

~~FE. 11. 85~~

30163



Battelle

New England

Marine Research

Laboratory

Report



New England Marine Research Laboratory
 397 Washington Street
 Duxbury, Massachusetts 02332
 Telephone (617) 934-5682

July 29, 1985

Dr. Joy Geiselman
 Contracting Officer's Representative
 Minerals Management Service
 Alaska, OCS Region
 949 East 36th Avenue
 Anchorage, Alaska 99510

Dear Dr. Geiselman:

It gives me pleasure to send you our Final Annual Report "Beaufort Sea Monitoring Program: A analysis of Trace Metals and Hydrocarbons From Outer Continental Shelf Activities - Year 1 Results" on Contract No. 14-12-0001-30163. We have addressed the comments on our draft report received on June 16, 1985, and have made use of additional text provided to us concerning the synopsis of drilling activities in the Beaufort Sea.

Although we have presented our results on the NOAA/NAF intercalibration sample in the report, we have not discussed apparent discrepancies between Battelle's results and those of NOAA. We have rechecked our results and stand by them. We plan to address this issue through the analysis of additional intercalibration materials to be supplied to us by NOAA as part of the Year 2 study.

Thank you for your useful comments. If you have any questions on the report as revised please contact me.

Sincerely,

Paul D. Boehm, Ph.D.
 Program Manager

PDB:dcw

cc: Mr. Jeffrey Petrino

Bill McLane NOAA Hydrocarbon Anal.

FINAL ANNUAL REPORT

on

BEAUFORT SEA MONITORING PROGRAM:
ANALYSIS OF TRACE METALS AND
HYDROCARBONS FROM OUTER CONTINENTAL
SHELF (OCS) ACTIVITIES - YEAR 1 RESULTS

July 29, 1985

by

Paul D. Boehm, Eric Crecelius
William Steinbauer, Margarete Steinbauer
Steven Rust and Jerry Neff

CONTRACT NO. 14-12-0001-30163

BATTELLE
New England Marine Research Laboratory
397 Washington Street
Duxbury, MA 02332

Submitted to:

Minerals Management Service
Alaska, OCS Region
Anchorage, AK 99510

"This study was funded by the Alaska Outer Continental Shelf Region of the Minerals Management Service, U.S. Department of the Interior, Anchorage, Alaska, under Contract No. 14-12-0001-30163.

PROJECT ORGANIZATION

Report Authors

	<u>Major Author(s)</u>	<u>Contributor(s)</u>
SECTION 1. INTRODUCTION	P. Boehm	J. Neff
SECTION 2. SAMPLING METHODOLOGY	W. Steinhauer	H. Steinhauer
SECTION 3. ANALYTICAL METHODOLOGY	U. Steinhauer E. Crecelius	
SECTION 4. PRESENTATION OF RESULTS	M. Steinhauer	E. Crecelius
SECTION 5. ANALYSIS AND INTERPRETATION OF DATA	P. Boehm	E. Crecelius S. Rust D. Burrell D. Shaw
SECTION 6. STUDY CRITIQUE AND RECOMMENDATIONS FOR YEAR 2 STUDY	P. Boehm	

This report has been reviewed by the Bureau of Minerals Management Service and approved for publication. Approval does not signify that the content necessarily reflect the views and policies of the Bureau, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	i
1. INTRODUCTION	1
1.1 Study Framework	1
1.2 Study Objectives and Technical Approach	1
1.3 Design Rationale	2
1.3.1 Sampling Rationale	5
1.3.2 Analytical Rationale	9
1.3.3 Data Analyses and Hypothesis Testing	10
1.4 Study Area Background	10
1.4.1 The Diapir Field	10
1.4.2 The Physical Environment of the Study Area	13
1.4.3 The Trace Metal and Hydrocarbon Geochemical Environment	17
1.4.4. The Sedimentological Environment	18
1.4.5 The Biological Environment	19
1.5 Potential Environmental Effects of Offshore Oil and Gas Development	19
1.5.1 Drilling Fluids and Cuttings	20
1.5.2 Produced Water	3
1.5.3 oil spills	36
1.6 Study Organizations	38
2. SAMPLING METHODOLOGY	38
2.1 Sampling Locations and Data	38
2.2 Sampling Methods and Locations	43
2.2.1 Field Survey Team	43
2.2.2 Survey of Vessel	43
2.2.3 Navigation	43
2.2.4 Communication	44
2.2.5 Field Data Management	44
2.2.6 Sampling Equipment and Methods	44
2.2.7 Sample Preservation and Transfer	45
2.3 Cruise Narrative and Sampling Limitations	46
3. ANALYTICAL METHODOLOGIES	47
3.1 Detailed Analytical Rationale	47
3.1.1 Measured Parameters	50
3.1.2 Pooling Strategy and Selection of Samples	55
3.2 Analytical Chemistry of Metals	59
3.2.1 Methods and Materials	59
3.2.2 Quality Control Methods	59

TABLE OF CONTENTS (Cont'd)

	<u>Page</u>
3.3 Analytical Chemistry of Hydrocarbons	61
3.3.1 Sample Processing.....	61
3.3.2 Sample Analysis.....	62
3.3.3 Quality Control Methods.....	63
3.4 Auxiliary Parameters	63
3.4.1 Hydrography.....	63
3.4.2 Sediment Grain Size Determinations.....*	66
3.4.3 Total Organic Carbon	67
4. PRESENTATION OF RESULTS.....	67
4.1 Introduction	67
4.2 Metals Data.....	67
4.2.1 Metals in Sediments.....	67
4.2.2 Metals in Tissues	70
4.3 Hydrocarbon Data.....	70
4.3.1 Saturated Hydrocarbons	75
4.3.2 Aromatic Hydrocarbons	81
4.3.3 Hydrocarbons in Tissues	81
4.3.4 Historical Data	81
4.4 Auxiliary Data.....*	89
4.4.1 Total Organic Carbon	89
4.4.2 Grain Size	89
4.5 Hydrographic Data	89
4.6 Quality Control Results.....	93
4.6.1 Metals.....	93
4.6.2 Hydrocarbons	93
4.6.3 Total Organic Carbon	103
4.6.4 Grain Size	103
5. ANALYSIS AND INTERPRETATION OF DATA.....	103
5.1 Introduction	103
5.2 Metals Chemistry	103
5.2.1 Sediment Sources and Dynamics	109
5.2.2 Relationships Between Metals and Properties of Sediment	109
5.2.3 Comparison of Metals Chemistry With Historical Data	113
5.2.4 Geographical Trends	113
5.2.5 Metals in Bivalve Tissues.....	113

TABLE OF CONTENTS (Cont'd)

	<u>Page</u>
5.3 Hydrocarbon Chemistry.....	117
5.3.1 General Interpretational Framework.....	117
5.3.2 Sediment Hydrocarbons.....	117
5.3.3 Bivalves.....	135
5*4 Statistical Analysis.....	136
5.4.1 Data Transformation.....	136
5.4.2 Data Normalization.....	139
5.4.3 Parameter Variability.....	144
6. STUDY CRITIQUE AND RECOMMENDATIONS FOR YEAR 2 STUDY	144
7. REFERENCES.....	151

LIST OF TABLES

Table 1.1 Drilling Sites in Federal Lease Areas.....	7
Table 1.2 Significant Potential Sources of Contaminants from o CS Operations.....	11
Table 1.3 Major Permitted Discharges and Potential Impact-Causing Agents Associated With Offshore Oil and Gas Exploration in the Beaufort Sea.....	21
Table 1.4 Concentrating Ranges of Several Metals in Natural Marine Sediments and Drilling Fluids From Alaska.....	23
Table 1.5 Projected Drilling Fluids/Cuttings Discharges to Alaska Coastal/OCS Waters During the Next Ten Years.....	25
Table 1.6 Organic Composition of Produced Water Effluents From Alaska.....	31
Table 1.7 Concentration Ranges of Metals in Seawater and in Produced Waters Discharged to the Gulf of Mexico.....	32
Table 1.8 Concentrations of Selected Petroleum Hydrocarbons in Produced Water Effluents From the Buccaneer Platform in the Northwest Gulf of Mexico.....	33
Table 2.1 Station Locations, Sampling Dates and Depths for Proposed and Sampled Stations for the 1984 Beaufort Sea Monitoring Program.....	40
Table 3.1 Analytical Plan for 1984 Sediment Samples.....	48
Table 3.2 Analytical Plan for 1984 Bivalve Samples.....	49

LIST OF TABLES (Cent'd)

		<u>Page</u>
Table 3.3	Analytical Methods Used for the Analysis of Trace Metals in Marine Sediments and Bivalves	51
Table 3.4	Compounds Determined by Fused Silica Capillary Gas Chromatography	53
Table 3.5	Key Diagnostic Parameters Determined by Fused Silica Capillary Gas Chromatography	54
Table 3.6	Aromatic Hydrocarbons and Heterocyclics Quantified Using High Resolution Capillary Gas Chromatography/Mass Spectrometry	5 6
Table 3.7	Key Diagnostic Parameters Determined by GC/MS and Used for Statistical Analysis	57
Table 3.8	Summary of Analytical Conditions for Metals in Sediments and Tissues	60
Table 3.9	Fused Silica Capillary Gas Chromatography/Flame Ionization Detection Analytical Conditions	64
Table 3.10	Gas Chromatography/Mass Spectrometry Instrumental Conditions	65
Table 4.1	Total Organic Carbon Means and Standard Deviations, and Percent Silt & Clay for all Sediment Stations	90
Table 4.2	Summary of Grain-Size Data for all Sediment Stations	91
Table 4.3	Hydrographic Data for 1984 BSM P Survey	92
Table 4.4	Analysis of Replicate Samples of Hess-1, a Standard Reference Sediment	94
Table 4.5	Analysis of Replicate Samples of Oyster Standard 1566, a Standard Reference Tissue	95
Table 4.6	Analysis of Replicate Procedural Blanks for Sediment Digestion	96
Table 4.7	Analysis of Replicate Procedural Blanks for Tissue Digestion	97
Table 4.8	Analysis of Replicate Samples of Reagents to Establish Reagent Blank for Sediment Digestion	98
Table 4.9	Analysis of Replicate Samples of Reagents to Establish Reagent Digestion for Tissue	99
Table 4.10	Comparison of Techniques for Determination of the Concentration of Metals in Sediments	100

LIST OF TABLES (Cont'd)

		<u>Page</u>
Table 4.11	Recoveries of PAH Contained in NBS-SRM-1647 Subjected to Hydrocarbon Analytical Scheme	101
Table 4.12	Analytically-Determined UVF Total Oil Concentrations in Sediments Fortified With Varying Concentrations of Prudhoe Bay Crude Oil	102
Table 4.13	Concentrations of Total Saturated Hydrocarbons (F1) and Selected Hydrocarbon Parameters in NOAA Reference Sediments	104
Table 4.14	Concentrations of n-Alkanes in NOAA Reference Sediment	105
Table 4.15	Concentrations of Polycyclic Aromatic Hydrocarbons (PAH) in NOAA Reference Sediments	106
Table 4.16	Quality Control Data for Total Organic Carbon Analysis *00* . . . ** . . .	107
Table 4.17	Quality Control Data for Gram-Size Analysis	108
Table 5.1	Range of Total Metal Concentrations in Arctic Coastal Sediments	114
Table 5.2	Regional Differences in the Co-reposition of Sediments Collected in 1984 from the Beaufort Sea	115
Table 5.3	Concentration of Metals in Bivalve Tissue	116
Table 5.4	Saturated Hydrocarbon Quantitative Parameters (GC/FID) Used to Test Null Hypotheses H ₀₁ {Sediment Concentrations} and H ₀₃ (Bivalve Concentrations)	118
Table 5.5	Saturated Hydrocarbon Parameters Source Ratios (GC/FID) Used to Test Null Hypotheses H ₀₂ (Sediment Hydrocarbon Sources) and H ₀₄ (Bivalve Hydrocarbon sources)	119
Table 5.6	PAH Quantitative Parameters (GC/MS) Used to Test Null Hypotheses H ₀₁ (Sediment Concentrations) and H ₀₃ (Bivalve Concentrations)	120
Table 5.7	PAH Source Parameters (GC/MS) Used to Test Null Hypotheses H ₀₂ (Sediment Sources) and H ₀₄ (Bivalve Sources)	121
Table 5.8	Tabulation of Several Key Saturated Hydrocarbon, Parameters and Diagnostic Ratios by Means at Each Station ^a	129
Table 5.9	Summary of Aromatic Hydrocarbon Diagnostic Ratios	134
Table 5.10	F Values From Levene's Test for Homogeneity of Variance	140

LIST OF TABLES (Cont'd)

		<u>Page</u>
Table 5.11	Pooled Within-Station Standard Deviation Estimates for Unnormalized and Normalized Logarithmic Data	141
Table 5.12	Correlation Matrix for Metal Parameters with TOC, % Silt, % Clay Using Station Averages	142
Table 5.13	Correlation Matrix for Selected Organic Parameters with TOC, % Silt, and % Clay Using Station Averages	143
Table 5.14	Detectable Multiplicative Changes in Concentrating as a Function of Pooled Standard Deviation on a Logarithmic (Natural) Scale	145
Table 5.15	Standard Deviation on a Logarithmic (Natural) Scale for the Metal Parameters and the Organic Parameters TOC and TOC	146
Table 5.16	Standard Deviation on a Logarithmic (Natural) Scale for Selected Organic Parameters by Station	147
Table 5.17	Detectable Multiplicative Changes in Concentrations as a Function of Standard Deviation on a Logarithmic (Natural) Scale	148

LIST OF FIGURES

Figure 1.1	Sediment Monitoring Network Blocks Showing Assumed Risk Levels and Locations of Potential Sampling Sites	4
Figure 1.2	Proposed Tracts for Lease Sale 71	5
Figure 1.3	Lease Sale BF, Leased Tracts	6
Figure 1.4	Beaufort Sea 97	12
Figure 1.5	Proposed Endicott Development of Sag River/Duck Island Area	14
Figure 1.6	The Seal Island Discovery, With Paths of Exploratory and Delineation D	15
Figure 1.7	Lisburne Development Proposal Offshore Construction	16
Figure 1.8	Time Sequence Illustrating Fate of Discharged Drilling Fluid Particulates; Side View of Plume During 1000bb/hr Discharge (From Ayers et al., 1980)	27
Figure 1.9	Graphical Presentation of Results of Five Drilling Fluid Dispersion Studies Performed in U.S. Outer Continental Shelf Waters	28
Figure 1.10	Relationship Between Distance From Produced Water Discharge Point and Dilution Ratio	34

LIST OF FIGURES (Cent'd)

	<u>Page</u>
Figure 1.11 Schematic Representation of How TSM (Total Suspended Matter) Levels Promote Sorption and Sedimentation of Oil From Spills and Produced Water Chemicas.	35
Figure 1.12 Program Organization Showing Task Leaders and Principal Investigators	39
Figure 2.1 Beaufort Sea 1984 Monitoring Program Study Area Showing all Station Locations	41
Figure 2.2 Detail of Prudhoe Bay-Gwydyr Bay Area Station Locations	42
Figure 3.1 Analytical Scheme for Hydrocarbons in Sediments and Bivalve Tissues	52
Figure 3.2 Laboratory Sample Splitting Procedure	58
Figure 4.1 Summary of Metal Concentrations, Silt and Clay Fractions, and Total Organic Carbon in Eastern Study Area Sediments	68
Figure 4.2 Summary of Metal Concentrations, Silt and Clay Fractions, and Total Organic Carbon in Endicott Field Transect Station Sediments	69
Figure 4.3 Summary of Metal Concentrations, Silt and Clay Fractions, and Total Organic Carbon in Prudhoe Bay-Gwydyr Bay Area Sediments	71
Figure 4.4 Summary of Metal Concentrations, Silt and Clay Fractions, and Total Organic Carbon in East Harrison Bay Sediments	72
Figure 4.5 Summary of Metal Concentrations, Silt and Clay Fractions, and Total Organic Carbon in West Harrison Bay Sediments	73
Figure 4.6 Summary of Metal Concentrations in Bivalve Tissues and Corresponding Sediments	74
Figure 4.7 Summary of Saturated and U V/l? Hydrocarbon Concentration, Silt and Clay Fractions, and Total Organic Carbon in Eastern Study Area Sediments	76
Figure 4.8 Summary of Saturated and U V/F Hydrocarbon Concentrations, Silt and Clay Fractions, and Total Organic Carbon in Endicott Transect Stations Sediments	77
Figure 4.9 Summary of Saturated and U V/F Hydrocarbon Concentration, Silt and Clay Fractions, and Total Organic Carbon in Prudhoe Bay-Gwydyr Bay Area Sediments	78

LIST OF FIGURES (Cont'd)

		<u>Page</u>
Figure 4.10	Summary of Saturated and U V/F Hydrocarbon Concentration, Silt and Clay Fractions, and Total Organic Carbon in East Harrison Bay Sediments	79
Figure 4.11	Summary of Saturated and U V/F Hydrocarbon Concentrations, Silt and Clay Fractions, and Total Organic Carbon in West Harrison Bay Sediments	80
Figure 4.12	Summary of Aromatic Hydrocarbon Concentrations, Silt and Clay Fraction% and Total Organic Carbon in Eastern Study Area Sediments	82
Figure 4.13	Summary of Aromatic Hydrocarbon Concentrations, Silt and Clay Fractions, and Total Organic Carbon in Endicott Transect Station Sediments	83
Figure 4.14	Summary of Aromatic Hydrocarbon Concentration, Silt and Clay Fractions, and Total Organic Carbon in Prudhoe Bay-Gwydyr Bay Area Sediments	84
Figure 4.15	Summary of Aromatic Hydrocarbon Concentrations, Silt and Clay Fractions, and Total Organic Carbon in East Harrison Bay Sediments	85
Figure 4.16	Summary of Aromatic Hydrocarbon Concentrations, Silt and Clay Fractions, and Total Organic Carbon in West Harrison Bay Sediments	86
Figure 4.17	Summary of Hydrocarbon Concentrations in Bivalve Tissues and Corresponding Sediments	87
Figure 4.18	Summary of 1984 BSMP Survey and Historical Hydrocarbon Data	88
Figure 5.1	The Linear Correlation Between Total Barium and Percent Mud (Silt Plus Clay) in 27 Surface Sediments from the Beaufort Sea	110
Figure 5.2	The Linear Correlation Between Total Barium and Percent TOC in 27 Surface Sediments from the Beaufort Sea	111
Figure 5.3	The Linear Correlation Between Total Vanadium and Percent Mud in 27 Surface Sediments from the Beaufort Sea	112
Figure 5.4	The Average Concentrations of Total saturated Hydrocarbons (TOT) as Determined by GC-FID, and Percent Mud, at Each Station	122
Figure 5.5	Results of U V/F Determined Hydrocarbon Content of Sediments Showing Averages for Each station	123
Figure 5.6	Typical UV/F Spectra of, A-Prudhoe Bay Crude Oil Reference Standard and B-Sediment Extract	124

LIST OF FIGURES (Cent'd)

Page

Figure 5.7	Regression of Saturated Hydrocarbons Against Silt Plus Clay Content for Study Area Sediments.	125
Figure 5.8	Regression of Saturated Hydrocarbons Against Total Organic Carbon Content for Study Area Sediments.....	126
Figure 5.9	Representative G C-FID Traces for Beaufort Sea Sediment Saturated Hydrocarbons, A-Station 6B; B-Station 5-1; C-Station 7G.....	128
Figure 5.10	Typical Sediment Saturated Hydrocarbon G C-FID Traces <u>Illustrating</u> the Difference Between Oiled and Unoiled Sediments	130
Figure 5.11	Aromatic Hydrocarbon Relative Abundance Plots from Representative Sediment Stations	132
Figure 5.12	Aromatic Hydrocarbon Relative Abundance Plots of Sediments and Prudhoe Bay Crude Oil	133
Figure 5.13	UV/F Spectra of Prudhoe Bay Crude Oil(A) and Benthic Bivalve Sample Extracts, Stations 6D <u>Astarte</u> (B) and Station 5F <u>Cyrtodaria</u> (C).....	137
Figure 5.14	Total Hydrocarbons G C-FID Trace of Benthic Bivalve Sample Extract.	138

ABSTRACT

Oil exploration and production activities in offshore waters of the Alaskan Beaufort Sea have been increasing in recent years. A research program designed to implement an environmental monitoring program and to detect and quantify **long-term** changes in the concentrations of metals and hydrocarbons **sourced** in exploration and production discharges, was begun in 1984.

The first year of the study focused on establishing a series of **benthic** stations at which surface sediment (0-1 cm) and **bivalve molluscs** were sampled using a modified grab sampler designed to obtain an undisturbed sediment sample. Twenty-seven stations were occupied at which eight replicate sediment samples were collected. A sampling strategy consisting of combination of randomly placed stations, stations chosen to examine offshore **gradients**, gradients away from a major exploration/production activity, and stations chosen to reoccupy stations previously in other programs was employed. The collection success of **bivalves** was limited due to the **sparsity** of animals, but samples of sufficient biomass for chemical analyses were obtained at three stations.

The analysis of **metal** constituents (Ba, Cr, V, Pb, Cu, **Zn**, Cd) in sediments by a variety of analytical techniques revealed a wide range of concentrations. However, highest concentrations were associated with fine **grained** sediments and were located near discharges to major rivers. The within-station variability of metals in sediments was examined at each station and the minimum detectable change at each station determined. **Similarly**, hydrocarbon concentrations were determined on replicates at each station. Detailed hydrocarbon determinations of individual saturated hydrocarbons (by GC/FID) and **polynuclear** aromatic hydrocarbons (PAH) (by GC/MS) were performed on replicates at seven stations and on composite samples from the remaining stations. Concentrations of hydrocarbons also **covariied** with the quantity of **fine** sediment (i.e., silt plus clay) and were related to the **proximity** of the station to river discharges. The **detailed** PAH compositions revealed that sediments at all stations **contained** significant quantities of **fossil** hydrocarbons. However, this composition did not result from exploration/production discharges, but probably was related to the nature of sediment source material which contains organic-rich peat, and possible smaller quantities of coal particles from river drainage. No evidence for inputs from any oil and gas exploration activities were detected in any sediment or bivalve samples.

Based on the Year 1 results, a **statistically** valid method for monitoring incremental additions of metals and hydrocarbons to the **benthic** environment has been established and the most useful chemical parameters, to ascertain these changes, developed. Suggestions for implementation of the Year 2 program are presented in this report as well.

1. INTRODUCTION

1.1 Study Framework

Although the north slope of Alaska has been a significant oil producing region for several years, offshore exploration in state waters only began about five years ago and, at present, is growing steadily in federal leasing areas. The Outer Continental Shelf (OCS) Lands Act Amendments of 1978 charge the Department of the Interior, Minerals Management Service (MMS) to monitor the marine environment with the purpose of identifying changes in the quality of the environment and to identify the causes of such changes.

The unique physical and biological environment of the Alaskan Beaufort Sea makes exploration for, and development and production of offshore oil and gas resources extremely difficult and hazardous. In addition, it raises serious questions about the environmental fate and effects of intentional or accidental discharges and activities, and the applicability of results of studies in other U.S. OCS regions for predicting impacts in the Beaufort Sea. A scientific appraisal of the feasibility of conducting a monitoring program in the Beaufort Sea to measure changes in environmental quality attributable to oil and gas exploration and production activities, and the framework for the design of such a program was discussed at a workshop held in Alyeska, Alaska on September 27-29, 1983. The MMS and National Oceanic and Atmospheric Administration (NOAA) sponsored workshop resulted in a document (Dames and Moore, 1984) which recommended the implementation of an initial phase of the Beaufort Sea Monitoring Program (BSMP), to be based on determining whether changes in key toxic and source-diagnostic chemical concentrations were detectable in the region. This consensus recommendation formed the basis of the study design framework and the study results presented in this report.

1.2 Study Objectives and Technical Approach

The objectives of the BSMP were to establish and implement a monitoring program over an initial three-year period:

- To detect and quantify long-term change in the concentrations of trace metals and hydrocarbons that might:
 1. result from discharges of OCS oil and gas exploration and production activities;
 2. adversely affect, or suggest other adverse effects on humans or those parts of their environment by which they judge quality; and
 - 3* influence Federal OCS regulatory management decisions.
- To determine the probable cause(s) of such change(s).

Over the three-year period of this initial phase of the BSMP, the technical approach consists of:

- Collecting the necessary bottom sediment and benthic bivalve species.
- Performing the appropriate laboratory analyses for trace metal, hydrocarbon and auxiliary parameters.
- Performing the appropriate statistical analyses to test the following null hypotheses for evaluating effects of OCS oil and gas development-related perturbations:

H₀1: There **will** be no change in sediment concentrations of selected metals or hydrocarbons.

H₀2: Changes in concentrations of selected metals or hydrocarbons in sediments are not related to oil and gas development activity.

H₀3: There will be no change in concentrations of selected metals or hydrocarbons in selected sentinel organisms.

H₀4: Changes in concentrations of selected metals or hydrocarbons in selected sentinel organisms are not related to OCS oil and gas development activity.

- o **C**ollecting concurrent, localized physical and water quality data to aid in the evaluation and interpretation of the data collected.
- Evaluating the efficacy of the monitoring design based on each year's results and to recommend refinements as needed.
- Evaluating the need for the addition or deletion of elements to this core chemical program at the end of the three-year study and to make such recommendations to MMS.

As in all monitoring programs, the first year of the study was devoted to establishing of a monitoring design including the selection of sampling stations, sampling methods, analytical targets and associated methods, and interpretive tools. Thus, while the above study objectives and technical approaches were operative, our additional objectives for Year 1 of the study were to:

- Establish a sampling design to be modified as needed based on an assessment of sampling success and other logistical factors.
- Assess the variability in the measurement of analytical parameters resulting from combined sampling variability (small scale heterogeneity) and analytical variability.
- Determine what degree of change can be validly statistically determined for the contaminants of interest, given such variability and given realities of financial constraints.
- From the variety of analytical measurements and their variability, establish a blend of effective monitoring parameters to be focused on during subsequent hypothesis testing to begin in Year 2 of the study.

In order to accomplish both the Year 1 and longer term objectives, a study design (described in the next section) was initially adopted.

1.3 Design Rationale

Guiding the design of the field sampling, analytical and interpretive segments of the program was the overall objective of the study: to detect changes due to OCS activities over time. Thus, the placement of stations, the sampling replication scheme,

the analytical targets chosen and the variability analysis of measured parameters, together with eventual testing of statistical hypotheses, were geared to a monitoring **philosophy**. During the **first** year of the program the monitoring **design** was established without a **firm** knowledge of key factors such as: 1) the environmental **variability** in selected analytical parameters, 2) the best choice of analytical targets and/or parameter ratios, and 3) in the case of **benthic** bivalve **molluscs**, the availability of animals at selected station locations. The program began with the expectation that the initial **sampling** and analytical design would most likely be **refined** as actual data were analyzed. However, prior to the acquisition of data, it was decided to establish a design which, based on **OCS** activity, would maximize the ability to detect actual chemical perturbations due to an on-going activity.

The historical data base was generated during the mid- 1970's under **NOAA/MS** funding as part of an environmental baseline or reconnaissance philosophy, and it was clear that while existing data might **aid** in station selection, these data would not shed much light on environmental variability due to the lack of replicate analyses in those previous programs.

The choice of sample types, bottom sediment and benthic bivalve **molluscs** stem **from** the design workshop conclusions (Dames and Moore, 1984). Bottom sediments were chosen since they represent a natural accumulator or sink of particulate pollutants. Bivalves were selected because of their established utility (National Academy of Sciences, 1983) as environmental sentinels. In this capacity, bivalves process large amounts of seawater during normal feeding activity and accumulate water-borne pollutants **from** dilute solutions. Thus, bivalves represent a surrogate seawater sample reflecting a time-integrated exposure regime (the direct analysis of seawater itself **being** ill-advised in a **monitoring** program due to large variability and generally **low** ambient levels requiring a very large volume sample to be processed).

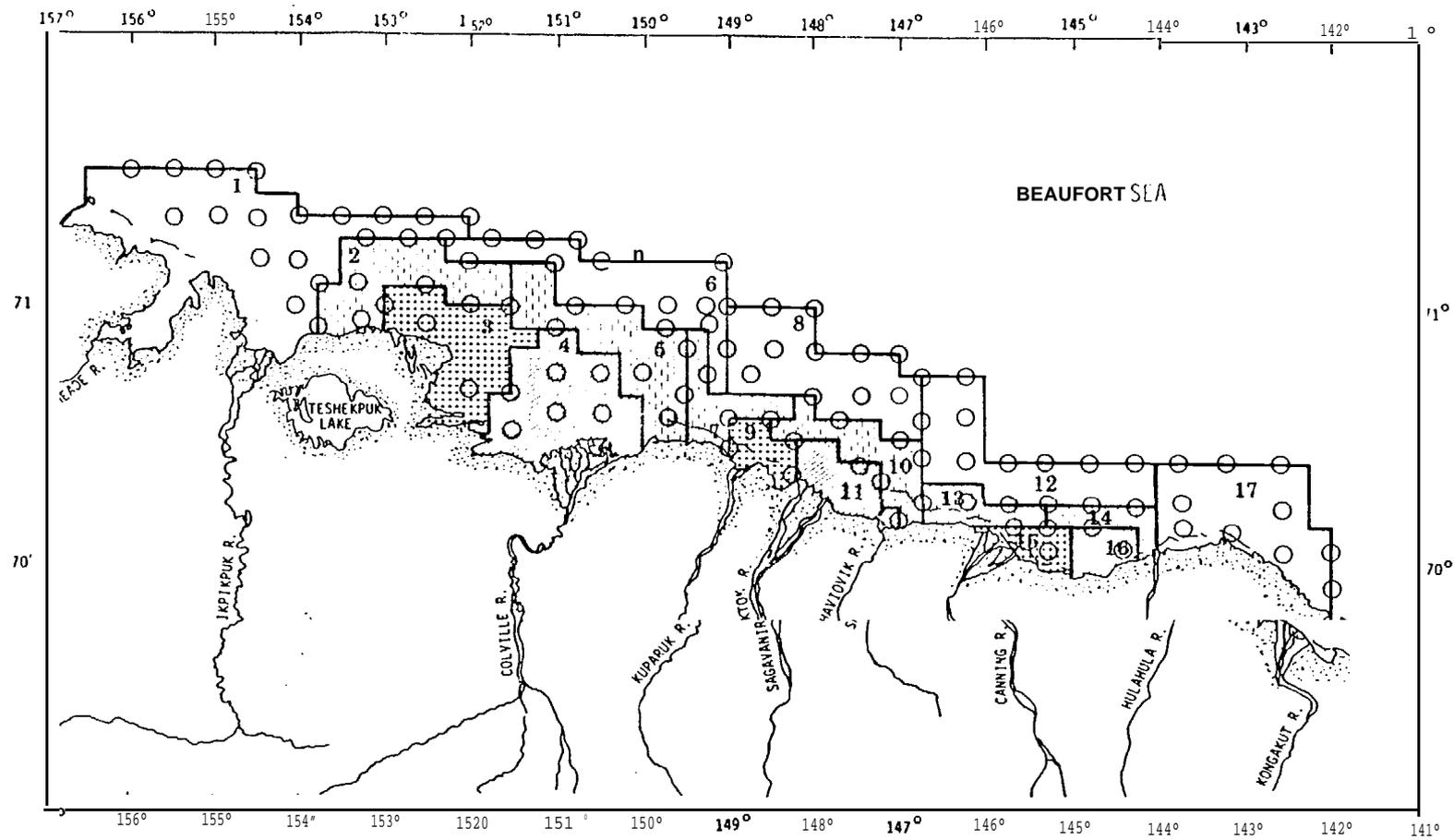
1.3.1 sampling Rationale

In addition to the important mechanics of the actual **sampling** activity, several major considerations entered into the design of the sampling program and **will** be discussed in Section 2.2 of this report. Those considerations focused on the selection of sampling stations and the specification of a replication scheme.

Present levels of **OCS** **oil** and gas exploration and production activities, and oil company interest **in** future exploration sites were considered very important in the design of the program. This activity and interest was factored into the design through the areal relative risk assessment proposed by the Dames and Moore (1984) report. A summary of their **findings** appears in Figure 1.1 in which **'low'**, **'medium'**, **'high'** and **'highest'** risk areas (risk in terms of probability of **detecting** environmental change) were **designated**. The **assessment** for **med** an overall **template** on the sampling design.

The rationale for the development of the sampling plan focused on the Diapir Field Lease Sale 71 area and the joint State/Federal Lease Sale BF (Figures 1.2 and 1.3). We chose to consider sampling locations within state boundaries (i.e., within the 3-mile limit) as **well**. If chemical inputs to the marine system attributable to oil and gas development are to be detected during the initial phase of the **BSMP**, they are likely to occur **within** the lease sale **sites** and in nearshore areas where considerable exploration activities have and are presently occurring (Alaska **Oil** and Gas **Commission**, 1983). During the next several years large scale development is only likely to occur within state waters. To date, exploratory drilling in Federal lease areas has been restricted to operations summarized in Table 1.1, although drilling permit applications have been **filed** for other sites.

The program **design** rationale focused on the midfield to **farfield** regions surrounding and adjacent to present and **future** exploration and development activities. Data on **nearfield** (within 1000 m of a **specific** activity) distributions of drilling muds, cuttings and other discharges surrounding **OCS** activities are **acquired** as part of required National Pollutant Discharge Elimination System (**NPDES**) permit monitoring.



Legend

- O Monitoring locations
- 1 Monitoring block
- Low risk
- Medium risk
- High risk
- Highest risk

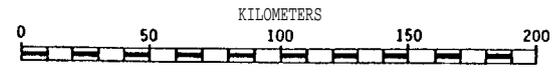


Figure 1.1 Sediment Monitoring Network Blocks Showing Assumed Risk Levels and Locations of Potential Sampling Sites.

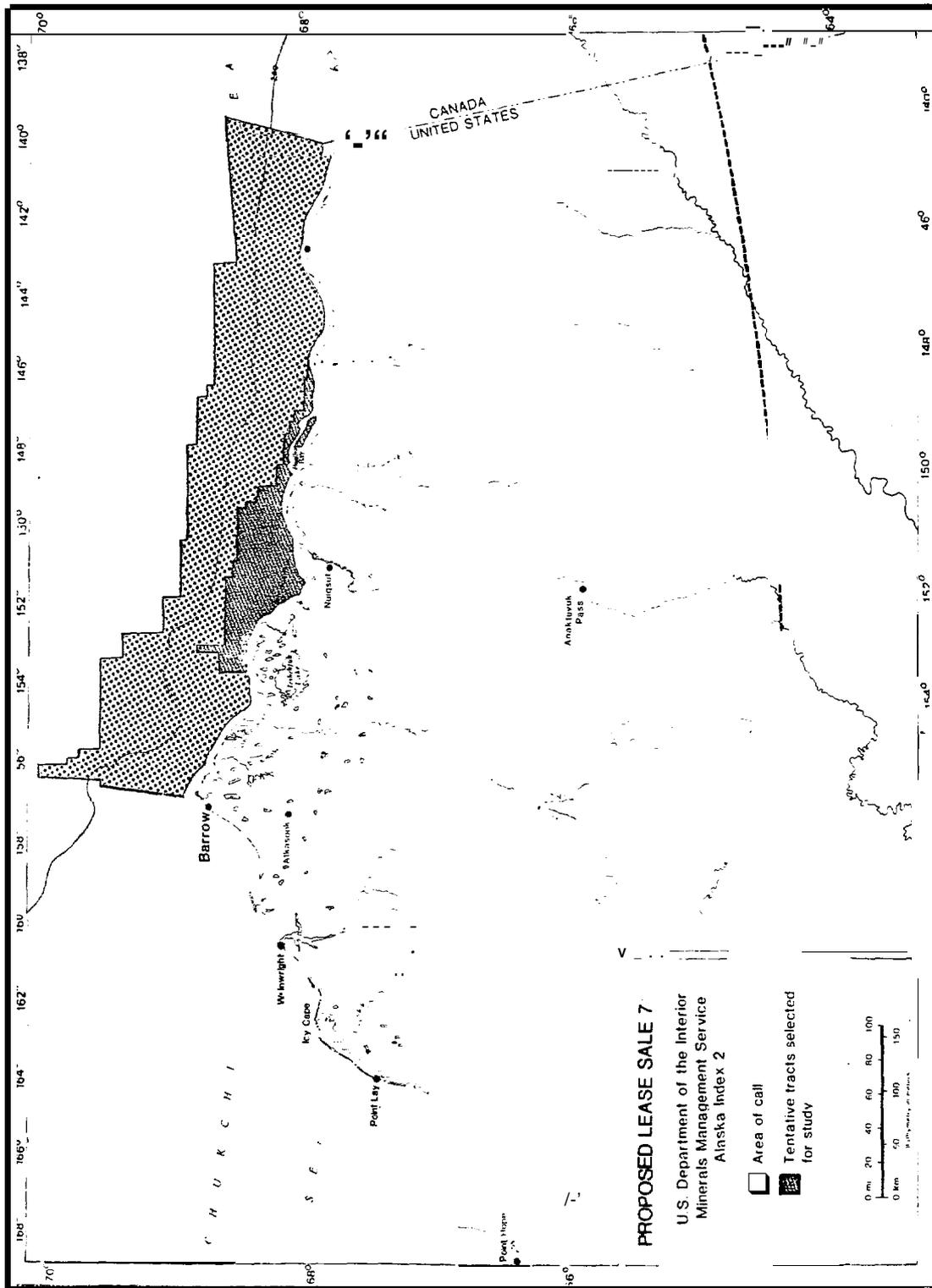


Figure 2 Proposed Tracts for Lease Sale 71. (Adapted from Jackson and others, 1981, Arctic Summary Outer Continental Shelf and Onshore Oil and Gas Activities and Impacts in the Arctic: A Summary Report, October 1981; prepared by Rogers, Golden & Halpern, USGS Open-File Report 81-621, p. 41.)

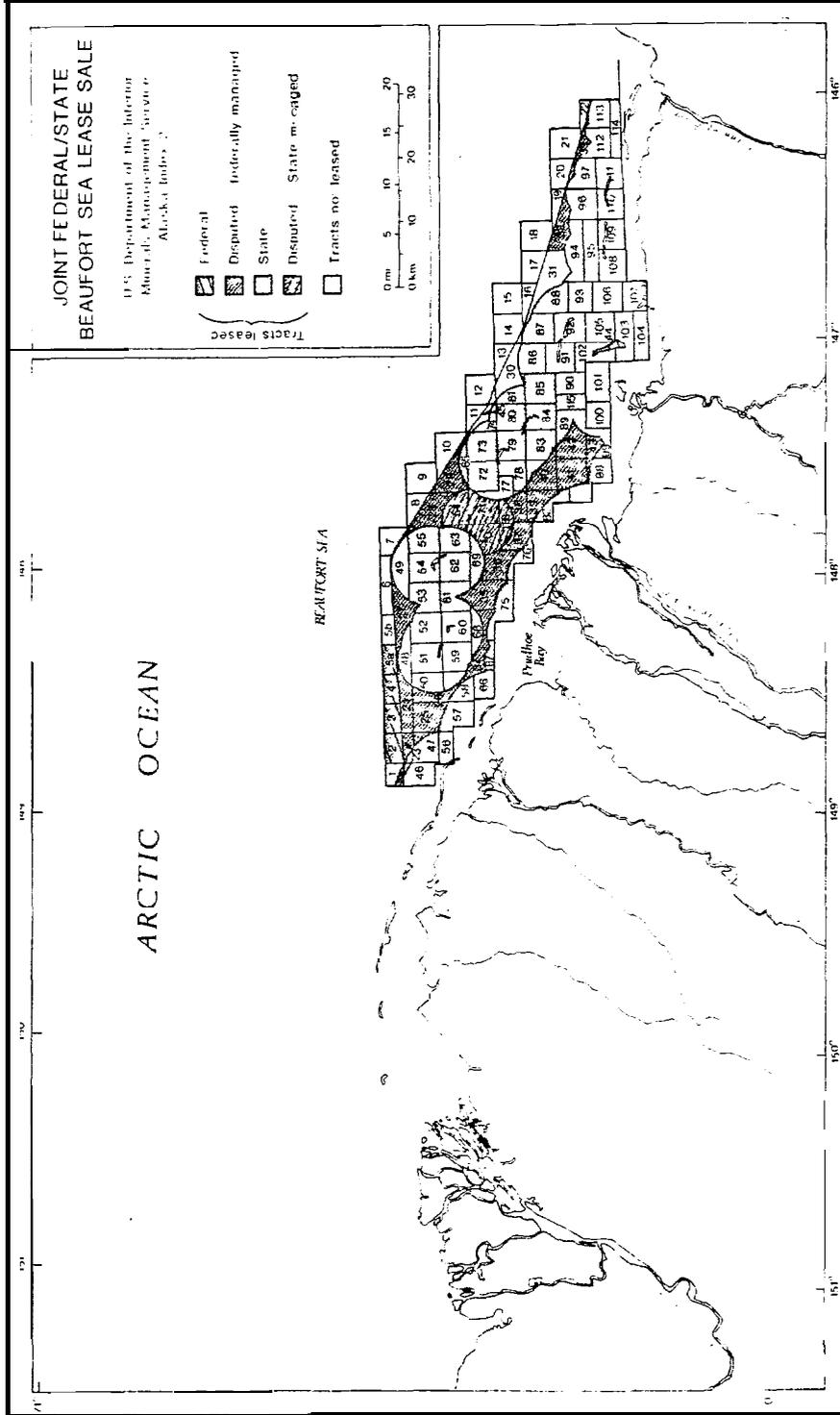


Figure 3 Lease Sale BF, Leased Tracts. (Adapted from Jackson and others, 1981, Arctic Summary Report, Outer Continental Shelf and Onshore Oil and Gas Activities and Impacts in the Arctic: A Summary Report, October 1981: prepared by Rogers, Golden & Halpern, USGS Open-File Report 81-621, p. 39.)

Table 1.1. **Drilling Sites in Federal Lease Areas.**

	<u>LATITUDES / LONGITUDES</u>	
Existing Sites:		
Exxon Beachy Petit	70023°1107911N	147°53'27.98" W
Shell-Tern Island	70°16'46.02"N	147°29'45.61" W
Sohio-M ukluk Island	70°4 1'0.039"N	150055' 11.89" W
Proposed Sites:		
"Seal" Prospect (Currently Being Drilled on State Land)	70°29'31 .435"N	148041'35.803° W
Exxon - Lease 0281	a. 71°2'9.29" N	152°43'25.32" W
	b. 71°1'38.75"N	152°39'27.95" W
	c. 71°1'55.21"N	152°47'33.05" W
	d. 71°1'7.06"N	153°26'6.99" w
	e. 71 °0'12.44"N	153°26'23.90" W
	f* 71 00'51.85'1N	153022 ^s 10.94" W
	g. 71 00'31.69"N	153°17'28.1 6" W
	h. 7 1°3'2.02"N	152°46'21.20" W
	i. 71°4'35.32"N	152°32'53.88" w
	j. 71°2'46.00" N	152°30'28.05" W
	k. 70 °56'18.90" N	151053'00.04'1 w
Shell - Harvard (Single Gravel Island)	70°3 5'4.74"N	149°05'48.804" w

Our specific rationale for monitoring the selected stations included the following approaches:

1. An Area-Wide approach, with a mixed placement and random selection of stations within the "high" and "highest" risk blocks specified by Dames and Moore (1984);
2. An Activity-Specific approach, with stations selected downstream from an actual or proposed major development activity;
3. A Gradient approach, which was incorporated as part of 1 and 2 above. As chemicals are introduced into the Study Area from point sources, material will be distributed by physical processes and gradients will be established. Gradients will be maintained as long as discharges continue. Station placements in both the Area-Wide and Activity-Specific approaches were designed to detect contaminant gradients. In the Area-Wide segment, these gradients were to be examined through establishing offshore transects skewed in the *direction* of net sediment transport direction (i.e., to the west). In the Activity-Specific approach, these gradients were sought downstream (to the west) of the activity at midfield to **farfield** distances (i.e., 1 to 10 miles).
4. Reoccupation of a limited number of baseline stations from which data are available from NOAA A-O CSEAP supported studies.

In addition to the above rationale, other design elements included: limiting sampling to areas with water depths of approximately 2 to 25 m; focusing some attention in the sensitive lagoon areas along the nearshore (Sirepson Lagoon - Gwydyr Bay and Stefansson Sound); sampling of sediments and bivalves at the same stations.

Actual placement of stations for the Year 1 study were based on the above four considerations.

Stations in Camden Bay, east of the Carming River, were selected randomly within the "highest risk" (block 15) and "high risk" (block 16) regions (see Figure 1.1) defined in Dames and Moore (1984). Both shallow and deeper stations were selected randomly to examine offshore gradients within these areas.

In addition, three Shaw et al. (1979) baseline stations were chosen to be reoccupied (Stations 1A, 1D and 2D). Stations to the west of the Canning River delta (i.e., Stations 2E, 2F) were chosen to examine discharges from the river. These stations were considered to be at "medium risk" due to their distance from proposed exploration areas. Stations 3A, 3B and 3C were randomly located in another "medium risk" area offshore of the Stefansson Sound area. These stations were selected to represent possible offshore, fine-grained sediment depositional areas, reflecting possible long range transport west from the Camden Bay area or east from the Sagavanirktok River, Prudhoe Bay area. Station 3C also represents a Shaw (1979) baseline station.

The Stations 4A, 4B, 4C and 4D were selected to represent a transect offshore from the Stefansson Sound (Boulder Patch area). This location was selected to cover two possible scenarios: 1) that this transect represented an upstream reference when considering the Endicott Field development; 2) that this transect would reflect storm-driven eastward drift of Endicott discharges if indeed net transport was to the east. Nearshore sediment and water transport is not known well enough to differentiate between these two possibilities. The northernmost station (4D) in this transect also represented a Kaplan and Venkatesan [1981] baseline station.

Stations 5(1), 5(2), 5(5) and 5(10) were selected as part of the activity -specific rationale to represent a possible transect downstream of the Endicott Field development. Stations 5F and 5 G were specifically placed to correspond with baseline stations of Shaw (1981). These stations were also considered to be in the "highest risk" area. A series of stations was selected to examine possible distributions of chemicals from the Seal Island vicinity. Station 5 A was selected as a midfield monitoring site for the Seal Island activity and 5B and 5 E were randomly placed, generally corresponding to farfield stations "downstream" from the Seal Island, Endicott and general Prudhoe Bay activities.

In the Harrison Bay area stations were randomly placed within the "high" and "highest risk" areas. Stations 6B, 6 C, 6 D and 6E were selected to generally represent an offshore transect from the major seasonal discharges of the Colville River. Two stations (6A and 6B) were chosen to reoccupy a Shaw (1979) baseline station. Stations 7 D (Shaw baseline station) and 7F (Kaplan baseline station) were selected to represent stations downstream from the exploration activity off Cape Halkett. In addition, several stations (7A, 7B, 7C, 7E, 7G) were randomly selected in the West Harrison Bay region, an area classified along with the Cape Halkett/Pitt Point area as one at "highest risk" due to industry interest and potential exploration activity.

All of the above station selections were made according to the basic strategy of selecting most stations in "high" and "highest risk" area vis-a-vis potential industry activity, and according to the "area-wide" and "activity-specific" strategies. Obviously these stations were selected randomly (except for those corresponding to previously occupied baseline stations) prior to actual data acquisition. It was anticipated that, based on the first year's results, stations might have to be moved, eliminated or additional stations added.

While the above design rationale holds for sediments and bivalve samples, several specific considerations should be noted for the bivalve collections. A limited number of sampling stations were selected for bivalves. Unlike the sediment sampling, in which sediments are available from all stations, bivalve distributions in the Beaufort Sea are uneven and species composition changes as one moves offshore. Based on the best available bivalve distribution data, and abundance of species composition and animal sizes, a target list of bivalves suitable for chemical analyses was developed:

1. Nearshore Area: Cyrtodaria kurriana
Portlandia arctica
Liocyma fluctuosa
2. Offshore Area: Arctinula groenlandica
Macoma calcarea
Portlandia arctica

Methods for collection are described in Section 2.2.

In order to form the foundation of a statistically valid monitoring program, a degree of replication was essential to the sampling design. Based on information available on the variability of environmental chemical measurements from other areas, the degree of areal coverage desired (i.e., number of stations), and budgetary constraints inherent in any environmental monitoring program, a degree of replication (four replicates per station, later increased to six) was incorporated into the program as was a degree of oversampling, (eight replicates collected) to allow for any possible additional analytical data points if required in the future.

1.3.2 Analytical Rationale

The analytical targets were chosen on the basis of their importance vis-a-vis their toxicity and on the basis of being indicative of OCS oil and gas exploration, and production activity discharges. The analytical program focused on trace metals, specific individual petroleum hydrocarbons and, regarding sediments, two key auxiliary

parameters, total organic carbon, and sediment grain size distributions that are used as geochemical tools in interpreting metal and hydrocarbon distributions. OCS activities may result in the permitted and accidental discharges of materials through drilling mud discharges, produced water or formation water discharges, or accidental spillages. The relative importance of these discharges and their chemical and physical composition is summarized in Table 1.2.

The metals analytical program focused on barium (Ba), Chromium (Cr), Zinc (Zn), lead (Pb), copper (Cu), cadmium (Cd) and vanadium (V), while the hydrocarbon program focused on total hydrocarbon content as well as detailed saturated hydrocarbon (normal and isoprenoid alkanes) and aromatic hydrocarbon (homologous series of two- to five-ringed polycyclic aromatics) distributions.

A more extensive discussion of exploration and development discharges is found in Section 1.5.

1.3.3 Data Analyses and Hypothesis Testing

As discussed in Section 1.2, the overall objectives of the three-year study centered on statistically testing four hypotheses concerning temporal trends in contaminant inputs and sources of these inputs reflected in sediment and bivalve analytical contaminant findings.

The data analysis task in the first year's program involved two activities: 1) determining the variability in observed metal and hydrocarbon parameters at each station, and 2) examining the geochemical (sediments) and biogeochemical (bivalves) data to determine the sources of materials and factors affecting their observed distributions. The first activity involved an examination of the data to determine their statistical qualities and the distribution (normal or non-normal) of the results. Once determined, the variability in chemical parameters and parameter ratios could be ascertained, followed by an assessment of the ability to validly detect subsequent changes in these parameters through the existing replication scheme. Which parameters or ratios should be focused on in subsequent year's hypotheses testing would then be determined from a combination of variability analysis and geochemical determinations.

1.4 Study Area Background

1.4.1 The Diapir Field

The Beaufort Sea, a part of the Arctic Ocean, lies north of Alaska and western Canada at latitudes mostly higher than 70° N. In U.S. federal waters, the Diapir Field Oil Lease Planning Area covers more than 21 million hectares containing 9,649 potential lease blocks. The Federal Planning area extends from the 4.8 km geographic federal/state boundary to approximately 73°N latitude (60 m water depth) and from the disputed U.S./Canada jurisdiction line (approximately 141° W longitude) to 162° W longitude in the Chukchi Sea to the west. The first lease offering in the area was the joint Federal/State Beaufort Sea Oil and Gas Lease Sale (BF) held on December 11, 1979. Twenty-four federal and 62 state tracts were leased for a primary lease term of 10 years.

The second federal lease offering (Sale 71) was held on October 13, 1982. The Lease Sale 71 area lies between 146.00° W and 153.300° W longitude. Of the 338 tracts offered, 125 received bids and 121 tracts were leased, covering an area of 268,450 hectares. The third lease offerings in the Diapir Field was held in August, 1984 and lease offering 97 is scheduled for June, 1986.

By the end of the 1984-85 drilling season, at least 34 exploratory wells had been drilled in State land that was leased primarily in the Stefansson Sound and Simpson Lagoon areas. Nine exploratory wells had been drilled in Federal land that was leased in the Sales BF and 71 in Stefansson Sound, Harrison Bay and Pitt Point areas (see Figure 1.4). During the next drilling season, two exploratory wells may be drilled in blocks that were leased during Sale 87 in the Camden Bay area. This offshore exploratory drilling activity has led to the following discoveries and planned development.

Table 1.2 Significant Potential Sources of Contaminants From OCS Operations

Activity/Source	Petroleum Hydrocarbons	Other Organics	Trace Metals	solids
Exploration/ Drilling Muds and Cuttings	+ (++) ^a	++	+++	++++
Production/Produced Waters	+++	+++	++ ^b	+
Exploration & Production/ Petroleum Spillages	++++	++	+	+

a Oil-based muds or diesel additives; also cuttings may contain higher layers of formation hydrocarbons.

b Very variable; may be more significant in some instances.

++++ Most important contaminant.

+++ Very important contaminant.

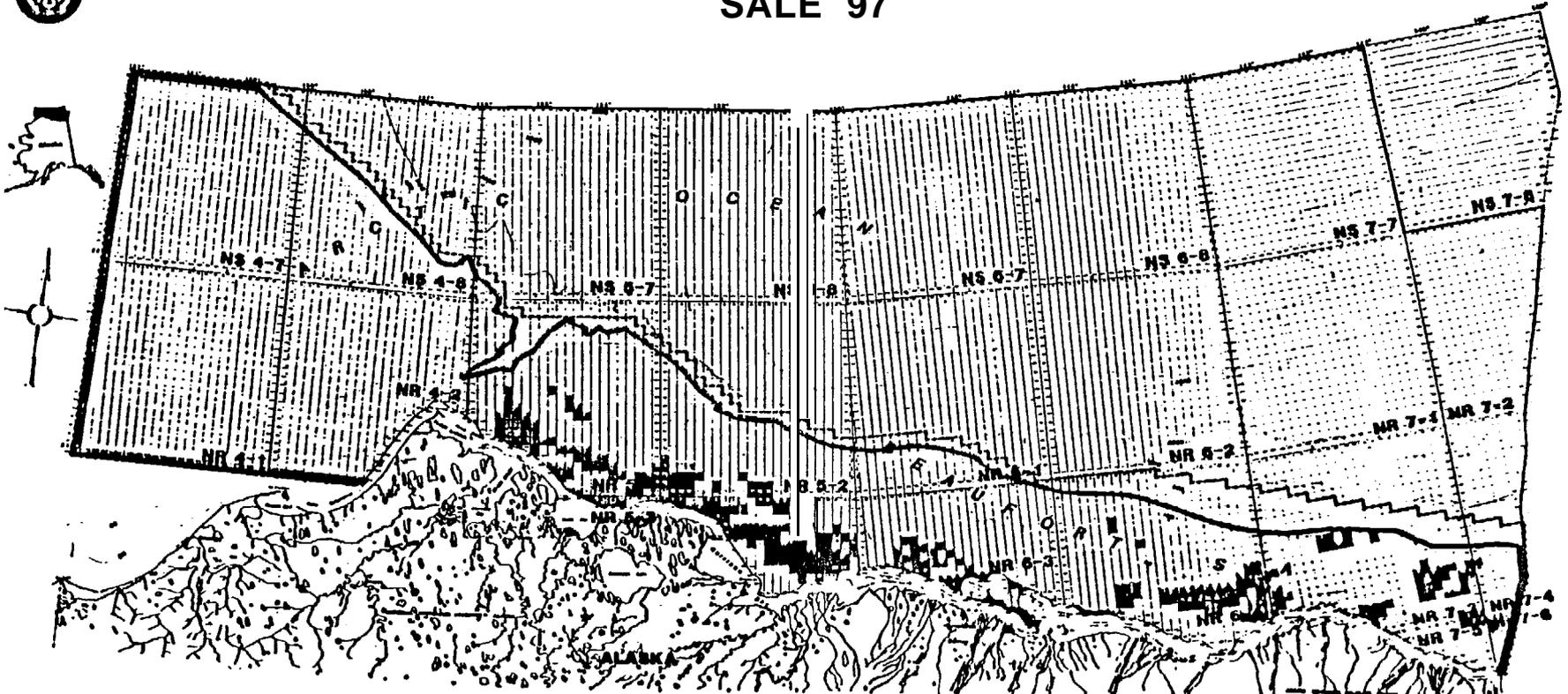
++ Contaminant of **lesser importance**.

+ Detectable contaminant.



BEAUFORT SEA

SALE 97



-  Area Selected For Further Study
-  Area of Call
-  Area of Hydrocarbon Potential
-  Blocks Leased - Sales BF and 71
-  Blocks Leased - Sale S7



Reference to maps

January 1986
ALASKA OCS REGION

Figure 1.4 Beaufort Sea Sale 97.

On May 5, 1982, **Sohio** and **Exxon** announced tentative plans to develop the Sagavanirktok River/Duck **Island** area by tapping the **Endicott reservoir**. Figure 1.5 illustrates the proposed development. The **Endicott** project is designed to support up to 200 production wells over the life of the **field**. Daily production is estimated at 75,000 to 150,000 barrels (12,000-24,000 cubic m) of **oil** and 250 million cubic feet (7.1 million cubic m) of natural gas.

In January 1984, Shell Western announced the **discovery** of a new oil reserve at its Seal Island prospect (Figure 1.6). Results of initial delineation drilling, released in July 1984, were **issued** along with conservative estimates by Shell that the discovery held reserves in the range of 300 **million barrels** of oil--one of the largest **finds** in North America in the past decade.

In January 1984, ARCO committed **itself** to developing the Lisburne **oil field** on the northwest edge of the Sadlerochit formation (Figure 1.7). Estimates are that the reservoir holds between 1 and 3 billion barrels of **oil**. The complicated geology of **Lisburne** will necessitate the drilling of 180 wells **from** six new **drill** sites. One of the **sites** will be a gravel island approximately 13,000 feet offshore in Prudhoe Bay, as shown in Figure 1.7.

1.4.2 The Physical Environment of the Study Area

The near-shore coastal zone of the U.S. Beaufort Sea contains abundant narrow, low, sand and gravel barrier islands, particularly between Harrison Bay and Camden Bay. In addition, there are numerous east-west oriented shoals which probably are extensions of the barrier island chain. Several small to medium **size** rivers discharge to the Beaufort Sea south of the Diapir Field. These include, **from** east to west, the **Carming, Shaviovik, Kadleroshilik, Sagavanirktok, Putuligayuk, K uparuk** and **Colville** Rivers. The **largest** is the **Colville** River. Runoff **from** the rivers is highly seasonal with approximately 80 percent of the estimated total annual runoff of 40 km³ to the Alaskan Beaufort Sea occurring in June (Antonov, 1958). The spring runoff carries high loads of suspended sediment. **Naidu and Mo welt** (1974) have estimated that sediment discharge **from** the **Colville** River **alone** is 4.5 to 9 **million** metric tons per year. The sediment may be carried more than 100 km **from** the river mouth and be deposited in water depths up to 40 m.

Because spring runoff to the **Beaufort** Sea begins in May before breakup of shore-fast ice, the river discharge flows out over the sea ice, flooding large areas out to at least the barrier islands (Barnes and **Reimnitz**, 1972; Cannon, 1981). The **fresh** water flow, carrying high concentrations of suspended sediments then drains through cracks and holes in the ice during breakup of the shore-fast ice. The fresh water may **drain** quite forcefully through cracks in the ice causing strudel scouring of seafloor sediments. The resulting depressions may be up to 25 m in diameter and 4 m deep (**Reimnitz** and Barnes, 1974).

The outer continental shelf of the Alaskan Beaufort Sea is quite shallow. In most areas, the shelf break occurs at a water depth of about 60 m, but in some regions, the shelf extends out to 200 to 800 m (**Sharma**, 1979; Grantz et al., 1981). The average depth of the Alaskan Beaufort Sea continental shelf **is** only 37 m. Its width ranges **from** 55 km **in** the east to 110 km in the west. The main **physiographic** features of this continental shelf include a gently sloping inner shelf (0.060 slope) extending **from** shore to the 30-m **isobath**, a slightly steeper outer shelf (0.90 slope) between the **30 and 60 to 70 m isobaths, and a steep continental slope**.

Water depths of the Diapir Field lease tracts range **from** 5 to 40 m, with an average of 16 m. At the present time, exploratory **drilling is** restricted to water depths of 20 m or less **from** barrier islands, man-made gravel islands or artificially-created ice islands. However, the **National** Petroleum Council (1981) has suggested that technology and relevant experience are now or soon **will be available** to operate safely in water depths up to 60 m in the more extensively ice-covered areas of the Beaufort Sea.

A **dominant** oceanographic feature of the Beaufort Sea is sea ice. In the Diapir Field Planning Area there are three major zones of winter ice: the landfast ice

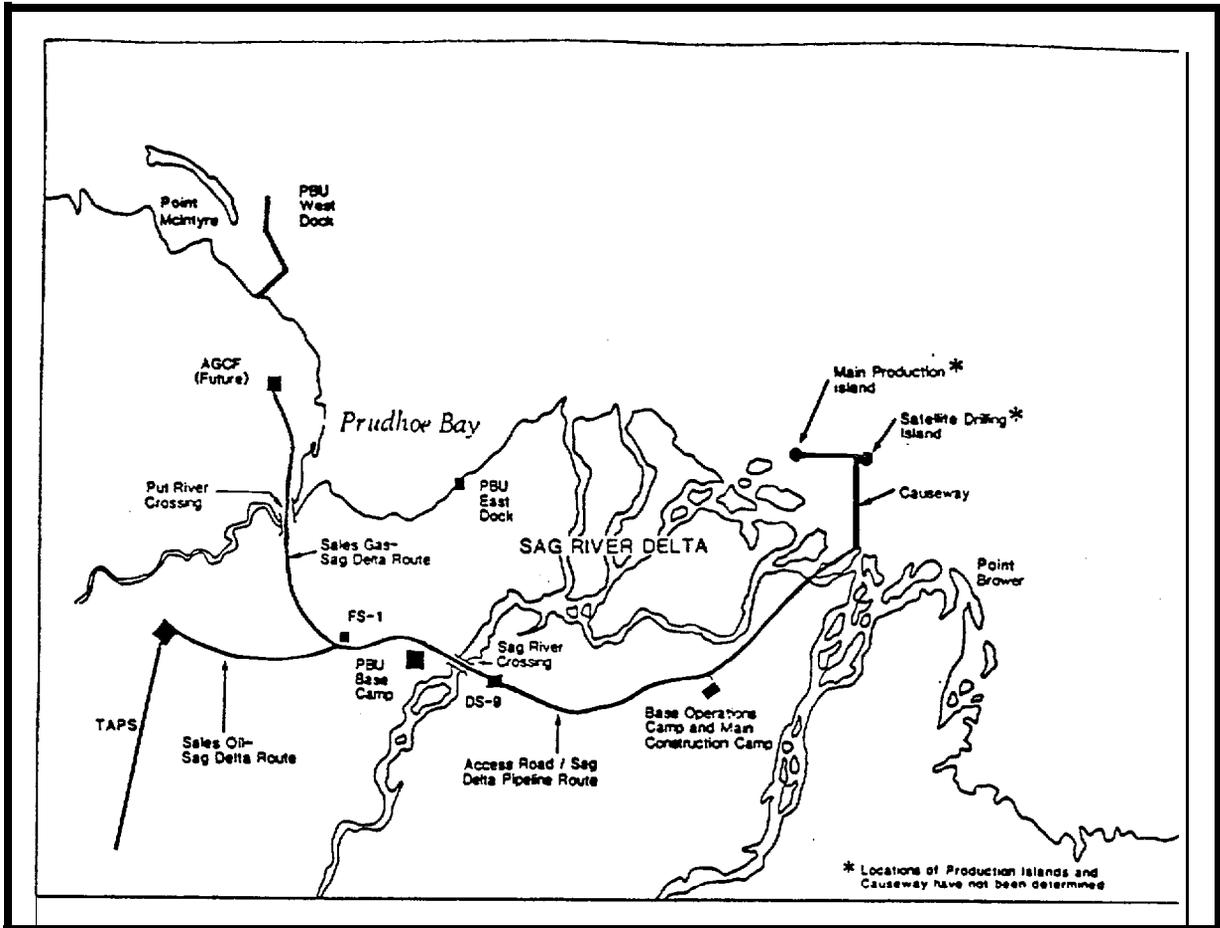


Figure 1.5 Proposed Endicott Development of Sag River/Duck Bland area. (Sohio, 1982). From Deis and Pierson (1983).

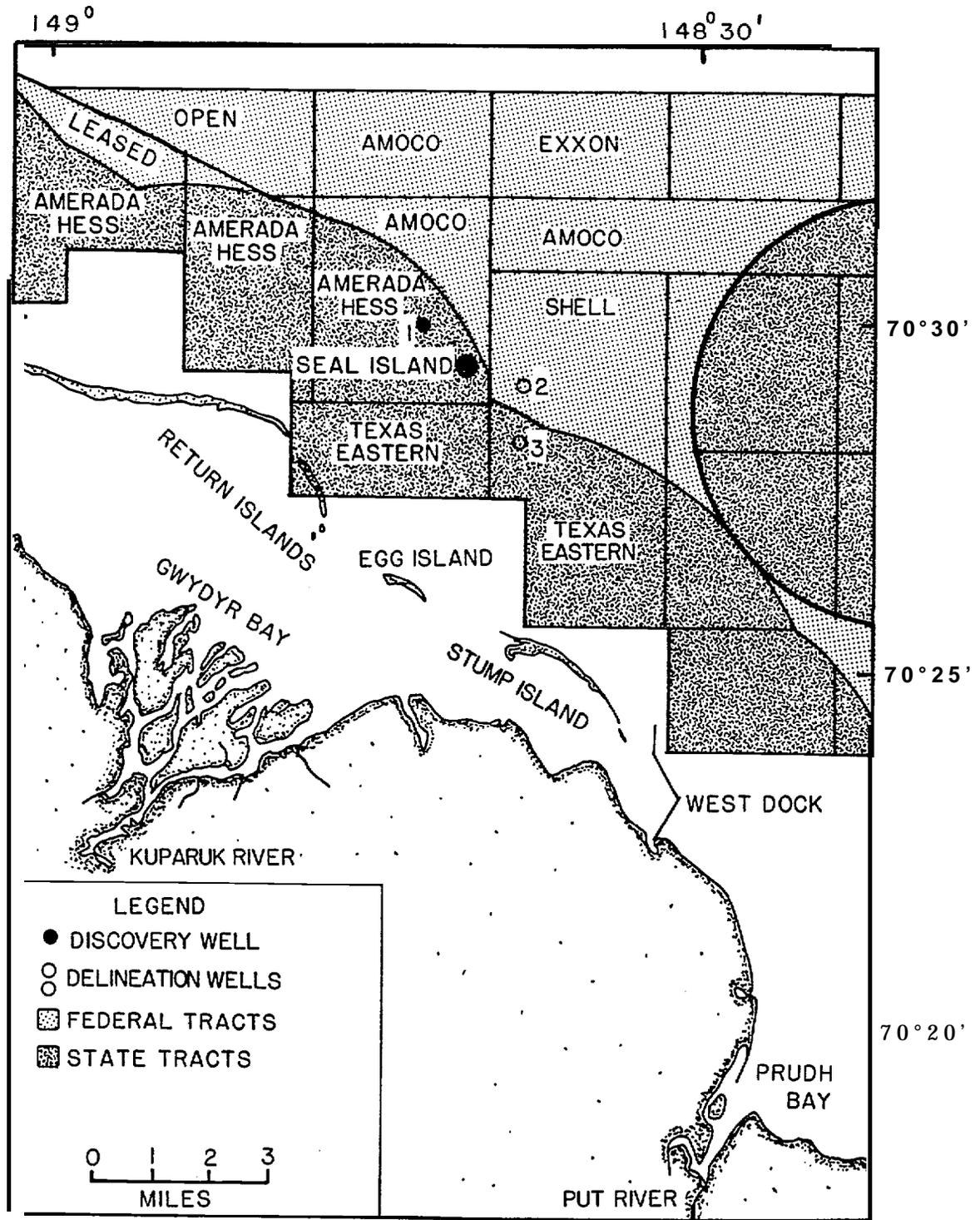


Figure 1.6 The Seal Island Discovery, With Paths of Exploratory and Delineation Drilling. From Lynch, Rudolph and Slitor (1984).

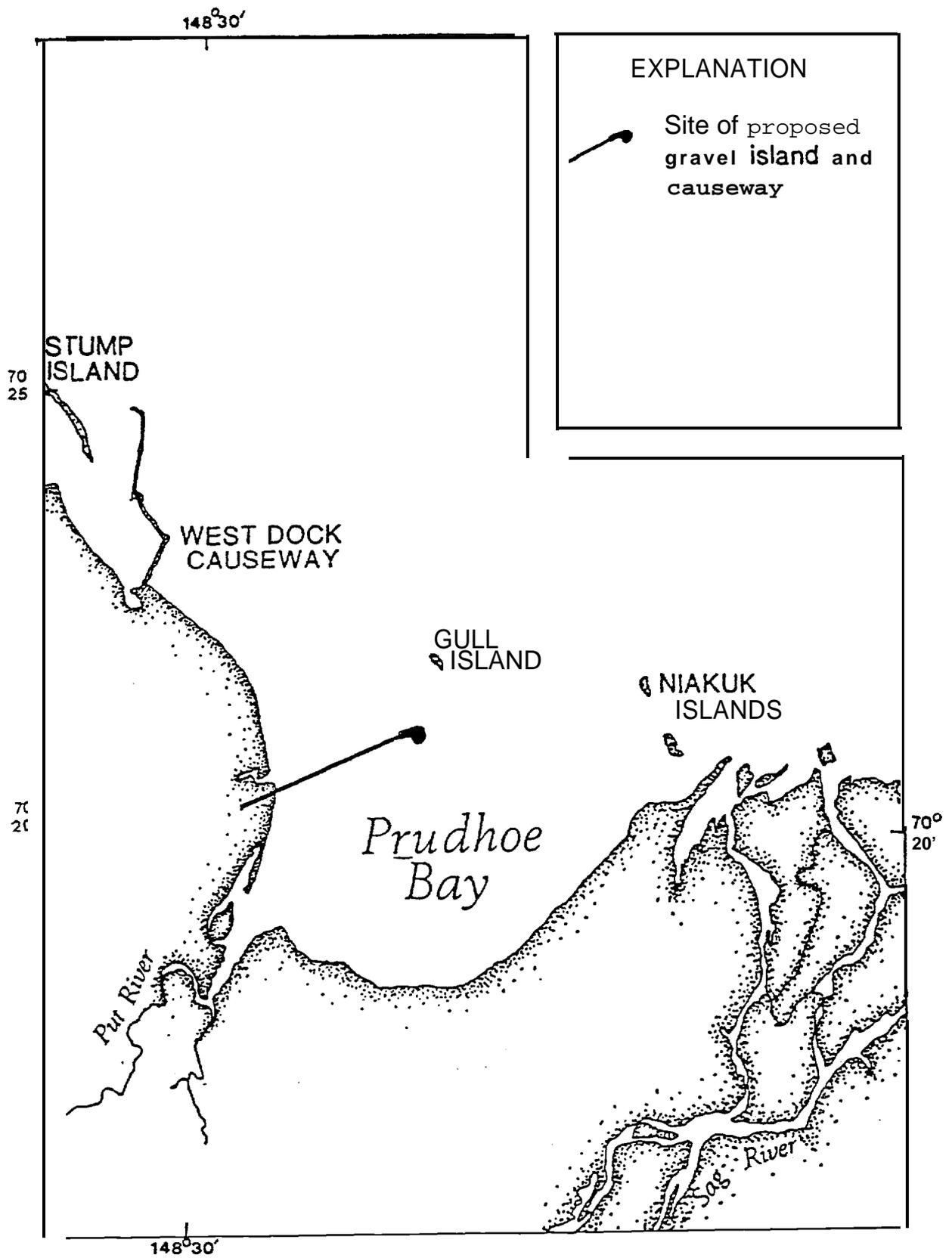


Figure 1.7 Lisburne Development Proposals Offshore Constructing. From Lynch, Rudolph and Sliator (1984).

zone, the Sta m ukhi zone, and the pack ice zone. The Planning Area is primarily in the landfast ice zone, which extends fro m the shore to the grounded ridge ice or Sta m ukhi zone. The Sta m ukhi zone first forms in about 8 to 15 m of water and by late winter may extend out to 20 to 30 m water depth, depending in part on the coastal geometry (Barry, et al., 1979). The shorefast ice reaches a thickness of about 2.0 to 2.4 m. It can be divided into a nearshore zone of bottom-fast ice out to water depth of about 2 m and a seaward zone of floating ice.

In the Alaskan Beaufort Sea, new ice generally begins to form from about mid-September to October and the first continuous sheet of fast ice has formed by mid-October (Barry, 1979). A stable shorefast ice sheet extending to about the 15-m isobath persists fro m January/February to April/ May. Breakup may begin in late June or early July and usually is complete by the beginning of August. At Point Barrow, breakup has been observed to occur as early as June 15 or as late as August 22, while fall freezeup has been observed to occur as early as September 3 or as late as December 19. By late August or early September, an ice-free zone usually extends 20 to 25 km offshore but may extend offshore to about 100 km in the region of Harrison Bay (Pritchard and Stringer, 1981). However, summer storms may drive pack ice into the shore.

Offshore, there is an ice shear zone where the relatively im mobile shorefast ice encounters the highly mobile arctic pack ice. This zone is called the Sta mukhi zone and is characterized by the pile up of the opposing ice sheets into vertical ridges which may extend downward as much as 30 to 40 m. Significant ice scouring of bottom sediments occurs in this zone.

Sea ward of the the Sta m ukhi zone is the pack ice zone, which contains first-year ice up to about 1 m thick, multi-year ice flo ws, ridges and flo wbergs, and ice islands. The pack ice is not continuous but is broken by fractures, leads and polynyas. U nder the influence of storm winds and ocean currents, the pack ice drifts at a rate up to about 7 km/day and exceptionally to 32 km/day (Shapiro and Barry, 1978). The net movement of pack ice in the Beaufort Sea is from east to west in response to the Beaufort Sea gyre.

Water currents in the Diapir Field Planning Area are m airily wind-driven. Tides are se midiurnal with an a m plitude of only 15 to 20 cm (Mathews, 1981; Northern Technical Services, 198 1), and do not contribute substantially to current flo ws, especially in the summer. The nearshore wind-driven current regime extending out to the 40 to 50 m isobath flows predominantly toward the west parallel to local isobaths during normal conditions, but may reverse during storms (K ozo, 198 1). Current speeds during the summer may range fro m 2 cm/see during normal conditions to more than 95 cm/see during storms. Off the Sagavanirktok River delta at 5.5 m water depth, mean current speeds were 13 cm/see and maximum velocity was 53 cm/sec during August-September, 1976 (Barnes et al., 1977). Under the ice in water depths of 5 to 8 m current speed averages about 2 cm/see with occasional pulses to 10 cm/see. H o wever, near the edge of bottom-fast ice at about 2 m depth, prism effects can cause 10 to 15 cm/see tidal currents (Barnes, 1981).

Coastal waters of the Alaskan Beaufort Sea tend to be salinity-stratified, particularly near the mouths of rivers and out to the 6-m isobath. In the summer, the warmer fresh water fro m river input lies over the colder more saline ocean water. In general, mean summer seawater salinities in the near-shore Beaufort Sea range fro m 1 to 30 ppt (Barnes et al., 1977; Kozo, 1981). Surface water temperatures in August-September range fro m about -0.9 to 7.5° C, averaging about 1.7° C.

1.4.3 The Trace Metal and Hydrocarbon Geochemical Environment

Several recent studies have examined the distribution of hydrocarbons and metals in Beaufort Sea sediments (Shaw et al., 1979; Kaplan and Venkatesan, 1981; Venkatesan and Kaplan, 1982; Naidu et al., 1981). Shaw et al. (1979) examined the hydrocarbon geochemistry of nearshore sediment along a transect from Point Barrow to Barter Island. Total hydrocarbon concentration in the nearshore range between 0.3 and 20 µg/g dry sediment. The saturated hydrocarbons are dominated by n-alkanes ranging in chain length bet w een 23 and 31 carbon atoms with a strong odd-even preference and no

unresolved complex mixture (U C M) evident. This distribution is consistent with a **prevalent biogenic input** of terrigenous plant material, most likely resulting from transport of **riverine** suspended particulate matter during the spring runoff. Shaw et al. (1979) also examined sources of aromatic hydrocarbons in **nearshore** sediments using the **alkyl homolog** distribution of selected aromatic hydrocarbon series determined by G C/ MS. Distributions characteristic of both **pyrogenic** and **petrogenic origins** were observed, with the geographic distribution of **pyrogenic** aromatic compounds indicative of a long range transport source of **anthropogenic** combustion products rather than **localized** inputs. Their **analysis** also ruled out natural seepage or spills of Prudhoe Bay crude oil as the source of aromatic hydrocarbons in the region.

The hydrocarbon geochemistry of the Beaufort Sea Outer Continental Shelf (O C S) has been studied by Kaplan and Venkatesan (1981), and Venkatesan and Kaplan (1982). The **range** of total hydrocarbon concentrations reported was 20 to 50 ug/g dry sediment, which is **slightly** greater than that found in the nearshore sediments. Whether these differences are due to differences in the analytical methods employed or to a greater abundance of fine-grained, organic-rich **sediments** in the O C S region was not investigated. As with the nearshore sediments, the major source of saturated sedimentary hydrocarbons was found to be higher plant debris, with no evidence of a U C M indicative of **anthropogenic** inputs. A marine **biogenic** origin for some of the organic matter was also indicated by the occurrence of the hydrocarbons pristane and n-heptadecane. The occurrence of several **alkanes**, together with **steranes**, diterpanes and triterpanes also attested to the **biogenic** origin of the organic matter. Measurable concentrations of aromatic hydrocarbons were found in **almost all** the Beaufort Sea O C S sediments examined. The distribution of **alkylated homologues** determined by G C/MS was found to be characteristic of a **pyrogenic** origin. The available organic geochemical data for the region indicate that hydrocarbons found in nearshore and offshore sediments originate **primarily** through natural processes, with **little** evidence of anthropogenic petroleum inputs.

The geochemistry of several metals (Fe, Mn, Cu, Co, Cr, Ni, V and Zn) was examined by Naidu et al. (1981) in four depositional regions of the Beaufort Sea (O C S, Harrison Bay, Simpson and Beaufort lagoons). Concentrations of all **metals** in O C S sediments were greater than those found in the nearshore or the coastal lagoons. Total metal concentrations in sediments of the arctic lagoons were **comparable** with those of non-polluted temperate **sediments**. Neither vanadium or **nickel, metals** which might be indicative of petroleum contamination, exhibited a regional geographic distribution consistent with localized petrogenic inputs. Other studies of metal distributions in O C S sediments have been conducted by Sweeney (1984) and Robertson and Abel (1979).

Data on the concentrations of **metals** and hydrocarbons in bivalves from the region are sparse with Shaw et al. (1979) presenting some evidence attesting to **very low levels** of hydrocarbons in **bivalves** from the area.

1.4.4 The Sedimentological Environment

The sediment characteristics of the lagoons along the Beaufort Sea coast have been studied by Naidu et al. (1984). Primary sources of sediments in the **Diapir** Field are **riverine** input of suspended particulate matter, erosion of coastal bluffs, and ice rafting. The riverine and erosional **particulates** include a significant concentration of, tundra peat (Schell, 1983) **which** may contribute significant amounts of organic carbon and fossil hydrocarbons to coastal **sediments**. It has been estimated that 700 metric tons of peat per km per year enter the **Beaufort** Sea from coastal erosion. **Nearshore surficial** sediments are predominantly **mud** (Grantz et al., 1982; Naidu, 1982). **Coarse-grained** sand and gravel sediments in nearshore areas are primarily relict deposits. In some **areas, the** sandy and muddy substrate is interrupted by aggregations of cobbles and boulders, termed boulder patches. These boulder patches usually contain a **single** layer of boulders about 70 cm thick (Duntan et al., 1982). The dominant clay mineral in Beaufort Sea **sediments** is illite (Naidu, 1982). Major mechanisms of large **scale** sediment transport and dispersion in the region include: transport in suspension; on-ice transport from river **overflows**; storm-driven bed transport; and ice rafting and in-ice sediment transport (Sharma, 1983).

Transport and deposition of coastal sediment are influenced by seasonal variations in hydrodynamics and sediment supply. During winter months, nearshore sediment transport nearly ceases, while considerable ice gouging, occurring in the Stamukhi zone at water depths of 15 to 45 m, acts as the major sediment disturbance further offshore (Barnes et al., 1984). At spring breakup, the ice cover nearshore is subject to high turbid riverine overflows. The Colville River is the largest single source of material and, during a three-week period in the spring, can discharge 74 percent of its annual load (Naidu et al., 1984). Sedimentation rates in the lagoons have been estimated to range from 0.5 to 1.6 cm/yr.

Prevailing westerly winds occurring in the open water season transport river plumes and resuspended bottom sediment westward. Westerly storms, characteristic of the late summer-fall can account for cataclysmic beach transport and net shoreline erosion amounting to as much as 1500 m³/day or overall a net erosion and transport rate of 1-4 m/yr (Hume and Schalk, 1967; Short et al., 1974).

Other commonly observed sediment transport processes include ice-scouring and sediment rafting. Samples of sea ice show a sediment concentration range of 40 to 730 mg/L melted ice which is far greater than ambient seawater suspended loads of approximately 1 mg/L. (Naidu et al., 1984). Suspended loads may be greater (10 to 100 mg/L) during flash floods.

1.4.5 The Biological Environment

The major sources of primary production of the Beaufort Sea food web include terrestrial vegetation (primarily peat), phytoplankton, epibiotic algae (living on or near the under-surface of the ice), attached macrophytes (especially in boulder patches), and benthic microalgae (Schell and Homer, 1981). It is at present uncertain whether microalgae or organic detritus, derived in part from peat are the major sources of nutrition for consumers (Schell, 1983).

The nearshore benthic infauna and epifauna are extremely depauperate due to seasonal scour from bottom fast ice (Broad, 1979). Similar scouring resulting in depauperate benthic fauna may occur in the depth interval of 15 to 30 m due to ridge ice in the Stamukhi zone. These regions do contain small populations of annual species or juvenile immigrants from adjacent unscoured zones. Benthic faunal diversity increases with water depth seaward from the bottom fast ice zone, with the exception of the Stamukhi zone. Dominant taxa include polychaetes, gammarid amphipods, isopods, and bivalve mulluscs. The highly motile forms such as amphipods and isopods may invade the area in large numbers during the open-water season (Griffiths and Dillinger, 1981; Northern Technical Services, 1981). Infaunal biomass ranges from a mean of 3.1 g/m² in waters less than 2 m to 42.05 g/m² in coastal lagoons, and 30.6 g/m² at water depths to 2 to 20 m (Wacasey, 1975; Broad et al.; 1981). Higher trophic levels, including a wide variety of marine and anadromous fish as well as the bowhead whale, apparently depend primarily on epibenthic and planktonic crustaceans for sustenance and there is little concrete evidence of benthic-pelagic trophic coupling in the nearshore Beaufort Sea.

1.5 Potential Environmental Effects of Offshore Oil and Gas Development

During exploration for and development of offshore oil and gas reserves on the outer continental shelf of the U.S. Beaufort Sea, there will be physical disturbances and generation of a variety of solid and liquid wastes, some of which will be discharged to the ocean (see Table 1.2; Section 1.3). Such discharges are regulated by the Environmental Protection Agency (EPA) through issuance of National Pollutant Discharge Elimination System (NPDES) permits in compliance with provisions of the Clean Water Act (Federal Water Pollution Control Act, as amended: 33 U.S.C. 1251 et seq.). Liquid and solid wastes that may be permitted for discharge to the ocean include drilling fluids, drill cuttings, deck drainage, sanitary and domestic wastes, several non-contact or clean once-through

process waters, and produced waters. Produced water and other waste waters possibly containing oil are processed through an oil-water separator while sanitary sewage is treated in an activated sludge treatment system before discharge. Treated waste water containing up to 48 pp m oil and grease is presently permitted for discharge to the ocean. However, New Source Performance Standards (N SPS), which have been proposed by EPA, include a daily maximum of 59 pp m and a monthly average of 23 pp m oil and grease (William Telliard, EPA, Washington, DC, personal communication). The chemical contaminants associated with various OCS operations are summarized in Table 1.3.

The major permitted discharges (in terms of volume and environmental concern) associated with exploration and development drilling are drilling fluids and drill cuttings. During development drilling of a field, the usual practice is to bring wells into production as they are drilled. Thus, drilling and production go on simultaneously from a development platform during much of the development phase. The major effluent, often associated with oil and gas production, is produced water. Ocean disposal of treated produced water is permitted in the Gulf of Mexico, in some regions off southern California and in Cook Inlet, Alaska. Currently there is some doubt and considerable debate about whether such discharges will be permitted in the Alaskan Beaufort and Bering Seas.

Exploration and development drilling will take place from barrier islands, man-made gravel islands, artificially-created ice islands or reusable concrete island drilling systems (CIDS). Other platform designs and configurations, compatible with the harsh Beaufort Sea conditions are under design and consideration. During development of a field, from 10 to 50 and occasionally up to 100 wells may be drilled from each platform. Preliminary plans for unitization of the Endicott Reservoir off the Sagavanirktok River, the first proposed offshore development in the Alaskan Beaufort Sea, call for the construction of two gravel islands. As many as 80 wells may eventually be drilled from each island (Redburn and Wheeler, 1983). One or occasionally two wells can be drilled at a time from each platform and each well may require two to six months to drill. Thus development of a field may take as long as 20 years.

Two other impact-causing agents associated with offshore oil and gas development should be mentioned. The physical presence of the platform or artificial island, or the added bottom relief provided by a pile of drill cuttings on the bottom produces a reef effect (Davis et al., 1982). Reef-associated foraging fish are attracted to the structure and may produce profound effects on the benthic epifauna and infauna through predation. Accidents during field development and production may result in oil spills or even blowouts which would represent acute, possible massive-scale inputs of petroleum to the shallow Beaufort Sea.

1.5.1 Drilling Fluids and Cuttings

Drilling fluids are specially formulated mixtures of natural clays and/or polymers, weighting agents and other materials suspended in water or a petroleum material. Water-base, but not oil-base drilling fluids may be allowed by NPDES permit to be discharged to U.S. coastal and OCS waters. Water-base drilling fluids (in which the continuous phase is fresh- or seawater) are used almost exclusively for drilling in U.S. coastal and OCS waters. The five major ingredients in water-base drilling fluids (barite, bentonite clay, lignosulfonate, lignite, and caustic) account for over 90 percent of the total mass of additives used in water-base drilling fluids (Perricone, 1980). The other major ingredient is fresh water or seawater. The remaining ingredients include a wide variety of specialty additives used to solve particular down-hole problems. From an environmental perspective the most important of these include diesel oil or mineral oil (0.1 to 4 percent sometimes used for fluids control or to improve the lubricating properties of the mud when drilling a slanted hole), chromate salts, surfactants, and biocides. Current NPDES permits for the Beaufort Sea prohibit discharge of drilling fluids containing diesel oil, mineral oil, chromates or chlorinated phenol biocides.

When NPDES permits were granted for offshore drilling on the mid-Atlantic outer continental shelf in 1978, the Offshore Operators Committee Task Force on

Table 1.3 Major Permitted Discharges and Potential Impact-Causing Agents Associated With Offshore Oil. and Gas Exploration in the Beaufort Sea.

-
-
- Physical Structure of Platform or Artificial Island

 - Drill Cuttings - 1100 m t/Exploration Well, Less for Development Well

 - Drilling Fluids - 900 m t/Exploration Well, 25 % Less for Development Well

 - Cooling Water, Deck Drainage, Ballast Water - May be Treated in an Oil/ Water Separator

 - Domestic Sewage - primary Activated sludge Treatment

 - Sacrificial. Anodes, Corrosion, Antifouling Paints - May Release Small Amounts of Several Metals (Al, Cu, Hg, Sn, Zn)

 - Produced Water (Production Only) - Treated in Oil/Water Separator to Reduce Total Hc to Mean of 48 ppm, Daily Max. 72 ppm.
-
-

Environmental Science, and EPA Region II developed a list of eight general or genetic **drilling** mud types that included **virtually** all types of water-base muds commonly used on the U.S. OCS. The genetic mud concept has been incorporated into NPDES permits issued by EPA Regions I, II, III, IX, and X (including Alaska) and is under **consideration** for future permits in other regions (Ayers et al., 1983). **Bioassays** performed according to the EPA Region II protocols are conducted on **field** samples of muds representative of the eight genetic **drilling** fluid types. Operators then may be **allowed** to discharge drilling fluids of the eight generic types without conducting additional **bioassays**. If specialty additives are used, bioassay and approval of the **EPA Regional Administrator** is required before the muds containing additives are discharged to the ocean.

Barite (barium sulfate) is used as a **weighting** agent in **drilling** fluids. It has a density of 4.1 to 4.3 g/cc and a solubility in seawater of about 50 to 52 $\mu\text{g/liter}$ as Ba (Burton et al., 1968; Chan et al., 1977). The amount of **barite** added to a **drilling** mud may vary from 0 to about 2 kg/liter (700 lb/bbl) and **usually** increases with depth of the well (National Academy of Sciences, 1983).

Bentonite clay (sodium montmorillonite), or sometimes **attapulgite** clay, is the major ingredient of most water-base **drilling** fluids. It is used to maintain the gel strength required to suspend and carry **drill** cuttings to the surface. It also helps coat the wall of the bore-hole preventing loss of drilling fluids to permeable formations.

Lignosulfonates are organic polymers derived from the **lignin** of wood and are byproducts of the wood pulp and paper industry. When complexed with certain inorganic ions such as chromium, **iron**, or **calcium**, they are effective in preventing flocculation of clays. They are used to control the viscosity of drilling fluids. Chrome or **ferrochrome lignosulfonate** is used most frequently in water-base muds for offshore drilling. Lignite (a soft coal) is used with **lignosulfonate** as a clay deflocculant and filtration control agent.

Caustic (sodium hydroxide) is used to maintain the **pH** of **drilling** fluid in the range of 10 to 12. A high **pH** is needed for optimum clay **deflocculation** by chrome **lignosulfonate**, and to inhibit corrosion of **drill** pipe and growth of hydrogen sulfide-producing bacteria.

Several metals are found in **drilling** fluids (Table 1.3). **The metals of major** environmental concern, because of their potential toxicity and/or abundance in drilling fluids, include arsenic, barium, chromium, cadmium, copper, iron, lead, mercury, **nickel**, and zinc. Some of these metals are added intentionally to drilling muds as metal salts or **organometallic** compounds. Others are trace contaminants of major **drilling** mud ingredients. The metals most frequently present in drilling fluids at concentrations significantly higher than in natural marine sediments include barium, chromium, lead, and **zinc** (Table 1.4).

Barium in drilling fluids is derived almost exclusively from barite. Bentonite clay may also contain some barium.

Chromium in **drilling** fluids is derived primarily from chrome and **ferrochrome lignosulfonates**. Different brands of chrome or **ferrochrome lignosulfonate** may contain from 1,000 to 45,000 mg/kg chromium (Neff, 1982). Barite and lignite may also contain some chromium. In addition, inorganic chromium salts sometimes are added to drilling fluids for **stabilization** of chrome **lignosulfonate** at high temperatures, corrosion control, or **H₂S-scavenging**. Used offshore, drilling fluids may contain 0.1 to about 1,400 mg/kg dry weight and rarely to about 6,000 mg/kg total chromium. Chromium complexed to **lignosulfonate** is in the **+3 valency** state (Skelly and Dieball, 1969). **Hexavalent** chromium added to **drilling** muds is quickly reduced to the trivalent state by the **lignosulfonate** and becomes absorbed to the clay **fraction** (McAtee and Smith, 1969). **Chrome-lignosulfonate**-clay complexes are quite stable at normal operating temperatures. Above about 150°C, these complexes begin to break down, due to thermal degradation of lignosulfonate.

Most of the other metals detected in some **drilling** fluids (mercury, lead, **zinc**, nickel, arsenic, cadmium, and copper) are present primarily as trace impurities in **barite**, **bentonite**, and sedimentary rocks in the formations penetrated by the drill. The average concentrations of these metals in marine sediments are as high as or higher, in most cases, than their concentrations in **drilling** muds (Table 1.4). The **metallic** impurities in **pure barite** are associated with highly insoluble sulfide mineral inclusions, particularly

Table 1.4 Concentration R anges of Several Metals in Natural Marine Sedim ents and Drilling Fluids fro m Alaskaa. Concentrations are in mg/kg Dry Wt. (ppm).

M etal	Alaskan O CS Drilling Muds	Sediments	
		Norton Sound	Beaufort Sea
* Barium ^b	520 - 360,000	350 - 500	135 - 4,200
* Chromium	17 - 1,300	30- 80	4- 110
Cobalt	38- 52	20 - 30	13 - 53
Copper	1.5- 88	20 - 50	16 - 53
Nickel	44- 88	20 - 45	30 - 50
Strontium	NA	200 - 300	NA
* zinc	34- 389	50- 110	65- 103
Iron	9,420- 76,300	NA	13,800 - 30,000
Manganese	138 - 350	NA	138 - 258
*Lead	2.4 - 106	NA	3 - 21
Vanadium	160 - 235	NA	55 - 155
Mercury	<i>0.015 - 0.217</i>	NA	NA
Cadmium	10.02 - 1.80	NA	NA

^a Data from NO RTEC, 1981, 1982, 1983; Sharma, 19'79; Ecomar, 1983.

^b Barium values obtained by A A and may be 10 w.

N A. Not analyzed

* May be present at substantially higher concentration in drilling fluid than in sediments.

with sphalerite (ZnS) and galena (PbS) in it (Kramer et al., 1980; MacDonald, 1982). Mercury is of particular concern because of its high toxicity. Although mercury from mercuric sulfide can be methylated to highly mobile and toxic methylmercury compounds by sediment bacteria, the speed and efficiency of this transformation is only 10-3 times that of methylation of ionic Hg^{+2} (Fagerstrom and Jernelov, 1971) and the rate-limiting step appears to be oxidation of sulfide to sulfate (Gavis and Ferguson, 1972). This reaction will be oxygen-limited in most marine sediments. Pipe thread compound (pipe dope) and drill collar dope may contain several percent metallic lead, zinc, and copper (Ayers et al., 1980a). Some pipe dope gets into the drilling mud. However, metals from this source are in the form of fine metallic granules and are biologically relatively inert. Finally, inorganic zinc salts, such as zinc carbonate, zinc chromate, or zinc sulfonate may be added to drilling muds as H₂S scavengers. In such cases, zinc is precipitated as zinc sulfide.

Drill cuttings are particles of crushed sedimentary rock produced by the action of the drill bit as it penetrates into the earth. Drill cuttings range in size from clay to coarse gravel and have an angular configuration. Their chemistry and mineralogy reflect that of the sedimentary strata being drilled.

During drilling of a typical 3,000-m, offshore exploration well, approximately 900 metric tons of drilling fluid solids and 1,100 metric tons of drill cuttings will be discharged. Slightly smaller amounts of drilling fluids and cuttings are discharged during drilling of a development well. Drill cuttings are discharged more or less continuously during actual drilling, which may actually occur only one-third to one-half the time during a two to three month drilling operation (Ray, 1979). Discharged cuttings may contain 5 to 10 percent drilling fluid solids. Whole used drilling fluids may be discharged intentionally in bulk quantities several times during drilling and at the end of the drilling operation.

Unless restricted by N P DES permit, the rate of bulk drilling mud discharges ranges from 500 to 2,000 barrels per hour and may require 0.5 to 3 hours (Ayers et al., 1980b; Ray and Meek, 1980). Some permits for the Beaufort Sea include a rate limit of 1,000 barrels per hour and require predilution (10-fold with seawater) under some conditions.

Exploration and development drilling is expected to take place in several OCS regions of Alaska in the next 10 years (Table 1.5). Most activity is expected to take place in the Beaufort and Bering Seas. If all 128 exploration and development wells projected by the Minerals Management Service for the Diapir Field for the next 10 years are drilled, then a total of approximately 215,000 metric tons of drilling fluid and cuttings solids would be discharged. Substantial additional drilling will take place in state waters. Several major development projects are being considered in the Beaufort Sea, including the Endicott, Seal Island, and Lisburne fields. More than 100 wells could be drilled in the Endicott Field alone.

A water-base drilling fluid is a slurry of solid particles of different sizes and densities in water. Drilling fluid additives may be water-soluble, colloidal, or particulate. Clay, silt, and cuttings have a density of about 2.6 g/cc. Silt and unflocculated clays settle in calm seawater at estimated rates of about 1.4×10^{-2} to 5.8×10^{-5} cm/sec (Smedes et al., 1981). However, much of the clay in drilling mud tends to flocculate upon contact with seawater, resulting in more rapid settling of this fraction. Barite, despite its fine grain size ($<64\mu m$), may settle more rapidly because of its high density. Because of this physical/chemical heterogeneity, drilling fluids and cuttings undergo rapid and substantial fractionation and dispersion upon discharge to the ocean.

According to a dispersion/dilution model developed by Brandsma et al. (1980), drilling mud discharged from a submerged discharge pipe can be viewed as going through three distinct phases: convective descent of the jet of material, dynamic collapse, and passive diffusion and convective mixing of the ambient medium. Of the material discharged, about 10 percent remains as a plume in the upper water column. This fine grained material generally contains less than 10 percent of the drilling fluid solids. The remaining 90 percent settles directly to the bottom. Critical determinants of the impacts of discharged drilling fluids and cuttings on water column biota are the rate and extent of these dispersion/dilution processes.

Table 1.5 Projected Drilling Fluids/Cuttings Discharges to Alaska Coastal/OCS Waters During the Next Ten Years.

Region	Wells Next 10 Years		Total Discharges (MT) ^a		
	Exploration	Production	Mud	cuttings	Total
Gulf of Alaska	3	6	6,800	8,200	15,000
Kodiak	2	3	3,800	4,700	8,500
Cook Inlet	2	3	3,800	4,700	8,500
N. Aleutian Basin	14	27	30,800	37,700	68,500
St. George	17	63	57,800	70,700	128,500
N avarin Basin	18	57	54,700	66,800	121,500
Norton Sound	19	33	39,400	48,100	87,500
Hope	6	9	11,500	14,000	25,500
Barro W	6	16	16,200	19,800	36,000
Diapir	45	83	96,500	118,000	214,500
Totals	132	300	321,300	392,700	714,000

^aBased on a discharge of 900 metric tons (MT) drilling fluids and 1100 M T cuttings per exploration well and 25 percent less of each per production w en.

Several field studies have shown that drilling fluids discharged to the ocean are diluted rapidly to very low concentrations, usually within 1,000 to 2,000 m down-current from the discharge pipe and within 0.1 to 4 hours of discharge (Figure 1.8 from Ayers et al., 1980b; Eco mar, 1978, 1983; Houghton et al., 1980; Northern Technical Services, 1983). Quite frequently, dilutions of 1,000-fold or more are encountered within a short time and distance of discharge. (Figure 1.9).

The distance from an exploratory platform to which drilling fluid solids are dispersed and their concentration in bottom sediments depends on the types and quantities of drilling fluids discharged, hydrographic conditions at the time of discharge, and height above the bottom at which discharges are made (Gettleson and Laird, 1980). Because barite (barium sulfate) is a major ingredient of many drilling fluids used on the U.S. outer continental shelf and is both very dense and insoluble in seawater, barium frequently is used as a marker for the settleable fraction of drilling fluid. In several investigations performed to date, the barium concentration in bottom sediments was highest near the rig and decreased markedly with distance from the rig (Dames and Moore, 1978; Crippen et al., 1980; Gettleson and Laird, 1980; Meek and Ray, 1980; Trocine et al., 1981; Northern Technical Services, 1981, 1982, 1983; Bothner et al., 1982, 1983; EG & G Environmental Consultants, 1982; Boothe and Presley, 1983). Barium concentrations may reach concentrations 10 to 20 times above background in sediments near the discharge. Concentrations of barium in surficial sediments of 5,000 mg/kg have been reported near an exploratory rig site (Trefry et al., 1983; Trocine and Trefry, 1983), compared to a normal background of 200 to 300 mg Ba/kg in sediments from the area. Barium concentrations in excess of 40,000 ppm above background have been reported in surficial sediments within about 100 m of the discharge from a multiple-well development platform in the Gulf of Mexico (Petrizzuolo, 1983). Usually the increment in barium concentration is restricted primarily to the upper few centimeters of the sediments. In most cases, there is a steep gradient of decreasing barium concentration in surficial sediments with lateral distance to background concentrations 1,000 to 1,500 m down-current of the discharge point.

Other drilling mud-associated metals are much less elevated than barium in bottom sediments near the rig. Visible accumulations on the bottom of drilling discharges, primarily drill cuttings, have been reported near drilling rigs in the Gulf of Mexico (Zingula, 1975), offshore southern California (Bascom et al., 1976), on the mid-Atlantic outer continental shelf (EG & G Environmental Consultants, 1982), and the Beaufort Sea (Northern Technical Services, 1981), but not on Georges Bank (Battelle/W. H.O.I., 1983, 1984) or Cook Inlet, Alaska (Dames and Moore, 1978). These cuttings piles may be as much as a few meters high and 100 to 200 m in diameter. In non-depositional and high-energy environments, accumulations of drilling fluid and cuttings solids are dispersed from their deposition site by current-induced resuspension, bed transport and bioturbation (National Academy of Sciences, 1983). Bothner et al., (1983) estimated the half-time for wash-out of barite from sediments near an exploratory rig on Georges Bank to be about 0.4 years.

In the shallow Beaufort Sea, drilling fluids and cuttings may be discharged by above-ice or below-ice disposal (Northern Technical Services 1981, 1982). In either case, because of the shallow water, mud and cuttings will tend to settle initially on the bottom in the vicinity of the disposal site. It is generally agreed now, that because of their relatively low acute toxicity, "drilling fluids will have little adverse impact on water column organisms (Auble et al., 1983; Neff, 1982; Petrizzuolo, 1983). Acute and long-term impacts of mud and cuttings discharges will tend to be restricted to the benthos in areas where significant amounts of mud and cuttings accumulate on the bottom. Impacts may be due to outright burial, chemical toxicity of the mud or cuttings, or a change in the texture and grain size of the sediments.

Benthic communities in the vicinity of a C. O.S.T. well in lower Cook Inlet, Alaska were studied before, during and after drilling (Dames and Moore, 1978; Lees and Houghton, 1980; Houghton et al., 1981). The well was located in 62 m of water in a dynamic high-energy environment characterized by 4 to 5 m tides and tidal currents in the range of 42 to 104 cm/sec. Drill cuttings and elevated levels of barium were not detected

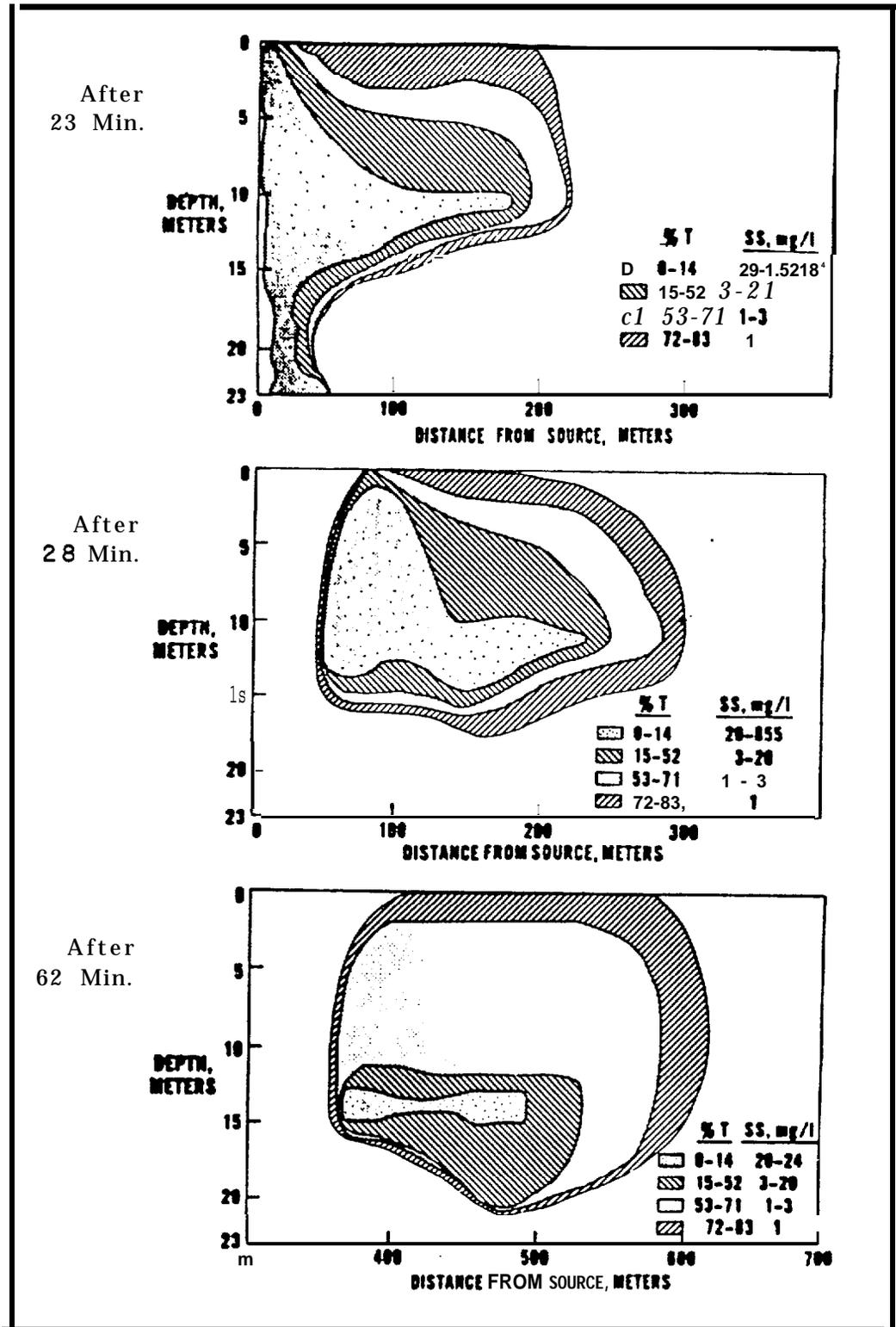


Figure 1.8 Time Sequence Illustrating Fate of Discharged Drilling Fluid Particulates; Side View of Plume During 1000 bbl/hr Discharge (from Ayers et al., 1980b).

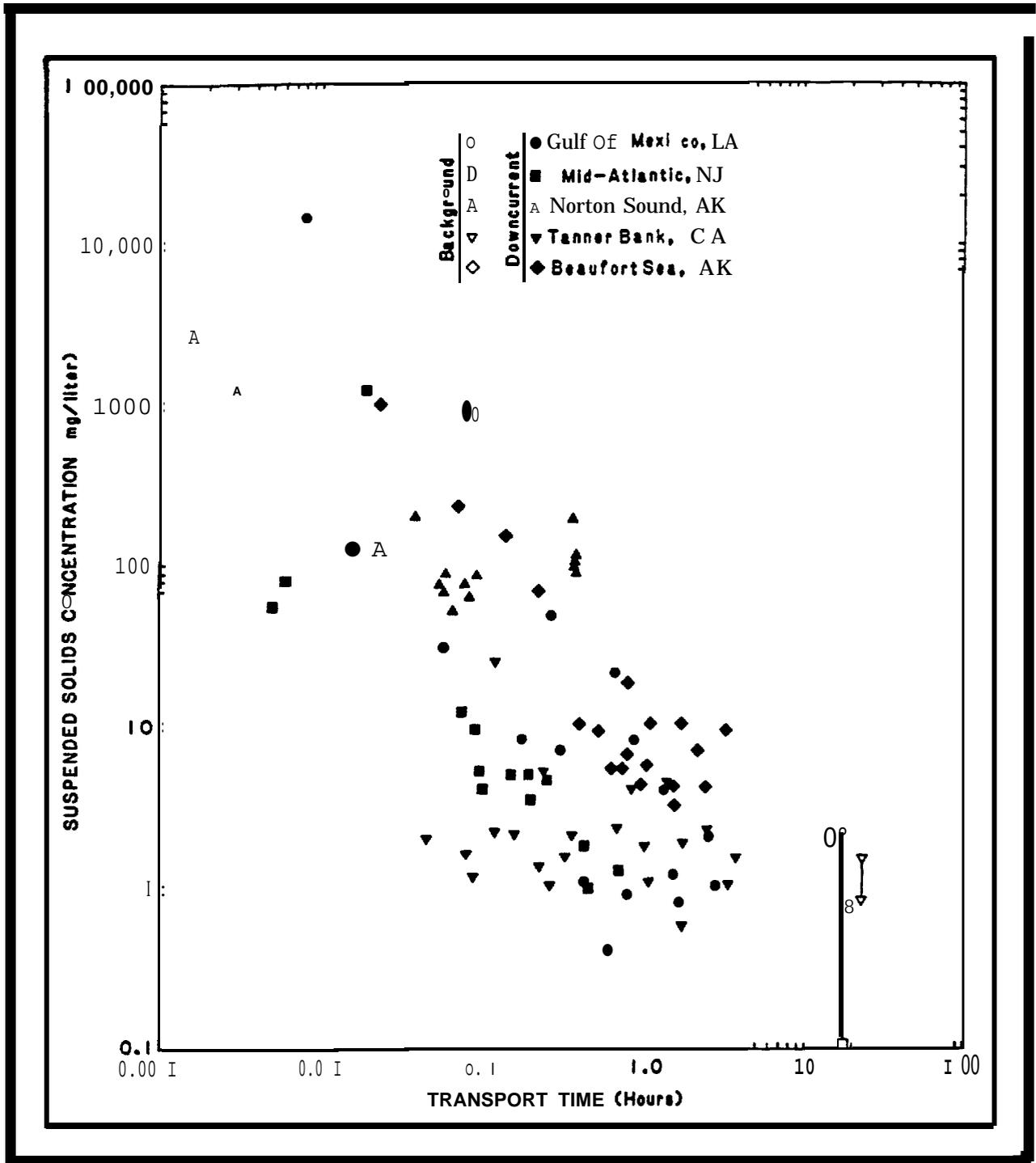


Figure 1.9 Graphical Presentation of Results of Five Drilling Fluid Dispersion Studies Performed in US. Outer Continental Shelf' Waters. Concentration of suspended solids is used as an indicator of drilling fluid solids concentration and is plotted against transport time (distance from rig divided by current speed). Undiluted drilling fluids contained from 200,000 to 1,400,000 ppm suspended solids before discharge. Data from Ayers et al., 1980b; EG & G Environmental Consultants, 1982; Ecomar, 1978, 1983; Northern Technical Services, 1981.

in sediments near the rig. Some changes in **benthic** communities were observed near the **drilling rig** during drilling. However, the investigators had difficulty in **relocating** and resampling stations established during the **predrilling** survey. Because of this and because of extreme patchiness and **seasonality** of the **benthic** fauna in the area, the investigators were unable to demonstrate a statistically significant impact that could be attributed to drilling discharges. Pink salmon fry, shrimp and hermit crabs were suspended in live boxes at 100, 200, and 1,000 m downcurrent from the drilling **fluid** discharge. After four days, there were no mortalities or sublethal effects that could be attributed to the **mud** discharge plume.

Crippen et al. (1980) studied the effects of exploratory drilling from an artificial gravel island on **benthic** fauna of the Canadian Beaufort Sea. Dredging to obtain materials for construction of the island and subsequent erosion of the island caused changes in local **hydrographic** conditions, and increased suspended sediment loads and rates of sedimentation such that it was not possible to distinguish effects of drilling fluid discharges from those resulting from island construction.

Crippen et al. (1980) also measured concentrations of metals in **drilling** fluids, sediments and **benthic animals** from the **drilling** site. Several metals, including mercury, lead, zinc, cadmium, and arsenic were present at elevated levels in the drilling fluids due to use of an impure grade of **barite**. Concentrations of these metals, as well as barium, increased in sediments near the **rig** during **drilling**. However, no correlation was detected between the concentrations of these metals in the **sediments** and their concentrations in tissues of **benthic** animals from the **site**.

More recently, Northern Technical Services (1981) investigated the effects of above-ice and below-ice disposal of **drilling** fluids and cuttings on the near-shore benthos of the U.S. Beaufort Sea off Prudhoe Bay, Alaska. Experimental and reference sites were located in 5 to 8 m of water. The maximum amount of material collecting on the bottom immediately after both types of test discharges of drilling fluid and cuttings ranged from 1 to 6 cm. Analyses of grain size and metals concentrations in bottom sediments indicated that the drilling fluids and cuttings were swept out of the area rapidly. The abundance of some species of **benthic** animals changed in the 3 to 6 months after the experimental discharges. In particular, the numbers of **polychaete** worms and harpacticoid copepods decreased at a discharge site in comparison to a nearby reference site. However, sediment grain size was different at experimental and reference sites and may have been the main factor responsible for the observed differences in seasonal population fluctuations.

Amphipods and bivalve molluscs were placed in live boxes or trays near the discharge sites before the discharge for up to 89 days after the discharge. The amphipods suffered few mortalities. More molluscs died or were missing in the tray from the discharge site than in trays from a reference site. However, the experimental tray had been disturbed, possibly contributing to the differences.

Concentrations of most metals were higher in animals from the reference sites than in those from the disposal sites. **Polychaete** tubes and **acroalgae**, **Eunephyta rubriforis**, from the disposal sites contained elevated levels of barium. However, these values were obtained by atomic absorption spectrometry and may not be reliable. The **acroalgae** also had a slightly elevated concentration of copper in their tissues.

There have been several laboratory investigations of the **bioavailability** of metals from **drilling** fluids (Neff, 1982; Petrazzuolo, 1983; National Academy of Sciences, 1983). Several of these studies have demonstrated a **statistically** significant accumulation of barium and chromium, and an indication of a slight accumulation of copper, cadmium and lead in several species of marine invertebrates. In all cases, the magnitude of metal bioaccumulation was small.

1.5.2 Produced Water

Produced water is fossil (connate) water that is trapped in the reservoir with the fossil fuel, or water that has leaked or been pumped into the formation during drilling or production. The produced water is pumped to the surface with the oil and gas, and must be separated from the hydrocarbons before they are processed further. Some wells generate no produced water at all; others may generate 90 percent produced water and 10 percent fossil fuel. In Cook Inlet, Alaska some of the oil, gas, and water produced offshore is piped to onshore production facilities at Trading Bay and Kens-i where oil and water are separated (Table 1.6). The Trading Bay facility generates 10.65 million liters (67,000 barrels) of oil and 9.86 million liters (62,000 barrels) of produced water which are discharged to the Inlet each day. Discharges from production platforms in the Gulf of Mexico generally are less than 1.59 million liters (10,000 barrels) per day (Menzie, 1982).

Produced water usually, but not always, is a saline brine with total dissolved solids concentrations up to about 10 times that of seawater (300 ppt salinity). The major inorganic ions present are the same as those in seawater. In addition, produced water may contain elevated levels of several heavy metals (Table 1.7) and slightly water-soluble 10 w molecular weight aliphatic and aromatic hydrocarbons (Table 1.8).

Dilution of produced water upon discharge to the ocean is very rapid, the actual rate being dependent upon such factors as total dissolved solids concentration of the produced water, current speed, vertical convective mixing of the water column and water depth (Figure 1.10). Based on a model developed by the Massachusetts Institute of Technology, it was estimated that saturated brine (about 320 ppt salinity) from the Bryan Mound Strategic Petroleum Reserve salt dome would be diluted to within 5 ppt of ambient sea water salinity within 30 m of the discharge point (Federal Energy Administration, 1977). In Trinity Bay, Texas, a shallow estuary physiographically somewhat similar to the near-shore Beaufort Sea, total dissolved hydrocarbon concentrations in produced water were diluted by 2,400-fold within 15 m down-current of the discharge pipe located 1 m above the bottom in 2 to 3 m of water (Armstrong et al., 1979). Crude oil tanker ballast water (with a hydrocarbon composition similar to that of produced water) discharged to Valdez Harbor from the Valdez ballast treatment facility (Lysyj et al., 1981) or to the Red Sea at Yanbu, Saudi Arabia from crude oil tankers (Neff et al., 1983), was diluted 500-fold or more within 150 m of the discharge and 1,000 to 3,000 fold within 500 to 1,000 m of the discharge.

Where suspended sediment concentrations are high, as in the Beaufort Sea, dissolved and colloidal hydrocarbons and metals from produced water tend to become absorbed to suspended particles and settle to the bottom (Figure 1.11). In Trinity Bay, Texas, sediments 15 m down-current from a produced water discharge, contained high concentrations of C₁₀-C₂₈ alkanes and aromatic hydrocarbons from C₃-benzenes to C₃-phenanthrenes (Armstrong et al., 1979). A gradient of decreasing sediment naphthalene concentrations extended away from the discharge in all directions for up to 5,000 m of the discharge. In deeper water, more typical of OCS drilling activities, elevated levels of hydrocarbons are restricted to a much smaller area of the bottom or are not detected at all. In the Buccaneer Field, located in about 20 m of water, elevated levels of n-alkanes were detected in surficial sediments within a radius of about 15 to 20 m of the discharge (Middleditch, 1981). However, sediment resuspension and transport resulted in rapid changes in sediment hydrocarbon concentrations on almost a daily basis.

Elevated levels of barium, cadmium, chromium, copper, lead, strontium, and zinc have been detected in surficial sediments in the vicinity of production platforms in the northwest Gulf of Mexico (Tillery and Thomas, 1980; Wheeler et al., 1980). These metals may be derived from discharge of drilling fluids and produced water, and by corrosion or leaching of submerged rig structures, antifouling paints, and sacrificial anodes. The magnitude of elevation in the concentration of metals other than barium in sediments usually is small.

Produced waters have also been shown to contain significant levels of radionuclides, from geological strata in the formation, in particular ²²⁶Ra and ²²⁸Ra and are directly related to salinity values of produced waters. These levels are generally

Table 1.6 Organic Composition of Produced Water Effluents from Alaska^a.

Parameter	Trading Bay ^b Final Effluent		Kenai ^c Final Effluent		Cook Inlet ^d Offshore Platform	
	Cone.	% Red.	Cone.	% Red.	Cone.	% Red.
Total Organic Load mg C/L	435		288	47	188	
Suspended Petroleum mg C/L	5.3	1.2	14	93	36	91
Dissolved Non-Volatile mg C/L	423	97	264	22	141	-
Volatile Hydrocarbons mg C/L	6.5	1.6	10	40	11	65
Volatile Aliphatics mg/L	1.5		1.0	38	0.8	91
Volatile Aromatics mg/L	6.1	-	10.2	40	11.3	55

a From Lysyj et al. (1981)

b Onshore processing of 4 offshore platforms
 o 131,000 bbl total fluids per day
 o 62,000 bbl produced water per day

c Onshore processing of 30 offshore platforms
 o 21,000 bbl total fluids per day
 o 8,000 bbl produced water per day

d Single offshore platform
 o 13,000 bbl total fluids per day
 o 11,000 bbl produced water per day

Table 1.7 Concentration Ranges of Metals in Sea water and in Produced Waters Discharged to the Gulf of Mexico. Concentrations are in $\mu\text{g}/\text{kg}$ (parts per billion).

Metal	Concentration in Sea water ^a	Concentration in Produced Water ^b
Antimony	0.5	0.061
Arsenic	3.0	0.32
Barium	10 - 63	6.4 - 3,500
Beryllium	0.0005	0.25 - 2.7
Cadmium	0.11	0.057 - 32
Chromium	0.13- 0.25	0.83 - 260
Copper	0.5 - 3.5	0.55 - 120
Iron	1.7 - 150	260 - 2,900
Lead	0.6 - 1.5	0.78 - 760
Manganese	0.1 - 8.0	0.84 - 4.3
Mercury	0.15- 0.27	0.16 - 0.4
Nickel	2.0	0.35 - 1,200
Silver	0.145	0.028 - 110
Strontium	8,000	230 - 71,000
Thallium	0.01	0.33
zinc	1.5- 10	15 - 610

a From Goldberg (1963)and Hood (1963)

b From Middleditch (1981)

Table 1.8 Concentrations of Selected Petroleum Hydrocarbons in Produced Water Effluents From the Buccaneer Platform in the Northwest Gulf of Mexico. Concentrations are in $\mu\text{g/liter}$ (parts per billion)

Compound	From Middleditch (1981)	From Sauer (1981)
Aromatic Hydrocarbons		
Benzene	6100	1150
Toluene	5460	7460
Ethylbenzene	1200	850
m- p- & o-xylenes		3570
Total C ₃ -Benzenes	24.2	5590
C ₄ -Benzenes	22.2	830
C ₅ -Benzenes	4.5	NA
C ₆ -Benzenes	3.2	NA
C ₇ -Benzenes	0.9	NA
C ₈ -Benzenes	1.2	NA
C ₉ -Benzenes	2.4	NA
C ₁₀ -Benzenes	1.0	NA
C ₁₁ -Benzenes	0.3	NA
Naphthalene	11.1	170
Methylnaphthalenes	7.2	20
C ₂ -Naphthalenes	10.4	NA
C ₃ -Naphthalenes	4.3	NA
C ₄ & C ₅ -Naphthalenes	0.9	NA
Biphenyl or Acenaphthene	2.8	NA
C ₁ & C ₂ -Biphenyls	2.9	NA
Alkanes		
C ₁ - C ₁₃	3120	3100
Cycloalkanes	2580	1060
Alkenes	580	NA
C ₁₄ - C ₂₉	1476	NA
Total Aromatics Measured	12,860	16,070
Total Alkanes Measured	4,596	3,170
Total Cycloalkanes Measured	2,580	1,060
Total Alkenes Measured	580	NA
Total Hydrocarbons Measured	<u>20,616</u>	<u>20,300</u>

NA , Not Analyzed.

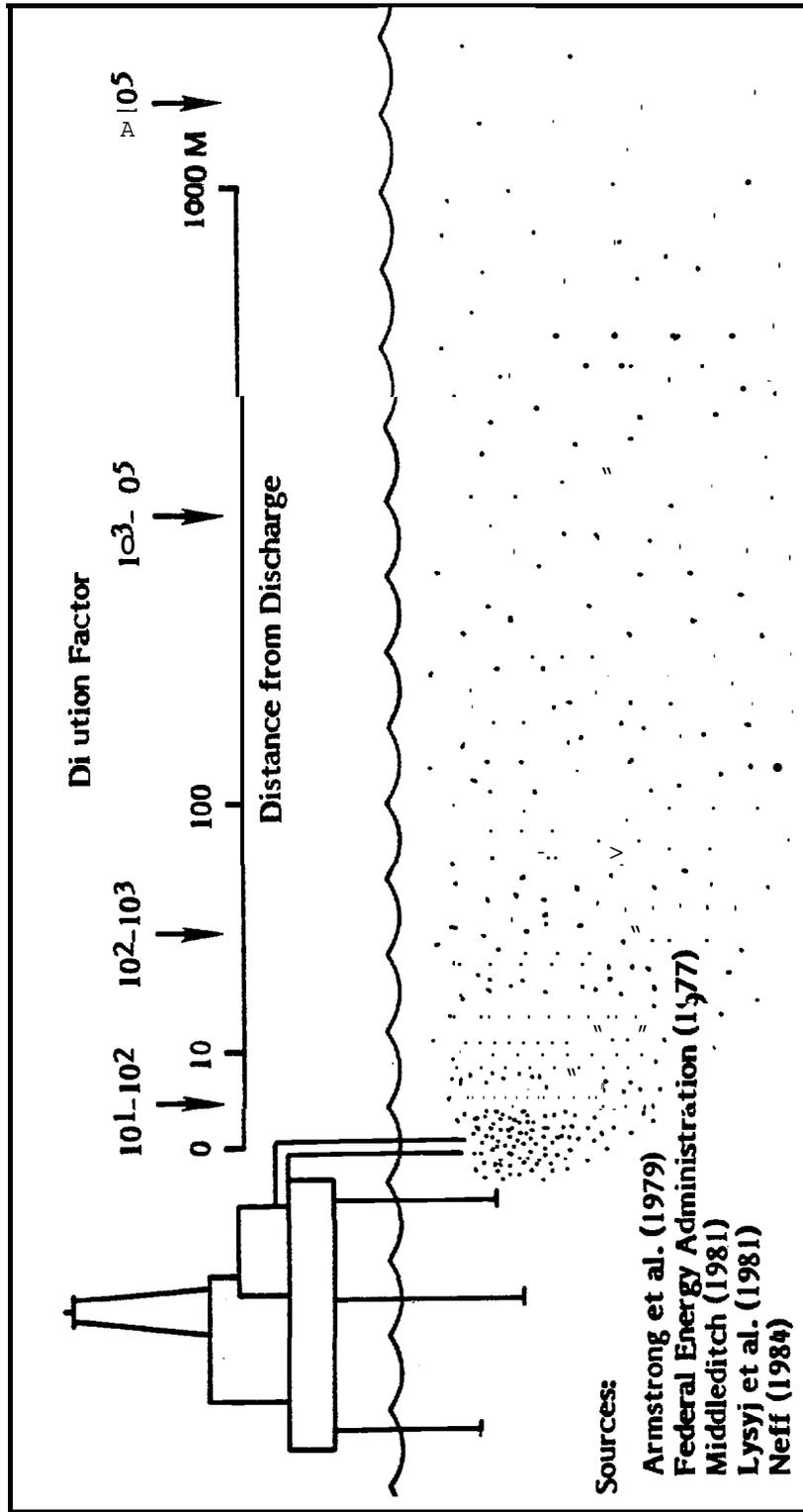


Figure 1.10 Relationship Between Distance from Produced Water Discharge Point and Dilution Ratio.

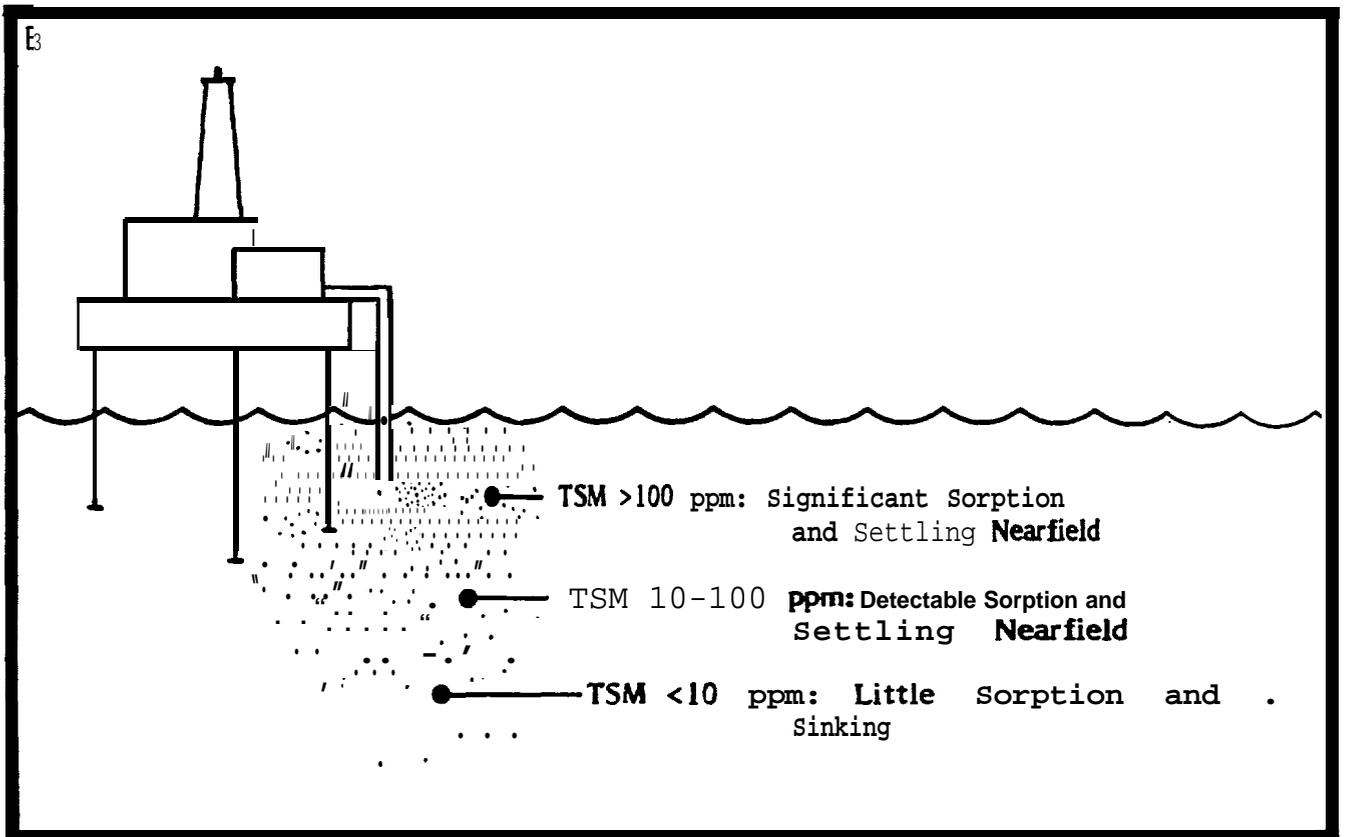
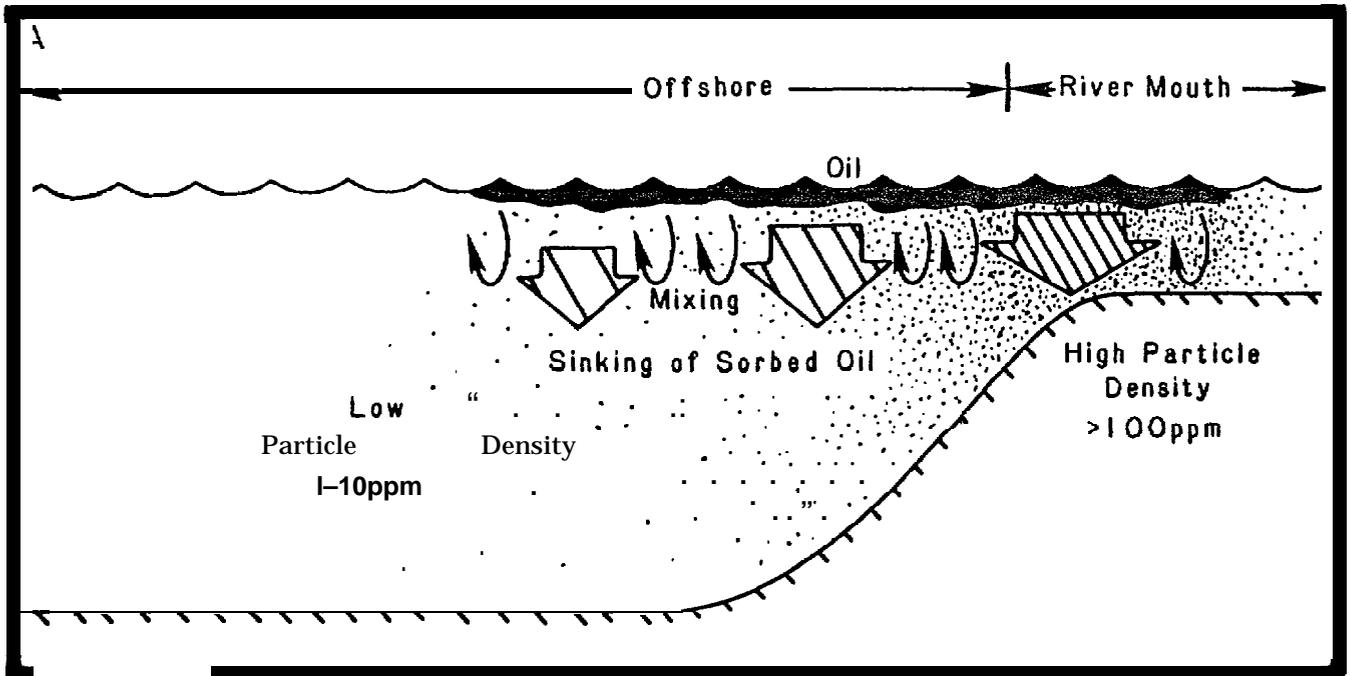


Figure 1.11 Schematic Representation of How TSM (Total Suspended Matter) Levels Promote Sorption and Sedimentation of Oil from Spills and Produced Water Chemicals.

higher than ambient sea water values. Depending on dilution rates of produced water and the levels in produced water. These **radionuclides** may be potentially sorbed and **sedimented** and/or **bioaccumulated** by **marine** organisms.

The very limited information available suggests that produced water has a low acute and chronic toxicity to marine animals (Neff, 1984). There have been no published reports of **bioaccumulation** of metals from produced water by marine animals. Clams *Rangia cuneata* placed in trays on the bottom near the produced water **outfall** of a separator platform in Trinity Bay, Texas **accumulated** aromatic hydrocarbons to high concentrations (Fucik et al., 1977). When placed in clean seawater in the laboratory, the clams released the accumulated hydrocarbons rapidly. Barnacles, shrimp, some **benthic** organisms and several species of fish from the vicinity of the Buccaneer production platform in the northwest Gulf of Mexico contained slightly elevated levels of **n-alkanes**, some of which were identified as **petrogenic** and may have been derived in part from produced water (Middleditch, 1981).

1.5.3 Oil Spills

Accidental oil **spills** can occur any **time** during exploration for and development of offshore oil and gas reserves in the Beaufort Sea, though the danger of such an event increases as the **field** comes into production, and large volumes of crude oil must be stored and then transported out of the area. During exploration and development, significant volumes of diesel fuel and petroleum-based lubricants are stored on-board the drilling platform or island for operation of diesel engines and other machinery. Small spills of these **materials** can occur **during** normal supply, storage, transfer and usage operations. Such spills rarely involve more than one or a few barrels of oil. Any spillage on the **drill** floor is collected by the deck **drainage** system and passed through an oil-water separator before discharge.

During development **drilling** or production, **spills** of crude oil can occur. Well blowouts or pipeline breaks are the most likely causes of major spills. If ice breaker tankers are used to transport crude oil to refineries, then **spills** associated with ballast or **bilge** water discharges or tanker accidents would be another important potential source of oil spill.

The chemical composition of crude oils from different producing regions or even different production zones in a single well can vary tremendously. Crude petroleum and most refined petroleum products are extremely complex **mixtures** of many thousands of organic compounds. Hydrocarbons (compounds containing only hydrogen and carbon) are the most abundant accounting for 50 to 98 percent of the weight of the **oil** (Speers and Whitehead, 1969; Clark and Brown, 1977). The **remainder** is made up **primarily** of **various** sulfur, oxygen and nitrogen-containing organic compounds and small amounts of several metals (V, Ni, Fe, Al, Na, **Ca**, **Cu**, and U).

Petroleum contains a significant fraction (0 to 20 percent) of higher molecular weight material (1,000 to 10,000) **consisting** of both hydrocarbon and NSO compounds called **asphaltenes**. These compounds, consisting of 10 to 20 fused rings with **aliphatic** and **naphthenic** side chains, contribute significantly to the properties of petroleum in geochemical formations and in spill situations as well (e.g., related to emulsification "behavior").

Vanadium and nickel are the most abundant metallic constituents of crude petroleum, sometimes reaching concentrations of thousands of parts per million, but most often lower. They are present in porphyrin complexes and as **free** metals as well.

The petroleum hydrocarbons consist of **aliphatic**, open-chain compounds, **alicyclic**, ringed compounds, and aromatic compounds containing at least one benzene ring.

The most **toxic** components of petroleum include low molecular weight aromatic hydrocarbons (benzene through **fluorene**), and related low molecular weight sulfur, oxygen and nitrogen **heterocyclics** (Neff, 1979; Neff and Anderson, 1981). Some 4- and 5-ring **polycyclic** aromatic hydrocarbons are potent carcinogens.

Although spilled petroleum may cause severe acute effects in the water column (i.e., fish kills), chronic effects are most likely to occur when oil sinks or is transported to the bottom and is incorporated into bottom sediments where it becomes a long-term source to benthic animals.

Studies of several oil spills have shown that, in order for significant quantities of oil to reach the bottom, oil must sorb to suspended sediment and sink. The Santa Barbara oil spill is a good example of this (Kolpack et al., 1971), where transport and deposition of large quantities of flood runoff material occurred during the spill. This appears to be the major transport route of oil to the benthos, although other mechanisms can become significant in certain cases. Most notably, the water column to benthic transport of oil can occur by fecal pellet transport (Boehm et al., 1982a; Johanssen et al., 1980), by sinking due to Langmuir circulation, by direct sinking of dense (cold, weathered) oil in areas of low density water (fresh water input at river mouths or near ice melting) or by sinking of saline brines during formation of sea ice. Oil deposition by sorption and sinking is more likely where riverine inputs of suspended material (i.e., from the Sagavanirktok, Colville and Kuparuk Rivers) occur and where total suspended concentrations approximate 100 ppm (Figure 1.11). Suspended sediment concentrations in the Beaufort Sea can be very high, especially during spring breakup when the riverine overflow onto the shorefast ice mixes with seawater, or following summer storms (Naidu, 1979; Northern Technical Services (1981)).

Petroleum hydrocarbon transport to nearshore subtidal sediments may occur if the oil beaches and the beach is subsequently exposed to seasonal erosion or ice scour. Studies in the Canadian Arctic (Baffin Island Oil Spill Program) (Boehm et al., 1982b; 1985) and in the Amoco Cadiz spill (Marchand and Caprais, 1981; Boehm et al., 1982c; Atlas et al., 1981) have shown that large amounts of oil (> 100 ppm in sediments) can be expected to impact nearshore (subtidal sediments) if shoreline impact is allowed to occur.

Sorbed or otherwise sedimented oil will tend to follow normal offshore sedimentation patterns in which the oil will eventually be transported to low energy basins, through features or other depositional areas. This will occur unless the amount of oil sedimented is so great that the texture of the sediment changes, or a "tar mat" is formed. In the Tsesis and other spills (e.g., Santa Barbara blowout), offshore basins served as traps of oil (Boehm et al., 1982a; Kolpack et al., 1971).

Many studies have been published concerning the biodegradation of petroleum hydrocarbons in sediments (see Bartha and Atlas, 1984 for a review). Given the availability of oxygen and nutrients, resident microbial populations will utilize hydrocarbons as substrates at varying rates. Sedimented oil was observed to be rapidly biodegraded in the Amoco Cadiz spill (Atlas et al., 1981) and in the Tsesis spill (Boehm et al., 1982d), while little biodegradation was evident from chemical results in the IXTOC I blowout and Baffin Island Experiment spill (Boehm and Fiest, 1982; Boehm, 1983). Haines and Atlas (1982) determined that biodegradation of petroleum proceeds slowly in Arctic environments with significant degradation occurring only after a year or more of environmental exposure.

Once buried or mixed in the sediment below the oxic zone, which may be on the order of as little as several millimeters deep, no significant biodegradation will proceed due to limited oxygen availability (Ward et al., 1982). Any physical or biological motions would tend to accelerate biodegradation due to inputs of oxygen. There is evidence that bioturbation of marine sediments enhances oxygen irrigation and, hence, biodegradation of oiled sediments (Gordon et al., 1978; Bartha and Atlas, 1984). Studies examining the distribution of polycyclic aromatic hydrocarbons (PAH) in coastal and offshore sediments (e.g., Farrington et al., 1983) suggest that PAH sources from petroleum are more readily degraded than associated PAH from pyrolytic inputs due to their availability to microbial populations.

Evidence exists (Boehm et al., 1982d; Boehm, 1983) for the biodegradation of petroleum within the gut of arctic bivalves, owing probably to an indigenous concentrated microbial population within the animal. These observations were made in an area where no chemical evidence for biodegradation is seen outside of the animals (i.e., in the sediments). It is not known whether this may represent a significant removal mechanism of oil from low level oiled substrates.

Boehm and Fiest (1982) reported rapidly decreasing levels of oil in the water column initially at 10 ppm, 1 km from the blowout site to 1 ppm with 10 km, down to 0.1 ppm at 20 km from the I X T O C I blowout. Lower water column levels (100 ppb to 1 ppm) would be more typical. In acute impact zones of blowouts of lesser dimension and which occur at or above the sea surface (e.g., Ekofisk). McAuliffe et al. (1975) observed levels as high as 36 ppm in the water following a blowout. Much lower concentrations of oil (10 to 120 ppb) were found in the water column (Marchand and Caprais, 1981; Calder and Boehm, 1982) after the A m o c o C a d i z spill with lower quantities (10 to 20 ppb) offshore and 100 ppb to 1 ppm in the estuaries where large quantities of oil were transported. Those water column levels can have differing impacts on marine biota.

Studies of transport of oil to the offshore benthos following the I X T O C I blowout (Boehm and Fiest, 1981) indicate that 10 to 100 ppm could be found near the massive blow out site, but little was found in offshore sediments further away. Offshore sediments at the A m o c o C a d i z spill were found to contain 30 to 220 ppm, with much greater quantities (500 to 1000 ppm) within the estuaries (Marchand and Caprais, 1981; Gundlach et al., 1983). McAuliffe et al. (1975) observed oil-in-sediment levels on the order to 100 ppm in the vicinity of a Gulf of Mexico blowout in areas of high concentration of suspended sediments. Low levels (1 to 8 ppm) of oil were found in the sediments around the Ekofisk blowout (Johnson et al., 1978). Very high values of oil in sediments were obtained after the Santa Barbara blowout (Kolpack et al., 1971).

Hydrocarbons in solution or dispersion in seawater are much more bioavailable than hydrocarbons sorbed to sediments or detritus (Neff, 1979; Neff and Anderson, 1981; Anderson, 1983). The bioaccumulation factor (concentration in tissues divided by concentration in sediment) for aromatic hydrocarbons associated with sediments and detritus usually is less than 1, but may be as high as 11. Bioavailability is inversely related to sediment organic carbon content. However, because sediments represent by far the most concentrated source of hydrocarbons in the contaminated environment, sediments are a major source of chronic contamination of benthic and demersal fauna in an oil-impacted area. It appears that filter-feeding bivalves accumulate petroleum hydrocarbons primarily from the water column, while deposit-feeding bivalves accumulate hydrocarbons primarily from sediments (Boehm et al., 1982a; Anderson, 1983).

1.6 Study Organizations

The BSMP is being conducted by scientists from Battelle's Marine Laboratories in Duxbury, Massachusetts and Sequim, Washington with logistical assistance from personnel at Battelle's Anchorage office. Scientists from the University of Alaska's Marine Sciences Institute are siding in data analysis and interpretation. The program's efforts are being reviewed by a Scientific Review Board. The program organization is summarized in Figure 1.12.

2. SAMPLING METHODOLOGY

2.1 Sampling Locations and Dates

Field sampling for the 1984 BSMP was conducted during the period between September 1 and September 17. Twenty-seven stations were visited and sampled. Of the 38 proposed stations, 24 were occupied and successfully sampled. Ice conditions prevented sampling of the remaining proposed stations (outermost stations and Camden Bay site). Three new stations were occupied and sampled (2E, 2F and 7G).

Sampling dates, station locations and their depths are detailed in Table 2.1. The Beaufort Sea Study Area with locations of all stations is shown in Figures 2.1 and 2.2.

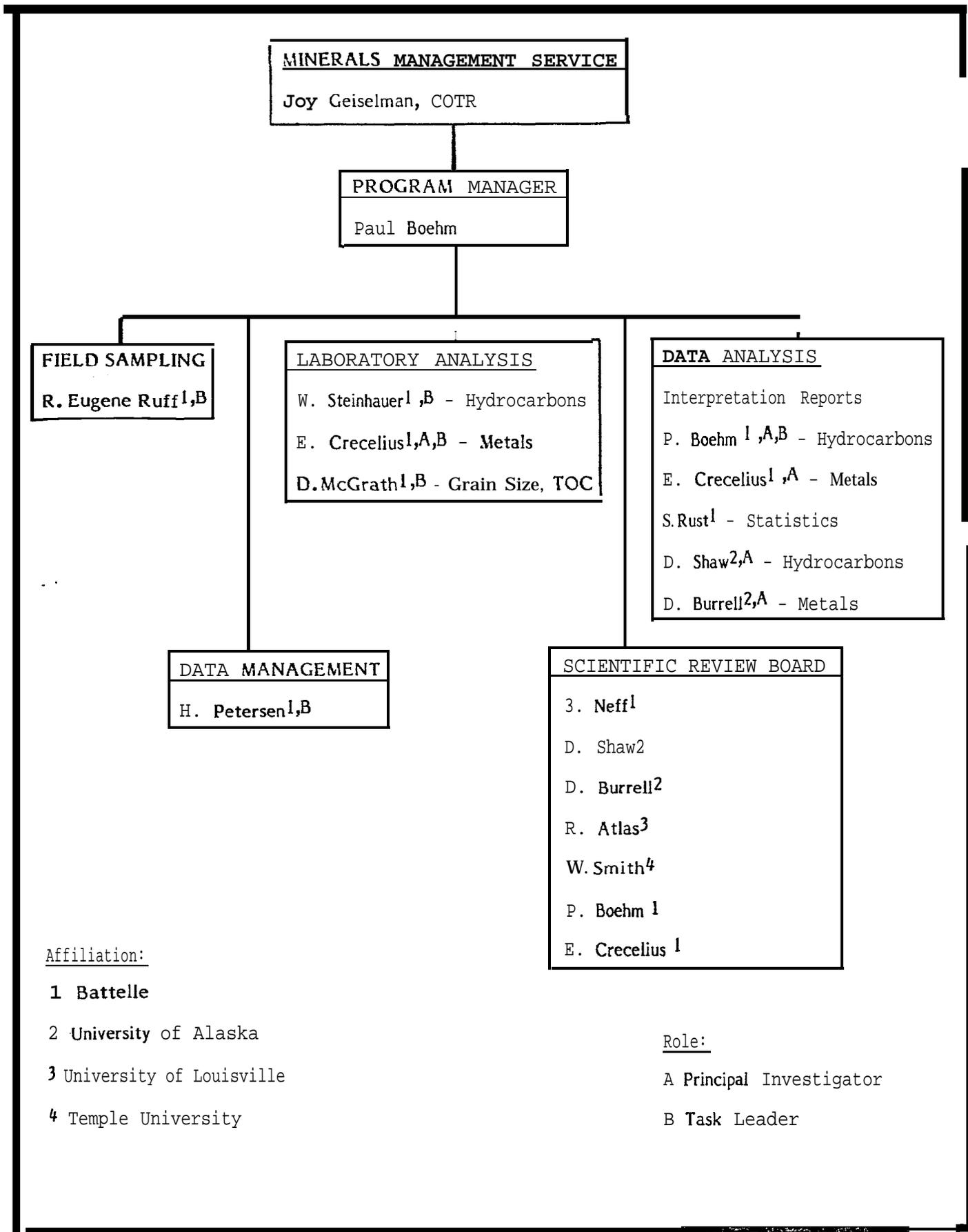


Figure 1.12 Program Organization Showing Task Leaders and Principal Investigators

Table 2.1 **Station Locations, Sampling Dates and Depths for Proposed and Sampled Stations for the 1984 Beaufort Sea Monitoring Program.**

Station No.	Sampling Date	Depth (m)	Position	
			N. Lat.	W. Long.
1A	not sampled	8	70°01.6'	144032.3'
1B	not sampled	15	70°04.0'	144041.5'
1C	not sampled	23	70°10.0'	145000.0'
1D	not sampled	5	70°05.7'	145005.6'
2A	not sampled	5	70°01.5'	145°305.0'
2B	not sampled	11	70°04.0'	145010.0'
2C	not sampled	25	70°10.0'	145020.0'
2D	not sampled	7	70°03.4'	145018.0'
2E	11 Sept.	7.6	70°12.8'	146011.5'
2F	12 Sept.	1.8	70°10.3'	146°01.9'
3A	12 Sept.	6.1	70°20.3'	147005.6'
3B	13 Sept.	3.7	70°17.9'	147002.0'
3C	not sampled	14	70°22.0'	146036.0'
4A	2 Sept.	4.3	70°18.4'	147040.0'
4B	2 Sept.	7.3	70°21.0'	147039.6'
4C	2 Sept.	9.1	70°26.1'	147042.6'
4D	not sampled	22	70°35.0'	147040.0'
5(1)	14 Sept.	6.4	70°25.1'	148004.9'
5(2)	14 Sept.	5.8	70°25.4'	148°07.2'
5(5)	14 Sept.	7.0	70°26.0'	148016.8'
5(10)	14 Sept.	8.2	70°27.1'	148030.6'
5A	14 Sept.	11.6	70°29.9'	148045.8'
5B	17 Sept.	16.5	70°34.6'	148°54.8'
5C	not sampled	22	70°35.0'	148025.0'
5D	1 Sept.	2.0	70°24.31"	148032.9'
5E	17 Sept.	19.2	70°38.9'	149016.1'
5F	16 Sept.	1.5	70°26.4'	148049.2'
5G	13 Sept.	9.1	70°29.4'	148002.4'
6A	4 Sept.	3.0	70°32.2'	149°56.7'
6B	4 Sept.	5.2	70°33.3'	150°24.9'
6C	4 Sept.	15.2	70°40.3'	150°32.1'
6D	5 Sept.	18.3	70°44.7'	150029.2'
6E	not sampled	22	71°00.0'	150045.0'
6F	5 Sept.	12.5	70°40.2'	151012.0'
7A	7 Sept.	1.5	70°37.6'	152°10.1'
7B	6 Sept.	5.5	70°47.4'	151056.0'
7C	6 Sept.	14.3	70°54.8'	152°00.7'
7D	not sampled	5	70°56.5'	153015.3'
7E	6 Sept.	2.7	70°43.5'	152°04.2'
7F	not sampled	20	70°10.0'	153000.0'
7G	7 Sept.	3.0	70°39.41'	151053.7'

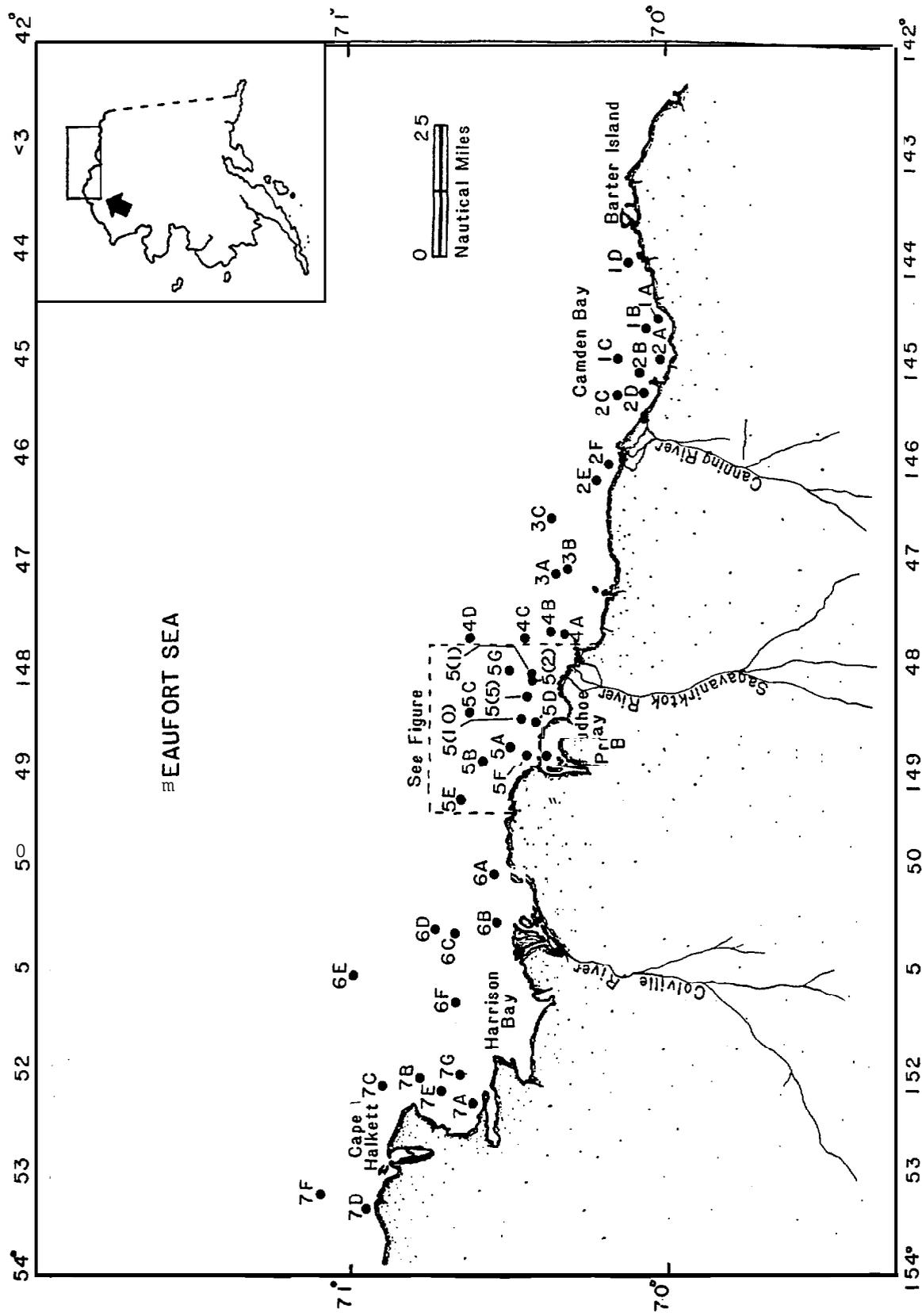


Figure 2. Beaufort Sea 1984 Monitoring Program Study Area Showing all Station Locations.

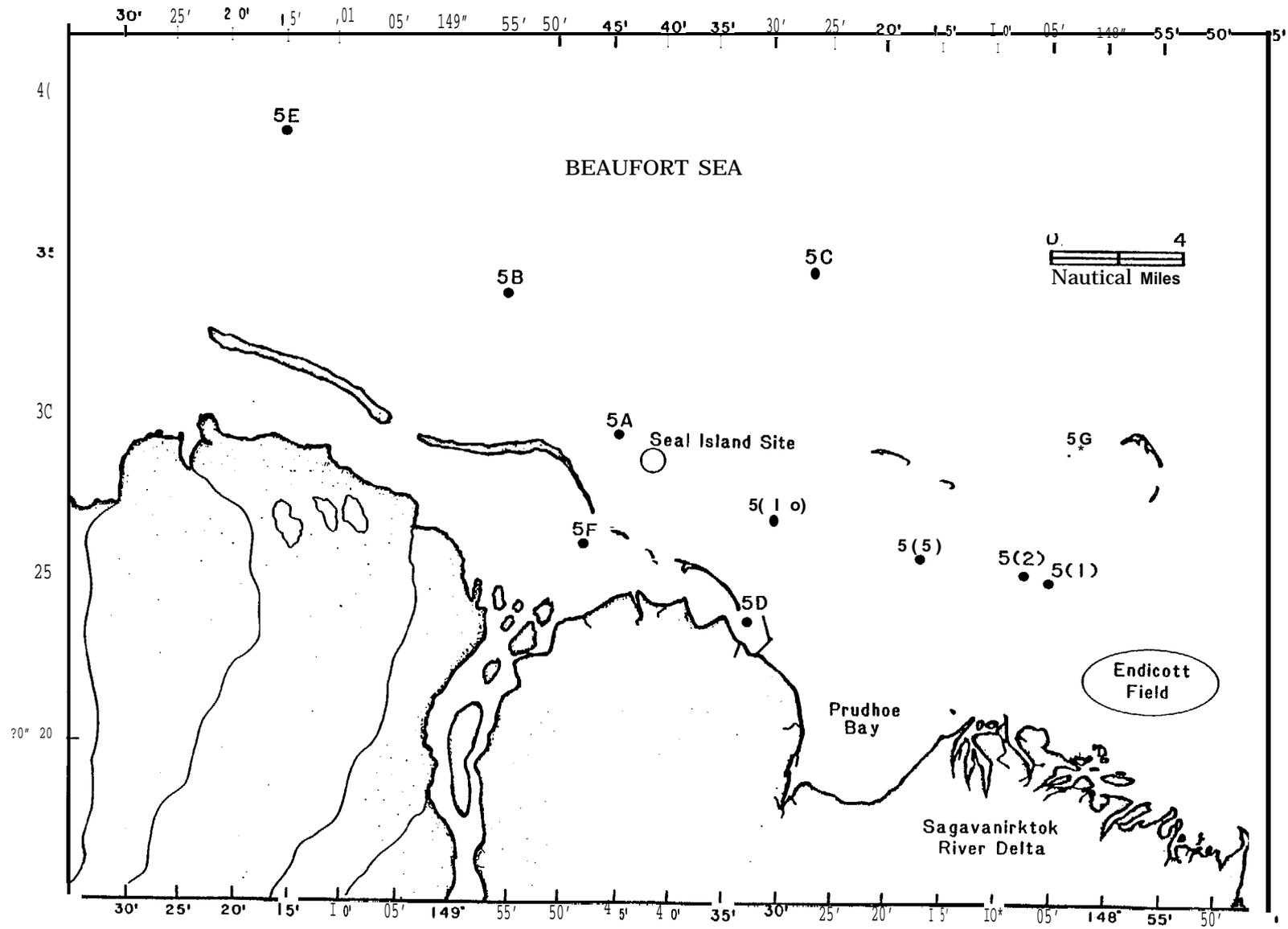


Figure 2.2 Detail of Prudhoe Bay-Gw ydyr Bay Area Station Locations.

2.2 Sampling Methods and Logistics

2.2.1 Field Survey Team

2.2.1.1 Scientific Party. The Scientific Party for the 1984 Field Season consisted of R. Eugene Ruff, William Steinhauer, and James Campbell. Mr. Ruff served as Field Party Chief and was responsible for the overall success of the sampling program. In addition to coordinating all field and logistic activities, Mr. Ruff served as the formal liaison between the scientific party and Battelle management staff at B N E M R L. He maintained the ship's station log (navigation log) and chief scientist's log throughout the survey. Mr. Steinhauer collected all the sediment and bivalve samples, and was responsible for overall integrity of the sampling, sample storage and transfer operations. He maintained the cast logs, sediment collection logs, bivalve collection logs, and sample transfer forms. Mr. Campbell collected all hydrographic data, performed dissolved oxygen analyses and maintained the hydrographic log.

2.2.1.2 Ship's Crew. The N O A A research vessel No. 1273 was skippered by Mr. Eric Gardner, a N O A A Corps Officer from Seattle, Washington. He was assisted by Mr. Steven Pace. Mr. Pace has had extensive experience navigating in the Beaufort Sea and, therefore, provided invaluable assistance in navigation and piloting the research vessel.

Preparation of the N O A A vessel was coordinated by Mr. George Lapienne of the N O A A Office, Juneau, Alaska. Mr. Lapienne and Mr. Gardner performed pre-survey maintenance, and held a shake-down cruise to assure that the vessel was sea-worthy for the field survey.

2.2.2 Survey Vessel

N O A A 1273, the survey vessel provided by the government for use on the BSMP was a Bristol Bay gill netter, aluminum-hulled 11 m overall length, with a 3-m beam, and 0.76 m draft. The vessel was powered by a 3208 catapillar engine with a 1900 L usable fuel tank and had a 645 km cruising range. The working deck was 2.6 m by 3.9 m, and was equipped with hydraulic winch with 900 kg line pull and 615 m of 0.63 cm stainless steel wire, and with a hydraulic A-frame 1.8 m wide and 2.6 m high above deck with 1.5 m clearance over rails. The survey vessel was equipped with the following electronics:

- Radar, 38.6 km sea scan
- VHF marine radio
- HF radio tunable to 30 MHz
- Recording depth recorder
- TRACOR BRIDGESTAR satellite navigation system

2.2.3 Navigation

The Tracer Omega-2 navigation system, expected to be the primary navigational aid for use during the cruise, was not available by the start-up date. Therefore, the on-board satellite navigation system was employed to determine station locations. The ship's radar, fathometer, and dead reckoning were used to position the vessel as close as possible to the desired station location. Then the Tracer Bridgestar SATNAV receiver was monitored until an accurate position could be obtained. Satellite passes were irregular in timing, but a satisfactory reading was nearly always obtained during the period that the station was being sampled. Since the vessel could be anchored at most of the stations,

this method was adequate for establishing the initial station positions and resulted in very little lost time.

2.2.4 Communication

The anticipated nightly communications link with the Battelle Alaska Operations office via upper side band contact with Radio Broadcast in Fairbanks proved unreliable, possibly due to electrical problems within the ship and/or disturbances in the atmosphere. Alternate communication channels were established through Colville River Radio and through Bill Koplun aboard the Anika Marie. Since reliable communications are difficult to maintain in the remote Arctic environment, communications needs and requirements will be reassessed prior to the next field effort.

2.2.5 Field Data Management

Shipboard data forms (Station Log, Cast Log, Sediment Sample Log, Bivalve Sample Log, and Hydrolab Data Sheets), and Sample Transmittal Forms comprise the media used for recording field operation and sample tracking data. Carbon copies of the forms were maintained by two of the scientific party members during the performance of the survey and while samples were in transit from the field to the laboratory, so as to provide redundancy.

The Station Log contains station position and depth data, and as well as date and length of occupation. In addition, the Station Log contains information on the type of positioning equipment used and any drift in position which may have occurred during station occupation.

Each lowering of sampling gear was recorded by station, date and time, and assigned a cast number in the Cast Log. In addition, sampling success and sample number were recorded on this form, providing redundancy in sample identification and tracking with the Sediment Sample Log and Bivalve Sample Log. Information on sample type (i.e., sediment chemistry or grain size, bivalve species) and replicate number were also recorded on the two sample logs. Hydrographic data generated by the CTD sonde, as well as dissolved oxygen data, and quality control test measurements and samples (temperature and salinity) were recorded on the Hydrolab Data Sheet.

Each sample collected (sediment, chemistry, grain size, bivalve, salinity, and QC) was confirmed and recorded on a Sample Transmittal Form which accompanied the samples throughout the transfer from Deadhorse, Alaska to BNEMRL. Upon return to the lab, all samples were compared with appropriate data forms to validate the sample transfer.

2.2.6 Sampling Equipment and Methods

2.2.6.1 Sediment Sampling. Sediment samples were collected with a 0.1-m² stainless steel Kynar-coated, modified Van Veen grab (T. Young, Sandwich, Massachusetts). A second Teflon-coated grab sampler was stored at the Prudhoe Bay logistics center in Deadhorse, Alaska. After the grab sampler was deployed and retrieved, the top centimeter of sediment was removed with a Teflon-coated scoop and placed into 250 ml Teflon jars. Both the grab sampler and the scoops were soap and water washed, then rinsed with methanol and methylene chloride before use. Teflon jars were prepared at BNEMRL using the following procedure: soap and water wash, followed by nitric acid soak (overnight), weak hydrochloric acid rinse, and distilled water rinse. Jars were then rinsed with methanol and methylene chloride. A second methylene chloride rinse was performed in the field just prior to use of the jars. Sediment replicates were stored over dry ice (-78°C) in polystyrene shipping containers for field storage and transfer to BNEMRL. Each grab sample was photographed before subsampling to document the integrity of the undisturbed sediment surface.

The field survey manual called for two chemistry replicates, comprised of the upper 1 cm of sediment from either side of the grab sampler, to be collected every 6 min

(10 grabs/ hr). This sampling schedule was easily achieved at most stations. However, at stations containing a high silt and clay content, the pace was difficult to maintain since relatively more time was required washing and preparing the grab sampler between 10 workings. In addition, undisturbed sediment surface was not always achieved at every 10 working. Repeat 10 workings were made until acceptable replicates were obtained.

The Teflon-coated grab sampler and Teflon-coated scoops were Molly provided by Dr. Michael Bothner, USGS, Woods Hole, Massachusetts for use on the first field survey. This equipment was restored to its original condition and returned at the end of the survey.

2.2.6.2 Infaunal Bivalve Sampling. Infaunal bivalves were collected with the O. 1-m 2 Kynar-coated stainless steel modified Van Veen grab. The sediment collected by the grab was sieved for bivalves through a 5-mm Nytex screen. Seawater for washing the sediment was obtained from a submersible pump (Rule 1500) fitted with Bev-a-line lined tubing. Bivalves were identified and individuals of the species of interest were pooled in clean polyethylene jars and stored over dry ice.

Infaunal bivalve sampling on the first field survey did not proceed as anticipated. It was proposed that 10 stations were to be sampled for infaunal bivalves and that one or two pooled samplers would be collected at each station. Historical information indicated that infaunal bivalve populations were patchy, but that adequate densities (20/grab) of target species could be encountered at selected stations. Actual infaunal populations at all stations (including sediment stations) were much lower than expected; the average density at stations sampled was 3-4 bivalves/0.1 m² grab. A larger, more efficient washing system is proposed for the next field survey in order to process biota grabs more quickly.

2.2.6.3 Epifaunal Bivalve Sampling. Epifaunal bivalves (Arctinula groenlandica) were collected with a miniature semi-balloon Gulf of Mexico shrimp trawl fitted with a 1-3 cm stretch mesh, uncreosoted net (Marinovich Co., Biloxi, Mississippi). The contents of the trawl were sieved through a 5-mm Nytex screen with uncontaminated sea water, and species of interest sorted and segregated in polyethylene jars and frozen over dry ice.

Due to extensive ice cover in all offshore areas the boat was unable to reach relatively deep water (>25 m) and travel in the habitat areas of Arctinula. The field team did travel in 18-20 m water at Station 5B to test the sampling methods but insufficient numbers of Arctinula were collected (4 individuals/5 min bottom contact time) and a successful sampling was not achieved.

2.2.6.4 Hydrographic Data. A Hydrolab series 4000 conductivity, temperature, dissolved oxygen meter was the primary instrument used in collection of hydrographic data. Discrete sea water samples were also collected with a Niskin bottle for the determination of salinity (Beckman salinometer, B N W) and dissolved oxygen (Winkler method, shorebased facility, Deedhorse, AK). Surface water temperatures were also taken with a bucket thermometer.

2.2.7 Sample Preservation and Transfer

All sediment and bivalve samples collected for chemical analysis were placed in either Teflon (sediment samples) or polyethylene (Bivalve samples) jars and immediately placed in coolers containing dry ice (-78°C). Teflon jars were prepared as described in Section 2.2.6.1. Polyethylene jars were prepared in the same manner but were not rinsed with methylene chloride. This method of sample preservation worked well for the field program as the coolers took little room and required no maintenance. Dry ice was routinely supplied by the Battelle Alaska office in Anchorage. For shipment to B N E M R L, samples were repacked with dry ice and first shipped to Anchorage, Alaska where they were repacked with dry ice and sent on a direct flight to Boston. Upon arrival at B N E M R L, samples were immediately transferred to a commercial freezer and maintained at -200 C.

2.3 Cruise Narrative and Sampling Limitation

Field sampling for the first year of the BS M P was initiated on Saturday, September 1, 1984, five days after contract award. A field team which included R .E. Ruff, field party chief, W .G. Steinhauer, and J.F. Campbell was mobilized from BN E M R L. During the period of August 27 to August 31 all of the necessary cruise gear and equipment was ordered, assembled, packaged, and rushed to Prudhoe Bay, Alaska, for loading aboard the N O A A research vessel. During this same period, the N O A A field staff including George Lapienne and Lt. Eric Gardiner were in Prudhoe Bay preparing the government-supplied boat and performing sea trials.

The first station sampled, 5D, just outside of the lee of West Dock, east of Stump Island, served as a shakedown cruise and enabled the scientific party to assess the applicability of proposed sampling procedures aboard the 11-m boat. Based on the experience of the first sampling station, the weighted sediment grab (908 kg of steel weight) was exchanged for the unweighted grab which was then used throughout the survey. In addition, a data station was fabricated to fit forward of the winch, a sieve frame was built to fit on the transom, and the grab stand modified to fit between the legs of the hydraulic U-lam e. Other than these minor modifications and changes the sampling equipment was used as planned for the remainder of the survey.

The major problem encountered in the shakedown cruise was the size and physical limitations of the 11-m research vessel. As a scientific platform, the deck space was adequate for all of the sampling operations. However, deck and cabin space were limited, and with five people aboard, the boat was quite cramped. Due to limited deck space, extra fuel could not be carried as anticipated. This had no effect on the 1984 field survey. However, longer excursions to the east and west are anticipated during ice-free conditions and fuel reserve may be limiting in future surveys. Also, because of limited deck space, the second grab sampler could not be carried on-board, but had to remain at the Nana Camp logistics center. Deck space for cold storage of food and samples was also limited and barely adequate for 5-day survey legs. Careful planning for the 1985 field survey should provide an additional 0.7 to 0.11 m³ of frozen storage space to allow for longer duration at sea.

Since sampling did not begin until September, the increasing presence of sea ice throughout the Study Area was the major factor in determining the eventual cruise trackline. Ice was very much in evidence in all but the shallowest stations. In general, a heavy band of polar pack ice completely prevented the vessel from reaching the furthest offshore stations (Stations 6E, 4D, and 3C). To the west across Harrison Bay this accumulation followed the 15-m contour and prevented sampling at the western-most stations. East of Prudhoe, it remained up against the barrier islands and impinged upon the coast at Brownlow Point, thereby preventing passage into Camden Bay and sampling at the eastern-most stations. At times, the ship was taken into the pack ice in order to reach a particular station location. Since the floes in the pack were constantly in motion relative to each other, care had to be taken in order to keep the vessel from being pinched or caught in the ice. This ice movement also meant that the leads that were followed into the pack were not necessarily still present to follow back toward open water. Therefore, the stations had to be completed early enough to allow sufficient daylight to locate alternate paths back out of the ice. Grease ice was actively forming around the ice floes and inside the barrier islands and, by 12 September, this new ice stretched completely across the lagoon between Flaxman Island and the mainland. The presence of numerous ice floes and newly-formed ice considerably slowed the cruise progress and made seeking shelter behind protective barrier islands a nightly necessity. The net result was that transit time took far longer than planned, slowing the progress of the survey.

Sampling proceeded essentially as projected in the Battelle field survey handbook. Inability to sample at some stations due either to ice conditions or mechanical problems was partially offset by sampling three additional stations not on the original sampling plan. Sediment samples could be quickly and efficiently collected with the Kynar-coated modified Van Veen grab. A total of 220 sediment samples were obtained from 27 stations occupied between the western part of Harrison Bay and Flaxman Island

to the east. The photographic documentation and the hydrographic measurements were easily accomplished at each of these stations. Bivalve molluscs were more difficult to locate, and occurred in very low abundances at most of the stations occupied. Concentrations of Astarte borealis were encountered at two of the mid-depth stations, and Cyrtodaria kurriana was found at the shallowest station in Gwydyr Bay. At stations containing a high sediment silt-clay content the flow rate of water available from the submersible pump proved to be inadequate for washing the large volumes of sediments necessary to obtain hundreds of bivalves. The abundant offshore scallop Arctinula groenlandica could not be obtained since the pack ice precluded reaching the deepest stations. However, one otter trawl sample was taken to demonstrate that no unforeseen problems might be encountered in deploying or retrieving the net.

Several mechanical problems related to the relative newness of the vessel and to the fact that the BSMP was essentially used as a shakedown cruise, had a direct bearing on the results obtained. The ship's alternator failed during the cruise leg into Harrison Bay. This problem essentially negated any options to occupy the offshore stations in the ice pack or to steam toward the western-most stations off Pitt Point. Since the ship was limited to battery power, the emphasis was placed on heading back toward Prudhoe Bay, and station occupation became secondary in importance. An additional full day of cruise time was lost while a replacement alternator was located and flown up from Fairbanks. During the cruise leg to the east, a faulty relay caused the low engine oil alarm to sound intermittently. This resulted in a reduction of cruising speed and frequent stops to check the engine oil level, and it contributed to the decision not to try to push through the ice pack and into Camden Bay. Other mechanical problems which interfered with the progress of the cruise included a sticking compass, limited range on the radar, malfunctioning panel instruments, and the lack of proper trim on the vessel which held the top speed down to only 8 kt. These and other mechanical and design problems were communicated to MMS with the request to have modifications made before the next field effort.

The Tracer Omega-2 navigation system, that was expected to be the main navigational aid for use during the cruise, was not available at the start-up date. Therefore, the on-board satellite navigation system was relied upon to determine the station locations.

In spite of all of the problems encountered, the first cruise of the BSMP should be rated as a success. The problems inherent with arctic research were addressed, on-board techniques and procedures were worked out, and valuable experience was obtained for planning the future field efforts. In addition, "a majority of the projected stations were occupied and the requisite samples obtained for laboratory analysis. The overall success of the field effort would not have been possible without the considerable efforts of George Lapierre in preparing and maintaining the NOAA vessel, and those of Eric Gardiner, the ship's skipper, and Steve Pace for assistance throughout the cruise.

3. ANALYTICAL METHODOLOGY

3.1 Detailed Analytical Rationale

The analytical strategy and specific analytical methodologies used in the BSMP were designed to meet the study objectives stated in Section 1.2. These objectives were to rigorously test the four null hypothesis, H_01 through H_{04} , through appropriate sampling, analytical and statistical designs. The philosophy of the analytical design was that it must result in a set of statistically rigorous measurements and not merely descriptive information.

The analytical plan for 1984 field samples is presented in Table 3.1 and 3.2. The laboratory analyses involved the determinations of hydrocarbons, trace metals, grain size and total organic carbon in sediments, and hydrocarbons and trace metals in bivalves. Frozen samples were returned to the laboratory and carefully split for the various analyses, thus creating "paired analysis" for all chemical parameters measured. Grain

Table 3.1 Analytical Plan for 1984 Sediment Sam ples.

No. of Stations	Number of Replicates	<u>Level 1</u>	<u>Level 2</u>	<u>Metals</u>	<u>Grain Size and TOC</u>
		UV/F	GC/FID (Saturates) GC/MS (Aromatics)		
27	6	162		162	162
20	1 (pooled)		2 0		
T	6		42		

Table 3.2 Analytical Plan for 1984 Bivalve Sam pies.

Station	Species	Number of Replicates	U V/F	G C-FID G C/US	Metals
6D	<u>Macoma</u>	2	2	2	3
	<u>Astarte</u>	4	4	4	
SF	<u>C yrtodaria</u>	5	5	1	5
	<u>C yrtodaria</u>	1 (pooled)			
3A	<u>Astarte</u>	5	5	5	5

size samples were "paired" in the sense that they were taken from the same grab sample, but they were not part of the same homogeneous sample split in the laboratory for chemical analysis.

3.1.1 Measured Parameters

3.1.1.1 Trace Metals. The seven elements determined in sediments and bivalves included Ba, Cr, V, Pb, Cu, Zn, and Cd which were measured by a combination of flame (FAA) and/or graphite furnace atomic absorption (ZGFAA), inductively-coupled plasma emission spectrophotometry (ICAP), and energy dispersive x-ray fluorescence (XRF) (Table 3.3). As a quality control check, some concentrations were determined by more than one method. In other instances when initial results consisted of "non-detectable" values, samples analyzed by one technique were reanalyzed using a more sensitive technique.

3.1.1.2 Hydrocarbons. A hierarchical analytical strategy was applied to the analyses of hydrocarbons in sediments and organics (Figure 3.1). The strategy consisted of screening large numbers of samples by UV/Fluorescence Spectroscopy (UV/F) followed by a more detailed component-specific analysis by gas chromatography flame ionization detection (GC-FID) and gas chromatography/mass spectrometry (GC/MS).

Under a given set of conditions the intensity of molecular fluorescence is linearly proportional to the concentration of the fluorescing material. However, the UV/F approach is limited by interference characteristic of impurities and solvent which become more significant as concentration is reduced. For the BSM P samples, UV/F was used as a first level method to screen for the presence of petrogenic residues and to determine the "semi-quantitative content" of aromatic compounds relative to a reference oil (Prudhoe Bay crude oil). The parameters measured by UV/F were fluorescence peaks at 312, 355, and 425 nm, corresponding to 2-, 3-, 4- and 5-ring aromatic hydrocarbons, respectively. Solvent and matrix interferences at 312 nm, and moderate amounts of the highly fluorescing perylene at 425 nm prevented useful and accurate quantitation at these wavelengths.

All sample replicates were analyzed by UV/F. At each station, the replicate extracts were pooled to yield a single sample for more detailed GC-FID and GC/MS analyses. At seven selected sediment stations and one selected bivalve station, all individual replicates were analyzed by GC-FID and GC/MS to obtain statistical variability information.

The GC-FID and GC/MS techniques revealed the composition of specific saturated and aromatic hydrocarbons isolated from the total extractable material by column chromatography. Results can be used to distinguish between petrogenic, marine, and terrestrial biogenic and other anthropogenic sources when compared to results of GC-FID and GC/MS of these source materials.

The analytical data outputs from GC-FID are listed in Table 3.4. The concentrations of n-alkanes and isoprenoids in sediments are reported on a dry weight basis and, in bivalves, on a wet weight basis. From these concentrations a series of key diagnostic parameters were calculated (Table 3.5). The absolute concentrations of individual alkanes and isoprenoid alkanes and/or the sum of alkanes will be used to test null hypothesis H_01 in subsequent years. The source ratios are useful in establishing the source of the observed hydrocarbon distribution, the contributions of biogenic hydrocarbons, and the degree to which petroleum hydrocarbons from exploration or production-related discharges have been detected in the samples (i.e., testing null hypothesis H_02).

Detailed analysis also included identification and quantification of polycyclic aromatic hydrocarbons (PAH) by computer-assisted fused silica capillary gas chromatography/mass spectrometry (GC/MS). The concentrations of a series of PAH from 2 to 5 rings including parent (unsubstituted) and alkylated compounds, (in particular, the substituted naphthalenes), phenanthrenes and dibenzothiophenes, served as useful source indicators. These source ratios have been shown to be important in distinguishing between different generic residues in other study regions, and were envisioned to be important in distinguishing between different generic PAH sources in the Beaufort Sea.

Table 3.3 Analytical Methods Used for the Analysis of Trace Metals in Marine Sediments and Bivalves.

Element	Analytical Method	
	Sediments	Bivalves
Ba	ICAP and XRF	ICAP
Cr	ZGFAA	ZGFAA
v	ZGFAA	ZGFAA
Pb	ZGFAA	ZGFAA
Cu	FAA or ZGFAA	FAA
Zn	FAA or ZGFAA	FAA
Cd	ZGFAA	ZGFAA

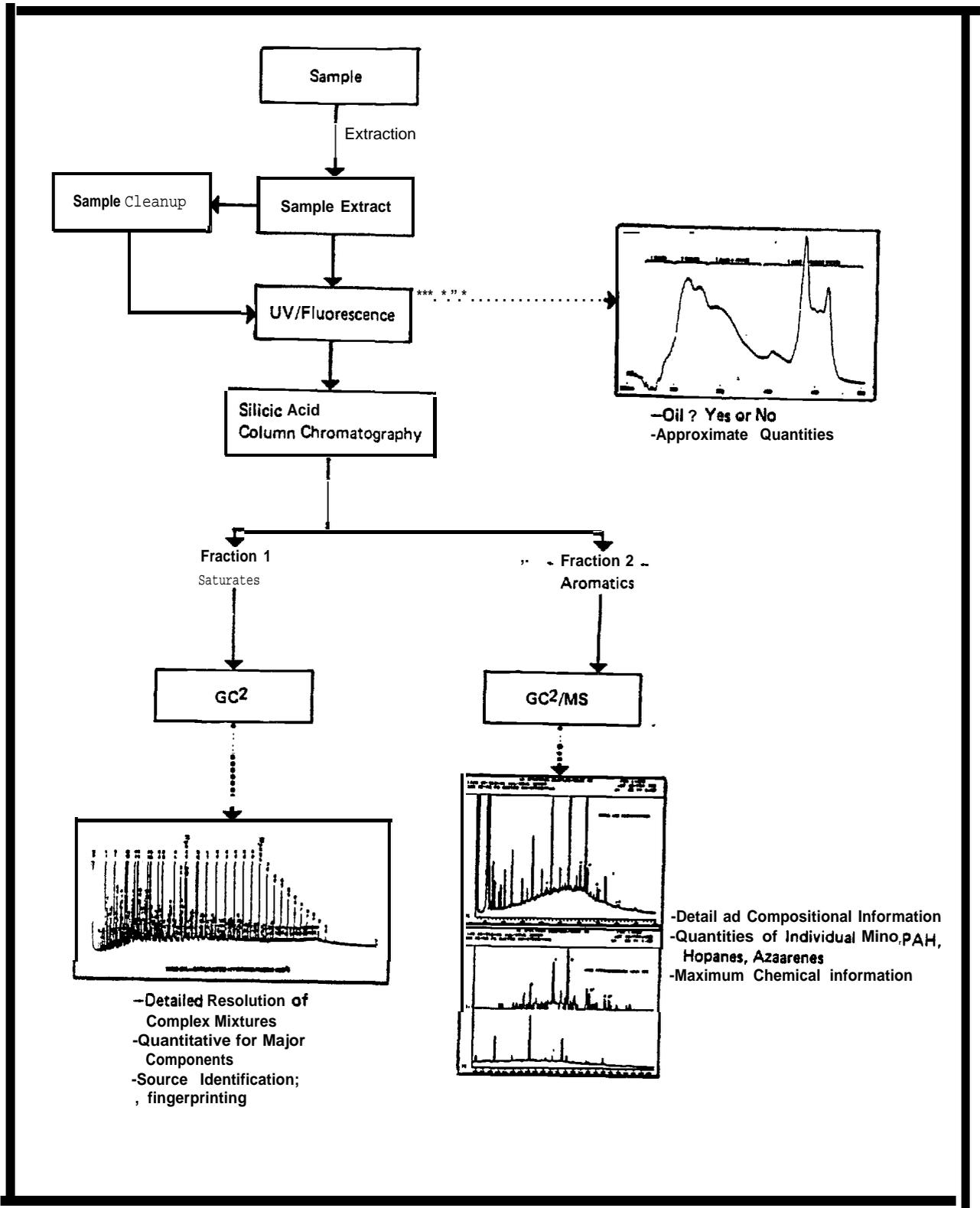


Figure 3.1 Analytical Scheme for Hydrocarbons in Sediments and Bivalve Tissues.

Table 3.4 Compounds Determined by Fused Silica Capillary Gas Chromatography.

Compound	Revelance
1. <u>Saturated Hydrocarbons</u>	
n-alkanes (<i>n-C10</i> to n-C 34)	W eathering and source indicators, especially when ratios are derived
Isoprenoids (1380,1470,1650,1708,1810) ^a	Weathering indicator (marker co m pounds as a group in lightly weathered sa m pies)
2. <u>Unresolved Complex Mixture</u>	Indicator of weathered petroleum although microbial activity can result in formation of these G C/FID unresolved co m pounds.

^a Where 1300 = retention index of n-C 13, 1400 = retention index of n-C 14, 1800=retention index of n-C 18.

Table 3.5 Key Diagnostic Parameters Determined by Fused Silica Capillary Gas Chromatography.

Variable	Abbreviation	Units
Sum of n-alkanes, C ₁₀ -C ₃₄	TALK	μg/g
Sum of n-alkanes, C ₁₀ -C ₂₀	LALK	μg/g
Sum of isoprenoids, 1380 + 1470 + 1650 + 1708+ 1810	ISO	μg/g
Sum of n-alkanes, C ₁₄ -C ₁₈	ALK	μg/g
Isoprenoid, 1708 (Pristane)	PRIS	μg/g
Isoprenoid, 1810 (Phytane)	PHY	μg/g
TALK/TOC ^a		μg/mg TOC
TALK/% SILT		
LALK/TALK		
ISO/ALK		

^a T O C = Total Organic Carbon

The aromatic compound pounds reported from the GC/MS analyses and used to test the four null hypotheses are listed in Table 3.6. Aromatic parameter ratios (e.g., Table 3.7), which are extremely useful for examining the nature of the observed aromatic compound position (testing of H_2 and H_0^4), were also computed.

3.1.1.3 Grain Size and TOC. In addition to the metal and hydrocarbon parameters measured, each sediment sample was also analyzed for sediment grain size and total organic carbon (TOC) content. The analysis of sediment samples for sand, silt and clay content was based on a rapid wet-sieving procedure. Further division of the silt and clay fractions into phi classes was accomplished by the pipet method (Plumb, 1981). TOC analysis was performed by high temperature combustion. TOC and grain size data are paired with metals and hydrocarbon data for inclusion in the geochemical data set.

3.1.2 Pooling Strategy and Selection of Samples

The statistical design of the analytical program called for the random selection of sediment replicates and the pooling of bivalve specimens to meet the study objectives. Frozen samples were returned to the laboratory and carefully split or composited for the various analyses (Tables 3.1 and 3.2), creating statistically paired analyses for parameters of interest.

3.1.2.1 Sediment Samples. Six of the eight sediment replicate samples collected at each of the 27 stations were selected at random for chemical analysis. Samples were thawed and carefully homogenized under controlled laboratory conditions. Jars containing thawed sediments were shaken by hand until overlying water was incorporated into sediment. Then, in a laminar flow hood, the jars were opened and the contents stirred until the sediment appeared well mixed. The homogenized sediment was split into subsamples for replicate analyses of metals, UV/F hydrocarbons and TOC, and for archival (for possible future analyses). Based on results of the UV/F analysis, seven stations were selected for complete hydrocarbon characterization by GC-FID and GC/MS. At the remaining 20 stations, one-half of each of the six replicate extracts were combined to create one pooled station extract. The remainder of each extract was archived.

The selection of stations for individual replicate hydrocarbon analysis was based on a requirement that broad areal coverage was desired and that, in general, the mean UV/F determined hydrocarbon concentration at these stations was similar. Additionally, replicates were chosen for individual analyses at a station with relatively high hydrocarbon concentrations and at a station with low concentrations.

3.1.2.2 Bivalve Samples. Bivalve specimens, from each station where sampling was successful, were pooled in the field to create one sample. Upon return to the laboratory, this pooled sample was partially thawed and split into subsamples for metals and hydrocarbon analyses. In general, five times as many individuals were reserved for hydrocarbon analysis as were needed for metals analysis (Figure 3.2). The subsamples were further split into random replicates for chemical analysis. For the extremely small Cyrtodaria species, individual organisms were pooled to create a tissue sample which was then split by weight. For the larger species, numbers of individual organisms were recorded along with wet weight in each pooled sample. Subsampling for metals analysis was performed under a laminar flow hood at Battelle-Northwest Marine Research Laboratory (BNW). Subsampling for analysis of hydrocarbons was performed at Battelle-New England Marine Research Laboratory (BNEML).

Thirteen individual replicate samples, including poolings of Astarte and Cyrtodaria, were analyzed for the suite of metals (Table 3.2). Sixteen replicate samples, including the species Astarte, Cyrtodaria, and Macoma, were analyzed for hydrocarbons by UV/F. One set of replicates was pooled for detailed GC-FID and GC/MS analysis (Table 3.2).

Table 3.6 Aromatic Hydrocarbons and Heterocyclics Quantified Using High Resolution Capillary Gas Chromatography/Mass Spectrometry.

m/e ION SEARCH	COMMON IDENTIFICATION AND ABBREVIATION
128	Naphthalene (CON)
142	Methyl Naphthalenes (C ₁ N)
156	C ₂ Naphthalenes (C ₂ N)
170	C ₃ Naphthalenes (C ₃ N)
184	C ₄ Naphthalenes (C ₄ N)
152	Acenaphthene (ACE)
154	Biphenyl (BPHN)
166	Fluorene (FLOR)
180	Methyl Fluorenes (C ₁ F)
194	C ₂ Fluorenes (C ₂ F)
208	C ₃ Fluorenes (C ₃ F)
178	Phenanthrene, Anthracene (PHEN)
192	Methyl Phenanthrenes, Anthracenes (C ₁ P)
206	C ₂ Phenanthrenes, Anthracenes (C ₂ P)
220	C ₃ Phenanthrenes (C ₃ P)
234	C ₄ Phenanthrenes (C ₄ P)
202	Fluoranthene, Pyrene (FLAN, PYRN)
216	Methyl Fluoranthene or Methyl Pyrene (C ₁ PYR)
228	Chrysene, Benzo(a)anthracene (CHRY, BAA)
242	Methyl Chrysene (C ₁ C)
256	C ₂ Chrysenes (C ₂ C)
252	Benzo(a)pyrene, Benzo(e)pyrene, Benzofluoranthene, Perylene (BAP, BEP, BFA, PERY)
184	Dibenzothiophene (DBT)
198	Methyl Dibenzothiophenes (C ₁ DBT)
212	C ₂ Dibenzothiophenes (C ₂ DBT)
226	C ₃ Dibenzothiophenes (C ₃ DBT)

Table 3.7 Key Diagnostic Parameters Determined by GC/MS and Used for Statistical Analysis.

Variable	Definition of Abbreviation	Units
Naphthalene series (C ₀ N + C ₁ N + C ₂ N + C ₃ N + C ₄ N)	N	μg/g
Fluorene series (F ₀ R + C ₁ F + C ₂ F + C ₃ F)	F	μg/g
Phenanthrene series (P ₀ HEN + C ₁ P + C ₂ P + C ₃ P + C ₄ P)	P	μg/g
Dibenzothiophene series (D ₀ BT + C ₁ DBT + C ₂ DBT + C ₃ DBT)	D	μg/g
4- and 5-ringed Polynuclear Aromatic Hydrocarbons (F ₁ LAN + PYEN + BAA + CHRY + BFA + BAP + BEP + PERY)	4-, 5-PAH	μg/g
(N + F + P + D) / (N + F + P + D + 4-, 5-PAH)	FFPI	
(N + F + P + D) / TOC	A1TOC	μg/mg TOC
(N + F + P + D + 4-, 5-PAH) / TOC	ATTOC	μg/mg TOC
(N + F + P + D) / % SILT	ALSILT	
(N + F + P + D + 4-, 5-PAH) / % SILT	ATSILT	
(N + F + P + D) / % CLAY	Al CLAY	
(N + F + P + D + 4-, 5-PAH) / % CLAY	AT CLAY	

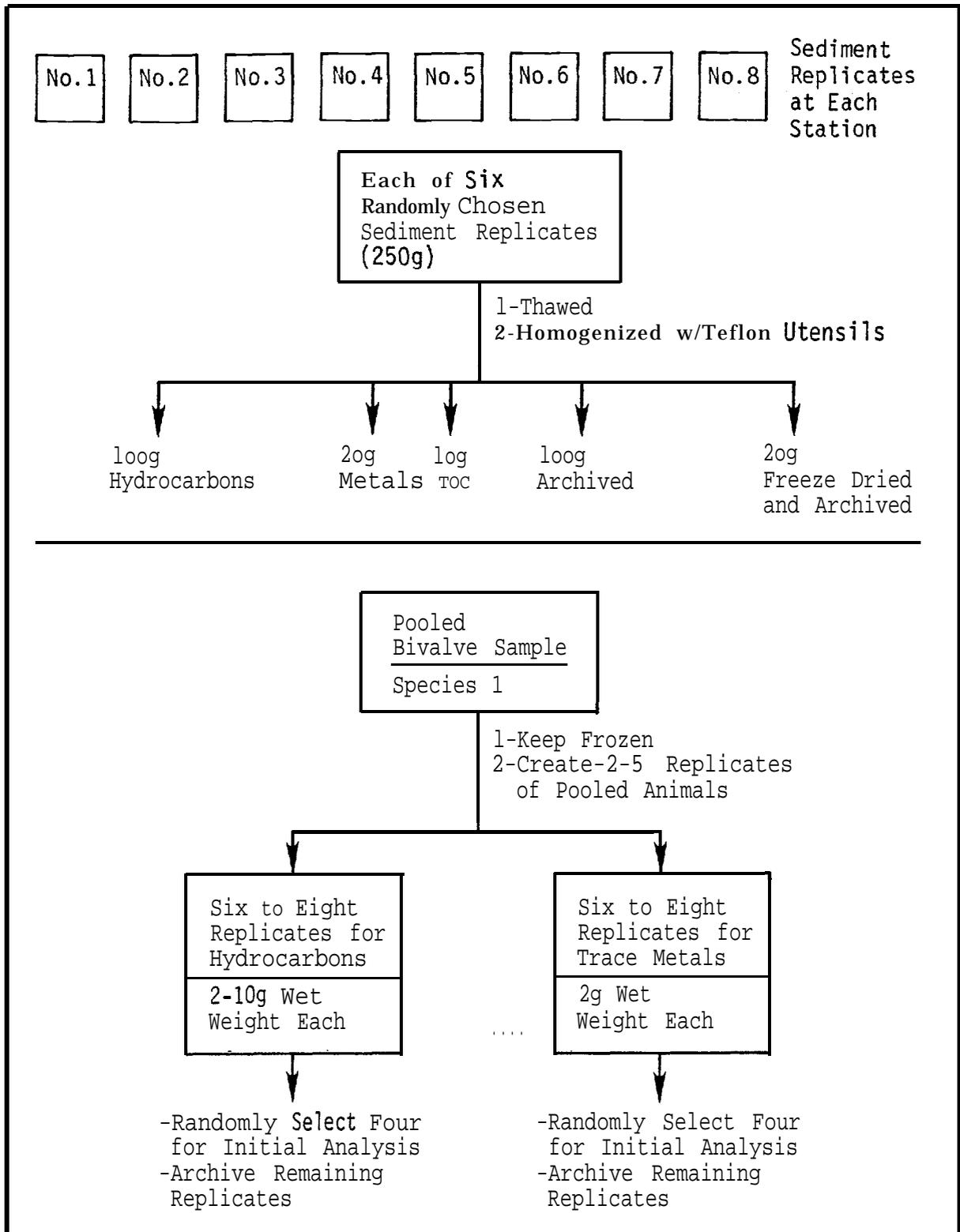


Figure 3.2 Laboratory Sample Splitting Procedure.

3.2 Analytical Chemistry of Metals

3.2.1 Methods and Materials

The analyses for trace metals in both marine sediments and bivalve tissues were carried out by the BN W. Concentrations were determined for the following elements: Ba, Cd, Cr, Cu, Pb, V, and Zn. The various procedures employed in each of the analyses are summarized in Table 3.8 and detailed below.

Aliquots of sediment were received frozen and stored at -20°C until freeze dried to constant weight in a Virtis freeze-dryer. The dry sediment was ground in a Spex ceramic ball mill. Sediments which contained gravel were sieved through a 2-mm nylon screen to remove gravel before grinding.

Two digestion procedures were used to totally dissolve sediment. Sediments were prepared for analysis by IC A P (Applied Research Laboratory Model 3560) by digesting 0.25 g of dry ground sediment in a Teflon vial with 2 ml of aqua regia and 6 ml of hydrofluoric acid. The vial was sealed with a screw cap and heated for 2 hrs on a hot plate at $80-90^{\circ}\text{C}$. After cooling, the contents were transferred to polystyrene containers, 3 g of ultra-pure boric acid added, and diluted to 50 ml with double deionized water.

For Z G F A A Perkin Elmer Model 5000 analysis, sediments were digested by adding 7 ml of hydrochloric acid to 0.1 g of sediment in a 15-ml Teflon vial. The vial was sealed and heated in an $80-90^{\circ}\text{C}$ water bath for 1 hr. After cooling, 3 ml of nitric acid was added and the heating procedure repeated. After cooling, 0.5 ml hydrofluoric acid was added, the vial sealed and heated again for 1 hr. at $80-90^{\circ}\text{C}$. After cooling, the digestate was transferred to a polystyrene container and diluted to 50 ml with double deionized water.

Bivalves were received frozen and stored at -20°C until thawed for dissection. The bivalves were cleaned of foreign matter using Teflon forceps followed by rinsing in double deionized water. For each tissue sample, 5-10 individual bivalves of the same species were removed from their shells using Teflon forceps and a titanium knife. The pooled tissue was placed in an acid-cleaned, pre weighed plastic jar, the wet weight recorded, and the tissue freeze dried, to constant weight. After recording the tissue dry weight, the dry tissue was ground to powder in an all-plastic Spec 8000 ball mill.

Two digestion procedures were used to totally dissolve tissue. Tissues were prepared for Z G F A A analysis by digesting a mixture of 0.25 g dry tissue and 5 ml nitric acid in a Teflon screw top vial. The contents of the vial were digested (unsealed) for 8 hr. at 130°C . After cooling, 1 ml hydrofluoric acid was added, cap sealed and heated for 2 hr, and the solution evaporated to near dryness. The sample was further diluted to 25 ml with double deionized water and acidified with 25 μl of nitric acid.

For IC A P analysis, tissue was digested by adding 5 ml of reagent grade nitric acid to 0.25 g tissue and heating 8 hr at 130°C , followed by overnight heating at 800°C in a loosely capped Teflon vial. After cooling, 1 ml hydrofluoric acid was added and the sealed vial heated for 2 hr at $80-90^{\circ}\text{C}$. The sample was again cooled, transferred to a polyethylene bottle and diluted to 25 ml with double deionized water.

Approximately 10% of the sediments was analyzed for Ba by X R F to verify the data obtained by the IC A P method. In addition, some sediment samples were also analyzed for Cu, Pb, and Zn by X R F. Sediments were prepared for X R F by pressing 0.5 g of powdered sample into a 25-mm diameter pellet. A gadolinium secondary target was used for excitation of Ba and a zirconium secondary target was used for Cu, Pb, and Zn. The analysis was performed on a Kevex spectrometer and the data reduced methods described by Nielson (1977).

3.2.2 Quality Control Methods

The QC activities involved with the analyses of sediment and bivalve tissue included the following procedures:

Prior to analysis of environmental samples, lab ware and reagent blanks were analyzed in triplicate for each lot to determine that blanks were acceptable.

Table 3.8 Summary of Analytical Conditions for Metals in sediments and Tissues

Element	Instrument	Instrument Condition	ppm (dry weight)	
			Detection Limit	Procedural Blank
<u>Sediment</u>				
Ba	ICAP	493.41 nm 1st order (Forward Power) FP 2.3 Kw observation height 20 mm nebulizer flow 2.5 l/min	0.4	1.8
Ba	XRF	Tungsten tube 70 Kv, 20 ma gadolinium secondary source counting time 3000 sec	50	0
Cd	ZGFAA	Pyrolytic tube NH ₄ H ₂ PO ₄ matrix 10 g/l 228.8 nm, slit 0.7 nm hollow cathode lamp 4 ma gas 50 l/min 80 & 140°C dry 250 & 500°C ash 15000 atomization 26000 clean	0.04	0.1
Cr	ICAP	266.72 3rd order FP 1.2 Kw observation height 20 mm nebulizer flow 2.5 ml/min	1.2	9.1
Cu	ICAP	324.75 2nd order FP 1.2 Kw Observation height 20 mm Nebulizer flow 2.5 ml/min	0.9	0.9
Cu	XRF	Tungsten tube 40 Kv, 20 ma zirconium secondary source counting time 3000 sec	0.5	0
Pb	XRF	Tungsten tube 40 Kv, 20 ma zirconium secondary source counting time 3000 sec	0.5	0
Pb	ZGFAA	Pyrolytic tube NH ₄ H ₂ PO ₄ matrix 10 g/l 283.3 nm, slit 0.7 nm electrodeless discharge lamp 10 W gas 50 ml/min 80 and 140°C dry 250 and 800°C ash 2100°C atomization 26000 clean	0.3	1.5
V	ICAP	292.40 2nd order FP 1.2 Kw observation height 20 mm nebulizer flow 2.5 ml/min	0.4	1.4
Zn	ICAP	213.86 3rd order FP 1.2 Kw observation height 20 mm nebulizer flow 2.5 l/min	6.0	u.8
Zn	XRF	Tungsten tube 40 Kv, 20 ma zirconium secondary source counting time 3000 sec	0.5	0
<u>Tissue</u>				
Ba	ICAP	Same as for sediment	0.01	0.04
Cu	ICAP	Same as for sediment	0.5	0.5
V	ICAP	Same as for sediment	1.2	1.1
Zn	ICAP	Same as for sediment	0.1	1.0
Cd	ZGFAA	Same as for sediment except gas flow 200 ml/min 250 and 600°C ash	0.04	0.06
Cr	ZGFAA	Pyrolytic tube 357.9 nm, slit 0.7 nm hollow cathode lamp 25 ma gas flow zero 80 and 140°C dry 250 and 1300°C ash 2300°C atomization 26000°C clean	0.04	0.7
Pb	ZGFAA	Same as for sediment except gas flow zero 250 and 750°C ash 2000°C atomization	0.06	0.5

Procedural blanks were run through the entire analytical process to recognize any unusual contamination, to establish a blank value to be subtracted from sample results, and to determine detection limits. Five procedural blanks were run with every batch of samples.

The detection limit for each element in both sediment and tissue was defined as two times the standard deviation of the background signal for the procedural blanks.

Standard reference materials (sediment MESS-1 and oyster tissue NBS-SRM 1566) were analyzed along with each batch of samples to verify accuracy and precision of the analytical results. At least one SRM was analyzed for every 20 samples.

The precision of each analytical instrument for each metal was determined by analysis of five replicates of a certified homogeneous SRM sediment and bivalve tissue. Field samples and SRMs were analyzed for Ba, Cu, Pb, and Zn by two different techniques to verify that the sediment digestion procedures totally dissolved the sediments. The XRF technique determined total metals without sediment digestion.

The method of standard additions was used to evaluate matrix effects for both ICAP and ZGFAA. Ammonium phosphate was used as a matrix modifier in the ZGFAA analysis of Cd and Pb to improve the analytical signal and precision. The Zeeman effect background correction system was used for all ZGFAA analyses.

3.3 Analytical Chemistry of Hydrocarbons

The general analytical strategy for the chemical assessment consisted of two levels (Figure 3.1). On the first level, sample replicates were extracted and analyzed by UV/F to measure approximate concentrations of petroleum. Sample replicates of additional interest were carried through individually to the second level, which consisted of GC-FID and computer-assisted GC/MS.

Sediments and tissues were each analyzed by slightly different analysis schemes. Each sample type required a unique initial processing/sample extraction protocol and followed its own analytical scheme. All samples were spiked with internal standards, androstane or cholestane (saturated hydrocarbons), and o-terphenyl (aromatic hydrocarbons), prior to solvent extraction.

3.3.1 Sample Processing

3.3.1.1 Sediment Sample Processing. Six surface sediment sample replicates from each station were analyzed for high molecular weight hydrocarbons using UV/F. One hundred-fifty gram subsamples of 150 g were analyzed by UV/F using the analytical method described below. Selected individual samples from seven stations as well as all pooled extracts were analyzed by GC-FID and GC/MS.

The extraction methods for the UV/F, GC-FID and GC/MS analysis of sediment samples were based on methods of Brown et al. (1979) and Boehm et al. (1982 e). Approximately 150 g of wet sediment was weighed into a 250-ml Teflon jar and dried by extracting three times with 50 ml of methanol. Five micrograms of two internal standards, androstane and o-terphenyl were added to the sediment. The dry sediment was then extracted three times with 100 ml of dichloroethane:methanol (9:1) by shaking on a platform shaker for a minimum of 4 hr for each extraction. All solvent extracts were transferred into a 1-L separator funnel containing 100 ml of water (Millipore RO) to which 10 g sodium chloride had been added. The dichloroethane layer was drawn off and the aqueous methanol phase extracted three times with 50 ml of dichloroethane. The combined dichloroethane extracts from each sample were dried, combined, reduced in volume to 1 ml by rotary evaporation and displaced with hexane. Single aliquots of extracts for subsequent analysis by GC-FID and GC/MS were weighed on a Cahn Model 25 electrobalance to determine total extractable organics. The extracts were fractionated by silica gel/alumina column chromatography into saturated and unsaturated/aromatic fractions which were analyzed by GC-FID and GC/MS, respectively.

Column chromatography was performed using a 100% activated silica/5% deactivated alumina/activated copper (1 g, 1g, 2g, respectively) 1-cm i.d.

chromatography column that was wet-packed in methylene chloride and prepared by eluting with 30 ml each dichloromethane and hexane. The sample, of no more than 50 mg extract weight in 0.5 ml hexane, was charged to the column which was then eluted with 18 ml hexane followed by 21 ml hexane:dichloromethane (1:1) to isolate the saturated (f₁) and unsaturated/aromatic (f₂) hydrocarbons, respectively.

3.3.1.2 Bivalve Tissue Samples. Five samples consisting of three species of benthic bivalves (*Cyrtodaria kurriana*, *Macoma calcaria* and *Astarte borealis*) were analyzed. All individual replicates were analyzed by U V/F. Subsequently, either individual or pooled extracts were analyzed by GC-FID and GC/MS.

Samples of 2-10 g wet weight tissue (approximate wet weights of individual bivalves; 0.25 g/*Cyrtodaria*, 2.5 g/*Astarte*, 3.0 g/*Macoma*) were extracted and analyzed by the procedure of Boehm et al. (1982d). Clam tissues (guts, muscle, gills) were removed from the shells with solvent-rinsed utensils. Wet tissue was digested overnight with a 5 N aqueous potassium hydroxide. The digestate was neutralized with hydrochloric acid and extracted in a separator funnel three times with hexane. Hexane extracts were combined, dried with sodium sulfate and concentrated to 0.5 ml by rotary evaporation. Polar and biogenic compounds which interfered with the U V/F analysis were removed from the extracts by alumina column chromatography which contained 6.5 g of 7.5% water-deactivated alumina. The column was eluted with 25 ml of hexane/dichloromethane (9:1) to isolate the saturated, unsaturated and aromatic compounds. The fraction was concentrated and transferred into hexane for U V/F analysis.

After U V/F analysis, the individual or pooled extracts were concentrated by rotary evaporation and displaced with hexane. The total extracts were then analyzed by GC-FID and GC/MS directly. Due to the low lipid weight of the total extracts, column chromatography was not required prior to GC-FID or GC/MS analysis.

3.3.2 Sample Analysis

3.3.2.1 U V/F Analysis. The technique of synchronously scanning the corrected excitation and emission monochrometers of a scanning spectrofluorometer was based on the methods of Wakeham (1977), Gordon et al. (1976), John and Soutar (1976), Boehm et al. (1982f), and Boehm and Fiest (1982). This method was used to analyze all sediment and bivalve extracts, and to determine the presence and semi-quantitative amounts of aromatic hydrocarbons in all samples.

The sample extract (or a dilution thereof) was dissolved in hexane and analyzed by U V/F. The intensity of the fluorescence emission was measured from 250 to 500 nm while synchronously scanning the excitation monochrometer at a wavelength 25 nm shorter than the wavelength of the emission monochrometer. This technique measured 2- to 5-membered aromatic hydrocarbons (Lloyd, 1971) and yielded the spectral detail needed for this study.

The intensities of the fluorescence spectra were measured at several wavelengths (e.g., 312, 355 and 425 nm) which correspond to approximate peak maxima of the 2-, 3-, and 4- plus 5-membered aromatics present in the samples and those present in the Prudhoe Bay crude oil reference standard characterized in this study. Calibration curves, based on the analysis of a Prudhoe Bay crude oil standard, were used to quantify sample extracts in this study. One or several dilution series of the hexane solutions of the oil were used to quantify sample extracts and to calibrate the method daily. The resulting U V/F data is presented in $\mu\text{g/g}$ Prudhoe Bay crude oil equivalents.

3.3.2.2 GC-FID. GC-FID analysis served to identify and quantify the saturated petroleum hydrocarbon compounds present in the sample. The concentrations of certain compounds were also used to calculate indicator ratios that reveal the type of hydrocarbons present, i.e., biogenic or petroleum.

Each fraction was analyzed by fused silica capillary gas chromatography on a Shimadzu GC-9A gas chromatograph equipped with a splitless injection port, a flame ionization detector, and a Shimadzu C-R 3A data system. Wall-coated open tubular (WCOT) fused silica columns (0.25 mm x 30 m, J&W Scientific) coated with SE30 or bonded DB-1 stationary phases were used to analyze the saturated hydrocarbon fractions

from the column chromatography procedure. The instrumental conditions are listed in Table 3.9. Concentrations were calculated by the internal standard method on the Shimadzu C-R3A. The computerized data system automatically identified compounds by comparing retention indices of peaks in the samples to retention indices of known compounds in a standard mixture that was analyzed daily. Concentrations were calculated by comparing the integrated areas of peaks with the area of the appropriate internal standard (androstane or cholestane) and applying a determined response factor. The total concentrations of saturated hydrocarbons were determined by integrating the unresolved area (UCM) on the C-R 3A and adding it to the total resolved integrated area (i.e., peaks) and, calculating a concentration using the internal standard method.

The concentrations of n-alkanes and isoprenoids in sediments were determined from GC-FID on a dry weight basis and on a wet weight basis for bivalves.

3.3.2.3 GC/MS. The aromatic hydrocarbon fractions of the adsorption column of either individual sample replicate or pooled extracts were analyzed by GC/MS to measure the concentration and column position of the aromatic hydrocarbons in the samples.

An aliquot of the aromatic fraction was analyzed using a Finnigan 4530 GC/MS instrument equipped with a 0.25 mm id. x 30 m DB-5 fused silica capillary column (J&W Scientific) which was threaded directly into the ion source. Instrumental conditions are listed in Table 3.10.

Selected ion searches were used to obtain ion chromatograms for aromatic compounds with known retention indices. Concentrations of the identified compounds were determined by measuring peak areas (ion currents) of the appropriate peaks in the selected ion chromatograms and relating them to that of the internal standard. Relative response factors for each component were calculated from analyses of analytical standards, if available, or were extrapolated. The compounds reported from the GC/MS analyses are listed in Table 3.6.

3.3.3 Quality Control Methods

The quality assurance program in the geochemistry laboratory was part of the formal laboratory-wide quality assurance program instituted at B N E M R L. The requirement of this program consisted of an initial demonstration of laboratory capability and analysis of spiked samples as an on-going check on performance. Specific measures taken before the initiation of study and during the course of this study included a rigorous on-the-job training program including analysis of triplicate samples and blanks, adherence to strict sample transfer and custody procedures, laboratory notebook audits, documented calibration of UV/F, GC-FID and GC/MS on a daily basis, and an on-going analytical QC program.

The on-going analytical QC program consisted of the analysis of procedural blank samples with every batch of sediment or tissue analyzed, analysis of blank spikes for the determination of recoveries of selected compounds, re-extraction of samples to monitor efficiency of extraction, and the analysis of reference samples for an additional check on precision and accuracy.

Discussion of the results of the analytical QC program are presented in Section 4.6.

3.4 Auxiliary Parameters

3.4.1 Hydrography

Hydrographic data included of temperature, salinity, and dissolved oxygen measurements taken at the 27 stations sampled for sediments or bivalves. When possible these measurements were recorded at three depths in the water column, although at some extremely shallow stations only surface and bottom measurements could be recorded. Failure of the dissolved oxygen probe and lack of storage or work space on the boat for

Table 3.9 Fused Silica Capillary Gas Chromatography/Flame Ionization Detection Analytical. Conditions.

Instrument:	Shim adzu G C-9A gas chro m atograph Shim adzu C-R 3A <i>integrator/data</i> processor
Features:	Split/splitless capillary inlet system Microprocessor-controlled functions Auto m atic data reduction/Floppy Disk data storage
Inlet:	Splitless
Detector:	Flame ionization
Column:	
f ϕ :	0.25 mm I. D. x30 m SE 30 fused silica (J&W Scientific) DB1 fused silica (J& W Scientific)
Gases:	
Carrier:	Helium 2 ml/min
Make-up:	Helium 30 ml/min
Detector:	Air 300 ml/min Hydrogen 30 ml/min
Temperatures:	
Injection port:	250° C
Detector:	300° c
C olu m n oven:	40°-290° 30 C/min
D aily calibration:	Alkane/mixture
Quantification:	Internal standard (F ϕ androstane; cholestane)

Table 3.10 Gas Chromatography/Mass Spectrometry Instrumental Conditions.

INSTRUMENT:	Finnegan 4530 gas chromatograph/mass spectrometer
FEATURES:	Data General Nova 4 data system with Inco data system Finnegan MAT 9610
INLET:	Splitless
DETECTOR:	Quadrupole mass spectrometer
SCAN RATE:	450 amu/sec (45-450 amu)
IONIZATION VOLTAGE:	70 eV
COLUMN:	0.25 mm i.d. x 30 m SE54 fused silica (J&W Scientific)
INTERFACE:	Direct insertion of column into source
CARRIER GAS:	Helium 2 ml/min
TEMPERATURES:	
INJECTION PORT:	270° C
SEPARATOR OVEN:	280° C
SOURCE:	250° C
GC OVEN:	40-290° C, 10° C/rein (temperature program)
DAILY CALIBRATION:	FC43, DFTPP and aromatic mixture
QUANTIFICATION:	Internal standard (o-terphenyl) (response factors)

Winkler titrations apparatus limited the number of dissolved oxygen measurements performed on the survey. The hydrographic data was collected in support of the analytical program and was not used to characterize water masses.

Primary hydrographic measurements were taken with a Hydrolab Series 4041 in-situ instrument with digital read-out. The Hydrolab consists of a probe (Sonde) attached to an electronics module by an electro-mechanical cable. The probe contains sensors of temperature, conductivity and dissolved oxygen. The precision of the instrument is listed below by parameter:

<u>Parameter</u>	<u>Precision</u>
Temperature	+ 0.05°C
Salinity	+ 0.050/00
Dissolved Oxygen	+ 0.05 ppm

Calibration of the temperature probe at each station was performed with a bucket thermometer using a thermometer complying with all requirements of the National Bureau of Standards. The conductivity probe was calibrated at each station with a secondary sea water standard of known salinity. A analysis of the secondary standard was performed on a Beckman salinometer both before and after the cruise. The dissolved oxygen probe was calibrated at each station using a wet air calibration that relies on the known solubility of oxygen in distilled water at any given temperature. Discrete water samples were also collected by Niskin bottle and preserved for oxygen analysis by the Winkler method. This analysis was originally intended to provide a quality control check on the dissolved oxygen probe, but became the primary measurement after the failure of the probe. Due to lack of storage/work space these analyses were performed at the shore base.

3.4.2 Sediment Grain Size

The analysis of sediment samples for sand, silt and clay content was based on a sieve-pipet procedure. Division of the sand fraction into phi classes was accomplished by graded sieving of the dried sand material (Holme and McIntyre, 1971). Division of silt and clay into phi classes was based on the pipet method (Fork, 1974).

A subsample of approximately 25 g of homogenized sediment was dried to a constant weight at 100°C cooled in a desiccator, and weighed to within 0.01 mg on a Mettler analytical balance. The oven-dried material was added to a dispersant solution of aqueous sodium metaphosphate (5.0 g/L), stirred with a glass rod, and agitated for 10-15 min on a Junior Orbit Shaker. The solution was allowed to stand overnight then shaken for 10 min. The sediment suspension was poured into a 0.063 mm sieve and the sieve gently agitated in a basin of water. The silt and clay fractions (particles of less than 0.063 mm) which passed through the screen, were resuspended in 1 L of dispersing solution in a graduated cylinder. At specific time intervals, 25, ml aliquots were removed, dried at 105°C for 24 hr, cooled to room temperature and weighed to the nearest 0.1 g.

The sand fraction retained on the sieve was rinsed into an aluminum weighing pan and dried to constant weight. To divide the sand component into phi intervals, the dried sand material was placed in a graduated series of nested sieves (2.0 mm, 1.0 mm, 0.5 mm, 0.25 mm, 0.125 mm, and 0.063 mm screen sizes) and shaken for 10 min on a Ro-Tap Testing Sieve Shaker.

For the purposes of data reporting, the phi classes were recorded separately but were also combined to generate sand, silt and clay sediment size classes for data interpretation.

3.4.3 Total Organic Carbon

T O C analyses were determined using a Leco model W R-12 carbon analyzer. The dried sample was homogenized and a 150 - 250 mg aliquot placed in a ceramic crucible. The sample was washed twice with 6 N H Cl to remove carbonate carbon. If reaction was vigorous on the second wash a third treatment with H Cl was conducted. Following decarbonation, the sample was rinsed with distilled water until neutral and dried at 450C. Copper and zinc accelerators were added to the sample crucibles and combusted with an induction furnace. The C O₂ evolved was scrubbed of water, halide and sulfur, and the percent T O C calculated. The carbon analyzer was calibrated daily with series of known calibration standards to provide a calibration curve covering the range of interest.

4. PRESENTATION OF RESULTS

4.1 Introduction

This section presents the data generated from the 1984 B S M P survey. These data include results of the laboratory analyses for metals and hydrocarbons, auxiliary parameters (grain size and total organic carbon), the hydrographic data collected on-site, and the quality control results.

Because of the large volume of data derived from the survey, each data set is discussed in a separate subsection. This tabular presentation of the analytical results is limited to those parameters most relevant to the interpretation and synthesis with historical data. A complete listing of each data set is stored in our database management system to be transmitted to The National Oceanic Data Center (N O D C).

All results are presented in tabular form, arranged by separate geographical groupings of stations from east to west within the Study Area, and accompanied by a station location map.

4.2 Metals Data

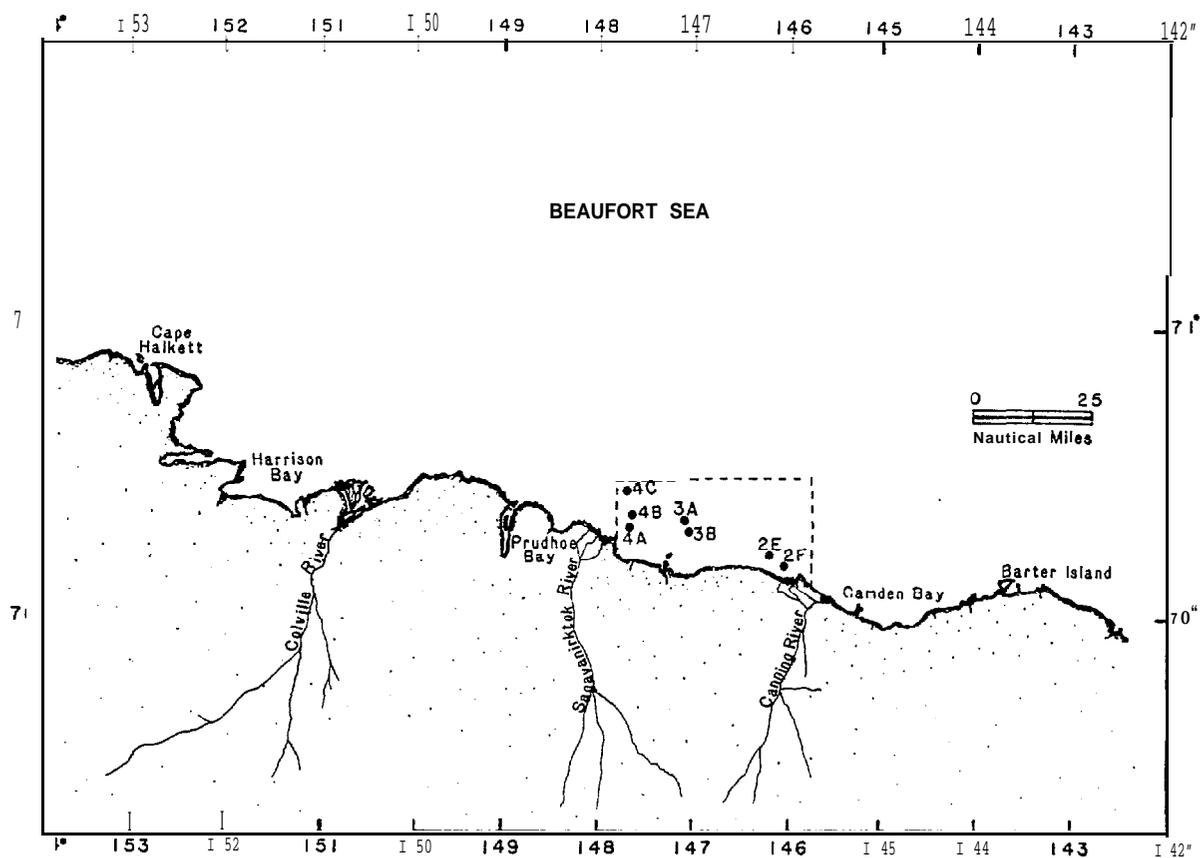
Data for metals in sediments were collected at each of the 27 stations. Since six replicate samples were analyzed at each station, the concentrations are reported as a mean + one standard deviation for each of the seven metals. Values for the silt and clay fractions, as well as total organic carbon, are included for each station for reference.

With the exception of Ba and Cr, which ranged from 186 to 745 $\mu\text{g/g}$ and 17 to 91 $\mu\text{g/g}$ in sediment% respectively, the range for all other metal concentrations in sediments encompasses two orders of magnitude. The highest levels of all metals occur at Station 6B, while the 10 west sediment metal concentrations are associated with Station 5B. Similarly, combined silt and clay fractions are highest at Station 6B and 10 west at 5B.

4.2.1. Metals in Sediments

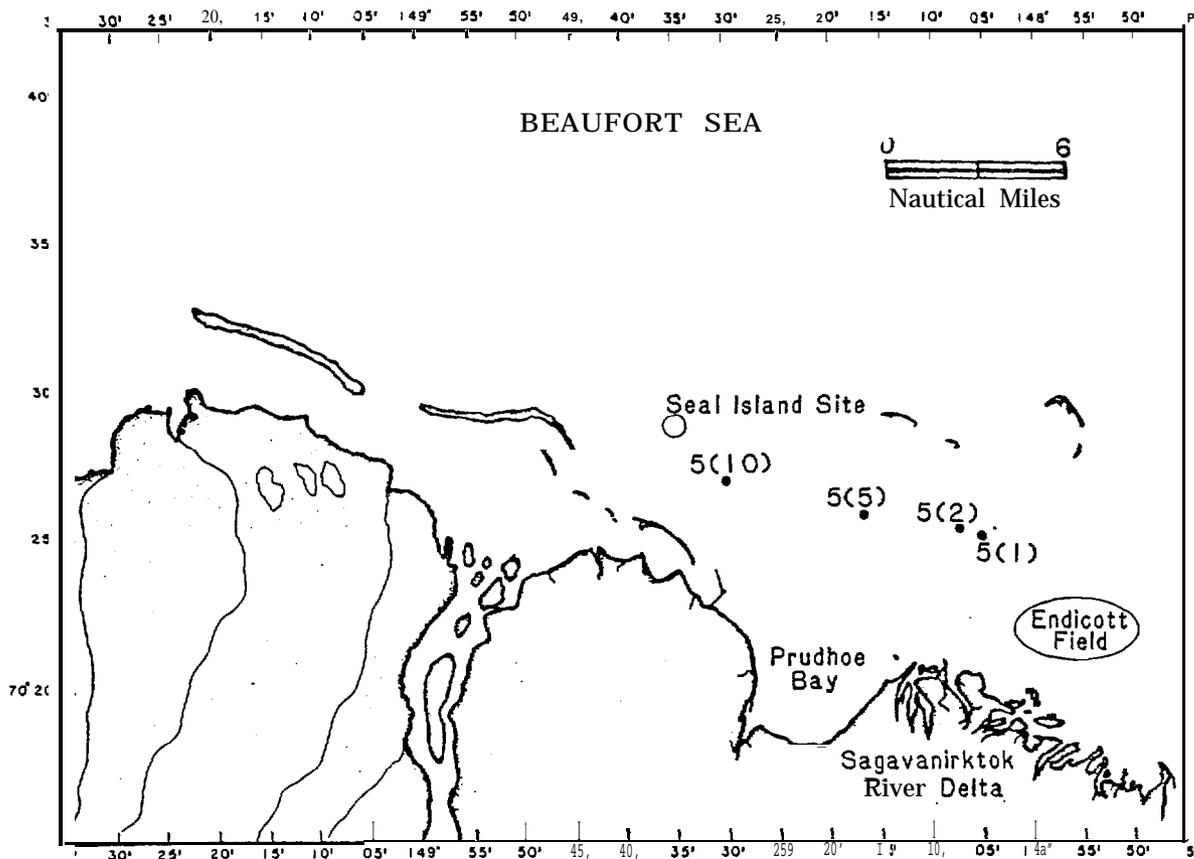
Figure 4.1 presents the data for stations in the eastern section of the Study Area, which includes the Carming River Delta (the "2" stations), the Mikelson Bay - Stockton Island area (the "3" stations), and the Foggy Island Bay transect (the "4" stations). Except for Cd and Pb, the sediments of Station 3B show the highest overall concentrations of metals in this area, followed by Stations 4A and 3A. Silt and clay fraction values exhibit a similar trend. Low est overall metal concentrations in this area are associated with Station 2E sediments.

The Prudhoe Bay-Gw ydyr Bay region in the central part of the Study Area includes the "5" stations and is divided into two station groupings. Figure 4.2 presents data for the Endicott Field transect stations, selected to represent 1-, 2-, 5- and 10- mile locations from the Endicott Field (i.e., the activity-specific gradient). The concentrations of metals do not follow a gradient away from the Endicott Field area but, rather, may be a function of the sediment grain size at individual stations. Stations 5(5) and 5(10)



	STATION						
	4A	4B	4C	3A	3B	2E	2F
METALS ($\mu\text{g/g}$)							
Ba	367 \pm 7	194 \pm 11	254 \pm 44	346 \pm 20	382 \pm 15	193 \pm 10	261 \pm 7
Cr	52 \pm 2	36 \pm 4	39 \pm 6	52 \pm 5	58 \pm 2	37 \pm 3	46 \pm 1
V	93 \pm 4	48 \pm 6	57 \pm 14	88 \pm 4	97 \pm 3	50 \pm 4	73 \pm 3
Pb	8.1 \pm 0.8	6.1 \pm 0.9	4.1 \pm 1.0	6.1 \pm 0.8	6.1 \pm 2.5	4.7 \pm 0.3	6.7 \pm 0.3
Cu	25.0 \pm 3.2	18.5 \pm 3.8	18.7 \pm 6.2	23.0 \pm 1.1	29.0 \pm 5.5	15.3 \pm 3.8	16.4 \pm 1.1
Zn	64 \pm 2	35 \pm 5	33 \pm 9	58 \pm 3	64 \pm 5	33 \pm 2	50 \pm 9
Cd	0.14 \pm 0.03	0.18 \pm 0.04	0.06 \pm 0.02	0.16 \pm 0.03	0.15 \pm 0.02	0.13 \pm 0.03	0.21 \pm 0.02
SILT (%)	17.0 \pm 4.1	4.0 \pm 1.7	9.0 \pm 3.4	28.0 \pm 1.8	47.0 \pm 3.5	4.6 \pm 0.9	10.0 \pm 2.8
CLAY (%)	16.0 \pm 11.0	3.6 \pm 2.4	8.0 \pm 4.9	14.0 \pm 1.3	18.0 \pm 1.3	3.1 \pm 0.9	4.8 \pm 1.1
TOC (mg/g)	7.2 \pm 1.0	3.0 \pm 0.8	3.1 \pm 1.6	8.4 \pm 0.6	9.2 \pm 0.5	2.4 \pm 0.2	5.6 \pm 1.0

Figure 4.1 Summary of Metal Concentrations, Silt and Clay Fractions, and Total Organic Carbon in Eastern Study Area Sediments.



	STATION			
	5(1)	5(2)	5(5)	5(10)
<u>METALS (µg/g)</u>				
Ba	236 ± 16	186 ± 14	294310	286 ± 6
Cr	23 ± 6	22 ± 5	40 ± 3	39 ± 2
V	45 ± 4	44 ± 7	69 ± 3	66 ± 3
Pb	4.9 ± 0.3	5.3 ± 0.6	6.2 ± 0.3	5.5 ± 0.5
Cu	9.7 ± 2.9	9.9 ± 0.5	15.7 ± 1.2	17.3 ± 2.3
Zn	35 ± 2	78 ± 9	50 ± 3	48 ± 1
Cd	0.15 ± 0.03	0.12 ± 0.03	0.22 ± 0.03	0.25 ± 0.03
<hr/>				
SILT (%)	5.4 ± 1.8	1.8 ± 0.5	23.0 ± 3.0	23.0 ± 10.0
CLAY (%)	4.1 ± 1.2	1.8 ± 0.7	13.0 ± 2.4	11.0 ± 4.2
<hr/>				
TOC (mg/g)	4.5 ± 0.9	3.1 ± 1.7	9.7 ± 4.6	12.9 ± 9.2

Figure 4.2 Summary of Metal Concentrations, Silt and Clay Fractions, and Total Organic Carbon in Endicott Field Transect Station Sediments.

generally show the higher sediment metal concentrations while Stations 5(1) and 5(2) have the lower values.

Data for the remaining stations in the Prudhoe Bay-Gwydyr Bay site are shown in Figure 4.3. The highest metal concentrations, silt, clay, and total organic carbon levels generally appear in the sediments from Stations 5A and 5D. The 10 west values are clearly found at Station 5B.

The western section of the Study Area includes stations in Harrison Bay. Sediment data for the East Harrison Bay stations are displayed in Figure 4.4. Stations 6B, 6C and 6D represent an offshore transect away from the Colville River Delta. The metal concentrations, grain size data and total organic carbon values at these stations clearly follow the offshore gradient, with the highest levels occurring at Station 6B and the 10 west at Station 6D.

Figure 4.5 presents the data for the West Harrison Bay stations. Although trends are less obvious at this site, the highest overall metal concentrations appear in Station 7C sediments, while Station 7B generally has the 10 west values. Grain size trends are similar when values for silt and clay are combined.

4.2.2 Metals in Tissues

Metals data were also collected from bivalve samples at three stations within the Study Area. Figure 4.6 presents this data along with corresponding sediment data. At Stations 6D and 3A Astarte was collected, while the sample at Station 5F was comprised of Cyrtodaria. The concentrations of Ba, Cr, V, and Pb in tissues are lower than in corresponding sediments. Cu, Zn and Cd concentrations, however, are nearly equal to or greater in tissue samples than in the sediments. The highest levels of metals in tissues clearly occur at Station 6D where Astarte was collected.

4.3 Hydrocarbon Data

Replicate sediment samples for hydrocarbons were collected at each of the 27 stations, and analyses were performed sometimes on both pooled sediment samples and individual replicates, and sometimes only on pools. The UV/F scan was conducted on each of six replicates per station, with concentrations reported as a mean \pm one standard deviation. GC-FID analyses for saturated hydrocarbons and GC/MS analyses for aromatics were conducted on each of six replicates only at seven stations. These concentrations are also reported as a mean \pm one standard deviation. The six replicates at the remaining 20 stations were pooled, analyzed and reported as one sample, essentially representing a mean at these stations.

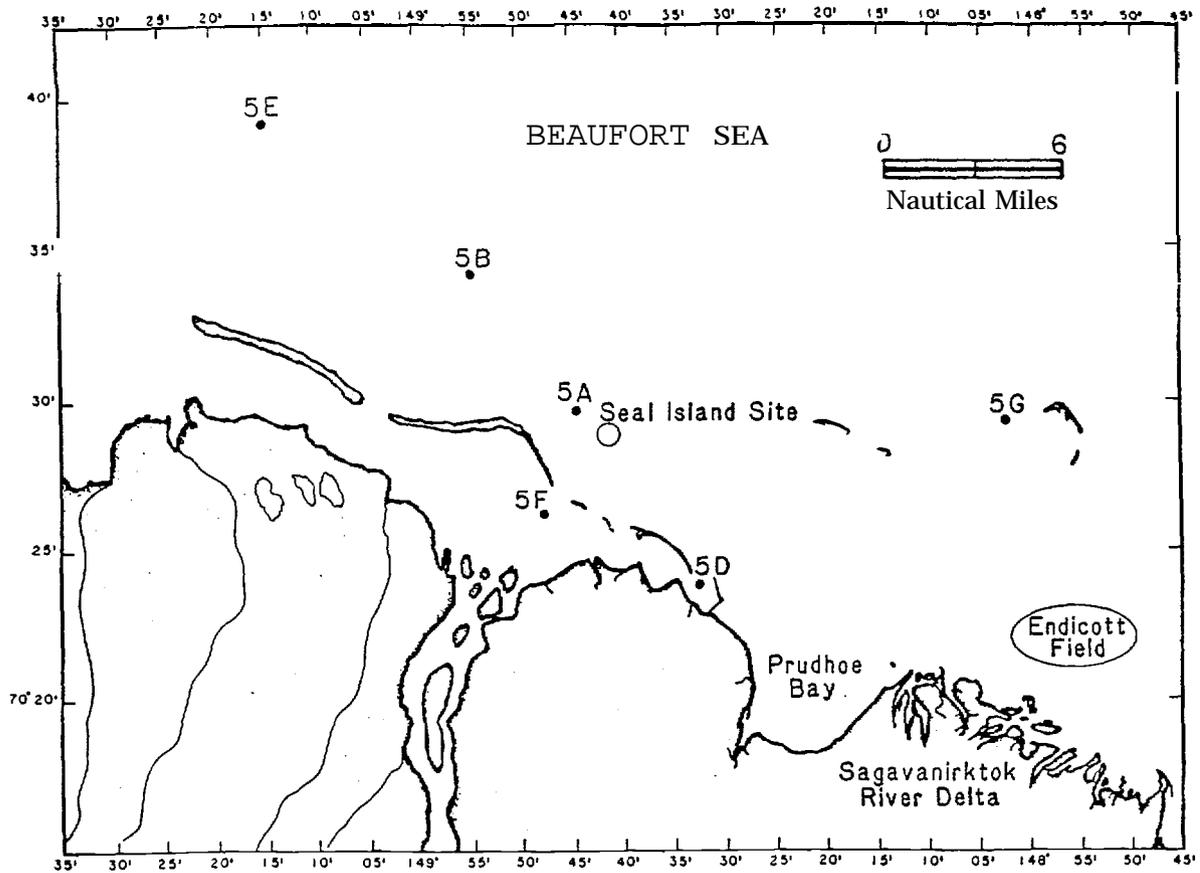
In the tabulation of hydrocarbon data, individual compounds are combined and presented as several selected parameters most relevant to the interpretations and discussion of the data. For the saturated hydrocarbons, these parameters include:

- Total Alkanes (TALK) = n-C₁₀ through n-C₃₄
- Low Molecular Weight Alkanes (LALK) = n-C₁₀ through n-C₂₀
- TOT = Total Resolved plus Total Unresolved Complex Mixture

The concentrations of the individual isoprenoid alkanes (pristane and phytane) and the results of the UV/F, reported as concentrations of Prudhoe Bay crude (0.7) equivalents at 355 nm, are also included in the tabulations of the saturated hydrocarbons.

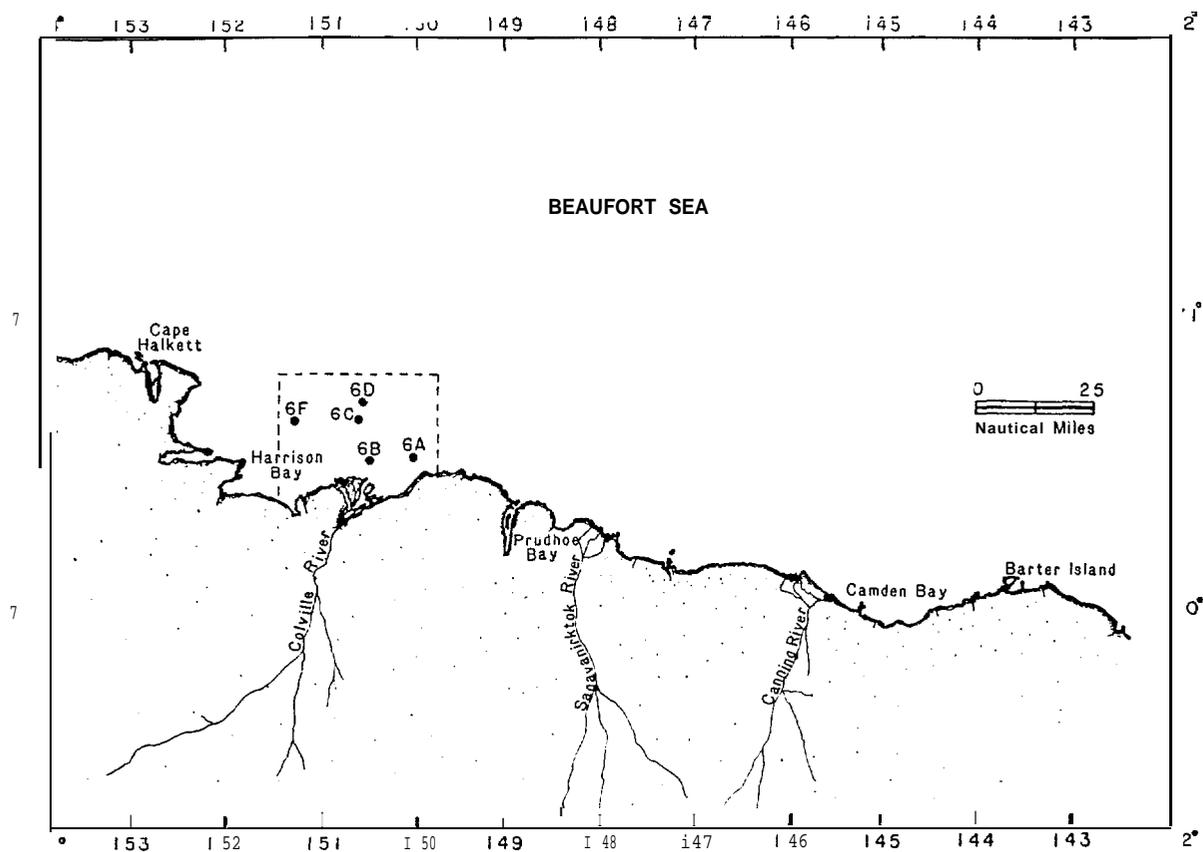
The aromatic hydrocarbons are presented in terms of the following parameters:

- N = Naphthalene + Methyl Naphthalene + C₂
Naphthalenes + C₃ Naphthalenes + C₄
Naphthalenes



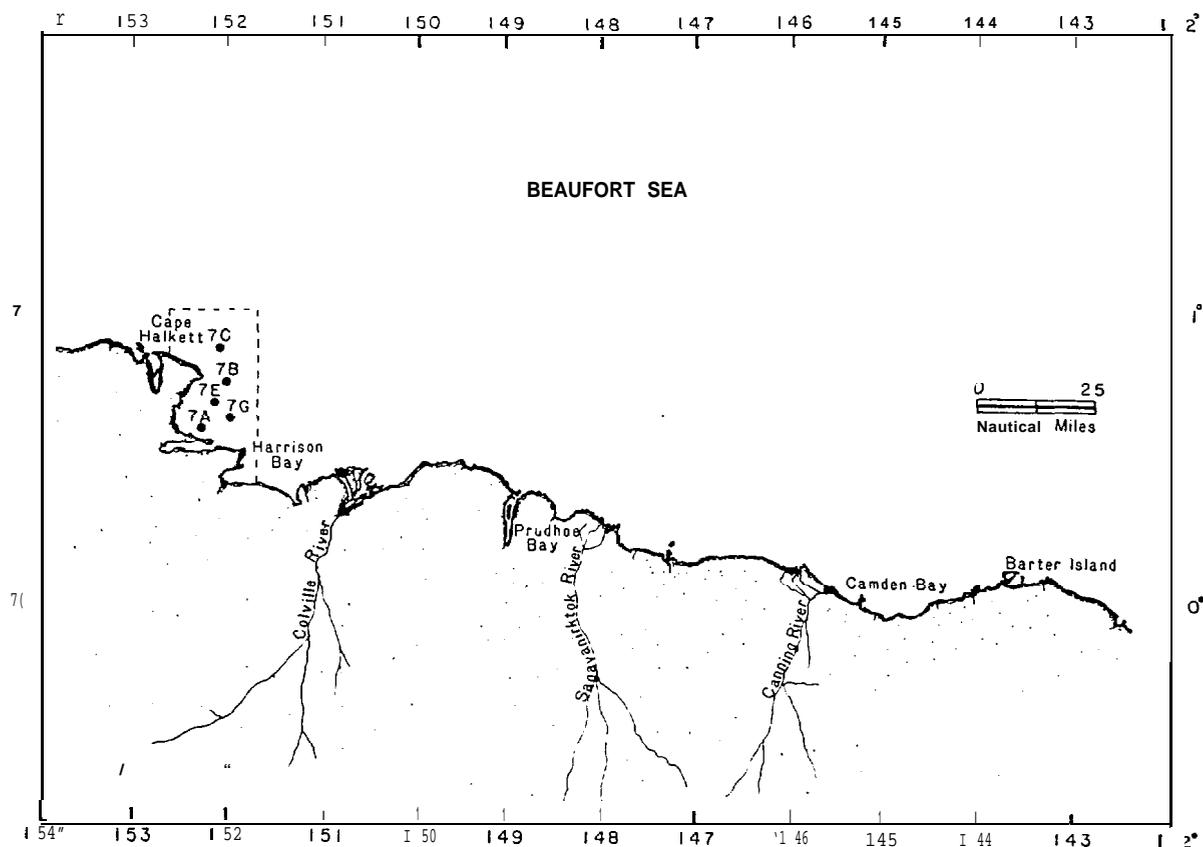
	STATION					
	5G	5D	5F	5A	5B	5E
METALS ($\mu\text{g/g}$)						
Ba	286 \pm 33	373 \pm 10	330 \pm 12	554 \pm 74	192 \pm 6	347 \pm 131
Cr	34 \pm 4	55 \pm 2	49 \pm 3	55 \pm 3	17 \pm 1	36 \pm 26
V	62 \pm 9	92 \pm 2	79 \pm 2	95 \pm 4	33 \pm 2	69 \pm 50
Pb	6.1 \pm 0.9	9.9 \pm 0.5	7.8 \pm 0.8	9.1 \pm 0.9	3.9 \pm 0.9	6.5 \pm 4.9
Cu	10.6 \pm 1.4	24.9 \pm 1.2	18.1 \pm 0.6	20.6 \pm 1.0	4.9 \pm 0.7	12.8 \pm 9.2
Zn	39 \pm 5	76 \pm 2	64 \pm 3	66 \pm 5	19 \pm 3	42 \pm 34
Cd	0.11 \pm 0.04	0.22 \pm 0.01	0.21 \pm 0.03	0.22 \pm 0.03	0.04 \pm 0	0.08 \pm 0.04
SILT (%)	10.0 \pm 1.6	60.0 \pm 4.1	51.0 \pm 4.8	50.0 \pm 9.8	1.6 \pm 0.5	11.0 \pm 11.0
CLAY (%)	8.2 \pm 1.8	12.0 \pm 2.0	10.0 \pm 2.5	22.0 \pm 2.0	1.6 \pm 0.9	18.0 \pm 25.0
TOC ($\mu\text{g/g}$)	6.4 \pm 1.8	29.2 \pm 2.1	17.0 \pm 2.2	10.1 \pm 0.2	2.1 \pm 0.3	4.5 \pm 3.9

Figure 4.3 Summary of Metal Concentrations, Silt and Clay Fractions, and Total Organic Carbon in Prudhoe Bay-Gwydyr Bay Area Sediments.



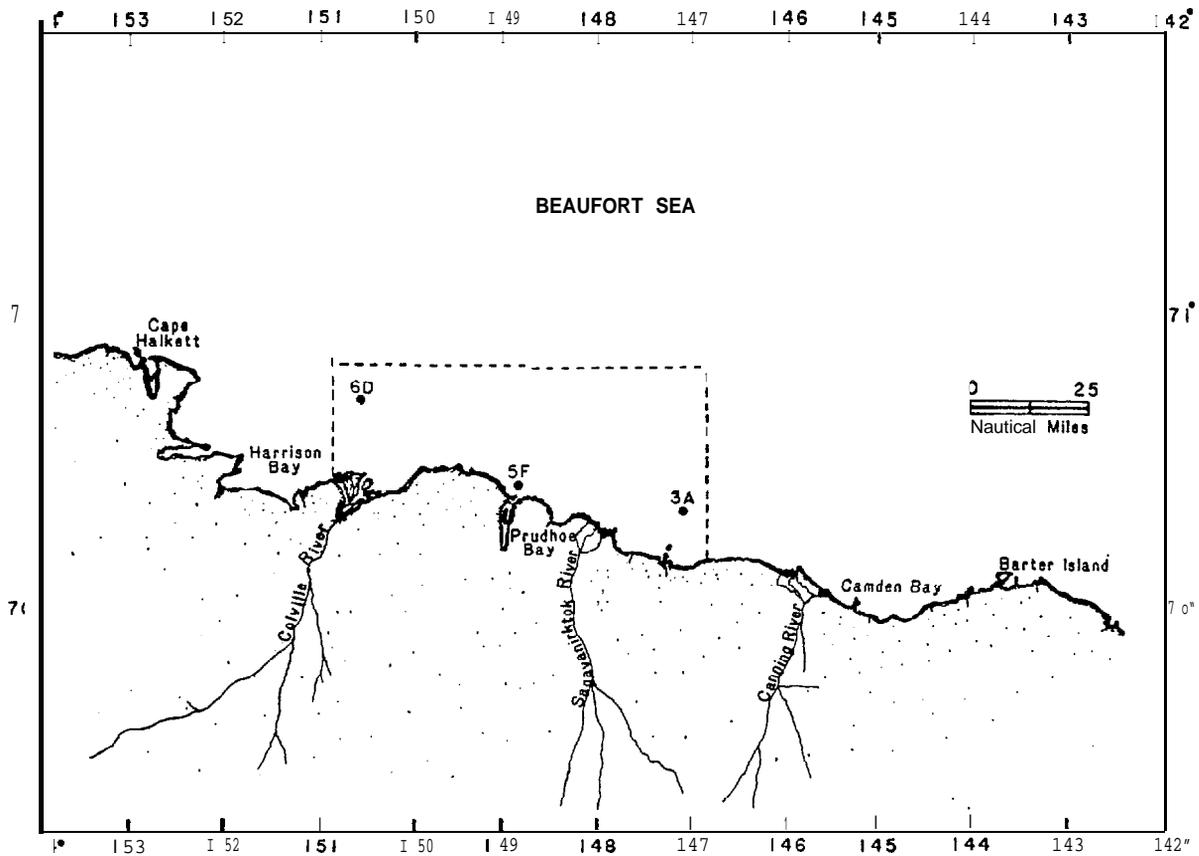
	STATION				
	<u>6B</u>	<u>6C</u>	<u>6D</u>	<u>6F</u>	<u>6A</u>
METALS ($\mu\text{g/g}$)					
Ba	745 \pm 42	398 \pm 122	282 \pm 22	407 \pm 141	385 \pm 11
Cr	91 \pm 4	65 \pm 18	38 \pm 4	63 \pm 11	60 \pm 4
V	153 \pm 10	98 \pm 29	66 \pm 7	109 \pm 26	91 \pm 4
Pb	16.7 \pm 1.0	8.4 \pm 2.1	7.1 \pm 0.6	12.5 \pm 4.1	8.7 \pm 1.3
Cu	36.7 \pm 1.6	20.7 \pm 4.2	9.1 \pm 1.7	21.2 \pm 5.6	23.5 \pm 1.4
Zn	112 \pm 7	68 \pm 19	45 \pm 3	63 \pm 16	70 \pm 2
Cd	0.29 \pm 0.03	0.06 \pm 0.01	0.07 \pm 0.02	0.13 \pm 0.04	0.13 \pm 0.03
SLT (%)	63.0 \pm 6.6	13.0 \pm 8.3	4.3 \pm 2.5	35.0 \pm 12.0	48.0 \pm 3.1
CLAY (%)	26.0 \pm 2	17.0 \pm 7.3	6.5 \pm 3.4	30.0 \pm 14.0	18.0 \pm 1.6
TOC (mg/g)	18.0 \pm 0.7	6.2 \pm 1.4	3.811.1	10.5 \pm 3.4	11.5 \pm 1.2

Figure 4.4 Summary of Metal Concentrations, Silt and Clay Fractions, and Total Organic Carbon in East Harrison Bay Sediments.



	STATION				
	7A	7E	7B	7C	7G
METALS ($\mu\text{g/g}$)					
Ba	698 \pm 29	605 \pm 13	456216	568 \pm 9	607 \pm 39
Cr	63 \pm 4	62 \pm 5	49 \pm 2	77 \pm 2	42 \pm 7
V	87 \pm 3	92 \pm 4	68 \pm 3	145 \pm 4	68 \pm 10
Pb	8.5 \pm 0.9	8.3 \pm 0.4	6.6 \pm 0.5	14.7 \pm 0.9	11.1 \pm 0.6
Cu	13.8 \pm 2.2	16.811.3	9.7 \pm 1.0	27.0 \pm 0.9	11.5 \pm 6.6
Zn	75 \pm 5	71 \pm 2	51 \pm 3	97 \pm 1	53 \pm 2
Cd	0.10 \pm 0.03	0.15 \pm 0.03	0.06 \pm 0.01	0.13 \pm 0.02	0.07 \pm 0.02
<hr/>					
SILT (%)	58.034.4	58.0 \pm 4.7	8.0 \pm 2.8	44.0 \pm 2.2	8.850.6
CLAY (%)	7.8 \pm 1.8	13.0 \pm 1.9	5.3 \pm 2.0	41.0 \pm 2.8	1.2 \pm 0.4
<hr/>					
TOC (mg/g)	11.4 \pm 4.2	17.3 \pm 1.8	5.6 \pm 0.8	13.4 \pm 0.6	26.3 \pm 10.2

Figure 4.5 **Summary of Metal Concentrations, Silt and Clay Fractions, and Total Organic Carbon in West Harrison Bay Sediments.**



	STATION					
	6D		5F		3A	
	<u>Tissues^a</u>	<u>Sediments</u>	<u>Tissues^b</u>	<u>Sediments</u>	<u>Tissues^a</u>	<u>Sediments</u>
METALS ($\mu\text{g/g}$)						
Ba	29.7 \pm 6.4	282 \pm 22	16.8 \pm 4.9	330 \pm 12	8.3 \pm 1.5	346 \pm 20
Cr	4.5 \pm 0.4	38 \pm 4	3.2 \pm 0.7	49 \pm 3	2.4 \pm 0.5	52 \pm 5
V	5.3 \pm 0.5	66 \pm 7	3.3 \pm 0.8	79 \pm 2	1.9 \pm 0.4	88 \pm 4
Pb	0.80 \pm 0.12	7.1 \pm 0.6	0.48 \pm 0.08	7.8 \pm 0.8	0.61 \pm 0.16	6.1 \pm 0.8
Cu	27.7 \pm 0.6	9.13 1.7	16.2 \pm 4.0	18.1 \pm 0.6	11.8 \pm 3.4	23.0 \pm 1.1
Zn	96.0 \pm 3.0	45 \pm 3	68.4 \pm 8.3	64 \pm 3	72.6 \pm 8.5	58 \pm 3
Cd	11.24 \pm 1.20	0.07 \pm 0.02	1.42 \pm 0.12	0.21 \pm 0.03	9.29 \pm 3.05	0.16 \pm 0.03

a Astarte tissue
 b Cyrtodaria tissue

Figure 4.6 Summary of Metal Concentrations in Bivalve Tissues and Corresponding Sediments.

- e P = Phenanthrene+ Methyl Phenanthrene+ C₂ Phenanthrenes+ C₃ Phenanthrenes + C₄ Phenanthrenes
- D = Dibenzothiophene + Methyl Dibenzothiophene + C₂ Dibenzothiophenes+ C₃ Dibenzothiophenes
- F = Fluorene + Methyl Fluorene + C₂ Fluorenes + C₃ Fluorenes
- PAH = Fluoranthene + Pyrene + Benzo(a)anthracene + Chrysene + Benzofluoranthene + Benzo(a)pyrene + Benzo(e)pyrene + Perylene

4.3.1 Saturated Hydrocarbons

For the saturated and UV/F hydrocarbon parameters, the range generally encompasses two orders of magnitudes. Total alkanes (TALK), the n-C₁₀ through n-C₃₄ compounds, range from 0.68 µg/g to 22.8 µg/g while the low molecular weight alkanes (LALK), or n-C₁₀ through n-C₂₀ compounds, range from 0.24 to 4.0 µg/g. The highest sediment concentrations of pristane and phytane are 0.305 µg/g and 0.144 µg/g, respectively, while the low end of the range is represented by 0.008 µg/g and 0.003 µg/g, respectively for pristane and phytane. UV/F, measured at 355 nm, varies from 5 µg/g to 309 µg/g. The total resolved plus unresolved hydrocarbons (TOT) ranges from 2.7 µg/g to 68.0 µg/g. The highest values for all the above parameters are clearly associated with the sediments from Station 6B, for which the highest silt and clay grain size fractions, as well as the highest metal concentrations, are also reported.

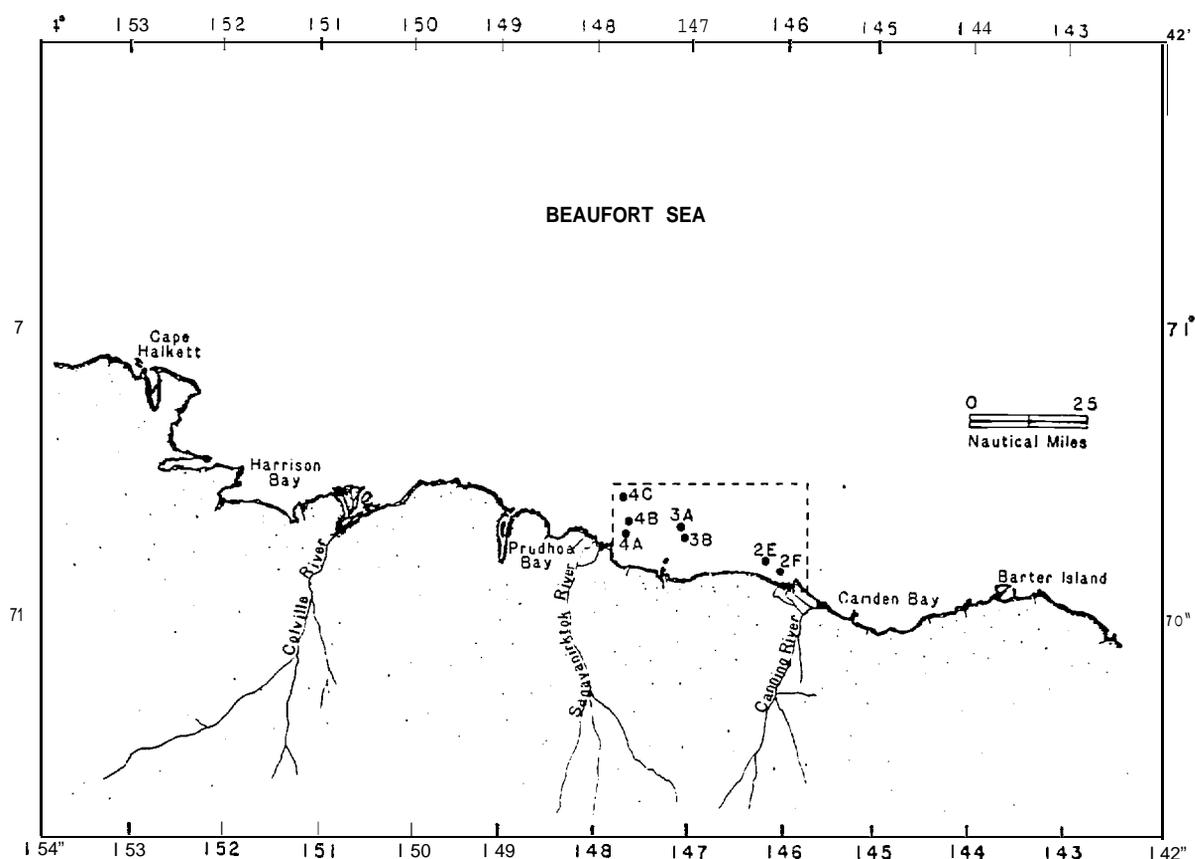
Figure 4.7 presents the data for the seven stations located in the eastern section of the Study Area, which include the Carling River Delta (the "2" stations), the Mikelson Bay - Stockton Island area (the "3" stations) and the Foggy Island Bay transect (the "4" stations). Three of the stations (4A, 3B and 2F) represent those at which complete replicate sets were analyzed. The highest concentrations of hydrocarbons are generally found at Stations 3B and 4A. Low est levels of all parameters occur at Station 2E. The nearshore-to-offshore transect stations (4A, 4B and 4C) do not appear to show a gradient for any of the parameters. Grain size and total organic carbon data appear to follow the same pattern indicated by the hydrocarbon data.

In the central portion of the Study Area, the Prudhoe Bay-Gwydyr Bay region includes the "5" stations which are divided into two station groupings for presentation. Figure 4.8 presents the data for the Endicott Field transect stations, selected to represent 1-, 2-, 5-, and 10-mile distances from the Endicott Field locations. As was found with the metals data, the hydrocarbon concentrations at these stations do not presently indicate a gradient away from the proposed area of activity. The higher levels of all parameters occur at Stations 5(5) and 5(10) while the lowest concentrations are found at Stations 5(2) and 5(1). The grain size and total organic carbon data follow a similar pattern.

Figure 4.9 presents the data for the remaining stations in the offshore Prudhoe Bay-Gwydyr Bay site. The highest saturated hydrocarbon concentrations are generally associated with Stations 5A, 5D and 5F, or the stations nearer to shore, while the lowest levels are found at those stations further offshore.

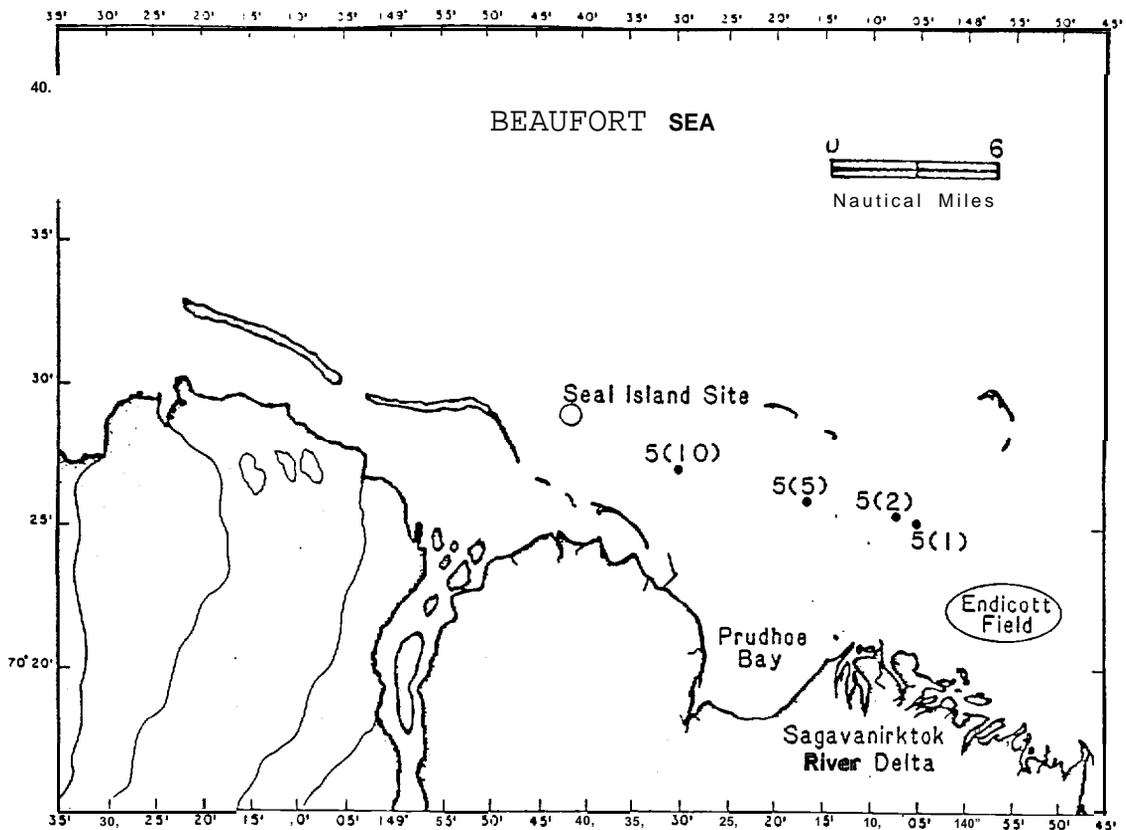
Data for East Harrison Bay (the "6" stations) are displayed in Figure 4.10. Highest sediment hydrocarbon concentrations are clearly associated with Stations 6B and 6A, the stations nearest to the Colville River mouth, while Stations 6C, 6D and 6F, those furthest offshore, show lowest concentrations. A transect out from the Colville River mouth is represented by Stations 6B, 6C and 6D. Hydrocarbon concentrations, grain size and total organic carbon data at these stations clearly follow an offshore gradient, with highest concentrations associated with Station 6B and lowest levels at Station 6D.

Figure 4.11 presents the data for the West Harrison Bay stations. Trends at these stations are less clear, although Station 7E generally exhibits the highest overall concentrations. The lowest levels are associated with Station 7B. The relationship



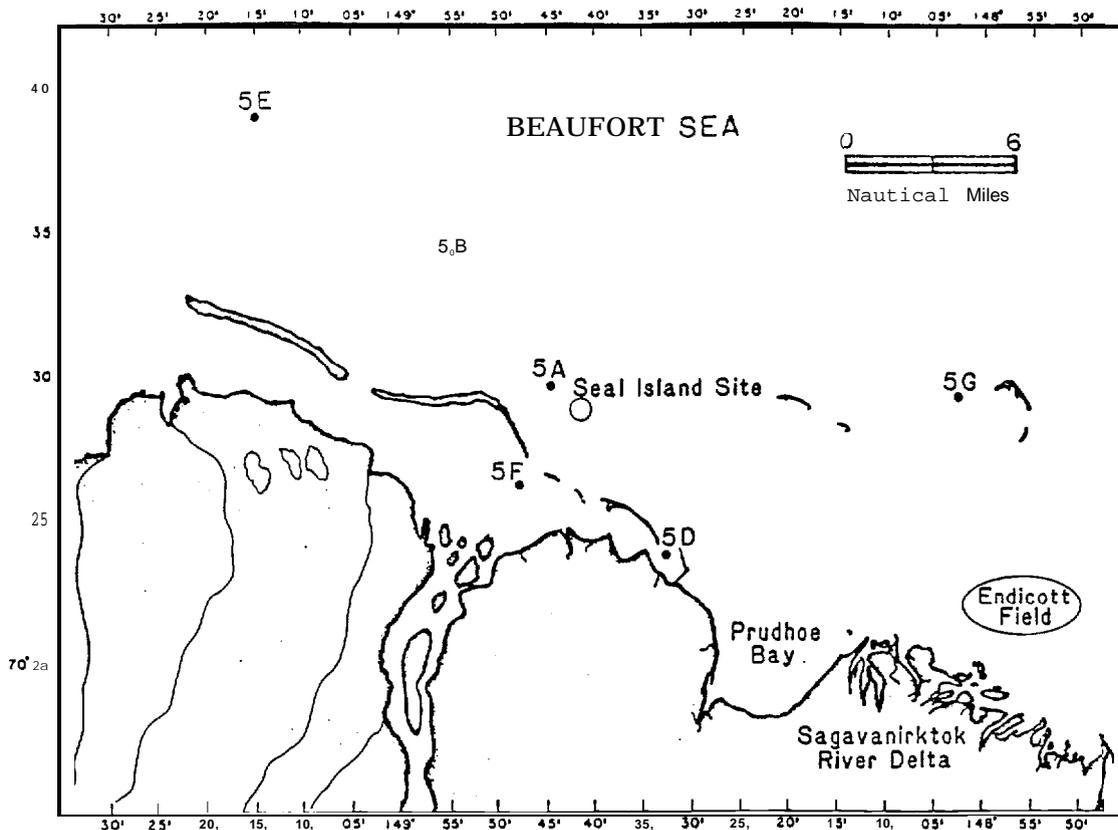
	STATION						
	4A	4B	4C	3A	3B	2E	2F
SATURATED HYDROCARBONS (ug/g)							
TALK	3.41 ± 0.33	0.92	1.86	2.78	4.46 ± 1.19	0.30	1.42 ± 0.26
LALK	0.62 ± 0.03	0.24	0.51	0.49	0.82 ± 0.23	0.25	0.39 ± 0.05
Pristane	0.046 ± 0.004	0.016	0.028	0.035	0.047 ± 0.013	0.009	0.026 ± 0.001
Phytane	0.019 ± 0.003	0.007	0.012	0.017	0.023 ± 0.006	0.004	0.010 ± 0.002
TOT	12.42 ± 1.69	3.62	6.87	9.91	13.91 ± 3.34	2.94	5.59 ± 0.73
U V/F (355 nm)	35 ± 6	8 ± 2	21 ± 8	33 ± 2	34 ± 7	7 ± 1	19 ± 4
SILT (%)	17.0 ± 4.1	4.0 ± 1.7	9.0 ± 3.4	28.0 ± 1.8	47.0 ± 3.5	4.6 ± 0.9	10.0 ± 2.8
CLAY (%)	16.0 ± 11.0	3.6 ± 2.4	8.0 ± 4.9	14.0 ± 1.3	18.0 ± 1.3	3.1 ± 0.9	4.8 ± 1.1
TOC (mg/g)	7.2 ± 1.0	3.0 ± 0.9	3.1 ± 1.6	8.4 ± 0.6	9.2 ± 0.5	2.4 ± 0.2	5.6 ± 1.0

Figure 4.7 Summary of Saturated and UV/F Hydrocarbon Concentrations, Silt and Clay Fractions, and Total Organic Carbonic Eastern Study Area Sediments.



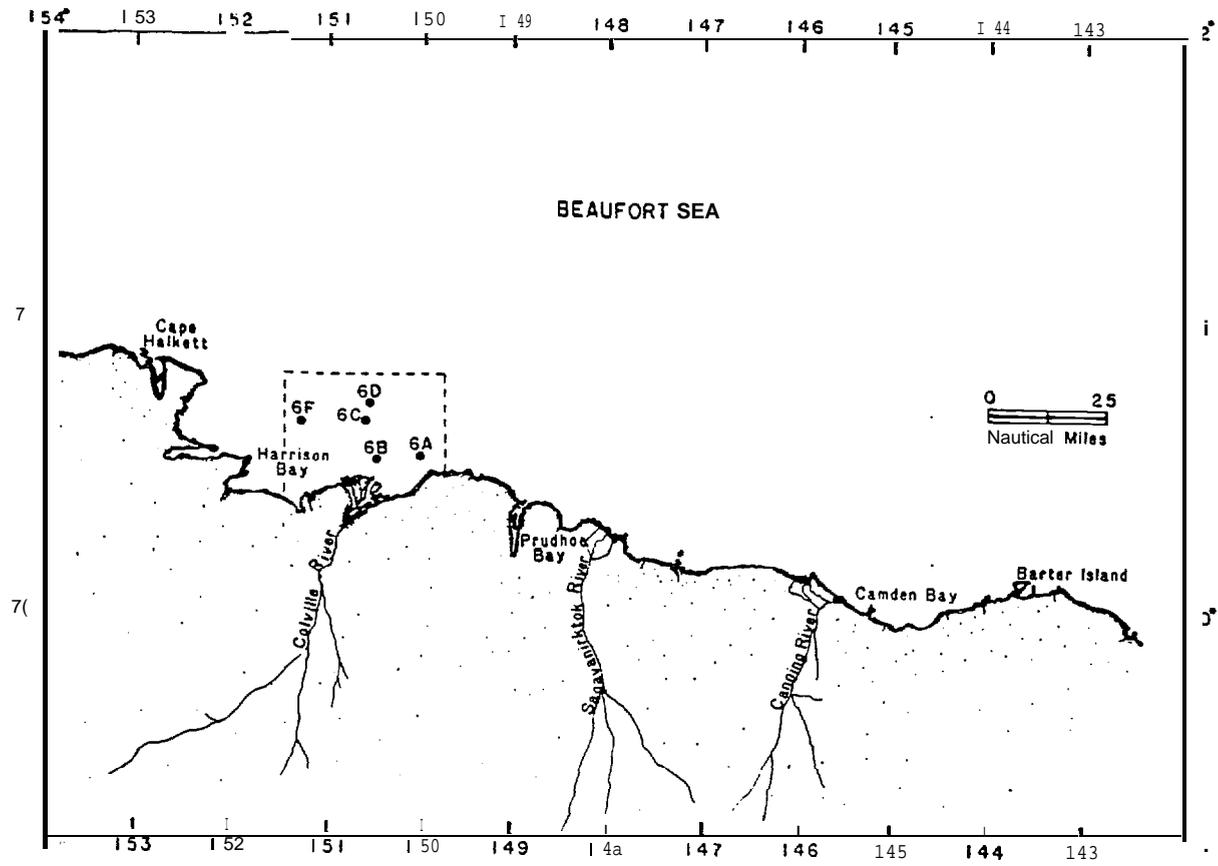
	STATION			
	<u>5 (1)</u>	<u>5 (2)</u>	<u>5 (5)</u>	<u>5 (10)</u>
SATURATED HYDROCARBONS (µg/g)				
TALK	1.23	0.68	3.48	3.59
LALK	0.30	0.27	0.67	0.71
Pristane	0.016	0.008	0.055	0.053
Phytane	0.007	0.003	0.027	0.018
TOT	4.67	2.69	13.26	13.96
UV/F (355 nm)	17 ± 12	5 ± 1	28 ± 5	21 ± 3
SILT (s)	5.4 ± 1.8	1.8 ± 0.5	23.0 ± 3.0	23.0 ± 10.0
CLAY (%)	4.1 ± 1.2	1.8 ± 0.7	13.0 ± 2.4	11.0 ± 4.2
TOC (mg/g)	4.5 ± 0.9	3.1 ± 1.7	9.7 ± 4.6	12.9 ± 9.2

Figure 4.8 Summary of Saturated and UV/F Hydrocarbon Concentrations, Silt and Clay Fractions, and Total Organic Carbon in Endicott Field Transect Stations Sediments



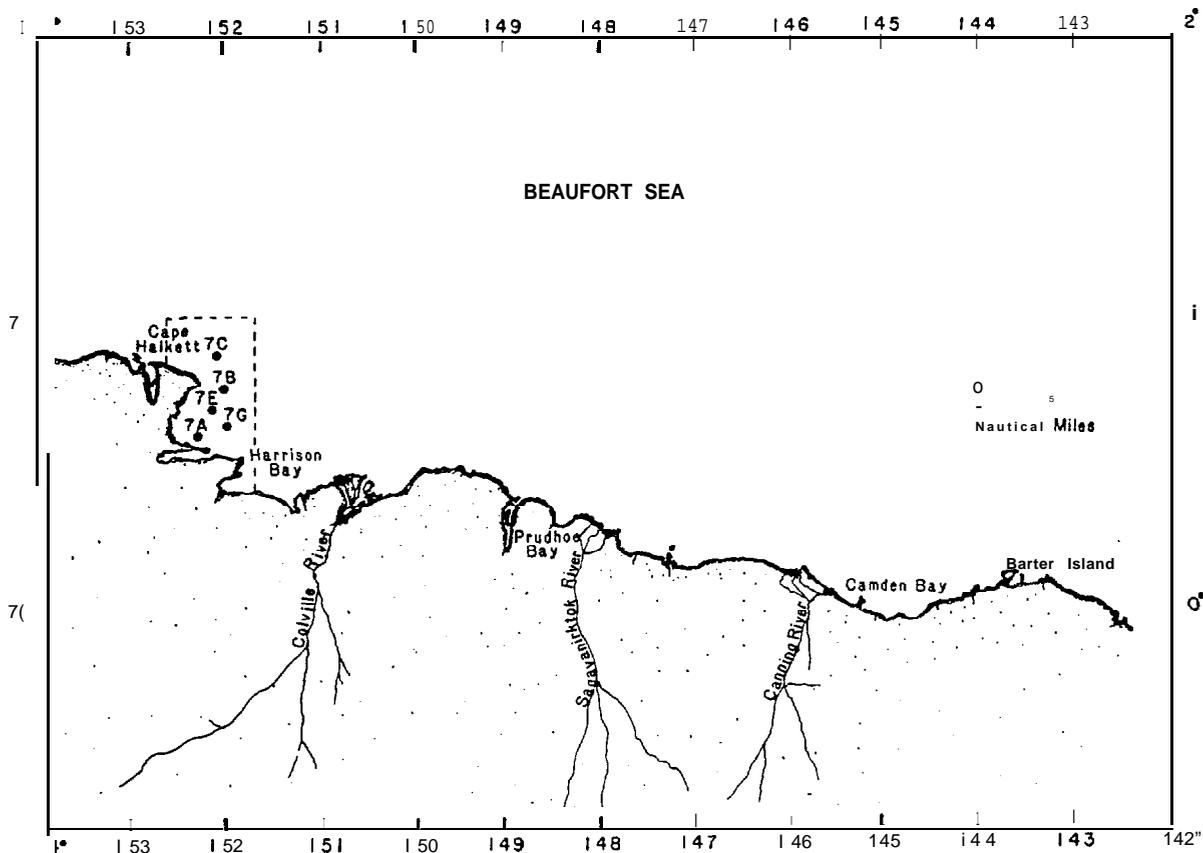
	STATION					
	5G	5D	5F	5A	5B	5E
SATURATED HYDROCARBONS (g/g)						
TALK	2.97	10.78 ± 3.60	11.43	5.92	0.77	2.35
LALK	0.75	1.14 ± 0.38	1.32	1.00	0.28	0.61
Pristane	0.056	0.072 ± 0.023	0.072	0.086	0.010	0.044
Phytane	0.022	0.034 ± 0.010	0.032	0.041	0.004	0.019
TOT	10.93	35.51 ± 4.36	37.00	20.51	2.78	9.01
UV/F (355 nm)	40 ± 15	71 ± 4	44 ± 2	67 ± 10	7 ± 2	43 ± 51
SILT (%)	10.0 ± 1.6	60.0 ± 4.1	51.054.8	50.039.8	1.6 ± 0.5	11.0 ± 11.0
CLAY (%)	8.2 ± 1.8	12.0 ± 2.0	10.0 ± 2.5	22.0 ± 2.2	1.6 ± 0.9	16.0 ± 25.0
TOC (mg/g)	6.4 ± 1.8	29.2 ± 2.1	17.0 ± 2.2	10.1 ± 0.2	2.1 ± 0.3	4.5 ± 3.9

Figure 4.9 Summary of Saturated and UV/F Hydrocarbon Concentrations, Silt and Clay Fractions, and Total Organic Carbon in Prudhoe Bay-Gwydyr Bay Area Sediments.



	STATION				
	6B	6C	6D	6F	6A
SATURATED HYDROCARBONS (µg/g)					
TALK	22.75	3.99 ± 1.50	2.50 ± 0.87	7.25	8.47
LALK	4.02	1.21 ± 0.42	1.27 ± 0.87	1.39	2.43
Pristane	0.305	0.067 ± 0.029	0.032 ± 0.008	0.091	0.096
P hytane	0.144	0.030 ± 0.017	0.130 ± 0.003	0.037	0.039
TOT	68.63	15.75 ± 6.31	7.75 ± 2.47	24.21	70 ± 11
UV/F (355nm)	309270	60 ± 14	23 ± 7	97 ± 46	70 ± 11
SILT (%)	63.0 ± 6.6	13.0 ± 8.3	4.3 ± 2.5	35.0 ± 12.0	48.0 ± 3.1
CLAY (%)	26.0 ± 2.0	17.0 ± 7.3	6.5 ± 3.4	30.0 ± 14.0	18.0 ± 1.6
TOC (mg/g)	18.0 ± 0.7	6.2 ± 1.4	3.8 ± 1.1	10.5 ± 3.4	11.5 ± 1.3

Figure 4.10 Summary of Saturated and UV/F Hydrocarbon Concentrations, Silt and Clay Fractions, and Total Organic Carbon in East Harrison Bay Sediments.



	STATION				
	<u>7A</u>	<u>7E</u>	<u>7B</u>	<u>7C</u>	<u>7G</u>
SATURATED HYDROCARBONS ($\mu\text{g/g}$)					
TALK	5.76 \pm 2.63	7.94	3.65	7.33	3.99
LALK	1.33 \pm 0.53	1.72	1.17	1.65	1.05
Pristane	0.080 \pm 0.034	0.142	0.043	0.099	0.214
Phytane	0.031 \pm 0.011	0.041	0.016	0.045	0.045
TOT	21.88 \pm 5.78	25.99	11.38	23.71	17.67
UV/F (355nm)	61 \pm 8	109 \pm 4	136 \pm 4	104 \pm 6	121 \pm 37
SILT. (%)	58.0 \pm 4.4	58.0 \pm 4.7	8.0 \pm 2.8	44.0 \pm 2.2	8.8 \pm 0.6
CLAY (%)	7.8 \pm 1.8	13.0 \pm 1.9	5.3 \pm 2.0	41.0 \pm 2.8	1.2 \pm 0.4
TOC (mg/g)	11.4 \pm 4.2	17.3 \pm 1.8	5.6 \pm 0.8	13.4 \pm 0.6	26.2 \pm 10.2

Figure 4.11 Summary of Saturated and UV/F Hydrocarbon Concentrations, Silt and Clay Fractions, and Total Organic Carbon in West Harrison Bay Sediments.

bet ween hydrocarbon data, and grain size and total organic carbon is also somewhat unclear at all stations except 7B, for which the 10 west values are reported.

4.3.2 Aromatic Hydrocarbons

The aromatic hydrocarbon data for station areas "2", "3" and "4" in the eastern section of the Study Area are presented in Figure 4.12. Trends similar to those established for the metals data and saturated hydrocarbon data in this area are also observed with the aromatics. Stations 4A, 3B and 3A reveal the highest sediment concentrations for this group of parameters, while the 10 west levels always occur at Station 2E. Of the nearshore-to-offshore transect stations, 4 C, or the furthest offshore station, has 10 west concentrations of aromatics than Station 4B which occupies the middle station of the transect.

In the Prudhoe Bay-Gwydyr Bay region, data for the Endicott Field transect stations are shown in Figure 4.13. Once again, the aromatics data follow the same trends found with the metals and saturated hydrocarbon data. The higher sediment aromatics levels occur at Stations 5(5) and 5(10) while the 10 west concentrations are associated with Stations 5(1) and 5(2). No indication of a gradient away from the Endicott Field is obvious in the data set.

Aromatic hydrocarbon data for the six remaining Prudhoe Bay-Gwydyr Bay area stations are displayed in Figure 4.14. At Station 5 D, the station nearest to shore and to the West Dock, sediments generally reveal the highest concentrations of aromatics. Lowest values appear to be associated with Station 5G sediments. Data for the remaining stations vary by individual parameters.

Figure 4.15 presents the data for the five stations in East Harrison Bay. Highest concentrations of aromatics are found in sediments from Station 6B which is nearest to the Colville River mouth. Lower levels are associated with those stations further offshore (6C, 6D and 6F). The stations comprising a transect out from the Colville River Delta (6B, 6 C and 6D) clearly reveal a decrease in aromatic hydrocarbon levels with distance from the river outlet.

Data for the West Harrison Bay stations are shown in Figure 4.16. Higher aromatics levels are generally associated with Station 7 A which is nearest to shore, while the 10 west concentrations most often occur at Station 7B. For the remaining stations in this area, data vary by station as well as by parameter.

4.3.3 Hydrocarbons in Tissues

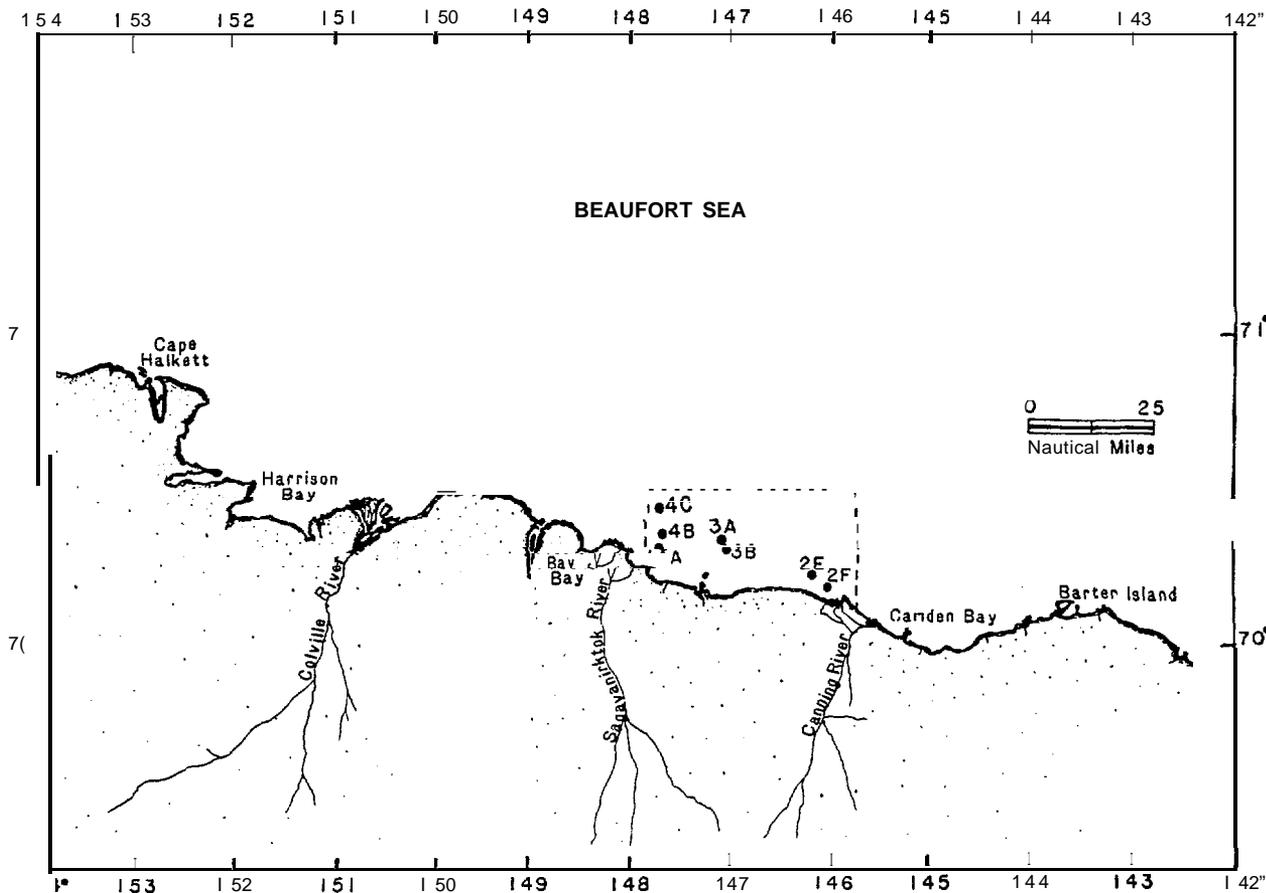
Pooled bivalve tissue samples collected from three stations were analyzed for hydrocarbons. These data, along with corresponding sediment data, are shown in Figure 4.17. Hydrocarbon concentrations in tissues are detected for the saturates and by the UV/F scan. However, with the exception of phenanthrenes in Station 6D macro samples, no other aromatics are found in the tissues.

4.3.4 Historical Data

The sampling strategy, as outlined in Section 1, specified that the 1984 BSM P survey would occupy several stations for which baseline data were available. Nine stations in our survey are in the proximity of eight nearshore sediment baseline stations of Shaw et al. (1979). Figure 4.18 presents the locations of these stations and the corresponding hydrocarbon data. Only quantitative saturated hydrocarbon data are available for comparison.

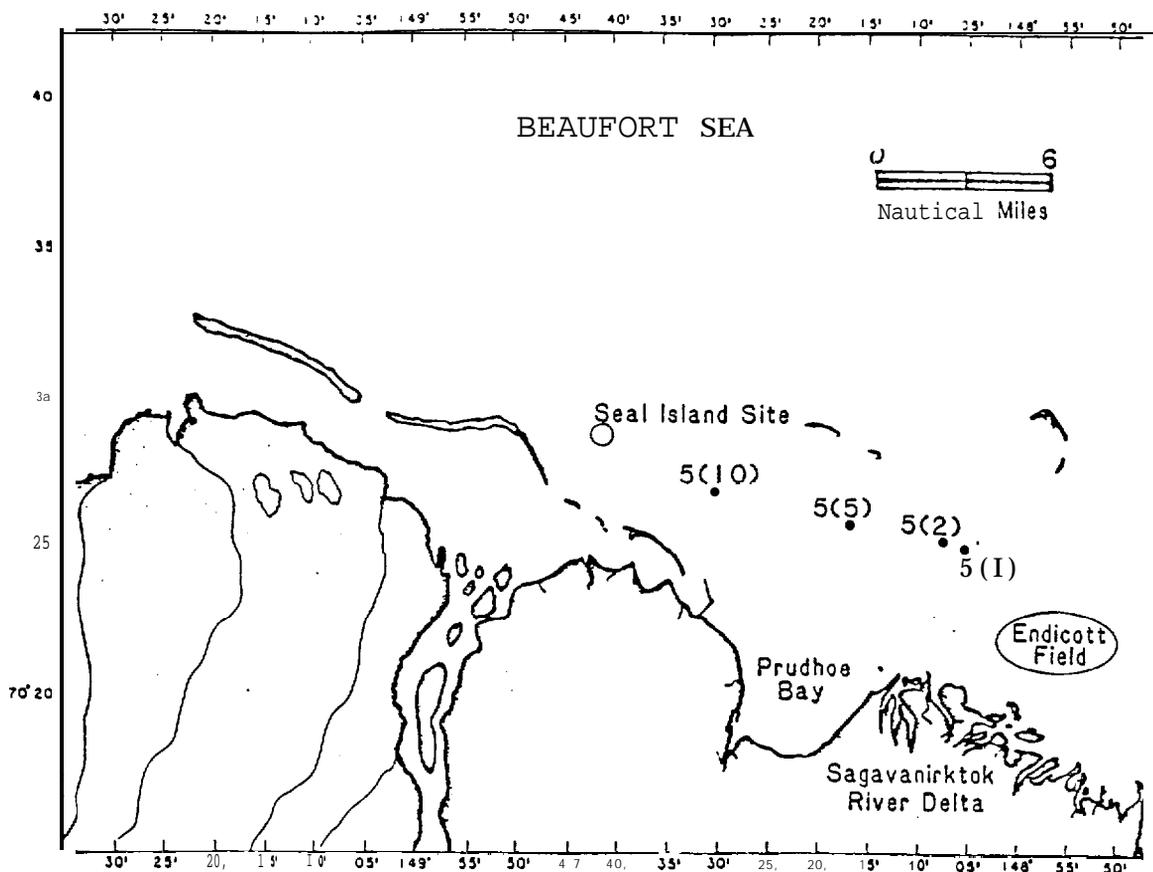
In comparing the two data sets, considerations must be given to several factors. Shaw's (1979) data set does not include grain size and total organic carbon analyses, parameters which are highly valuable in interpreting the hydrocarbon data. Differences in analytical methodologies may also contribute to the disparity in some of the data.

In general, the best agreement between the two data sets is in the LAL K/TALK and pristane/phytane ratios. Stations 5F (BSMP, 1984) and 10 (Shaw et al.,



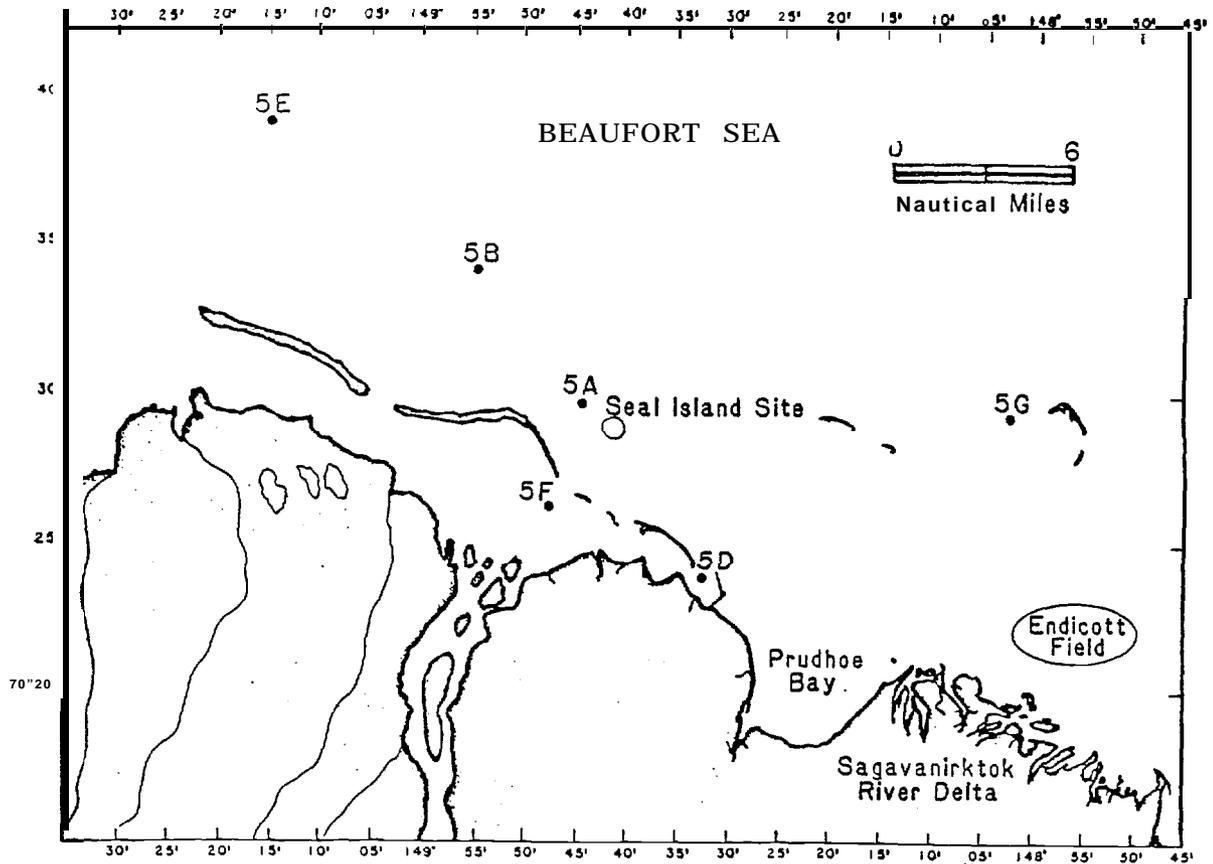
	STATION						
	4A	4B	4C	3A	3B	2S	2P
AROMATIC HYDROCARBONS ($\mu\text{g/g}$)							
N	0.17 \pm 0.02	0.04	0.07	0.14	0.15:0.05	0.02	0.03 \pm 0.01
P	0.19:0.01	0.04	0.09	0.18	0.17 \pm 0.05	0.03	0.07 \pm 0.02
D	0.04 \pm 0.00	0.01	0.02	0.02	0.02 \pm 0.00	<0.01	<0.01 \pm 0.00
F	0.04 \pm 0.01	0.01	0.02	0.04	0.03 \pm 0.01	0.01	0.01:0.01
PAH	0.10 \pm 0.03	0.01	0.04	0.09	0.08 \pm 0.04	0.01	0.03 \pm 0.01
<hr/>							
SILT (%)	17.05:4.1	4.0 \pm 1.7	9.0:3.4	28.0 \pm 1.8	47.0 \pm 3.5	4.6 \pm 0.9	10.0 \pm 2.8
CLAY (%)	16.0 \pm 11.0	3.6 \pm 2.4	8.0:4.9	14.0 \pm 1.3	18.0 \pm 1.3	3.1 \pm 0.9	4.8:21.1
<hr/>							
TOC (mg/g)	7.2 \pm 1.0	3.0 \pm 0.8	3.1 \pm 1.6	8.4 \pm 0.6	9.2:10.5	2.4 \pm 0.2	5.6 \pm 1.0

Figure 4.12 Summary of Aromatic Hydrocarbon Concentrations, Silt and Clay Fractions, and Total Organic Carbon in Eastern Study Area Sediments.



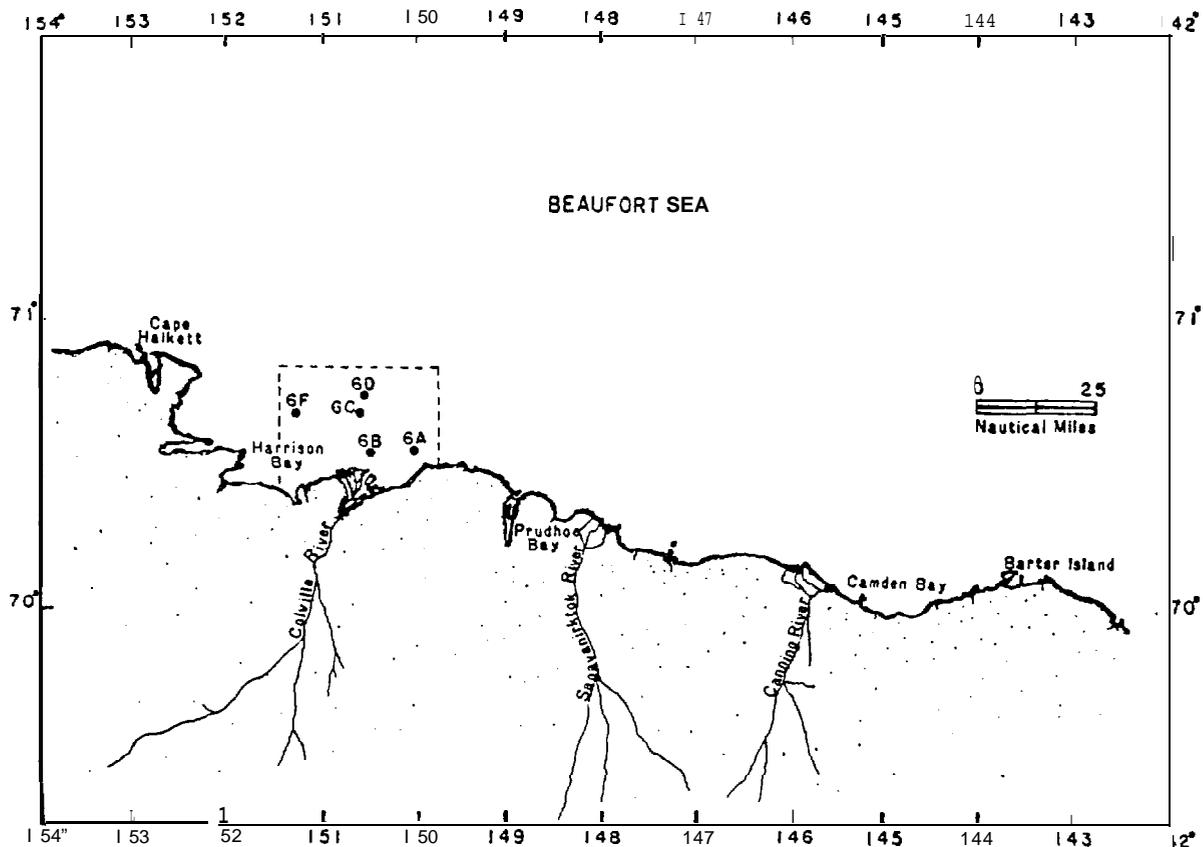
	<u>STATION</u>			
	<u>5(1)</u>	<u>5(2)</u>	<u>5(5)</u>	<u>5(10)</u>
<u>AROMATIC HYDROCARBONS (µg/g)</u>				
N	0.04	0.01	0.13	0.13
P	0.06	0.02	0.17	0.16
D	0.01	0.01	0.03	0.03
F	0.01	<0.01	0.03	0.04
PAH	0.04	0.01	0.12	0.07
SILT (%)	5.4 ± 1.8	1.8 ± 0.5	23.0 ± 3.0	23.0 ± 10.0
CLAY (%)	4.1 ± 1.2	1.8 ± 0.7	13.0 ± 2.4	11.0 ± 4.2
TOC (rig/g)	4.5 ± 0.9	3.1 ± 1.7	9.7 ± 4.6	12.9 ± 9.2

Figure 4.13 Summary of Aromatic Hydrocarbon Concentrations, Silt and Clay Fractions, and Total Organic Carbon in Endicott Field Transect Station Sediments.



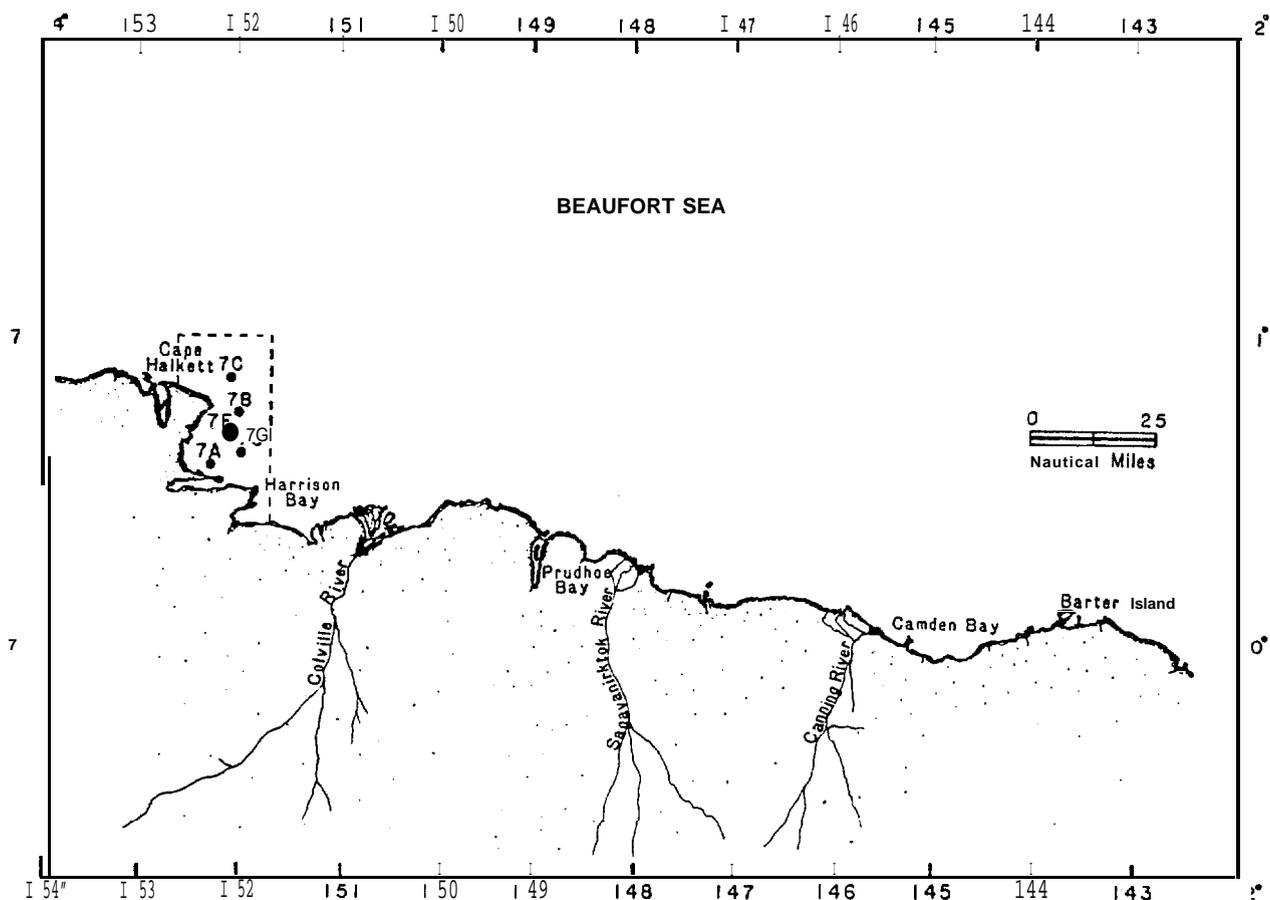
	STATION					
	5G	5D	5P	5A	5B	5E
AROMATIC HYDROCARBONS ($\mu\text{g/g}$)						
N	0.13	0.36 \pm 0.07	0.20	0.29	0.22	0.16
P	0.13	0.40 \pm 0.03	0.23	0.26	0.27	0.18
D	0.02	0.07 \pm 0.01	0.03	0.03	0.07	0.04
F	0.02	0.05 \pm 0.01	0.02	0.03	0.08	0.04
PAH	0.08	0.22 \pm 0.08	0.21	0.15	0.13	0.07
SLT (S)	10.0 \pm 1.6	60.0 \pm 4.1	51.0 \pm 4.8	50.0 \pm 9.8	1.6:0.5	11.0 \pm 11.0
CLAY (%)	8.2 \pm 1.8	12.0 \pm 2.0	10.0 \pm 2.5	22.0 \pm 2.0	1.6 \pm 0.9	18.0 \pm 25.0
TOC (mg/g)	6.4 \pm 1.8	29.2 \pm 2.1	17.0 \pm 2.2	10.1 \pm 0.2	2.1 \pm 0.3	4.5 \pm 3.9

Figure 4.14 Summary of Aromatic Hydrocarbon Concentrations, Silt and Clay Fractions, and Total Organic Carbon in Prudhoe Bay-Gwydyr Bay Area Sediments



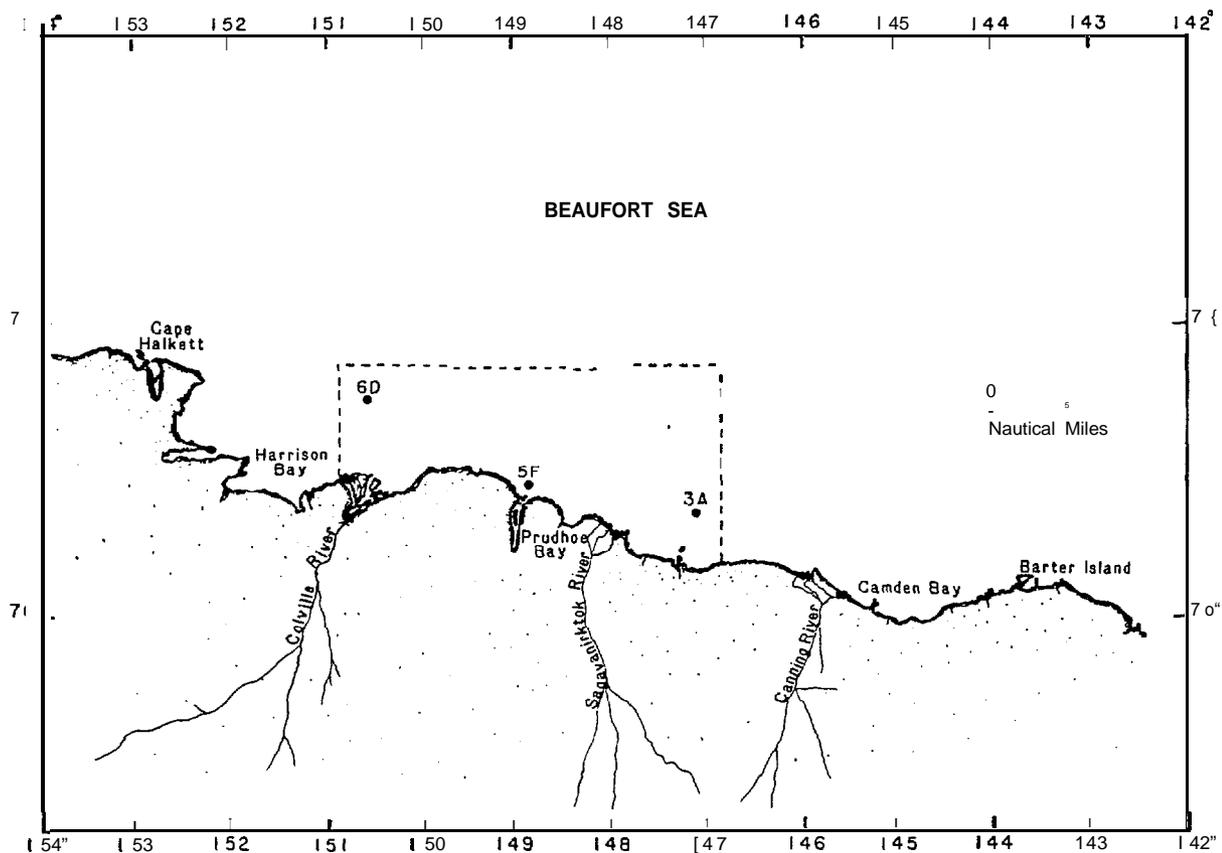
	STATION				
	6B	6C	6D	6F	6A
AROMATIC HYDROCARBONS ($\mu\text{g/g}$)					
N	3.50	0.41 ± 0.33	0.08 ± 0.03	0.47	0.44
P	2.03	0.41 ± 0.25	0.08 ± 0.03	0.43	0.45
D	0.33	0.10 ± 0.09	0.02 ± 0.00	0.08	0.13
F	0.62	0.09 ± 0.06	0.01 ± 0.01	0.11	0.14
PAH	1.12	0.16 ± 0.07	0.05 ± 0.01	0.24	0.24
SILT (%)	63.0 ± 6.6	13.0 ± 8.3	4.3 ± 2.5	35.0 ± 12.0	48.0 ± 3.1
CLAY (%)	26.0 ± 2.0	17.0 ± 7.3	6.5 ± 3.4	$30.0314.0$	$18.0311.6$
TOC (mg/g)	18.0 ± 0.7	6.2 ± 1.4	3.8 ± 1.1	10.5 ± 3.4	11.5 ± 1.3

Figure 4.15 Summary of Aromatic Hydrocarbon Concentrations, Silt and Clay Fractions, and Total Organic Carbon in East Harrison Bay Sediments.



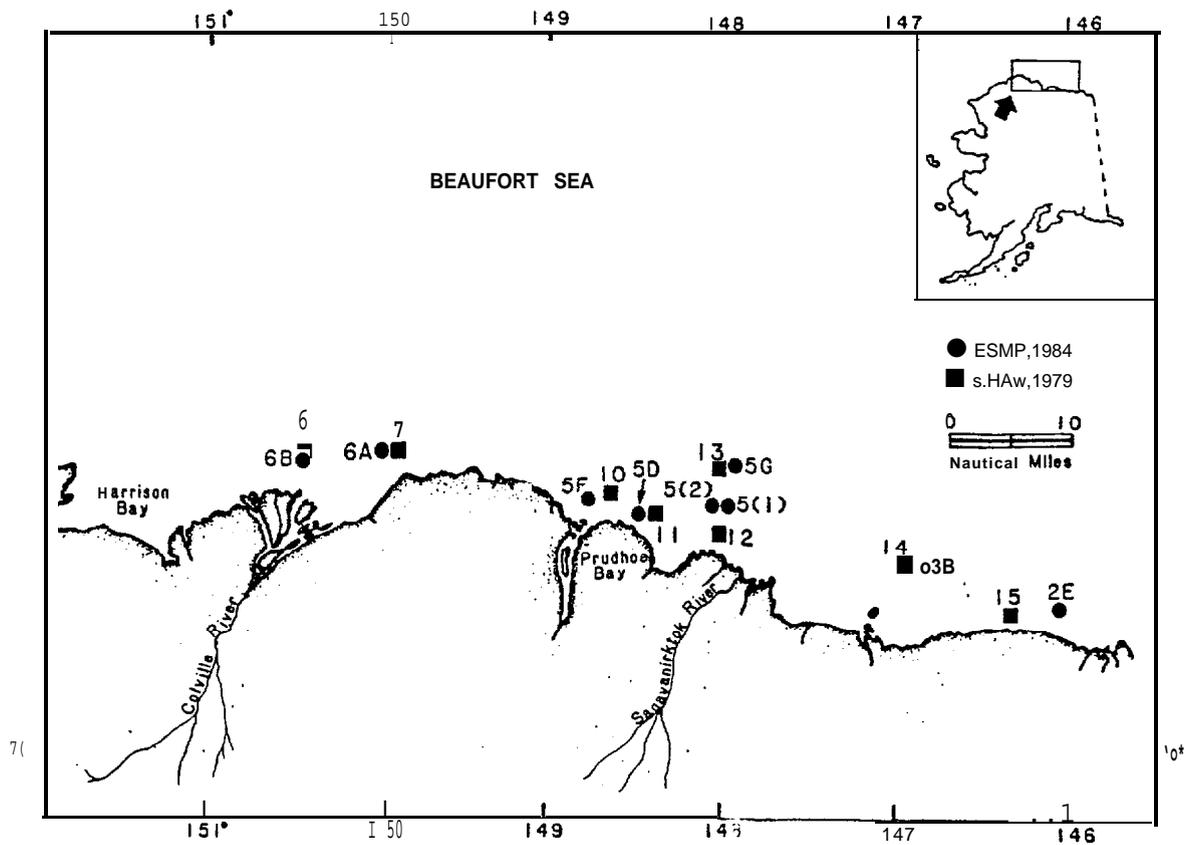
	STATION				
	7A	7B	7B	7C	7G
AROMATIC HYDROCARBONS ($\mu\text{g/g}$)					
N	0.96 \pm 0.87	0.89	0.19	0.69	0.99
P	0.76 \pm 0.66	0.51	0.18	0.61	0.58
D	0.14 \pm 0.13	0.07	0.04	0.11	0.05
F	0.12 \pm 0.11	0.07	0.04	0.12	0.01
PAH	0.24 \pm 0.13	0.22	0.11	0.32	0.20
<hr/>					
SILT (%)	58.0 \pm 4.4	58.0 \pm 4.7	8.0 \pm 2.8	44.0 \pm 2.2	8.8 \pm 0.6
CLAY (%)	7.8 \pm 1.8	13.0 \pm 1.9	5.3 \pm 2.0	41.0 \pm 2.8	1.2 \pm 0.4
<hr/>					
TOC (mg/g)	11.4 \pm 4.2	17.3 \pm 1.8	5.6 \pm 1.8	13.4 \pm 0.6	26.3 \pm 10.2

Figure 4.16 Summary of Aromatic Hydrocarbon Concentrations, Silt and Clay Fractions, and Total Organic Carbon in West Harrison Bay Sediments.



	STATION							
	6D			3A		5F		
	<u>Astarte</u>	<u>Macoma</u>	<u>Sediment</u>	<u>Astarte</u>	<u>Sediment</u>	<u>Cyrtodaria</u>	<u>Sediment</u>	
SATURATED HYDROCARBONS ($\mu\text{g/g}$)								
TALK	9.24	8.32	2.50	7.36	2.78	0.89	11.43	
LALK	1.76	0.67	1.27	0.32	0.49	0.22	1.32	
TOT	78.93	42.67	7.75	72.90	9.91	37.69	37.00	
UV/F (355 nm)	0.6 ± 0.6	0.8 ± 0.2	23 ± 7	0.1 ± 0.1	33 ± 2	1.0 ± 0.2	44 ± 2	
AROMATIC HYDROCARBONS ($\mu\text{g/g}$)								
N	0	0	0.082	0	0.143	0	0.196	
P	0	0.04	0.083	0	0.181	0	0.227	
O	0	0	0.016	0	0.021	0	0.034	
F	0	0	0.014	0	0.037	0	0.024	
PAH	0	0	0.052	0	0.088	0	0.214	

Figure 4.17 Summary of Hydrocarbon Concentrations in Bivalve Tissues and Corresponding Sediments.



STATIONS		TALK ^a ($\mu\text{g}/\text{g}$)	LALK ^b ($\mu\text{g}/\text{g}$)	LALK/ TALK	PRIS ($\mu\text{g}/\text{g}$)	PHY ($\mu\text{g}/\text{g}$)	PRIS/ PHY	OEPI ^c
BSMP, 1984	60	20.81	3.63	.17	0.305	0.144	2.1	5.7
Shaw, 1979	6	11.34	1.64	0.14	0.220	0.080	2.7	7.4
BSMP, 1984	6A	8.47	2.43	0.29	0.096	0.039	2.5	7.0
Shaw, 1979	7	9.34	0.60	0.06	0.130	0.050	2.6	2.9
BSMP, 1984	5F	11.43	1.32	0.12	0.072	0.032	2.2	7.8
Shaw, 1979	10	4.29	0.52	0.12	0.070	0.020	3.5	5.5
BSMP, 1984	5D	10.78	1.14	0.11	0.072	0.034	2.1	8.1
Shaw, 1979	11	5.78	0.54	0.09	0.070	0.030	2.3	2.7
BSMP, 1984	5(1)	1.23	0.30	0.24	0.016	0.007	2.3	5.7
BSMP, 1984	5(2)	0.68	0.27	0.40	0.008	0.003	2.7	5.5
Shaw, 1979	12	0.27	0.08	0.30	0.010	0.010	1.0	10.0
BSMP, 1984	5G	2.97	0.75	0.25	0.056	0.022	2.5	5.5
Shaw, 1979	13	1.99	0.22	0.11	0.010	0.020	0.5	3.9
BSMP, 1984	3B	4.46	0.82	0.18	0.047	0.023	2.0	7.1
Shaw, 1979	14	3.45	0.44	0.13	0.080	0.030	2.7	6.5
BSMP, 1984	2E	0.80	0.25	0.31	0.009	0.004	2.2	6.0
Shaw, 1979	15	3.72	0.45	0.12	0.090	0.030	3.0	5.1

^a BSMP, 1984 n-C₁₀ through n-C₃₄
Shaw, 1979 n-C₁₄ through n-C₃₂

^b BSMP, 1984 n-C₁₀ through n-C₂₀
Shaw, 1979 n-C₁₄ through n-C₂₀

^c Odd Even Carbon Preference Index as defined by Boehm (1983)

Figure 4.18 Summary of 1984 BSMP Survey and Historical Hydrocarbon Data.

1979) see m to show the sm allest variability in the data across all parameters. Reasonable agree m ent is seen in the data for Stations 6 A and 7 as w en, although no temporal trends can be invoked as explanation for any of the data in Figure 4.18.

4.4 Auxiliary Data

At all sediment stations, total organic carbon and grain size data were collected fro m each replicate grab. These data are used to characterize the properties of the sediments, and to supplement the interpretation and discussion of the sediment metals and hydrocarbon data. In addition, correlations between grain size, total organic carbon content, metal and hydrocarbon concentrations have been established and are discussed in Section 5.

4.4.1 Total Organic Carbon

Table 4.1 presents the data for the total organic carbon analyses. M cans \pm one standard deviation represent six replicate analyses at each station. Since total organic carbon generally has a positive correlation to sedi nent grain size, values for the combined silt and clay fractions are included in the data presentation.

The T O C range covers two order of magnitude: 2.10 mg/g at Station 5B to 29.2 m g/g at Station 5 D. The 10 w est T O C levels are generally associated with the eastern half of the Study Area. Although the highest single T O C value occurs at Station 5D (near West Dock, Prudhoe Bay), the highest area T O C levels generally occur in the West Harrison Bay area ("7" stations).

4.4.2 Grain Size

Table 4.2 presents the grain size m cans and standard deviations for the sediment replicate sa m pies at all stations. Although the analyses deter mined the individual -1 to >10 phi size categories for each sa m pie, the data are grouped into gravel, sand, silt, and clay fractions for the convenience of interpretation.

The sediment grain sizes of the Beaufort Sea appear to vary enormously by region. As can be deduced from the large standard deviations of grain size categories at many of the stations, large variations in the texture of the sediments are found even a m ong replicates of the same station. Thus, general trends in sediment co m position are difficult to infer from these data alone.

M cans for the silt and clay fractions range fro m 63 % and 40%, respectively, to 1% for both fractions. The range for the sand fraction is 11 % to 97 %, while gravel ranges between 0 % and 36%. R egionally, the sediments from stations in the eastern segment of the Study Area (the "2", "3" and "4" stations) are generally dominated by sand and gravel fractions, while combined silt and clay are most often dominant in the West Harrison Bay station sediments (the "7" stations). High percents of gravel are associated with sediments fro m Stations 4 A and 4 C (36% and 26 %, respectively).

4.5 Hydrographic Data

The hydrographic data collected on-site at all stations (except. 5D) are presented in Table 4.3. Water temperature and salinity were measured on the surface (1 m) at all stations, and at mid-depth and bottom where depth permitted. Due to instrument and/or equip m ent problems, data for dissolved oxygen are into m plete.

Salinities range fro m 16.54 ‰ at the surface to 31.78 ‰ at bottom depth. Water stratification, resulting fro m the freshwater inputs of nearby rivers, can be noted at most all stations, particularly from the salinity data and to a lesser extent by the water temperatures. A relatively fresh surface layer appears throughout the Study Area with the exception of Stations 6B and 7B, and several extremely shallow locations. (Stations 7A, 7E, 7G, 5F). The similarity in surface and bottom water te m peratures at Stations 6B and 7B may suggest recent mixing of the water colu m n, creating the saltwater wedges observed at these locations.

Table 4.1 Total Organic Carbon Means and Standard Deviations, and Percent Silt + Clay for all Sediment Stations.

STATION	TOC (mg/g)	SILT + CLAY (%)
2E	2.4 ± 0.2	7.6
2F	5.6 ± 1.0	14.7
3A	8.4 ± 0.6	41.9
3B	9.2 ± 0.5	64.8
4A	7.2 ± 1.0	32.8
4B	3.0 ± 0.8	6.5
4C	3.1 ± 1.6	16.0
5(1)	4.5 ± 0.9	9*5
5(2)	3.1 ± 1.7	3.6
5(5)	9.7 ± 4.6	36.4
5(10)	12.9 ± 9.2	33*7
5A	10.1 ± 0.2	72.4
5B	2.1 ± 0.3	3.3
5D	29.2 ± 2.1	72.5
5E	4.5 ± 3.9	25.4
5F	17.0 ± 2.2	61.3
5G	6.4 ± 1.8	17.5
6A	11.5 ± 1.3	66.5
6B	18.0 ± 0.7	88.6
6C	6.2 ± 1.4	28.5
6D	3.8 ± 1.1	10.9
6F	10.5 ± 3.4	61.5
7A	11.4 ± 4.2	65.5
7B	5.6 ± 0.8	13.3
7C	13.4 ± 0.6	84.6
7E	17.3 ± 1.8	68.2
7G	26.3 ± 10.2	10.1

Table 4.2 Summary of Grain-Size Data for all Sediment stations.

STATION	Sediment Type			
	% GRAVEL	% SAND	% SILT	% CLAY
2E	0.22 ± 0.20	92.00 ± 1.60	4.64 ± 0.68	2.95 ± 0.80
2F	0.04 ± 0.07	84.84 ± 3.55	10.12 ± 2.99	4.58 ± 1.50
3A	0.01 ± 0.02	58.03 ± 1.79	28.18 ± 1.57	13.77 ± 1.15
3B	0.30 ± 0.59	34.46 ± 4.22	46.39 ± 3.30	18.45 ± 1.22
4A	36.44 ± 19.76	29.91 ± 5.16	16.97 ± 6.71	15.80 ± 10.51
4B	3.19 ± 6.33	89.17 ± 5.89	3.48 ± 1.57	3.05 ± 2.09
4C	26.09 ± 19.05	56.88 ± 22.90	8.73 ± 3.31	7.29 ± 4.01
5(1)	1.08 ± 1.62	88.01 ± 1.80	5.34 ± 1.99	4.21 ± 1.27
5(2)	0.01 ± 0.01	96.41 ± 1.21	1.77 ± 0.42	1.86 ± 0.54
5(5)	0.32 ± 0.28	63.77 ± 2.42	23.73 ± 2.70	12.66 ± 3.14
5(10)	0.03 ± 0.06	65.07 ± 14.71	22.44 ± 8.53	11.23 ± 3.36
5A	0.05 ± 0.10	27.55 ± 9.99	51.02 ± 8.84	21.72 ± 1.96
5B	0.01 ± 0.02	96.92 ± 0.95	1.72 ± 0.47	1.60 ± 0.97
5D	1.01 ± 1.33	25.70 ± 2.60	58.92 ± 3.63	13.56 ± 1.26
5E	2.18 ± 1.84	68.50 ± 36.74	9.41 ± 10.53	15.96 ± 23.41
5F	4.57 ± 5.59	34.08 ± 7.43	51.00 ± 4.28	10.35 ± 2.20
5G	0.08 ± 0.16	81.58 ± 3.05	9.72 ± 1.50	7.78 ± 1.56
6A	0.24 ± 0.18	33.47 ± 3.50	48.65 ± 23.02	17.85 ± 1.58
6B	0	11.37 ± 8.48	62.80 ± 5.62	25.80 ± 1.55
6C	0.16 ± 0.16	69.00 ± 15.53	12.29 ± 7.93	16.18 ± 7.27
6D	0.10 ± 0.18	89.03 ± 5.80	4.33 ± 2.25	6.54 ± 3.02
6F	0.34 ± 0.38	34.83 ± 26.53	32.86 ± 11.88	28.62 ± 13.42
7A	0.01 ± 0.03	34.58 ± 5.60	58.05 ± 4.12	7.46 ± 1.80
7B	0	86.68 ± 4.52	8.02 ± 2.83	5.30 ± 1.96
7C	0.35 ± 0.56	15.07 ± 1.79	44.42 ± 1.93	40.17 ± 2.61
7E	0.51 ± 1.01	31.72 ± 2.88	54.95 ± 4.05	13.26 ± 1.55
7G	0	89.95 ± 1.01	8.83 ± 0.57	1.24 ± 0.38

Table 4.3 Hydrographic Data for 1984 BSMP Survey

Station	Station Depth (m)	TEMPERATURE °C			SA LINITY (‰)			DISSOLVED OXYGEN (ppm)		
		Surface	Mid	Bottom	Surface	Mid	Bottom	Surface	Mid	Bottom
2E	7*5	-0.4/1m	-1.2/3m	-1.3/6m	22.44	30.69	31.27			
2F	2.0	-0.9/1m		-0.5/2m	21.10		25.56			
3A	6.0	-0.4/1 m	-0.7/3m	-1.0/5 m	23.57	25.99	28.65			
3B	4.0	-0.5/1 m	-0.5/2m	-0.5/3 m	23.71	24.07	26.28			
4A	5.0	2.1/1m		1.6/4m	18.88		18.95	12.1		12.5
4B	8.0	1.5/1m	1.4/4m	0.2/7 m	19.02	19.08	26.52	13.5	13.3	13.4
4C	9.0	-0.2/1 m	-0.4/5 m	-0.7/9 m	17.43	24.14	29.52	13.0	13.4	13.7
5A	12.0	0.0/1 m	-1.2/6 m	-1.2/11m	22.37	31.13	31.64			12.6 ^a
5B	16.5	-0.3/1 m	-1.2/8 m	-1.3/15m	25.20	29.38	31.78			12.2 ^a
5D										
5E	18.0	-0.4/1 m	-1.2/9 m	-1.2/17 m	24.85	30.83	31.64			
5F	2.0	-0.6/1 m			28.22					
5G	9.0	-0.6/1 m	-1.0/5m	-1.0/8m	22.72	30.18	31.64			11.9 ^a
5(1)	5.5	-0.2/1 m	-0.2/3m	-0.9/5 m	23.57	23.78	30.03			
5(2)	5.5	-0.3/1 m	-0.4/3 m	-0.8/5 m	23.50	23.71	30.47			12.6 ^a
5(5)	7.0	-0.4/1 m	-0.5/3m	-0.8/6 m	23.57	23.50	30.03			
5(10)	9.0	-0.3/1 m	-0.6/4m	-1.1/7.5m	22.09	28.58	31.56			12.7 ^a
6A	3.0	2.2/1 m		0.1/2 m	17.64		30.47	12.0		13.0
6B	6.0	0.5/1 m		0.4/5 m	29.96		30.32	12.1		11.8
6C	15.0	0.6/1 m	0.0/7 m	-0.6/14m	17.50	23.00	30.62	12.2	12.8	13.8
6D	18.0	0.6/1m	-0.5/9 m	-0.8/17 m	17.16	27.28	31.34			
6F	13.0	0.3/1 m	-0.1/6m	-0.5/12m	19.71	28.44	31.34			
7A	2.0	2.0/1 m			16.54					
7B	6.0	0.6/1 m	0.6/3m	0.5/5 m	21.52	21.52	22.86			
7C	15.0	0.6/1 m	0.37 m	-0.7/14m	17.70	31.20	31.71			
7E	3.0	1.9/1m		1.9/3m	20.06		20.06			
7G	3.0	1.2/1m		1.2/5 m	23.71		23.71			

aA analyzed by Winkler Titration Method.

Blanks indicate no sample was analyzed

The fluctuations in water temperatures are small with changes in depth as well as between stations. Temperatures range between -1.3°C and 2.2°C. The dissolved oxygen data, although limited, suggest well-oxygenated waters throughout the water column. Values for dissolved oxygen range between 11.8 ppm and 13.8 ppm.

4.6 Quality Control Results

4.6.1 Metals

Accuracy was determined by analyzing Standard Reference Materials (SRM) sediment standard MESS-1 and oyster tissue NBS-SRM 1566. Results for analysis of five replicates of these standards and the certified or best values are shown in Tables 4.4 and 4.5. Generally the range of values obtained overlaps with the range of best values, verifying that the methods employed are accurate.

Analytical precision was also determined by analyzing replicates of the SRM (Table 4.4 and 4.5). The precision (coefficient of variation, CV) for metals in sediment is 10% or less. With the exception of Cr which showed greater variability, the precision is also excellent for tissue samples.

Detection limits were calculated from the procedural blanks by using twice the standard deviation of the mean for replicate procedural blanks (Tables 4.6 and 4.7). The detection limits were mostly in the range of tenths to several ppm dry weight and did not prevent quantification of metals in samples. Reagent blanks were determined before the field samples were analyzed to verify that detection limits would not be adversely affected by reagents (Tables 4.8 and 4.9).

Because Ba in sediments can be a difficult metal to dissolve, approximately 10% of the sediment samples were analyzed by both XRF and ICP. The XRF technique does not require sediment dissolution. The results of the technique comparisons are shown in Table 4.10. The means of five replicate field grab samples are within two standard deviations for the different techniques.

4.6.2 Hydrocarbons

The hydrocarbon QC program consisted of the analysis of procedural blanks, blank spikes, the reextraction of samples, and the analysis of a National Oceanic and Atmospheric Administration/National Analytical Facility (NOAA/NAF) reference sediment. Blanks analyzed by UV/F at 312 and 355 nm emission wavelength yielded total laboratory background concentrations between 0 and 35.6 µg Prudhoe Bay oil equivalent which, when divided by a sample weight (e.g., 150 g of sediment) are within an acceptable range. Some of this background at 312 nm may be due to the o-terphenyl internal standard. The same blanks analyzed by GC-FID showed a series of small peaks (probably phthalic acid esters) eluting around n-C 25. Potential interferences from these components were considered minimal.

Blank spikes consisted of a mixture of n-alkanes (range n-C 10 to n-C 34) and a 1-ml ampule of NBS-SRM 1647 (PAH in acetonitrile). Recoveries of the n-alkanes, calculated versus added androsane internal standard, ranged between 50 and 100%, with lower recoveries associated with the more volatile components. Recoveries of individual PAH in NBS-SRM 1647 are listed in Table 4.11. Recoveries of several PAH were low and somewhat variable. Steps have now been taken to modify analytical procedures (in particular solvent concentration methods, which are a major source of volatilization losses) in order to gain higher and more uniform PAH recoveries.

In order to determine the adequacy of the extraction methods, sediment samples were reextracted and found to contain between 0.01 and 0.09 µg/g dry weight total saturated hydrocarbons, indicating that the extraction method employed thoroughly extracted all hydrocarbons.

Four sediments were fortified with Prudhoe Bay crude oil following initial extraction, then reextracted and analyzed by UV/F to determine total oil concentrations. The results, shown in Table 4.12, indicate recovery of the spike ranges between 60 to 75%.

Table 4.4 Analysis of Replicate Samples of Mess-1, a Standard Reference Sediment.

	METALS (ppm Dry Weight)						
	Ba	Cd	Cr	Cu	Pb	v	Zn
	270	0.720	63	23	35.4	77	161
	270	0.740	62	29	31.9	81	168
	284	0.760	62	26	33.5	79	171
	279	0.685	64	24	37.9	77	176
	279	0.631	66	27	34.5	81	176
	275	0.667	64	30	36.5	81	170
	273	0.707	64	24	32.7	77	164
	275	0.706	63	28	32.7	84	167
Mean	275	0.702	64	26	34.4	80	169
S.D. ^a	4.8	0.041	1.3	2.6	2.1	2.6	5*3
CV(%) ^b	2	6	2	10	6	3	3
Best Value ^c	270	0.59	71	25.1	34.0	72.4	191
S.D.		0.10	11	3.8	6.1	5*3	17

^a Standard Deviation

^b Coefficient of Variation

^c Values reported by the Marine Analytical Chemistry Standards Program, National Research Council, Canada

Table 4.5 Analysis of Replicate Samples of Oyster Standard 1566, a Standard Reference Tissue.

	METALS (ppm Dry Weight)						
	Ba	Cd	Cr	Cu	Pb	V	Zn
	4*43	3.84	0.69	59*7	0.50	1.34	823
	4.78	4.05	.86	59.2	0.50	0.94	815
	5.48	4.16	2.01	59.7	0.46	1.14	832
	4.98	3*95	3.88	59.7	0.46	1.14	827
	5*33	3.89	0.75	58.7	0.46	1.14	827
Mean	5.00	3.98	1.64	59.4	0.48	1.14	8.25
S.D.	0.42	0.13	1.36	0.5	0.02	0.14	6
CV(%)	8	3	83	1	5	12	1
Best Value	N/A	3.5	0.69	63.0	0.48	N/A	852
S.D.		0.4	0.27	395	0.04	-	14

N/A = Not Available.

Table 4.6 Analysis of Replicate Procedural Blanks for Sediment Digestion.

	METALS (ppm Dry Weight)						
	Ba	Cd	Cr	Cu	Pb	v	Zn
	1.8	0.100	8.6	1.60	1.60	1.0	3.0
	1.6	0.100	8.4	0.80	1.60	1.80	4.0
	1.8	0.100	9.2	0.80	1.60	1.60	3.8
	1.6	0.100	9.2	0.40	1.28	1.0	3.4
	2.0	0.100	10.0	0.80	1.60	1.6	10.0
Mean	1.8	0.100	9.08	0.88	1.54	1.4	4.84
S.D.	0.17	0.0	0.63	0.44	0.14	0.37	2.91
CV (%)	9	0	7	50	9	27	60
Detection Limit	0.4	0.04	1.2	0.9	0.3	0.4	6.0

Table 4.7 Analysis of Replicate Procedural Blanks for Tissue Digestion.

	METALS (ppm Dry Weight)						
	Ba	Cd	Cr	Cu	Pb	v	Zn
	0.040	0.053	0.04	0.40	0.55	0.80	0.90
	0.040	0.053	0.07	0.40	0.50	2.20	1.00
	0.060	0.107	0.07	1.00	0.55	1.00	1.00
	0.040	0.053	0.08	0.40	0.50	0.80	1.00
	0.040	0.053	0.09	0.40	0.55	0.80	1.00
Mean	0.044	0.064	0.07	0.52	0.53	1.12	0.98
S.D.	0.009	0.024	0*02	0.27	0.03	0.61	0.05
CV (%)	20	38	27	52	5	54	5
Detection Limit	0.01	0.04	0.04	0.5	0.06	1.2	0.1

Table 4.8 A nalysis of Replicate Sam ples of Reagents to Establish Reagent Blank for Sedim ent Digestion.

	METALS (ppm Dry Weight)						
	Ba	Cd	Cr	Cu	Pb	v	Zn
	6.0	0.100	2.6	700	1.92	10.0	8.1
	5.0	0.120	2.6	3.0	1.60	6.0	7.0
	<u>5.0</u>	<u>0.140</u>	<u>2.4</u>	<u>3.0</u>	1.92	<u>5.0</u>	7.0
Mean	5.3	0.12	2.5	4.3	1.81	7.0	7.4
S.D.	0.58	0.02	0.12	2.3	0.18	2.65	0.64
CV (%)	11	17	5	54	10	38	9

Table 4.9 Analysis of Replicate Samples of Reagents to Establish Reagent Blank for Tissue Digestion.

	METALS (ppm Dry Weight)						
	Ba	Cd	Cr	Cu	Pb	v	Zn
	0.2	0.107	.04	0.2	0.50	0.4	0.4
	0.2	0.160	.07	0.2	0.63	1.1	0.5
	<u>0.3</u>	<u>0.040</u>	<u>.07</u>	<u>0.5</u>	0.55	<u>0.5</u>	0.5
Mean	0.23	0.10	0.06	0.3	0.56	0.67	0.47
S.D.	0.05	0.06	0.02	0.14	0.07	0.31	0.05
CV (%)	22	60	29	47	12	46	10

Table 4.10 Comparison of Techniques for Determination of the Concentration of Metals in Sediments.

	METALS			
	Ba	Cu	Pb	Zn
<u>Station 5(1) (5 Replicate Field Grab Samples)</u>				
Mean XRF	235	14.4	7.06	41.7
S.D.	18	2.7	1.30	3*9
Mean ICAP	237	9.0		34.6
S.D.	18	2.7		2.2
Mean ZGFAA			4.92	
S.D.			0.33	
<u>Station 5A (5 Replicate Field Grab Samples)</u>				
Mean XRF	456	23.2	10.52	86.2
S.D.	167	2.8	2.06	5.3
Mean ICAP	541	20.6		65.4
S.D.	74	1.1		5.4
Mean ZGFAA			9.13	
S.D.			0.87	

Table 4.11 Recoveries of PA H Contained in NBS-SR 14-1647 Subjected to Hydrocarbon Analytical Scheme. Data Reported Relative to o-Terphenyl Internal Standard.

	Percent Recovery Relative to o-Terphenyl					x	±	sd
	1	2	Replicate No.		5			
			3	4				
Naphthalene	30	24	11	30	22	23	±	8
Fluorene	64	62	141	69	58	79	±	35
Phenanthrene + Anthracene	131	131	92	132	116	120	±	17
Fluoranthene	46	48	60	53	43	50	+	7
Pyrene	48	49	62	55	43	51	±	7
Benzo(a)anthracene	38	45	122	48	37	58	±	36
Chrysene	43	46	112	51	38	58	±	31
Benzo(a)fluoranthene	95	119	81	113	97	101	±	15
Benzo(a)pyrene	30	38	86	30	30	43	±	24

Table 4.12 Analytically-Determined U V/F Total Oil Concentrations in Sedim ents Fortified with Varying Concentrations of Prudhoe Bay Crude Oil.

Sample Replicate	Concentration Added ($\mu\text{g/g}$ dry weight)	UV/F (312 nm) Concentration ($\mu\text{g/g}$ dry weight)	UV/F (355 nm) Concentration ($\mu\text{g/g}$ dry weight)
1	181.8	136.2	145.7
2	149.0	94.7	94.7
3	228.8	135.5	145.9
4	148.4	9 3 * 5	97.6

The concentration of **total** saturated hydrocarbons and selected hydrocarbon parameters in the N O A A/N A F reference sediment samples are shown in Table 4.13. Since the **values** determined by the N O A A/N A F are not known, we are unable to comment on the agreement of our data with those of N O A A laboratories. However, it is evident from Table 4.13 that excellent agreement was attained among the three replicates analyzed, indicating good analytical precision. A similar conclusion can be derived from the concentration of individual **n-alkanes** (Table 4.14) and P A H (Table 4.15). Since no S R M was included in the analyses, a determination of accuracy could not be made in this sample set.

4.6.3 Total Organic Carbon

Table 4.16 presents the results of the Q C data obtained for the **total** organic carbon analyses. Single replicate samples from two stations were randomly chosen and split. Three analyses were performed on **each** sample to determine **reproducibility** of the analytical method. As can be noted from the data, variability between splits is minimal and indicates acceptable analytical precision.

Since no S R M or spiked samples were analyzed, accuracy could not be determined.

4.6.4 Grain Size

The quality control program maintained by sediment laboratory is part of a Battelle laboratory-wide Q C program. **Project-specific** measures carried out include documentation of sample custody and data handling, reagent Q C checks, and the analysis of numerous split samples to ascertain method **variability**.

Table 4.17 presents results of nine duplicate sediment grain size analyses performed during the course of the analytical work. These data indicated that, for the wide range of sediment textures analyzed, reproducibility of the methods is acceptable. As can be expected, the greatest variability occurs in the -1 phi category (gravel). In the higher phi classes (or smaller grain sizes), less variability between split samples is observed.

Since no S R M was included in the analyses, a determination of accuracy could not be made in this sample set.

5. ANALYSIS AND INTERPRETATION OF DATA

5.1 Introduction

The task of analyzing and interpreting the data consisted of two basic approaches. The first approach dealt with an examination of the data from **geochemical** and **biogeochemical** perspectives. In this approach, spatial distributions of metals and hydrocarbons were examined along with compositional aspects of the data which suggested generic sources of observed distributions. It is the **geochemical** perspective which sets up the framework for null hypothesis testing, insofar as the interpretation of the data suggests key diagnostic parameters and parameter ratios to be used in hypothesis testing.

The second interpretive approach was a **statistical one** which, during the **Year 1** program, examined the statistical aspects of the data set, including the **within-station** variability in the key parameters and parameter ratios. Thus, the statistical analysis was geared towards determining what degree of change might be detectable given the **variability**, and the **existing** and **alternate** replication schemes.

5.2 Metals Chemistry

During the **first** year of this program, we have established the concentrations of seven metals in sediments collected during September 1984 from the **Beaufort** Sea continental shelf. Sediments were collected and **analyzed** from 27 stations with 6

Table 4.13 Concentrations of Total. Saturated Hydrocarbons (F 1) and Selected Hydrocarbon Parameters in N O A A Reference Sediments.

Parameter	Replicate No.			\bar{x}	\pm	sd
	1	2	3			
Total Saturated Hydrocarbons ($\mu\text{g/g}$ dry weight)	10.39	10.89	9*93	10.40	+	0.48
% Resolved	15	15	14	15	\pm	1
% Unresolved	85	85	86	85	\pm	1
Pris/n- C 17	0.70	0.61	0.62	0.64	\pm	0.05
Phy/n- C 18	0.29	0.22	0.26	0.26	\pm	0.03
Pris/Phy	1.21	1.73	1.45	1.46	\pm	0.26
O E PI ^a	6.44	5.91	5.87	6.07	\pm	0.32

^a Odd Even Predominance Index as defined by Boehm (1984).

Table 4.14 Concentrations of n- Alkanes in N O A A Reference Sediment.

n-Alkane Carbon No.	Concentration (rig/g dry wt.)					
	Replicate No.			\bar{x}	\pm	sd
	1	2	3			
10	8	3	3	5	+	3
11 ^a	308	357	285	317	+	37
12	3	4	3	3	+	1
13	4	4	4	4	+	0
14	3	5	4	4	+	1
15	9	10	10	10	+	1
16	24	21	20	22	+	2
17	9	12	11	11	+	2
18	18	18	8	15	+	6
19	16	12	15	14	+	2
20	8	8	8	8	+	0
21	50	50	48	49	+	1
22	18	14	12	15	+	3
23	26	20	17	21	+	5
24	26	16	14	19	+	6
25	41	34	30	35	+	6
26	30	23	20	24	+	5
27	75	73	62	70	+	7
28	38	34	29	34	+	4
29	160	178	149	162	+	15
30	6	28	23	19	\pm	12
31	237	267	220	241	+	24
32	24	22	19	22	+	3
33	90	113	75	93	+	19

a Elevated value due to contamination.

Table 4.15 Concentrations of Polycyclic Aromatic Hydrocarbons (PAH) in NOAA Reference Sediment.

Compound	Concentration (ng/g dry wt.)					
	Replicate No.			\bar{x}	\pm	sd
	1	2	3			
Naphthalene	1	2	3	2	+	1
C 1-Naphthalenes	1	2	1	1	+	1
C 2-Naphthalenes	1	2	2	2	+	1
C 3-Naphthalenes	1	2	1	1	+	1
C 4-Naphthalenes	ND	ND	ND			
Biphenyl	<1	1	3			
C 1-Biphenyls	<1	<1	<1			
C 2-Biphenyls	ND	<1	ND			
C 3-Biphenyls	ND	ND	ND			
C 4-Biphenyls	ND	ND	ND			
Phenanthrenes	3	4	2	3	\pm	1
C 1-Phenanthrenes	6	8	5	6	\pm	2
C 2-Phenanthrenes	4	7	4	5	\pm	2
C 3-Phenanthrenes	1	3	1	2	\pm	1
C 4-Phenanthrenes	1	1	<1			
Dibenzothiophene	<1	<1	<1			
C 1-Dibenzothiophene	<1	1	<1			
C 2-Dibenzothiophene	1	2	<1			
C 3-Dibenzothiophene	ND	1	ND			
Fluoranthene	6	10	6	7	+	2
Pyrene	8	11	8	9	+	2
Benzo(a)anthracene	3	13	3	6	+	6
Chrysene	5	12	4	7	+	4
Benzofluoranthene	25	56	25	35	+	18
Benzo(a)pyrene	9	20	9	13	+	6
Benzo(e)pyrene	6	18	6	10	+	7-
Perylene	41	61	43	48	+	11

Table 4.I6 Quality Control Data for Total.
Organic Carbon Analyses.

<u>STATION 7E-1005</u>	<u>TOC (mg/g)</u>
Split A	18.2
Split B	15.9
split c	18.9

<u>STATION 7G-1006</u>	
Split A	16.9
Split B	17.8
split c	28.2

Table 4.17 Quality Control Data for Grain Size Analysis.

ϕ	STATION 4A-1003		STATION 5(1)-1001		STATION 5B-1003	
	A	B	A	B	A	B
-1	38.79	58.86	0.33	0.06	0	0
0	4.91	3.60	0.75	0.53	0.04	0
1	4.43	3.46	2.19	2.58	0.46	0.47
2	10.72	7.37	11.14	11.89	16.45	17.42
3	8.82	5.94	60.97	60.59	77.28	76.19
4	3.13	2.12	12.16	10.53	3.37	3.42
5	4.21	2.09	2.08	3.00	1.91	2.00
6	3.98	2.65	2.61	2.33	0	0
7	3.98	2.76	1.47	2.04	0	0
8	3.48	2.38	1.49	1.39	0	0
9	4.01	2.06	1.13	0.88	0.48	0.52
10	1.55	1.39	0.90	1.31	0	0
>10	7.99	5.32	2.79	2.88	0	0

ϕ	STATION 6F-1004		STATION 5E-1 003		STATION 2F-1007	
	A	B	A	B	A	B
-1	0.91	0.47	4.92	2.52	0	0
0	0.47	0.08	2.20	1.84	0	0.02
1	0.68	0.28	11.11	11.42	0.07	0.07
2	0.48	0.50	15.49	17.76	1.53	1.46
3	1.38	1.25	34.66	37.11	42.87	41.73
4	14.36	11.77	8.36	8.11	37.42	35.13
5	7.58	12.24	1.54	0.56	3.63	4.80
6	11.67	9.36	2.22	2.95	4.16	4.38
7	13.53	13.70	3.20	2.64	2.99	3.80
8	10.93	11.04	3.70	3.71	1.71	2.42
9	8.73	9.90	3.17	3.37	1.83	1.59
10	6.87	8.22	2.70	1.64	0.65	1.03
>10	22.42	21.18	6.73	6.36	3.11	3.58

ϕ	STATION 5F-1003		STATION 7A-1001		STATION 7E-1001	
	A	B	A	B	A	B
-1	4.92	2.52	0	0	2.02	0
0	2.20	1.84	0.09	0.10	0.38	0.38
1	11.11	11.42	0.22	0.19	0.61	0.71
2	15.49	17.76	0.26	0.38	1.34	1.60
3	34.66	37.11	1.82	1.90	4.06	3.92
4	8.36	8.11	26.19	27.21	28.30	25.98
5	1.54	0.56	39.88	37.94	25.97	30.88
6	2.22	2.95	13.80	13.16	12.66	11.86
7	3.20	2.64	4.68	5.18	6.72	6.84
8	3.70	3.71	3.65	3.95	4.03	4.96
9	3.17	3.37	2.99	2.62	2.62	2.74
10	2.70	1.64	1.26	1.81	1.41	1.94
>10	6.73	6.36	5.16	5.57	9.88	8.19

replicate grabs per station analyzed for metals. The mean, range, standard deviation, and other measures of within-station variance for metals are presented in Section 4. The concentrations of metals are similar to those reported for other sandy and muddy continental shelf sediments from both Alaska and other coastal regions of the United States. The within-station variances are often in the range of 4-15% for coefficients of variation (C V), although occasionally the C V exceeds 30%.

The correlations between metals, T O C, and sediment grain size indicate approximately 50% of the variability in the metal concentrations can be predicted by either T O C, silt, or clay content. These three parameters are about equally positively correlated with metal concentrations. Usually, the stations with high C V for metals also have high variance for T O C and grain size. This indicates that within-station variability will be the factor that limits our ability to resolve differences between stations and resolve temporal trends (see Section 5.4).

5.2.1 Sediment Sources and Dynamics

During the last 20 years there have been several studies that investigated the sources and movement of sediments in the Beaufort Sea. The major riverine source of sediment is the Colville River which enters eastern Harrison Bay (Carlson, 1976). Most of the river-borne sediments are deposited in deltas or lagoons (Naidu et al., 1982). Shoreline erosion is the other source of sediment to the area, estimated at 1-4 m /yr along some regions of the coast (Hume and Schalk, 1967; Short et al., 1974).

The prevailing easterly winds transport both river plumes and resuspended nearshore sediments westward during the open-water season. Westerly storms, which occasionally occur during summer and fall, can be important in the easterly transport of nearshore sediments (Dygas and Burrell, 1976). Ice-scouring and sediment rafting may also be important sediment transport processes.

5.2.2 Relationships Between Metals and Properties of Sediment

The broad regional variations in grain size, T O C and metals of the Beaufort Sea surface sediments have been discussed by Naidu et al. (1982). The general pattern they observed is an increase in % mud (silt + clay) in sediment, T O C, and heavy metals with distance offshore. Generally, the middle and outer continental shelf areas are carpeted by poorly sorted sandy muds. The inner shelf and bay sediments are mainly silty sand and sandy silt with minor amounts of clay and gravel. The gravel on the outer shelf sediments may be relict deposits, indicating that much of the mud transport on the shelf is apparently bypassing the shelf area and depositing in deeper water. The poorly sorted sediments on the shelf are probably a result of mixing by ice gouging and bioturbation.

The correlation coefficient for metals, silt, clay, and T O C are all relatively high. These correlations indicate the metals are either associated with the organic matter in the sediment, the clay minerals or the coatings on the sediment particles. Metals correlate approximately the same with either grain size as T O C. (A correlation matrix is presented in Section 5.4).

The relationships between Ba, % mud, and % T O C are shown in Figures 5.1 and 5.2. The line in these figures is the least squares linear relationship. The mean concentrations for 27 sediment stations were used to establish these relationships. Also plotted on these figures are the mean and standard deviation for four regions of the Beaufort Sea Study Area. Based on these data, the present concentrations and distributions of Ba in the sediments appear to be controlled by grain size and T O C.

The relationship between V and % mud (Figure 5.3) has a correlation coefficient 0.86. The regional differences in V appear to be related to grain size, as well. Sediments from Station 6B in East Harrison Bay contained the highest metal concentrations and the highest silt plus clay content. Station 6B is nearest the Colville River delta. Other stations in both East Harrison Bay (6A-6F) and West Harrison Bay (7A-7G) which contain high concentrations of silt and clay are similarly high in concentrations of metals. However, stations with relatively low silt and clay contents (e.g., 6D) contain lower metal concentrations.

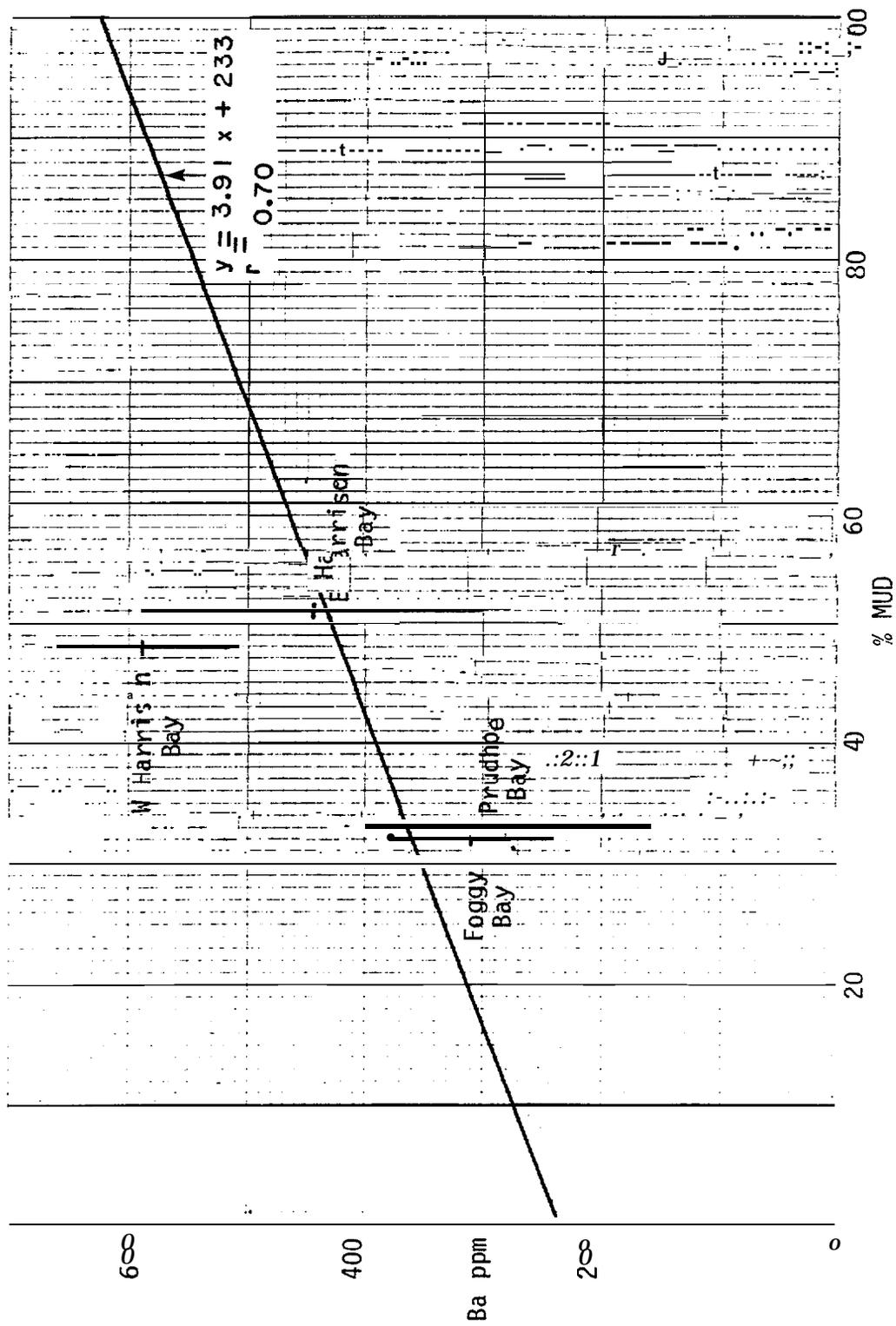


Figure 5.1 The Linear Correlation Between Total Barium and Percent Mud (Silt Plus Clay) in 27 Surface Sediments from the Beaufort Sea.

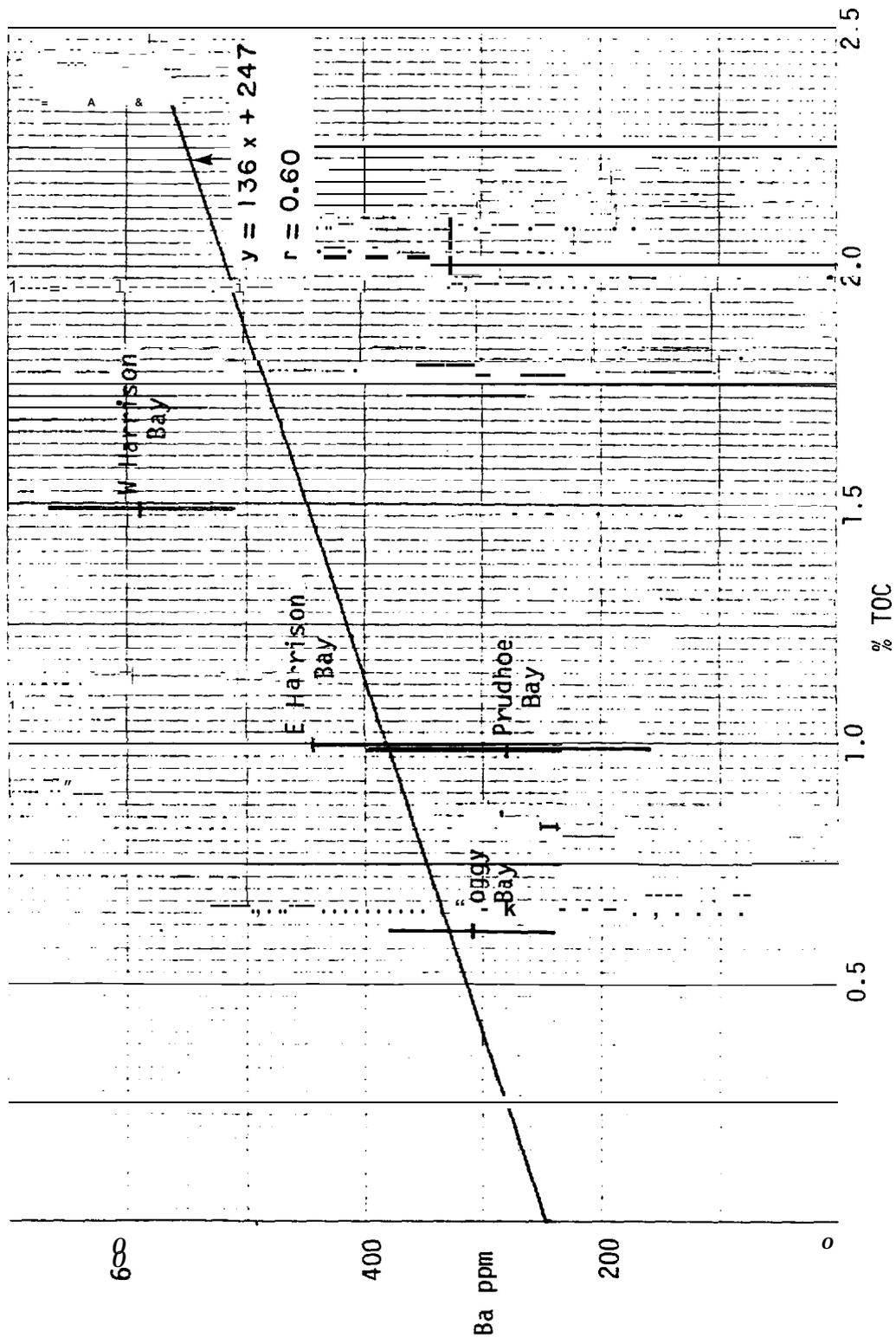


Figure 5.2 The Linear Correlation Between Total Barium and Percent TOC in 27 Surface Sediments from the Beaufort Sea.

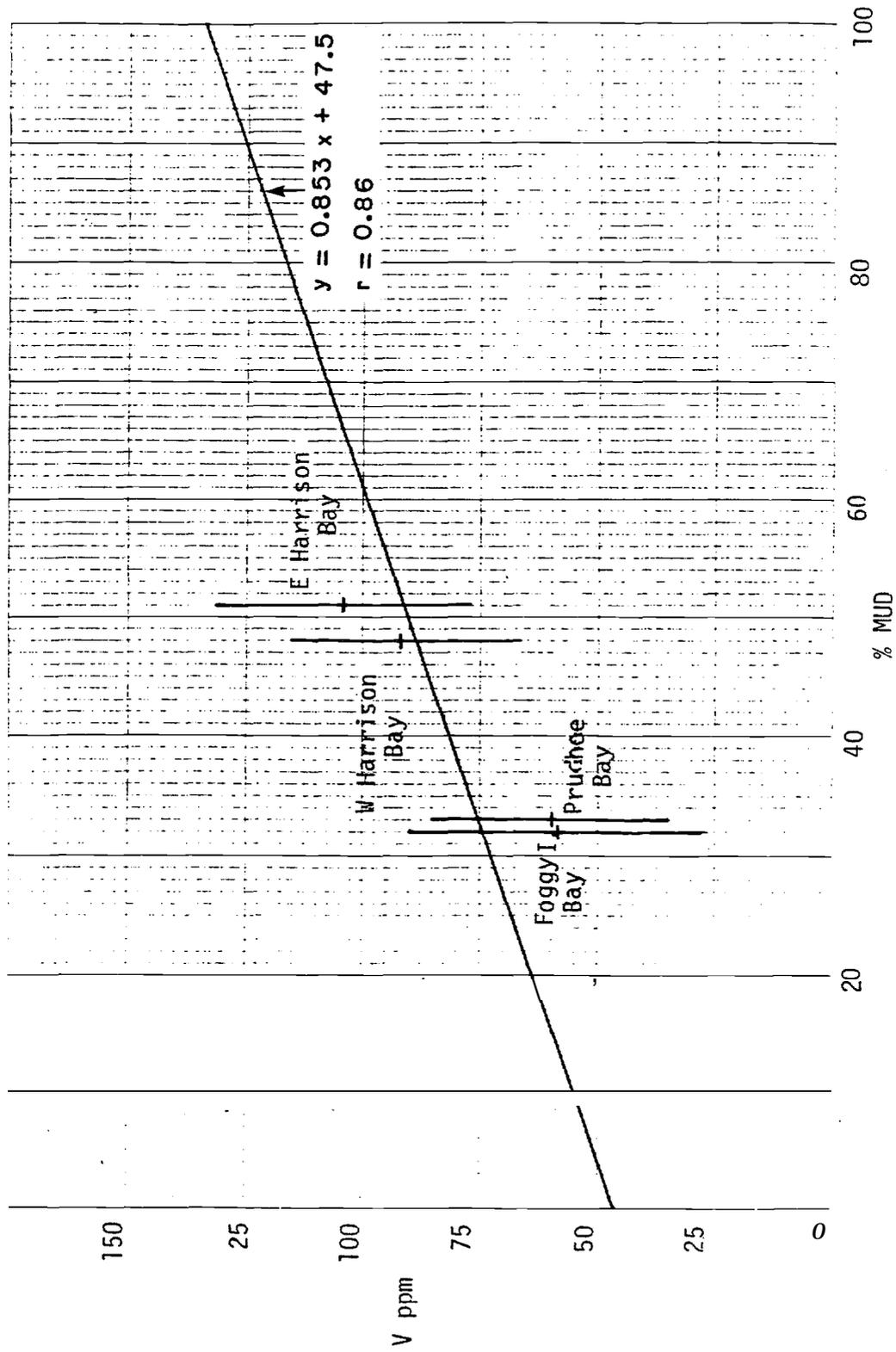


Figure 5.3 The Linear Correlation Between Total Vanadium and Percent Mud in 27 Surface Sediments from the Beaufort Sea.

5.2.3 Comparison of Metals Chemistry with Historical Data

The concentrations of metals reported by this study are similar to values reported by Robertson and Abel (1979) and Naidu et al. (1982) for the Beaufort Sea and by Campbell and Loring (1980) for Baffin Bay in the Canadian Arctic. There are considerable ranges in metal concentrations shown in Table 5.1 due to both variation in sediment texture and possible differences in analytical techniques. All sediment chemistry studies in the Arctic have reported the strong positive correlation between increasing metals content and decreasing particle size. For example, Campbell and Loring (1980) report the correlation coefficient for Cu with % mud, nearly identical to that determined in the present study; $r=0.76$ and $r=0.85$, respectively.

The metal concentrations in Beaufort Sea sediments are in the range of those reported for similarly textured sediments on both the East and West coast of the United States (Bothner et al., 1983; Katz and Kaplan, 1981).

5.2.4 Geographical Trends

Based on the data for the 27 stations sampled, there do not appear to be geographical trends in the concentration of metals in the sediments other than those differences attributable to changes in T O C and grain size. The mean sediment concentrations of metals, T O C and mud in four regions of the Beaufort Sea are shown in Table 5.2. There is almost no difference in the concentrations of Cd, Cr, Cu, and Zn in the four regions. There are increases in the concentrations of Ba, Pb, V, T O C and mud in the sediments from East Harrison Bay area (the "6" stations) and West Harrison Bay stations (the "7" stations) compared to the Foggy Island Bay (the "3" and "4" stations) and Prudhoe Bay (the "5" stations) sediments. The concentrations of metals in the two stations from West Camden Bay are not included in Table 5.2 but are similar to those determined for stations near Foggy Island and Prudhoe Bay. These limited data suggest that either there are no major differences in the chemical composition of sediments supplied to the Beaufort Sea by rivers and shoreline erosion or the differences in composition are lost as the sediments are mixed and dispersed on the shelf. There maybe a significant trend of increasing T O C toward the west that is not due to grain size. The sources of the T O C are probably the rivers and shoreline erosion.

5.2.5 Metals in Bivalve Tissues

The mean concentrations of metals in bivalve tissue are listed in Table 5.3. Because of the difficulties in collecting adequate numbers of bivalves only three stations were analyzed for metals. The mean concentrations and standard deviations represent either three or five replicate analyses. Each sample was a composite of 5-10 individual bivalves. The standard deviations are usually about $\pm 25\%$ of the mean, indicating that means which differ by a factor of two may be significantly different.

The only metal that appears to vary between species is Cd which is approximately six times higher in Astarte than in Cyrtodaria. There appear to be between-station differences in metal concentrations for Astarte, particularly for Cu. Three metals (Cu, Zn and Cd) are present in bivalve tissues in concentrations equal to or greater than the concentration of metals in the sediments from which the bivalves were collected. Both Cu and Zn, which are necessary micronutrients to animals, are present in tissue at approximately the sediment concentrations. Cd, which has not been demonstrated to be a necessary element, is bioaccumulated in the tissue to between 7-15 times the concentration in the sediment. The other four metals (Ba, Cr, V and Pb) are approximately 10 times lower in tissue than in sediment. If the bivalves were bioaccumulating metals from sediment there could be a correlation between tissue and sediment concentrations. There is no obvious relationship between the concentration of a given metal in tissue and sediment. However, the data are limited to sediments that were sandy and similar in metal content.

Additional bivalve samples to be collected during the second year will allow comparison of difference within species and between species, and relationship to sediment chemistry.

Table 5.1 Range of Total Metal Concentrations in Arctic Coastal Sediments.

	ppm Dry Weight		
	This Study	Naidu et al. (1982)	Campbell and Loring (1980)
Ba	193 - 745		
Cd	0.04 - 0.29		
Cr	17 - 92	82 - 97	16 - 139
Cu	5 - 37	10 - 61	4 - 42
Pb	3 - 17		4 - 42
v	32 - 153	25 - 275	47 - 156
Zn	19 - 112	38 - 130	17 - 83

Table 5.2 Regional Differences in the Composition of Sediments Collected in 1984 from the Beaufort Sea.

Study Region (No. of stations)		Ba	Cd	Cr	Cu	Pb	V	Zn	TOC	Mud	
		Dry Weight ppm								% Dry Weight	
Foggy Island (5) (the '3" and '4" Stations)	Mean	309	0.14	47	23	6.	1	59	51	0.62	32
	S.D.	73	0.04	10	3	1.3	32	14	0.26	20	
Prudhoe Bay (10) (the '5" Stations)	Mean	279	0.16	37	15	6.5	60	53	0.99	33	
	S.D.	120	0.07	13	5	1.8	26	17	0.78	26	
East Harrison (5) Bay (the '6" Stations)	Mean	444	0.14	64	22	10.7	104	73	1.00	51	
	S. D.	157	0.08	17	9	3.5	28	21	0.49	28	
West Harrison (5) Bay (the '7" Stations)	Mean	587	0.10	58	16	9.9	92	69	1.48	48	
	S. D.	78	0.03	12	6	2.8	28	17	0.89	31	

Table 5.3 Concentration of Metals in Bivalve Tissue.

	Ba	Cd	Cr	Cu	Pb	v	Zn
	ppm dry weight						
Station 5F (5 replicate composites of <u>Cyrtodaria</u>)							
Mean	17	1.4	3.2	16	0.48	3.3	68
S.D.	5	0.1	0.7	4	0.08	0.8	8
Station 3A (5 replicate composites of <u>Astarte</u>)							
Mean	8.3	9.3	2.4	12	0.61	1.9	73
S.D.	1.5	3.1	0.5	3	0.16	0.4	9
Station 6D (3 replicate composites of <u>Astarte</u>)							
Mean	30	11.2	4.5	28	0.80	5.3	96
S.D.	6	1.2	0.4	1	0.12	0.5	3

5.3 Hydrocarbon Chemistry

5.3.1 General Interpretational Framework

The data generated as part of the hydrocarbon chemistry task consisted of generally two types of data: U V/F data which describe gross-fluorescence properties of the sample converted to quantitative data based on the arbitrary, but relevant Prudhoe Bay Crude oil (P B C) standard; G C -FID and G C/ MS data which yield the concentration of individual saturated (normal and isoprenoid alkanes) and aromatic (2- to 5- ring homologous series) hydrocarbons, respectively. While U V/F data may be precise and informative in a relative sense, spatially the gross property data are insensitive to subtle compositional changes and incremental additions of sub-ppm inputs of "new" material (i.e., pollutants). G C -FID and G C/ M S yield accurate and precise data at lower quantitative levels and, in addition, key source diagnostic ratios can be calculated and also used, along with quantitative data, to address the composition of ambient hydrocarbon concentrations, and to address changes in the composition overtime.

Our approaches to interpreting the hydrocarbon data, in light of the four null hypotheses to be tested, are summarized in Table 5.4 through 5.7.

5.3.2 Sediment Hydrocarbons

5.3.2.1 Overview of Hydrocarbon Data. The analytical results have been summarized in Section 4.3. Total saturated hydrocarbon concentrations in surface sediments (G C-FID data) range from 2.7 ppm to 69 ppm as shown in Figure 5.4, while total hydrocarbons (U V/F data) in Prudhoe Bay oil equivalents range from 7.5 ppm to 310 ppm as shown in Figure 5.5. Note that the two sets of values, G C-FID and U V/F data, are not directly comparable. However, G C -FID (saturated hydrocarbon) and U V/F (total hydrocarbons) are highly correlated, with $r = 0.88$. Taking mean data from each station we find that the area-wide ratio of saturates (G C-FID)/total (U V/F) = 0.34 ± 0.11 . It should be reemphasized here that U V/F determinations were obtained for all six sediment sampling replicates at each station while six extracts were pooled at 20 of the 27 stations to yield a single G C-FID and G C/ M S analysis at these 20 stations. At the remaining seven stations, each of the six sediment sampling replicates were analyzed by G C-FID (saturates) and G C/ MS (aromatics).

Highest hydrocarbon concentrations (greater than 60 ppm P B C equivalents) were observed in the Colville River area (E. Harrison Bay) and in Harrison Bay in general, (Stations 6B, 6A, 6F, 7A, 7C, 7E), as well as at the mouth of Gwydyr Bay (Station 5F) and near the West Dock/Stump Island area (Station 5 D). In general, these stations contained greater than 60% silt plus clay and greater than 10 mg T O C.

5.3.2.2 U V/F Spectra. The U V/F spectral characteristics of the sediment extract were quite uniform throughout the Study Area. As illustrated in Figure 5.6, which depicts a representative sediment U V/F spectrum along with that of P B C, the major spectral bands for Study Area sediments are at 355 nm, corresponding to the 3-ringed aromatics; 312 nm, corresponding to the 2-ringed aromatics; and the spectral doublet corresponding to the compound perylene of diagenetic origin. Spectral characteristics of PBC are similar, with maxima at 312 and 355 nm although the 312 nm peak shows greater abundance than the 355 nm peak. No perylene doublet is observed in the oil. Due to the large background fluorescence in the area's sediments, it is highly doubtful whether U V/F results will be effective in detecting small incremental additions of petroleum hydrocarbons to the sediment.

5.3.2.3 Gas Chromatographic Composition of Saturated Hydrocarbons. The saturated hydrocarbon composition of the Beaufort Sea Study Area sediments is quite uniform despite absolute concentration differences that range over one and a half to two orders of magnitude. This compositional homogeneity strongly suggests that the sediments from the entire Study Area are similarly sourced.

The moderately strong dependence of the saturated hydrocarbon concentrations on silt/clay content ($r = 0.8$ for saturates versus silt, and $r = 0.55$ for saturates versus clay) and on T O C content ($r = 0.7$ for saturates versus T O C) is illustrated in Figures 5.7 and 5.8.

Table 5.4

Saturated Hydrocarbon Quantitative Parameters (G C/FID)
 Used to Test Null Hypotheses H_0^1 (Sediment Concentrations)
 and H_0^3 (Bivalve Concentrations)

PARAMETER	SIGNIFICANCE
1. Total n-alkanes (TALK):	Quantifies n-alkanes from n-C 10 to n-C 34; baseline data are available at area wide stations in the Beaufort . This total is directly related to the fineness of the sediment and, hence, to the total organic carbon content.
2. n-alkanes C 10-C20 (L A L K):	Crude petroleum contains abundant amounts of n-alkanes in this boiling range; unpolluted samples are very low in many of these alkanes .
3. Phytane:	This isoprenoid alkane is low in abundance in unpolluted sediment; crude oil contains significant quantities of phytane.
4. Unresolved Complex Mixture (UC M):	The U C M is generally a feature of weathered petroleum although microbial activity can contribute to formation of these G C/ FID - unresolved components.

Table 5.5 **saturated Hydrocarbon Parameter Source Ratios (G C/FID) Used to Test Null Hypotheses H₀₂ (Sediment Hydrocarbon Sources) and H₀₄ (Bivalve Hydrocarbon Sources).**

PARAMETER	SIGNIFICANCE
1. LA LK/TALK	This ratio has been applied to monitoring studies to indicate the relative abundance of C ₁₀ -C ₂₀ alkanes characteristic of light crude and refined oils, over the total alkanes which are diluted by terrigenous plant waxes.
2. Isoprenoid Alkane/Straight Chain Alkane Ratio	This parameter ratio measures the relative abundance of branched, isoprenoid alkanes to straight chain alkanes in the same boiling range. This ratio is a useful indicator of the extent of biodegradation and a source indicator as well.
3* Pristane/Phytane Ratio:	The source of phytane is mainly petroleum, while pristane is derived from both biological matter and oil. In "clean" samples, this ratio is very high and increases as oil is added.
4. n-alkanes/Total Organic Carbon (TOC):	The ratio of total saturated hydrocarbons (TOT) to TOC, or n-alkanes (a subset of the saturated hydrocarbons) to TOC has been used to monitor oil inputs. In sediments receiving "normal" pollutant inputs within a given region, a specific TOT/TOC or n-alkanes/TOC ratio is characteristic of the "geochemical province". TOC, n-alkanes, and other pollutants are associated with finer particles (i.e., high silt/clay content). Small (tens of ppm) additions of petroleum to the sediment cause the ratio to increase dramatically, since n-alkanes (K/g) increase and TOC (µg/g) does not.
5* OEPI (odd-even carbon preference index):	The range of OEPI values for Beaufort Sea sediments has been established. Oil lowers the OEPI value. OEPI values in areas of low hydrocarbon content have been used as an effective monitor of oil additions.

Table 5.6

PAH Quantitative Parameters (G C/MS) Used to Test Null Hypotheses Ho 1 (Sediment Concentrations) and H₃ (Bivalve Concentrations).

PARAMETER	SIGNIFICANCE
1. Total Polycyclic Aromatic Hydrocarbons (PAH)	The sum of 2-5 ringed aromatics is a good quantitative indicator of petrogenic addition if statistical limits are determined. The sum of 2-3 ringed PAH is a better indicator since these components are more prevalent in oil.
2. Individual PAH and PAH homologous series (i.e., naphthalenes, phenanthrenes and dibenzothiophenes)	Key individual PAH compounds may be quantitatively less variable than the total PAH parameter. Also, several individual marker compounds (e.g., the alkylated dibenzothiophenes) may be extremely sensitive key monitoring parameters.

Table 5.7

PAH Source Parameters (G C/MS) Used to Test Null Hypotheses H₀₂ (Sediment Sources) and H₀₄ (Bivalve Sources).

PARAMETERS	SIGNIFICANCE
1. Fossil Fuel Pollution Index (FFPI) ^a	Pyrogenic or combustion-derived PAH assemblages are relatively more enriched in 3-5 ringed PAH compounds; fossil fuels are highly enriched in 2-3 ringed PAH and polynuclear organo-sulfur compounds (e.g., dibenzothiophene and its alkyl homologues). This ratio is designed to determine the approximate percentage of fossil fuel to total PAH.
2. Alkyl Homologue Distribution	Used to assess the importance of fossil fuel and combustion PAH sources.
3. Specific PAH ratios	For example, the ratio of phenanthrenes to dibenzothiophenes appear to be related to specific sources of PAH (and others).
4. PAH/TOC	Analogous to total hydrocarbon/TOC ratio.

^a

$$FFPI = \frac{N + \dots + \dots + \dots + \dots}{\text{Total PAH}} \times 100$$

= 100 for fossil PAH (oil, coal)
= 0 for combustion PAH

where:

N = CON, C₁N, C₂N, C₃N, C₄N (naphthalenes)
P = C₀P, C₁P, C₂P, C₃P, C₄P (phenanthrenes)
F = C₀F, C₁F, C₂F, C₃F (fluorenes)
DBT = CO DBT, C₁DBT, C₂DBT, C₃DBT (dibenzothiophenes)

Total. PAH = N + P + F + DBT + FLAN + PYRN + BAA + CHRY + BAP + BEP + BFA + PERY

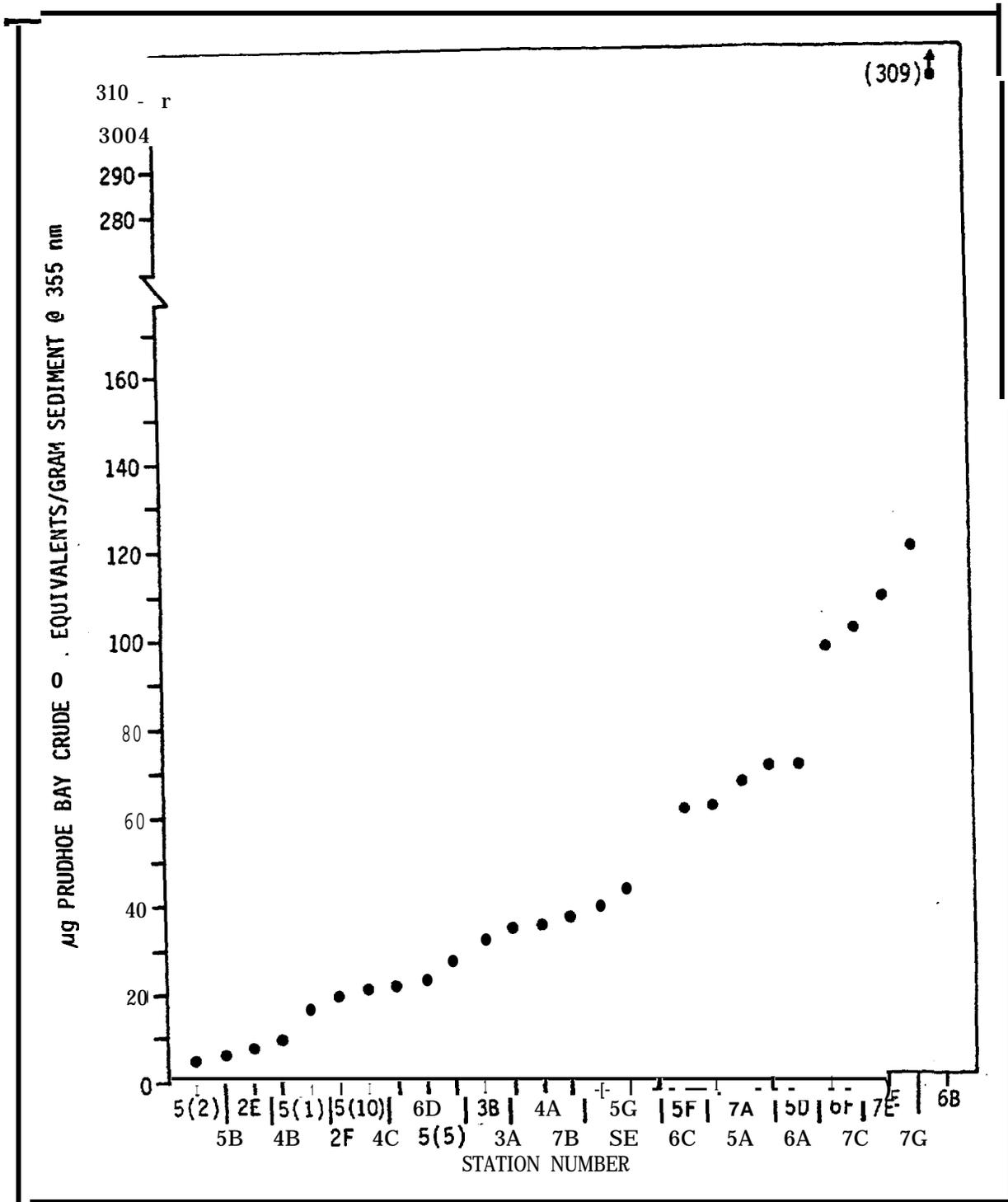


Figure 5.5 Results of UV/F Determined Hydrocarbon Content of Sediments Showing Averages for Each Station.

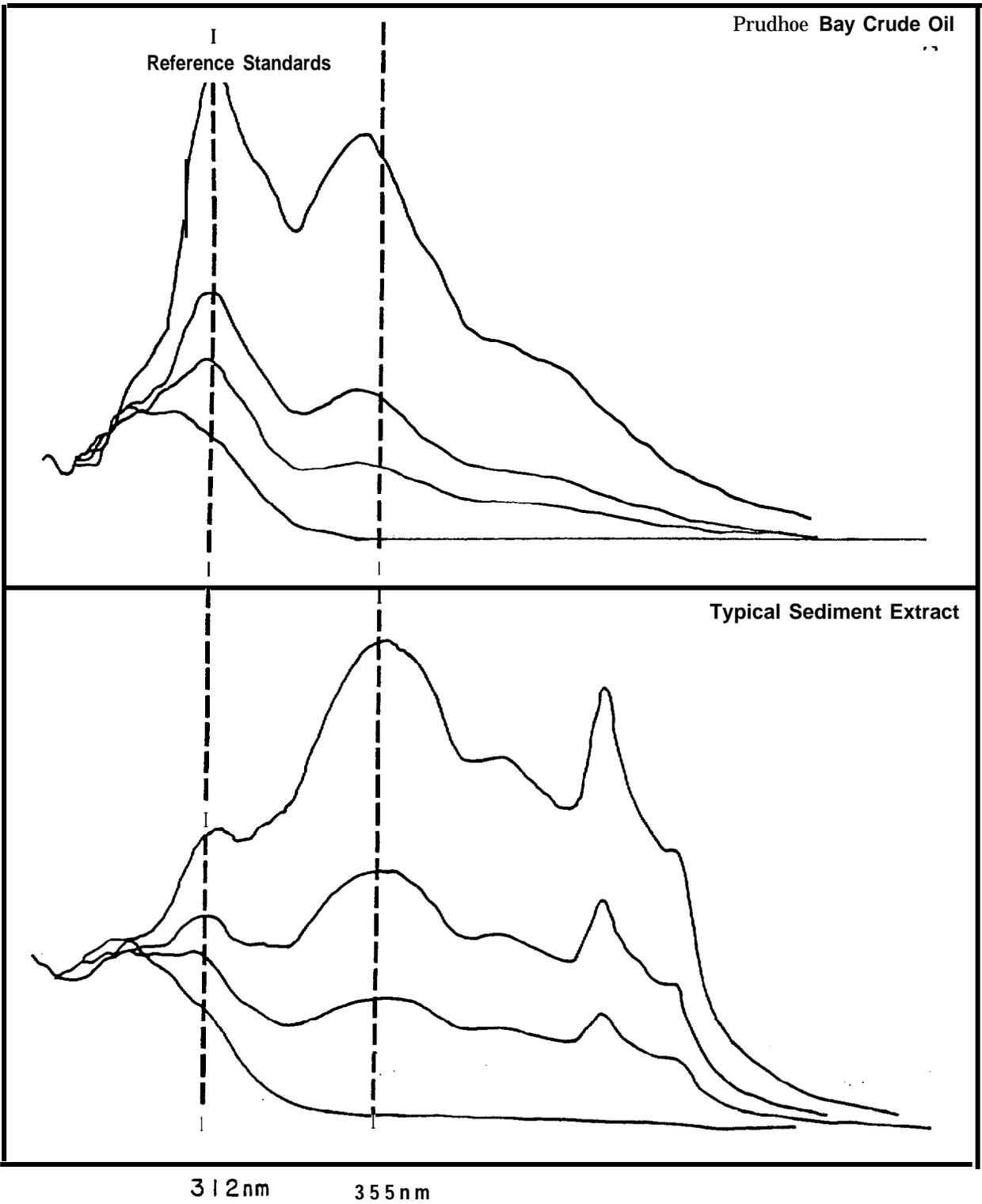


Figure 5.6 Typical UV/F Spectra of A-Prudhoe Bay Crude Oil Reference Standard and B-Typical Sediment Extract.

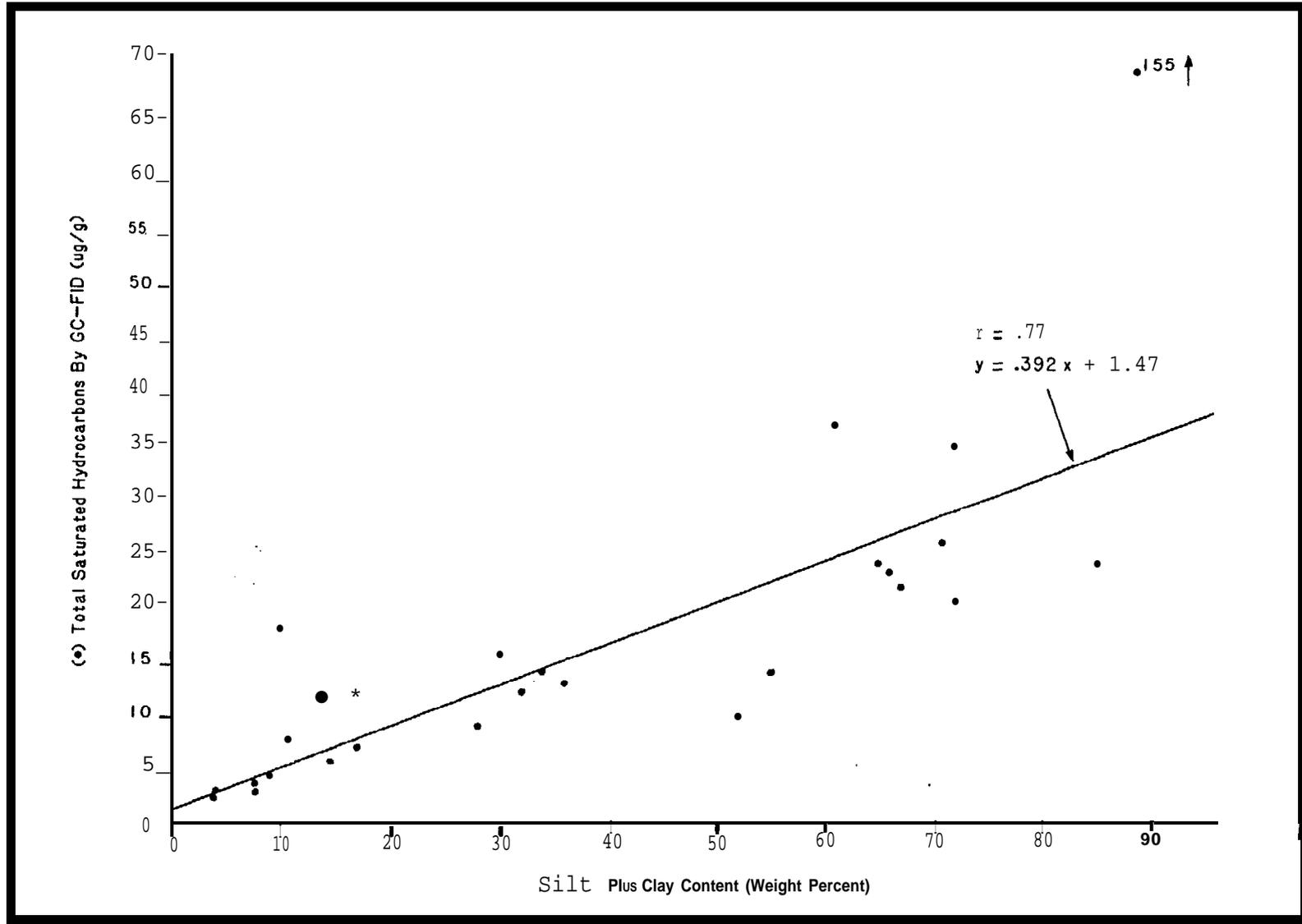


Figure 5.7 Regression of Saturated Hydrocarbons Against Silt + Clay Content for Study Area Sediments.

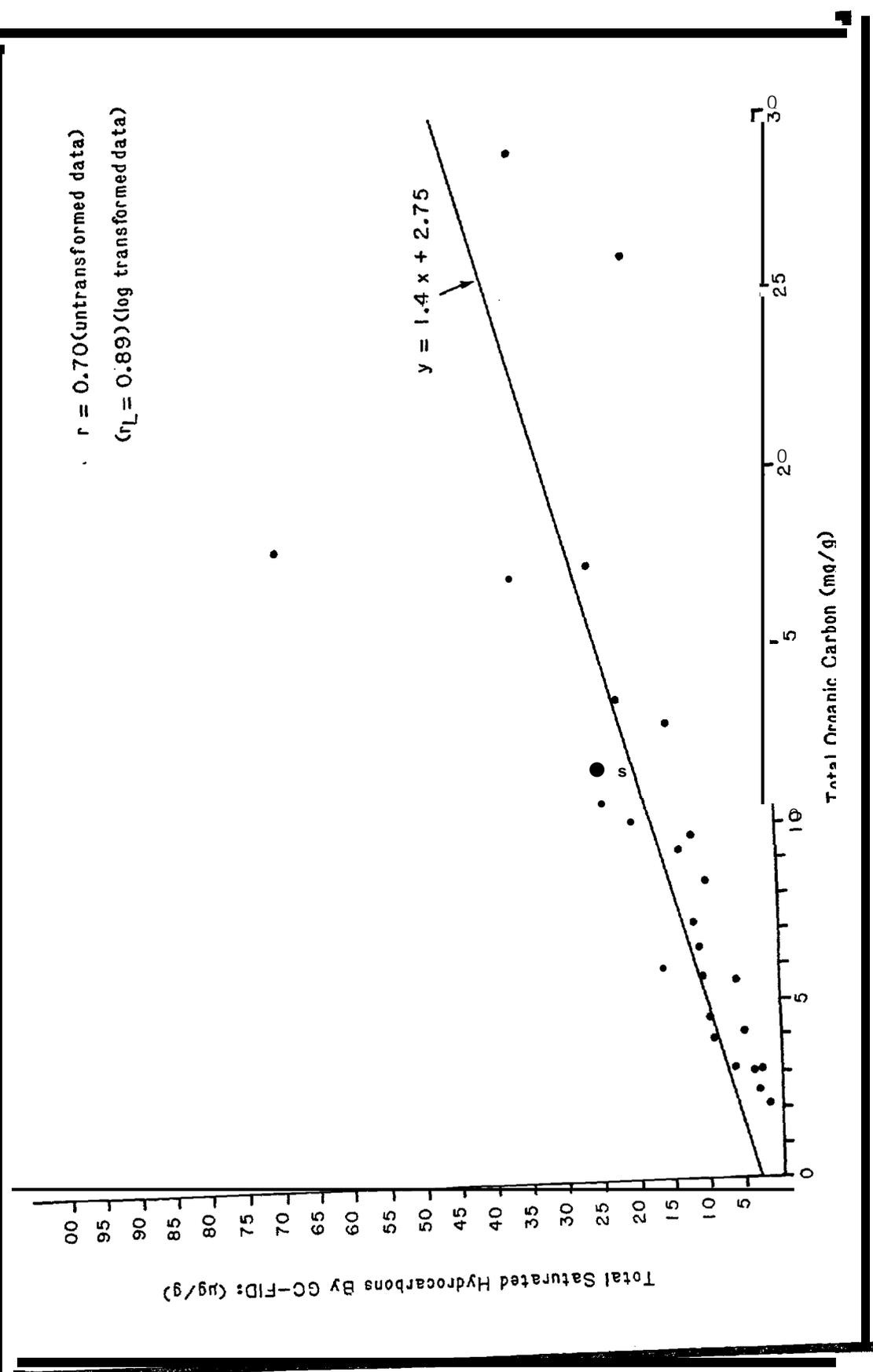


Figure 5.8 Regression of Saturated Hydrocarbons Against Total Organic Carbon Content for Study Area Sediments.

Figure 5.9 presents several G C- FID traces representing stations of low, medium and high (Stations 5(1), 7 G and 6B, respectively) hydrocarbon concentration. The chromatograms illustrate a n-alkane composition containing a full suite of alkanes from n-C₁₀ through n-C₃₃. There are two distributions superimposed on one another: the n-alkanes from n-C₁₀ to n-C₂₀ consisting of similar quantities of odd carbon number and even carbon number alkanes; the n-alkanes from n-C₂₁ through n-C₃₃ exhibiting a strong odd carbon number predominance. The higher molecular weight alkane odd carbon predominance can be expressed as:

$$\frac{2(C_{27} + C_{29})}{(C_{26} + 2C_{28} + C_{30})}$$

(Barrington and Tripp, 1977; Boehm, 1984). This odd-even predominance index (OEPI) is relatively high in all study area sediments, ranging from 2.7 to 8.1 (Table 5.8). These high OEPI values attest to the important contribution of terrigenous plant wax material transported by fluvial discharge to coastal waters. These terrigenous plant waxes have been observed commonly elsewhere (Wakeman and Barrington, 1980).

The more interesting distribution concerns the C₁₀ to C₂₀ n-alkanes, the sum of which is equal to the LALK parameter in Table 5.8. This alkane distribution very much resembles petroleum-like distributions. As often is the case for oil spill studies (e.g., Figure 5.10), the presence of LALK signifies petroleum inputs superimposed on a background consisting mainly of terrigenous plant wax alkanes. This distribution was observed for all Beaufort sediments. Either all of the sediments are significantly contaminated with petroleum hydrocarbons or another diagenetic source must be postulated. This source is almost certainly peat which is found abundantly in the sediments and which is sourced to the sediments from tundra cliff erosion. No direct analyses of peat from the area are available for comparison.

Although the total alkanes, n-C₁₀ through n-C₃₄ (TALK in Table 5.8) range over almost two orders of magnitude, the ratio of LALK to TALK is relatively constant. The LALK/TALK ratio ranges narrowly from 0.12 at Station 5D to 0.48 at Station 6D and for the entire study area averages 0.27 ± 0.08 . This ratio value is quite precise within a given station (see Section 5.3) with \sqrt{x} values (coefficients of variation = CV) typically 0.04 to 0.12, thus making it a good monitoring candidate due to the fact that fresh petroleum will add preferentially to the n-C₁₀ to n-C₂₀ range. The variability in the TALK and LALK parameters themselves are much greater, with CV values ranging from 0.05 to 0.68 for LALK and 0.10 to 0.45 for TALK.

The G C-FID traces shown in Figure 5.9 also exhibit other features common to petroleum and other diagenetic sources (i.e., peat). Branched alkanes are abundant in the chromatograms. The highly branched isoprenoid alkanes have been examined in detail as source indicators and possible monitoring parameters. Table 5.8 presents mean data on pristane and phytane concentrations as well as the pristane/phytane ratio. Another possibly useful parameter ratio is ISO/ALK, which expresses the ratio of five isoprenoid alkanes with chromatographic retention indices of 1380, 1470 (farnesane), 1650, 1708 (pristane), 1810 (phytane) to the five adjacent n-alkanes, C₁₄ through C₁₈. We prefer to use this ratio over the single ratios of pristane/n-C₁₇ or phytane/n-C₁₈. The mean ISO/ALK and pristane/phytane ratios for each station are presented in Table 5.8. Note the remarkable constancy of the ISO/ALK value which ranges from 0.39 to 0.55, excluding Stations 7E and 7G values which are discussed below. This constancy suggests a strong uniformity in alkane source to the sediments, perhaps peat again. Similarly, the pristane/phytane values (excluding Stations 7E and 7G) range narrowly from 2.0 to 2.9.

An anomalous biogenic pristane input at Stations 7E and 7G results in higher pristane/phytane ratios (3.5 and 4.7, respectively) at these stations. Likewise, the ISO/ALK values 0.62 and 0.92 are influenced by pristane inputs. The elevated pristane value at Station 7G is noted in the G C-FID trace presented in Figure 5.9.

Pristane and phytane are highly correlated in the Study Area ($r=0.93$) although neither isoprenoid is particularly highly correlated with TOC or grain size parameters (see Section 5.2.2.5). Alkane parameters TALK and LALK are highly correlated with each

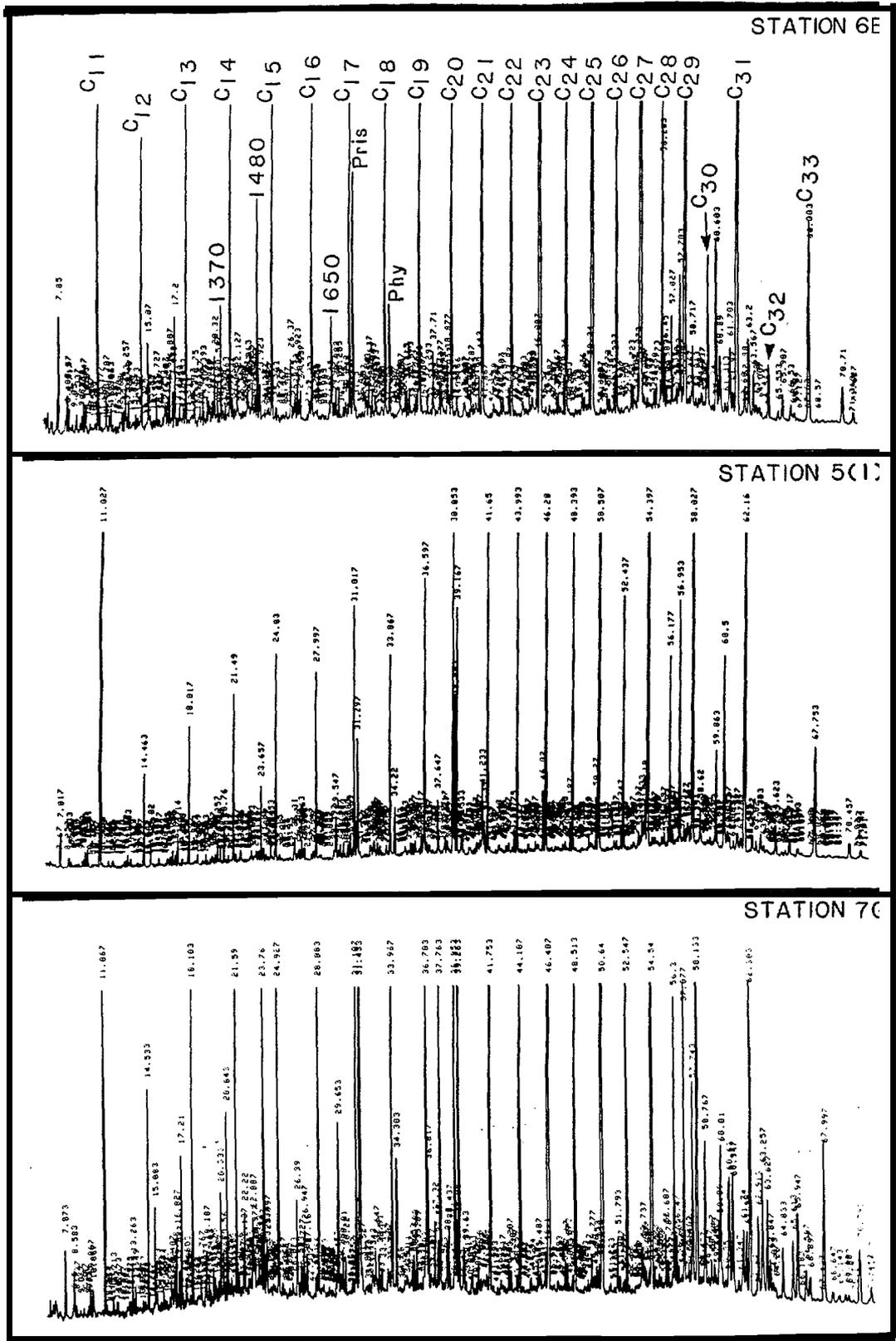


Figure 5.9 Representative G C-FID Traces for Beaufort Sea Sediment Saturated Hydrocarbons.

Table 5.8 Tabulation of Several Key Saturated Hydrocarbon, Parameters and Diagnostic Ratios by M cans at Each Station^a.

Station	LALK ($\mu\text{g/g}$)	TALK ($\mu\text{g/g}$)	$\frac{\text{LALK}}{\text{TALK}}$	PRIS ($\mu\text{g/g}$)	PHY ($\mu\text{g/g}$)	$\frac{\text{PRIS}}{\text{PHY}}$	$\frac{\text{ISO}}{\text{ALK}}$	OEPI
2E	0.26	0.80	0.32	0.010	0.004	2.5	0.44	6.0
2F	0.39	1.42	0.27	0.026	0.010	2.6	0.48	6.2
3A	0.50	2.78	0.18	0.035	0.017	2.1	0.45	7.0
3B	0.82	4.46	0.18	0.047	0.023	2.0	0.44	7.1
4A	0.62	3.41	0.18	0.046	0.019	2.4	0.43	6.2
4B	0.24	0.92	0.27	0.016	0.007	2.3	0.44	2.7
4C	0.51	1.86	0.27	0.028	0.012	2.3	0.43	4.9
5(1)	0.30	1.23	0.24	0.016	0.007	2.3	0.46	5.7
5(2)	0.27	0.68	0.39	0.008	0.003	2.7	0.39	5.4
5(5)	0.67	3.48	0.19	0.056	0.027	2.1	0.52	5.2
5(10)	0.71	3*59	0.20	0.053	0.018	2.9	0.47	6.5
5A	1.00	5.92	0.17	0.086	0.041	2.1	0.52	6.1
5B	0.28	0.77	0.36	0.010	0.004	2.5	0.45	4.0
5D	1.14	10.8	0.12	0.072	0.034	2.1	0.41	8.1
5E	0.61	2.31	0.26	0.044	0.019	2.3	0.45	4.2
5F	1.32	11.5	0.12	0.072	0.032	2.3	0.42	7*9
5G	0.75	2.97	0.25	0.056	0.022	2.5	0.47	5*5
6A	2.43	8.47	0.29	0.096	0.039	2.5	0.49	7*0
6B	4.02	22.8	0.18	0.305	0.144	2.1	0.51	5.7
6C	1.21	3.99	0.30	0.067	0.030	2.2	0.47	5.4
6D	1.27	2.50	0.48	0.032	0.013	2.5	0.47	5.2
6F	1.39	7.24	0.19	0.091	0.038	2.4	0.46	7.3
7A	1.33	5.76	0.23	0.080	0.031	2.6	0.55	6.6
7B	1.17	3.65	0.32	0.043	0.016	2.7	0.45	5*9
7C	1.65	7.32	0.23	0.099	0.045	2.2	0.47	6.2
7E	1.72	7*93	0.22	0.142	0.041	3.5	0.62	7.1
7G	1.05	3.99	0.26	0.214	0.045	4.7	0.92	3.7

^a See Section 4.3 for explanation of terms

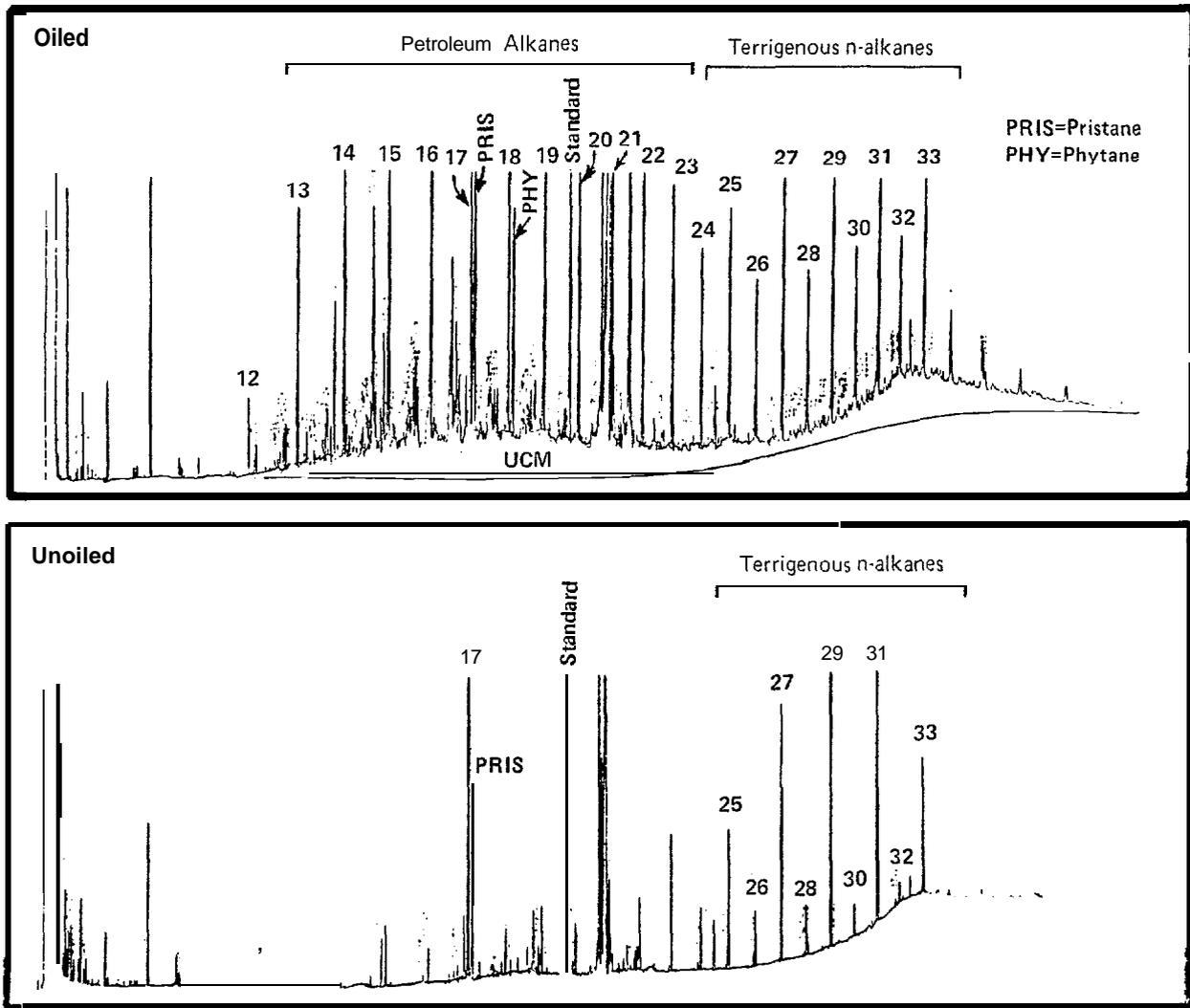


Figure 5.10 Typical Sediment Saturated Hydrocarbon GC-FID Traces Illustrating the Difference Between Oiled and Unoiled Sediments.

other ($r=0.92$) and, as discussed in the next section, to aromatic hydrocarbons as well.

5.3.2.4 G C/MS Co reposition of Aromatic Hydrocarbons. Analytical results on the extensive set of aromatic hydrocarbon (A H) determinations have previously been presented in Section 4.3. As was the case for the saturated hydrocarbon composition, the A H composition is remarkably constant, with the 2- and 3-ringed A H (i.e., naphthalene and phenanthrene homologous series) more abundant than the 4- and 5-ringed A H.

Three typical A H compositional plots from Stations 2F, 5F and 6B, and from Stations 7G and 6A and PB C reference material are shown in Figures 5.11 and 5.12, respectively. These compositional plots, each normalized to the compound or homolog in greater abundance, reveal the three similar types of compositions. In all three the abundance of the naphthalene and phenanthrene compounds greatly exceeds the 4- and 5-ringed compounds. This situation is unusual for marine sediments where, except for areas of marked fossil fuel pollution inputs, coastal sediments contain greater relative quantities of A H characteristic of combustion or pyrolytic sources, with the 4- and 5-ringed compounds dominating. It is highly unusual to see the ratio of fossil A H to combustion A H exceeding 0.5 (even in heavily industrialized areas) due to the input of considerable amounts of combustion A H products (i.e., burning of fossil fuel) followed by deposition and runoff of combustion particulate (Boehm et al., 1984). Of course, since the Beaufort Sea is not heavily industrialized, what we are probably seeing is the product of tundra cliff erosion and the resultant transport of high organic, diagenetic peat to the offshore stations.

The Fossil Fuel Pollution Index FFPI (Boehm, 1983; Boehm and Barrington, 1984), which is a ratio of fossil (coal, oil, peat) aromatics to total aromatics is consistently greater than 0.7 at all stations (Table 5.9). Note that the denominator of this ratio is comprised of all aromatics including the abundant diagenetic compound perylene. If perylene, a 5-ringed AH, were omitted from the FFPI then all FFPI values would be near unity, making this ratio unuseable for a diagnostic source indicator for future petroleum additions, despite its relatively high precision within each station (s/\bar{x} ranges from 0.04 to 0.08, except at station 7A where $s/\bar{x} = 0.22$).

The most abundant single aromatic compound in most of the sediment samples was perylene which is a common diagenetic aromatic compound in offshore marine sediment (Wakeham et al., 1980). It is either produced in situ in the sediments (Aizenshtat, 1973; Gschwend et al., 1983) or is transported offshore from terrigenous sources (Venkatesan and Kaplan, 1982).

In order to provide diagnostic source-type information from the G C/ M S data, we have explored the exploitation of the relative abundances of specific homologous series as graphically depicted in Figures 5.11 and 5.12. Specifically, the quantitative ratios of the homologous series N/P and P/D (N =naphthalenes; P =phenanthrenes; D =dibenzothiophenes) are presented in Table 5.9, with higher ratios found near the Colville River mouth in Harrison Bay. At each particular station in which replicates were analyzed, the N/P ratio is fairly precise with s/\bar{x} values ranging narrowly from 0.10 to 0.20, much more precise than the absolute N and P values themselves. Similarly, the P/D ratio precision ranges from 0.10 to 0.20, excluding station 2F. Values of P/D range from 3.5 to 12. Note, in Table 5.9, the N/P and P/D values of a typical relevant crude oil sample. The N/P and P/D ratios, 4.0 and 1.1 are very much different than ambient ratios. If indeed the source of sedimentary aromatics is largely natural, then these specific aromatic homologous series ratios may be used to distinguish aromatic inputs from other diagenetic inputs. The dibenzothiophene series seems to be an especially important petroleum indicator amid the significant overall A H background.

5.3.2.5 Statistical Correlations. In order to view the individual parameter distributions within the entire Study Area in a more holistic sense, Pearson correlation coefficients were determined between the major parameters. As shown in Section 5.4, all of the organic parameters are highly correlated ($r=0.8$), illustrating that the entire hydrocarbon assemblage co-varies strongly throughout the Study Area. Much weaker correlations are exhibited between the hydrocarbons and grain size (silt + clay) and TOC parameters. The total alkanes (TALK) and total saturates (TOT) appear to correlate well with silt-sized particles ($r=0.8$) but the A H correlate much less ($r=0.4$ to 0.7) with both grain size and TOC. Additional statistical considerations are presented in Section 5.4.

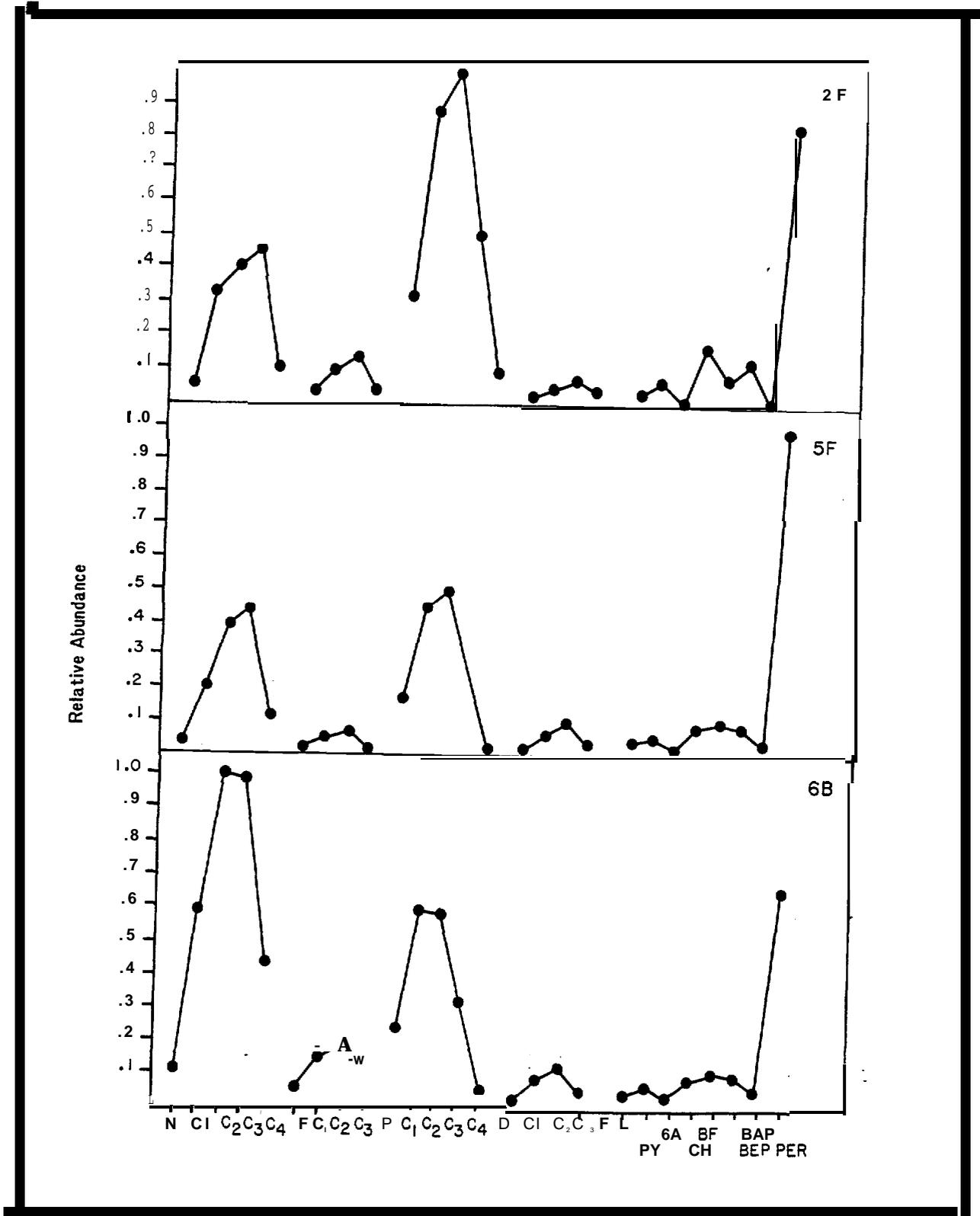


Figure 5.11 Aromatic Hydrocarbon Relative Abundance Plots from Representative Sediment Stations.

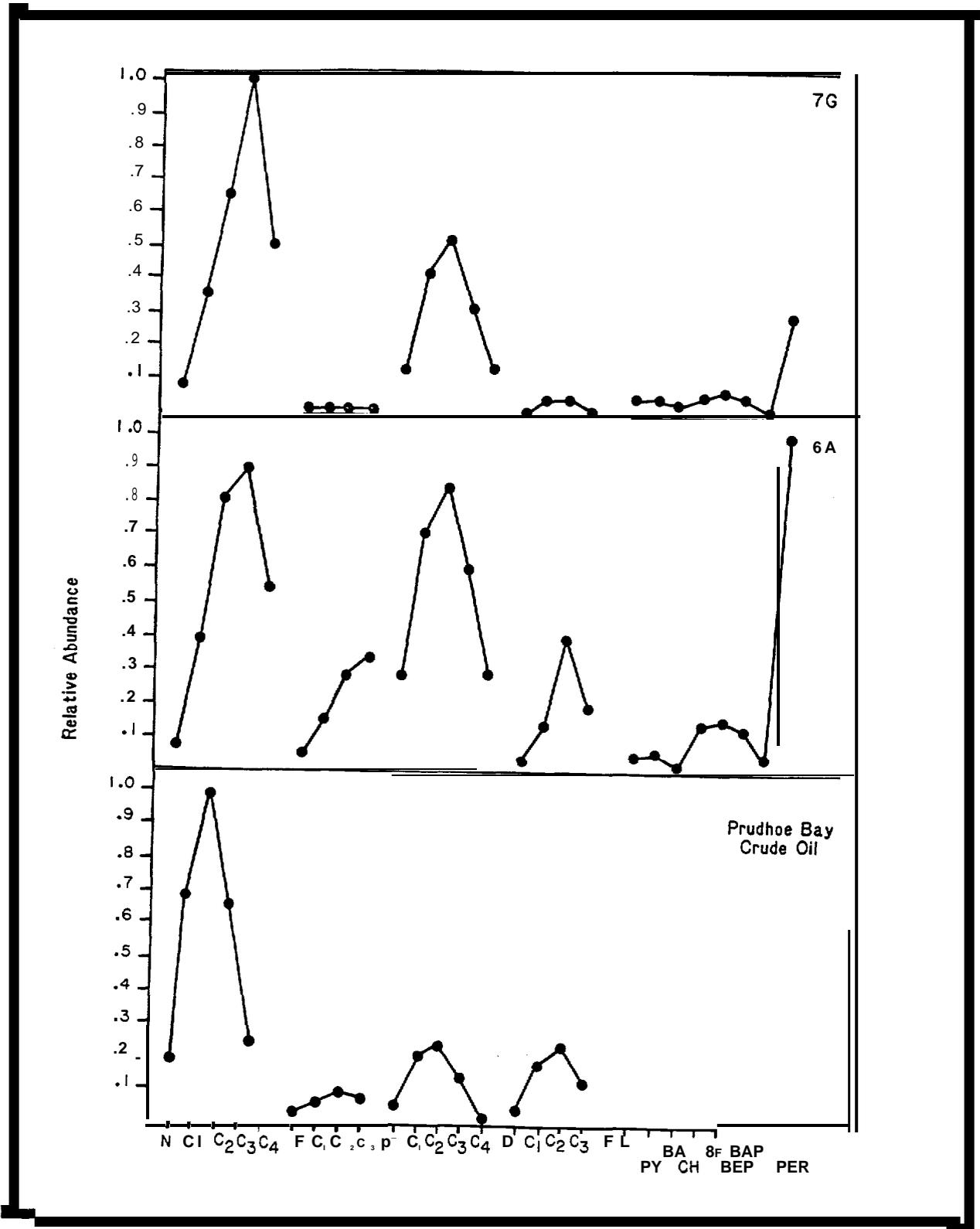


Figure 5.12 Aromatic Hydrocarbon Relative Abundance Plots of Sediments and Prudhoe Bay Crude Oil.

Table 5.9 Summary of Aromatic Hydrocarbon Diagnostic Ratios.

Station	FFPI ^a	N/P ^b	P/D ^c
2E	0.85	0.59	7.9
2F	0.76 ± 0.04	0.46 ± 0.06	12.7 ± 7.3
3A	0.81	0.79	8.6
3B	0.84 ± 0.06	0.92 ± 0.14	8.4 ± 1.4
4A	0.82 ± 0.03	0.93 ± 0.09	4.5 ± 0.49
4B	0.87	1.0	3.4
4C	0.82	0.74	4.5
5(1)	0.83	0.79	501
5(2)	0.76	0.56	3.8
5(5)	0.76	0.74	5.4
5(10)	0.83	0.81	5.0
5A	0.81	1.11	9.4
5B	0.83	0.81	4.0
5D	0.79 ± 0.06	0.91 ± 0.20	5.8 ± 0.59
5E	0.85	0.91	4.6
5F	0.69	0.86	6.7
5G	0.79	0.94	7.5
6A	0.83	0.99	3.5
6B	0.85	1.72	6.2
6C	0.83 ± 0.07	0.96 ± 0.18	4.5 ± 0.90
6D	0.79 ± 0.04	1.00 ± 0.17	5.1 ± 0.83
6F	0.82	1.08	5.3
7A	0.83 ± 0.019	1.29 ± 0.20	5.6 ± 1.1
7B	0.80	1.07	4.9
7C	0.83	1.13	5.7
7E	0.88	1.73	7.4
7G	0.88	1.70	12.1
Prudhoe Bay Crude oil	1.00	3*97	1.14

^a Fossil Fuel Pollution

Index:
$$\frac{\text{Naphthalenes} + \text{Phenanthrenes} + \text{Dibenzothiophenes} + \text{Fluorenes}}{\text{Total PAH}}$$

^b N/P = Naphthalenes (C₀N - C₄N)/Phenanthrenes (C₀P - C₄P)

^c P/D = Phenanthrenes (C₀P - C₄P)/Dibenzothiophenes (C₀DBT - C₃DBT)

5.3.2.6 Geographical Analysis. The distribution of hydrocarbons in Harrison Bay can be understood in terms of input from the Colville River and the general east to west flow in the coastal Alaskan Beaufort. The Colville, although smaller than the Mackenzie River in Canada, is the largest Alaskan river emptying into the Beaufort Sea. The Colville drains most slope of the Brooks Range (but not the coastal plain) between 150° and 160° W; the annual flow is 1010 m³ with an average TOC content of 12 mg/L. The region drained by the Colville contains numerous outcropping coal deposits as well as natural petroleum seep areas and oil shale outcrops. In particular, there is a 1.5-mile long Oil. Lake (70° 18'N, 151° 09'W) slightly west of the Colville and 5 miles from the coast. This lake was named for the natural seep oil which forms a slick on its surface. The terrain drained by the Colville, like the terrain of the entire Alaskan north slope, does not have well developed soil, but rather contains various depths of seasonally thawed peat-like material.

Consequently, the organic matter carried by the Colville includes fractions derived from peat, coal and oil. Additional peat enters the marine environment from direct erosion of 10 w bluffs which are a common feature on the Beaufort coast. Although these natural sources may account for the fluorescent material and diagenetic PAH found in Harrison Bay sediments, anthropogenic sources cannot be entirely excluded. Suspended material discharged by the Colville moves west following the general coastline of Harrison Bay as can be seen in satellite photos of the Colville sediment plume (see Naidu et al., 1984). Material can be deposited in shallow water, resuspended, and finally deposited in deeper water. This sediment transport pathway is consistent with the high UV/F and (UV/F)/TOC results at Station 6B and values at other Harrison Bay stations (6A, 6c, 6D, 6F, 7A, 7E, and 7G) which, compared to other stations, are elevated in all saturated and aromatic compounds. Five of ten sediment samples from Harrison Bay were > 50 % silt + clay, compared to four of sixteen for stations to the east of Oliktok Point. This tendency toward finer grained sediments indicates that at least portions of Harrison Bay will receive preferential deposition of low density organic detritus.

Two stations within Harrison Bay, 7E and 7G, exhibit anomalous marine biogenic inputs as reflected in higher absolute and relative quantities of pristane. These stations may be the site of elevated productivity, perhaps due to nutrient loadings from the Colville River.

Marine sediments collected between the mouths of the Colville and Canning Rivers, including the Prudhoe Bay area, showed lower UV/F, (UV/F)/TOC, and total hydrocarbon values than those from Harrison Bay. Higher hydrocarbon concentrations are generally associated with finer grained (3B, 5A, 5D, and 5F) and more organic rich (5D and 5F) stations. There are probably fewer natural petroleum seeps and coal outcrops to the east of the Colville. Also, the drainage system east of the Colville consists of smaller rivers which discharge material more uniformly along the coast. These factors will lead to greater dispersion and lower concentrations of hydrocarbons.

However, in overall aromatic and saturated hydrocarbon composition, sediments from this area are quite similar to the sites further west. From sediment data of the stations near Prudhoe Bay or adjacent to Seal Island there is no evidence of anthropogenic inputs related to petroleum exploration activities.

5.3.3 Bivalves*

The data on hydrocarbon content and composition of benthic bivalves collected in Year 1 of the study were sparse due to generally low bivalve abundances at selected sediment sampling stations, and an inability to sample further offshore due to ice conditions. Samples collected in sufficient quantity for analysis included:

Astarte borealis: Stations 3A and 6D

Cyrtodaria kurriana: Station 5F

Macoma calcarea: Station 6D

Analytical results are summarized in Section 4.3.

All animals exhibited extremely low abundance of UV/F-detectable fluorescent AH. A greater relative amount of 312 nm aromatics were detected by UV/F. Two typical spectra are presented in Figure 5.13. These spectra show two main features: the 312 nm response and evidence for perylene in the samples, the latter perhaps from a sediment source.

Detailed analyses of these samples by GC-FID and GC/MS were conducted, but revealed very low levels of detectable material. A characteristic GC-FID trace in Figure 5.14 illustrates primarily a biogenic background totally different from the sediment chromatograms. These biogenic compounds are unidentified. Normal alkanes were detected at very low levels in the samples. No systematic differences are seen between the same species collected at different stations (i.e., Astarte). While low levels of n-alkanes were detected in the samples, the amounts of these compounds are very small compared to the biogenic background.

GC/MS analyses of the sample replicates revealed low or no detectable AH in all of the samples in spite of a positive UV/F spectral response at 312 nm. This apparent paradox has been noted in other studies (e.g., Boehm and Fiest, 1980). The absence of detectable aromatics in background tissues indicates that the significant sedimentary reservoir of AH is not readily available to filter feeding bivalves. Thus, aromatic analyses of bivalves may serve as sensitive indicators of water-borne petroleum exposure, rather than sediment petroleum exposure.

5.4 Statistical Analysis

The initial goals of the statistical analysis for this reporting period are to address the issues of data transformation and data normalization. With respect to data transformation, the effect of a logarithmic transformation on the homogeneity of the within-station variances is examined. Based on the results of this analysis, a logarithmic transformation is applied to all measurements prior to any statistical analyses.

The effects of normalizing the data with division by percent silt (% SILT), percent clay (% CLAY) and total organic carbon (TOC) are also examined. There is no apparent reduction in within-station variability due to normalization by these parameters. It is concluded that normalization of the data by % SILT, % CLAY, or TOC is not warranted. All statistical analyses are, thus, based on unnormalized metal and organic parameter measurements to which a logarithmic transformation has been applied.

Finally, the variability of each parameter is characterized and the magnitude of temporal change that will be detected is determined for the current replication scheme. These calculations and determinations are based on the pooled within-station variability of the parameters and the power of the two-sample t-test for detecting changes in average concentration.

In the following analyses, within-station variability was estimated at all stations for metals, %SILT, %CLAY, UV/F at 355, and TOC. Within-station variability for all other parameters was measured only at Stations 2F, 3B, 4A, 5D, 6c, 6D, and 7A since data from remaining stations were based on pooled nonreplicated samples.

5.4.1 Data Transformation

A goal of the statistical analysis for this reporting period is to determine if a logarithmic transformation of the raw data will stabilize the within-station variability. It is important that within-station variability be comparable among stations because one of the overall goals of this study is to examine potential spatial gradients in chemical concentrations. Furthermore, heterogeneity of within-station variability across stations may reflect a general relationship between within-station means and variances. Such a relationship will affect hypothesis tests concerning temporal changes in variables within particular stations. In either case, reduction of variance heterogeneity will improve statistical tests of the hypotheses proposed in this study.

Heterogeneity of within-station variances was examined using the results of Levene's test produced by the statistical computing package BMDP7D. For all untransformed variables tested, the F values produced by Levene's test caused rejection

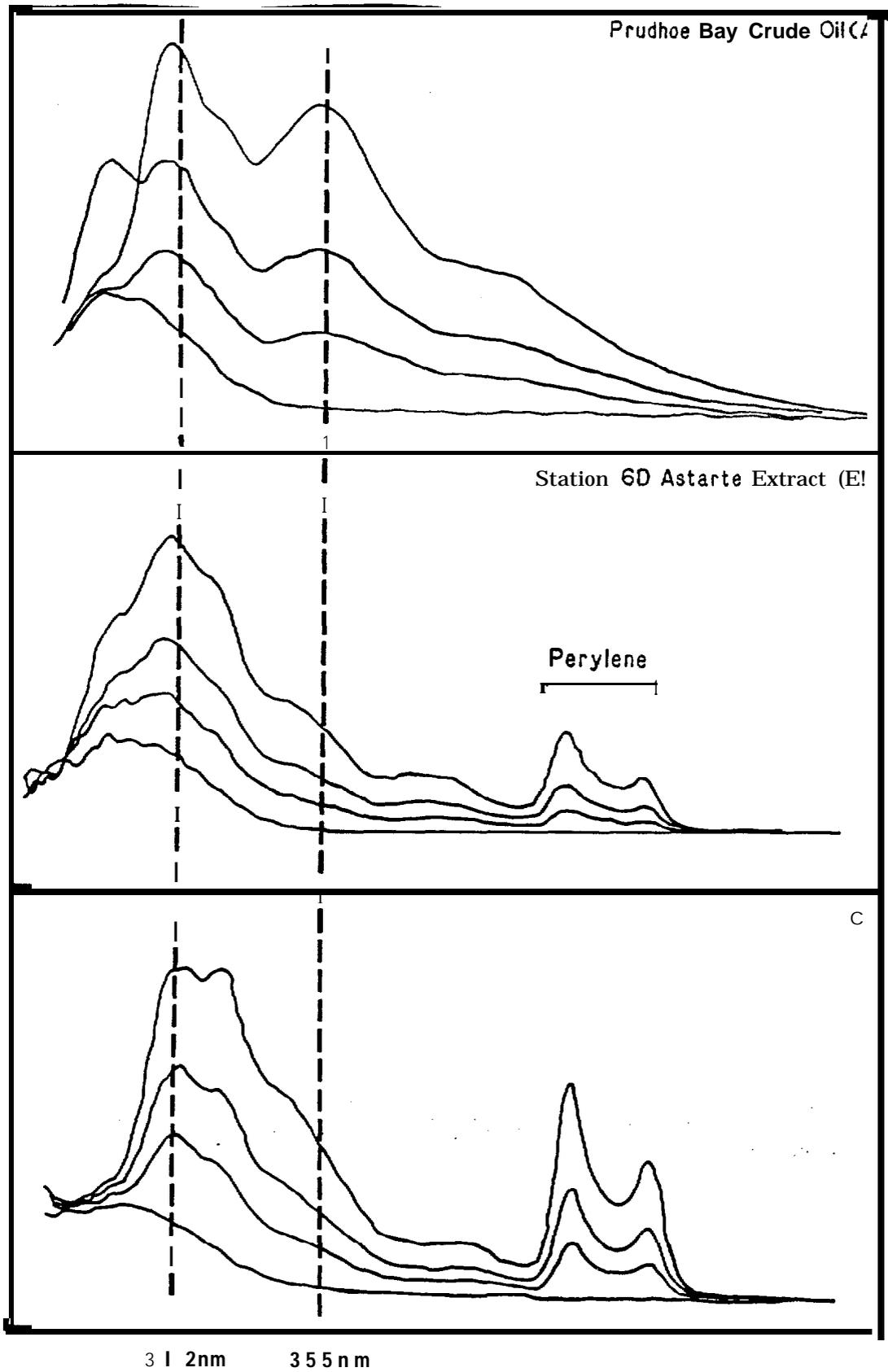


Figure 5.13 UV/F Spectra of **Prudhoe** Bay Crude Oil (A) and **Benthic Bivalve Sample** Extracts, Stations 6D Astarte (B) and Station 5F Cyrtodaria (C).

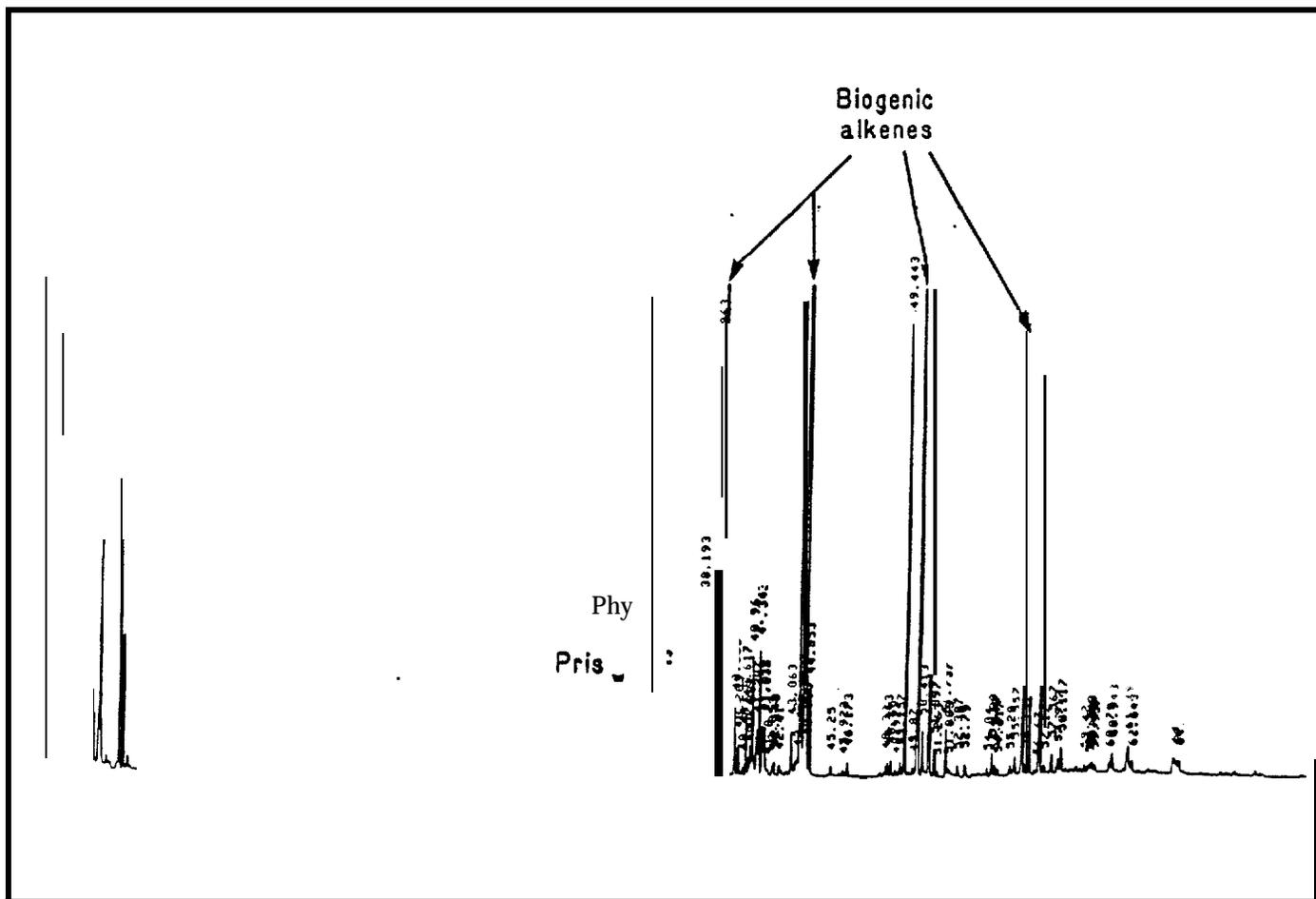


Figure 5.14 Total Hydrocarbons GC-FID Trace of Benthic Bivalve Sample Extract.

of the null hypothesis that within-station variances were equal among stations. A logarithmic transformation reduced the F values for 15 of 18 organic parameters and for four of these parameters, the null hypothesis of equal variances could not be rejected (Table 5.10). Only one of seven log-transformed metal concentrations showed a reduction in Levene's F value but, in most cases, the differences between F values for transformed and untransformed metal parameters are small (Table 5.10).

Based on the consistent reduction in Levene's F value when organic parameters are subjected to a logarithmic transformation, all variables were subsequently transformed. This decision also rests on a general historical precedent for using logarithmic transformations when analyzing chemical concentration data. Although the transformation reduced Levene's F for most variables tested, for only four of these variables did transformation result in failure to reject the null hypothesis of homogeneous variance. Thus, it must be realized that the station variances are probably heterogeneous for most of the parameters even after the log-transformation.

It is important to note that the standard deviation of log-transformed data (natural logarithm) may be interpreted as an approximate coefficient of variation for the data on the original scale for standard deviation values smaller than 0.70. This relationship is easily illustrated using the lognormal distribution as an example. Suppose that $\ln(Y)$ has a normal distribution with mean μ and standard deviation σ ; that is, suppose that a measurement Y follows a lognormal distribution with parameters μ and σ . The mean and standard deviation of Y are $\exp(\mu + \sigma^2/2)$ and $(\exp(\sigma^2)-1)^{1/2} \exp(\mu + \sigma^2/2)$, respectively. Thus, the coefficient of variation of Y is $CV = (\exp(\sigma^2) - 1)^{1/2}$.

For small values of ($\sigma < 0.7$), $\exp(\sigma^2) \approx 1 + \sigma^2$ and, therefore, $CV \approx \sigma$. The actual CV value is always larger than σ with the difference increasing as σ increases. The maximum relative difference in the range $0 < \sigma < 0.7$ is 12% for $\sigma = 0.7$. Similar relationships hold for the coefficient of variation and the standard deviation of log-transformed data that follow distributions other than the lognormal.

5.4.2 Data Normalization

Reduction of within-station variability would improve the power of the statistical tests used to test the proposed hypotheses in this program. If the variables of interest are highly correlated with an ancillary variable, then normalization with this variable may reduce within-station variability.

The following method was used to determine if normalization of the raw data with TOC, % SILT, % CLAY would reduce within-station variability. A one-way ANOVA using stations as treatments was conducted by applying the SAS statistical procedure GLM to the log-transformed parameters and log-transformations of parameters normalized by dividing the raw data by either TOC, % SILT, or % CLAY. In this analysis the root mean square (RMS) of the model error term is a pooled estimate of within-station standard deviation.

Table 5.11 shows that normalization with TOC results in a small reduction in standard deviation for most organic parameters but normalization results in no reduction in standard deviation for metal parameters. Except for the organic UVF 355 parameter, normalization with % SILT or % CLAY produced no decrease in standard deviation (Table 5.11). These results suggest that data normalization with TOC, % SILT, % CLAY would not be effective in reducing within-station variability.

Another method used to examine the variance reduction potential of data normalization was to calculate correlation matrices using only the 27 within-station averages. These correlations reflect only the between-station relationships of the variables and do not include any within-station correlations. Table 5.12 contains the correlation coefficients and observed significance levels (below) for the log-transformed metal parameters with themselves and log(TOC), % SILT, and % CLAY. Table 5.13 contains similar information for selected log-transformed organic parameters. The observed significance level may be interpreted as the probability that a correlation coefficient as large as that observed would be observed if the two variables were uncorrelated. The relative large correlations with TOC, % SILT and % CLAY in Tables

Table 5.10 F Values^a From Levene's Test for Homogeneity of Variance

Metal Parameter	Untransformed Data	Log-transformed Data
Cd	1.47	2.91
Pb	4.74	3.65
Ba	5.89	5.75
Cr	4.08	6.19
Cu	4.61	5.14
Zn	8.40	9.91
V	6.39	8.99

Organic Parameter	Untransformed Data	Log-transformed Data
N	10.10	6.99
F	5.50	19.41
P	11.38	10.47
D	8.17	6.29
PAH	2.80	2.80
FFPI	3.32	2.59
P/D	5.41	4.11
TALK	5.17	1.89 ^b
LALK	3.78	3.02
ISO	3.52	2.48
ALK	3.47	2.01 ^b
LALK/TALK	7.89	3.63
ISO/ALK	2.45	2.45
1708	3.24	2.38
1810	2.71	1.20 ^b
TOT	4.30	1.19 ^b
TOC	11.62	5.22
355	5.15	4.15

^a For the metal parameters, the hypothesis of homogeneous variance is rejected if F exceeds 1.3; for the organic parameters, the F value is 2.37.

^b Null hypothesis not rejected.

Table 5.11 Pooled Within-Station Standard Deviation Estimates for Unnormalized and Normalized Logarithmic Data.

Metal Parameter	ln (x)	ln (X/TOC)	ln (X/%Silt)	ln (X/%Clay)
Cd	0.1784	0.3350	0.3760	0.4299
Pb	0.1448	0.2795	0.3189	0.4301
Ba	0.1637	0.2682	0.3226	0.3820
Cu	0.2144	0.2950	0.3339	0.3871
Cr	0.0394	0.2747	0.2977	0.3721
Zn	0.2003	0.2975	0.3212	0.3873
v	0.1603	0.2613	0.2876	0.3585

Organic Parameter	ln (x)	ln (X/TOC)	ln (X/%SILT)	ln (X/%Clay)
N	0.6007	0.5929	0.7260	0.7555
F	1.244	1.2358	1.3339	1.3836
P	0.5873	0.5703	0.7046	0.7412
D	1.0219	0.9908	1.1105	1.1423
PAH	0.7716	0.8001	0.8273	0.8817
TALK	0.3362	0.2931	0.4571	0.4667
LALK	0.3643	0.3578	0.5165	0.4973
1708	0.3219	0.2722	0.4396	0.4658
1810	0.3265	0.2871	0.4326	0.4780
TOT	0.2915	0.2556	0.3912	0.3988
355	0.3834	0.3403	0.3673	0.4285

Table 5.12 Correlation Matrix for Metal Parameters with TOC, % Silt, % Clay Using Station Averages.

PEARSON CORRELATION COEFFICIENTS / PROB > |R| UNDER HO:RHO=0 / N = 27

	LCDCONC	LPBCONC	LBACONC	LCRCONC	LCUCONC	LZNCNC	LVCONC	LTOCCONC	PSILT	PCLAY
LCDCONC	1.0000 0.0000	0.30214 0.1256	0.12529 0.5335	0.34450 0.0785	0.61401 0.0007	0.45707 0.0165	0.38930 0.0447	0.46702 0.0140	0.53450 0.0041	0.31005 0.1059
LPBCONC	0.30274 0.1256	1.0000 0.0000	0.80711 0.0001	0.79598 0.0001	0.58192 0.0015	0.80520 0.0001	0.85654 0.0001	0.74219 0.0001	0.63904 0.0003	0.71159 0.0001
LBACONC	0.12529 0.5335	0.80711 0.0001	1.0000 0.0000	0.80806 0.0001	0.45060 0.0167	0.70758 0.0001	0.80897 0.0001	0.76038 0.0001	0.71065 0.0001	0.56880 0.0020
LCRCONC	0.34450 0.0785	0.79590 0.0001	0.80806 0.0001	1.0000 0.0000	0.80838 0.0001	0.79867 0.0001	0.96039 0.0001	0.67849 0.0001	0.74548 0.0001	0.72378 0.0001
LCUCONC	0.61401 0.0007	0.58192 0.0015	0.45600 0.0167	0.80838 0.0001	1.0000 0.0000	0.68832 0.0001	0.80746 0.0001	0.53806 0.0038	0.65225 0.0002	0.69907 0.0001
LZNCNC	0.45707 0.0165	0.80520 0.0001	0.70758 0.0001	0.79867 0.0001	0.68832 0.0001	1.0000 0.0000	0.84804 0.0001	0.70911 0.0001	0.72066 0.0001	0.64778 0.0003
LVCONC	0.38930 0.0447	0.85654 0.0001	0.80897 0.0001	0.96039 0.0001	0.80746 0.0001	0.84804 0.0001	1.0000 0.0000	0.71569 0.0001	0.75347 0.0001	0.84146 0.0001
LTOCCONC	0.46702 0.0140	0.74219 0.0001	0.76038 0.0001	0.67849 0.0001	0.53806 0.0038	0.70911 0.0001	0.71569 0.0001	1.0000 0.0000	0.76939 0.0001	0.47147 0.0130
PSILT	0.53450 0.0041	0.63904 0.0003	0.71065 0.0001	0.74548 0.0001	0.65225 0.0002	0.72066 0.0001	0.75347 0.0001	0.76939 0.0001	1.0000 0.0000	0.61079 0.0007
PCLAY	0.31805 0.1059	0.71159 0.0001	0.56880 0.0020	0.72378 0.0001	0.60907 0.0001	0.64778 0.0003	0.84146 0.0001	0.47147 0.0130	0.61079 0.0007	1.0000 0.0000

Table 5.13 Correlation Matrix for Selected Organic Parameters with TOC, % Silt, and % Clay Using Station Averages.

PEARSON CORRELATION COEFFICIENTS / PROB > |R| UNDER H₀: RHO=0 / N = 27

	LN	LF	LP	LD	LPAH	LTALK	LLALK	LC355	LC1708	LC1810	LTOT
LN	1.00000 0.0000	0.85998 0.0001	0.98838 0.0001	0.93503 0.0001	0.95389 0.0001	0.83384 0.0001	0.84850 0.0001	0.89799 0.0001	0.88877 0.0001	0.87563 0.0001	0.84404 0.0001
LF	0.85998 0.0001	1.00000 0.0000	0.88751 0.0001	0.93138 0.0001	0.87081 0.0001	0.73264 0.0001	0.74638 0.0001	0.72481 0.0001	0.67056 0.0001	0.72518 0.0001	0.71840 0.0001
LP	0.98838 0.0001	0.88751 0.0001	1.00000 0.0000	0.94410 0.0001	0.97224 0.0001	0.84005 0.0001	0.83901 0.0001	0.88227 0.0001	0.86947 0.0001	0.87061 0.0001	0.85103 0.0001
LD	0.93503 0.0001	0.93138 0.0001	0.94410 0.0001	1.00000 0.0000	0.92557 0.0001	0.77027 0.0001	0.80086 0.0001	0.77878 0.0001	0.75798 0.0001	0.77178 0.0001	0.77345 0.0001
LPAH	0.95389 0.0001	0.87081 0.0001	0.97224 0.0001	0.92557 0.0001	1.00000 0.0000	0.88206 0.0001	0.86364 0.0001	0.87291 0.0001	0.85924 0.0001	0.87862 0.0001	0.88358 0.0001
LTALK	0.83384 0.0001	0.73264 0.0001	0.84005 0.0001	0.77027 0.0001	0.88206 0.0001	1.00000 0.0000	0.93137 0.0001	0.91042 0.0001	0.91274 0.0001	0.94932 0.0001	0.99518 0.0001
LLALK	0.84850 0.0001	0.74638 0.0001	0.83901 0.0001	0.80086 0.0001	0.86364 0.0001	0.93137 0.0001	1.00000 0.0000	0.90010 0.0001	0.89667 0.0001	0.90879 0.0001	0.91760 0.0001
LC355	0.89799 0.0001	0.72481 0.0001	0.88227 0.0001	0.77878 0.0001	0.87291 0.0001	0.91042 0.0001	0.90010 0.0001	1.00000 0.0000	0.96844 0.0001	0.97020 0.0001	0.92232 0.0001
LC1708	0.88877 0.0001	0.67056 0.0004	0.86947 0.0001	0.75798 0.0001	0.85924 0.0001	0.91274 0.0001	0.89667 0.0001	0.96844 0.0001	1.00000 0.0000	0.98077 0.0001	0.93375 0.0001
LC1810	0.87583 0.0001	0.72518 0.0001	0.87061 0.0001	0.77178 0.0001	0.87862 0.0001	0.94932 0.0001	0.90879 0.0001	0.97028 0.0001	0.98077 0.0001	1.00000 0.0000	0.96247 0.0001
LTOT	0.84464 0.0001	0.71840 0.0001	0.85103 0.0001	0.77345 0.0001	0.88358 0.0001	0.99518 0.0001	0.91780 0.0001	0.92232 0.0001	0.93375 0.0001	0.96247 0.0001	1.00000 0.0000
LTOCCONC	0.73441 0.0001	0.47383 0.0125	0.73815 0.0001	0.59930 0.0010	0.75444 0.0001	0.86711 0.0001	0.73527 0.0001	0.81374 0.0001	0.87006 0.0001	0.85024 0.0001	0.89285 0.0001
PSILT	0.88889 0.0001	0.64054 0.0003	0.70904 0.0001	0.63042 0.0004	0.72883 0.0001	0.85799 0.0001	0.72839 0.0001	0.70700 0.0001	0.69597 0.0001	0.75333 0.0001	0.84448 0.0001
PCLAY	0.56594 0.0021	0.67559 0.0001	0.59400 0.0011	0.58557 0.0013	0.61891 0.0006	0.66782 0.0001	0.62115 0.0006	0.86792 0.0001	0.58482 0.0014	0.67785 0.0001	0.65014 0.0002

5.12 and 5.13 indicate that the norm alization parameters may be used to reduce the between-station variability in station averages even though no reduction in within-station variability is achieved by normalization.

5.4.3 Parameter Variability

The magnitude of temporal change that will be detected by the current monitoring program is a direct function of the underlying variability in the parameters being measured and the number of replicate samples analyzed each year. Table 5.14 lists the metal parameters and selected organic parameters along with a pooled estimate of the within-station standard deviation. Also listed is the minimum multiplicative change that will be detected (with **80 % probability**) by the current monitoring program for three different second-year sample sizes. A detectable multiplicative difference of 1.5 is a 50% change and 2.1 represents a 110 % change.

For the metal parameters, changes on the order of 1.1 to 1.5 will be detectable with a second-year sample size of 6. This range only increases to 1.2 through 1.8 for a sample size of 2 which indicates that a large second-year sample size is not crucial to the detection of changes in the metal parameters. This statement is also true for the organic parameters that have a pooled standard deviation 0.30 or less. A reduction of the second-year sample size to 4 would not appreciably affect the organic parameters with pooled standard deviations of 0.60 or less. Since this category includes most of the organic parameters, it appears that a reduction in sample size to 4 for the second year would have no significant detrimental effect on the ability to detect changes.

Caution should be used when drawing conclusions based on Table 5.14. Because of the heterogeneity of variance from station to station, the pooled standard deviations in Table 5.14 should be viewed as average variability estimates. Standard deviation values are reported by station in Tables 5.15 and 5.16. These values may be used in conjunction with Table 5.17 to determine detectable multiplicative changes for the individual stations in subsequent years.

6. STUDY CRITIQUE AND RECOMMENDATIONS FOR YEAR 2 STUDY

Of the Year 1 and overall (Years 1-3) objectives of the BSMP, most have been met or are in the process of being met through the activities conducted during this first year of study. In spite of the extremely short lead time given, the less than ideal open water conditions during September, 1984, and the lack of a shakedown period for the sampling vessel and several shortcomings of the vessel, the 1984 field sampling program was initiated and successfully concluded during its first year.

The first year's sampling design was intended to yield monitoring data from Barter Island to Cape Halkett as far offshore as the 25 m isobath. The design was intended to obtain surface sediment and benthic bivalve samples such that adequate replication could be attained. Due to ice conditions and boat problems, the Year 1 program did not succeed in obtaining the complete areal coverage desired. Bivalve collections were inadequate due to the sparsity of animals at pre-selected locations, which were chosen primarily for sediment characteristics and secondarily for expected bivalve abundance. Logistically, the low sea water flow rates afforded by our washdown system was of lesser significance in the inability to obtain sufficient numbers of animals. Offshore ice conditions further hindered the ability to sample the abundant offshore glass scallop, Arctinula.

Analytically and statistically the Year 1 program was successful in identifying the key parameters and parameter ratios to be used in long-term monitoring of oil and gas exploration, and development inputs. The within-station variability of these parameters and ratios was documented. Based on these results, we are able to document the magnitudes of detectable changes for these parameters and are able to confidently plan our replication scheme for the Year 2 study.

Table 5.14 Detectable Multiplicative Changes in Concentration as a Function of Pooled Standard Deviation on a Logarithmic (Natural) Scale.

Metal Parameter	Pooled Standard Deviation	Second Year Sample Size		
		6	4	2
Cd	0.18	1.4	1.5	1.7
Pb	0.13	1.3	1.4	1.5
Ba	0.16	1.4	1.4	1.6
Cu	0.21	1.5	1.6	1.8
Cr	0.05	1.1	1.1	1.2
Zn	0.21	1.5	1.6	1.8
v	0.16	1.4	1.4	1.6

Organic Parameter	Pooled Standard Deviation	Second Year Sample Size		
		6	4	2
N	0.60	3.0	3*5	5.2
F	1.24	9.4	13.1	30.6
P	0.60	3.0	3.5	5.2
D	1.01	6.2	8.2	16.3
PAH	0.78	4.1	5.1	8.7
TALK	0.34	1.9	2.1	2.6
LALK	0.37	2.0	2.2	2.8
1708	0.32	1.8	2.0	2.5
1810	0.32	1.8	2.0	2.5
TOT	0.28	1.7	1.8	2.2
355	0.39	2.1	2.3	3.0
FFPI	0.11	1.3	1.3	1.4
P/D	0.60	3.0	3.5	5.2
1S0	0.32	1.8	2.0	2.5
ALK	0.32	1.8	2.0	2.5
LALK/TALK	0.18	1.4	1.5	1.7
ISO/ALK	0.14	1.3	1.4	1.5
TOC	0.30	1.8	1.9	2.3.

Table 5.15 Standard Deviation on a Logarithmic (Natural) Scale for the Metal Parameters and the Organic Parameters 355 and TOC.

Station	Metal Parameter							355	TOC
	cd	Pb	Ba	Cr	Cu	Zn	v		
2E	0.23	0.07	0.05	0.09	0.21	0.05	0.07	0.12	0.09
2F	0.09	0.05	0.02	0.02	0.09	0.21	0.05	0.18	0.18
3A	0.16	0.14	0.05	0.09	0.05	0.05	0.05	0.07	0.07
3B	0.14	0.12	0.05	0.02	0.18	0.07	0.02	0.21	0.05
4A	0.21	0.09	0.02	0.02	0.12	0.02	0.12	0.53	0.28
4B	0.28	0.18	0.05	0.12	0.21	0.14	0.12	0.53	0.28
4C	0.41	0.28	0.16	0.16	0.32	0.25	0.25	0.34	0.48
5(1)	0.23	0.07	0.07	0.32	0.37	0.05	0.09	0.55	0.23
5(10)	0.14	0.09	0.02	0.05	0.14	0.02	0.05	0.16	0.69
5(2)	0.32	0.12	0.05	0.05	0.05	0.53	0.02	0.25	0.46
5(5)	0.14	0.05	0.05	0.07	0.07	0.05	0.05	0.18	0.41
5A	0.12	0.09	0.14	0.05	0.05	0.07	0.05	0.16	0.02
5B	0.00(a)	0.28	0.02	0.07	0.14	0.14	0.05	0.28	0.16
5D	0.05	0.05	0.02	0.05	0.05	0.02	0.02	0.32	0.07
5E	0.55	0.53	0.34	0.62	0.55	0.67	0.62	1.01	0.69
5F	0.14	0.09	0.05	0.05	0.02	0.05	0.02	0.05	0.12
5G	0.37	0.14	0.12	0.09	0.12	0.12	0.14	1.03	0.30
6A	0.30	0.16	0.02	0.07	0.05	0.02	0.05	0.14	0.12
6B	0.12	0.05	0.05	0.05	0.05	0.07	0.07	0.23	0.05
6C	0.28	0.23	0.28	0.25	0.21	0.28	0.28	0.21	0.21
6D	0.28	0.09	0.07	0.09	0.18	0.07	0.12	0.30	0.28
6F	0.34	0.39	0.51	0.16	0.28	0.23	0.25	0.60	0.44
7A	0.34	0.12	0.05	0.07	0.16	0.07	0.02	0.12	0.34
7B	0.14	0.07	0.02	0.05	0.12	0.07	0.05	0.12	0.14
7C	0.16	0.07	0.02	0.02	0.02	0.01	0.02	0.07	0.05
7E	0.21	0.05	0.02	0.07	0.07	0.02	0.05	0.05	0.09
7G	0.25	0.05	0.07	0.16	0.51	0.05	0.14	0.30	0.37

(a) All measurements were below the detection limit.

Table 5.16 Standard Deviations on a Logarithmic (Natural) Scale for Selected Organic Parameters by Station.

Organic Parameter	Station						
	2F	3B	4A	5 D	6 c	6D	7A
N	0.46	0.34	0.12	0.18	0.67	0.34	1.27
F	0.92	0.28	0.30	0.16	0.55	0.44	2.99
P	0.34	0.34	0.07	0.09	0.58	0.32	1.31
D	1.04	0.28	0.14	0.12	0.69	0.28	2.32
PAH	0.25	0.80	0.25	0.32	0.44	0.30	1.70
TALK	0.12	0.28	0.09	0.14	0.30	0.30	0.55
LALK	0.09	0.28	0.05	0.41	0.30	0.60	0.46
1708	0.05	0.25	0.09	0.41	0.34	0.25	0.53
1810	0.16	0.25	0.12	0.39	0.44	0.25	0.48
TOT	0.14	0.23	0.14	0.39	0.32	0.30	0.25
FFPI	0.05	0.07	0.05	0.07	0.09	0.05	0.28
P/D	0.69	0.18	0.12	0.09	0.21	0.16	1.33
ISO	0.09	0.25	0.05	0.41	0.37	0.25	0.55
ALK	0.16	0.25	0.07	0.41	0.34	0.25	0.46
LALK/TALK	0.12	0.05	0.07	0.09	0.12	0.39	0.09
ISO/ALK	0.07	0.02	0.07	0.02	0.02	0.02	0.07

Table 5.17 Detectable Multiplicative Changes in Concentration as a Function of Standard Deviation on a Logarithmic (Natural) Scale.

Standard Deviation	Second Year Sample Size		
	6	4	2
0.1	1.2	1.3	1.4
0.2	1.5	1.6	1.8
0.3	1.8	1.9	2.3
0.4	2.1	2.3	3.1
0.5	2.5	2.9	4.0
0.6	3.0	3.5	5.3
0.7	3.6	4.3	6.9
0.8	4.3	5.3	9.1
0.9	5.1	6.5	11.9
1.0	6.1	7*9	15.7
1.2	8.7	12.0	27.1
1.4	12.4	18.1	47.0
1.6	17.7	27.3	81.4
1.8	25.4	41.3	141.0
2.0	36.3	62.4	244.3

The lack of replication for the organic parameters at 20 of the 27 stations sampled creates some uncertainty as to how the pooled measurements from these stations should be used. The original intent was to extrapolate the within-station variances from the seven replicated stations to the remaining 20, based on some similar station characteristic(s): grain size distribution, absolute concentration levels, geographical region, etc. We have not yet determined the most valid approach, if indeed one exists. To partly alleviate this problem, replicates should be analyzed at these stations during subsequent years. Making the assumption that the magnitude of variability remains constant from year to year, would allow the testing of hypotheses concerning temporal trends in average parameter levels at those stations. Fewer replicates could be analyzed per station (perhaps 2, 3 or 4) so that variability information can be obtained for a larger number of stations. A reduction in sample size from 6 to 3 or 4 still would allow for the estimation of the magnitude of variability, whereas estimating variability at stations with only one pooled sample requires unverifiable assumptions concerning the equality of variability levels among stations.

Based on the metals data and on a subset of the hydrocarbon data from the Year 1 study, and from similar monitoring studies on Georges Bank and in the Gulf of Mexico, small incremental additions can be detected. However, due to the expected low level inputs from well drilling and well production activities, OCS activities are in the short term, most likely to be detected only within the near- to mid-field distances (1-10km) from point sources.

The utilization of Year 2 resources should reflect the expectation of detecting inputs only in the near- to mid-field; should reflect a need to obtain absolute concentration and variability data at those offshore and eastern-most stations which were proposed but not sampled during the Year 1 study; and should reflect an acute need to obtain nearshore and offshore bivalves.

An important information gap exists pertaining to the relation of source materials, in particular peat material, to the observed sediment hydrocarbon and metal distributions. Representative peat samples need to be obtained and analyzed for target elements and hydrocarbon compounds. As the distinction between diagenetic peat and fossil fuel becomes more difficult due to molecular similarities, there is an important need to apply molecular marker techniques to peat and to offshore sediments. The tri-, tetra- and pentacyclic hydrocarbons derived from terpenes and the sterane compounds have been shown to be valuable markers in differentiating diagenetic and fossil hydrocarbons.

One recommended Year 2 study plan includes the following elements.

station selections

- The sampling of the Camden Bay Area stations not sampled during the Year 1 program.
- The resampling of the 27 stations sampled during the Year 1 program.
- The selection of three additional nearshore bivalve sampling sites with documented abundances of bivalves, and intensive bivalve sampling.
- The establishment and sampling of additional sediment stations corresponding to the bivalve stations.

Logistics

- Modification of bivalve washdown system to increased flow rate and on-board processing throughput.

Analytical

- The elimination of the U V/F measurement due to **high** background fluorescence and the limited potential use of U V/F in monitoring studies in the B eaufort.
- The inclusion of triterpane and sterane measurements **in** selected sediment sa m pies and source materials (see below).
- The inclusion of iron (Fe) and manganese (M n) into the metals analytical plan for use as important potential normalizers.
- The examination of the fine sediment **fraction** for che **mical** content and co m position.

Source Materials

- The sampling and detailed analysis of several sa m pies of coastal peat deposits and **riverine** source m aterials.

The action items *mentioned* above should be included **in** the tactical design of the Year 2 program. All of these items are reco m mended as necessary approaches to meeting the overall objectives of the multi-year program.

7. REFERENCES

- Aizenshtat, Z. 1973. Perylene and its geochemical significance. *Geochim. Cosmochim. Acta* 37:559-567.
- Alaska Oil and Gas Conservation Commission (1983). 1983 Statistical Report, Anchorage, Alaska.
- Anderson, J.W. 1983. The transport of petroleum hydrocarbons from sediments to benthos and the potential effects. Pages 165-180 In: G.F. Mayer, ed. Ecological Stress and the New York Bight: Science and Management, Estuarine Research Federation, Columbia, S. C.
- Antonov, V.S. 1958. The role of continental runoff in the current regime of the Arctic Ocean. *Problemy Severa* 1:52-64.
- Armstrong, H. W., K. Fucik, J.W. Anderson and J.M. Neff. 1979. Effects of oilfield brine effluent on sediments and benthic organisms in Trinity Bay, Texas. *Mar. Environ. Res.* 2:55-69.
- Atlas, R. M., P.D. Boehm and J.A. Calder. 1981. Chemical and biological weathering of oil from the Amoco Cadiz oil spillage within the littoral zone. *Estuar. Coastal Mar. Sci.* 12:589-608.
- Auble, G. T., A.K. Andrews, D.B. Hamilton and J.E. Rolelle. 1983. A Workshop Model Simulating the Fate and Effects of Drilling Muds and Cuttings on Benthic Communities, Western Energy and Land-Use Team. U.S. Fish and Wildlife Service, Fort Collins, CO.
- Ayers, R. C., Jr., T.C. Sauer, Jr., R.P. Meek and G. Bowers. 1980a. An environmental study to assess the impact of drilling discharges in the Mid-Atlantic. I. Quantity and fate of discharges. Pages 382-418 In: Symposium on Research on Environmental Fate and Effects of Drilling Fluids and Cuttings. Courtesy Associates, Washington, D.C.
- Ayers, R. C., Jr., T.C. Sauer, Jr., D.O. Stuebner and R.P. Meek. 1980b. An environmental study to assess the effect of drilling fluids on water quality parameters during high rate, high volume discharges to the ocean. Pages 351-381 In: Symposium on Research on Environmental Fate and Effects of Drilling Fluids and Cuttings. Courtesy Associates, Washington, D. C.
- Ayers, R. C., Jr., T.C. Sauer, Jr. and P.W. Anderson. 1983. The Generic Mud Concept for Offshore Drilling for NPDES Permitting. IAD C/SPE 1983 Drilling Conference. New Orleans, LA. February 1983. Society of Petroleum Engineers, Dallas, TX. 75206. IAD C/SPE Paper No. 11399. 8 pp.
- Barnes, P.W. 1981. Physical characteristics of the Sale 71 area. Chapt. 3 In: D. W. Norton and W. M. Sackinger, eds. In: Proceedings of a Synthesis Meeting. Beaufort Sea-Sale 71 Synthesis Report, Chena Hot Springs, AK, 22-23 April, 1981, U.S. D. C.-NOAA, OCSEAP, Juneau, AK.
- Barnes, P. W. and E. Reimnitz. 1972. River overflow into sea ice off the northern coast of Alaska, Spring 1972. *Trans. Amer. Geophys. Union.* 53: 1020.
- Barnes, P. W., E. Reimnitz and D. Drake. 1977. Marine Environmental Problems in the Ice Covered Beaufort Sea Shelf and Coastal Regions. NOAA/O C S E A P Annual Report., R. J. 205, 229 pp.

- Barnes, P. W., D.M. Rearic and E. Reimnitz. 1984. Ice gauging characteristics and processes. Pages 185-212 In: P. Id. Barnes, D.M. Schell, E. Reimnitz eds. The Alaskan Beaufort Sea-Ecosystems and Environments, Academic Press, New York.
- Barry, R.G. 1979. Study of Climatic Effects on Fast Ice Extent and Its Seasonal Decay Along the Beaufort-Chukchi Coasts. Final Reports of Principal Investigators, Environmental Assessment of the Alaskan Continental Shelf. U.S. D. C. -NO AA-OCSEAP, Boulder, CO.
- Barry, R. G., R.E. Moritz and J.C. Rogers. 1979. The Fast Ice Regimes of the Beaufort and Chukchi Sea Coasts, Alaska. Appendix I, **Final Reports** of Principal Investigators, Research Unit No. 244. U.S. D. C.- NO AA- OCSEAP-OCSEAP, Boulder, CO.
- Bartha, R. and R.M. Atlas. 1984. Transport and transfer mechanisms of petroleum: Biological processes. In: Federal Interagency Committee on Pollution Research, Development and Monitoring (CORDM) Report on Assessment of the Long-Term Environmental Effects of U.S. Offshore Oil and Gas Development Activities. NOAA, Rockville, MD.
- Bascom, W., A.J. Mearns and M.D. Moore. 1976. A biological survey of oil platforms in the Santa Barbara Channel. *J. Petrol. Technol.*, Nov. 1976. Pages 1280-1284.
- Battelle/Woods Hole Oceanographic Institution. 1983. **Georges Bank Benthic Infauna Monitoring Program. Final Report, Year 1.** Prepared for U.S. Dept. of the Interior, Minerals Management Service, New York OCS Office, New York. Contract No. 14-12-001-29192.
- Battelle/Woods Hole Oceanographic Institution. 1984. **Georges Bank Benthic Infauna Monitoring Program. Final Report, Year 2.** Prepared for U.S. Dept. of the Interior, Minerals Management Service, Atlantic OCS Office. Vienna, VA. Contract No. 14-12-0001-29192.
- Boehm, P.D. 1983. The long term fate of crude oil spilled in an Arctic nearshore environment. In: Proceedings of the Sixth Arctic Marine Oil Spill Program Technical Seminar, EPS, Canada.
- Boehm, P.D. 1984. The Status and Trends Program: Recommendations for the Design and Implementation of the Chemical Measurements Segment: Final Report of Workshop held October, 1983, NOAA/OA/D Rockville, MD.
- Boehm, P.D. and Barrington, J.W. 1984. Aspects of the polycyclic aromatic hydrocarbon geochemistry of recent sediments in the Georges Bank Region. *Env. Sci. Tech.* 18:840-845.
- Boehm, P.D. and D.L. Fiest. 1980. Determination of Hydrocarbon Composition and Concentration in Major Components of the Marine Ecosystem. Vol VI, In: Jackson W.B. and G.M. Faw, eds. Biological/Chemicals Survey of Texas and Capline Sector Salt Dome Brine Disposal Sites Off Louisiana 1978-1979. NOAA Technical Memorandum. NMFS-SEFC-30. 136 pp.
- Boehm, P.D. and D.L. Fiest. 1981. The transport of hydrocarbons from the water column to the benthos during the IX TOCI blowout. In: Proceedings of Symposium on the Research Results of the OCS Researcher-Cruise. June 9-10, 1979, Miami, FL. NOAA.

- Boehm, P.D. and D.L. Fiest. 1982. Subsurface distributions of petroleum from an offshore well blow out. The IXTO C I blowout, Bay of Campeche. Environmental Sci. and Technol. 16:67-74.
- Boehm, P. D., J.E. Barak, D.L. Fiest and A. Elskus. 1982a. A chemical investigation of the transport and fate of petroleum hydrocarbons in littoral and benthic environments: The Tsesis oil spill. Marine Environmental Res. 6: 157-188.
- Boehm, P. D., D.L. Fiest and A. Elskus. 1982b. Comparative weathering patterns of hydrocarbons from the A m oco C adiz oil spill observed at a variety of coastal environments. In: Proceedings, International Symposium on the Am oco Cadiz; Fates and Effects of the Oil Spill. Brest, France, November 19-22, 1979. (1981) CO B/ CNE XO Brest, France.
- Boehm, P. D., D.L. Fiest and P. Hirtzer. 1982c. Chemistry 2. Analytical Biogeochemistry 1981 Study Results. (BIOS) Baffin Island Oilspill Working Report 01-2, 354 pp.
- Boehm, P. D., D.L. Fiest, P. Hirtzer, L. Scott, R. Norstrom and R. Engelhardt. 1982d. A biogeochemical assessment of the BIOS experimental spills: Transport pathways and fates of petroleum in benthic animals. Pages 581-618 In: Proceedings of the Fifth Arctic Marine Oil Spill Program Technical Seminar. Environmental Protection Service, Ottawa, Canada.
- Boehm, P. D., D.L. Fiest, D. Mackay and S. Peterson. 1982e. Physical-chemical weathering of petroleum hydrocarbons from the IX T O C I blowout. Chemical measurements and a weathering model. Environmental Sci. Technol. 16:498-505.
- Boehm, P. D., A.D. Wait, D.L. Fiest and D. Pilson (1982f) Chemical Assessment-Hydrocarbon Analysis, Section Two. In: P. Boehm, ed. IXTO C Oil Spill Assessment. Final Report Contract No. AA851-CTO-71, BLM/MMS, New Orleans, LA.
- Boehm, P. D., Steinhauer, W. and Brown, J. 1984. Organic Pollutant Biogeochemistry Studies of the Northeast U.S. Marine Environment. Part 1: The State of Organic Pollutant Contamination of The Boston Harbor, Massachusetts Bay, Cape Cod Bay System: Sediments and Biota, Final Report, Contract NA-83-FA-C-00022, NOAA National Marine Fisheries Service, Sandy Hook, NJ. 61 pp.
- Boothe, P.N. and B.J. Presley. 1983. Distribution and Behavior of Drilling Fluids and Cuttings around Gulf of Mexico Drill Sites. Draft Final Report to American Petroleum Institute. Dept. of Oceanography, Texas A & M University, College Station, TX. 65 pp.
- Bothner, M.H., R.R. Rendigs, E. Campbell, M.W. Doughton, P.J. Aruscavage, A.F. Dorrzapf, Jr., R.G. Johnson, C.M. Parmenter, M.J. Pikerling, D.C. Brewster and F.W. Brown. 1982. The Georges Bank Monitoring Program. Analysis of Trace Metals in Bottom Sediments. First Year Final Report to U.S. Dept. of the Interior, Minerals Management Service, New York OCS Office, New York. U.S. Department of the Interior, Geological Survey, Woods Hole, MA. Interagency Agreement No. AA851-IA2-18.

- Bothner, M. H., R.R. Rendigs, E. Campbell, M.W. Doughten, C.M. Parmenter, M.J. Pickering, R.G. Johnson and J.R. Gillison. 1983. The Georges Bank Monitoring Program Analysis of Trace Metals in Bottom Sediments During the Second Year of Monitoring. Final Report to U.S. D.I., Minerals Management Service, Washington, D. C., U.S. Dept. of the Interior, Biological Survey, Woods Hole, MA.
- Brandsma, M. G., L.R. Davis, R.E. Ayers, Jr. and T.C. Sauer, Jr. 1980. A computer model to predict the short-term fate of drilling discharges in the marine environment. Pages 588-610 In: Symposium on Research on Environmental Fate and Effects of Drilling Fluids and Cuttings. Courtesy Associates, Washington, D.C.
- Broad, A.C. 1979. Environmental assessment of selected habitats in the Beaufort and Chukchi littoral system. Pages 361-544 In: Environmental Assessment of the Alaskan Continental Shelf. Annual Reports of Principal Investigators for the Year ending March, 1979. Volume III: Receptors-Fish, Littoral, Benthos. Outer Continental Shelf Environmental Assessment Program. Boulder, CO.
- Broad, A. C., W. Griffiths and A.G. Carey, Jr. 1981. Invertebrates. Pages 27-31 In: D. W. Norton and W.M. Sackinger, eds. Proceedings of a Synthesis Meeting: Beaufort Sea-Sale 71 - Synthesis Report. Chen. Hot Springs, AK. 21-23 April, 1981. U. S. D. C.-N OAA-OCSEAP, Juneau, AK.
- Brown, D. W., L.S. Ramos, J.J. Friedman, and W.D. MacLeod. 1979. Analysis of trace levels of petroleum hydrocarbons in marine sediments using a solvent/slurry extraction procedure. Pages 161-167 In: Trace Organic Analysis: A New Frontier in Analytical Chemistry. National Bureau of Standard Special Publication 519. Washington, D. C.
- Burton, J. D., N.J. Marshall and A.J. Phillips. 1968, Solubility of barium sulfate in sea water. *Nature* 271:834-835.
- Calder, J.A. and P.D. Boehm. 1982. The Chemistry of Amoco Cadiz Oil in the Aber Wrath. In: Proceedings, International Symposium on the Amoco Cadiz: Fates and Effects of the Oil Spill. Brest, France, November 19-22, 1979. COB/CNE XO Brest, France.
- Campbell, J.A. and D.H. Loring. 1980. Baseline levels of heavy metals in the waters and sediments of Baffin Bay. *Mar. Poll. Bull.* 11:257-261.
- Cannon, P.J. 1981. The Environmental Geology and Geomorphology of the Barrier Eland-Lagoon System Along the Beaufort Sea Coastal Plain from Prudhoe Bay to the Colville River. NOAA/O CSEAP Annual Rept., R.U. Unit 530, 52 pp.
- Carlson, R.F. 1976. A Theory of Spring River Discharge into the Arctic Ice. Pack' Pages 165-166 In: D.C. Burrell and D.W. Rood, eds. Proceedings of 3rd International Conference Port. Ocean Engin. Arctic Condt., Vol. I. Inst. Mar. Sci., Univ. Alaska, Fairbanks, AK.
- Chan, L. H., D. Drummond, J.M. Edmond and B. Grant. 1977. On the barium data from the Atlantic GE OSE CS expedition. *Deep-Sea Res.* 24:613-649.
- Clark, R. C., Jr. and D.W. Brown. 1977. Petroleum: Properties and analyses in biotic and abiotic systems. Pages I-89 In: Vol. I, D.C. Malins, ed. Effects of Petroleum on Arctic and Subarctic Marine Environments and Organisms. Academic Press, NY.

- Crippen, R. W., S.L. Hodd and G. Greene. 1980. Metal levels in sediment and benthos resulting from a drilling fluid discharge into the Beaufort Sea. In: Pages 636-669 Symposium on Research on Environmental Fate and Effects of Drilling Fluids and Cuttings. Courtesy-Associates, Washington, D. C.
- Dames and Moore, Inc. 1978. Drilling Fluid Dispersion and Biological Effects Study for the Lower Cook Inlet C. O. S.T. Well. Report submitted to Atlantic Richfield Co. 309 pp.
- Dames and Moore, Inc. 1984. Proceedings of the Beaufort Sea Monitoring Workshop, sponsored by National Oceanic and Atmospheric Administration-Minerals Management Service, September 1983. Draft Report.
- Davis, N., G.R. van Blaricom and P.K. Dayton. 1982. Man-made structures on marine sediments: Effects on adjacent benthic communities. Mar. Biol. 70:295-303.
- Deis, Jeffrey L. and Robert Pierson. 1983. Arctic Summary Report Update, September 1983. Outer Continental Shelf Oil and Gas Activities in the Arctic and their Onshore Impacts. Rogers, Golden and Halpern, 11872 Sunrise Valley Drive, Reston, VA 22901.
- Dunton, K. H., E. Reimnitz and S. Schonberg. 1982. An Arctic kelp community in the Alaskan Beaufort Sea. Arctic 35(4):465-484.
- Dygas, J.A. and D.C. Burrell. 1976. Dynamic sedimentological processes along the Beaufort Sea coast of Alaska. Pages 189-203 In: D.W. Wood and D.C. Burrell, eds. Assessment of the Arctic Marine Environment. Inst. Mar. Sci., Univ. Alaska, Fairbanks, AK.
- Ecomar, Inc. 1978. Tanner Bank Fluids and Cuttings Study. Conducted for Shell Oil Company, January through March, 1977. Ecomar, Inc., Goleta, CA. 495 pp.
- Ecomar, Inc. 1983. Mud Dispersion Study. Norton Sound Cost Well No. 2. Report for A R C O Alaska, Inc. Ecomar, Inc., Goleta, CA. 91 pp.
- E G & G Environmental Consultants. 1982. A Study of Environmental Effects of Exploratory Drilling on the Mid-Atlantic Outer Continental Shelf. Final Report of the Block 684 Monitoring Program. Waltham, MA. Available from Offshore Operators Committee, Environmental Subcommittee, P.O. Box 50751, New Orleans, LA. 70150.
- Fagerstrom, T. and A. Jernelov. 1971. Formation of methyl mercury from pure mercuric sulfide in anaerobic organic sediment. Wat. Res. ~:121-122.
- Barrington, J. W. and B. W. Tripp. 1977. Hydrocarbons in western North Atlantic surface sediments. Geochim. Cosmochim. Acta. 41:1627-1641.
- Barrington, J. W., J.M. Teal, B.W. Tripp, J.B. Livramento and A. McElroy. 1983. Biogeochemistry of Petroleum Components at the Sediment-Water Interface. Final Report, U.S. DOE, Div. Biomedical-Environmental Programs. Contract D E-A C02-77EV04256A007, and U.S. D.I., MMS.
- Federal Energy Administration. 1977. Strategic Petroleum Reserve. Draft Supplemental Final Environmental Impact Statement. Bryan Mound Salt Dome. FEA/S77/211.
- Fork, R.L. 1974. Petrology of Sedimentary Rocks. Hemphill Publishing Co., Austin, Texas, 182 pp.

- Fucik, K. W., H. W. Armstrong and J.M. Neff. 1977. The uptake of naphthalenes by the clam, Rangia cuneata, in the vicinity of an oil platform in Trinity Bay, Texas. Pages 637-640 The 5th Conference on the Prevention, Behavior, Control and Clean-up of Oil Pollution, Washington, D. C., American Petroleum Institute.
- Gavis, J. and J.F. Ferguson. 1972. The cycling of mercury through the environment. Water Res. 6:989-1008.
- Gettleton, D.A. and C.E. Laird. 1980. Benthic barium levels in the vicinity of six drill sites in the Gulf of Mexico. Pages 739-788 In: Symposium Research on Environmental Fate and Effects of Drilling Fluids and Cuttings. Courtesy Associates, Washington, D. C.
- Goldberg, E.D. 1963. Chemistry of seawater. In: W.N. Hill, ed. The Seas, VOL 2. Interscience Publ, NY.
- Gordon, D. C., P.D. Keizer, W.R. Hardstaff, and D.G. Alduos. 1976. Fate of crude oil spilled in seawater contained in outdoor tanks. Environmental Sci. Technol. 10:580-585.
- Gordon, D. C., Jr., J. Dale and P.D. Keizer. 1978. Importance of sediment working by the deposit-feeding polychaete Arenicola marina on the weathering rate of sediment-bound oil. J. Fish. Res. Bd. Can. 35:591-603.
- Grantz, A., S.E. Eittreim and O.T. Whitney. 1981. Geology and physiology of the continental margin north of Alaska and implications for the origin of the Canada Basin. Pages 439-492 In: A.E. M. Nairn, M. Churkin, Jr. and F.C. Slehti, eds. The Arctic Ocean. Plenum Press, NY.
- Grantz, A., O.T. Whitney and S.E. Eittreim. 1982. Geological Framework, Hydrocarbon Potential, and Environmental Conditions for Exploration and Development of Proposed Oil and Gas Lease Sale 87 in the Beaufort and Northeast Chukchi Seas. Open File Report 82-48. U.S. D.I., Geological Survey, 73 pp
- Griffiths, W.B. and R.E. Dillinger. 1981. Beaufort Sea barrier island-lagoon ecological process studies: Final report, Simpson Lagoon. Part V: Invertebrates. Pages 1-198 In: Environmental Assessment of the Alaskan Continental Shelf. Final reports of principal investigators. Volume 8: Biological Studies. National Oceanic and Atmospheric Administration, Boulder, CO.
- Gschwend, P. M., P.H. Chen and R.A. Hites. 1983. On the formation of perylene in recent sediments: kinetic models. Geochim. Cosmochim. Acta 47:2115-2119.
- Gundlach, E. R., P.D. Boehm, M. Marchand, R.M. Atlas, D.M. Ward and D.A. Wolfe. 1983. Fate of Amoco Cadiz oil. Science. 221:122-129.
- Haines, J.R. and R.M. Atlas. 1982. In situ microbial degradation of Prudhoe Bay crude oil in Beaufort Sea sediments. Mar. Environ. Res. 7:91-102.
- Holme, N.A. and I.A. McIntyre, Eds. 1971. Methods for the Study of Marine Benthos. Blackwell Scientific Publications, Oxford.
- Hood, D. W. 1963. Chemical oceanography. Oceanog. Mar. Biol. Ann. Rev. 1: 129-155.
- Houghton, J. P., D.L. Beyer and E.D. Thielk. 1980. Effects of oil well drilling fluids on several important Alaskan marine organisms. Pages 1018-1043 In: Symposium on Research on Environmental Fate and Effects of Drilling Fluids and Cuttings. Courtesy Associates, Washington, D. C.

- Houghton, J. P., K.R. Critchlow, D.C. Lees, R.D. Czapinski, R.C. Miller, R.P. Britch and J.A. Mills. 1981. Fate and Effects of Drilling Fluids and Cuttings Discharges in Lower Cook Inlet, Alaska, and on Georges Bank. Final Report to NOAA and BLM. Dames and Moore, Seattle, WA.
- Hume, J.E. and M. Schalk. 1967. Shoreline processes near Barrow, Alaska: A comparison of the normal and the catastrophic. Arctic 20:86-103.
- Johanssen, S., V. Larsson and P. Boehm. 1980. The Tsesis oil spill impact on the pelagic ecosystem. Mar. Poll. Bull. 11:284-293.
- John, P. and I. Soutar. 1976. Identification of crude oils by synchronous excitation spectrofluorometry. Anal. Chem. 48:520-524.
- Johnson, J. H., P.W. Brooks, A.K. Aldridge, S.J. Rowland. 1978. Presence and sources of oil in the sediment and benthic community surrounding the Ekofisk field after the blowout at Bravo. Pages 488-514 In: Proceedings of the Conference on Assessment of Ecological Impacts of Oil Spills, American Institute of Biological Sciences, Washington, D. C.
- Kaplan, I.R. and M.I. Venkatesan, 1981. Characterization of organic matter in sediments from Gulf of Alaska, Bering and Beaufort Seas (Final Report). U.S. National Oceanic and Atmospheric Administration, Outer Continental Shelf Environmental Assessment Program, Juneau, Alaska.
- Katz, A., and I.R. Kaplan. 1981. Heavy metals behavior in coastal sediments of southern California: A critical review and synthesis. Marine Chemistry 10:261-299.
- Kolpack, R. L., J.S. Mattson, J.B. Mark, Jr. and T.C. Tu. 1971. Hydrocarbon content of Santa Barbara Channel sediments. In: R.L. Kolpack, Ed. Biological and oceanographical Survey of the Santa Barbara Channel Oil Spill 1969-1970. II. Physical, Chemical, and Geological Studies. Allan Hancock Foundation, University of Southern California, Los Angeles, CA.
- Kozo, T.L. 1981. Winds. Pages 59-69 In: D. W. Norton and W. M. Sackinger, Eds. Beaufort Sea (Sale 71) Synthesis Report 1981. National Oceanic and Atmospheric Administration, Bureau of Land Management.
- Kramer, J. R., H.D. Grundy and L.C. Hammer. 1980. Occurrence and volatility of trace metals in barite for ocean drilling operations. In: Symposium on Research on Environmental Fate and Effects of Drilling Fluids and Cuttings. Courtesy Associates, Washington, D. C. pp. 789-798.
- Lees, D.C. and J.P. Houghton. 1980. Effects of drilling fluids on benthic communities at the Lower Cook Inlet C. O.S. T. well. Pages 209-350 In: Symposium on Research on Environmental Fate and Effects of Drilling Fluids and Cuttings. Courtesy Associates, Washington, D. C.
- Lloyd, J.B.F. 1971. The nature and evidential value of the luminescence of automobile engine oils and related materials. J. Forensic Sci. 11:83-94, 153-210, 235.
- Lynch, Christopher W., Robert W. Rudolph, and Douglas L. Slitor. 1984. Arctic Summary Report, December 1984 (Field Draft). Outer Continental Shelf Oil and Gas Activities in the Arctic and their Onshore Impacts. Rogers, Golden and Halpern, 11710 Bowman Green Drive, Reston, VA 22090.

- Lysyj, I., G. Perkins, J.S. Farlow and W. Lamoreaux. 1981. Effectiveness of offshore produced water treatment. Pages 63-67 In: Proc. 1981 Oil Spill Conference. American Petroleum Institute, Washington, D. C.
- MacDonald, R.W. 1981. An examination of metal inputs to the southern Beaufort Sea by disposal of waste barite in drilling fluid. Ocean Manage. 8:29-49.
- Marchand, M. and M.P. Caprais. 1981. Suivi de la pollution de l'Amoco Cadiz dans l'eau de mer et les sediments marins. Pages 23-54 In: Amoco Cadiz: Fate and Effects of the Oil Spill, Proceedings of the International Symposium. November 19-22, 1979, C N E X O, Brest, France.
- Mathews, J.B. 1981. Tides, storm surges. Pages 70-71 In: D.W. Norton and W.M. Saker, Eds. Beaufort Sea (Sale 71) Synthesis Report 1981. National Oceanic and Atmospheric Administration, Bureau of Land Management.
- McAtee, J.L. and N.R. Smith. 1969. Ferrochrome lignosulfonates. I. X-ray absorption edge fine structure spectroscopy. II. Interaction with ion exchange resin and clays. J. Colloid Interface Sci. 29:389-398.
- McAuliffe, C. D., A.E. Smalley, R.D. Groover, W.M. Welsh, W.S. Pickle and G.E. Jones. 1975. Chevron main pass Block 41 oil spill: Chemical and biological investigations. Pages 555-566 In: Proceedings 1975 Oil Spill Conference, American Petroleum Institute, Washington, D. C.
- Meek, R.P. and J.P. Ray. 1980. Induced sedimentation, accumulation, and transport resulting from exploratory drilling discharges of drilling fluids and cuttings. Pages 259-284 In: Symposium on Research on Environmental Fate and Effects of Drilling Fluids and Cuttings. Courtesy Associates, Washington, D.C.
- Menzie, C.A. 1982. The environmental implications of offshore oil and gas activities. Environ. Sci. Technol. 16:454A-472A.
- Middleditch, B.S. (Ed.). 1981. Environmental Effects of Offshore Oil Production. The Buccaneer Gas and Oil Field Study. Plenum Press, NY.
- Naidu, A.S. 1979. Sources, Transport Pathways, Depositional Sites and Dynamics of Sediments in the Lagoon and Shallow Marine Region, Northern Arctic Alaska. NO AA/O CSEAP Annual Report, 81 pp.
- Naidu, A.S. 1982. Aspects of Size Distributions, Clay Mineralogy and Geochemistry of Sediments of the Beaufort Sea and Adjacent Deltas, North Arctic Alaska. NO AA/O CSEAP Annual Report, R.U. 529, 121 pp.
- Naidu, A.S. and T.C. Mowalt. 1974. Clay mineralogy and geochemistry of Continental Shelf sediments of the Beaufort Sea. In: J. C. Reed and J.E. Sater, Eds. The Coast and Shelf of the Beaufort Sea. Proceedings of a Symposium on Beaufort Sea Coast and Shelf Research, January, 1974. Arctic Institute of North America, Arlington, VA.
- Naidu, A.S., M.D. Sweeney and L. Klein. 1981. Aspects of size distributions, clay mineralogy, and geochemistry of sediments in the Beaufort Sea and adjacent deltas, North Arctic Alaska: synthesis report. In: Environmental Assessment of the Alaska Continental Shelf: Annual reports of principal investigators for the year ending March 1981. Volume V. U.S. National Oceanic and Atmospheric Administration and U.S. Bureau of Land Management, Anchorage, Alaska.

- Naidu, A.S., L.H. Larsen, T.C. Mowatt, M.D. Sweeney, H.V. Weiss. 1982. Aspects of Size Distributions, Clay Mineralogy and Geochemistry of Sediments of the Beaufort Sea and Adjacent Deltas, North Arctic Alaska; Final Report, 121 pp.
- Naidu, A.S., T.C. Mowatt, S.E. Rawlinson and H.V. Weiss. 1984. Sediment characteristics of the lagoons of the Alaskan Beaufort Sea coast and evolution of Simpson Lagoon. Pages 275-294 In: P.W. Barnes, D.M. Schell, E. Reimnitz, eds., The Alaskan Beaufort Sea-Ecosystems and Environments. Academic Press, New York.
- National Academy of Sciences. 1983. Drilling Discharges in the Marine Environment. Panel on Assessment of Fates and Effects of Drilling Fluids and Cuttings in the Marine Environment. Marine Board, Commission on Engineering and Technical Systems, National Research Council, Washington, D. C. 180 pp.
- National Petroleum Council. 1981. U.S. Arctic Oil and Gas. National Petroleum Council., Washington, D.C. 286 pp.
- Neff, J.M. 1979. Polycyclic Aromatic Hydrocarbons in the Aquatic Environment. Sources, Fates, and Biological Effects. Barking Essex, England: Applied Science Publ. 262 pp.
- Neff, J.M. 1982. Fate and Biological Effects of Oil Well Drilling Fluids in the Marine Environment: A Literature Review. U.S. EPA, Environmental Research Laboratory, Gulf Breeze, FL. EPA-600/53-82-064.
- Neff, J.M. 1984. Biological effects of drilling fluids, drill cuttings and produced waters. In: Federal Interagency Committee on Pollution Research, Development and Monitoring (CORDM) report on Assessment of the Long-Term Environmental Effects of U.S. Offshore Oil and Gas Development Activities. NOAA, Rockville, MD.
- Neff, J.M. and J.W. Anderson. 1981. Response of Marine Animals to Petroleum and Specific Petroleum Hydrocarbons. Heisted Press, New York. 177 pp.
- Neff, J. M., J.P. Marum and J.S. Warner. 1983. Coreposition and Fate of Clean Ballast Water Discharged from Crude Oil Tankers. Proc. 1983 Oil Spill Conference. American Petroleum Institute, Washington, D. C.
- Nielson, K.K. 1977. Matrix corrections for energy dispersive x-ray fluorescence analysis of environmental samples with coherent/incoherent scattered x-rays. Analyt. Chem. 48(4):645-648.
- Northern Technical Services. 1981. Beaufort Sea Drilling Effluent Disposal Study. Performed for the Reindeer Island Stratigraphic Test Well Participants Under the Direction of Sohio Alaska Petroleum Company. Northern Technical Services, Anchorage, AK. 329 pp. Available from Sohio Alaska Petroleum Co., Anchorage, AK.
- Northern Technical Services. 1982. Above-Ice Effluent Disposal Tests. Sag Delta No. 7, Sag Delta No. 8 and Challenge Island No. 1 Wells, Beaufort Sea, Alaska. Report for Sohio Alaska Petroleum Co. Northern Technical Services, Anchorage, AK. 185 pp.
- Northern Technical Services. 1983. Open-Water Drilling Effluent Disposal Study. Tern Island, Beaufort Sea, Alaska. Report for Shell Oil Co. Northern Technical Services, Anchorage, AK. 87 pp.

- Perricone, D. 1980. Major drilling fluid additives. 1979. Page 15-29 In: Symposium on Environmental Fate and Effects of Drilling Fluids and Cuttings. Courtesy Associates, Washington, D.C.
- Petrizzuolo, G. 1983. Draft Final Technical Report Document. Environmental Assessment: Drilling Fluids and Cuttings Released onto the OCS. Submitted to Office of Water Enforcement and Permits, U.S. EPA, Washington, D.C. by Technical Resources, Inc., Bethesda, MD.
- Plumb, R.H., Jr. 1981. Procedures for Handling and Chemical Analysis of Sediment and Water Samples. Prepared under contract EPA -48055720 10. U.S. Army Engineer Waterways Experiment Station. Vicksburg, Miss.
- Pritchard, R.S. and W. Stringer. 1981. Ice characteristics and sea ice motions. Pages 81-87 In: D.W. Norton and W.M. Sackinger, Eds. Beaufort Sea (Sale 71) Synthesis Report 1981. National Oceanic and Atmospheric Administration, Bureau of Land Management.
- Ray, J.P. 1979. Offshore discharge of drill. muds and cuttings. In: Proc. of the OCS Frontier Technology Symposium. Dec. 6, 1979. Washington, D.C.
- Ray, J.P. and R.P. Meek. 1980. Water column characterization of drilling fluids dispersion from an offshore exploratory well on Tanner Bank. Pages 223-258 In: Symposium on Research on Environmental Fate and Effects of Drilling Fluids and Cuttings. Courtesy Associates, Washington, D. C.
- Redburn, D.R. and M.E. Wheeler. 1983. Offshore drilling mud and cuttings disposal in the Alaskan Arctic: An issue analysis. Paper presented at the Joint Northern Canada-Alaska Environmental Technical Exchange Workshop. Alaska Dept. Environ. Conserv., Juneau, AK. 26 pp.
- Reimnitz, E. and P.W. Barnes. 1974. Sea ice as a geologic agent on the Beaufort Sea shelf of Alaska. Pages 301-353 In: J.C. Read and J.E. Sater, Eds. The Coast and Shelf of the Beaufort Sea. Arctic Institute of North America, Arlington, VA.
- Robertson, D.E. and K.H. Abel, 1979. Natural Distribution and Environmental Background of Trace Heavy Metals in Alaskan Shelf and Estuarine Areas. Final Report to the National Oceanic and Atmospheric Administration supported by the Bureau of Land Management through interagency agreement, Outer Continental Shelf Environmental Assessment Program, Juneau, AK.
- Sauer, Jr., T.C. 1981. Volatile liquid hydrocarbon characterization of underwater hydrocarbon vents and formation waters from offshore production operations. Environ. Sci. Technol. 15:917.
- Schell, D. M. 1983. Carbon-13 and carbon-14 abundances in Alaskan aquatic organisms: Delayed production from peat in Arctic food webs. Science 219:1068-1071.
- Schell, D.M. and R.A. Homer. 1981. Primary production, zooplankton, and trophic dynamics of the Harrison Bay and Sale 71 area. Pages 3-12 In: D.W. Norton and W. M. Sackinger, Eds. Beaufort Sea (Sale 71) Synthesis Report. National Oceanic and Atmospheric Administration, Bureau of Land Management.
- Shapiro, L.H. and R.G. Barry (Eds.). 1978. The sea ice environment. Pages 3-55 In: Environmental Assessment of the Alaskan Continental Shelf. Interim Synthesis Report: Beaufort/Chukchi. U.S. D.O.A.-NOAA-OCSEAP, Boulder, CO.

- Sharma, G.D. 1979. The Alaskan Shelf: Hydrographic, Sedimentary and Geochemical Environments. Springer-Verlag, New York, NY. 498 pp.
- Sharma, G.D. 1983. Fate of drilling discharge and solids disposal in the Beaufort Sea and Diapir Field. In: Testimony of the Alaska Oil and Gas Association on Draft General NPDES Permits for the Beaufort Sea, submitted to U.S. EPA, Region 10.
- Shaw, D. G., D.J. McIntosh and E.R. Smith. 1979. Arene and alkane hydrocarbons in nearshore Beaufort Sea Sediments. Estuar. Coast. Mar. Sci. 2:435-439.
- Short, A. D., J.M. Coleman and L.D. Wright. 1974. Beach Dynamics and Nearshore Morphology of the Beaufort Sea Coast, Alaskan. Pages 477-488 In: J.C. Reed and J.E. Sater, Eds. The Coasts and Shelf of the Beaufort Sea. Arctic Inst. North America, Arlington, VA.
- Skelly, W.G. and D.E. Dieball. 1969. Behavior of chromate in drilling fluids containing chromate. Proc. 44th Ann. Meeting Society of Petroleum Engineers of AIME. Paper No. SPE 2539. 6 pp.
- Smedes, G. W., R.P. Herbst and J. Calman. 1981. Hydrodynamic modeling of discharges. Pages 387-402 In: B.S. Middleditch, Ed. Environmental Effects of Offshore Oil Production. The Buccaneer Gas and Oil Field Study. Plenum Press, N.Y.
- Speers, G.C. and E.V. Whitehead. 1969. Crude petroleum. Pages 638-675 In: G. Eglinton and M.R.J. Murphy, Eds. Organic Geochemistry: Methods and Results. Springer-Verlag, Berlin.
- Sweeney, M.D. 1984. Heavy metals in the sediments of an arctic lagoon, northern Alaska. M.S. Thesis, University of Alaska, Fairbanks, AK. 256 pp.
- Tillery, J.B. and R.E. Thomas. 1980. Heavy metal contamination from petroleum production platforms in the Gulf of Mexico. Pages 562-587 In: Symposium on Environmental Fate and Effects of Drilling Fluids and Cuttings. Courtesy Associates, Washington, D. C.
- Trefry, J. H., R.P. Trocine and K.E. Yhip. 1983. Drilling Mud Discharges: Minimizing Environmental Mismatches. Proc. 3rd Symp. Coastal and Ocean Management, ASCE/San Diego, CA. June 1-4, 1983. pp. 1228-1237.
- Trocine, R.P. and J.H. Trefry. 1983. Particulate metal tracers of petroleum drilling mud dispersion in the marine environment. Environ. Sci. Technol. 17(9):507-512.
- Trocine, R. P., J.H. Trefry and D.B. Meyer. 1981. Inorganic tracers of petroleum drilling fluid dispersion in the northwest Gulf of Mexico. Reprint Extended Abstract. Div. Environ. Chem. A CS Meeting. Atlanta, GA. March-April, 1981.
- Venkatesan, M.J. and I. R. Kaplan. 1982. Distribution and transport of hydrocarbons in surface sediments of the Alaskan Outer Continental Shelf. Geochim. Cosmochim. Acta 46:2135-2149.
- Wacasey, J. W. 1975. Biological Productivity of the Southern Beaufort Sea: Zoobenthic Studies. Beaufort Sea Project, Technical Report No. 126, Victoria, B.C. Canada. 39 pp.

- Wakeham, S. G., 1977. Synchronous fluorescence spectroscopy and its application to indigenous and petroleum-derived hydrocarbons in lacustrine sediments. *Environ. Sci. Technol.*, 1:272-276.
- Wakeham, S.G. and Barrington, J.W. 1980. Hydrocarbons in contemporary aquatic sediments. Pages 3-32 In: R .A. Baker, ed. Contaminants and Sediments. Ann Arbor Press, Ann Arbor, MI.
- Wakeham, S. G., C. Schaffner and W. Giger. 1980. Polycyclic aromatic hydrocarbons in recent lake sediments II. Compounds derived from biogenic precursors during early diagenesis. *Geochim. Cosmochim. Acta* 44:415-429.
- Ward, D. M., M.R. Winfrey, E. Beck and P. Boehm. 1982. Amoco Cadiz pollutants in anaerobic sediments: Fate and effects on anaerobic processes. Pages 159-190 In: Ecological Study of the Amoco Cadiz Oil Spill. Report of the NOAA/CNEXO Joint Scientific Commission. U.S. D. C.-NOAA, Rockville, MD.
- Wheeler, R .B., J.B. Anderson, R .R. Schwarzer and C.L. Hokanson. 1980. Sedimentary processes and trace metal contaminants in the Buccaneer oil/gas field, northwestern Gulf of Mexico. *Environ. Geol.* 3: 163-175.
- Zingula, R .P. 1975. Effects of drilling operations on the marine environment. Pages 433-448 In: Environmental Aspects of Chemical Use in Well-Drilling Operations. U.S. EPA. EPA-560/ 1-75-004.



Battelle

New England
Marine Research Laboratory
397 Washington Street
Duxbury, Massachusetts 02332
Telephone (61 7) 934-5682