# Hydrocarbon Levels in the Marine Environment of the Southern Beaufort Sea

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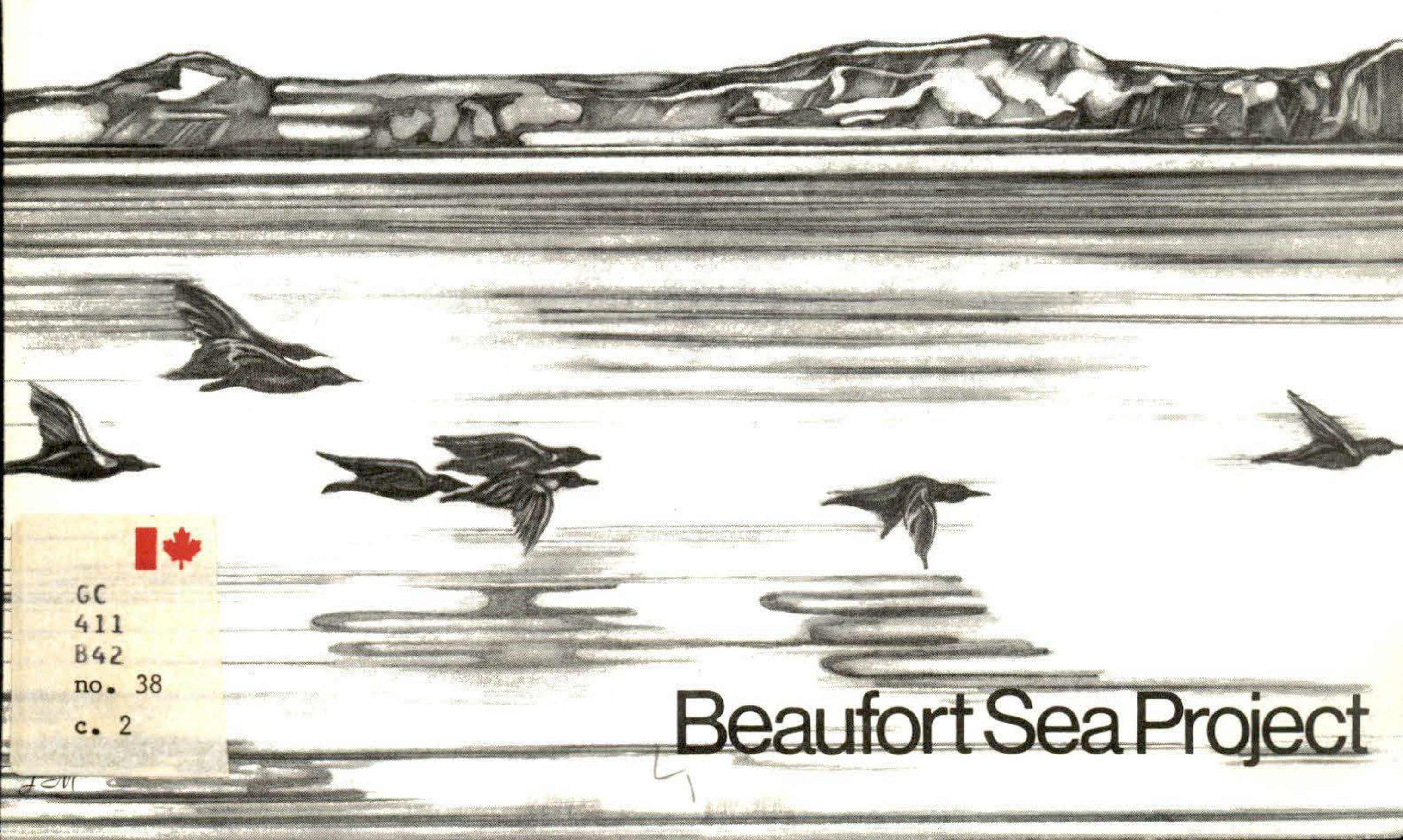
Technical Report No. 38



Beaufort Sea Project

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# HYDROCARBON LEVELS IN THE MARINE ENVIRONMENT OF THE SOUTHERN BEAUFORT SEA

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## 1. SUMMARY

This report summarizes the objectives of the project, the study area, methods, sources of data and field and laboratory results of the hydrocarbon baseline studies in the Southern Beaufort Sea during the summers of 1974 and 1975. The objectives of the investigation are: (1) to establish the baseline hydrocarbon levels in the Southern Beaufort Sea drilling area by measuring classes of hydrocarbons and identifying some specific hydrocarbons in sea water, marine organisms, fish and surface sediments, (2) to assess the origin of present day hydrocarbons, whether anthropogenic or naturally-occurring, and (3) to understand the probable hydrocarbon pathways in case an oil spill or blow-out occurs in the area. To achieve this, two cruises were conducted: a preliminary cruise on the M. V. THETA in the summer of 1974 and a major cruise on the M. V. PANDORA II in the summer of 1975, covering the summer open-waters from 139° W to 130° W and from the 10 m contour to the ice edge very close to the 100 m contour along 70.5° N to 71.5° N. Shipboard and shore-laboratory measurements of hydrocarbons were made in contaminant-free clean rooms on samples collected by hydrocarbon-free samplers. Results include polycyclic aromatic hydrocarbons and low-molecular weight hydrocarbons in sea water, polycyclic aromatic hydrocarbons and non-polar hydrocarbons in fish, mixed plankton and sediments. The baseline data show that the marine environment in Southern Beaufrot Sea is clean in general. No tar or plastic wastes were collected by neuston-net tows on the surface sea water. The levels of polycyclic aromatic hydrocarbons in sea water are low, comparable in cleanliness to uncontaminated oceanic waters in N.E. Pacific Ocean. The levels of low-molecular weight hydrocarbons, with the exception of methane in near-bottom water are low or close to the detectable limits indicating the absence of petrogenic inputs. The high methane is due to natural influx from the sediment. The polycyclic aromatic hydrocarbons in marine organisms appear to be low and levels in marine sediments have a very wide range. There is a paucity of data for organisms and sediments from other world areas for a useful comparison. The non-polar hydrocarbons in fish suggest marginal presence of petroleum hydrocarbons in the tissues, taking into account the small number of samples, the biological variability and the limitation of the analytical technique used. The non-polar hydrocarbons in marine sediments show characteristics typical of a mixture of marine and terrestrial hydrocarbons, suggesting influx of terrestrial plant material via the Mackenzie River, which also flows through areas with known natural seepage and petroleum drillings.

# 2. INTRODUCTION

## 2.1 General Nature and Scope of Study

This study covers investigations of the baseline hydrocarbon levels and characteristics in the marine environment of the Southern Beaufort Sea. To assess any environmental impact of possible hydrocarbon pollution arising from offshore drilling for oil or gas in future, it is essential to establish the existing levels of classes of hydrocarbons and specific hydrocarbon pollution indicators in sea water, biota and surface sediments so that any environmental changes and the rates at which such deterioration occurs can be estimated from present and future investigations. It is impossible to yield answers to all the questions on the hydrocarbon levels in the Arctic environment from an 18-month study, but this study should provide the first few essential steps towards grasping the dimensions of the chemical aspects. The scope of the study includes baseline hydrocarbon data from two chemical oceanographic cruises in the Southern Beaufort Sea area: a THETA cruise in the summer of 1974, a PANDORA II cruise in the summer of 1975 and from a beach walk program to investigate hydrocarbon pollution or natural seeps along the Southern Beaufort Sea Coastline in the summers of 1974 and 1975.

The work was planned and co-ordinated by C. S. Wong with W. J. Cretney as the co-investigator. It also involved substantial contribution from staff of the Ocean Chemistry Division, Ocean and Aquatic Sciences, Pacific Region, in the Department of the Environment. Part of the work was carried out by contracts to C. E. L. L. (DSS Contract File Ref. 01SX-KF832-0095), CHEMEX (DSS Contract File Ref. ST02-KF832-4-0785) and SEAKEM (DSS Contract File Ref. VIC46915/1) in 1974, and to SEAKEM (DSS Contract File Ref. SZ02. KF832-4-2062 and SZ02. KF832-4-2135), W. Richardson (SS08. KF832-5-0425) and Thalassic Data (SZ02. KF832-4-2107) in 1975.

The personnel in the Ocean Chemistry Division and in industries involved in this study includes the following:

### Ocean Chemistry Division

| | |
|---|---|
| Dr. C. S. Wong | (Chief, Ocean Chemistry Division) |
| Dr. W. J. Cretney | (Head, Marine Hydrocarbons Section) |
| Dr. R. W. Macdonald | (NRC postdoctoral fellow) |
| Dr. P. Christensen | (NRC postdoctoral fellow) |

Industries

| | |
|---|---|
| Mr. P. Erickson | (C. E. L. L., 1974; SEAKEM, 1975) |
| Mr. B. McIntyre | (CHEMEX, 1974) |
| Mrs. B. Hubbard | (SEAKEM, 1974) |
| Mr. D. Macdonald | (C. E. L. L., 1974; Thalassic Data, 1975) |
| Mrs. J. Stuart | (SEAKEM, 1975) |
| Miss W. Richardson | (Personal contract, 1975) |

Petroleum, or crude oil, is a very complex substance (Bestougeff, 1967) consisting of over 75% of hydrocarbons and usually 5-10% of non-hydrocarbons. The elements found in crude oil are C, H, O, N and S and trace amounts of metals, usually Ni, V, Fe, Na, Ca and Cu. The predominant classes of hydrocarbons are paraffins, cycloparaffins, aromatics (mono-, di- and poly-cyclic), naphteno-aromatics and asphaltene residual (including hetero-cyclics). Important physico -chemical properties of petroleum classes are summarized in Table 1 (Maritime Administration, U. S. Department of Commerce, 1973). Some environmentally significant compounds are shown in Figure 1.

Petroleum natural gases are complex mixtures too (Speers and Whitehead, 1969; Maritime Administration, U. S. Department of Commerce, 1973) consisting of volatile low-molecular weight (LMW) hydrocarbons, naphthenes aromatics and substantial amounts of non-hydrocarbons. The non-hydrocarbons include non-toxic nitrogen, carbon dioxide, helium and toxic hydrogen sulphide. The hydrocarbons include mainly $C_1$-$C_4$ gases of methane, ethane, propane, i- and n-butanes and some gaseous i- and n-pentanes, hexanes as well as gases above carbon number 7 ($C_7$+ aliphatics). The naphenes and aromatics include cylcopentane, methylcyclopentane, cyclohexane and benzene.

A large number of possible toxic constituents of crude oil exist (Speers and Whitehead, 1969). These include:

(1) Low-molecular weight aromatics such as benzene, toluene, xylene and other monocyclic aromatics.

(2) Acids and phenols such as napthenic acids, aliphatic acids, phenols, cresols, xylenols and naphthols.

(3) Sulphur compounds such as thiols, sulphides and thiophenes.

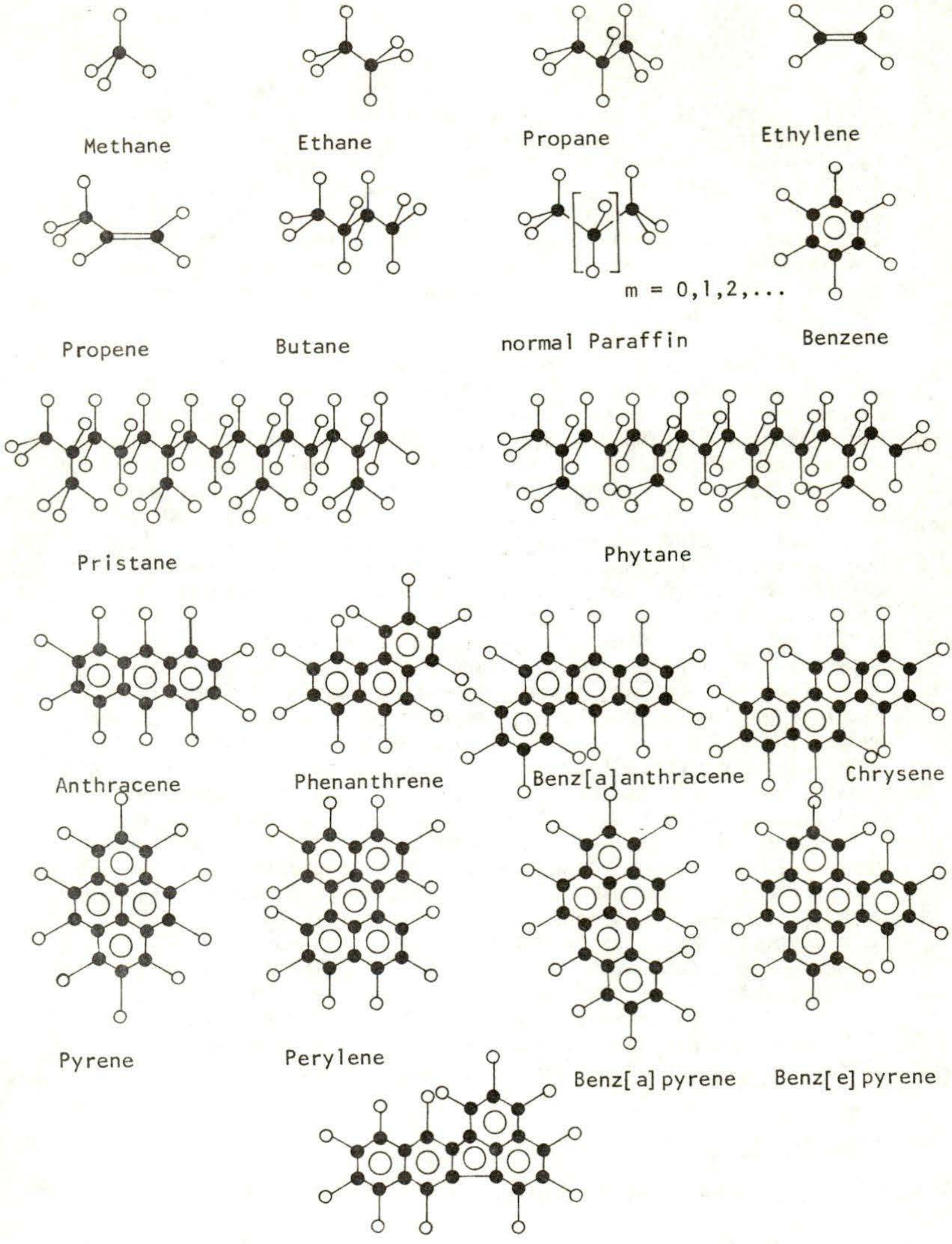
(4) Polynuclear aromatic hydrocarbons (PAH) such as 3,4 benzpyrene (BaP), 1,2-benzanthracenes 1,2-benzphenanthrene (chrysene), diphenylmethane, fluorene, phenanthrene and dibenzthiophene.

## TABLE 1

## PETROLEUM HYDROCARBONS--PHYSICO-CHEMICAL PROPERTIES

(After Table IV-13, Draft Environmental Impact Statement NTIS Report No. EIS 730392D)

| Fraction | Hydrocarbons | % by wt. in Crude Oil | Density (gm/ml) | Boiling Point ($^oC$) | Molecular Weight | Vapor Press. @ 20$^oC$ (mm) | Solubility (gm/10$^6$ gm distilled $H_2O$ |
|---|---|---|---|---|---|---|---|
| 1 | Paraffin $C_6$-$C_{12}$ | .1-20 | .66-.77 | 69-230 | 86-170 | 110-.1 | 9.5-.01 |
| 2 | Paraffin $C_{13}$-$C_{25}$ | 0+-10 | .77-.78 | 230-405 | 184-352 | .1 | .01-.004 |
| 3 | Cycloparaffin $C_6$-$C_{12}$ | 5-30 | .75-.9 | 70-230 | 84-164 | 100-1. | 55-1. |
| 4 | Cycloparaffin $C_{13}$-$C_{23}$ | 5-30 | .9-1. | 230-405 | 156-318 | 1.-0 | 1.-0 |
| 5 | Aromatic (Mono- and di-Cyclic $C_6$-$C_{11}$ | 0-5 | .88-1.1 | 80-240 | 78-143 | 72-.1 | 1780.-0 |
| 6 | Aromatic (Poly-Cyclic) $C_{12}$-$C_{18}$ | 0+-5 | 1.1-1.2 | 240-400 | 128-234 | .1-0 | 12.5-0 |
| 7 | Napheno-Aromatic $C_9$-$C_{25}$ | 5-30 | .97-1.2 | 180-400 | 116-300 | 1.-0 | 1.-0 |
| 8 | Residual(including heterocycles) | 10-70 | 1.-1.1 | 400 | 300-900 | 0 | 0 |



Methane

Ethane

Propane

Ethylene

Propene

Butane

normal Paraffin

Benzene

Pristane

Phytane

Anthracene

Phenanthrene

Benz[a]anthracene

Chrysene

Pyrene

Perylene

Benz[a]pyrene

Benz[e]pyrene

Benz[k]fluoranthene

Figure 1. Some Typical Petroleum HC with Environmental Significance.

(5) Heavy metals such as nickel, vanadium, mercury, lead, cadmium.

The present state of art in analytical chemistry would not permit a complete indentification and quantification of these compounds in the marine environment. In fact, even for petroleum, only about 340 individual hydrocarbons have been identified so far (Bestougeff, 1967). Our approach in this study is the application of known and reliable sampling and analytical techniques to obtain a general idea of the levels of marine hydrocarbons under existing environmental conditions, bearing in mind that the study has to be completed in a short duration of 18 months.

Thus, for the marine hydrocarbon study in the summer of 1974 using the M. V. THETA, the work was limited to testing of sampling technique using well-established Blumer samplers for organics, finding out the precision of our sampling method by repeated collections at one spot and estimating the reliability of our preservation technique by running storage tests. Some sea water and surface sediment samples were also collected for a preliminary study of the spatial distribution of hydrocarbons. Due to storage problems, shipboard determination of low-molecular weight hydrocarbons were made immediately after sample collection. In the summer of 1975, a major cruise was conducted using the M. V. PANDORA II. Chemical oceanographic work appearing in a separate report was performed along with the marine hydrocarbons studies. Sampling of sea water by contaminant-free Blumer samplers was made and shipboard measurements of LMW hydrocarbons by gas chromatography and of polynuclear aromatic hydrocarbons (PAH) by fluorescence technique were conducted. Surface sediment samples were collected by a pipe dredge. Plankton samples were collected by sub-surface Miller nets and surface floating debris by Neuston net tows. The samples to be analyzed in shore laboratory would be stored frozen. Shipboard extractions for aromatics and shipboard analysis for PAH were made in portable laboratory with the ambient air cleaned by filtration through dust filters to remove oil particles from the ship's exhaust and oil. This portable clean laboratory (See Fig. 2) is the first of its kind built specifically for shipboard hydrocarbon studies and has been very successful in eliminating laboratory contamination problems often plaguing marine chemists trying to measure ultra-trace levels of environmental contaminants.

## 2.2 Specific Objectives

This study hopes to achieve the following objectives:

(1) To establish the baseline hydrocarbon levels in the Southern Beaufort Sea drilling area by measuring classes

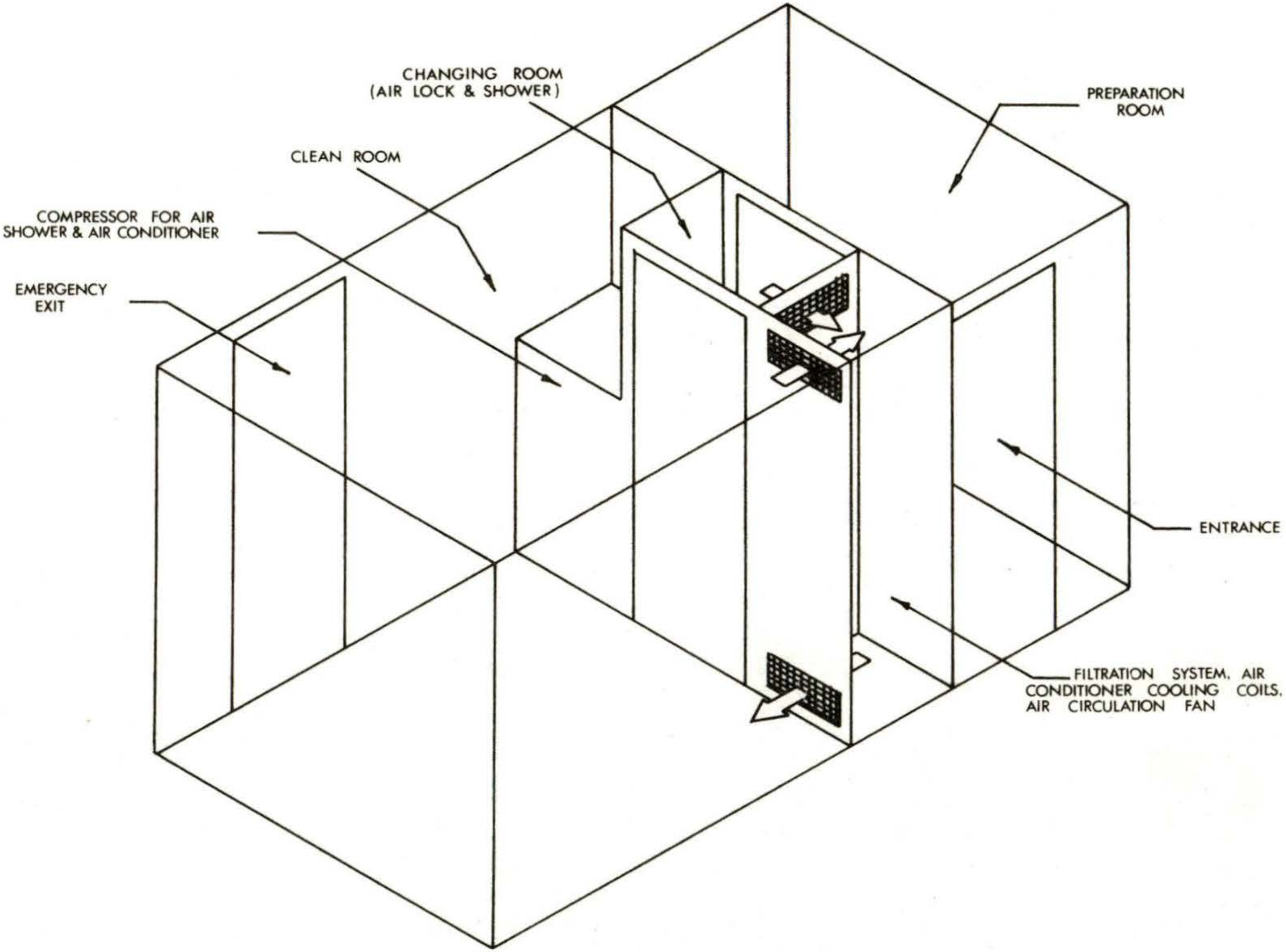


FIGURE 2. SHIPBOARD CLEAN LABORATORY

of hydrocarbons and identifying some specific hydrocarbons in sea water, marine organisms, fish and surface sediments.

(2) To assess the origin of present day hydrocarbons, whether anthropogenic or naturally-occurring.

(3) To understand the probable hydrocarbon pathways in case an oil spill or blowout occurs in the area.

## 2.3 General Relationship to Concerns of Offshore Exploratory Drilling

There is a general concern on the environmental effect of offshore exploratory drilling. We are facing not only a short-term problem arising from accidental spillage and blowouts but also a long-term chronic effect on the marine environment. The extremely cold weather in the Arctic poses an additional threat due to the low biodegradation rate which tends to preserve the pollutants and prolong the environmental damage. To predict the ecological effects of oil pollution is a complex problem and to do so for the Arctic ice and waters is even more difficult. The first hurdle we have to overcome is the general lack of information on the present-day hydrocarbon levels in the Arctic marine environment. There is a general agreement that the Arctic waters and ice are now "very clean" in a qualitative sense. However, no scientific data are available to tell us how clean they are. Very careful analyses for hydrocarbons in sea water, marine organisms, fish and surface sediments are required to establish, in future, any chronic pollution introduced by offshore drilling for oil and gas, or if any residual effects remain after an accidental spill or blowout. The baseline hydrocarbon data can be regarded as an insurance policy designed to ensure that the future Arctic marine environment will be maintained at the present level of cleanliness with respect to hydrocarbons.

## 3. RESUME OF CURRENT STATE OF KNOWLEDGE

No knowledge exists on the hydrocarbon levels in sea water, sea ice, fish, marine organisms, marine mammals, marine flora, and surface sediments in the drilling area of the Southern Beaufort Sea. Only scarce data exist for Western Beaufort Sea off the Alaskan Coast and at Prudhoe Bay. One set of data on the straight-chain hydrocarbons in phytoplanktons was collected in the Beaufort Sea off the U. S. Alaskan Coast (Clark, R. C., Jr., loc. cit.). Total extractable hydrocarbons in benthic sediment and in fish were investigated off Prudhoe Bay (Shaw and Cheek, unpublished manuscript) and aromatic hydrocarbons in fish and sediment in Prince William Sound/NE Gulf of Alaska (Chester et al. 1976). The U. S. data off the Northern Alaskan Coast did not include aromatics and low-molecular weight hydrocarbon gases, which should be a much better indication of possible increases in levels of hydrocarbons resulting from drilling or human activities.

Up to the present, there has been no data on gaseous hydrocarbon concentrations in the Beaufort Sea. Swinnerton and Lamontagne (1974) have compiled extensive data on the oceanic distribution of low-molecular weight hydrocarbons but the part relevant to comparison with Beaufort Sea data would be those in the Greenland Ice Pack. In view of the prospective oil drilling operations, the gaseous hydrocarbon data from the Louisiana Shelf area in the Gulf of Mexico should be useful for comparison, However, drilling operations, ballast tank dumping, industrial and domestic inputs have been taking place for some time in this area before the required sensitivity of detection techniques (Swinnerton and Linnenbom, 1967a; Swinnerton and Linnenbom, 1967b; Swinnerton et al.,1962) was developed. Thus, those shelf data (Brooks and Sackett, 1973; Brooks et al., 1974; Sackett and Brooks, 1974; Frank et al., 1970; Brooks et al., 1973) collected later cannot be used as "baseline". Some of the gaseous hydrocarbons, such as $CH_4$, $C_2H_4$ and $C_3H_6$, may be derived biologically. Other saturated hydrocarbons, such as $C_2H_6$ and $C_3H_8$ should be good petrogenic hydrocarbon tracers, despite the possible natural production of these gases in anoxic waters. These light hydrocarbons do not appear to be detrimental to marine organisms. However, they could serve as useful tracers of anthropogenic inputs and warn us of the presence of other not so innocuous petroleum components.

## 4. STUDY AREAS

The area covers the summer open-waters between the Yukon-Alaskan boundary in the west and Cape Parry in the east, including the offshore permits in the Southern Beaufort Sea and the two Canmar (Canadian Marine Drilling Ltd.) wildcat sites. For the summer cruise of 1974, the surveyed area by Ocean Chemistry Division on the M. V. THETA extended from Herschel Island (about 139°W) to offshore areas off Atkinson Point (about 131°W), and from the 10 m. contour along the coastal area to about 70°N and 71°N. The station locations and the cruise area are shown in Figure 3. The cruise in the summer of 1975 (August 2-25, 1975) covered a much wider area extending from 130°W and from the 10 m contour to the ice edge very close to the 100 m. contour along 70.5°N to 71.5°N, as shown in Figure 4. The locations of nearshore sediments for polycyclic aromatic hydrocarbons collected under a coastal pollutant study (Wong et al., 1976) are shown in Figure 5.

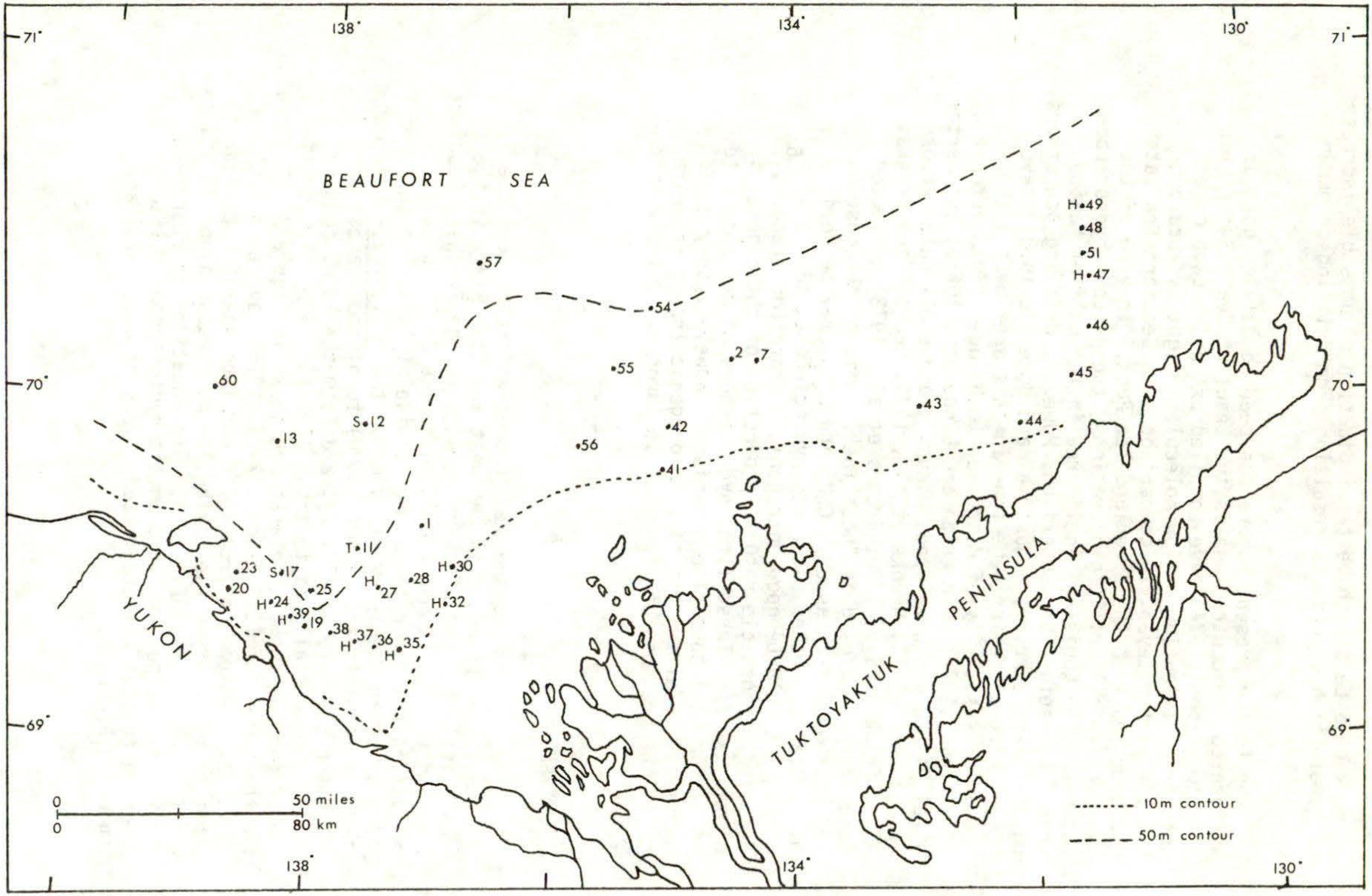


Figure 3. Station Locations for Cruise OC-BSP-74

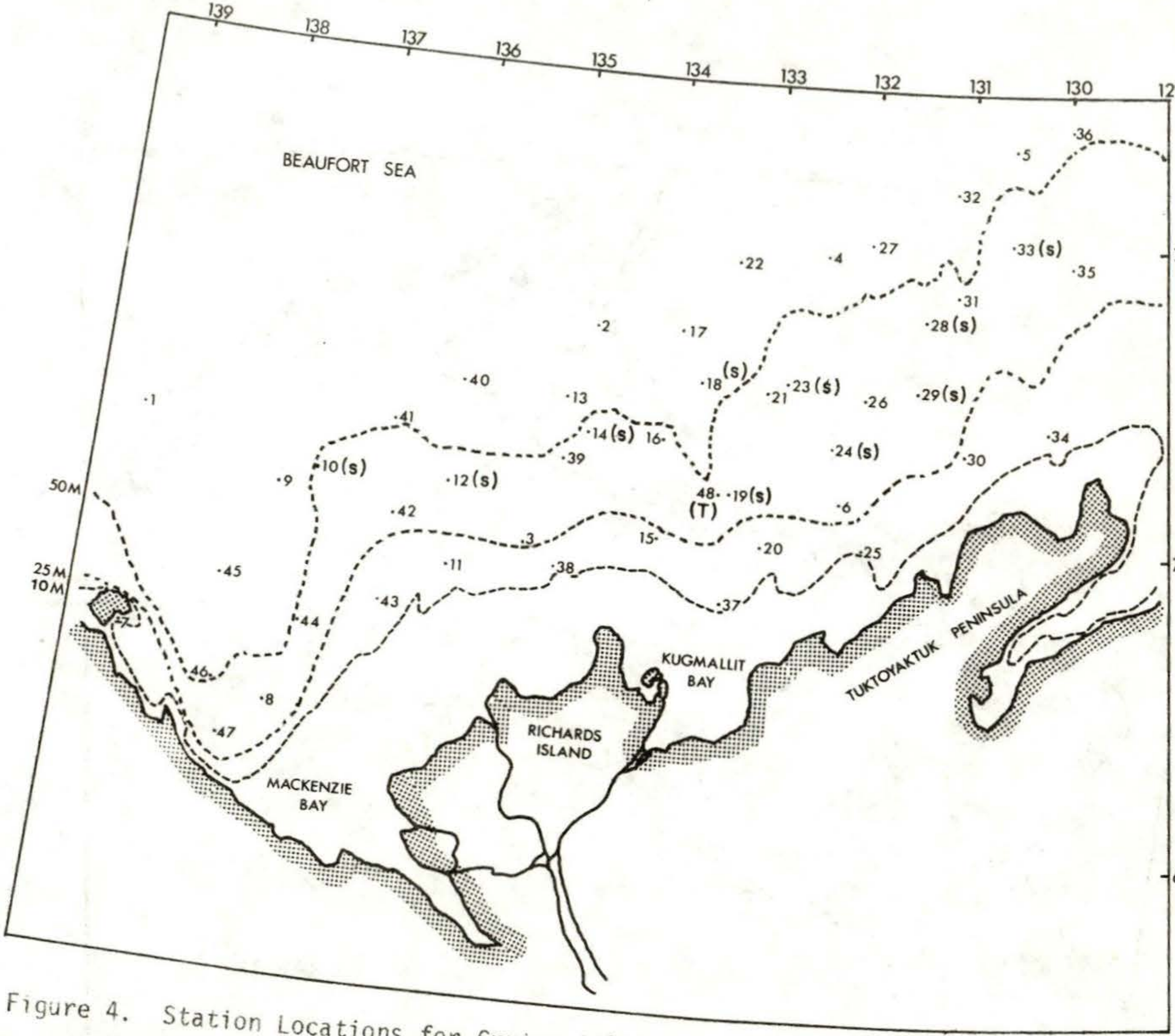


Figure 4. Station Locations for Cruise OC-BSP-75.

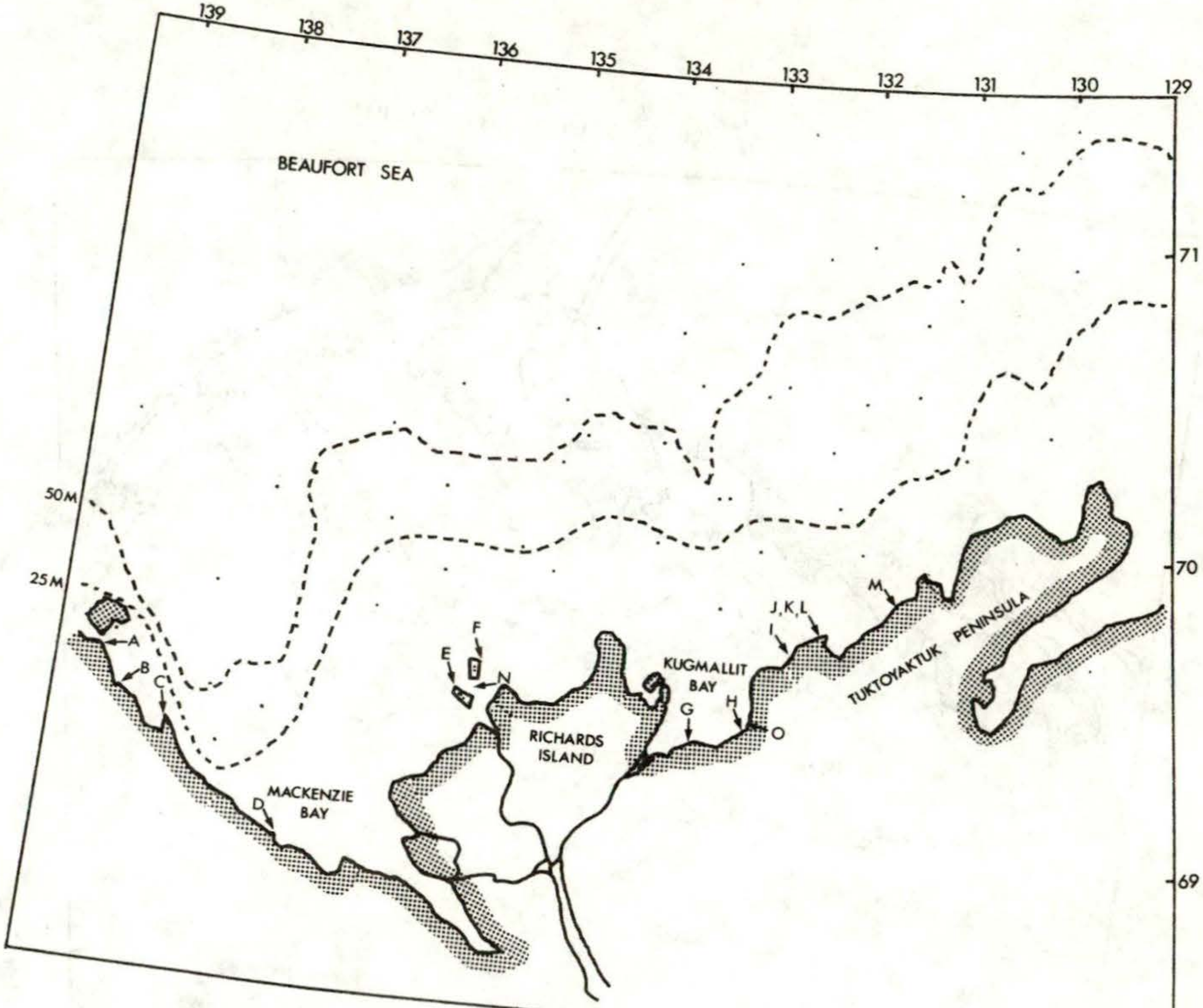


Figure 5. Station Locations for Nearshore Sediment Samples.

## 5. METHODS AND SOURCES OF DATA

### 5.1 Cruises

Sampling for hydrocarbon studies in the marine environment of the Southern Beaufort Sea during August 1974 was carried out from the charter M. V. THETA. The ship was loaded during the week of June 22 and left for Beaufort Sea June 28. However, because of heavy ice conditions, the THETA did not arrive in the sampling area until August 8. Ocean Chemistry personnel joinedthe ship on August 9 from Stokes Point and sampling was conducted August 11 to September 1. In 1975, sampling and shipboard analysis for hydrocarbon studies were conducted from the charter M. V. PANDORA II. Loading was done in Victoria in early July and the ship arrived in the sampling area as late as August 2, due to delay by heavy ice. Ocean Chemistry personnel joined the ship on August 2 from Stokes Point, and equipment preparations for chemical measurements and sampling were ready by August 4. Due to time constraints and rough seas, only six stations were occupied in the first leg. A north-west gale forced the ship to seek shelter in the lee of Herschel Island August 9-11 and had pushed the ice-field into Mackenzie Bay to as far south as 69°15'N. The remaining Ocean Chemistry personnel joined the ship on August 11 from Stokes Point for the second leg. The Eastern Mackenzie Bay and shelf waters off the Tuktoyaktuk Peninsula were ice-free and sampling at a series of 38 stations from August 12-21 was conducted in a zig-zag pattern between the 15 m. contour line and the ice edge at approximately the 70-80 m. depth contour. A time-series station was occupied August 23-24 about 45 miles north of Tuktoyaktuk. Chemical studies were completed on August 25. Due to a heavy ice field blocking the western passage, the M. V. PANDORA II had to return via the ice-free eastern passage in mid-September through M'Clintock Channel, Franklin Strait and Gulf of Boothia. The ship reached Halifax on October 13 and later Victoria via the Panama Canal on November 24. Thus, the 1975 samples had to be kept for an extra three months of storage on board.

### 5.2 Sampling and Storage

In 1974, heavy ice conditions throughout the summer had limited the sampling to Mackenzie Bay and a narrow stretch of water along the Tuktoyaktuk Peninsula between Herschel Island and Atkinson Point. The stations with hydrocarbon sampling are shown in Table 2.

In 1975, a heavy ice field was mainly on the Alaskan side of the Southern Beaufort Sea leaving the Eastern Mackenzie Bay and shelf water off the Tuktoyaktuk Peninsula relatively ice-free.

TABLE 2. 1974 Cruise Observations Listing (Southern Beaufort Sea)

Observation Code:
T - Temperature
S - Salinity
$O_2$ - Diss. Oxygen
A - Alkalinity
Sed - Sediment
N - Nutrients
HC - Hydrocarbon Sampling
NT - Net Tow

| STATION | DATE(GHT) | LOCATION | | SONIC DEPTH(Meters) | OBSERVATIONS |
|---|---|---|---|---|---|
| | | N | W | | |
| | 11/8/74 | 69°44' | 138°40' | | HC - 9 Surface Samples |
| 1 | 12/8/74 | 69°40'38" | 137°11'19" | 48 | T,S,$O_2$,N,A,HC,Sed |
| 2 | 13/8/74 | 70°07'15" | 134°37'07" | 30 | T,S,$O_2$,N,A,HC,Sed |
| 7 | 14/8/74 | 70°07'12" | 134°20'44" | 30 | T,S,$O_2$,N,A,HC |
| 11<br>+time series<br>25 hour | 16/8-17/8/74 | 69°36' | 137°41'00" | 64 | T,S,$O_2$,N,A,HC,Sed |
| 12 | 18/8/74 | 69°51'19" | 137°41'10" | 81 | NT,Sed |
| 13 | 18/8/74 | 69°48'35" | 138°23'09" | 191 | T,S,$O_2$,N,A,Sed |
| 17 | 19/8/74 | 69°26'11" | 138°09'32" | 66 | Sed |
| 19 | 19/8/74 | 69°18'28" | 138°05'25" | 42 | T,S,N,A,Sed,HC |
| 20 | 21/8/74 | 69°26'42" | 138°48'54" | 70 | T,S,$O_2$,N,A,Sed, HC |
| 23 | 22/8/74 | 69°30'53" | 138°37'59" | 15 | T,S,$O_2$,N,A,Sed,HC |
| 24 | 22/8/74 | 69°28'10" | 138°18'20" | 70 | HC |
| 25 | 23/8/74 | 69°28'34" | 138°00'12" | 65 | T,S,$O_2$,N,A,Sed,HC |
| 27 | 23/8/74 | 69°30'09" | 138°28'19" | 47 | HC |
| 28 | 23/8/74 | 69°29'29" | 137°10'17" | 43 | T,S,$O_2$,N,A,Sed |
| 30 | 23/8/74 | 69°33'32" | 136°50'16" | 9 | HC |
| 32 | 23/8/74 | 69°24'21" | 136°53'25" | 8 | HC |
| 35 | 23/8/74 | 69°18'19" | 137°01'10" | 7 | HC,Sed |
| 36 | 23/8/74 | 69°18'08" | 137°10'34" | 9 | T,S,N,$O_2$,A |
| 37 | 23/8/74 | 69°12'26" | 137°32'19" | 31 | HC |
| 38 | 24/8/74 | 69°18'00" | 137°53'32" | 35 | T,S,$O_2$,N,A |

Table 2 (cont'd)

| STATION | DATE(GHT) | LOCATION N | LOCATION W | SONIC DEPTH(Meters) | OBSERVATIONS |
|---|---|---|---|---|---|
| 39 | 24/8/74 | 69°18'10" | 138°14'16" | 35 | HC,NT |
| 41 | 25/8/74 | 69°49'13" | 135°00'05" | 11 | T,S,$O_2$,N,A,Sed |
| 42 | 25/8/74 | 69°57'10" | 134°59'31" | 19 | T,S,$O_2$,N,A,Sed,HC |
| 43 | 26/8/74 | 70°00'16" | 132°55'02" | 24 | T,S,$O_2$,N,A |
| 44 | 26/8/74 | 69°58'14" | 132°01'34" | 13 | T,S,$O_2$,N,A,HC,Sed |
| 46 | 26/8/74 | 70°12'00" | 131°41'47" | 22 | T,S,$O_2$,N,A |
| 47 | 26/8/74 | 70°19'25" | 131°41'22" | 31 | HC |
| 48 | 27/8/74 | 70°26'32" | 131°41'29" | 33 | T,S,$O_2$,N,A,Sed |
| 49 | 27/8/74 | 70°30'54" | 131°43'40" | 37 | HC |
| 51 | 27/8/74 | 70°24'31" | 131°40'53" | 35 | T,S,$O_2$,N,A,HC |
| 54 | 29/8/74 | 70°09'09" | 134°51'26" | 51 | T,S,$O_2$,N,A,Sed |
| 55 | 30/8/74 | 70°06'46" | 135°29'21" | 42 | T,S,$O_2$,N |
| 56 | 30/8/74 | 69°56'14" | 135°47'51" | 20 | T,S,$O_2$,N,A |
| 57 | 30/8/74 | 70°31'28" | 137°35'41" | 57 | T,S,$O_2$,N,A |
| 60 | 1/9/74 | 70°05'33" | 139°08'03" | 205 | T,S,$O_2$,N,A |

Forty-four stations were occupied with a total of 57 sea water samples for LMW hydrocarbons, 36 sea water samples for PAH, 22 surface sediment samples by pipe dredge, 37 Miller net tows for hydrocarbon levels in planktons, and 18 surface Neuston net tows for tar and other particulate pollutants. The detailed listing of stations with hydrocarbon sampling is shown in Table 3.

### 5.2.1 Sea water

Sea water for aromatic and polycyclic hydrocarbons was collected with a 5-liter Blumer sampler (Clark, Jr. et al., 1967), which consisted of an aluminium pressure case with an evacuated glass liner and a valve activated by pressure supplied by a tank of nitrogen on board as shown in Figure 6. The glass liners were pre-cleaned in a shore laboratory with rinses of hydrocarbon-free methanol and methylene chloride and fitted with pre-cleaned ground glass stoppers. Excess solvent was drained from the glass liners just before being inserted into the aluminium casing; then it was capped and tightened to 130 inch-lbs with a torque wrench. The sampler was then evacuated for three to five minutes, closed at the activated valve, and connected through an 1/8" nylon tubing to a cyliner of nitrogen. After lowering to the desired depth, the valve was activated by 125 psi pressure from a pressurized nitrogen cylinder to fill the evacuated glass liner with sea water for about five minutes. On raising the sampler to the surface, the expansion of sea water collected at greater depth and the very narrow inlet tubing prevented possible contamination of the sample by waters at shallower depths. The glass insert with the full sea water sample was immediately plugged with a ground-glass stopper after opening the pressure casing. The sea water sample was then poisoned with about 35 mg of mercuric chloride to prevent biological degradation and stored in the dark inside a wooden box lined with insulation. In 1974, the storage temperature on the ship was generally at 2-4°C and never exceeded 9°C. In 1975, the samples were stored in a refrigerator at 4°C. on board. After unloading in Victoria, the samples for both years were stored in a cold room at 4°C prior to chemical analysis, usually two to four months after collection.

Sea water samples at all depths for LMW hydrocarbons were collected by a Blumer sampler in the same way as described. However, a set of glass liners were used specifically for the LMW gases and all samples were processed immediately within a few minutes of sampling.

In 1974, surface grab samples for aromatic hydrocarbons were also taken using a solvent-washed stainless steel bucket suspended from a nylon line cast off the bow of the ship.

## TABLE 3

### 1975 Cruise Observations Listing (Southern Beaufort Sea)

Observation Code:
T - Temperature
S - Salinity
$O_2$ - Diss. Oxygen
A - Alkalinity
Sed - Sediment
N - Nutrients
HC - Hydrocarbon Sampling
NT - Net Tow
PSi - Particulate Silicate
PTr - Particulate Trace Metal
V - Vanadium
cc - Particle size analysis (Coulter Counter)

| Station | Date (GMT) | Location | | Sonic Depth (Meters) | Observations |
|---|---|---|---|---|---|
| 1 | Aug. 5 | 70°15' N | 139°04' W | 461 | T, S, $O_2$, A |
| 2 | Aug. 5 | 70°41' N | 134°45' W | 55 | T, S, A, PSi |
| 3 | Aug. 6 | 69°57' N | 135°16' W | 33 | T, S, $O_2$, A, PSi, HC |
| 4 | Aug. 7 | 70°57' N | 132°29' W | 64 | T, S, $O_2$, A, PSi, HC |
| 5 | Aug. 8 | 71°19' N | 130°35' W | 72 | T, S, $O_2$, A, HC |
| 6 | Aug. 8 | 70° 9' N | 132°15' W | 30 | T, S, $O_2$, A, PSi, PTr, HC |
| 7 | Aug. 9 | 69°34' N | 138°55' W | 9 | T, S, $O_2$, A, PSi, PTr, HC |
| 8 | Aug. 12 | 69°22' N | 137°30' W | 20 | T, S, $O_2$, A, PSi, PTr, HC, NT, cc |
| 9 | Aug. 13 | 70°03' N | 137°41' W | 83 | T, S, $O_2$, A, PSi, PTr, NT, HC, cc |

TABLE 3 (Cont'd)

| Station | Date (GMT) | Location | | Sonic Depth (Meters) | Observations |
|---|---|---|---|---|---|
| 10 | Aug. 13 | 70°07' N | 137°20' W | 49 | |
| 11 | Aug. 13 | 69°52' N | 136°00' W | 17 | T, S, $O_2$, A, PSi, PTr, NT, HC, cc |
| 12 | Aug. 13 | 70°08' N | 136°03' W | 40 | T, S, A |
| 13 | Aug. 13 | 70°27' N | 134°59' W | 50 | T, S, $O_2$, A, PSi, PTr, NT, HC, cc |
| 14 | Aug. 14 | 70°20' N | 134°45' W | 45 | A |
| 15 | Aug. 14 | 70°01' N | 134°00' W | 20 | T, S, $O_2$, PSi, PTr, NT, HC, Sed, cc |
| 16 | Aug. 14 | 70°20' N | 134°00' W | 48 | T, S, $O_2$, A, cc |
| 17 | Aug. 15 | 70°41' N | 133°53' W | 64 | T, S, A, Psi, PTr, NT, HC, Sed, cc |
| 18 | Aug. 15 | 70°31' N | 133°40' W | 65 | T, S, A |
| 19 | Aug. 15 | 70°10' N | 133°20' W | 25 | T, S, A |
| 20 | Aug. 15 | 70°00' N | 133°00' W | 14 | T, S, A, $O_2$ PSi, PTr, NT, HC, cc, Sed |
| 21 | Aug. 15 | 70°30' N | 133°00' W | 40 | T, S, $O_2$ A, cc |
| 22 | Aug. 16 | 70°55' N | 133°22' W | 70 | T, S, $O_2$, A, PSi, PTr, NT, HC, Sed, cc |
| 23 | Aug. 16 | 70°32' N | 132°49' W | 45 | T, S, A |

TABLE 3 (Cont'd)

| Station | Date (GMT) | Location | | Sonic Depth (Meters) | Observations |
|---|---|---|---|---|---|
| 24 | Aug. 16 | 70°20' N | 132°20' W | 25 | T, S, A |
| 25 | Aug. 16 | 70°01' N | 132°00' W | 15 | T, S, $O_2$, A, PSi, PTr, NT, HC, Sed, cc |
| 26 | Aug. 16 | 70°29' N | 132°02' W | 35 | T, S, $O_2$, A, cc |
| 27 | Aug. 17 | 71°00' N | 132°03' W | 65 | T, S, $O_2$, A, PSi, PTr, HC, NT, Sed, cc |
| 28 | Aug. 17 | 70°45' N | 131°28' W | 48 | T, S, A |
| 29 | Aug. 17 | 70°31' N | 131°31' W | 38 | T, S, A |
| 30 | Aug. 17 | 70°19' N | 131°01' W | 18 | T, S, $O_2$, A, PSi, PTr, NT, HC, Sed, cc |
| 31 | Aug. 17 | 70°50' N | 131°09' W | 50 | T, S, $O_2$, A, HC, cc |
| 32 | Aug. 18 | 71°11' W | 131°11' W | 80 | T, S, $O_2$, A, PSi, PTr, NT, HC, Sed, cc |
| 33 | Aug. 18 | 71°01' N | 130°36' W | 45 | T, S, A |
| 34 | Aug. 18 | 70°24' N | 130°13' W | 18 | T, S, $O_2$, A, PSi, PTr, NT, HC, Sed, cc |
| 35 | Aug. 18 | 70°56' N | 129°59' W | 35 | T, S, $O_2$, A, HC, cc |
| 36 | Aug. 19 | 71°23' N | 130°01' W | 73 | T, S, $O_2$, A, PSi, PTr, NT, HC, Sed, cc |
| 37 | Aug. 19 | 69°49' N | 133°21' W | 10 | T, S, $O_2$, A, PSi, PTr, HC, Sed, cc |

TABLE 3 (Cont'd)

| Station | Date (GMT) | Location | | Sonic Depth (Meters) | Observations |
|---|---|---|---|---|---|
| 38 | Aug. 20 | 69°54' N | 134°58' W | 14 | T, S, $O_2$, A, PSi, PTr, NT, HC, Sed, cc |
| 39 | Aug. 20 | 70°14' N | 134°58' W | 45 | T, S, $O_2$, A. |
| 40 | Aug. 20 | 70°27' N | 136°00' W | 58 | T, S, $O_2$, A, PSi, PTr, HC, cc |
| 41 | Aug. 20 | 70°19' N | 136°38' W | 60 | T, S, $O_2$, A, PSi, PTr, NT, HC, Sed, cc |
| 42 | Aug. 20 | 70°01' N | 136°33' W | 30 | T, S, $O_2$, S, cc |
| 43 | Aug. 21 | 69°44' N | 136°36' W | 15 | T, S, $O_2$, PSi, PTr, NT, HC, Sed cc |
| 44 | Aug. 21 | 69°38' N | 137°19' W | 48 | T, S, $O_2$, Sed |
| 45 | Aug. 21 | 69°45' N | 138°07' W | 155 | T, S, $O_2$, A, PSi, PTr, HC, Sed, cc, V |
| 46 | Aug. 21 | 69°25' N | 138°04' W | 65 | T, S, $O_2$, Sed, cc |
| 47 | Aug. 21 | 69°38' N | 137°49' W | 27 | T, S, $O_2$, PSi, PTr, HC, NT, Sed, V, cc |
| 48 | Aug. 23 | 70°10' N | 133°25' W | 27 | T, S, $O_2$, HC, cc |

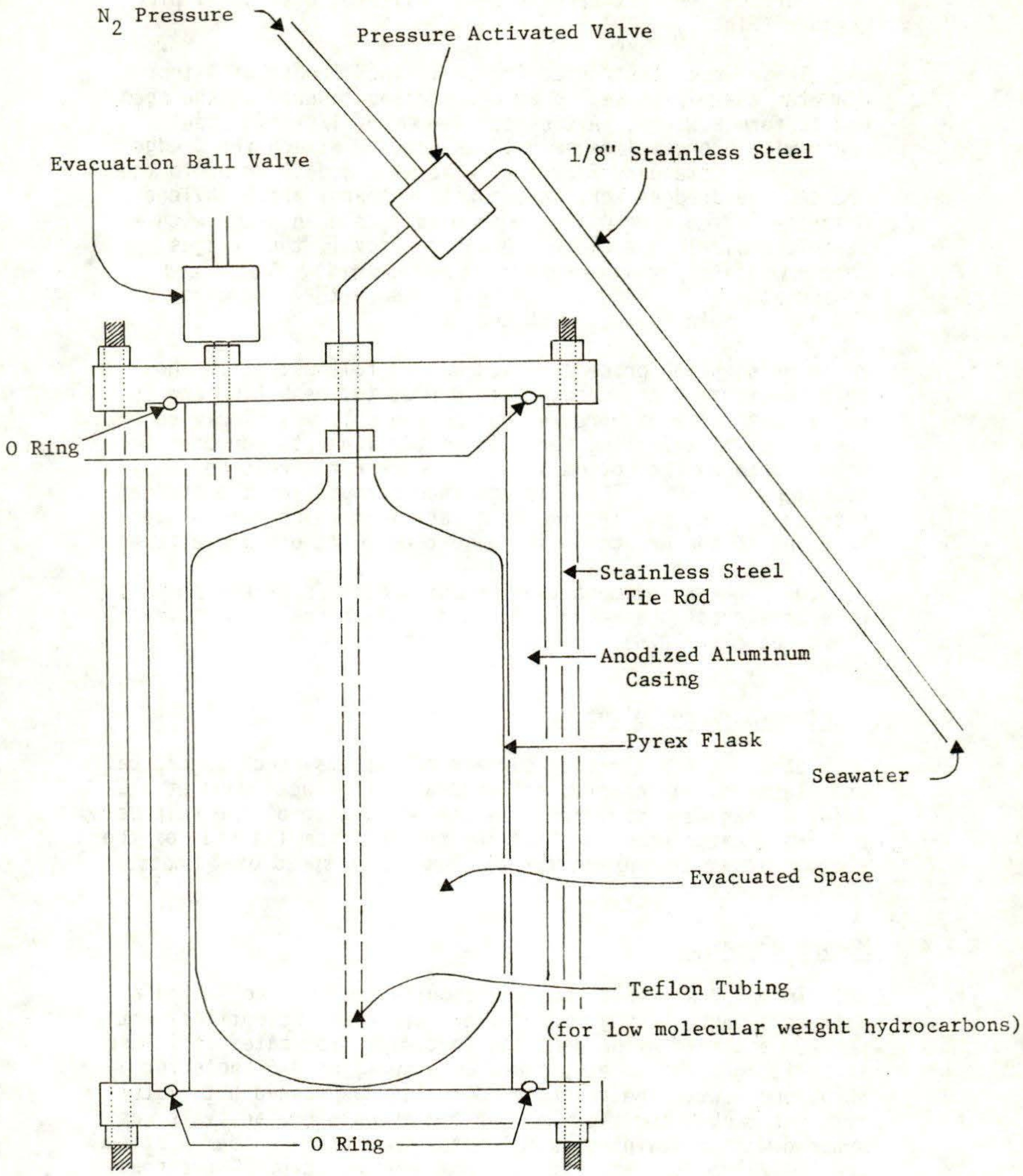


Figure 6 The Blumer Contaminant-Free Sampler

### 5.2.2 Sediments

Surface sediment samples were collected with steel pipe dredges (Fig. 7).

These were constructed from a 12-inch length of 4-inch diameter steel pipe sealed at one end and tapered at the open end to form a scoop. A two-foot length of 1/4-inch steel chain with a greaseless swivel was used to attach the dredge to the wire (standard 5/32-inch wire was used). Prior to the cruise, the dredges were washed with methanol and methylene chloride and covered with aluminum foil held in place with a stainless steel hose clamp. After retrieval, the dredges were immediately re-covered with aluminum foil, frozen and stored at -55°C. Care was taken to ensure that the dredges did not come in contact with the ship.

The sampling procedure used was as follows: with the ship stationary, the dredge was lowered to the bottom and an extra 10 to 15 m of wire let out as the ship was slowly edged forward. While feeling for tugs on the line, the dredge was dragged on the bottom until the wire angle reached approximately 50°. The ship was than stopped and the dredge retrieved. In some instances, a cast iron weight was placed in front of the dredge to increase the amount of sample taken.

Open beach sediment samples and benthic sediment samples were collected as already described in Technical Report No. 13 (Wong, et al., 1976).

### 5.2.3 Floating Surface Pollutants

Sampling for floating surface pollutants, such as tar balls and plastics, was carried out with a Neuston net (Wong et al., 1974). Tows were made from the starboard side of the ship using a forward cargo boom to place the net out from the side of the ship which towed the net for one hour at a speed of 4 knots.

### 5.2.4 Marine Organisms

In 1975, phytoplankton and zooplankton were collected at different depths using four Miller nets (Kahl Scientific) with No. 20 mesh size nylon nets and specially fabricated stainless steel (24 gauge) buckets, towed at a speed of 4-5 knots for about one hour. The plankton collected was washed with water into the bucket and the plankton for hydrocarbon analysis was spooned with a stainless steel spoon into a pre-washed aluminum can (3-1/2" o.d. x 2") with a tight aluminum cap. The capped aluminum can was stored frozen immediately. Some plankton was preserved in formaldehyde for biological identification.

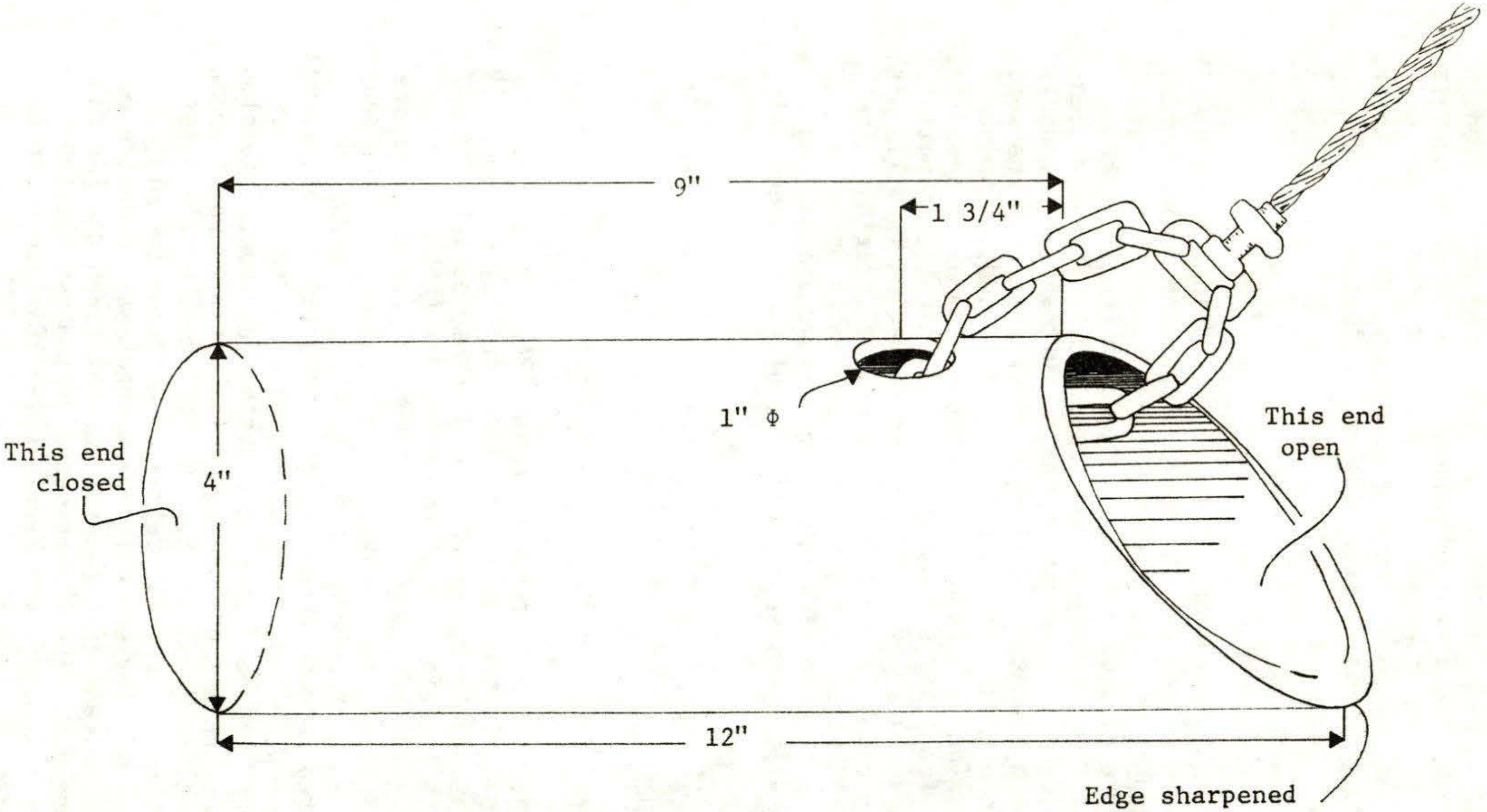


Figure 7. <u>Pipe Dredge Design</u>

The sampling equipments and containers were pre-cleaned prior to the cruise. The nylon nets were repeatedly soaked in distilled ethanol to remove hydrocarbon impurities. The buckets and fiberglass tows were washed with detergent, rinsed with distilled water and finally with distilled ethanol. The plankton buckets were given a final rinse with re-distilled methylene chloride. Aluminum cans were cleaned with soap and water, distilled water, redistilled methanol and finally methylene chloride.

### 5.2.5 Fish

Due to logistics problems, fish collected in the beach walk program had to be preserved with hydrocarbon-free formaldehyde, which had been previously extracted with redistilled hexane. Fish samples were also obtained by Dr. Roger Percy of the Freshwater Institute, Winnipeg, Manitoba. These fish had been frozen in the ice off Pt. Atkinson on the Tuktoyaktuk Peninsula. They were chipped from the ice shortly after freeze-up and kept frozen first in a plastic bag and then in individual aluminum foil wrappers. The fish samples remained frozen after sampling, in transit and for storage. Based on pathological examination, the most probable cause of death was ice formation in gills with death occurring about 12 hours before complete freezing. The samples had to be stored for at least four months prior to laboratory analysis. The foil in use contained about 75 ng polycyclic aromatic hydrocarbons per gram of the aluminum foil.

## 5.3 ANALYTICAL METHODS

### 5.3.1 Polycyclic Aromatic Hydrocarbons in Sea Water

The polycyclic aromatic hydrocarbons (PAH) in sea water were measured by a fluorescence technique (Cretney and Wong, 1974) using a combination of high speed liquid chromatograph with fluorescence or ultraviolet spectrophotometers (HSLC-FS, or HSLC-UVS). In 1974, the samples were brought back to the shore-laboratory in Victoria for analysis. In 1975, most of the samples were processed in a shipboard clean laboratory as shown in Figure 2. To separate suspended particulates (>0.5 μm) 4 litres of sea water in batches was centrifuged at $5^0$ using a Sorvall RC5 centrifuge with a GS-3 rotor and custom-fabricated stainless steel buckets. Centrifuged sea water (1.8 litres) was siphoned off into a pre-cleaned 2 litre separating funnel with a glass stopper and was extracted with methylene chloride (90 ml) in two portions. The methylene chloride extract was concentrated by removing the solvent in a rotary evaporator and the PAH was taken by cyclohexane. The fluorescence of the cyclohexane extract was determined using a Perkin-Elmer 204 fluorescence spectrophotometer.

Some methylene chloride extracts were brought back to Victoria for analysis. These extracts were kept in glass ampoules sealed with glass stoppers with teflon sleeves for transportation. In the shore clean-laboratory, the methylene chloride was removed and the residue redissolved in hexane. The hexane solution was analyzed using a combined HPLC-FS detection in two ways: (i) directly and (ii) passing the solution through a chromatographic column containing 5 μm silica gel (LiChrosorb Si-60, E. Merck Co.) In 1974, the preserved sea water samples were analyzed in the Victoria shore-laboratory using the same extraction and analytical techniques.

The suspended matter in the 1974 samples was allowed to settle while the samples were stored in the dark at $5^{0}C$. Sea water was siphoned off and the suspended particulates were extracted for PAH as above and analyzed with the silica gel column in the HPLC-FS system. In 1975, some of the centrifuged suspended matter was solvent-extracted immediately in the shipboard cleanroom as described, and the unprocessed samples and extracts were brought back to Victoria.

Chrysene was used as an external standard and the fluorescence responses of both the standard and the environmental samples were measured using an excitation wavelength of 308 nm and an emission wavelength of 383 nm. The analytical results were expressed as equivalent of chrysene. In this report, those fluorescent compounds which are present in sea water can be extracted with methylene chloride and have retention times on silica gel which are characteristic of 2- to 6-ring PAH and are designated as PAH. Validation of this designation must await further study with more sophisticated instrumentation and techniques, however. Those fluorescent compounds, including PAH, which are present in sea water and can be extracted with methylene chloride are referred to as fluorescent extractable compound or simply fluorescent extractables. This emphasis is necessary to make a distinction between fluorescence values obtained without prior elution of the solvent extract through silica gel and those obtained with prior elution of the solvent through silica gel to remove possible fluorescing material having polar functional groups (-OH, -COOH, =O etc.).

### 5.3.2 Polycyclic Aromatic Hydrocarbons in Nearshore Sediments

Thirteen open beach sediment samples and two benthic sediment samples collected along the Beaufort Sea Coasts were analyzed for polycyclic aromatic hydrocarbons using a modification of the method of Blumer and Giger (1974).

### 5.3.2.1 Modified Extraction Techniques of PAH

Wet sediments (110-205 g) were Soxhlet-extracted for 24 hours with 275 ml methanol, and for a further 24 hours with 75 ml benzene added. The extract was partitioned into n-pentane (125 ml, 3 x 75 ml) and washed with distilled water (2 x 250 ml). The solution was evaporated to dryness and the concentrate taken up in 2 ml benzene-pentane (1:1). This was applied to a copper column and eluted with a further 20 ml of that solvent (Blumer, 1957). The eluate was evaporated to dryness, taken up in 2 ml benzene-methanol (1:1) and applied to a Sephadex LH-20 column (1.6-cm i.d., 38-cm bed height). Elution with benzene-methanol was carried out at a flow rate of 6 ml/min, nitrogen (L grade) being used to maintain that flow. The first 50 ml of eluate were discarded, the second 50 ml collected and evaporated to dryness. The column was washed with 150 ml benzene-methanol and repacked after four runs. The concentrate in 1 ml n-pentane was applied to a column (1.2-cm i.d., alumina over silica gel, both 4 ml, deactivated with 3% water). The sample was eluted with 20 ml n-pentane, and the eluate discarded. The flask containing the concentrate was then washed with 2 ml methylene chloride. This was applied to the column along with 13 ml of the same solvent. The eluate was retained and evaporated to dryness. Trinitrofluorenone was added to the concentrate ( 2 mg for open beach sediments, 5 mg for benthic sediments) in 2 ml n-pentane. The solvent and a further four washings (2 ml each were pipetted off and discarded. Dowex 1-X2 (100-200 mesh) anion exchange resin was converted from chloride to sulphite ionic form by washing with sodium sulphite. The resin was washed with distilled water followed by methanol, and the Soxhlet-extracted for 36 hours in benzene-methanol (1:1). A column was packed in that solvent (1.2 cm i.d., 2 ml for open beach sediments, 5 ml for benthic sediments). The complexed material and excess TNF were applied to the column in 2 ml benzene-methanol (1:1) and eluted with 50 ml of that solvent. The sample was evaporated to dryness. The sample was taken up in 0.5 ml methylene chloride-pentane (1:4). A small portion (4-8%) was transferred to a Cahn electrobalance and weighed. The remainder of the sample was applied to an alumina column (0.6-cm i.d., 5 ml, deactivated with 1% water). The sample was eluted with 90 ml of 4% methylene chloride in pentane followed by 50 ml of 15% methylene chloride in pentane. Seven fractions were collected (cutpoints and column efficiency shown in Table 4). The fractions were adjusted to 25 ml and analyzed with a Beckman Acta II UV spectrophotometer (10-cm silica cell).

### 5.3.2.2 Recoveries of Ion Exchange Resin Columns

The resin has a styrene-divinylbenzene polymer lattice with quaternary ammonia exchange groups attached. It will partially degrade in the presence of sulphur-containing reducing agents

## TABLE 4

Alumina Column: Percentage of Standard Eluted in Each Fraction

| | I<br>0-10 ml | II<br>10-25 | III<br>25-75 | IV<br>75-100 | V<br>100-105 | VI<br>105-115 | VII<br>115-140 | |
|---|---|---|---|---|---|---|---|---|
| Phenanthrene | | 92 | 8 | | | | | |
| Anthracene | | | 100 | | | | | |
| Fluoranthene | | | 100 | | | | | |
| Pyrene | | 2 | 98 | | | | | |
| Benz(a)anthracene | | | | 100 | | | | |
| Chrysene | | | | 99 | 1 | | | |
| Perylene | | | | 10 | 82 | 8 | | |
| Benzo(a)pyrene | | | | 5 | 73 | 22 | | |
| Benzo(ghi)perylene | | | | | 2 | 91 | 7 | |
| Coronene | | | | | | 6 | 94 | |

and should therefore be prepared just prior to use. An analysis of benzene-methanol run through the column should be performed to ensure that no UV absorbing impurities are extracted.

Recoveries for five standards are shown to be 91-95% as in Table 5. Three analyses were run for each standard. TNF was added in a weight ration of 10:1 to the standards.

#### 5.3.2.3 Procedure Blank

Two methanol-benzene blanks were run through the entire procedure. No UV absorbance was detected.

#### 5.3.2.4 Recovery of the Modified Procedure

Three methanol-benzene blanks with five reference standards added were run through the entire procedure. Recoveries of the standards are given in Table 6. Recoveries were in all cases lower than those reported by Blumer and Giger. This can be accounted for by the large number of solvent evaporations involved in the method and use of a less efficient rotary evaporator than was employed by those authors.

### 5.3.3 PAH in Marine Organisms and Sediments

#### 5.3.3.1 Materials

Commercially available glass distilled iso-octane benzene and pentane were used without further purification. A purity check, however, was conducted on each new bottle prior to use and these solvents were redistilled if necessary. Ethanol was distilled three times in an all glass still or until adequately pure. Methanol and acetone were distilled once. Water was distilled from tap water in a Barnsted still and collected directly in glass bottles through a glass tube. Spectrograde carbon disulfide was used directly from the bottle. Potassium hydroxide (reagent grade, Fisher P-250) was extracted with benzene for three to four hours in a soxhlet apparatus and dried at 90°C for four hours. Sodium sulfate (Mallinkrodt, AR grade) was treated as the potassium hydroxide, but was heated at 600°C for an additional seven hours.

Florisil (60-100 mesh, Matheson, Coleman & Bell) was washed twice with methanol, dried at 90°C in a forced air oven for 20 hours and heated at 600°C for six or more hours. The florisil was allowed to cool, washed twice again with methanol and heated at 90°C for 20 hours in a vacuum dessicator under reduced pressure (25" of ltg). This procedure provided florisil of relatively constant activity from batch to batch. Of greater importance,

## TABLE 5

## Recovery of Standards Through Resin Column

| Compound | Present μg | Found μg | Recovery % | Standard Deviation % |
|---|---|---|---|---|
| Phenanthrene | 8.94 | 8.48 | 95 | 0.6 |
| Pyrene | 1.97 | 1.82 | 92 | 0.9 |
| Benzo[a] pyrene | 1.74 | 1.63 | 94 | 3.3 |
| Perylene | 1.87 | 1.76 | 94 | 3.9 |
| Coronene | 2.01 | 1.83 | 91 | 0.8 |

## TABLE 6

## Recovery of Standards Through Entire Procedure

| Compound | Present μg | Found μg | Recovery % | Standard Deviation % |
|---|---|---|---|---|
| Phenanthrene | 3.60 | 0.41 | 11 | 6 |
| Pyrene | 4.42 | 1.87 | 42 | 22 |
| Benzo[a] pyrene | 4.24 | 2.56 | 60 | 16 |
| Perylene | 3.32 | 1.88 | 57 | 15 |
| Coronene | 3.16 | 1.63 | 52 | 16 |

moreover, the florisil obtained gave maximal recoveries of standard PAH, particularly perylene.

### 5.3.3.2 Sample Preparation

The fish samples were either preserved in hydrocarbon-free formaldehyde and frozen or a frozen state and wrapped in aluminum foil. Each fish was defrosted and the fresh part separated for analysis. Organics in the fish samples were found to be leached out by formaldehyde.

The sediment sample, contained in the pipe dredge, was stored frozen immediately after collection. Sediment samples for chemical analysis were sub-sampled as follows. In 1974, the sub-samples were taken from completely thawed sediments in the dredge originally stored at -55°C. In 1975, the sub-samples were taken from the frozen dredge material at -55°C by use of a previously solvent-cleaned hand-drill and ice bit. The drillings were caught on aluminum foil and kept frozen until analysis.

### 5.3.3.3 Sample Extraction and Separation of Non-polar Hydrocarbons from PAH

Both the sediments and the organisms (fish and plankton) were extracted using essentially the same procedure. Organism samples (generally 20-40 g) were digested at reflux temperature in a solution of potassium hydroxide (7 g) in 95% ethanol (150 ml) to which had been added an aliquot of standard containing dotriacontane or hexatriacontane and perdeuterated phenanthrene, pyrene, chysene, 1,2 benzanthracene and perylene. Wet sediments (10-20 g) were treated in the same fashion. For the GC/MS analysis of PAH, however, it was found best to use larger amounts (about 90 g) of sediment with the amount of deuterated standard adjusted proportionally. Near the end of the reflux period, 150 ml of water was added to the mixture. In the case of an organism sample, if it did not appear to be completely digested, an additional 7 g of potasium hydroxide was added and the digestion carried on for a further 45 minutes. The hot organism digest was transferred to a separatory funnel by decanting the liquid and rinsing the flask with ethanol (2 x 25 ml) and iso-octane (2 x 100 ml). In the case of a sediment sample, the hot liquid phase was decanted into a separatory funnel after a brief period to allow the solid phase to settle. The solid material was then washed with vigorous agitation with ethanol (2 x 25 ml) and iso-octane (2 x 100 ml) and the washings were combined with the liquid phase. The hydrocarbons were partitioned into the iso-octane with vigorous shaking. Following a second partioning using a second 200 ml portion of iso-octane, the combined iso-octane extracts were washed with distilled water (3 x 150-200 ml). Emulsions, which formed with some sediment extracts, were broken satisfactorily by swirling and partial emmersion of the separatory funnel in an ultrasonic bath. The iso-octane extract was concentrated at 40°C on a rotary evaporator to less than 1 ml. The concentrate was applied with the aid of hexane: iso-octane (1:1, 2 x 5 ml) to a column (4 cm i.d.) of anhydrous sodium sulfate (60 g) over florisil (30 g). Elution with hexane: iso-octane (1:1, 90-120 ml) provided a fraction containing the non-polar hydrocarbons. Elution with benzene (about 120 ml) provided a fraction containing the PAH. The amount of eluant used varied with the activity of each batch of florisil. Exact cut points were determined using a standard mixture of n-paraffins and PAH. The fraction containing the non-polar hydrocarbons was evaporated down and taken up in carbon disulfide for injection in the GC. Similarly, the fraction containing the PAH was evaporated down and taken up in benzene for injection into the GC-MS.

#### 5.3.3.4 GC-MS Analysis of the PAH

Two types of GC-MS (Gas chromatograph-Mass spectrometer) analyses were employed using a Finnigan 3300 E GC-MS system: the ion-integration method and the programmable multiple-ion monitor (PROMIN) technique. The first method permits particular mass scan to be taken at various times during the GC temperature programming. The ion-integration trace is obtained by integrating all the fragmentation peaks between particular masses, very similar in principle to a normal GC FID trace.

The second method, more sensitive than the first one, employs a programmable multiple ion monitor which allows constant monitoring of specific masses throughout the run. The analytical technique has been developed in the Ocean Chemistry Division using a combination of this PROMIN technique and an isotopic dilution concept. A known amount of an isotopic species of the element or compound under consideration is used as a standard and the amount of the isotopic species is then physically compared to that of the indigenous species. The amount of the indigenous species is thus calculable. For PAH analyses, the compound added as a standard is a fully deuterated analogue of the PAH being studied. The PROMIN is set to the values of the deuterated and non-deuterated species and these masses monitored throughout the GC run(Fig.8 & 9). The amounts of deuterated and non-deuterated species at the appropriate retention times are then compared.

This method has an inherent advantage over most other methods of PAH determination in that it compares the amount of any specific compound to an internal standard of that same compound. The standard is added at the beginning of the sample preparation and any losses of compound should be the same for the deuterated and non-deuterated. This eliminates difficulties due to preferential loss through workup of one component compared to another. It also removes all discrepancies due to differences in the response to the analysis method between the compound being analyzed and the standard. Such difficulties arise in fluorescence, UV and GC determination where the response is obtained as the equivalent response of a specifiable amount of standard. In these methods, no correction is usually made for response differences. By GC-MS PROMIN isotope dilution all response and loss differences are accountable for and thus the values of any given compound reported are the actual values of that compound.

Certain assumptions that need to be made for successful practical application of the above method were confirmed. The retention time of the deuterated PAH was found to be the same. A large amount of one isotopic species does not cause a peak of the other species, which would be due to localized pressure changes in the source, of more than 0.25% of its own height. For the values used in practice, this effect is neglible. This result also helped to substantiate that the observed peaks are not being appreciably affected by a pressure carry-through by large amounts of other compounds. This is important since some of the samples have a large number of extraneous compounds in the working faction.

Originally, problems were experienced due to the ion integrator sensitivity being affected by column bleed-off in the OV-7 column. This was largely eliminated by replacement by a dexsil 300 column on a silanized support. Dexsil 300 has a lower vapor pressure than OV-7 and silanization tended to reduce tailing. However, on this column the added standards chrysene and benzanthracene could not be separated and so for calculation purposes their amounts are considered additive.

In a quadrupole mass spectrometer, the fragmentation envelope can be set via focusing. This is not true for a magnetic instrument where it is always constant. To reduce any difficulties arising from this, ionization was effected at 15 ev which gives least fragmentation and thus an abundance of molecular ion, and the machine was standardized daily for optimization of the $219^+$ peak of FC-43 (perfluorotributylamine). The fragmentation pattern becomes relatively constant via this latter procedure with the maximum of the envelope being set in the mass range of the molecular ions of the compounds being studied.

One problem that is still causing some difficulty is that sample preparation via the existing procedure tends to give compounds that have peaks at the masses being studied for PAH. In some samples this extraneous envelope is considerable. Usually the effect of these on the compounds being studied is small, as the contaminant retention time is usually longer than that of the studied PAH (Fig. 8 and 9 ).

Due to the PROMIN only having four channels, it was necessary to inject each sample twice with the mass spectrometer. The masses of $178^+$, $188^+$ (phenanthrene $d_0$ and $d_{10}$) and $202^+$, $212^+$ (pyrene $d_0$ and $d_{10}$) were used for one injection, with $228^+$, $240^+$ (chrysene and benzanthracene $d_0$ and $d_{12}$) and $252^+$, $264^+$ (perylene $d_0$ and $d_{12}$) for the second. A trace of each of these masses with respect to time was produced (Fig. 8, 9, 10 & 11). The height of the mass peak at the particular retention time was noted and the ratio of $d_0$:$d_x$ determined, accounting for a slight percentage of $d_0$ in the deuterated standards.

Analyses were carried out on a PROMIN equipped Finnigan MS connected to a Finnigan 9500 via a glass jet separator. The machine was standardized daily before use by optimization of the $219^+$ of FC-43. Promin drift was checked throughout the day. The GC employed a 1/8" x 5' dexsil 300 on silanized Chromosorb W solumn, with a flow rate of He at 26 ml/min and an injector temperature of $225^0$. The column was left at $100^0$ for the first two minutes after injection and then programmed at $8^0$/min to $300^0$ where it was held. All samples under consideration came off during the temperature programming.

### 5.3.3.5 GC Analysis of the Non-polar Hydrocarbons

Samples were chromatographed using a Hewlett-Packard gas chromatograph (Model 5700) equipped with two flame ionization detectors. Two columns were used: a 7' x 1/8" stainless steel column packed with 2% OV-7 on Chromasorb W (HP), 80-100 mesh and a 10' x 1/8" stainless steel column packed with 12.5% FFAP on Chromasorb W (HP), 80-100 mesh. Helium was used as the carrier gas and both columns were programed from $100^0$C to $270^0$C at $8^0$C/minute.

In the procedure reported here, hydrocarbons having the boiling point of hexadecane (n-$C_{16}$) or less were partially or completely lost through evaporation. The carbon preference index (CPI) for the sediment samples was calculated over the range n-$C_{19}$ to $C_{31}$ by the method of Cooper and Bray (1963) using weight percentages. The odd-even predominance (OEP) function was evaluated for n-paraffins in the range n-$C_{19}$ to n-$C_{30}$ using the method of Scelan and Smith (1970). An average OEP value was determined as the arithmetic mean of the individual OEP values for n-$C_{20}$ to n-$C_{30}$ inclusive.

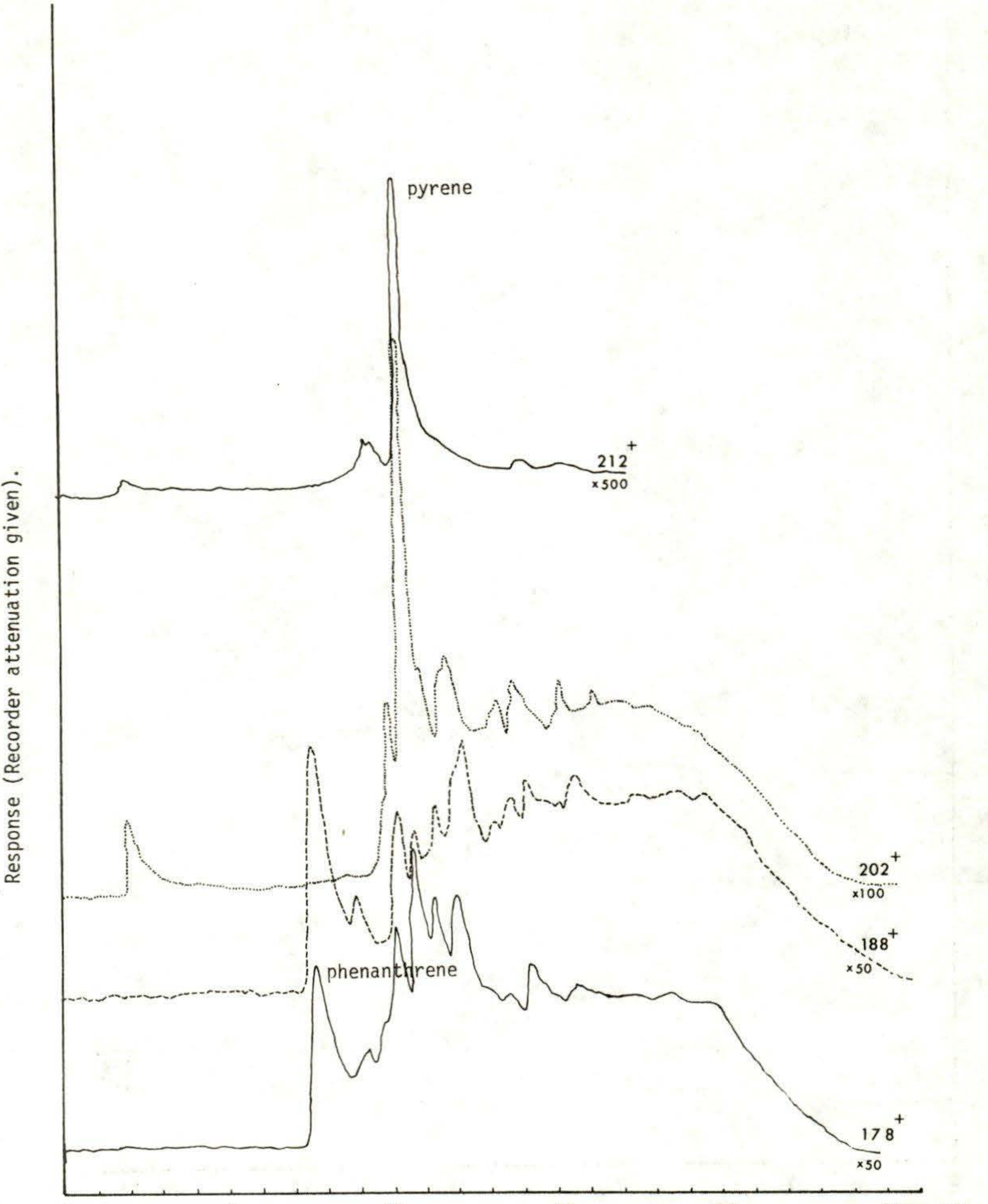


Figure 8. Promin traces for phenanthrene and pyrene on a sediment sample with deuterated standard added. (The baselines are displaced from zero for ease of observation.)

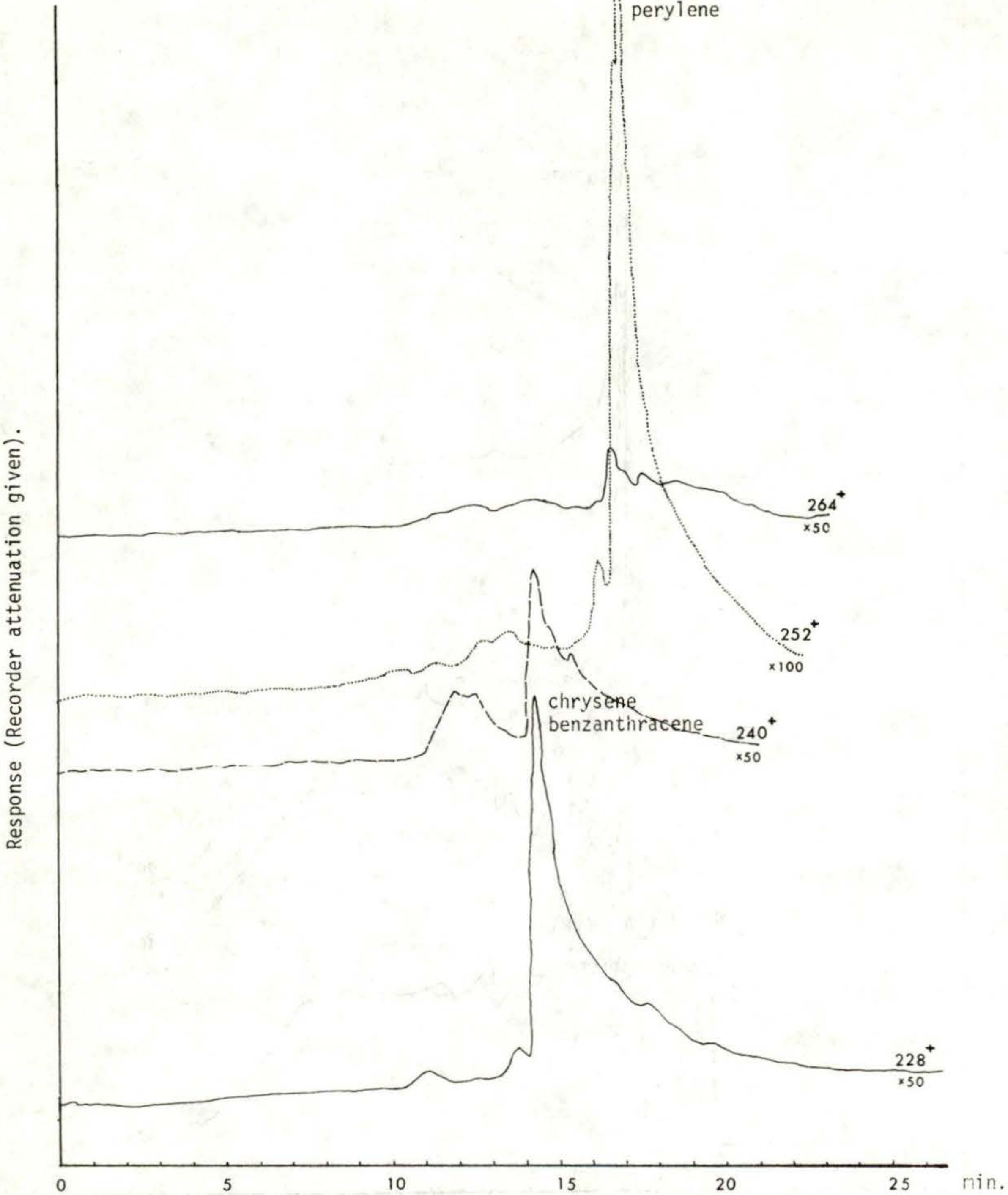


Figure 9. Promin traces for chrysene, benzanthracene and perylene on a sediment sample with deuterated standard added. (The baselines are displaced from zero for ease of observation.)

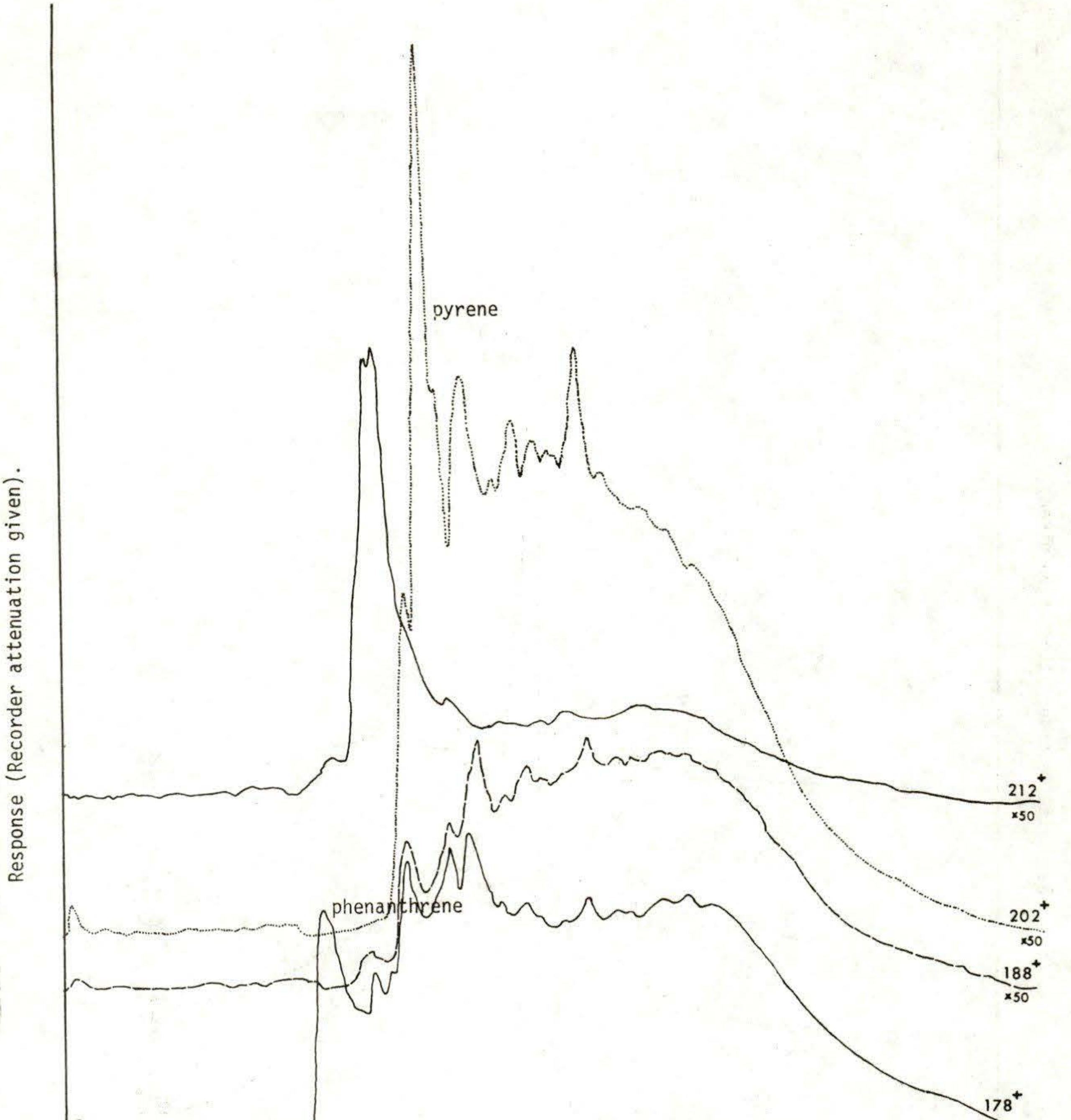


Figure 10. Promin traces for phenanthrene and pyrene on a sediment sample with no deuterated standard added. (The baselines are displaced from zero for ease of observation.)

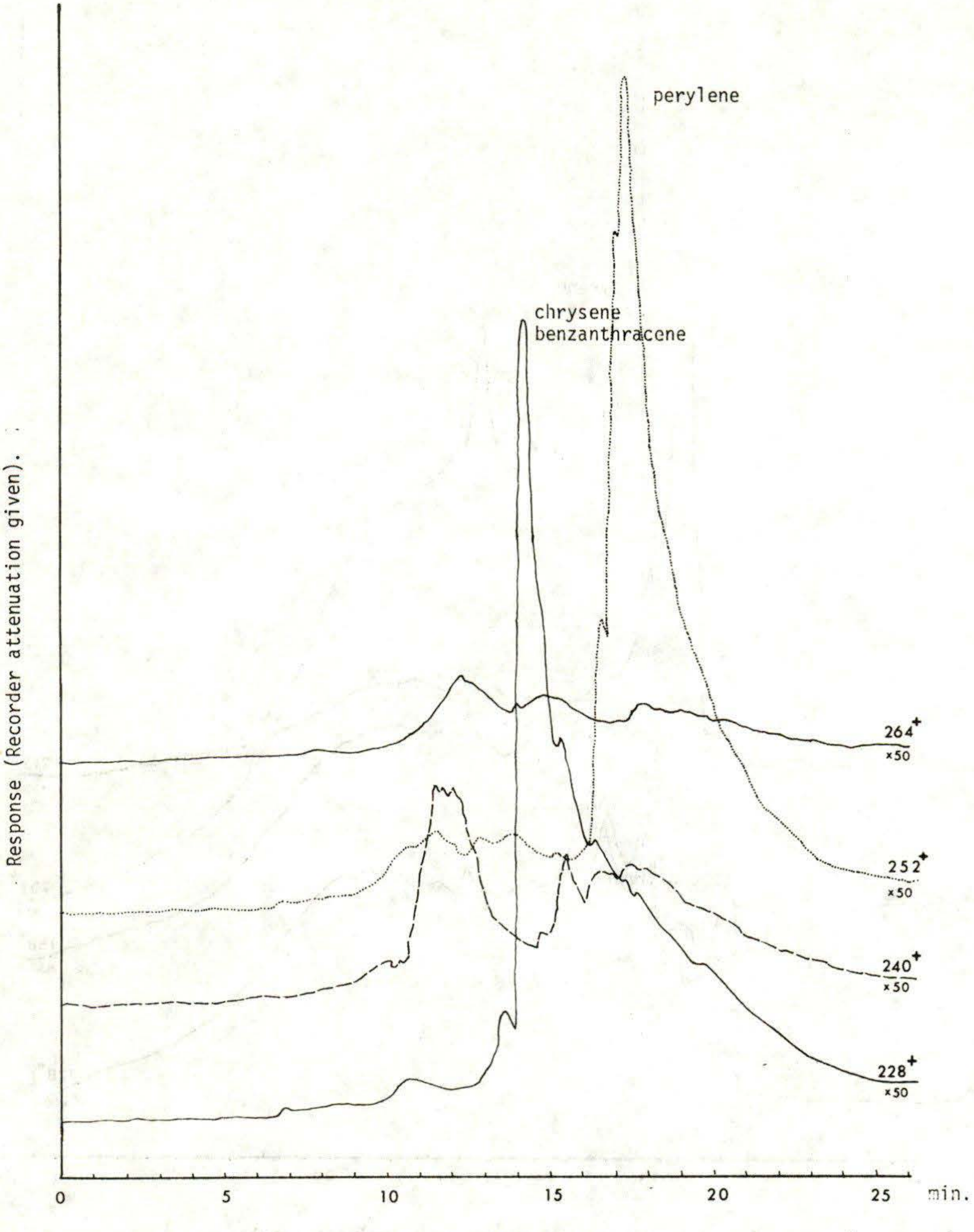


Figure 11. Promin traces for chrysene, benzanthracene and perylene on a sediment sample with no deuterated standard added. (The baselines are displaced from zero for ease of observation.)

## 5.3.4 Low-Molecular Weight Hydrocarbons in Sea Water

### 5.3.4.1 Experimental System

The equipment was designed to determine trace volatile gas components dissolved in sea water. Since a flame-ionization detector-gas chromatograph was used for the determination, the scope of the system is limited to those gases which respond to this method of detection. Attention was concentrated on the light $C_1$-$C_5$ hydrocarbons for the 1974 cruise, but with further modification such compounds as benzene and toluene were determined for the 1975 cruise.

The set up (Fig. 12) is much the same as that originally designed by Swinnerton and Linnenbom (1967 a). Two noteworthy modifications have been made; one affecting sample introduction, and the other affecting calibration.

### 5.3.4.2 Principle of Operation

Helium gas (Canadian Liquid Air, zero grade) is passed through an activated charcoal trap at -78°C to remove all residual hydrocarbons, and then through a 6-port Whitey ball valve to the stripping system. Depending on the ball valve position, the helium can either go directly through the stripper, or to the top of the calibrated sample volume (950 cc). When the helium goes directly through the stripper, the sample volume may be filled from the bottom up with sea water. Turning the 6-port valve then reroutes the helium to the top of the sample volume and causes the contained sea water to enter the stripper. In this manner a reproducible volume of sea water can be introduced to the stripper with a minimum of handling or exposure to the atmosphere. The stripped gases pass through a moisture trap (magnesium perchlorate) and into two cold traps connected in series.

The first, activated alumina, traps out the $C_2$ and higher molecular weight hydrocarbons, while the second, activated charcoal, traps out methane. The gases are separated in this manner because in natural waters methane occurs at much higher concentrations than the other hydrocarbons (approximately 100 fold). Therefore, determination of the higher hydrocarbons would become obscured due to the massive methane peak if all gases were determined simultaneously. The cold traps are cooled to -78°C (acetone-- dry ice) during the stripping operation, and are heated to 90°C prior to backflushing into the chromatograph. Two 6-port Carle valves have been used to allow each of the traps to be backflushed independently.

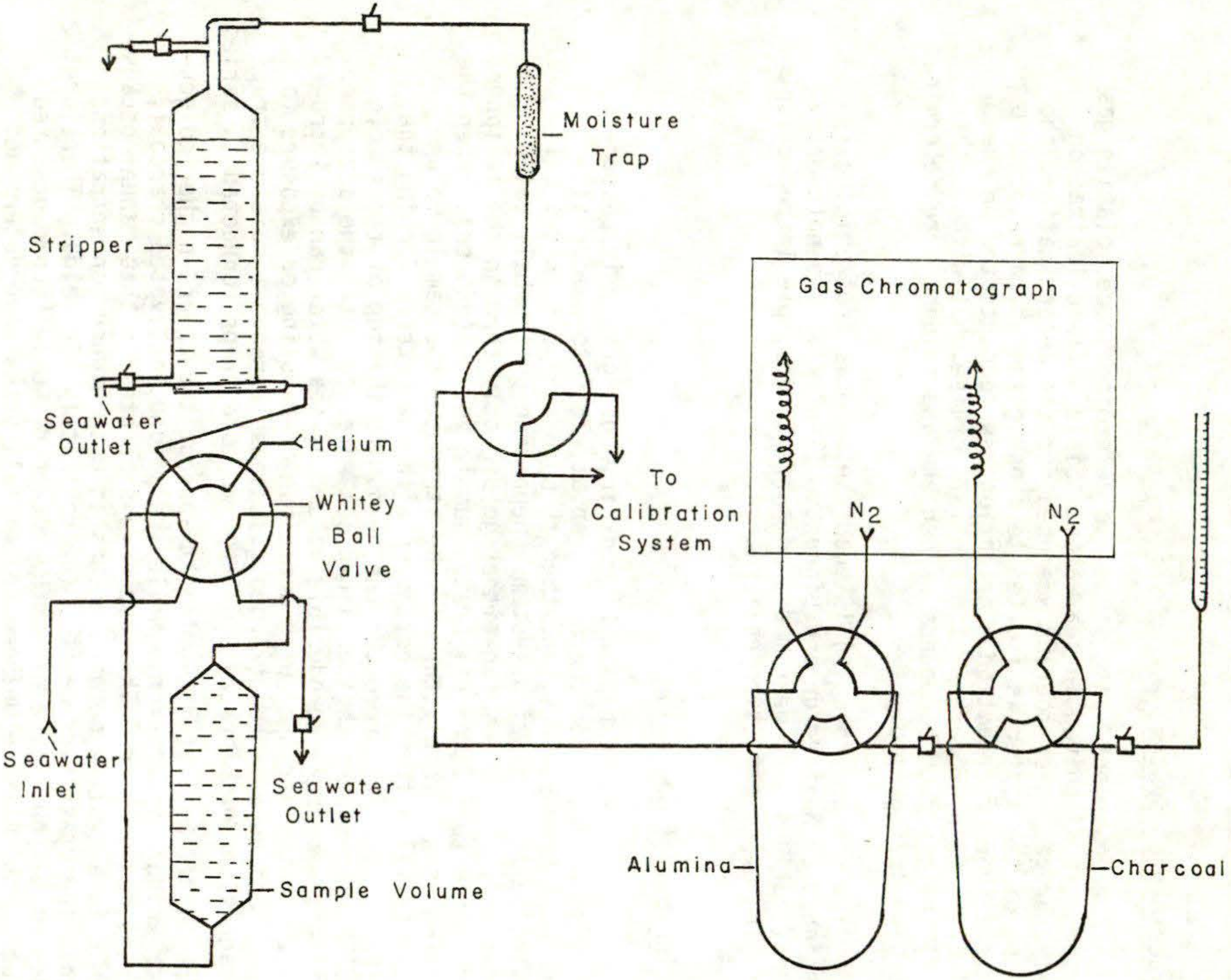


Figure 12. Schematic of Trace $C_1$-$C_4$ Hydrocarbon Analyzer

Two additional Carle valves have been included in the system to facilitate calibration. A 4-port Carle valve has been so arranged that the calibration portion may be bypassed. An 8-port valve has been connected as shown in Figure 13. Two loops of known volume are connected so that they can be evacuated via the vacuum system. A sample of calibration gas can then be introduced to one of the calibration loops, and the pressure measured on the Heise guage (0-1000 millibar). With the helium strip gas flowing, and the cold traps in place, a 90° turn of the 8-port valve introduces the calibration gas into the flow and allows it to be trapped out, and subsequently determined on the chromatograph. The two calibrated volumes, and the Heise guage together allow a 10,000 fold range in the amount of calibration gas to be introduced. With the correct choice of hydrocarbon concentration in the calibration gas, variations in natural levels will occur within the calibration range. In any event, the flame-ionization detector should be linear over seven orders of magnitude, so that good estimates are also possible for particularly high levels which lie outside the calibration range.

Before any sampling can be done, a blank on the equipment itself must be run. To do this all the normal stripping procedures are followed except that no sample is admitted. The helium strip gas is trapped and injection of the trapped sample into the chromatograph takes place as usual.

Blanks were run every day to insure that the stripping system was contamination free. Unusual results were also followed by a check blank. Based on the calibration curves (Fig. 14) and the reported accuracy of the standards, 95% confidence intervals for the various hydrocarbons were $CH_4$--2.82%, $C_2H_6$--6.7%, $C_2H_4$--4.2%, $C_3H_8$--6.8%, $C_3H_6$--4.7%, $C_4H_{10}$--34%. These intervals refer to the most commonly observed levels. Higher levels would have a lower percentage of uncertainty, whereas unusually low values would have a higher percentage of uncertainty. Duplicate analyses in the field and in the laboratory indicate that these confidence intervals are reasonable.

### 5.3.4.3 Problems

The largest problem encountered was that of obtaining a good blank. Although the light hydrocarbons purged very easily from the system, solvents such as methanol dichloromethane, chloroform and carbon tetrachloride adsorbed on the glass portions and were impossible to remove by purging with helium. At high attenuations these might not have caused any problems; but since the most sensitive (lowest) ranges and attenuations were necessary for the $C_2$ and higher hydrocarbons, traces of these solvents could not be tolerated. In general, they eluted as very broad peaks with high retention times; and therefore, although they did not interfere with the initial sample, caused great difficulty and obscured the

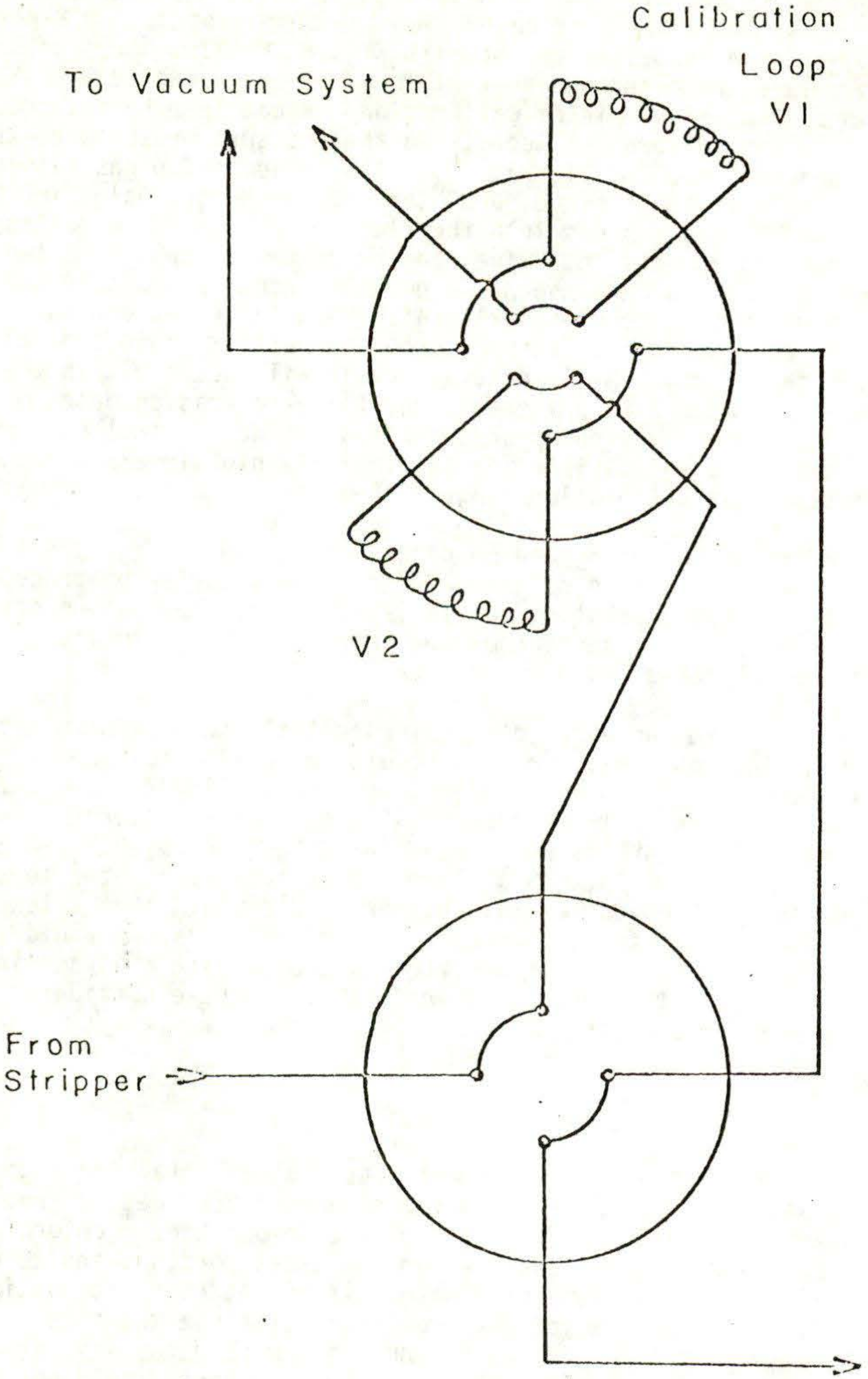


Figure 13. Details of Calibration System

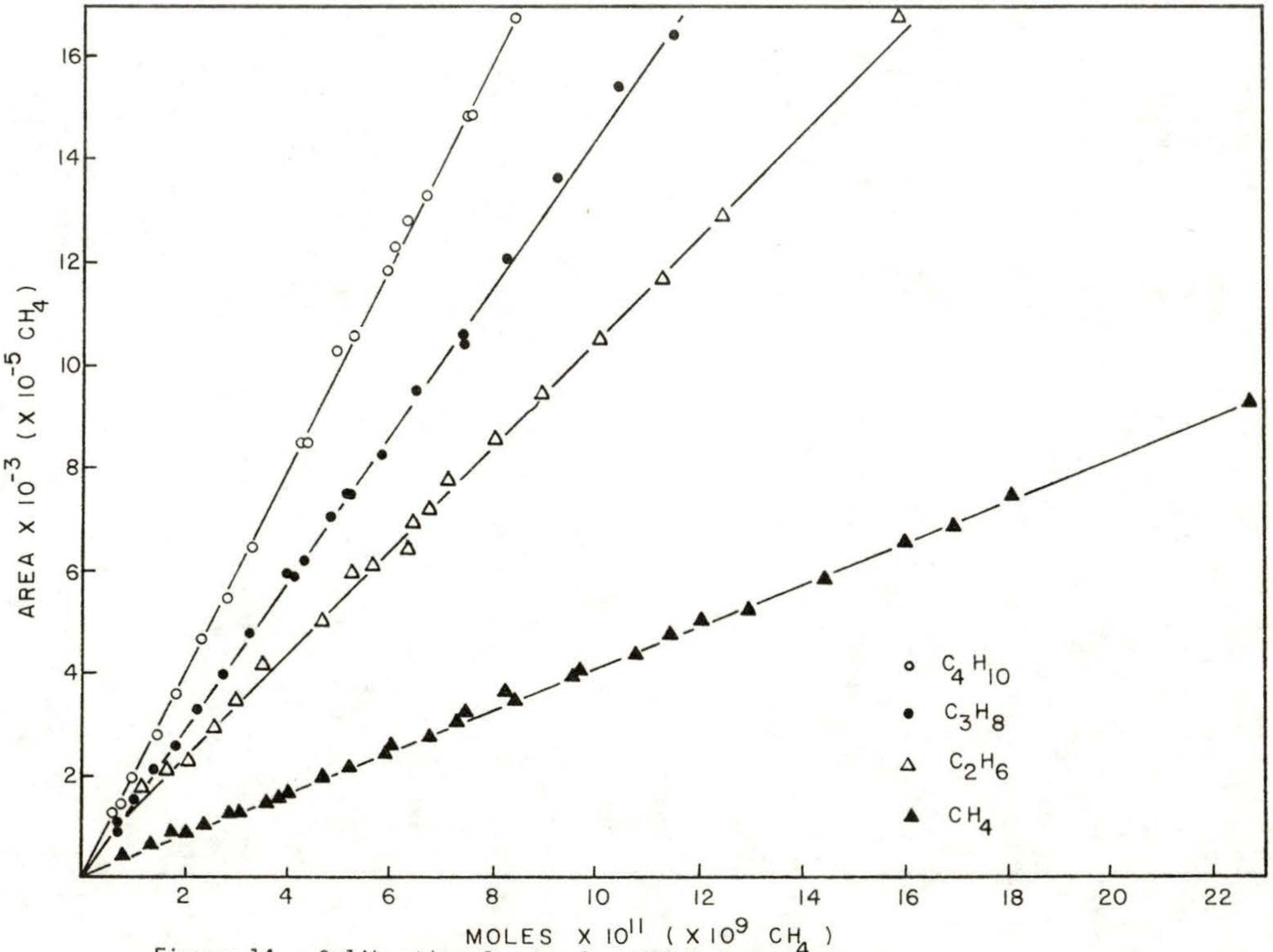


Figure 14. Calibration Curves for LMW Hydrocarbons

results of following analyses. It was discovered that these persistent solvents could only be removed by baking all the glassware at 300°C overnight with a purge gas constantly flowing. Although this problem and how to cope with it was originally discovered before the cruise, it recurred during the cruise because the glass Blumer inserts (5 litre) had been washed with some of these solvents. It is imperative, therefore, to scrupulously avoid the use of these solvents (particularly where they might come into contact with glass) for any of the $C_1$-$C_5$ equipment. Not only can they cause problems in the analysis, but there is a possibility that they could affect the samples. These absorbed solvents could remove some of the light hydrocarbons from samples with high hydrocarbon levels and reintroduce them into samples with lower hydrocarbon levels.

It was also found that the lifetime of the activated charcoal trap at the beginning of the helium line was limited, and that after approximately three days, some lighter hydrocarbons would show up in the blanks. This problem was removed by reactivating the trap. Heating the trap to 300°C with helium flow was adequate. Samples were not run until satisfactory blanks were obtained. These were usually zero, or less than 1% of the normally detected levels.

### 5.3.4.4 Experimental

Through experimentation it was found that with a helium pressure of 15 psi on the regulator and a flow rate of 50 ml/min measured at the exit, 45 minutes was more than adequate to strip the sample of light hydrocarbons. Second strips of the same sample for an additional 45 minutes gave levels comparable with the blanks. Although this procedure was certainly good for the $C_1$-$C_5$ hydrocarbons, some revision might be necessary for benzene or toluene.

For calibrations a slightly different procedure was followed to save time. The calibration volume was pumped out for five minutes, and the calibration gas was introduced and allowed to equilibrate for at least two minutes. After the traps were cold the helium gas was allowed to flow by opening the toggle valves. The calibration gas was injected into the flow and after three minutes the toggle valves were closed. This time was more than adequate to allow all the gases to be trapped out. Additional time could be saved by pumping out and preparing the next calibration while the analysis of the first calibration was taking place. In Table 7 are presented the calibration data for the Beaufort Sea Cruise. It was found that the response of the equipment remained constant over the whole cruise, and that all the calibrations could be treated as a single linear plot for each gas. The relative response factor shown in Table 7 is based on the slope of the linear least squares fit and is normalized to propane = 3. Since the F.I.D. is essentially a carbon counter,

# TABLE 7

## Linear Least Mean Squares Calibration Parameters

| Gas | a | b | Attenuation | Response Factor |
|---|---|---|---|---|
| $CH_4$ | -0.17 ± 2.73 | 2.406 ± .027 | 40 | 0.84 |
| $C_2H_6$ | -1.86 ± 1.79 | 2.748 ± .0211 | 1 | 2.02 |
| $C_2H_4$ | 2.57 ± 3.07 | 2.860 ± .0372 | 1 | 2.06 |
| $C_3H_8$ | -3.54 ± 3.02 | 2.045 ± .0259 | 1 | 3.00 |
| $C_3H_6$ | -1.16 ± 2.89 | 2.045 ± .0248 | 1 | 3.00 |
| $nC_4H_{10}$ | 0.06 ± 1.09 | 1.455 ± .0066 | 1 | 4.14 |

one expects that ethane and ethylene will be approximately 2, methane 1, and butane 4 (David, 1974). Allowance has been made for concentration of the hydrocarbon in the calibration gas and the attenuation. The concentrations of hydrocarbons in the calibration gases are reported in Table 8. (These standards were obtained from Matheson of Canada Ltd.). In Table 7, 95% confidence intervals are provided on slope and intercept, and the data was correlated as pressure = a + b area, where pressure refers to the pressure of the calibration gas in the calibration loop (9.88 cc) and area refers to the area under the peak. Peak areas were found to be the only reliable method of analyzing the data. Peak height varied with trapping time, temperature, and any slight variations in procedure while peak area did not.

Sea water samples were obtained in a 5 litre glass bottle (Blumer insert). To introduce the sample into the calibrated volume an arrangement shown in Figure 6 was used. Pressure was applied to the top of the 5 litre bottle (20 psi) with the aid of "Gelman" pump. This caused the sea water to flow up through the central 1/8" stainless steel tube and through the filter holder. Samples were filtered here to avoid the possibility of later clogging the coarse glass frit in the bottom of the stripper. Generally, GF/A filters were used, although any fiberglass filter finer than the frit would suffice. These filters became clogged rapidly when some of the surface Beaufort Sea water was sampled where there was a high sediment content. The filters could, however, be changed very quickly between samples without disturbing the system. The sample volume (950 cc) was rinsed out by allowing the first 900 cc of sea water to overflow. The Whitey ball valve was then switched causing the sample to enter the stripper. The pressure relief valve was opened at the top of the stripper to allow the excess helium already in the stripper to exit. When the sea water in the sample volume reached a level of 2" above the bottom, the pressure relief valve was closed and the two trap isolation toggle valves were opened to allow helium to flow through the system. A small dewar with a methanol-dry ice slurry had previously been placed over the traps allowing them to approach the temperature of the slurry. As soon as bubbles started to come up through the frit a stop watch was started and after 45 minutes the trap isolation toggle valves were closed to stop helium flow. A dewar filled with $90^{0}$+ hot water was placed on the activated charcoal trap for 30 seconds at which time the trapped out sample was injected into the chromatograph. (Before heating the traps, the chromatograph was checked to insure correct attenuation, that the baseline was zeroed, and that there were no problems of noise or drift.) The same procedure was followed later with the alumina trap after the methane had eluted from the column and the pen had returned to zero. In general, the majority of the Beaufort Sea samples could be handled by operating the gas chromatograph on attenuation 40 for methane and attenuation 1 for the higher molecular weight hydrocarbons.

TABLE 8

Concentration of Hydrocarbons in Calibration Standards

| Gas | Concentration (ppmv) |
|---|---|
| $CH_4$ | 100 ± 1 |
| $C_2H_6$ | 0.90 ± .02 |
| $C_2H_4$ | 0.88 ± .02 |
| $C_3H_8$ | 0.83 ± .02 |
| $C_3H_6$ | 0.83 ± .02 |
| $nC_4H_{10}$ | 0.85 ± .02 |

### 5.3.4.5 Chromatographic Parameters

The three zero grade gases: air, $H_2$ and $N_2$ were used to operate the chromatograph. The pressures and flow of these gases are given in Table 9. A moisture trap (supplied by Hewlett-Packard) was placed on the air line and the Nitrogen line and a .7μ brass filter was added to each of the three gas lines just before the connection ports on the back of the chromatograph. Methane was determined on a 4' silica gel column (1/8" diameter) while the $C_2$-$C_5$ hydrocarbons were determined on an 18' Durapak - phenyl-isocyanate column (1/8" diameter). Both columns were operated at slightly above room temperature (approximately $30^{o}C$).

### 5.3.4.6 Computing Gas Concentration

$T = 298^{o}C$ Room Temperature
$R = 83.14$ cc bar/$^{o}C$ gm mole (gas constant)
$V_2 = 9.88$ cc (calibration volume)
$V = 950$ cc (sampler volume)

P = pressure in bars
C = concentration of calibration gas (Table 2) in ppmv
n = moles/litre sample
$\begin{matrix} a \\ b \end{matrix}$ = linear least squares parameters (Table 1)
A = measured area of hydrocarbon
m = volume of gas in nanolitres (STP)/l

for any hydrocarbon whose area is A,

$$P = \frac{(a+bA)}{1000} \text{ bars} \times \frac{C}{10^6}$$

$$n = \frac{\frac{(a+bA)}{1000} \text{ bars} \times V_2 \text{ cc} \times \frac{C}{10^6}}{RT \times \frac{V}{1000}}$$

$$m \text{ nanolitres/l} = \frac{\frac{(a+bA)}{1000} \times V_2 \times \frac{C}{10^6}}{\frac{RTV}{1000}} \times 22.4 \times 10^9$$

$$= (a+bA) \times 9.40 \times 10^{-3} \times C$$

## TABLE 9

## Chromatograph Operating Parameters

| Gas | Pressure | Flow Rate |
|---|---|---|
| Air | 24 psi | 240 ml/min |
| $H_2$ | 15 psi | 30 ml/min |
| $N_2$ | 50 psi | 25 ml/min |

## 6. RESULTS

### 6.1 Polycyclic Aromatics Hydrocarbons in Sea Water

Some of the results of PAH in sea water suspended matter are shown in Tables 10, 11 and 12.

### 6.2 Polycyclic Aromatic Hydrocarbons in Marine Organisms, Surface Sediments and Nearshore Sediments

Some of the results of PAH as determined by GC/MS are shown in Table 13 (Fish samples), Table 14 (Surface sediment samples, 1974) and Table 15 (Surface sediment samples, 1975). PAH in nearshore sediments as determined by the fluorescent technique are shown in Table 16.

### 6.3 Low-Molecular Weight Hydrocarbons in Sea Water

Results of LMW hydrocarbons are shown in Table 17 ($C_1$-$C_4$ Hydrocarbons, 1974) and Table 18 ($C_1$-$C_4$ Hydrocarbons, 1975).

### 6.4 Tarballs and Plastics

Four neuston-net tows were made in 1974 and 17 in 1975. The locations of these tows are shown in Figure 15. No tar or plastics were found in 1974. In 1975, only one piece of styrofoam was found in one tow, and very small black pieces 0.1-2 mm in diameter occurred in 11 of the 17 tows. Tentatively, these black pieces, numbered ten to several hundreds per sample, were seeds, ash, dark terrestrial detritus, bark fragments, flying insects and occasionally what appeared to be tar specks. However, these tar-like material would not dissolve in carbon disulphide indicating their non-petroleum based characteristics. Even if the tar-like material was indeed tarballs, the concentration is less than 0.001 mg/$m^2$ or probably zero.

### 6.5 Non-polar Hydrocarbons in Fish, Mixed Plankton and Sediments

The results for non-polar hydrocarbons in fish samples in Southern Beaufort Sea are shown in Table 20 and sediments in Tables 21 and 22.

## 7. DISCUSSION

To assess the present state of the marine environment in the Southern Beaufort Sea with respect to petroleum pollution is a very difficult task. The levels of hydrocarbons are very low. There are few analytical methods available to detect such minute quantities in the marine environment. The sampling problem presents another great hurdle to getting reliable results such as the severe contamination which could result from the ship's exhaust and machine oils. Storage of samples collected without deterioration is another constraint. There is also the dilema

## Storage and Preservation of PAH Concentrations in Sea Water

### TABLE 10

The Effect of Time and Type of Poison on PAH Concentrations

| | Sample No. | Preservative Used | PAH Conc. (ng/l[b]) in Sea Water At PAH Adsorbed (ng/l[b]) | | | |
|---|---|---|---|---|---|---|
| Storage Time | | | 3 mo.[c] | 5 mo.[c] | 6 mo.[c,d] | On container |
| | 1 | None | 24 | 65 | 55 | 8 |
| | 2 | None | 21 } 23 | 36 } 49 | 41 } 52 | 7 |
| | 3 | None | 24 | 45 | 60 | 14 |
| | 4 | $NaN_3$ | 37 | 62 | 36 | 13 |
| | 5 | $NaN_3$ | 20 } 22 | 35 } 36 | 28 } 27 | 8 |
| | 6 | $NaN_3$ | 8 | 11 | 18 | 5 |
| | 7 | $HgCl_2$ | 11 | 23 | 87[e] | 7 |
| | 8 | $HgCl_2$ | 20 } 16 | 19 } 21 | n.d.[f] | 2 |
| | 9 | $HgCl_2$ | 17 | 23 | n.d. | 1 |

[a] These nine samples were collected just off Herschell Island at 69°44'N, 38°40'W. Four successive bucket casts were made over as short a time as possible.

[b] Chrysene equivalents.

[c] Time elapsed between collection and analysis of samples

[d] Analyses were performed on 0.5 l instead of customary 1.5 l.

[e] Some sediment was present in water sample.

[f] Not determined.

TABLE 11

PAH Concentrations in Mackenzie Bay Sea Water

| Station | Sample No. | Depth (m) | Salinity($^{o}$/oo) | PAH Conc. (ng/l[a]) | |
|---|---|---|---|---|---|
| | | | | In Water | On Container |
| 1 | 10 | 5 | 3.0 | 24, 32[b] | 11 |
| 1 | 11 | 22 | 30.0 | 39, 44 | 18 |
| 11 | 12 | 5 | 4.3 | 45, 59 | n.d.[c] |
| 11 | 13 | 5 | 4.3 | 32, 17 | n.d. |
| 11 | 14 | 35 | 31.5 | 23, 22 | 12 |
| 11 | 15 | 35 | 31.5 | 14, 15 | 6 |
| 42 | 19 | 5 | 3.9 | 17, 23 | 5 |
| 42 | 20 | 5 | 3.9 | 18, 28 | n.d. |
| 42 | 21 | 15 | 27.8 | 25, 26 | n.d. |
| 42 | 22 | 15 | 27.8 | 9, 13 | n.d. |

[a] Chrysene equivalents.

[b] Duplicate analysis.

[c] Not determined.

## TABLE 12

PAH Concentrations Associated with Particulate Matter in 1974 and 1975

| Year | Average Conc. mg/l of Particulate Matter | Average Conc. of PAH on Particulate Matter | |
|---|---|---|---|
| | | Sea Water ng/l | Particulate Matter ng/mg |
| 1974 | 31 | 140 | 5 |
| 1975 | 1 | 85 | 92 |

## TABLE 13

## Some PAH Compounds in Southern Beaufort Sea Fish

| Type of Fish | Condition | Amounts of Analyzed Material (μg/Kg wet weight) | | | |
|---|---|---|---|---|---|
| | | $178^+$ | $202^+$ | $228^+$ | $252^+$ |
| Pomfret | Frozen | | 1.26 | | |
| Least Cisco | Frozen | 8 | 3.6 | 5.1 | 2.7 |
| Least Cisco # 20 | Frozen | 15 | 4.0 | 4.4 | 2.9 |
| Least Cisco # 1 | Frozen | 3.8 | 0.4 | 3.2 | 18 |
| Least Cisco # 2 | Frozen | 1.4 | 1.1 | 4.3 | 1.9 |
| Arctic Cisco | Frozen | 7.2 | 2.3 | 10 | 12 |
| Arctic Cisco | Frozen | 8 | 2.0 | 1.7 | 1.8 |

## TABLE 14

## Some PAH Compounds in Southern Beaufort Sea Surface Sediments (1974 Cruise)

| Stn. No. | Sed. No. | Depth (m) | Type of Sample | Amounts of analyzed material (μg/Kg wet weight) $178^+$ | $202^+$ | $228^+$ | $252^+$ | Total |
|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 48 | Mud | 68 | 58 | 61 | 96 | 283 |
| 2 | 2 | 30 | Clay mud | 35 | 121 | 21 | 59 | 236 |
| 11 | 3 | 64 | Mud | 56 | 34 | 143 | 220 | 423 |
| 12 | 4 | 81 | Hard clay | 69 | 41 | 135 | 320 | 565 |
| 13 | 5 | 191 | Hard clay | 68 | 148 | 136 | 305 | 657 |
| 17 | 6 | 66 | | 165* | 57* | 60 | 285 | 567 |
| 19 | 7 | 42 | Clay | 82* | 27 | 72 | 182 | 363 |
| 20 | 8 | 70 | | 81* | 30 | 103 | 269 | 483 |
| 23 | 9 | 15 | | 77 | 20 | 42 | 151 | 290 |
| 23 | 10 | 15 | | 83 | 40 | 61 | 182 | 366 |
| 25 | 11 | 65 | | 76 | 30 | 118 | 307 | 531 |
| 28 | 12 | 43 | Sand, clay | 142 | 59 | 196 | 523 | 920 |
| 35 | 13 | 7 | Clay | 152 | 53 | 166 | 418 | 789 |
| 41 | 14 | 11 | Mud, clay | 114 | 57 | 144 | 200 | 508 |
| 42 | 15 | 19 | Mud, clay | 119 | 66 | 197 | 402 | 784 |
| 44 | 16 | 13 | Mud | 134 | 66 | 146 | 638 | 984 |
| 48 | 17 | 33 | | 50* | 19* | 31* | 168* | 268* |
| 54 | 18 | 51 | | 149 | 59 | 97 | 420 | 725 |

* small recovery of PAH

## TABLE 15

## Some PAH Compounds in Southern Beaufort Sea Surface Sediments (1975 Cruise)

| | | | | Amount of analyzed materials (μg/Kg wet weight) | | | | | Amounts of analyzed materials (μg/Kg dry weight) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Stn. No. | Sed. No. | Depth (m) | Type of Sample | $178^+$ | $202^+$ | $228^+$ | $252^+$ | Total | $178^+$ | $202^+$ | $228^+$ | $252^+$ | Total |
| 08 | 1 | 20 | Fine clay | 93 | 45 | 235 | 882 | 1255 | 174 | 84 | 439 | 1649 | 2368 |
| 09 | 2 | 83 | Med. mud | 61 | 26 | 250 | 930 | 1267 | 139 | 59 | 570 | 2120 | 2888 |
| 11 | 3 | 17 | Med. mud | 152 | 63 | 169 | 710 | 1094 | 249 | 103 | 277 | 1164 | 1794 |
| 13 | 4 | 50 | Med. mud | 50 | 30 | 142 | 287 | 509 | 105 | 63 | 300 | 606 | 1074 |
| 15 | 5 | 20 | Fine clay | 112 | 43 | 116 | 380 | 651 | 188 | 72 | 194 | 638 | 1094 |
| 17 | 6 | 64 | Mud | 25 | 14 | 42 | 138 | 219 | 66 | 37 | 111 | 366 | 580 |
| 20 | 7 | 14 | Sand | 22 | 8 | 24 | 43 | 97 | 28 | 12 | 30 | 54 | 122 |
| 22 | 8 | 70 | Fine clay | 39 | 23 | 160 | 450 | 672 | 81 | 48 | 332 | 936 | 1398 |
| 25 | 9 | 15 | Fine clay | 69 | 66 | 202 | 1004 | 1341 | 106 | 101 | 309 | 1536 | 2051 |
| 27 | 10 | 65 | Med. mud | 36 | 25 | 110 | 228 | 459 | 75 | 75 | 54 | 230 | 959 |
| 30 | 11 | 18 | Fine clay | 75 | 37 | 107 | 277 | 496 | 128 | 63 | 183 | 474 | 848 |
| 32 | 12 | 80 | Coarse Mat. | 25 | 18 | 33 | 137 | 213 | 40 | 29 | 53 | 220 | 343 |
| 34 | 13 | 18 | Med. mud | 61 | 35 | 80 | 243 | 419 | 82 | 47 | 108 | 328 | 566 |
| 36 | 14 | 73 | Med. mud | 35 | 28 | 45 | 322 | 430 | 86 | 70 | 112 | 802 | 1071 |
| 38 | 15 | 14 | Fine clay | 90 | 32 | 107 | 278 | 507 | 141 | 50 | 168 | 436 | 796 |
| 41 | 16 | 60 | Med. mud | 50 | 24 | 77 | 337 | 488 | 110 | 50 | 162 | 708 | 1025 |
| 42 | 17 | 30 | Fine clay | 76 | 33 | 113 | 798 | 1020 | 135 | 59 | 201 | 1420 | 1816 |
| 43 | 18 | 15 | Fine clay | 73 | 48 | 218 | 750 | 1089 | 125 | 82 | 373 | 1272 | 1860 |
| 44 | 19 | 48 | | 81 | 45 | 178 | 226 | 530 | 152 | 85 | 325 | 424 | 995 |
| 45 | 20 | 155 | Fine clay | 62 | 29 | 49 | 834 | 974 | 126 | 59 | 100 | 891 | 1177 |
| 46 | 21 | 65 | Med. mud | 90 | 31 | 104 | 360 | 585 | 165 | 57 | 190 | 659 | 1070 |
| 47 | 22 | 77 | Fine clay | 93 | 41 | 185 | 448 | 762 | 173 | 76 | 344 | 833 | 1417 |

TABLE 16

Some PAH Compounds in Nearshore Sediments of Southern Beaufort Sea
($\mu$g/Kg dry sediment)

| Sample* | Sample Designation* | Total Actual Wt. PAH Concentrate | Pyrene | Benzo[a] pyrene** | Perylene | Coronene | Total Wt.*** From UV |
|---|---|---|---|---|---|---|---|
| A | S-75-23 | 840 | -- | -- | -- | -- | -- |
| B | S-75-25 | 1,800 | 0.7 | -- | -- | 0.2 | 0.9 |
| C | S-75-19 | 5,200 | 3.0 | 7.6 | 7.3 | 1.7 | 19.6 |
| D | S-75-27 | 1,600 | 0.9 | 0.5 | 0.3 | 0.6 | 2.3 |
| E | S-75-36 | 8,000 | 0.9 | 10 | 0.9 | 0.6 | 12.7 |
| F | S-75-39 | 29,000 | 1.1 | 2.5 | 2.3 | -- | 5.9 |
| G | S-75-17 | 1,100 | 0.5 | 0.4 | 0.7 | 0.5 | 2.1 |
| H | S-75-18 | 4,100 | 1.3 | 3.2 | 3.5 | 0.4 | 8.4 |
| I | CS-75-14 | 5,200 | -- | -- | -- | -- | -- |
| J**** | CS-74-70 | 3,600 | -- | 2.2 | 1.2 | 1.5 | 4.9 |
| K**** | CS-74-71 | 3,600 | -- | -- | -- | 0.4 | 0.4 |
| L**** | CS-74-72 | 9,100 | -- | -- | -- | 0.4 | 0.4 |
| M | CS-75-2 | 1,700 | -- | -- | -- | -- | -- |
| N***** | B-75-2 | 26,000 | 41 | 106 | 129 | 19 | 295 |
| O***** | B-75-11 | 99,000 | 52 | 131 | 85 | 31 | 299 |

Note: * For sample designations, see Wong, et al. (1976).

** In the alumina column chromatography, some overlap of benzo[a] pyrene into fraction VI occurs. Benzo[a] pyrene and benzo[ghi]perylene have coincident peak absorbances and nearly identical absorption extinction coefficients. Results are therefore given in benzo[a]pyrene equivalents.

*** All UV absorption traces exhibit smooth slowly-rising baselines. Pyrene, benzo[a]pyrene, perylene and coronene are readily discernable because their peak abosrbances lie in the 330 to 460 nm range. An unknown compound(s) produces a large peak in the 250 to 300 nm range which completely masks any contribution from phenanthrene, anthracene, fluoranthene, chrysene and benz[a]anthracene.

**** Core samples J, K and L were all collected at the same site. For any given fraction, the UV spectral traces of each were virtually identical.

***** Benthic sediments.

## TABLE 17

$C_1$-$C_4$ Hydrocarbons in Southern Beaufort Sea, 1974

(Concentration in nanolitres/litre of sea water)

| Station | Date(GMT) | Sonic Depth (Meters) | $CH_4$ | $C_2H_6$ | $C_2H_4$ | $C_3H_8$ | $C_3H_6$ | $nC_4H_{10}$ |
|---|---|---|---|---|---|---|---|---|
| 7 | Aug. 14 | 5 | 119.7 | ---- | 1.11 | .26 | .83 | .029 |
| 7 | Aug. 14 | 20 | 195.2 | ---- | 0.99 | .39 | .45 | .035 |
| 11 | Aug. 16 | 35 | 125.6 | ---- | 0.14 | .05 | .13 | .024 |
| 11 | Aug. 17 | 5 | 201.8 | ---- | 0.85 | .05 | .73 | .024 |
| 11 | Aug. 17 | 20 | 244.1 | ---- | 0.25 | .17 | .22 | .054 |
| 11 | Aug. 17 | 60 | 187.8 | ---- | 0.19 | .15 | .13 | .012 |
| 19 | Aug. 19 | 5 | 148.0 | ---- | 1.20 | .14 | .94 | .047 |
| 19 | Aug. 19 | 2 | 110.7 | ---- | 0.81 | .12 | .69 | .024 |
| 20 | Aug. 21 | 0 | 180.8 | ---- | 0.77 | .18 | .63 | .024 |
| 20 | Aug. 21 | 7 | 136.9 | ---- | 0.79 | .09 | .77 | .012 |
| 20 | Aug. 21 | 15 | Lost | ---- | 0.27 | .24 | .23 | .035 |
| 20 | Aug. 21 | 0 | 147.5 | ---- | 0.63 | .12 | .46 | .012 |
| 23 | Aug. 22 | 2 | 258.1 | ---- | 1.42 | .92 | 1.59 | .254 |
| 24 | Aug. 22 | 2 | 84.6 | ---- | 1.17 | .16 | 1.03 | .041 |
| 28 | Aug. 23 | 2 | 72.2 | ---- | 1.06 | .18 | .91 | .035 |
| 27 | Aug. 23 | 2 | 78.1 | ---- | 0.78 | .14 | .64 | .044 |
| 30 | Aug. 23 | 3 | 74.7 | ---- | 0.39 | .09 | .09 | ---- |
| 32 | Aug. 23 | 3 | 79.4 | ---- | 0.49 | .22 | .44 | .035 |
| 35 | Aug. 23 | 3 | ∿276 | ---- | 0.15 | .02 | .31 | .021 |
| 37 | Aug. 23 | 3 | 67.7 | ---- | 0.35 | .09 | .18 | .021 |
| 39 | Aug. 23 | 3 | 107.3 | ---- | 1.06 | .07 | .81 | .024 |
| 42 | Aug. 25 | 5 | 94.1 | ---- | 0.45 | .17 | .30 | .029 |
| 42 | Aug. 25 | 5 | 135.5 | ---- | 0.38 | .08 | .19 | .024 |
| 42 | Aug. 26 | 3 | ∿562 | ---- | 0.87 | .08 | .76 | .024 |
| 44 | Aug. 26 | 5 | 142.8 | ---- | 0.38 | .23 | .26 | .049 |
| 44 | Aug. 26 | 3 | 545.7 | ---- | 1.03 | .16 | 1.00 | .065 |

## TABLE 17
(cont'd)

| Station | Date(GMT) | Sonic Depth (Meters) | $CH_4$ | $C_2H_6$ | $C_2H_4$ | $C_3H_8$ | $C_3H_6$ | $nC_4H_{10}$ |
|---|---|---|---|---|---|---|---|---|
| 47 | Aug. 27 | 30 | ∿470 | ---- | 0.51 | .14 | .25 | .070 |
| 47 | Aug. 27 | 15 | ∿580 | ---- | 1.60 | .18 | .67 | .070 |
| 48 | Aug. 27 | 30 | 572.0 | ---- | 0.54 | .14 | .23 | .058 |
| 49 | Aug. 27 | 30 | 517.7 | ---- | 0.54 | .17 | .22 | .070 |
| 49 | Aug. 27 | 15 | 617.2 | ---- | 1.92 | .23 | .96 | .070 |
| 49 | Aug. 27 | 3 | 271.2 | ---- | 1.61 | .14 | 1.39 | .047 |
| 51 | Aug. 27 | 3 | 256.4 | ---- | 1.34 | .21 | 1.02 | .066 |
| 23 | Aug. 22 | Ice Floe | 112.0 | ---- | >2.8 | .77 | 4.68 | .174 |
| 24 | Aug. 23 | Ice Floe | 107.3 | ---- | 14.56 | .46 | 8.69 | .127 |

## TABLE 18

### $C_1$-$C_4$ Hydrocarbons in Southern Beaufort Sea, 1975

(Concentration in nanolitres/litre of sea water)

| Station | Date(GMT) | Sonic Depth (Meters) | $CH_4$ | $C_2H_6$ | $C_2H_4$ | $C_3H_8$ | $C_4H_{10}$ | $C_3H_6$ |
|---|---|---|---|---|---|---|---|---|
| 1 | Aug. 5 | 405 | 15.4 | ---- | 0.18 | 0.52 | 0.112 | 0.137 |
| 2 | Aug. 5 | 3 | 93.1 | 0.59 | 2.14 | 0.29 | 0.102 | 1.90 |
| 2 | Aug. 6 | 0 | 90.2 | 0.45 | 1.98 | 0.20 | 0.079 | 1.67 |
| 3 | Aug. 6 | 3 | 108.9 | 0.63 | 1.69 | 0.25 | 0.062 | 1.42 |
| 3 | Aug. 6 | 3 | 80.0 | 0.94 | 1.56 | 0.90 | 0.213 | 1.44 |
| 5 | Aug. 7 | 3 | 90.7 | 1.80 | 2.31 | 0.68 | 0.198 | 1.74 |
| 5 | Aug. 7 | 3 | 60.3 | 0.87 | 1.59 | 0.28 | 0.081 | 1.22 |
| 6 | Aug. 8 | 20 | 589.8 | 1.39 | 1.74 | 0.47 | 0.106 | 1.08 |
| 7 | Aug. 10 | 3 | 108.2 | 0.70 | 0.86 | 0.30 | 0.067 | 0.96 |
| 7 | Aug. 11 | 3 | 102.4 | ---- | 0.74 | 0.16 | 0.086 | 0.875 |
| 7 | Aug. 11 | 3 | 101.6 | 0.87 | 0.88 | 0.30 | 0.090 | 0.968 |
| 8 | Aug. 12 | 3 | 72.0 | 0.60 | 1.32 | 0.27 | 0.098 | 1.39 |
| 8 | Aug. 12 | 10 | 139.8 | 0.42 | 1.07 | 0.16 | ----- | 0.713 |
| 9 | Aug. 13 | 3 | 77.5 | 0.82 | 1.13 | 0.27 | 0.082 | 1.129 |
| 9 | Aug. 13 | 60 | 91.9 | 0.45 | 0.22 | 0.19 | 0.058 | .222 |
| 11 | Aug. 13 | 3 | 101.4 | 0.61 | 0.72 | 0.50 | 0.050 | .836 |
| 13 | Aug. 14 | 3 | 85.9 | 0.61 | 0.73 | 0.11 | 0.030 | .997 |
| 13 | Aug. 14 | 30 | 66.6 | 0.62 | 0.76 | 0.26 | 0.048 | .491 |
| 15 | Aug. 14 | 3 | 97.7 | 0.54 | 1.13 | 0.33 | 0.100 | 1.266 |
| 15 | Aug. 14 | 15 | 268.2 | ---- | 0.87 | 0.14 | 0.042 | 0.644 |
| 17 | Aug. 15 | 3 | 54.9 | ---- | 1.13 | 0.29 | 0.092 | 1.098 |
| 17 | Aug. 15 | 60 | 342.5 | 0.69 | 0.33 | ---- | 0.056 | 0.233 |
| 17 | Aug. 15 | 60 | 334.3 | 0.62 | 0.25 | ---- | 0.059 | 0.189 |
| 20 | Aug. 15 | 3 | 88.6 | 0.50 | 0.81 | 0.38 | 0.058 | 0.886 |
| 20 | Aug. 15 | 15 | 206.9 | 0.34 | 1.15 | 0.33 | 0.048 | 0.753 |
| 22 | Aug. 16 | 3 | 104.2 | 0.57 | 1.79 | 0.33 | 0.129 | 1.741 |

## TABLE 18
(cont'd)

| Station | Date(GMT) | Sonic Depth (Meters) | $CH_4$ | $C_2H_6$ | $C_2H_4$ | $C_3H_8$ | $C_4H_{10}$ | $C_3H_6$ |
|---|---|---|---|---|---|---|---|---|
| 22 | Aug. 16 | 60 | 294.0 | 0.34 | 0.31 | 0.25 | 0.101 | 0.143 |
| 25 | Aug. 16 | 3 | 81.7 | 1.57 | 0.85 | 0.39 | 0.084 | 0.793 |
| 25 | Aug. 16 | 15 | 1004.7 | 0.56 | 0.98 | 0.21 | 0.042 | 0.619 |
| 27 | Aug. 17 | 3 | 76.9 | 0.69 | 1.35 | 0.22 | 0.094 | 1.320 |
| 27 | Aug. 17 | 60 | 391.8 | 0.77 | 0.99 | 0.28 | 0.065 | 0.280 |
| 30 | Aug. 17 | 3 | 93.3 | 0.63 | 0.95 | 0.20 | 0.034 | 0.964 |
| 30 | Aug. 17 | 20 | 276.7 | 0.43 | 1.17 | 0.17 | 0.059 | 0.674 |
| 31 | Aug. 17 | 48 | 408.5 | 0.91 | 1.34 | 0.35 | 0.062 | 0.435 |
| 32 | Aug. 18 | 3 | 68.4 | 0.45 | 1.35 | 0.18 | 0.053 | 1.287 |
| 32 | Aug. 18 | 70 | 252.4 | 0.38 | 0.54 | 0.18 | 0.021 | 0.177 |
| 34 | Aug. 18 | 3 | 128.9 | 1.32 | 0.94 | 0.50 | 0.095 | 1.022 |
| 34 | Aug. 18 | 15 | 98.9 | 0.46 | 0.74 | 0.14 | 0.040 | 0.718 |
| 35 | Aug. 18 | 30 | 1151.2 | 1.34 | 1.53 | 0.38 | 0.057 | 0.566 |
| 36 | Aug. 19 | 3 | 82.2 | 1.32 | 1.69 | 0.35 | 0.163 | 1.648 |
| 36 | Aug. 19 | 60 | 399.3 | 0.51 | 0.88 | 0.31 | 0.059 | 0.251 |
| 37 | Aug. 19 | 3 | 156.2 | 0.75 | 1.45 | 0.21 | 0.080 | ----- |
| 38 | Aug. 20 | 3 | 159.0 | 1.48 | 0.88 | 0.46 | 0.109 | 1.125 |
| 38 | Aug. 20 | 13 | 482.0 | 1.05 | 0.97 | 0.30 | 0.069 | 0.665 |
| 41 | Aug. 20 | 3 | 78.9 | 0.99 | 1.42 | 0.43 | 0.114 | 1.413 |
| 41 | Aug. 20 | 55 | 76.4 | 0.55 | 0.20 | 0.20 | 0.032 | 0.260 |
| 43 | Aug. 21 | 3 | 84.1 | 0.48 | 0.97 | 0.26 | 0.057 | 0.990 |
| 43 | Aug. 21 | 15 | 352.3 | ---- | 0.60 | 0.25 | 0.094 | 0.484 |
| 45 | Aug. 21 | 3 | 102.1 | ---- | 4.14 | 0.89 | 0.169 | 3.554 |
| 45 | Aug. 21 | 145 | 241.4 | 0.81 | 0.72 | 0.33 | 0.064 | 0.343 |
| 47 | Aug. 22 | 3 | 87.7 | 0.85 | 2.24 | 0.45 | 0.145 | 2.410 |
| 48 | Aug. 23 | 3 | 85.5 | 0.93 | 1.87 | ---- | 0.181 | 2.499 |
| 48 | Aug. 23 | 25 | 222.8 | ---- | 1.04 | ---- | 0.091 | 0.573 |
| 48 | Aug. 23 | 15 | 294.0 | ---- | 1.50 | 0.87 | ----- | 0.884 |
| 48 | Aug. 23 | 25 | 185.0 | 0.46 | 1.92 | 0.83 | 0.066 | 1.126 |

### TABLE 18
### (cont'd)

| Station | Date(GMT) | Sonic Cepth (Meters) | $CH_4$ | $C_2H_6$ | $C_2H_4$ | $C_3H_8$ | $C_4H_{10}$ | $C_3H_6$ |
|---|---|---|---|---|---|---|---|---|
| 48 | Aug. 23 | 5 | 57.4 | 0.31 | .81 | 0.50 | 0.074 | 1.012 |
| 48 | Aug. 23 | 23 | 283.4 | 1.71 | 1.13 | 0.60 | 0.119 | 0.701 |
| 48 | Aug. 23 | 5 | 40.6 | 0.97 | .74 | 0.26 | ----- | 0.900 |
| 48 | Aug. 23 | 3 | 57.7 | 1.17 | 1.21 | 0.46 | 0.118 | 0.979 |

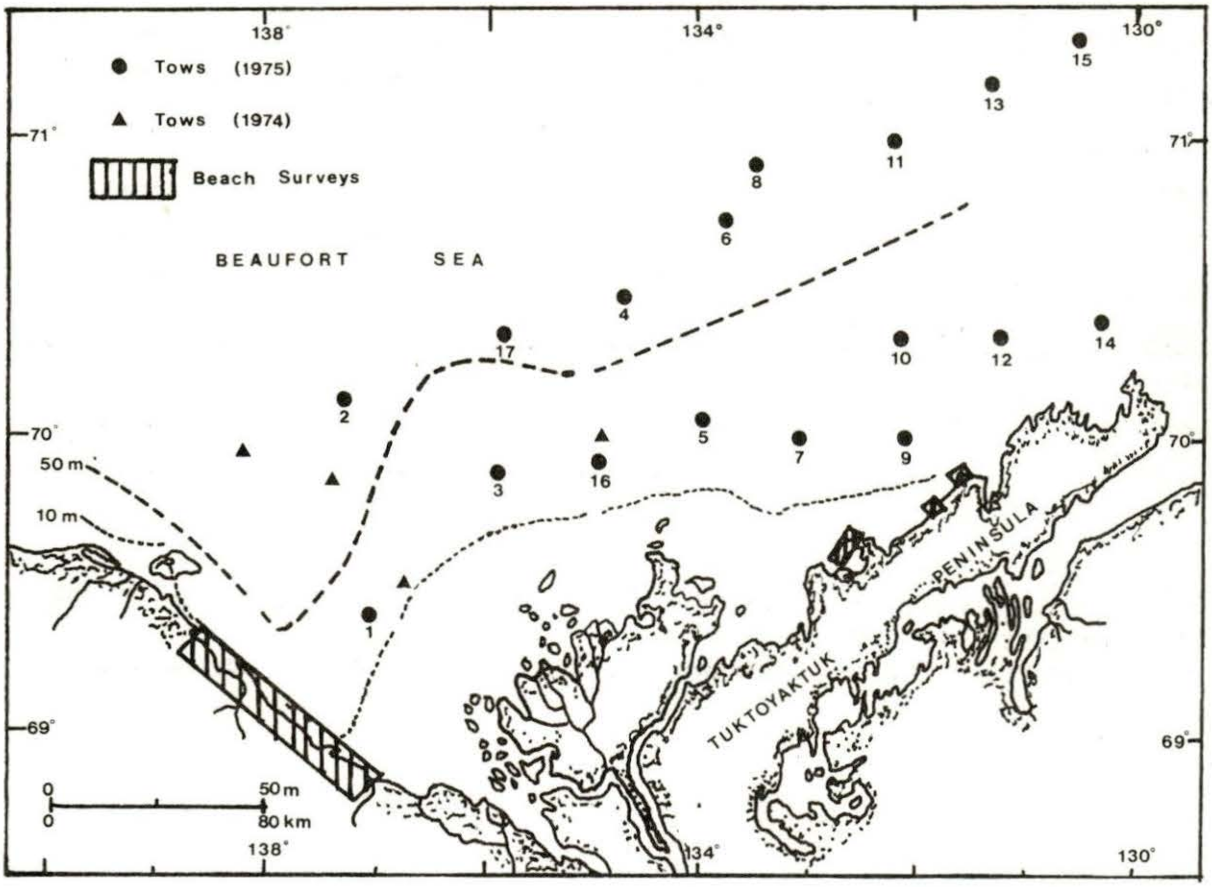


Figure 15. Locations of Neuston-net Tows for Surface Floating Tar and Plastics.

## TABLE 19.

### Non-polar Hydrocarbons in Southern Beaufort Sea Fish Samples

| Fish | Sample No. | Preserved State | Hydrocarbon Conc. (μg/g*) Unresolved | Total | % Unresolved |
|---|---|---|---|---|---|
| Arctic Cisco | 1 | Frozen | 1.37 | 4.03 | 34.1 |
| Arctic Cisco | 2 | Frozen | 0.67 | 2.76 | 24.3 |
| Arctic Cisco | 3 | Frozen | 1.36 | 2.03 | 66.5 |
| Arctic Cisco | 4 | Frozen | 1.20 | 3.27 | 37.0 |
| Least Cisco | 1 | Frozen | 0.60 | 1.98 | 30.1 |
| Least Cisco | 2 | Frozen | 1.46 | 4.9 | 30.0 |
| Least Cisco | 3 | Frozen | 1.82 | 7.8 | 23.4 |
| Arctic Cisco | F-14 | Formalin | 0.60 | 1.11 | 54.1 |
| Cisco** | F-13 | Formalin | 1.72 | 3.93 | 43.8 |
| Salmon[b] | 1 | Frozen | 0.14 | 0.90 | 15.5 |
| Tuna[b] | 1 | Frozen | 6.4 | 55.0 | 11.6 |

* Wet weight of fish flesh.

** This sample consisted of many small fingerlings. Identification of the type of Cisco was not made.

[b] Caught at Ocean Weather Station P and included for comparison purposes.

TABLE 20. Non-Polar Hydrocarbons in Southern Beaufort Sea Mixed Plankton

| Sample No. | Stn. No. | Depth (m) | Major Phytoplankton | $10^3$[a] cells/$m^3$ | Major Zooplankton | No./$m^3$[a] | Hydrocarbon Conc. Wet ($\mu g/g$) Total | Hydrocarbon Conc. Wet ($\mu g/g$) Unres. | Hydrocarbon Conc. Dry ($\mu g/g$) Total | Hydrocarbon Conc. Dry ($\mu g/g$) Unres. |
|---|---|---|---|---|---|---|---|---|---|---|
| 3 | 09 | 13 | *Ch. Wighami* | 543.5 | *Limnocalanus grimaldii* | 0.05 | 10.1 | 5.8 | 0.64 | 0.36 |
| | | | *Thalassiosira decipiens* | 34.1 | *Calanus fiamarchieus* | 0.05 | | | | |
| 9 | 15 | 6 | *Chaetoceros* | 172.4 | *Limnocalanus grimaldi* | 1.07 | 3.4 | 2.2 | 0.15 | 0.09 |
| | | | *Th. nordenskioldii* | 649 | *Spiratella helicina* | 0.13 | | | | |
| 10 | 17 | 3 | *Nitzschia* sp | 0.3 | | 0.00 | 11.4 | 7.3 | n.d. | n.d. |
| 11 | 17 | 10 | *N. seriata* | 10.0 | *P. libellula* | 0.04 | 1.5 | 1.4 | 0.18 | 0.16 |
| | | | *Ch. constrictus* | 7.2 | | | | | | |
| 12 | 17 | 20 | *Ch. constrictus* | 145.8 | *Calanus finmarchicus* + *C. hyperboreus* | 4.33 | 9.1 | n.d. | 0.57 | n.d. |
| | | | *N. Seriata* | 22.4 | | | | | | |
| 13 | 17 | 30 | *Ch. constrictus* | 47.3 | *Calanus finmarchicus* + *C. hyperboreus* | 55.10 | 203.0 | 5.4 | 2.88 | 0.05 |
| | | | *N. Seriata* | 12.0 | *P. libellula* | 0.08 | | | | |
| 16 | 22 | 20 | *Ch. constrictus* | 6.0 | *Calanus finmarchicus* + *C. hyperboreus* | 1.73 | 1.6 | 0.5 | n.d. | n.d. |
| | | | *Ch. convolutus* | | | | | | | |
| 17 | 22 | 30 | *Chaetoceros* sp | 11.2 | *Calanus finmarchicus* + *C. hyperboreus* | 2.77 | 7.4 | n.d. | 0.32 | n.d. |
| | | | *N. Seriata* | 5.6 | | | | | | |

TABLE 20. (Continued)

| Sample No. | Stn. No. | Depth (m) | Major Phytoplankton | $10^3$cells/$m^3$ [a] | Major Zooplankton | No./$m^3$ [a] | Hydrocarbon Conc. Wet (μg/g) Total | Unres. | Dry (μg/g) Total | Unres. |
|---|---|---|---|---|---|---|---|---|---|---|
| 21 | 27 | 20 | *N. Seriata*<br>*Ch. constrictus* | 320.2<br>101.8 | *Spiratella helicina* | 0.20 | 2.8 | 1.9 | 0.10 | 0.07 |
| 22 | 27 | 30 | *Ch. constructus*<br>*N. Seriata* | 220.3<br>92.6 | *Calanus finmarchicus* + *C. hyperboreus* | 3.58 | 20.3 | 2.0 | n.d | n.d |
| 24 | 30 | 20 | n.d | n.d | n.d | n.d | 3.7 | 3.1 | 0.37 | 0.32 |
| 25 | 32 | 20 | *N. Seriata*<br>*Ch. constrictus* | 350.9<br>95.9 | *P. Lebellula* | 0.06 | 1.8 | 1.3 | 0.10 | 0.07 |
| 26 | 32 | 40 | *Fragilariopsis* sp.<br>*Th. nordenskioldii* | 133.9<br>63.2 | *Calanus finmarchicus* + *C. hyperboreus* | 13.96 | 187.0 | n.d. | 6.06 | n.d. |
| 27 | 34 | 6 | *Fragilariopsis* sp.<br>*Melosira* sp. | 0.2<br>0.1 |  | 0.00 | 7.6 | 4.1 | 0.65 | 0.38 |
| 33 | 43 | 2 | n.d. | n.d. | *Limnocalanus grimaldii*<br>*Eurytemora herdmani* | n.d.<br>n.d. | 15.8 | 6.8 | 0.46 | 0.13 |

[a] No. of the specified cells or organisms obtained on the average from each cubic meter of water swept through the plankton net.

## TABLE 21

Non-polar Hydrocarbons in Southern Beaufort Sea Sediments
(1974 Cruise)

| | Sediment No.<br>Station No. | 3<br>11 | 6<br>17 | 7<br>19 | 8<br>20 | 10<br>23 | 11<br>25 | 12<br>28 |
|---|---|---|---|---|---|---|---|---|
| Paraffins | $n\text{-}C_{17}$ | 1.03[a] | 0.29 | 0.44 | 0.72 | 0.17 | 0.66 | 0.74 |
| | $n\text{-}C_{18}$ | 1.05 | 0.40 | 0.49 | 0.66 | 0.32 | 0.81 | 0.74 |
| | $n\text{-}C_{19}$ | 1.13 | 0.60 | 1.56 | 1.42 | 0.44 | 0.97 | 0.75 |
| | $n\text{-}C_{20}$ | 0.95 | 0.49 | 0.50 | 0.82 | 0.36 | 0.82 | 0.63 |
| | $n\text{-}C_{21}$ | 1.20 | 0.79 | 0.69 | 1.61 | 0.54 | 1.20 | 0.71 |
| | $n\text{-}C_{22}$ | 0.86 | 0.59 | 0.51 | 0.55 | 0.37 | 0.93 | 0.58 |
| | $n\text{-}C_{23}$ | 1.07 | 0.99 | 0.71 | 0.71 | 0.54 | 1.43 | 0.74 |
| | $n\text{-}C_{24}$ | 0.59 | 0.51 | 0.41 | 0.26 | 0.28 | 0.78 | 0.47 |
| | $n\text{-}C_{25}$ | 0.98 | 1.20 | 0.75 | 0.82 | 0.93 | 1.66 | 0.77 |
| | $n\text{-}C_{26}$ | 0.91 | 0.43 | 0.31 | 0.17 | 0.22 | 0.63 | 0.37 |
| | $n\text{-}C_{27}$ | 1.06 | 1.72 | 1.03 | 0.50 | 1.03 | 2.14 | 1.06 |
| | $n\text{-}C_{28}$ | 0.30 | 0.35 | 0.23 | 0.17 | 0.21 | 0.49 | 0.25 |
| | $n\text{-}C_{29}$ | 1.18 | 2.11 | 1.17 | 0.61 | 1.17 | 2.43 | 0.86 |
| | $n\text{-}C_{30}$ | 0.17 | 0.20 | 0.15 | 0.07 | 0.13 | 0.28 | 0.14 |
| | $n\text{-}C_{31}$ | 1.02 | 1.94 | 1.01 | 1.07 | 1.20 | 1.89 | 0.68 |
| | $n\text{-}C_{32}$ | 0.13 | 0.10 | 0.08 | 0.10 | 0.06 | 0.07 | 0.11 |
| | pristane | 1.00 | 0.29 | 0.44 | 2.79 | 0.15 | 0.63 | 0.73 |
| | phytane | 0.66 | 0.23 | 0.31 | 0.57 | 0.20 | 0.48 | 0.51 |
| | $\Sigma$n-paraffins | 13.1 | 12.7 | 9.1 | 10.3 | 8.0 | 17.2 | 9.6 |
| | unresolved hydrocarbons | 78.9 | 42.1 | 38.4 | 126.1 | 34.8 | 71.4 | 37.9 |
| | total hydrocarbons | 93.7 | 55.3 | 48.3 | 137.7 | 43.2 | 89.7 | 48.7 |
| | pristane/ phytane | 1.51 | 1.26 | 1.41 | 1.39 | 0.75 | 1.31 | 1.42 |
| Ratios | $n\text{-}C_{17}$/ pristane | 1.03 | 1.00 | 1.00 | 0.91 | 1.13 | 1.05 | 1.01 |
| | $n\text{-}C_{18}$/ phytane | 1.59 | 1.74 | 1.58 | 1.16 | 1.60 | 1.69 | 1.45 |

[a] All numbers except ratios are in units of μg/g (dry weight).

Table 21 (cont'd)

| | Sediment No. | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
|---|---|---|---|---|---|---|---|---|
| | Station No. | 35 | 41 | 42 | 44 | 48 | 58 | 60 |
| Parrafins | n-$C_{17}$ | 0.51 | 0.77 | 0.72 | 0.82 | 0.01 | 1.42 | 0.39 |
| | n-$C_{18}$ | 0.85 | 1.24 | 0.73 | 0.88 | 0.07 | 1.46 | 0.53 |
| | n-$C_{19}$ | 1.09 | 1.33 | 0.76 | 1.22 | 0.19 | 1.70 | 0.60 |
| | n-$C_{20}$ | 1.00 | 1.15 | 0.65 | 1.12 | 0.17 | 1.33 | 0.52 |
| | n-$C_{21}$ | 1.11 | 1.30 | 0.72 | 1.11 | 0.24 | 1.62 | 0.61 |
| | n-$C_{22}$ | 0.97 | 1.10 | 0.60 | 0.89 | 0.17 | 1.17 | 0.48 |
| | n-$C_{23}$ | 1.12 | 1.28 | 0.70 | 1.05 | 0.22 | 1.38 | 0.61 |
| | n-$C_{24}$ | 0.78 | 0.81 | 0.49 | 0.61 | 0.14 | 0.89 | 0.38 |
| | n-$C_{25}$ | 1.12 | 1.26 | 0.71 | 0.93 | 0.26 | 1.37 | 0.57 |
| | n-$C_{26}$ | 0.59 | 0.62 | 0.39 | 0.42 | 0.11 | 0.71 | 0.29 |
| | n-$C_{27}$ | 1.40 | 1.55 | 0.87 | 0.99 | 0.27 | 1.44 | 0.66 |
| | n-$C_{28}$ | 0.44 | 0.39 | 0.27 | 0.28 | 0.10 | 0.50 | 0.20 |
| | n-$C_{29}$ | 1.15 | 1.17 | 0.78 | 0.77 | 0.20 | 1.42 | 0.72 |
| | n-$C_{30}$ | 0.20 | 0.20 | 0.18 | 0.13 | 0.09 | 0.35 | 0.13 |
| | n-$C_{31}$ | 0.81 | 0.85 | 0.53 | 0.64 | 0.22 | 1.03 | 0.56 |
| | n-$C_{32}$ | 0.14 | 0.16 | 0.10 | 0.00 | 0.03 | 0.17 | 0.07 |
| | pristane | 0.53 | 0.70 | 0.70 | 0.84 | 0.01 | 1.53 | 0.35 |
| | phytane | 0.56 | 0.82 | 0.50 | 1.63 | 0.03 | 0.91 | 0.20 |
| | $\Sigma$n-paraffins | 13.3 | 15.2 | 9.2 | 11.9 | 2.6 | 18.0 | 7.3 |
| | unresolved hydrocarbons | 97.6 | 82.9 | 52.8 | 150.3 | 15.8 | 116.1 | 35.7 |
| | total hydrocarbons | 112.0 | 99.6 | 63.3 | 163.6 | 18.4 | 136.7 | 43.7 |
| Ratios | pristane/ phytane | 0.94 | 0.86 | 1.40 | 1.35 | 0.37 | 1.68 | 1.17 |
| | n-$C_{17}$/ pristane | 0.96 | 1.10 | 1.03 | 0.98 | 1.00 | 0.93 | 1.11 |
| | n-$C_{18}$/ phytane | 1.52 | 1.51 | 1.46 | 1.40 | 2.30 | 1.60 | 1.77 |

TABLE 22. Non-polar Hydrocarbons in Southern Beaufort Sea Sediments (1975 Cruise).

| | Sediment No.<br>Station No. | 1<br>08 | 2<br>09 | 4<br>13 | 8<br>22 | 10<br>27 | 11<br>30 | 14<br>36 | 15<br>38 |
|---|---|---|---|---|---|---|---|---|---|
| Paraffins | n-$C_{17}$ | 0.93[a] | 0.91 | 0.85 | 0.60 | 0.27 | 0.81 | 0.39 | 0.71 |
| | n-$C_{18}$ | 0.95 | 0.85 | 0.89 | 0.61 | 0.37 | 0.61 | 0.35 | 0.69 |
| | n-$C_{19}$ | 0.98 | 0.86 | 1.02 | 0.76 | 0.53 | 0.77 | 0.65 | 0.69 |
| | n-$C_{20}$ | 0.84 | 0.71 | 0.75 | 0.54 | 0.37 | 0.62 | 0.33 | 0.54 |
| | n-$C_{21}$ | 0.89 | 0.79 | 0.91 | 0.68 | 0.49 | 0.68 | 0.51 | 0.60 |
| | n-$C_{22}$ | 0.79 | 0.62 | 0.67 | 0.48 | 0.35 | 0.52 | 0.35 | 0.51 |
| | n-$C_{23}$ | 0.90 | 0.80 | 0.77 | 0.58 | 0.42 | 0.67 | 0.40 | 0.63 |
| | n-$C_{24}$ | 0.61 | 0.52 | 0.54 | 0.40 | 0.28 | 0.45 | 0.26 | 0.41 |
| | n-$C_{25}$ | 0.89 | 0.86 | 0.86 | 0.67 | 0.53 | 0.70 | 0.51 | 0.66 |
| | n-$C_{26}$ | 0.50 | 0.43 | 0.46 | 0.33 | 0.25 | 0.36 | 0.23 | 0.33 |
| | n-$C_{27}$ | 1.12 | 1.03 | 0.89 | 0.74 | 0.57 | 0.88 | 0.62 | 0.91 |
| | n-$C_{28}$ | 0.36 | 0.34 | 0.32 | 0.26 | 0.19 | 0.34 | 0.38 | 0.23 |
| | n-$C_{29}$ | 0.93 | 1.16 | 0.96 | 0.85 | 0.65 | 0.73 | 0.81 | 1.72 |
| | n-$C_{30}$ | 0.19 | 0.23 | 0.28 | 0.21 | 0.16 | 0.15 | 0.41 | 0.13 |
| | n-$C_{31}$ | 0.70 | 0.89 | 0.69 | 0.36 | 0.51 | 0.55 | 0.57 | 0.51 |
| | n-$C_{32}$ | 0.15 | 0.11 | 0.10 | 0.07 | 0.06 | 0.10 | 0.34 | 0.07 |
| | pristane | 0.95 | 0.89 | 0.92 | 0.70 | 0.29 | 0.70 | 0.47 | 0.67 |
| | phytane | 0.63 | 0.52 | 0.47 | 0.35 | 0.23 | 0.59 | 0.11 | 0.45 |
| | $\Sigma$n-paraffins | 11.8 | 11.1 | 10.9 | 8.1 | 6.0 | 8.9 | 7.1 | 8.4 |
| | unresolved hydrocarbons | 66.1 | 58.0 | 68.2 | 56.1 | 41.7 | 48.2 | 38.1 | 54.7 |
| | total hydrocarbons | 79.5 | 70.5 | 80.4 | 62.3 | 48.3 | 58.5 | 45.9 | 64.1 |
| Ratios | pristane/ phytane | 1.51 | 1.69 | 1.96 | 1.98 | 1.26 | 1.29 | 3.97 | 1.50 |
| | n-$C_{17}$/ pristane | 0.97 | 1.02 | 1.00 | 0.85 | 0.93 | 1.07 | 0.83 | 1.05 |
| | n-$C_{18}$/ phytane | 1.51 | 1.63 | 1.89 | 1.74 | 1.61 | 1.69 | 3.18 | 1.53 |

---

[a] All numbers except ratios are in units of μg/g (dry weight).

Table 22 (cont'd)

| | Sediment No.<br>Station No. | 16<br>41 | 17<br>42 | 18<br>43 | 19<br>44 | 20<br>45 | 21<br>46 | 22<br>47 |
|---|---|---|---|---|---|---|---|---|
| Paraffins | n-$C_{17}$ | 0.37 | 1.26 | 2.80 | 1.61 | 0.31 | 0.39 | 1.09 |
| | n-$C_{18}$ | 0.48 | 1.72 | 2.99 | 1.20 | 0.33 | 0.43 | 0.88 |
| | n-$C_{19}$ | 0.57 | 2.16 | 2.23 | 1.23 | 0.40 | 0.55 | 0.88 |
| | n-$C_{20}$ | 0.48 | 1.69 | 1.79 | 0.67 | 0.35 | 0.44 | 0.71 |
| | n-$C_{21}$ | 0.56 | 1.81 | 1.55 | 0.60 | 0.49 | 0.57 | 1.01 |
| | n-$C_{22}$ | 0.43 | 1.43 | 1.37 | 0.45 | 0.39 | 0.45 | 0.67 |
| | n-$C_{23}$ | 0.48 | 1.61 | 1.69 | 0.43 | 0.59 | 0.63 | 1.00 |
| | n-$C_{24}$ | 0.32 | 0.93 | 1.03 | 0.25 | 0.34 | 0.39 | 0.51 |
| | n-$C_{25}$ | 0.50 | 1.45 | 1.64 | 0.44 | 0.72 | 0.71 | 1.28 |
| | n-$C_{26}$ | 0.25 | 0.71 | 0.85 | 0.19 | 0.29 | 0.31 | 0.47 |
| | n-$C_{27}$ | 0.54 | 1.26 | 1.91 | 0.47 | 0.99 | 0.99 | 2.22 |
| | n-$C_{28}$ | 0.19 | 0.33 | 0.59 | 0.11 | 0.23 | 0.26 | 0.35 |
| | n-$C_{29}$ | 0.57 | 0.94 | 1.59 | 0.33 | 1.27 | 1.21 | 1.74 |
| | n-$C_{30}$ | 0.13 | 0.23 | 0.32 | 0.04 | 0.15 | 0.17 | 0.20 |
| | n-$C_{31}$ | 0.47 | 0.56 | 1.21 | 0.31 | 1.07 | 0.98 | 0.98 |
| | n-$C_{32}$ | 0.09 | 0.15 | 0.23 | 0.06 | 0.08 | 0.08 | 0.08 |
| | pristane | 0.46 | 1.33 | 3.07 | 1.52 | 0.34 | 0.47 | 1.39 |
| | phytane | 0.32 | 1.19 | 1.57 | 0.91 | 0.21 | 0.31 | 0.59 |
| | Σn-paraffins | 6.5 | 18.4 | 23.6 | 8.5 | 8.0 | 8.6 | 14.8 |
| | unresolved hydrocarbons | 43.1 | 65.2 | 54.5 | 98.3 | 28.3 | 36.5 | 59.6 |
| | total hydrocarbons | 50.3 | 86.1 | 82.7 | 109.1 | 36.9 | 45.9 | 76.2 |
| Ratios | pristane/ phytane | 1.43 | 1.13 | 1.95 | 1.66 | 1.61 | 1.51 | 2.31 |
| | n-$C_{17}$/ pristane | 0.80 | 0.91 | 0.91 | 1.05 | 0.97 | 0.83 | 0.84 |
| | n-$C_{18}$/ phytane | 1.50 | 1.42 | 1.59 | 1.31 | 1.51 | 1.39 | 1.48 |

of getting the right number and types of samples to produce a meaningful evaluation of the state of the environment. For this study, sampling methods, chemical detecting techniques and cleanliness of the analytical laboratory have all had to be pushed to the limits of the state of the art.

To establish the present levels of petroleum hydrocarbons for an assessment of the future change resulting from drilling activities, some chemical indicators of environmental contamination with respect to petroleum have to be established. Certain criteria are necessary in order to complete the program within the time and resources constraints imposed by the situation:

(1) They must be measureable by existing chemical techniques with minimum modification of the procedures.

(2) Reliable sampling techniques should be available for these indicators.

(3) Their distributions should be definitive in tracking down future environmental changes by petroleum contamination, should it happen.

The indicators thus selected are low-molecular weight hydrocarbons, in particular methane ($CH_4$), ethane ($C_2H_6$), propane ($C_3H_8$) and benzene ($C_6H_6$) in sea water, aliphatic hydrocarbons in sea water, and polycyclic aromatic hydrocarbons (PAH), in particular chrysene, pyrene, benzanthracene, benzpyrene and perylene, in sea water, marine organisms and surface sediments. Interpretation of the results obtained is not simple since some of these compounds have to be measured, not as a single chemical, but as a group of compounds, due to limitations of the separation or detection techniques. The variability of natural hydrocarbons poses another obstacle. Some of these compounds may be present both in petroleum and in the natural marine environment and some may interfere with the chemical detecting technique for petroleum hydrocarbons. Thus, great care has to be exerted in deriving any conclusion on the present baseline levels.

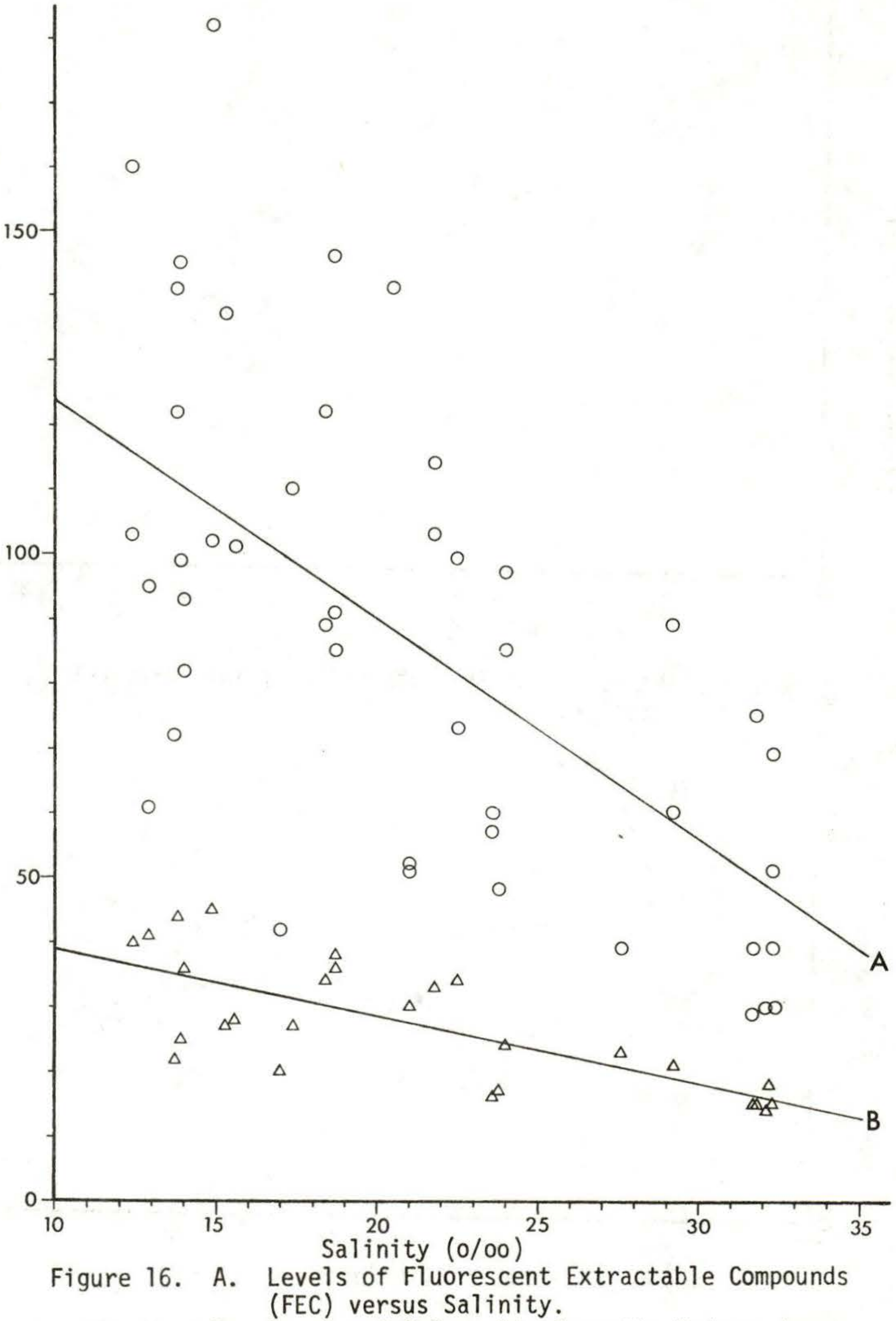
## 7.1 PAH in the Marine Environment

PAH has significant implication for petroleum pollution. It has been established to be carcinogenic (ZoBell, 1971; Andelman and Snodgrass, 1974). In crude oil, PAH usually occurs in quantities much less than 0.1% but on pyrolysis, its quantities can be increased greatly. Benzpyrene (BP) is the commonly measured PAH and the background value is of the order 10-100 ng BP/l in surface freshwater in remote areas (Il'nitskii et al., 1971). In sea water, PAH may come from petroleum pollution as well as from natural sources. It is a pyrolysis product of organic compounds; e.g., from the fuel combustion in heating, transport or industrial machinery. In nature, PAH may be synthesized by plants, bacteria, soil micro-organisms and phytoplanktons. In a special situation, such as the Clipperton Atoll Lagoon, which is a small closed system with high productivity, up to 4000 ng BP/l was observed due to accumulation of minute production of BP by phytoplankton and bacteria. The level and fate of PAH in the marine environment and especially in the Arctic has not been fully studied.

## 7.2 PAH in Sea Water

As discussed earlier in 5.3.1, the fluorescent extractable compounds (FEC) in sea water may be a combination of both PAH and non-PAH compounds. The levels of FEC in the Southern Beaufort Sea, as shown in Figure 16A, vary between 28 ng/l and 184 ng/l, expressed in chrysene equivalents. The concentrations of PAH, as shown in Figure 16B, vary between 14 ng/l and 45 ng/l. Both the PAH and FEC in sea water vary inversely with salinity showing high values at low salinities and vice versa. PAH accounts for about one-third of the fluorescence in the material extracted from sea water by methylene chloride, as indicated in Figure 16. A similar relationship was observed in sea water at ocean weathership station "P" (50°N, 145°W) in the Northeastern Pacific Ocean (Cretney and Wong, 1974), where 39 ng/l of FEC and 16 ng/l of PAH were found in the surface sea water of salinity 32$^{o}$/oo. For the deeper shelf water in Southern Beaufort Sea with salinity close to 32$^{o}$/oo, FEC amounts to an average of 50 ng/l and PAH 16 ng/l. The variation of PAH with salinity for nearshore stations is shown in Figure 17 and for offshore stations in Figure 18. PAH in nearshore waters shows much greater fluctuations than in the deeper offshore waters. The deeper shelf water with maximum salinity is oceanic in origin while the shallower waters with higher PAH or FEC are influenced by freshwater from the Mackenzie River. The deeper waters appear to have a minimum PAH burden at a level of about 16 ng/l in common with levels in surface waters at ocean weather station P in an area considered to be cleanest in the Pacific Ocean (Wong et al., 1976, in press). Future measurements of PAH in the deeper shelf waters of the Southern Beaufort Sea should provide a good chance of observing environmental changes resulting from drilling activities because of the more pristine state in the deeper waters relative to the surface waters which have wide fluctuations in PAH due to the Mackenzie River input.

The inverse relationship between PAH or FEC with salinity cannot be explained by the possibility of a small chemical extraction efficiency of PAH from sea water at higher salinity. Indeed, due to a "salting out" effect, the chemical extraction efficiency of non-polar materials such as PAH should increase with increasing ionic strength; i.e., with increasing salinity.



Salinity (o/oo)

Figure 16. A. Levels of Fluorescent Extractable Compounds (FEC) versus Salinity.
B. Levels of Polycyclic Aromatic Hydrocarbons (PAH) versus Salinity.

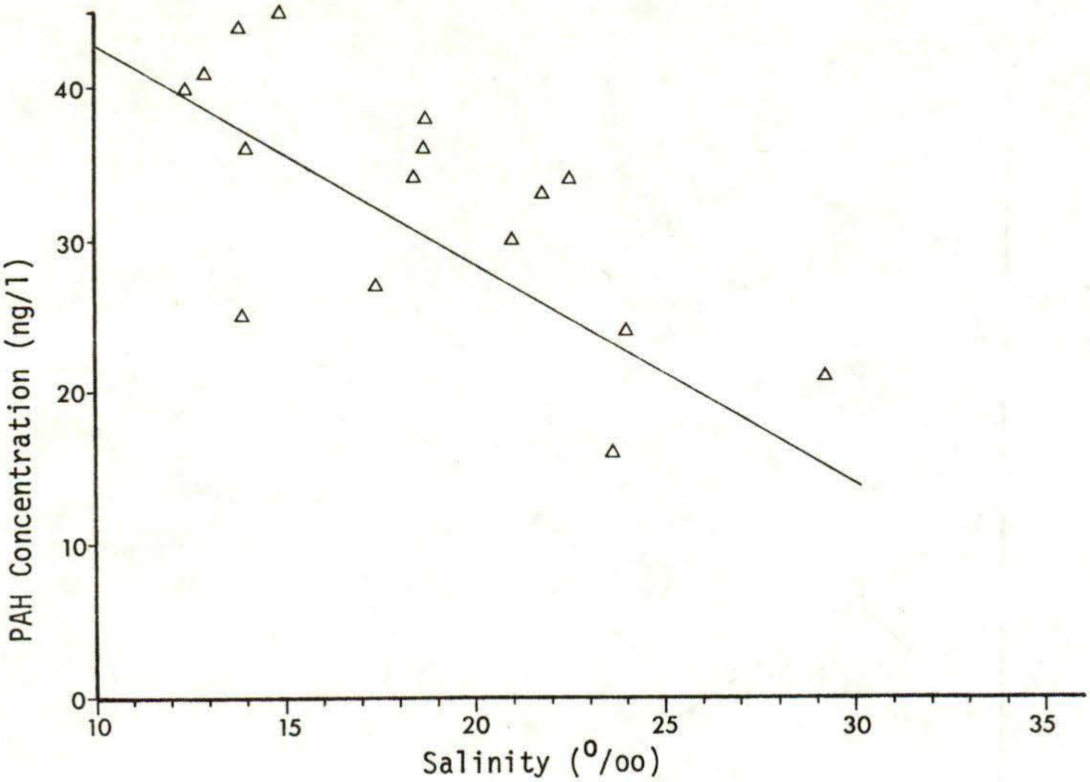


Figure 17. Variation of PAH with Salinity for Nearshore Stations.

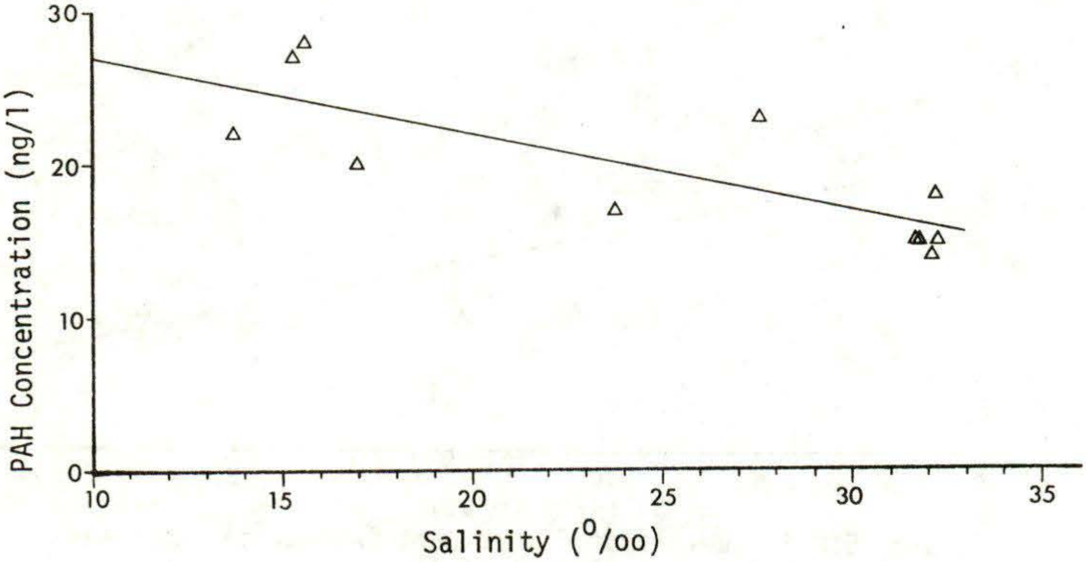


Figure 18. Variation of PAH with Salinity for Offshore Stations.

In the observations, however, the lower salinity waters have a higher burden of FEC or PAH than the more saline waters.

The occurrence of higher FEC or PAH in sea water with lower salinity can be attributed to several reasons: (i) supply of FEC and/or PAH from terrestrial sources, being carried into the Southern Beaufort Sea by Mackenzie River, (ii) in-situ production of FEC and/or PAH by marine organisms, (iii) atmospheric input from smokes produced by forest fires and underground combustion, such as in the Smoking Hills area east of the Tuktoyaktuk Peninsula, (iv) more rapid exchange of FEC and/or PAH with surface sediment in shallower waters.

The first source of FEC and/or PAH from terrestrial contributions via Mackenzie River was indicated by some qualitative evidence. Studies of the hydrocarbons in the sediments of the Southern Beaufort Sea (Peake et al., 1972; Wong et al., unpublished data) show the presence of paraffinic hydrocarbons of terrestrial plant origin brought to the shelf area by the Mackenzie River. Production of PAH by plants and microorganisms was observed in pristine, non-industrial and terrestrial areas, further confirmed by laboratory experiments (Borneff et al., 1968) and in forest soils (Mallet and Tissler, 1970). The drainage basins of the Mackenzie River through forested land and tundra soil could contribute greatly to the natural hydrocarbons as FEC or PAH. Mackenzie River also flows through regions with known fossil fuel deposits such as the Athabasca tar sand region and Norman Well natural seepage area. However, pending further study of the river burden of petroleum hydrocarbons or FEC, the magnitude of the river input of FEC and/or PAH cannot be assessed.

The second source is production by marine phytoplankton and bacteria. Bacterial production of PAH was summarized in detail by ZoBell (1971). Production of benz[a]pyrene by marine phytoplankton cultivated in vitro was observed by Niaussat, Mallet and Ottenwaelder (1969). BP was found in the Atlantic phytoplankton and in the Greenland to Gascony Gulf regions (De Lima-Zanghi, 1968) and in a tropical atoll in the Pacific Ocean (Mallet, 1971). The occurrence of the high level up to 4000 ng BP/l in a remote marine environment away from industrial source suggested natural production of PAH compounds and this was confirmed to be biosynthesized (Niaussat, 1970; Nuaussat, Ehrhardt and Ottenwaelder,1968; and Niaussat, Mallet and Ottenwaelder, 1969). However, this lagoon was essentially a closed system with high organic production due to high temperatures in the tropics. In the cold Southern Beaufort Sea shelf waters, the productivity is considered to be low and the system is open. Thus, although no quantitative data is available, it is suggested that the in-situ production of PAH and/or FEC is unlikely to be significant in a cold and unproductive environment.

The third source is the production by the pyrolysis of natural or industrial carbon compounds. The combustion of fossil fuels, refuse and industrial organic compounds may lead to PAH production (ZoBell, 1971; Andelman and Snodgrass, 1974). Combustion yields about 675 μg PAH/kg of gasoline (Hoffman and Wynder, 1968). Burning of fuel oil and crude oil produces variable amounts of PAH with an average of about 1000 μg BaP/kg of crude oil (ZoBell, 1971). Since existing traffic in the Southern Beaufort Sea is light and the population small, present anthropogenic input from fuel combustion is probably insignificant. The other pyrolytic source is forest fires or grass fires, possibly at a rate of 0.165-570 μg B[a]P/kg of organic carbon burned (ZoBell, 1971). In 1975, forest fires in the Yukon and N.W.T. have devastated 1,377,170 acres of vegetation (J. Lee, private communication). Based on a figure of 9 kg C/m$^2$ of plant biomass for a boreal forest (Whittaker and Likens, 1973) and an assumption of 0.02 g B[a]P/ton of coal burned (ZoBell, 1971) about 50 kg of B[a]P would be produced per year. Assuming a BaP to PAH ratio of 1:10, the total PAH is about 500 kg/year. The shelf waters of the Southern Beaufort Sea, based on an ice-free area of 105,000 km$^2$ in 1975 (Marko, private communication) have a volume of $5 \times 10^{15}$ litres. Taking an uppper limit of $10^{-7}$ g PAH/kg of sea water in Beaufort Sea, PAH amounts to $5 \times 10^8$ g or $5 \times 10^5$ kg. Thus, PAH produced by forest fire is hardly a significant contribution. Underground combustion has an unknown magnitude of PAH contribution, but if leakage into the atmosphere is insignificant, it is not expected to be a major budget term.

The last source, exchange with surface marine sediment in shallower waters, is unlikely to be large. In fact, clays tend to remove hydrocarbons from sea water (Meyers, 1972) and shallow surface sediments would more likely be a sink, rather than a source, for PAH.

## 7.3 Polycyclic Aromatic Hydrocarbons in Marine Organisms

A total of seven fish samples from the Southern Beaufort Sea area are shown in Table 13. The data are reported on a wet weight basis for the flesh of a frozen sample with the skin, bones and guts discarded. Formalin-preserved samples seemed to have leaching problems and were discarded. A comparison of the general range of PAH in the Southern Beaufort Sea fish and PAH or BP values for marine organisms obtained in other parts of the world is made in Table 23.

The PAH levels of $178^+$, $202^+$, $276^+$ and total PAH (defined as the sum of the four numbers) for the fish samples in the Southern Beaufort Sea appear to be less than or comparable to the values for samples in the N. E. Pacific Ocean, generally

## TABLE 23

PAH Levels in Marine Organisms

| Organisms | Area or State of Pollution | PAH Levels(μg/kg in wet weight) | | | | Total PAH | BP (μg/kg) | No.2 Fuel Oil (μg/kg) | Bunker C (μg/kg) |
|---|---|---|---|---|---|---|---|---|---|
| | | $178^+$ | $202^+$ | $228^+$ | $252^+$ | | | | |
| Fish | | | | | | | | | |
| Pomfret[a] | S. Beaufort Sea | | 1 | 5 | 3 | 9 | | | |
| Least Cisco #20[a] | S. Beaufort Sea | 8 | 4 | 4 | 3 | 19 | | | |
| Least Cisco # 1[a] | S. Beaufort Sea | 15 | 4 | 4 | 3 | 26 | | | |
| Least Cisco # 2[a] | S. Beaufort Sea | 4 | 1 | 3 | 18 | 26 | | | |
| Arctic Cisco # 1[a] | S. Beaufort Sea | 7 | 2 | 10 | 12 | 31 | | | |
| Arctic Cisco # 2[a] | S. Beaufort Sea | 8 | 2 | 2 | 2 | 14 | | | |
| Salmon # 1[a] | Stn. P, N.E. Pacific | 37 | 6 | 19 | 20 | 82 | | | |
| Salmon # 2[a] | Stn. P, N.E. Pacific | 9 | 3 | 7 | 1 | 20 | | | |
| Tuna # 1[a] | Stn. P, N.E. Pacific | 41 | 4 | 103 | 36 | 184 | | | |
| Cod[b] | Greenland Waters | | | | | | 15 | | |
| Fundulus, minnow[c] | Single Spill | | | | | | | 75,000 | |
| Anguilla liver, eel[c] | Single Spill | | | | | | | 85,000 | |
| Smelt[c] | Chronic Harbour Poll. | | | | | | 0-5,000* | | |
| Fish & Shell Fish[b] | French Coast | | | | | | 3-155 | | |
| Fish & Crustaceans[b] | French Coast | | | | | | 0-400 | | |
| Fish various[b] | Adriatic Coast, Italy | | | | | | 0-900 | | |
| Sardines[b] | Bay of Naples | | | | | | 65 | | |
| Oysters - Sample #1[a] | Vancouver Island | 20 | 43 | 26 | 17 | 123 | | | |
| Sample # 2[a] | Vancouver Island | 23 | 30 | 57 | 44 | 154 | | | |
| Sample # 3[a] | Vancouver Island | 18 | 26 | 46 | 57 | 147 | | | |
| Oysters - Commercial[b] | French Coast | | | | | | 1-70 | | |
| Crassostrea[c] | Chronic Poll. | | | | | | | 1,000 | |
| Oysters[b] | France, Atlantic Coast | | | | | | 0.4-3.5** | | |
| Oysters[b] | France, Channel Coast | | | | | | 70-112 | | |
| Mussels | | | | | | | | | |
| Modiolus[c] | Single spill | | | | | | 218,000 | | |
| Mytilus[c] | Single spill | | | | | | | | 74,000-100,000 |
| Mussels[b] | Greenland | | | | | | 18-55 | | |
| Mussels[b] | Bay of Naples | | | | | | 11-540 | | |

Table 23 (Cont'd) PAH Levels in Marine Organisms

| Organisms | Area or State of Pollution | PAH Levels(μg/kg in wet weight) | | | | Total PAH | BP (μg/kg) | No. 2 Fuel Oil (μg/kg) | Bunker C (μg/kg) |
|---|---|---|---|---|---|---|---|---|---|
| | | $178^+$ | $202^+$ | $228^+$ | $252^+$ | | | | |
| Clam | | | | | | | | | |
| Mya[c] | Single Spill | | | | | | | 26,000 | |
| Snail | | | | | | | | | |
| Littorina[c] | Single Spill | | | | | | | | 46,000-220,000 |
| Mulluscs[b] | Bay of Naples | | | | | | 2.4 | | |
| Mulluscs[b] | Greenland Waters | | | | | | 60 | | |
| Crustacean[b] | Arctic Ocean | | | | | | 0-230 | | |
| Shrimp, molluscs, oysters[b] | France | | | | | | 0-90 | | |
| Plankton[c] | Chronic Pollution | | | | | | 400 | | |

References--Note
(a) Oc. Chem Data
(b) Sullivan, 1974
(c) NAS, 1975

*dry weight
**μg/dozen

considered to be clean with respect to hydrocarbon pollution. The total PAH for fish in the Southern Beaufort Sea averaged to 21 μg/kg wet weight with values ranging from 9 to 31 μg/kg wet weight. The Pacific salmon and tuna have values of 20, 82 and 184 μg/kg wet weight. However, the species of fish collected in the Arctic and in the Pacific are different. Even within the same species, biological variability may contribute considerably to the difference observed in the same area. This variability can be the result of age, species, food habits or availability and migration. In Table 23 this may be illustrated in the case of benzpyrene (BP) for fish, oysters or mussels from various parts of the world. The upper limit of BP tends to be much higher by a factor of 100 in the case of chronic pollution and by a factor of 10,000 in case of an oil spill. Dunn and Stich (1975) obtained values for B[a]P at about 2 μg/kg wet weight for mussels on rocks 25-550 m distance from wharf structures in B. C. coastal waters. Thus, the BP contents in fish, molluscs and mussels of the Arctic Ocean and Greenland Sea are considered to be rather high, if there is no contamination problem in the sampling and analysis. The Beaufort Sea data on fish samples cannot be compared directly with the Arctic Ocean and Greenland Sea data since different compounds were studied.

### 7.4 PAH in Marine Sediments

The PAH data in marine sediments (from Table 14, 15 and 16) are summarized in Table 24, which also includes published results from other oceanic areas for comparison. PAH in marine sediments shows considerable variability within the same geographic location. This variability can be a factor of 10 or more. In the case of BaP, as summarized by ZoBell (1971), it may vary between nil to 3,400 μg/kg of sediment. Giger and Blumer (1974) did extensive identification work on nearshore sediments in Buzzards Bay, Massachusetts, U. S. A. Their work showed the high complexity of PAH in these nearshore sediments. Their chromatographic work from both A and B stations suggested contamination by diesel fuel, especially at station B, rather than by oil spills. Their station A was in an area which did not appear to be contaminated by a recent oil spill. The offshore surface sediments of Southern Beaufort Sea appear to be comparable in PAH content to the nearshore sediment at Buzzards Bay. The nearshore sediments which were beach core material contain much less PAH than benthic or offshore sediments. However, the nearshore beach material has much lower organic content, and is exposed to more extreme weathering. Due to the high variability of PAH in the natural environment, it is difficult to ascertain the characteristics of unpolluted sediments based on a small number of samples or on the analyses of a few specific compounds. The characterization would probably involve a more detailed study of the composition of different classes of compounds such as aromatics, cycloalkanes

## TABLE 24

## PAH Levels in Marine Sediments

| Material | Area | PAH Levels (in μg/kg wet weight) | | | | | Reference |
|---|---|---|---|---|---|---|---|
| | | $178^+$ | $202^+$ | $228^+$ | $252^+$ | Total | |
| Surface Marine Sediments (1974) | S. Beaufort Sea | 35-160 | 14-148 | 21-197 | 59-638 | 236-984 | Oc Chem Data |
| Surface Marine Sediments (1975) | S. Beaufort Sea | 22-152 | 8-66 | 24-250 | 43-1004 | 97-1341 | |
| Nearshore Sediment | Buzzards Bay, Mass. U. S. A. | | | | | | |
| | Stn. A | 33 | 100 | 40 | 26 | 199 | Giger & Blumer 1974 |
| | Stn. B | | 960 | 240 | 94 | 1294 | |

| Material | Area | PAH Levels (in μg/kg dry weight) | | | | | Reference |
|---|---|---|---|---|---|---|---|
| | | Pyrene | B[a]P | Perylene | Coronene | Total UV-PAH | |
| Nearshore Sediments | S. Beaufort Sea | 0.5-3.0 | 0.4-10 | 0.3-7.3 | 0.2-1.7 | 0.4-20 | Oc. Chem Data |
| Benthic Sediments | S. Beaufort Sea | 41,52 | 106,131 | 85,129 | 19,31 | 295,299 | |
| Nearshore Sediment | Buzzards Bay, Mass. U. S. A. | | | | | | |
| | Stn. A | 100 | 75 | 26 | 5 | 206** | Giger & Blumer 1974 |
| | Stn. B | 960 | 370 | 94 | 20 | 1444 ** | |

| Material | Area | B[a]P (μg/kg) | Reference |
|---|---|---|---|
| Mud (42 stations) | Tyrrhenean Sea | 1-3000 | Zo ell, 1971 |
| Mud from oyster beds | French Coast | 90-2840 | |
| Mud (17 stations) | Mediterranean Coast | up to 1800 | |
| Mud (8 stations) | Villefranche Bay, France | 16-5000 | |

TABLE 24

(cont'd)

| Material | Area | B[a]P (µg/kg) | | Reference |
|---|---|---|---|---|
| Mud (12 stations) | French Coast | nil to 1700 | | |
| Mud and Sand | Villefranche Bay, France | nil to 1700 | | |
| Calcareous deposits | French Coast | 8-59 | | |
| Surface Mud | Italian Coast | nil to 2500 | | |
| Mud (218 samples) | Adriatic Coast | nil to 3400 | | |

**Total PAH's as defined by Giger and Blumer, 1974 are 570 and 3600 µg/kg dry weight respectively.

and n-& iso-alkanes. (M. Tissier and Oudin, 1973). The information obtained for PAH in Southern Beaufort Sea sediments should be very useful as baseline data, especially in tracing any oil spill with input of specific types of aromatics.

## 7.5 LMW Hydrocarbons in Sea Water

The data obtained in 1974 and 1975 are summarized in Tables 17 and 18 respectively. In order to view the LMW hydrocarbon data for Beaufort Sea in the proper perspective, it is essential to examine the reported oceanic concentrations of hydrocarbons first.

Before examining in detail the data in Table 17 and 18, it is important to note the possible origins of various LMW-HC. The unsaturates, ethylene and propylene, appear to be biogenic and are not found at all in crude oils (Wilson, et al., 1970). Although refined products, for example gasoline, do contain unsaturated hydrocarbons, one does not expect to find any unsaturated hydrocarbons in water as a result of natural seepage or crude oil spillage.

The saturated hydrocarbons, methane, ethane, propane and iso and n-butane all occur as the low boiling fraction in crude oils. Natural gas also contains a large fraction of methane with approximately 3% by volume being made up of ethane and propane. (Moore, et al., 1966). Methane is also produced naturally in anoxic regions and can in fact reach remarkably high values in this manner (Atkinson and Richards (1967), Jannasch (1975), Lamontagne, et al., 1973). Although the higher saturated hydrocarbons are also naturally produced, they are not nearly as prevalent as methane, commonly occuring in concentrations which are more than two orders of magnitude lower (Sackett and Brooks, 1975).

### 7.5.1 Methane

Methane occurs in the atmosphere at a fairly constant level of 1.5 ppmv (Swinnerton and Lamontagne, 1974). Using the solubility data provided by Atkinson and Richards (1967), it can be shown that the expected concentration of methane in the water at atmospheric equilibrium would be 61-75 nl/l depending on temperature and salinity. Table 18 reveals that while many of the methane determinations lie close to this range, quite a large number were higher. A diagram of methane concentration plotted as a function of depth revealed no pattern, but if as in Figure 19, the concentration is plotted as a function of distance from the bottom it becomes clear that much of the methane found in the study area was originating from the bottom. Particle concentration and size distribution studies which were concurrently

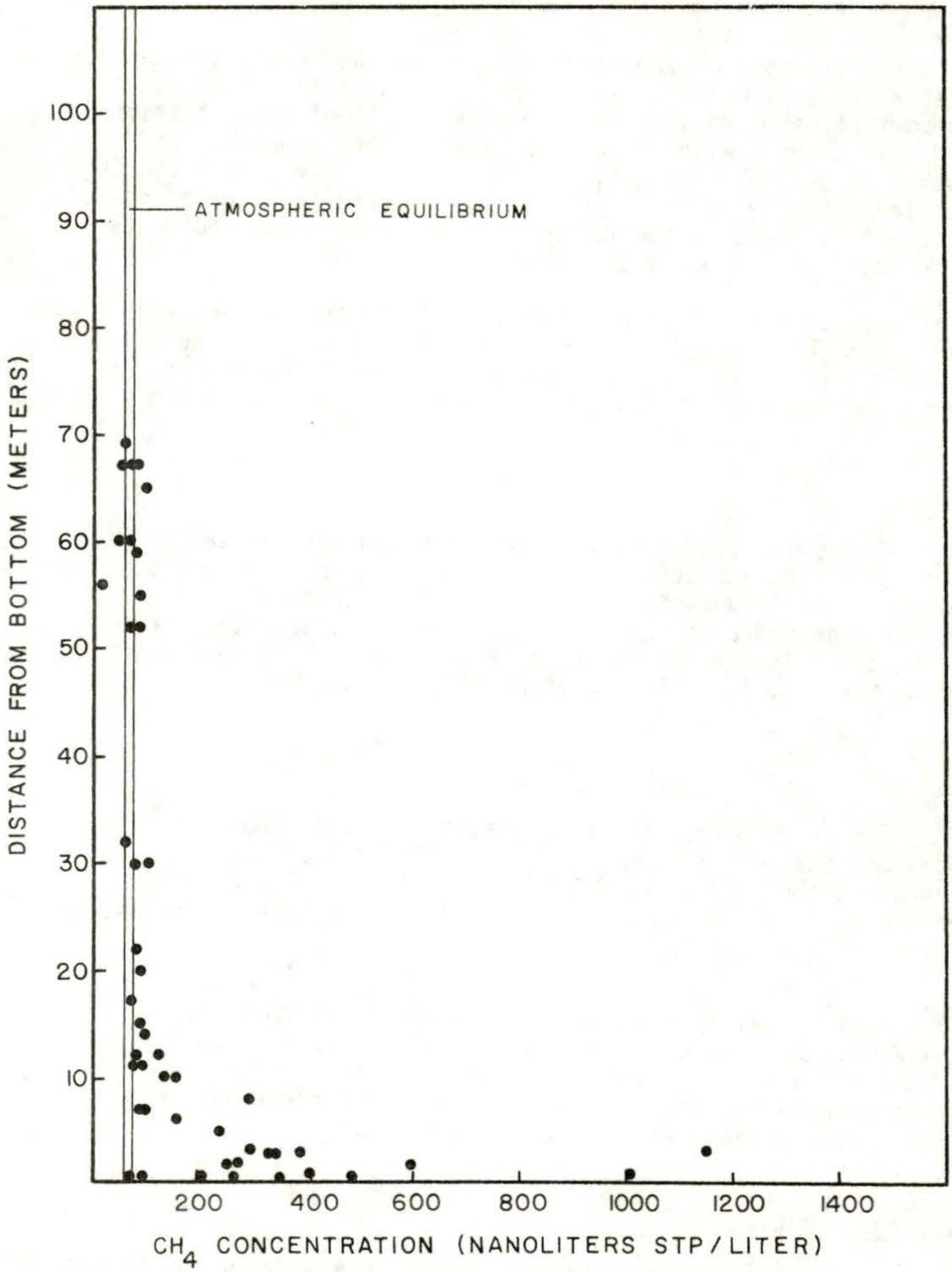


Figure 19. Variation of Methane Concentration with Distance from Bottom.

run as part of the 1975 chemical oceanography program revealed that bottom erosion was occuring at those stations where methane concentrations in excess of 300 nl/l were found.

In 1974 some of the near surface methane levels were high (Table 17, Stations 42, 44, 49 and 51) and at that time no supportable explanation could be given. All of these stations had been covered with ice a short time before sampling, and both grounded and moving ice was in the vicinity. Ice scouring coupled with ice coverage preventing atmospheric exchange could have put significant quantities of methane from the sediments into the water column and trapped it there.

Surface concentration of methane for both 1974 and 1975 are shown in Figure 20. There is no indication that the Mackenzie River is a source of high methane concentration, at least in the month of August for the two years of sampling.

### 7.5.2 Ethane

When solubility effects due to temperature and salinity are taken into account, the levels found in the Beaufort Sea compare very favourably with the oceanic average of 0.50 nl/l (Swinnerton and Lamontagne, 1974). Their average ethane concentrations in the Greenland Ice Pack of 1.7 nl/l, were over twice that found for the Beaufort Sea.

### 7.5.3 Propane

The average propane concentration found in Southern Beaufort Sea in 1974 was 0.17 nl/l while in 1975 a higher average concentration of 0.34 nl/l was found. The average open ocean baseline value of 0.34 nl/l was reported by Swinnerton and Lamontagne (1974).

Statistical analysis of the data indicate that the difference between the averages of 1974 and 1975 is significant at the 99% level. A possible explanation may be that the 1975 stations were more representative of the oceanic environment while 1974 stations were largely estuarine.

### 7.5.4 Iso and n Butane

These hydrocarbon gases were found only at very low levels in both years. Considering the accuracy of the method for such low values, it can only be safely reported that butane was detectable, but only in trace amounts.

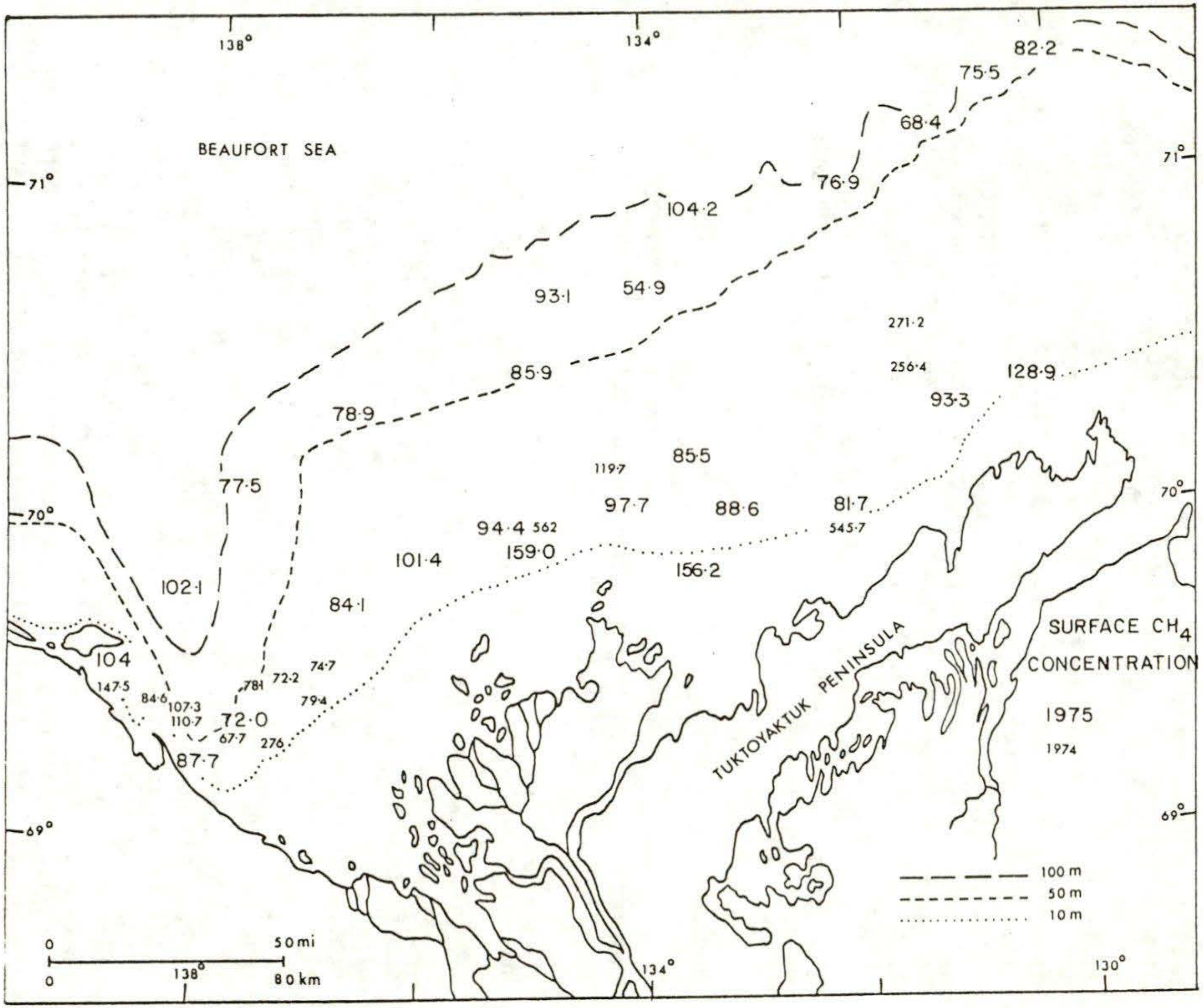


Figure 20. Methane Concentration in Surface Waters of Southern Beaufort Sea, 1974 and 1975.

### 7.5.5 Ethylene and Propylene

The levels of these two hydrocarbons found in the Beaufort Sea shelf area were quite low compared to those found in other regions. Since these two unsaturated hydrocarbons have been linked to biological productivity (Brooks, et al., 1973; Swinnerton and Lamontagne, 1974; Wilson, et al., 1970) the low levels found here may indicate a low primary productivity for the area in 1974 and 1975. In 1974 the extremely turbid top seven meters of water limited light penetration which could have reduced unsaturated hydrocarbon production in two ways. Firstly, the high turbidity would severly restrict phytoplankton growth (Grainger, 1975), and secondly, photochemical processes which can generate these gases from dissolved organic material (Wilson, et al., 1970) could not proceed at a significant rate.

Both ethylene and propylene tended to decrease with depth. The trend for propylene in Figure 21 clearly illustrates this. Variability also decreased with depth.

### 7.5.6 Benzene and Toluene

No detectable amount of these two aromatic hydrocarbons was found in 1975. They may serve as useful indicators of petroleum pollution in future.

## 7.6 Non-polar Hydrocarbons in Fish, Marine Plankton and Sediments

The search for evidence of contamination by minute quantities of petroleum hydrocarbons in the marine environment is difficult due to the masking effect of natural biogenic hydrocarbons, often present in very large amounts in marine organisms and sediments. To establish the presence of petroleum hydrocarbons, several techniques have been developed utilizing gas chromatography (NAS, 1975). These include studies of the presence of unresolved compounds in the gas chromatogram envelope (Farrington, et al., 1972; Burns and Teal, 1971; Farrington and Quinn, 1973), and the absence of odd carbon-number predominence for the $C_{25}$-$C_{33}$ range (NAS, 1975), the pristane/phytane ratio ($C_{19}$:$C_{20}$) in the $C_{16}$-$C_{20}$ range, the pristane/isoprenoid isoalkane ratio ($C_{19}$:$C_{18}$) (Blumer and Sass, 1972) and the ratio of n-$C_{16}$/total n-alkanes in $C_{14}$-$C_{17}$ range (Clark and Finley, 1973). In general, as the quantity of petroleum hydrocarbons becomes smaller and approaches the quantity of natural hydrocarbons, the analytical problem of distinguishing between the natural and petroleum compounds becomes increasingly more difficult. The detection limit of petroleum hydrocarbons is governed by the matrix of natural hydrocarbons in the sample, i.e., by the concentrations and types of the natural ones.

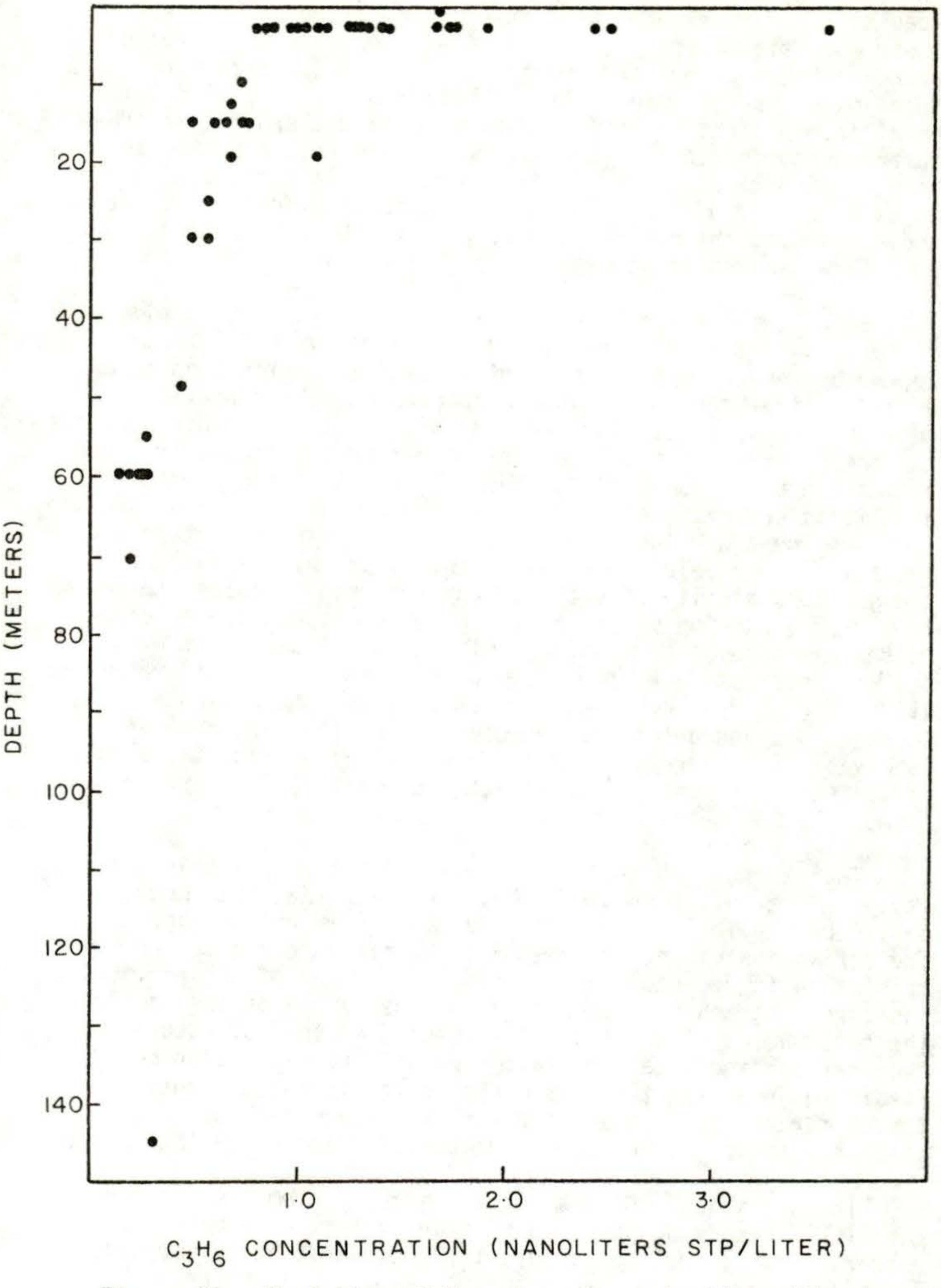


Figure 21. Variation of Propylene Concentration with Depth.

Natural hydrocarbons, like other natural organic compounds in general, are formed by specific biochemical pathways, which lead to the formation of certain organic carbon structures. These specific organic structures would occur in much greater abundance than others and provide useful characterization techniques, as first suggested by Eglinton, et al., (1962) for paraffins in plant material. Many land plants exhibit an odd-carbon predominance in their n-paraffin content, and the much higher concentrations of odd-carbon number n-paraffins also occur in lipids of organisms, as reviewed by Clark, Jr. (1966) and applied to characterization of natural hydrocarbons in benthic algae and in sea weeds (Clark and Blumer, 1967).

In contrast to the biochemical pathways leading to simple mixtures of natural hydrocarbons, petroleum hydrocarbons are formed by very non-specific chemical pathways which lead to a great proliferation of organic compounds and the formation of very complex mixtures (Ehrhardt and Blumer, 1972). This provides the basis for the gas chromatogram envelope technique for estimating petroleum hydrocarbons. Temperature-programmed gas-liquid chromatography (g.l.c.) is particularly useful because it shows the degree of complexity of a hydrocarbon mixture and lends itself to relatively easy quantification. Because of the great complexity of petroleum hydrocarbon mixtures, there is always a portion of a mixture appearing as a broad envelope in the gas chromatogram as a result of the inability of even the most sophisticated temperature programmed g.l.c. in resolving all the individual compounds present. Thus, the presence of such a broad and unresolved envelope accompanying the often resolvable natural hydrocarbons in a biological material should indicate the presence of petroleum hydrocarbons (Ehrhardt and Blumer, 1972).

The gas chromatogram envelope technique was used in this study. However, it should be kept in mind that this method has to be applied with much caution in the interpretation. The estimation of the petroleum contamination based on the resolution is dependent on the resolving power of the particular gas chromatograph used as well as on the matrix of the sample. The combination of an atypically complex mixture of natural hydrocarbons and a gas chromatograph of poor resolution could result in an artificial envelope of unresolved components. The difference in resolution power of various pack columns will lead to variation from laboratory to laboratory (NAS, 1975).

In this study, the gas chromatograph system used is comparable in resolving power to similar systems used by other workers (Clark, Jr. and Finley, 1973; Ehrhardt and Blumer, 1972; Burns and Teal, 1973; Farrington, et al., 1972) who have demonstrated the capability of such systems in resolving the natural hydrocarbons encountered in this study for marine organisms and sediments. Another problem is a tailing effect. Even if a gas chromatographic system can adequtely resolve a natural hydrocarbon mixture, an envelope may arise from the tailing of chromatographic peaks. In this case, the envelope is strictly an artifact, but does determine the lower limit to which an envelope can be attributed to a mixture of unresolved hydrocarbons in the presence of a greater amount of natural hydrocarbons. In order to estimate the tailing effect, a set of eleven n-alkanes covering the range of heptadecane ($C_{17}H_{36}$) to dotriacontane ($C_{32}H_{66}$) was chromatographed under conditions comparable to those by which the fish samples had been run. The artificial "envelope" generated by the tailing effect was determined to be 14% of the hydrocarbon total. This value represents probably the "worst case" as the upper limit of an artificial "envelope". It should not be used, however, to correct concentrations or percentages which have been determined using the envelope of unresolved hydrocarbons, since it depends on the concentration, distribution and type of hydrocarbons in a sample as well as on the gas chromatographic system itself.

### 7.6.1 Fish

A summary of the results of the hydrocarbon concentrations in fish samples from Beaufort Sea and Station P is given in Table 27. The average of the frozen fish samples from the Beaufort Sea is about 38%, and the formalin preserved samples 49%, for the percentage of unresolved to total hydrocarbons. In contrast, the tuna and salmon from Ocean Weathership Station P (50$^{O}$N, 145$^{O}$W) have percentages of 12 and 16% respectively; and within the 14% tailing effect discussed above, the fish samples from Ocean Station P are free from petroleum contamination as far as can be determined by the particular method on the same instrument system used. It is noteworthy that the apparently large concentration (6.4 μg/g wet weight) of unresolved hydrocarbons in the tuna fish is an artifact of its exceptional high hydrocarbon content compared to other fish in the study. Burns and Teal (1973), using the same criteria, had concluded that all their samples of Sagasso Sea plants and animals were contaminated by petroleum hydrocarbons. Their values for unresolved hydrocarbons and percentage of unresolved to total hydrocarbons were also included in Table 27. The petroleum hydrocarbons in these Sargasso Sea fish samples dominate the gas chromatograms for both resolved and unresolved ones. In the case of the Beaufort Sea fish samples, it is not possible to determine if the resolved hydrocarbons are of petroleum or natural origin except for a few natural ones which are present in major quantities. However, from evidence of the envelope of unresolved hydrocarbons, hydrocarbons of the petroleum type may be present in the sample levels approaching the limit of the analytical method, with the questionable assumption of unaltered ration of resolved and unresolved hydrocarbons by weathering or incorporation into the marine food chain (Blumer, et al., 1970).

TABLE 25

Non-polar Hydrocarbon Concentrations in Fish

| Fish | Area | Preserved State | Hydrocarbon Concentrations (µg/g wet weight) of fish flesh<br>Unresolved | <br>Total | <br>% Unresolved |
|---|---|---|---|---|---|
| Arctic Cisco (4 samples) | S. Beaufort Sea | Frozen | 0.7-1.4 | 2.0-4.0 | 24-67%<br>Av. 38% |
| Least Cisco (3 samples) | S. Beaufort Sea | Frozen | 0.6-1.8 | 2.0-7.8 | 23-30% |
| Arctic Cisco | S. Beaufort Sea | Formalin | 0.6 | 1.1 | 54% |
| Cisco (mainly fingerlings) | S. Beaufort Sea | Formalin | 1.7 | 3.9 | 44% |
| Salmon | Stn. P, N. E. Pacific Ocean | Frozen | 0.1 | 0.9 | 16% |
| Tuna | Stn. P, N. E. Pacific Ocean | Frozen | 6.4 | 55 | 12% |
|  | Tailing Effort |  |  |  | 14% |
| Sargassum** fish | Sargasso Sea** |  | 1.5 |  | 89% |
| Pipe fish | Sargasso Sea** |  | 7.4 |  | 81% |
| Trigger fish | Sargasso Sea** |  | 1.4 |  | 81% |

** Burns and Teal, 1973

## 7.6.2 Marine Plankton

The marine plankton and their non-polar hydrocarbon content are summarized in Table 20. The composition of the plankton would be mainly phytoplankton for shallower depths and zooplankton in deeper waters. Two major zooplankton hydrocarbons are tentatively identified: pristane ($C_{19}H_{40}$) and heneicosane or heneicohexane ($C_{21}H_{44}$ or $C_{21}H_{32}$), using retention data. Pristane is an important biological marker of the phytoplankton and other plant pigment (Blumer, 1965; Blumer and Snyder, 1965; and Eglington, 1969) and is incorporated into copepods feeding on the phytoplankton (Eglington, 1969). In samples of mainly phytoplankton composition, much lower hydrocarbon contents were found and less dominance by any particular hydrocarbon occurred.

An envelope of unresolved hydrocarbons was found in all the gas chromatograms of the zooplankton and phytoplankton samples (Table 20). The concentration of unresolved hydrocarbons ranges from 0.5 to 7.3 μg/g of plankton in wet weight. In the South Atlantic Ocean unresolved hydrocarbons for five zooplankton tows (Farrington and Teal, 1972) were undetected in three tows, and at levels of 0.3 and 20.4 μg/g (wet weight) in the other two. In Florida Strait and Yucatan Strait, gas chromatogram envelope was observed (Iliffe and Calder, 1974) but no quantitative data were given. In the western Gulf of Mexico (Parker, Winters and morgan, 1972), the hydrocarbons in a blue-green algae Trichodesmium e., had carbon numbers less than $C_{19}$ for samples from some locations, but at different locations, had a homologous series of n-paraffins out to at least n-$C_{34}$. The presence of n-$C_{19}$ to n-$C_{34}$ was suggested by these authors to be conclusive evidence for petroleum contamination. Although not mentioned in their report, the example of the chromatogram from the polluted Trichodesmium e. shows a huge envelope of unresolved hydrocarbons, in addition to the n-paraffin homologue.

Most of the chromatograms of plankton hydrocarbons in this study show a series of n-paraffins extending from n-$C_{16}$ to n-$C_{38}$ with a maximum in the range n-$C_{26}$. None of the chromatograms show more than a slight odd-carbon predominance in the n-paraffins. Since these characteristics in the hydrocarbons of plankton have been observed for plankton grown in culture free from oil contamination (Clark and Blumer, 1967; Blumer, et al., 1971), their presence does not indicate pollution by petroleum hydrocarbons. Thus, unless a certain n-paraffin series is absent, as in the case of the algae Trichodesmium e. discussed above, or has a known natural range in uncontaminated samples, the n-paraffins by themselves are not useful indicators of petroleum pollution. The n-paraffins have a proven utility only where the study organisms are well characterized and with both the temporal and spatial variabilities being considered (Clark and Finley, 1973).

It is inconclusive whether the unresolved hydrocarbons and n-$C_{16}$ to n-$C_{38}$ extension in the plankton analysis is indicative of actual petroleum pollution in the marine environment or of sampling contamination. Despite precautions taken in sampling, some problems did arise. First, the plankton sample is a mixture of living and non-living material retained by the net, including any tar or plastic particles. Plankton samples collected near lanes of tanker traffic may contain small 'tarballs' making it uncertain whether the petroleum contamination is in the plankton itself or just associated with it (Farrington and Quinn, 1972). however, this possibility is unlikely in Southern Beaufort Sea due to lack of tanker traffic and absence of tarballs in surface net tows. The other possible contaminant is plastic,of the polyethylene type, which may contain large amounts of n-paraffins in the n-$C_{14}$ to n-$C_{38}$ range and a complex of unresolved hydrocarbons (Douglas and Grantham, 1973). However, from data on Neuston-net tows and particulate pollutants on beaches (Wong, et al., 1976), the amount of plastics is unlikely to be high enough to cause contamination in the analysis. Other possibilities of accidental contamination may also happen, such as the discharge of waste waters from the research ship, oil from the ship's deck and machinery and plastics used in the freshwater system on the ship.

### 7.6.3 Sediments

The stations from which the analyzed sediments came are shown in Figures 22 and 23 for the 1974 and 1975 cruises respectively. The gas chromatograms of the paraffin containing fraction from the florisil chromatography of the sediment extracts are all characterized by the presence of a homologous series of n-paraffins, the isoprenoids pristane and phytane and an unresolved envelope. The contributions of the various resolved hydrocarbons and the unresolved envelope for each sediment are given in Tables 21 and 22 respectively. The concentration range of the n-paraffins is 2.6-23.6 μg/g with an average of 11.0 μg/g. The concentration of the unresolved envelope hydrocarbons is 28.3 to 136.7 μg/g with an average of 62 μg/g. The n-paraffin of greatest abundance is nonacosane (n-$C_{29}$) or heptacosane (n-$C_{27}$) except in some samples with maxima in the heptadecane (n-$C_{17}$) to tricosane (n-$C_{23}$) range. In many samples, the n-paraffin distribution is clearly bimodal. The n-paraffin distribution for three sediment samples are shown in Figure 24. In Figure 24a, the local maxima at nonadecane (n-$C_{19}$) and nonacosane (n-$C_{29}$) are very nearly equal, whereas in Figure 24b and 24c, which are extreme cases, one of the local maxima clearly dominates. Bimodal distributions of n-paraffins are found in sediment with mixed marine and terrestrial hydrocarbons (Brown, et al., 1972) although microbial modification of such distribution is possible (Johnson and Calder, 1973).

All the sediment samples show predominance of the n-paraffins having an odd number of carbon atoms over the n-paraffins having an even number of carbon atoms. An increase in this predominance is observed, moreover, on comparison of n-paraffins having increasing

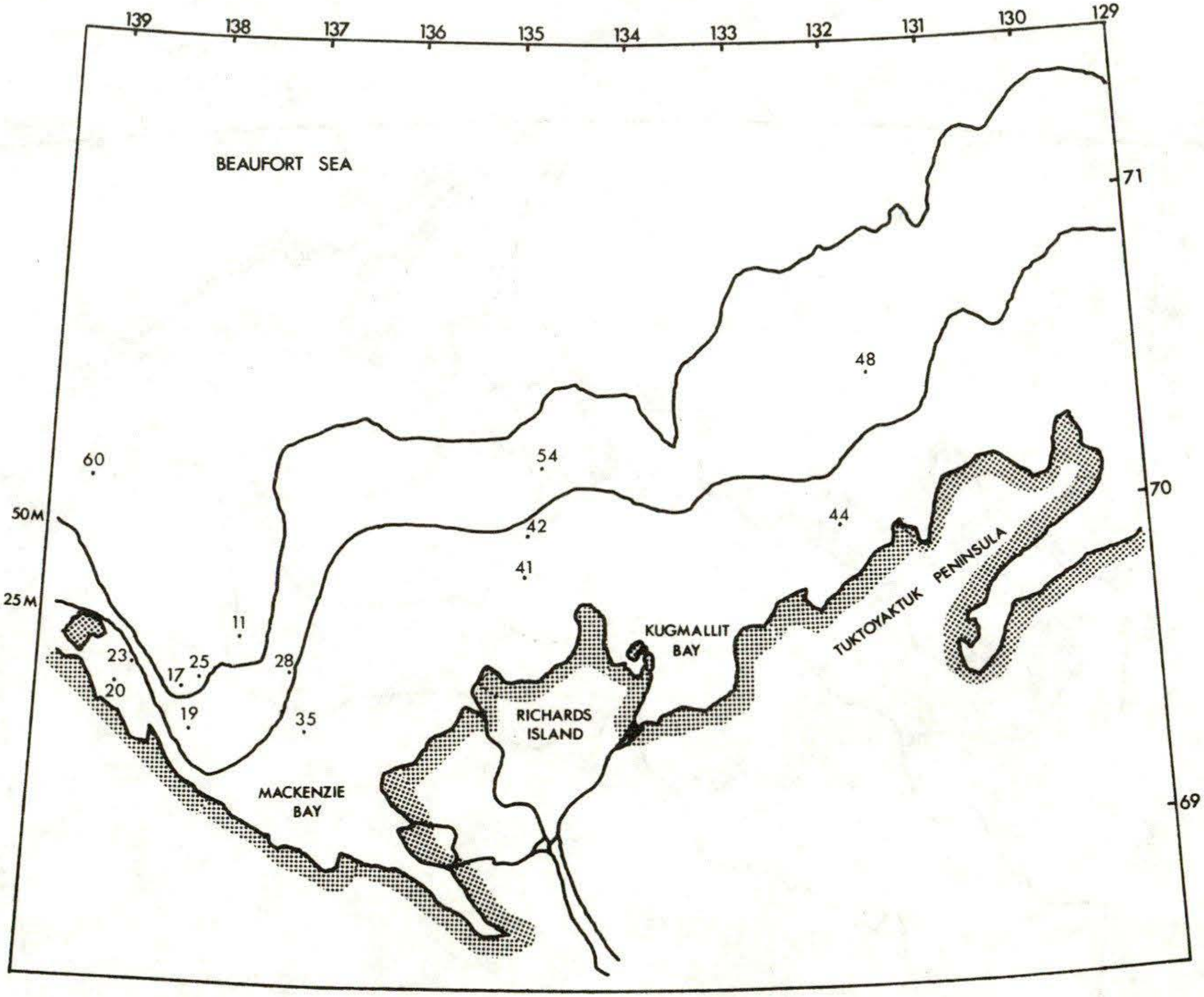


Figure 22. Locations of Sediment Samples for Non-polar Hydrocarbons for Cruise OC-BSP-74.

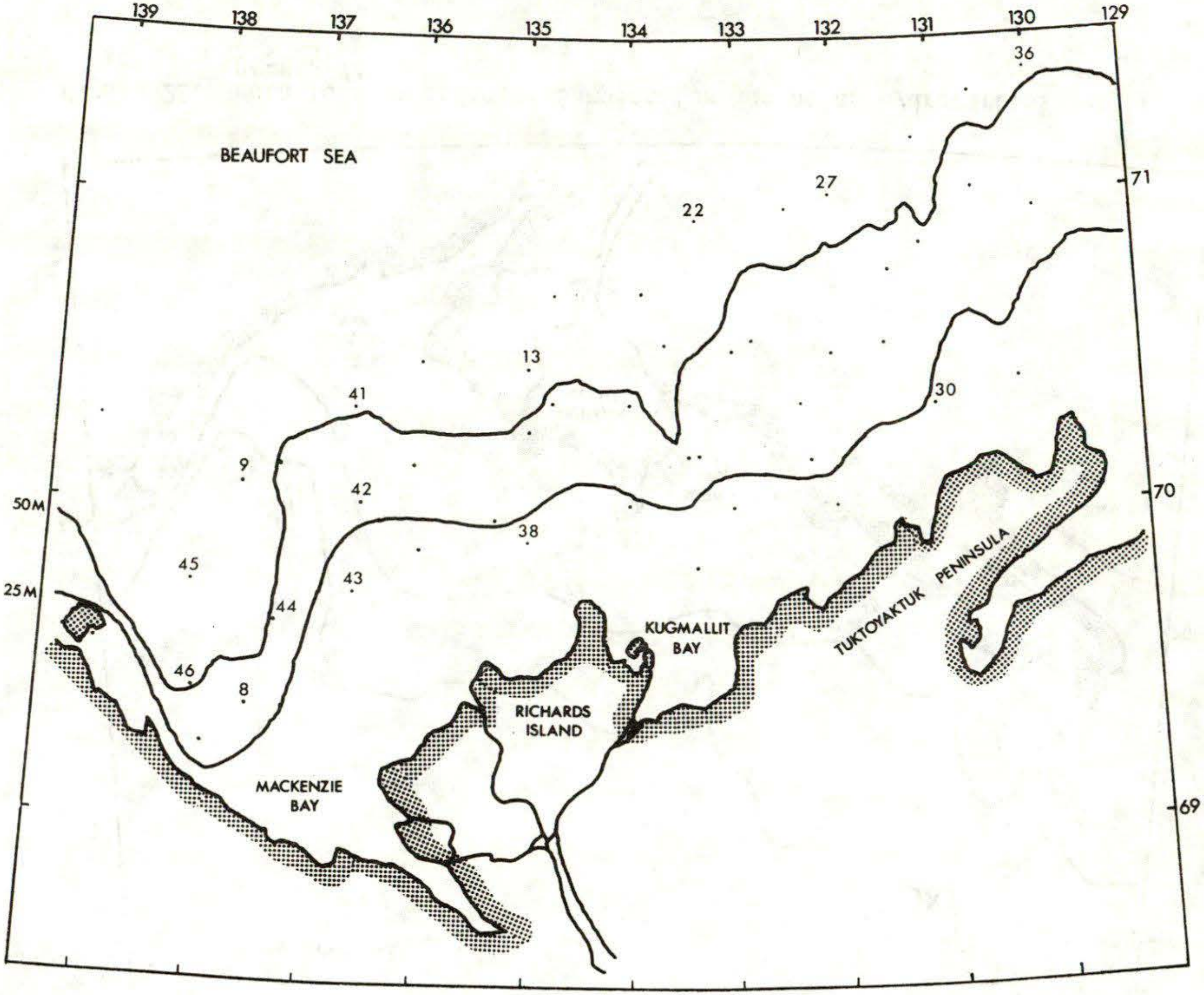


Figure 23. Locations of Sediment Samples for Non-polar Hydrocarbons for Cruise OC-BSP-75.

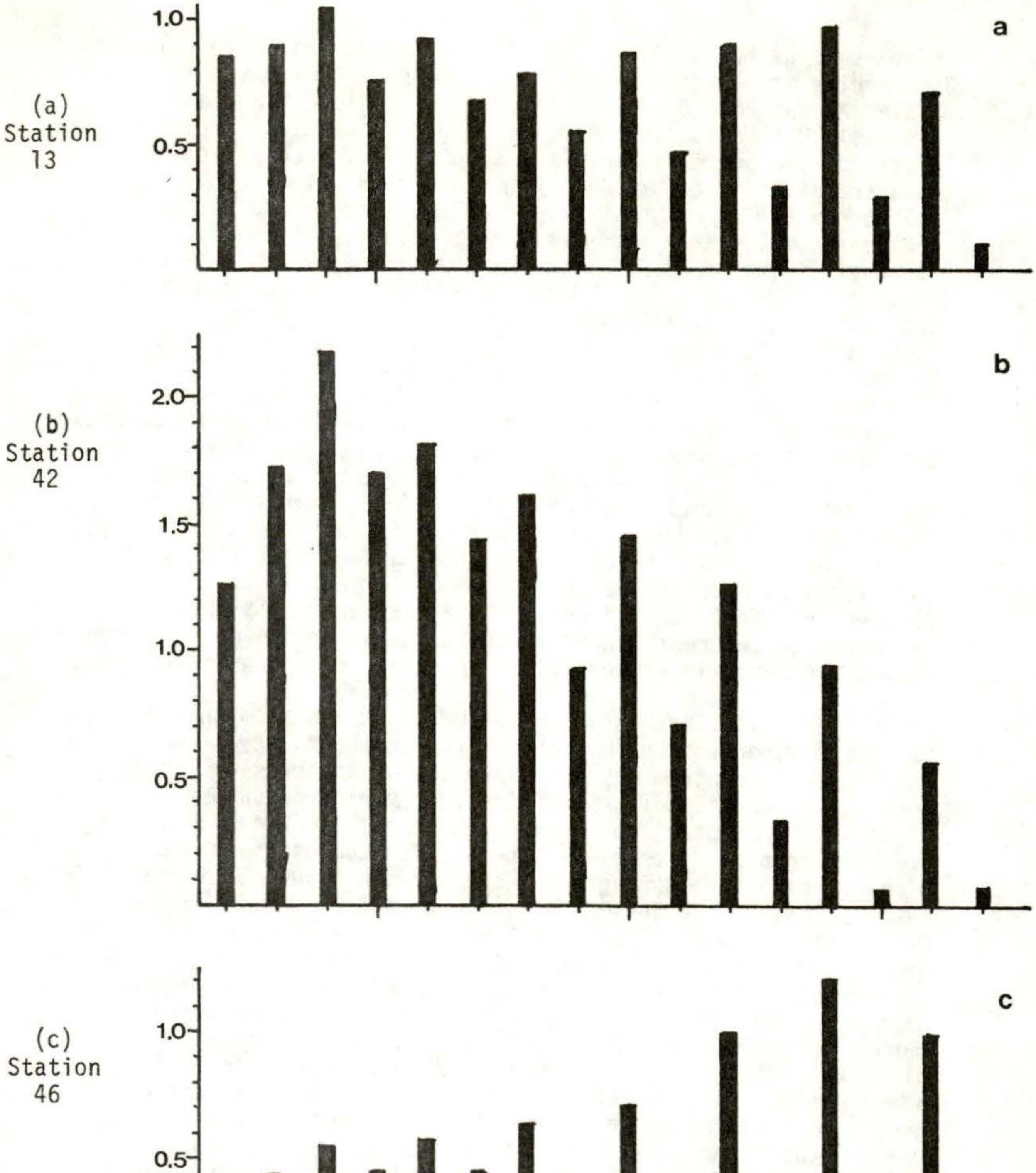


Figure 24. n-Parrafin Distributions in Southern Beaufort Sea Sediments (1975) for (a) Station 13, (b) Station 42 and (c) Station 46.

numbers of carbon atoms. The OEP(odd-even predominance) values for the series of n-paraffins from n-$C_{19}$ to n-$C_{30}$ are given in Tables 25 and 26. A CPI (Carbon Preference Index) and an average OEP is also given for each sediment sample. The OEP plots for two sediment samples from different geographical area are given in Figure 25. The sediment sample from station 46 (1975) has an OEP plot which is typical of other sediment samples from the same geographical location off Herschel Island. The OEP plot for the sediment sample from station 13 (1975) is typical of OEP plots for sediment samples from all other geographical locations. An area generally encompasing the western bank of Herschel Canyon, at least as far north as Herschel Island, has sediments with a remarkably high predominance of odd numbered n-paraffins over even numbered n-paraffins by comparison with the rest of the Southern Beaufort Sea bottom. The presence of an odd-carbon predominance in the higher molecular weight n-paraffins is regarded as evidence for their origin in land plants( Phillippi, 1974; Meinschein, 1969, 1959; Clark, 1966; Eglington, et al., 1962; Stevens, et al., 1956). Peake and co-workers (1972) have estimated an annual flux of $24 \times 10^8$ g of n-paraffins on suspended sediments into the Southern Beaufort Sea via the Mackenzie River. This annual flux was based on two representative Mackenzie River sediment samples having a n-paraffin content of 5.4 μg/g and 6.2 μg/g respectively.

Once n-paraffins enter the S. Beaufort Sea from the Mackenzie River and become part of the sediment, it is expected that their concentrations and distribution patterns will become modified. Addition of n-paraffins from marine organisms, diagenisis of n-paraffin precursor materials such as fatty acids, microbial alteration of n-paraffin compositions and biodegredation are some processes which can bring about modifications. Marine organisms contain n-paraffins for which the CPI is nearly unity (Clark and Blumer, 1967; Koons, et al., 1965). Geochemical production of n-paraffins results in a decrease of odd-carbon predominence ( Phillippi, 1974).Microbial alteration of n-paraffin profiles can also result in a decrease in odd-carbon predominance (Johnson and Calder, 1973; Dembicki, Jr., et al., 1976). Except for the so far unreported possibility of selective biodegredation of even n-paraffins, the common processes bringing about changes in the n-paraffin distribution would result in a diminishment of odd-carbon predominance. The relatively higher values for CPI and OEP found for samples obtained southeast of Herschel Island would seem to be consistent with the deposition of river material with high organic carbons in Mackenzie Canyon off Herschel Island ( Pelletier, 1975). The average concentration of n-paraffins in the Beaufort Sea sediments, which were analyzed for this report, is about double the average concentration on suspended material entering the Beaufort Sea as reported by Peake and co-workers. Peake and co-workers (1972b) also studied a limited number (10) of Beaufort Sea sediment and reported a range of total n-paraffins from 1.23 to 9.40 μg/g with an average of 5.1 μg/g. Although the

TABLE 26

Relative Distributions of OEP Values of n-Paraffins for Southern Beaufort Sea Sediments (1974 Cruise)

| Sample No. | 3 | 6 | 7 | 8 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | Central |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Station No. | 11 | 17 | 19 | 20 | 23 | 25 | 28 | 35 | 41 | 42 | 44 | 48 | 54 | 60 | Parrafin |
| OEP Value | 1.11 | 1.31 | 1.13 | 1.83 | 1.24 | 1.17 | 1.09 | 1.10 | 1.05 | 1.09 | 1.15 | 1.51 | 1.18 | 1.09 | n-$C_{19}$ |
| | 1.21 | 1.41 | 1.25 | 1.98 | 1.38 | 1.30 | 1.15 | 1.13 | 1.14 | 1.13 | 1.09 | 1.42 | 1.25 | 1.18 | n-$C_{20}$ |
| | 1.29 | 1.47 | 1.33 | 2.15 | 1.45 | 1.37 | 1.18 | 1.13 | 1.16 | 1.15 | 1.11 | 1.41 | 1.27 | 1.22 | n-$C_{22}$ |
| | 1.48 | 1.81 | 1.56 | 2.07 | 1.91 | 1.66 | 1.39 | 1.28 | 1.34 | 1.29 | 1.39 | 1.47 | 1.36 | 1.40 | n-$C_{23}$ |
| | 1.71 | 2.15 | 1.79 | 2.72 | 2.67 | 1.97 | 1.59 | 1.43 | 1.53 | 1.44 | 1.59 | 1.69 | 1.53 | 1.55 | n-$C_{24}$ |
| | 2.01 | 2.63 | 2.16 | 3.63 | 3.57 | 2.39 | 1.91 | 1.67 | 1.81 | 1.65 | 1.85 | 2.01 | 1.73 | 1.76 | n-$C_{25}$ |
| | 2.44 | 3.39 | 2.79 | 3.69 | 4.25 | 3.00 | 2.50 | 2.10 | 2.27 | 2.03 | 2.25 | 2.29 | 1.99 | 2.14 | n-$C_{26}$ |
| | 3.00 | 4.37 | 3.65 | 3.24 | 4.75 | 3.77 | 3.24 | 2.57 | 2.89 | 2.52 | 2.72 | 2.55 | 2.36 | 2.68 | n-$C_{27}$ |
| | 3.75 | 5.60 | 4.65 | 3.45 | 5.46 | 4.75 | 3.85 | 2.97 | 3.43 | 2.97 | 3.15 | 2.87 | 2.81 | 3.37 | n-$C_{28}$ |
| | 4.88 | 7.35 | 5.85 | 5.31 | 6.89 | 6.04 | 4.47 | 3.57 | 3.96 | 3.32 | 3.83 | 3.10 | 3.21 | 4.18 | n-$C_{29}$ |
| | 6.13 | 9.66 | 7.17 | 9.55 | 9.22 | 7.68 | 5.18 | 4.41 | 4.58 | 3.55 | 5.39 | 3.25 | 3.49 | 4.93 | n-$C_{30}$ |
| Av.OEP 20-30 | 2.66 | 3.76 | 3.06 | 3.63 | 3.92 | 3.22 | 2.52 | 2.13 | 2.30 | 2.02 | 2.33 | 2.13 | 2.03 | 2.37 | n-$C_{25}$ |
| CPI 18-32 | 2.00 | 3.32 | 2.49 | 2.82 | 3.37 | 2.70 | 1.97 | 1.75 | 1.78 | 1.71 | 1.75 | 2.05 | 1.75 | 1.90 | n-$C_{25}$ |

TABLE 27. Relative Distribution of OEP Values of n-Paraffins for Southern Beaufort Sea Sediments (1975 Cruise).

| Sample No.<br>Station No. | 1<br>08 | 2<br>09 | 4<br>13 | 8<br>22 | 10<br>27 | 11<br>30 | 14<br>36 | 15<br>38 | 16<br>41 | 17<br>42 | 18<br>43 | 19<br>44 | 20<br>45 | 21<br>46 | 22<br>47 | Central Paraffins |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| OEP Value * | 1.07 | 1.10 | 1.21 | 1.27 | 1.33 | 1.21 | 1.77 | 1.11 | 1.14 | 1.17 | 1.05 | 1.28 | 1.18 | 1.21 | 1.16 | n-$C_{19}$ |
| | 1.10 | 1.15 | 1.27 | 1.35 | 1.39 | 1.19 | 1.75 | 1.16 | 1.19 | 1.19 | 1.11 | 1.29 | 1.28 | 1.27 | 1.30 | n-$C_{20}$ |
| | 1.11 | 1.19 | 1.27 | 1.35 | 1.33 | 1.21 | 1.53 | 1.17 | 1.21 | 1.17 | 1.18 | 1.70 | 1.33 | 1.29 | 1.44 | n-$C_{21}$ |
| | 1.16 | 1.28 | 1.26 | 1.33 | 1.31 | 1.29 | 1.37 | 1.23 | 1.23 | 1.22 | 1.27 | 1.14 | 1.42 | 1.35 | 1.57 | n-$C_{22}$ |
| | 1.28 | 1.41 | 1.31 | 1.36 | 1.39 | 1.39 | 1.41 | 1.37 | 1.31 | 1.37 | 1.41 | 1.30 | 1.61 | 1.49 | 1.76 | n-$C_{23}$ |
| | 1.43 | 1.57 | 1.48 | 1.55 | 1.66 | 1.53 | 1.68 | 1.56 | 1.49 | 1.45 | 1.48 | 1.61 | 1.91 | 1.70 | 2.17 | n-$C_{24}$ |
| | 1.65 | 1.81 | 1.70 | 1.83 | 1.95 | 1.77 | 2.05 | 1.86 | 1.73 | 1.76 | 1.79 | 2.00 | 2.31 | 2.05 | 2.78 | n-$C_{25}$ |
| | 2.03 | 2.17 | 1.93 | 2.15 | 2.20 | 2.21 | 2.21 | 2.39 | 2.03 | 1.96 | 2.12 | 2.43 | 2.89 | 2.63 | 4.02 | n-$C_{26}$ |
| | 2.49 | 2.65 | 2.29 | 2.53 | 2.57 | 2.77 | 2.06 | 3.05 | 2.42 | 2.39 | 2.56 | 2.96 | 3.73 | 3.37 | 4.98 | n-$C_{27}$ |
| | 2.87 | 3.24 | 2.76 | 3.00 | 3.11 | 3.27 | 1.96 | 3.54 | 2.92 | 3.01 | 2.98 | 3.48 | 4.90 | 4.25 | 5.72 | n-$C_{28}$ |
| | 3.33 | 3.89 | 3.03 | 3.29 | 3.53 | 3.71 | 1.92 | 3.99 | 3.47 | 3.33 | 3.47 | 4.35 | 6.37 | 5.25 | 6.20 | n-$C_{29}$ |
| | 3.85 | 4.47 | 3.13 | 3.07 | 3.79 | 4.17 | 1.75 | 4.54 | 3.94 | 3.23 | 4.07 | 5.75 | 7.85 | 6.20 | 6.63 | n-$C_{30}$ |
| Av.OEP ** 20-30 | 2.02 | 2.26 | 1.95 | 2.07 | 2.20 | 2.23 | 1.79 | 2.35 | 2.08 | 2.01 | 2.14 | 2.55 | 3.20 | 2.80 | 3.50 | n-$C_{25}$ |
| CPI 18-32*** | 1.69 | 1.94 | 1.76 | 1.84 | 2.05 | 1.86 | 1.77 | 1.89 | 1.79 | 1.59 | 1.70 | 1.73 | 2.84 | 2.49 | 2.72 | n-$C_{25}$ |

* The odd-even predominance values (Scalan and Smith, 1970) were calculated using the formula:

$$\text{OEP} = \left[ \frac{C_i + 6C_{i+2} + C_{i+4}}{4C_{i+1} + 4C_{i+3}} \right]^{(-1)^{C+1}}$$

where $C_i$ is the relative weight per cent of an n-alkane containing $i$ carbon atoms per molecule.

** The average OEP values (Scalan and Smith, 1970) were calculated using the formula:

$$\text{OEP}_{\text{average}} = \frac{1}{11} \sum_{i=18}^{28} \left[ \frac{C_i + 6C_{i+2} + C_{i+4}}{4C_{i+1} + 4C_{i+3}} \right]^{(-1)^{i+1}}$$

where $C_i$ is defined as in the above formula. The average OEP values calculated according to the above formula are centered at the $C_{25}H_{52}$ n-alkane, pentacosane.

*** The carbon preference indices (Cooper and Bary, 1963; Scalan and Smith, 1970) were calculated using the formula:

$$\text{CPI} = \frac{\sum_{i=9}^{15} C_{2i+1}}{2} \left[ \frac{1}{\sum_{i=9}^{15} C_{2i}} + \frac{1}{\sum_{i=9}^{15} C_{2i+2}} \right]$$

where $C_n$ ( $n=2i$, $2i + 1$, $2i + 1$, $2i + 2$; $i = 9\ldots,15$) is the relative weight per cent of the n-alkane containing $n$ carbon atoms per molecule. The CPI ratios calculated according to the above formula are centered at the $C_{25}H_{52}$ n-alkane, pentacosane.

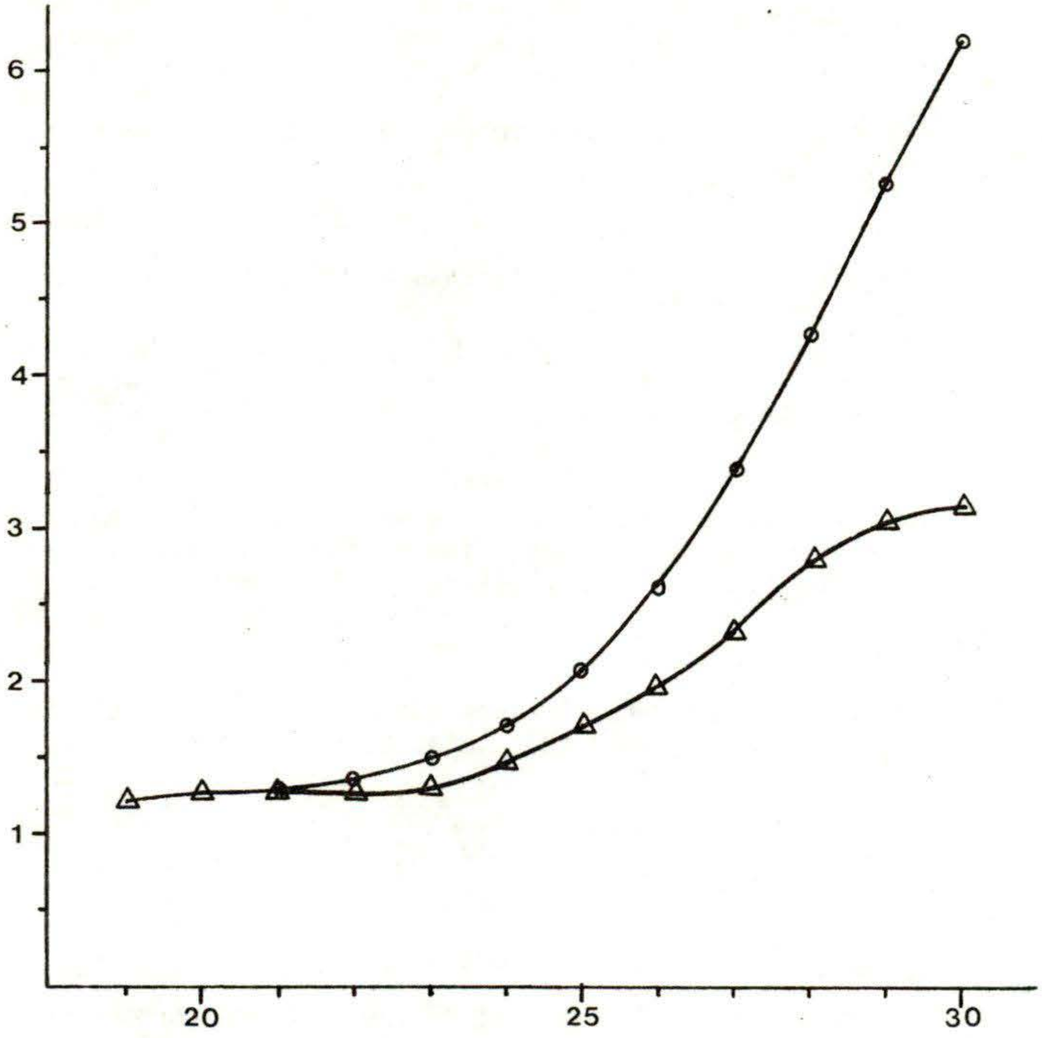


Figure 25. Odd-Even Predominance in Paraffinic Hydrocarbons for Southern Beaufort Sea Sediments (1975) from Station 14 (in triangles) and Station 46 (in circles).

average concentration value reported here for Beaufort Sea sediments is slightly more than double that reported by Peake and co-workers the large range in values found may account for the differences in the averages. A better comparison might be acheived knowing the geographical location of the sediments studied by Peake and co-workers. In any case, both sets of data are in accord with other results. For example, Brown and co-workers(1972) report two values for total n-parrafin concentrations in surface sediments obtained in Saanich Inlet, B.C.: 2.3 μg/g for a sediment from the oxidizing sill area and 32.7 μg/g for a sediment from the reducing central basin.

All the Beaufort Sea sediments, which have been analyzed, contain more than trace quantities of the isoprenoid hydrocarbon, phytane. In contrast, many recent sediments contain no detectable quantities of phytane suggested (Blumer and Snyder, 1965) to be the result of too slow production by geochemical conversion of phytol to phytane in the uppermost sedimentary layer. They also suggest that pristane, but not phytane, often found in recent sediments likely arises by conversion of phytol in the marine food chain. Since pristane and phytane are major constitutents in many crude oils and are present in nearly equal quantities (Speers and Whitehead,1969; Zafiriou, et al., 1972) the presence of phytane and pristane/phytane ratios approaching unity in marine sediments are often cited as evidence of oil pollution. However, Tissier and Oudin (1973) found a pristane/phytane ratio of almost unity in several unpolluted sediment samples in the estuarine environment on the French Coast of the English Channel and attributed the phytane occurrence to bacteria, in which both pristane and phytane are constituents. Bacterial production, therefore, could account for the presence of phytane in the Beaufort Sea sediments. Without specifying locations, Peake and co-workers(1972a) report the presence of phytane and pristane in sediments from the Mackenzie River drainage basin in quantities up to 0.18 and 0.25 μg/g respectively. Thus, suspended matter in the Mackenzie River may be a source of phytane in Beaufort Sea.

## 7.7 Tar and Plastics

As mentioned in 6.4, no tar or plastics were found in Southern Beaufort Sea.

## 8. CONCLUSION

From the baseline data collected on the THETA Cruise in the summer of 1974 and on the PANDORA II Cruise of 1975, with extensive hydrocarbon studies on sea water, fish, plankton and marine sediments by utilizing contaminant-free sampling techniques and shipboard clean-room sample-processing and analysis, the following conclusions can be drawn:

(1) Polycyclic Aromatic Hydrocarbons in Sea Water. The PAH concentrations in the Southern Beaufort Sea vary between 13 and 45 ng/l (in chrysene equivalents) inversely with salinity. Possibly due to the influence from the Mackenzie River, which flows through regions with known fossil fuel deposits and natural seepages, PAH in nearshore waters show much greater fluctuations than PAH in deeper offshore waters. The deeper shelf waters have a level of 16 ng/l, comparable in cleanliness to uncontaminated oceanic waters at Ocean Weathership Station P (50° N, 145° W) in N. E. Pacific Ocean.

(2) Polycyclic Aromatic Hydrocarbons in Marine Organisms. Total PAH, defined as the sum of chrysene, benzanthracene, perylene, phenanthrene and pyrene and certain isomers in the flesh of Southern Beaufort Sea fish (Pomfret, Least Cisco and Arctic Cisco) averages 21 μg/kg wet weight within a range of 9-31 μg/kg wet weight. It is difficult to compare these baseline data with those from other areas because of the differences in age, species, migration, food habits, analytical techniques and chemical compounds involved. For comparison, total PAH for fish caught in Station P waters, generally considered clean, amounts to 20-82 μg/kg wet weight for salmon and 184 for tuna.

(3) Polycyclic Aromatic Hydrocarbons in Marine Sediments. Total PAH (defined as for organisms) in marine sediments is in the range 236-984 μg/kg wet weight for samples collected in the 1974 cruise and 122-2,888 μg/kg dry weight for the 1975 cruise. Total uv-PAH, defined as the sum of pyrene, benz[a]pyrene, perylene and coronene, is 0.4-20 μg/kg dry weight for nearshore sediments and about 300 μg/kg dry weight for benthic sediments. There is a paucity of data from other areas for a useful comparison.

(4) Low Molecular Weight Hydrocarbons in Sea Water. The levels of LMW Hydrocarbons (in nanoliters/l of sea water) in Southern Beaufort Sea are 72-617 methane, 0 for ethane and 0.20-0.92 for propane in 1974 data; and 15-1,151 for methane, 0.31-1.80 for ethane, and 0.11-0.90 for propane in 1975 data. These levels, with the exception of high methane in near-bottom waters, are considered low in general, indicating the absence of petrogenic inputs. The high methane in near-bottom waters is due to an influx from the sediments. The unsaturates are low, with ethylene in the range 0.14-1.92 nanoliters/l of sea water for the 1974 cruise and 0.18-4.14 nanoliters/l for the 1975 cruise, and with propylene at levels of 0.09-1.59 nanoliters/l for 1974 and 0.14-1.90 nanoliters/l for 1975. These low levels of unsaturates are of biogenic origin resulting from the low primary production in the Arctic marine

environment. No detectable amount of LMW aromatic compounds (benzene and toluene) was found in the 1975 cruise.

(5) Non-polar Hydrocarbons in Fish. The few fish samples from Southern Beaufort Sea show percentages of unresolved to total hydrocarbons of 23%-67% compared to 12-16% for N.E. Pacific Ocean fish and over 80% for Sargasso Sea fish. Using these characteristics as a means of measuring petroleum contamination, N.E. Pacific fish is considered to be clean while Sargasso Sea fish definitely contaminated. Southern Beaufort Sea fish may be considered marginal in showing the presence of petroleum hydrocarbons taking into account the small number of samples analyzed, the biological variability and thelimitations of this unresolved hydrocarbon envelope technique.

(6) Non-polar Hydrocarbons in Marine Plankton. The n-paraffins in most of the marine plankton extend from n-$C_{16}$ to n-$C_{38}$ with a maximum in the n-$C_{26}$ range with an insignificant odd-carbon predominance and an envelope of unresolved hydrocarbons. Compared to similar baseline data in the Atlantic Ocean and the Gulf of Mexico, the presence of petroleum hydrocarbons is implied. However, it is inconclusive whether such hydrocarbons are incorporated into the plankton biomass or just associated with the plankton collecting technique, which filters off all particulates, living or non-living.

(7) Non-polar Hydrocarbons in Marine Sediments. The n-paraffins in the marine sediments show characteristics of a bimodal distribution typical of a mixture of marine and terrestrial hydrocarbons. An odd-carbon predominance characteristic of terrestrial plant material is evident in most marine sediments of the Southern Beaufort Sea, suggesting an influx of Mackenzie River water. Phytane, an isoprenoid not usually present in recent sediments, is found in all Beaufort Sea sediments. Phytane has been used to indicate the presence of petroleum contamination and it may originate from natural seeps and drilling operations in the drainage basin of the Mackenzie River, although the possibility of natural bacterial production, reported in unpolluted areas in the English Channel, should not be ruled out.

(8) Tar and Particulate Pollutants. Southern Beaufort Sea appears to be free of tarballs, floating domestic plastic wastes and plastics from seismic exploration activities, based on Neuston-net tows in the surface waters for 1974 and 1975. The debris collected in the net appears to be of natural, terrestrial origin from trees, seeds and vegetations.

# 9. IMPLICATIONS AND RECOMMENDATIONS

## 9.1 Implications

The very low levels of hydrocarbons now existing in sea water of the Southern Beaufort Sea would imply a marine environment of extreme cleanliness with respect to petroleum hydrocarbons.

In the case of LMW hydrocarbons, the clean environment in the Southern Beaufort Sea may be evident when compared to the Gulf of Mexico where extensive baseline data are available (Sackett and Brooks, 1975; Brooks et al., 1973; and Swinnerton and Lamontagne, 1974). In the Gulf of Mexico, wherever extensive shipping and drilling take place, extremely high levels of petrogenic LMW hydrocarbons are found. On the Louisiana Shelf and the Louisiana Texas Shelf, levels four to five times open ocean concentrations are routinely found, and frequently, levels fifty to a hundred times the baseline values are seen. High concentrations of the light saturated hydrocarbons have been found associated with every port examined (Brooks and Sackett, 1973).

LMW hydrocarbon input from offshore drilling platforms produces methane levels up to three orders of magnitude times the background. Ethane, propane and butane are also found at levels over a thousand times their open ocean concentration, and in the case of butanes, an increase up to a million times has been reported (Sackett and Brooks, 1975). High saturated hydrocarbon levels have been measured at a distance of half a mile from a tanker dumping "clean" ballast water.

Clearly, baseline levels of LMW hydrocarbons have been vastly altered over the majority of the continental shelf off Louisiana and Texas. Thus, with existing baseline data, future changes could be easily detected in the Southern Beaufort Sea. Since methane can be produced naturally and ubiquitously, interpretation of its source can often be in doubt. Considering that high natural levels are at present associated with near-bottom water and that these can influence surface concentrations particularly in shallow waters less than 10 m it would be poor practice to use methane concentration alone to look for future anthropogenic inputs. High concurrent levels of ethane, propane and butane would make a very clear case for petrogenic origin and therefore, future LMW hydrocarbon studies to assess the influence of oil exploration on the environment should emphasize measurements of all saturated LMW hydrocarbons.

Although the LMW hydrocarbons are not known to be exceptionally toxic, they can cause anaesthesia and narcosis in moderate concentrations, and even death at sufficiently high levels (Blumer, 1969). Oxidation and exchange processes will eventually remove most of these hydrocarbons from sea water. However, their occurrence may indicate the presence of other not so harmless hydrocarbons such as the di-, tri- and polycyclic aromatic hydrocarbons.

Polycyclic aromatic hydrocarbons are more persistent than LMW hydrocarbons in the marine environment, and as a result of their low biodegradability, PAH could be accumulated to high concentrations in marine organisms and sediments. The main concern for this class of compounds is its carcinogenic potential. However, it should be emphasized that only a few of the PAH out of thousands tested exhibit carcinogenic activity towards experimental animals (ZoBell, 1971) and their effects on marine organisms are essentially unknown. The most active carcinogenic hydrocarbons (Heidelberger, 1964) are 20-methylcholanthrene, 9,10-dimethyl-1,2,5,6-dibenzanthracene, 9,10-dimethyl-1,2-benzanthracene and 1,2,5,6-dibenzanthracene. Often, closely related compounds structurally may be inactive or vice-versa.

The PAH content in the Southern Beaufort Sea is low, implying either a very effective removal mechanism of PAH from sea water through biological uptake or sediment adsorption. The PAH content in the few fish samples from the Southern Beaufort Sea appear to be on the low side when compared to similar content in different species of fish in the N.E. Pacific Ocean. At least ten times more samples would be required to establish their presence in fish with statistically significant meaning. PAH in the marine sediments did not present many sampling problems since it is present in large quantities. However, the variability in the sediment in Beaufort Sea and in marine mud from other geographical areas (ZoBell, 1971) implies a very difficult interpretation problem.

The baseline data on non-polar hydrocarbons in fish imply the absence of petroleum contamination although this suggestion would be limited by the small number of samples and biological variability. Similar data in marine plankton and marine sediments imply the presence of petroleum hydrocarbons in the samples collected, possibly from the input from the Mackenzie River, which flows through areas with fossil fuel deposits and drilling operations. A lack of similar data in the Mackenzie River and the delta region prevents any firm conclusion on this possible explanation.

The absence of tar and plastics in the Southern Beaufort Sea implies a clean environment, at least visually free from anthropogenic influences.

## 9.2 Recommendations

It is recommended that:

(1) Year-to year fluctuations in hydrocarbon levels should be studied to establish the natural variability for a better assessment of the anthropogenic inputs. In future, hydrocarbons and possibly other pollutant levels should be monitored regularly in marine sediments, in sea water, in marine fauna and flora and in food fish species.

(2) Several selected oceanic and nearshore areas, representative of the Arctic environment, should be preserved. It is with

prohibition of drilling activities in these areas that changes can be discerned when comparisons are made with areas where drilling has taken place.

(3) Wintertime hydrocarbons and chemical oceanographic data should be obtained so that the environmental consequences of winter drilling operations and/or accidental blowouts or spills can be assessed effectively.

(4) Further development of sampling and analytical techniques for low levels of hydrocarbons in the marine environment should be pursued. At present, special equipment and analytical methods only permit very few laboratories of extremely high competence to perform baseline studies in a pristine environment. To be effective, simplication of existing sampling and analytical procedures to a degree that can be handled by chemical oceanographic consultant companies will be required.

(5) Further work to ascertain the required hydrocarbon parameters is necessary, so that resources to assess future environmental changes can be applied more effectively. For example, measurements of all saturated LMW hydrocarbons and LMW aromatics would be more useful than measurements of methane alone, which may be produced by nature. Measurements of polycyclic aromatic hydrocarbon levels in sea water and marine organisms may be more useful than similar measurements in marine sediments because of the extremely high variability in the sediments.

(6) Whenever possible, baseline hydrocarbon data should be collected, especially if the samples can be obtained routinely from the same location. What should be observed depends on the competence of the laboratory involved and the logistics problems in sampling, sample transportation and storage. Tentatively, the following sample collections should be made: (a) Neuston-net tows for tar and plastics, (b) fish frozen in ice, (c) freshly caught fish by the native population and (d) pipe-dredged surface sediment samples or sediment sampled by a gravity core sampler without using any lubricating grease or oil. Water sampling and storage should only be made when personnel are thoroughly familiar with the cleaning procedures and logistics of preserving the sample integrity.

## 10. NEEDS FOR FURTHER STUDY

Pollutants resulting from drilling operations, in particular trace metals, should also be studied simultaneously with hydrocarbons. These can result from drilling muds, spilled fuels, ship operations and increasing human activities. The cost is minimal since the major cost may be absorbed in a hydrocarbon study.

The environmental effects of pollutant uptakes, such as hydrocarbons, dispersants and trace metals, in the Arctic could be studied using C.E.P.E.X. techniques (Controlled Ecosystem Pollution Experiment) where sea water is enclosed with a small quantity of the test material added to study the sub-lethal effects. This work could be an extension of the present Ocean Chemistry work in Saanich Inlet. This approach has an important bearing on the interpretation of the chemical data on hydrocarbon levels and other contaminant levels.

After the initial work on finding the existing levels of chemicals and hydrocarbons is completed, future work should be initiated to fill the gap in the processes at work in the Arctic environment which could affect the distribution of petroleum-based hydrocarbons and other pollutants. Knowledge on the geochemical cycles is also required since adsorption of the pollutants on sediments and the dispersion of sediments would be important factors in the fate of these pollutants.

The present study is mainly a general investigation of the hydrocarbon levels in sea water, marine organisms and marine sediments in the Southern Beaufort Sea. In the immediate vicinity of the drilling sites and artificial islands, more concentrated efforts are required to monitor more acute environmental changes which may result from the drilling operations and associated increased marine traffic.

Hydrocarbon input from the Mackenzie River and the hydrocarbon level around the Mackenzie Delta should be studied in the future. This study has shown that the Southern Beaufort Sea sediments contain natural petroleum hydrocarbons of terrestrial origin. The magnitude of these inputs must be assessed with accuracy for any future assessment of the change in hydrocarbon levels resulting from drilling operations.

The conclusions reached in the present study are based on the best scientific techniques available which are not entirely satisfactory. When more advanced methods or new approaches are available in future, this study and its conclusions should be reviewed from time to time. Also, in future, when any compound is shown to be of environmental significance it may be checked using the sediment and tissue samples now being stored in an environmental sample bank at Ocean Chemistry.

## 11. REFERENCES

Atkinson, L.P. and F.A. Richards (1967) The occurence and distribution of $CH_4$ in the marine environment, Deep Sea Res., 14, 673-84.

Andelman, J.B. and J.E. Snodgrass (1974) Incidence and significance of polynuclear aromatic hydrocarbons in the water environment, pp. 69-83. In: CRC Critical Reviews in Environmental Control, (ed) Bond and Straub, (publ.) CRC Press, Inc., Cleveland, Ohio.

Bestougeff, M.A. (1967) Petroleum hydrocarbons, pp. 77-108. In: Fundamental aspects of petroleum chemistry, (ed) Nagy and Columbo, (publ.) Elsevier, New York, 388 pp.

Blumer, M. (1965) Organic pigments: Their long-term fate, Science, 149, 722.

Blumer, M. (1969) Oil pollution of the ocean, Oceanus, 15(2).

Blumer, M. and W. Giger (1974) Polycyclic aromatic hydrocarbons in the environment: Isolation and characterization by chromatography, visible, ultraviolet and mass spectrometry, Anal. Chem., 46, pp. 1663-1671.

Blumer, M. and J. Sass (1972) Indigenous and petroleum derived hydrocarbons in a polluted sediment, Mar. Poll. Bull., 3(6), pp. 92-94.

Blumer, M. and W.D. Snyder (1965) Isoprenoid hydrocarbons in recent sediments: Presence of pristane and probable absence of phytane, Science, 150, pp. 1588-1599.

Blumer, M., R.R.L. Guillard and T. Chase (1971) Hydrocarbons in marine phytoplankton, Mar. Biol., 8, pp. 183-189.

Blumer, M., G. Souza and J. Sass (1970) Hydrocarbon pollution of edible shellfish by an oil spill, Mar. Biol., 5, 195.

Borneff, J., F. Selenka, H. Kunte and A. Maximos (1968) Experimental studies on the formation of polycyclic aromatic hydrocarbons in plants, Environ. Res., 2, 22.

Brooks, J.M. and W.M. Sackett (1973) Sources, sinks, and concentrations of light hydrocarbons in the Gulf of Mexico, J. Geophys. Res., 78, pp. 5248-58.

Brooks, J.M., J.R. Gormley and W.M. Sackett (1974) Molecular and isotopic compositions of two seep-gases from the Gulf of Mexico, Geophys. Res. Letters, 1, pp. 213-6.

Brooks, J.M., A.D. Fredericks, W.M. Sackett and J.W. Swinnerton (1973) Baseline concentrations of light hydrocarbons in Gulf of Mexico, Environ. Sci. & Techn., 7, pp. 639-642.

Brown, F.S., M.J. Baedecker, A. Nissenbaum and I.R. Kaplan (1972) Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia - III. Changes in organic constituents of sediment, Geochim. et Cosmochim. Acta, 36, pp. 1185-1203.

Burns, K.A. and J.M. Teal (1971) Hydrocarbon incorporation into the salt marsh ecosystem from the West Falmouth oil spill, Woods Hole Oceanographic Tech. Rep., No. 71-69, Woods Hole, Mass., 14 pp.

Burns, K.A. and M. Teal (1973) Hydrocarbons in the pelagic Sargassum community, Deep Sea Res., 20, pp. 207-211.

Chester, S.N., B.H. Gump, H.S. Hartz, W.E. May, S.M. Dyszel and D.P. Enagonio (1976) Trace hydrocarbon analysis: The NBS Prince William Sound/NE Gulf of Alaska baseline study, NBS Tech. Note 889, 66 pp.

Clark, R.C., Jr. (private communication)

Clark, R.C., Jr. (1966) Saturated hydrocarbons in marine plants and sediments, M. Sc. Thesis, Mass. Inst. Technol., 96 pp.

Clark, R.C., Jr. and M. Blumer (1967) Distribution of n-paraffins in marine organisms and sediment, Limnol. Oceanogr., 12, pp. 79-87.

Clark, R.C., Jr. and J.S. Finley (1973) Techniques for analysis of paraffin hydrocarbons and for interpretation of data to assess oil spill effects in aquatic organisms. In: Proceedings of the 1972 Joint Conference on Prevention and Control of Oil Spills, American Petroleum Institute, Washington, D.C., pp. 161-172.

Cooper, J.E. and E.E. Bray (1963) A postulated role of fatty acids in petroleum formation, Geochim. Cosmochim. Acta, 27, pp. 1113-1127.

Cretney, W.J. and C.S. Wong (1974) Fluorescence monitoring study at Ocean Weather Station "P". In: Marine Pollution Monitoring (Petroleum) Symposium and Workshop, May 13-17, 1974 at National Bureau of Standards, Gaithersburg, Maryland, U.S.A., Preprint of contribution papers, pp. 85-88.

David, D.J. (1974) Gas chromatographic detectors, (ed) J. Wiley and Sons, N.Y.

De Lima-Zanghi, C. (1968) Marine plankton fatty acids and pollution with benzo (a) pyrene, Cah. Oceanogr., 20(3), 203, 1968 (French); C.A., 1968, 69, 45858b.

Dembicki, H., Jr., W.G. Meinschein and D.E. Hatlin (1976) Possible edological and environmental significants of the predominance of even-carbon number, $C_{20}$ - $C_{30}$ n-alkanes, Geochim. et Cosmochim. Acta, 40, pp. 203-208.

Douglas, A.G. and P.J. Grantham (1973) Docosane in rock extracts: A possible contaminative source, Chem. Geol., 12, pp. 249-255.

Dunn, B.P. and H.F. Stich (1975) The use of mussels in estimating benzo (a) pyrene contamination of the marine environment (38971), P.S.E.B.M., 150, pp. 49-51.

Eglington, G. (1969) Organic Geochemistry: The organic chemist's approach, pp. 20-73. In: Organic Geochemistry, (ed) Eglington and Murphy, (publ.) Springer-Verlag Berlin.

Eglington, G., A.G. Gonzales, R.J. Hamilton and R.A. Raphael (1962) Hydrocarbon constituents of wax coatings of plant leaves: a taxonomic survey, Phytochem., 1, pp. 89-102.

Ehrhardt, M. and M. Blumer (1972) The source identification of marine hydrocarbons by gas chromatography, Environ. Pollut., 3, pp. 179-194.

Farrington, J.W. and J.G. Quinn (1973) Petroleum hydrocarbons in Narragansett Bay. I. Survey of hydrocarbons in sediments and clams (Mercenaria mercenaria), Estuarine Coastal Mar. Sci., 1, pp. 71-79.

Farrington, J. and J. Teal (1972) Summary of intercalibration measurements and analysis of open ocean organisms for recently biosynthesis hydrocarbons and petroleum hydrocarbons. In: Proceedings of a workshop on baseline studies of pollutants in the marine environment, pp. 583-631. Sponsored by the National Science Foundation's Office for the International Decade of Ocean Exploration, Brookhaven National Laboratory, May 24-26, 1972.

Farrington, I.W., C.S. Giam, G.R. Harvey, P.L. Parker and J. Teal (1972) Analytical techniques for selected organic compounds, E.D. Goldberg, (ed.) Marine Pollution Monitoring: Strategies for a National Program. U.S. Department of Commerce, Washington, D.C.

Frank, D.J., W.M. Sackett, R. Hall and A.D. Fredericks (1970) Methane, ethane, and propane concentrations in the Gulf of Mexico, Amer. Ass. Petrol. Geol. Bull., 54, 1933.

Grainer, E.H. (1975) Biological productivity of the southern Beaufort Sea: The physical-chemical environment and the plankton, Technical Report No. 12 a.

Heidelberger, C. (1964) Studies on the molecular mechanism of hydrocarbon carcinogenesis, J. Cellular Comp. Physiol. Suppl., 64, pp. 129-148.

Hoffman, D. and E.L. Wynder (1968) Chemical analysis and carcinogenic bioassays of organic particulate pollution. In: Air Pollution, (ed) Stern, 2, pp. 187-247, Academic Pass., N.Y.

Iliffe, T.M. and J.A. Calder (1974) Dissolved hydrocarbons in the eastern Gulf of Mexico Loop Current and the Caribbean Sea, Deep Sea Res., 21, pp. 481-488.

Il'nitskii, A.P., K.P. Ershova, A.Y. Khesina, L.G. Rozhkova, V.G. Klubkov and A.A. Korolev (1971) Stability of carcinogens in water and various methods of decontamination, Gig. Sanit., 36(4), 8, 1971 (Russian); (Eng. transl., Hyg. Sanit., 36, 9, 1971).

Jannasch, H.W. (1975) Methane oxidation in Lake Kivu, Limnol. & Oceanog., 20, pp. 860-4.

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

Koons, C.B., G.W. Jamieson and L.S. Ciereszko (1965) Normal alkane distributions in marine organisms: Possible significance to petroleum origin, Bull. Am. Ass. Petrol. Geologists, 49, pp. 301-304.

Lamontagne, R.A., J.W. Swinnerton, U.S. Linnenbom and W.D. Smith (1973) Methane concentrations in various marine environments, J. Geophys. Res., 78.

Mallet, L. (1971) Bacterial biosynthesis of polycyclic hydrocarbons of the benzo (a) pyrene type in biological media, Gaz. Hop. Civ. Mil., 143(9), 605, 1971; C.A., 1972, 76, 2510j.

Mallet, L. and M. Tissier (1970) Biosynthesis of polycyclic hydrocarbons of the benzo (a) pyrene type in forest soil, C.R. Soc. Biol. (Paris), 163(1), 63, 1969 (French); C.A., 1970, 73, 44, 301k.

Maritime Administration, U.S. Dept. of Commerce (1973) Vol. 1, Draft, Environmental Impact Statement, Maritime Administration Tanker Construction Program, N. T.I.S. Report No. EIS 730 392D, 150 pp.

Meinschein, W.G. (1959) Origin of petroleum, Bull. Amer. Assoc. Petrol. Geologists, 41, pp. 925-943.

Meinschein, W.G. (1969) Hydrocarbons - saturated, unsaturated and aromatic. In: Organic Geochemistry: Methods and Results, (ed) Eglington and Murphy, (publ.) Springer-Verlag, New York, Heidelburg, Berlin, pp. 330-356.

Meyers, P. (1972) Association of fatty acids and hydrocarbons with mineral particles in sea water, Ph.D. Thesis, University of Rhode Island, 154 pp.

Moore, B.J., R.D. Miller and R.D. Shrewsbury (1966) Information circular 8302, 1-142, U.S. Bureau of Mines, Pittsburgh.

National Academy of Sciences (1975) Petroleum in the marine environment: Workshop on inputes, fates, and the effects of petroleum in the marine environment, May 21-25, 1973, 107 pp.

Niaussat, P. (1970) Pollution, pas biosynthèse "in situ" d'hydrocarbures cancérigenes, d'une biocoénose lagunaire. Reproduction "in vitro" de ce phénomène, Rev. Intrnat. Océanogr. Méd., 17, pp. 87-98.

Niaussat, P., J. Ehrhardt and J. Ottenwalder (1968) Presence of 3, 4 - benzopyrene in the Clipperton Atoll lagoon, CR. Acad. Sci. (Paris), 267(21), 1772, (French); C.A., 1969, 70, 40561 k.

Niaussat, P., L. Mallet and J. Ottenwaelder (1969) Presence of benzo (a) pyrene in various marine phytoplankton species cultivated in vitro, C.R. Acad. Sci. (Paris), Ser. D., 268(7), 1109, (French); C.A., 1969, 70, 112540 a.

Parker, P.L., J.K. Winters and J. Morgan (1973) A baseline study of petroleum in the Gulf of Mexico. In: Proceedings of a workshop on baseline studies of pollutants in the marine environment, pp. 555-581. Sponsored by the National Science Foundation's Office for the International Decade of Ocean Exploration, Brookhaven National Laboratory, May 24-26.

Peake, E., B.L. Baker and G.W. Hodgson (1972a) Hydrogeochemistry of the surface waters of the Mackenzie River drainage basin, Canada - II. The contribution of amino acids, hydrocarbons and chlorines to the Beaufort Sea by the Mackenzie River system, Geochim. Cosmochim. Acta, 36, pp. 867-883.

Peake, E., M. Strosher, B.L. Baker, R. Gosser, R.G. McCrossan, C.J. Yorath and G.W. Hodgson (1972b) The potential of Arctic sediments: hydrocarbons and possible precursors in Beaufort Sea sediments. In: Proceedings of the International Geological Congress, twenty-fourth session, Montreal.

Pelletier, B.R. (1975) Sediment dispersal in the southern Beaufort Sea, Technical Report No. 25a.

Phillippi, G.T. (1974) The influence of marine and terrestrial source material on the composition of petroleum, Geochim. Cosmochim. Acta, 38, pp. 947-966.

Sackett, W.M. and J.M. Brooks (1974) Use of low molecular weight hydrocarbon concentrations as indicators of marine pollution. In: Marine Pollution Monitoring (Petroleum) Symposium and Workshop, May 13-17, pp. 82-4.

Sackett, W.M. and J.M. Brooks (1975) Origin and distribution of low molecular weight hydrocarbons in Gulf of Mexico coastal waters, ACS Symposium series, No. 18, pp. 211-30.

Scalan, R.S. and J.E. Smith (1970) An improve measure of the odd-even predominance in the normal alkanes of sediment extracts and petroleum, Geochim. Cosmochim. Acta, 34, pp. 611-620.

Shaw, D.G. and L.M. Cheek (1976) Draft, Hydrocarbon studies in the benthic environment at Prudhoe Bay, Alaska.

Speers, G.C. and E.V. Whitehead (1969) Crude petroleum. In: Organic Geochemistry, (ed) Eglington and Murphy, (publ.) Springer-Verlag, New York, Heidelburg, Berlin, pp. 638-675.

Stevens, N.P., E.E. Bray and E.D. Evans (1956) Hydrocarbons in sediments of Gulf of Mexico, Bull. Amer. Assoc. Petrol. Geologists, 40, pp. 975-983.

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

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

Swinnerton, J.W. and V.J. Linnenbom (1967b) Gaseous hydrocarbons in sea water: determination, Science, 156, pp. 1119-1120.

Swinnerton, J.W., V.J. Linnenbom and C.H. Cheek (1962) Determination of dissolved gases in aqueous solutions by gas chromatography, Anal. Chem., 4, pp. 483-485.

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

Whittaker, R.H. and G.E. Likens (1973) Carbon in the biota, pp. 281-297. In: Carbon and the Biosphere, (ed) Woodwell and Pecan, (publ) Technical Information Center, Office of Information Services, U.S. Atomic Energy Commission.

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, pp. 1577-1579.

Wong, C.S., D.R. Green and W.J. Cretney (1974) Quantitative tar and plastic waste distribution in the Pacific Ocean, Nature, 247, pp. 30-32.

Wong, C.S., D. MacDonald and W.J. Cretney (1976) Tar and particulate pollutants on the Beaufort Sea coast, Technical Report No. 13.

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

ZoBell, C.E. (1971) Sources and biodegradation of carcenogenic hydrocarbons, Prev. Cont. of Oil Spills Joint Conf. Proc., pp. 441-451, (publ) A.P.I., Washington, June 15-17.