-	-	-
		143.6	0.7	1.3	0.4	0.5	0.1	0.1
1.8	471	148.2	2.1	4.3	1.2	2.7	0.1	0.3
		148.9	2.1	4.2	1.1	2.5	0.1	0.3
		152.1	2.2	4.1	1.2	2.5	0.1	0.3
6.0	1481	147.3	2.6	9.0	-	-	-	-
		147.0	2.7	9.4	1.6	8.0	0.3	0.3
		147.5	2.8	9.5	-	7.0	0.2	0.3
14.0	5506	146.2	3.4	18.9	2.0	19.7	0.2	0.5
		143.9	2.9	14.5	1.8	14.1	0.2	0.4
		144.5	3.3	16.8	1.9	17.1	-	-
18.0	7183	139.3	3.1	19.1	1.9	18.6	-	0.5
		141.6	3.4	19.4	2.1	20.6	0.2	0.5

Note: Nutrients were not analyzed because of interference with NaN_3. Light values are relative.

Table B-3. Results of Natural Modification of Light Hydrocarbons experiment for the "dark" bottles.

Time (days)	Methane	Ethane	Ethene	Propane (nl l^{-1})	Propene	iso-Butane	n-Butane	PO_4	SiO_2	NO_3 (μmol l^{-1})	NO_2	NH_3
0	149.3	0.8	1.4	0.4	0.5	0.1	0.2	1.8	12.5	7.3	0.3	1.5
	147.6	1.1	1.5	0.5	0.6	0.1	0.2					
	145.7	0.9	1.5	-	-	-	-					
	143.6	0.7	1.3	0.4	0.5	0.1	0.1					
1.8	-	-	1.5	0.4	0.5	0.1	-	1.7	12.2	7.5	0.4	1.3
	147.5	0.9	1.5	0.4	0.5	0.1	0.2	1.7	12.3	7.4	0.4	2.4
	146.0	0.7	1.5	0.4	0.5	0.1	0.2	1.7	12.4	7.5	0.4	3.1
6.0	143.7	0.8	1.5	0.4	0.6	0.1	0.1	1.1	12.5	7.5	0.2	2.0
	144.9	0.8	-	-	0.6	0.1	0.2	1.0	12.4	7.4	0.2	2.4
	146.1	0.8	1.6	0.5	0.7	0.1	0.1	1.0	12.4	7.4	0.2	2.0
14.0	145.3	0.8	2.0	0.5	0.8	0.1	0.1	1.2	12.6	7.4	0.2	3.3
	143.4	1.2	1.9	0.7	0.8	0.1	0.2	1.1	13.3	7.3	0.2	3.3
18.0	139.1	1.0	1.8	0.5	0.7	0.1	0.2	1.8	13.3	7.5	0.4	5.4
	141.4	0.9	1.7	0.6	0.8	0.1	0.1	2.0	13.3	7.5	0.3	4.2
	140.3	1.1	1.5	0.5	0.7	0.1	0.1	2.1	13.8	7.6	0.4	5.3