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ANALYSIS OF TRACE METALS
AND HYDROCARBONS FROM OUTER
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ABSTRACT

An environmental monitoring program, designed to assess potential areawide or cumulative effects of anticipated oil and gas exploration and development on the U.S. Beaufort Sea Continental Shelf, was initiated in 1984. This program was designed to detect and quantify long-term changes in the concentrations of metals and hydrocarbons in sediments and animal tissues.

In the first year of the study, a series of sediment sampling stations was established in the nearshore area between Barter Island and Cape Halkett. The strategy was to include stations that would be selected to detect onshore/offshore gradients, and gradients laterally away from major oil and gas expiration activities. Included also were previously sampled stations, as well as randomly chosen locations. Twenty-seven stations were occupied and surface sediments and bivalve samples collected during the first year. In Year-2 of the study, areal coverage of the Study Area was increased to 39 marine stations and 10 shoreline and river stations.

Analysis of six replicate sediment samples for Ba, Cr, Pb, Cu, Zn, and Cd revealed a wide range of concentrations. Generally, however, higher concentrations of metals were associated with finer grained sediments and were located near discharges to major rivers. For similarly textured sediments, no major change in trace metal concentrations was detected between Year- 1 and Year-2. Sediment concentrations of individual saturated hydrocarbons, determined by gas chromatography-flame ionization detection (GC-FID) and polynuclear aromatic hydrocarbons (PAH), determined by gas chromatography-mass spectrometry (GC/MS), were similarly correlated to sediment grain size and proximity to major rivers.

Shoreline peat and riverine sediments were analyzed in Year-2 to examine the influence of these source materials on the composition and distribution of marine sediment hydrocarbons and trace metals. Based on trace metal data, peat does not appear to influence the concentrations in marine sediment; riverine sediments may be more important sources. On the other hand, PAH content and composition indicate that both source materials contribute to the hydrocarbon character of marine sediments. Hydrocarbon composition of riverine sediments, however, was more similar to marine sediments than the shoreline peat deposits.

Both trace metal and hydrocarbon analyses of bivalve and crustacean tissues indicated concentration differences between species but no apparent relationship between animal body burdens and sediment concentrations.

1. INTRODUCTION

1.1 Program Overview and Objectives

The Beaufort Sea Monitoring Program (BSMP) was initiated to evaluate the impact of offshore oil, and gas exploration and production activities on environmental quality in the Beaufort Sea, and to quantify temporal changes in the concentrations of metals and hydrocarbons.

Specific objectives of the three-year program are the following:

1. To detect and quantify changes in the concentrations of trace metals and hydrocarbons in the Beaufort Sea sediments and sentinel organisms which may
 - result from OCS petroleum-related activities;
 - impact the environment; and
 - influence Federal regulatory and management decisions.
2. To identify potential causes of these changes.

The technical approach of the monitoring program consists of the following:

1. Collecting bottom sediment, and benthic amphipods and bivalves.
2. Performing laboratory analyses for trace metals, hydrocarbons, sediment grain size, and total organic carbon.
3. Performing the appropriate statistical analyses to test the following null hypotheses for evaluating effects of OCS oil and gas-related activities:
 - H_01 : There will be no change in sediment concentrations of selected metals or hydrocarbons.
 - H_02 : Changes in concentrations of selected metals or hydrocarbons in sediments are not related to oil and gas development activity.
 - H_03 : There will be no change in concentrations of selected metals or hydrocarbons in selected sentinel organisms.
 - H_04 : Changes in concentrations of selected metals and hydrocarbons in selected sentinel organisms are not related to OCS oil and gas development activity.
4. Evaluating the efficacy of the monitoring program design based on each year's results and recommending refinements as needed.
5. Evaluating the need for the addition or deletion of elements to this core chemical program at the end of the three-year study and making such recommendations to MMS.

1.2 Year-1 Goals

Despite an extremely short lead time and less-than-ideal sampling conditions, Year-1 of the BSMP concluded with successful field and analytical programs, and accomplished the goals of the first year of study. These goals were

1. To establish a sampling design which could be refined after the first year of data analysis.
2. To assess the sampling and analytical variabilities.
3. To determine the degree of statistically valid change in the contaminants of interest.
4. Based on statistical and data analyses, to identify key parameters to be used to monitor oil and gas activity inputs to the environment.

Results of the Year-1 effort were reported in Boehm et al. (1985).

1.3 Year-2 Sampling and Analytical Plan

The primary goals of the Year-2 sampling and analytical plan incorporated the basic monitoring program objectives (presented in 1.1 above) as well as the recommendations made by the Scientific Review Board (SRB) Committee after reviewing the Year-1 results. The Year-2 program goals were

1. To obtain definitive analytical data from all stations sampled.
2. To obtain replication data at all stations sampled, for all analytical measurements. This was accomplished by pooling two station replicates to form a composite and analyzing three replica te composite sam pies from each station.
3. To determine whe the r concentrations of metals and hydrocarbons have changed between Year-1 and Year-2. This goal was accomplished by resampling 26 Year-1 stations and comparing mean values of the chemical constituents measured.
4. To examine the hypothesis that within-station variability (i.e., combined sampling plus analytical variability) does not change with time. A statistical analytical plan was developed to exam ine this hypothesis.
5. To obtain sam pies from regions within the Study Area that were not sampled in Year-1. Thirteen additional stations were added to the Year-1 sampling plan and one Year-1 station was deleted. Thirty-nine sediment stations were succe ssfully occupied in Year-2.
6. To obtain chemical data on potential metal and hydrocarbon sources (i.e., peat/riverine sediments) other than those attributed to oil and gas exploration or production activities. To accomplish this goal, two riverine stations and eight coastal peat stations were added to the sampling plan.

7. To reorient the sediment metals program towards examining only the mud fraction (the combined silt and clay fractions or particles $<64 \mu\text{m}$). In order to accomplish a shift in this direction, sediment samples from the 26 Year-1 stations, which were resampled in Year-2, were analyzed for metals in both the bulk sediment and in the mud fraction. Only the mud fraction of new Year-2 station samples was analyzed for metals.
- 8* To examine the feasibility of reorienting the hydrocarbon sediment chemistry program towards the mud fraction. On three samples, both the bulk sediment and the mud fraction were analyzed for saturated and aromatic hydrocarbons.
9. To determine body burdens of metals and hydrocarbons in animal species from the entire areal extent of the Study Area.
10. To conduct additional hydrocarbon intercalibration studies at the direction of MMS.

Detailed sampling and analytical plans are discussed in Chapter 3.

1.4 Current and Planned Drilling Activities in the Beaufort Sea

Past and proposed drilling locations on the Outer Continental Shelf (OCS) of the Beaufort Sea are shown in Figures 1.1, 1.2, and 1.3. In addition to the nine major locations at which drilling has occurred, four new sites have been selected for future drilling. Of these, the Corona/Shell and Erik/Amoco sites in the Camden Bay area are scheduled to be put into operation during the summer of 1986. The Phoenix/Tenneco operation, north of the Colville delta, is currently scheduled for fall, 1986. However, the likelihood that those drilling activities will actually occur has been diminished by the current industry-wide slowdown in exploration.

In addition to activity centered on the shelf, a fair amount of drilling activity has been conducted along the outer and inner shelf, on barrier islands, in river deltas, and along the Beaufort Sea coast. These locations are shown in Figures 1.4, 1.5, and 1.6. Not included in Figure 1.4 are the numerous activities being conducted in State and Canadian territories in the Mackenzie River delta and adjoining shelf region approximately 350 km east of Barter Island.

The circled locations in Figures 1.7, 1.8, and 1.9 indicate those oil fields for which greatest development potential has been identified. These include Endicott and Seal/Northstar/Sandpiper offshore fields (Figure 1.8) and Pt. Thomson, Milne Pt., and Colville River delta coastal fields (Figures 1.7 and 1.9). The Year-2 monitoring program locations are presented in those figures as well.

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 (Table 1.1). 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.). Current NPDES permits for the

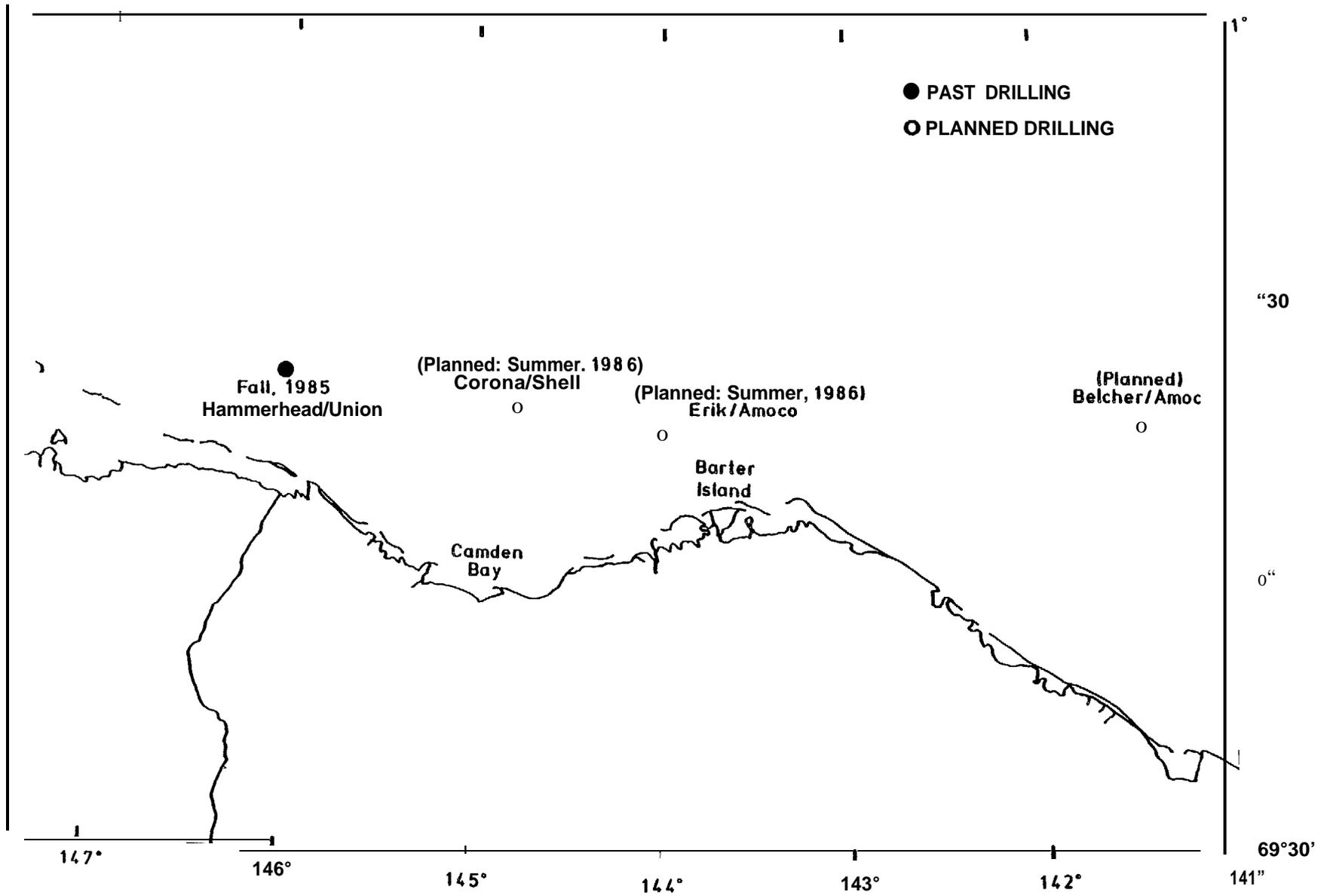


FIGURE 1.1. BEAUFORT SEA OUTER CONTINENTAL SHELF DRILLING LOCATIONS--EASTERN STUDY AREA.

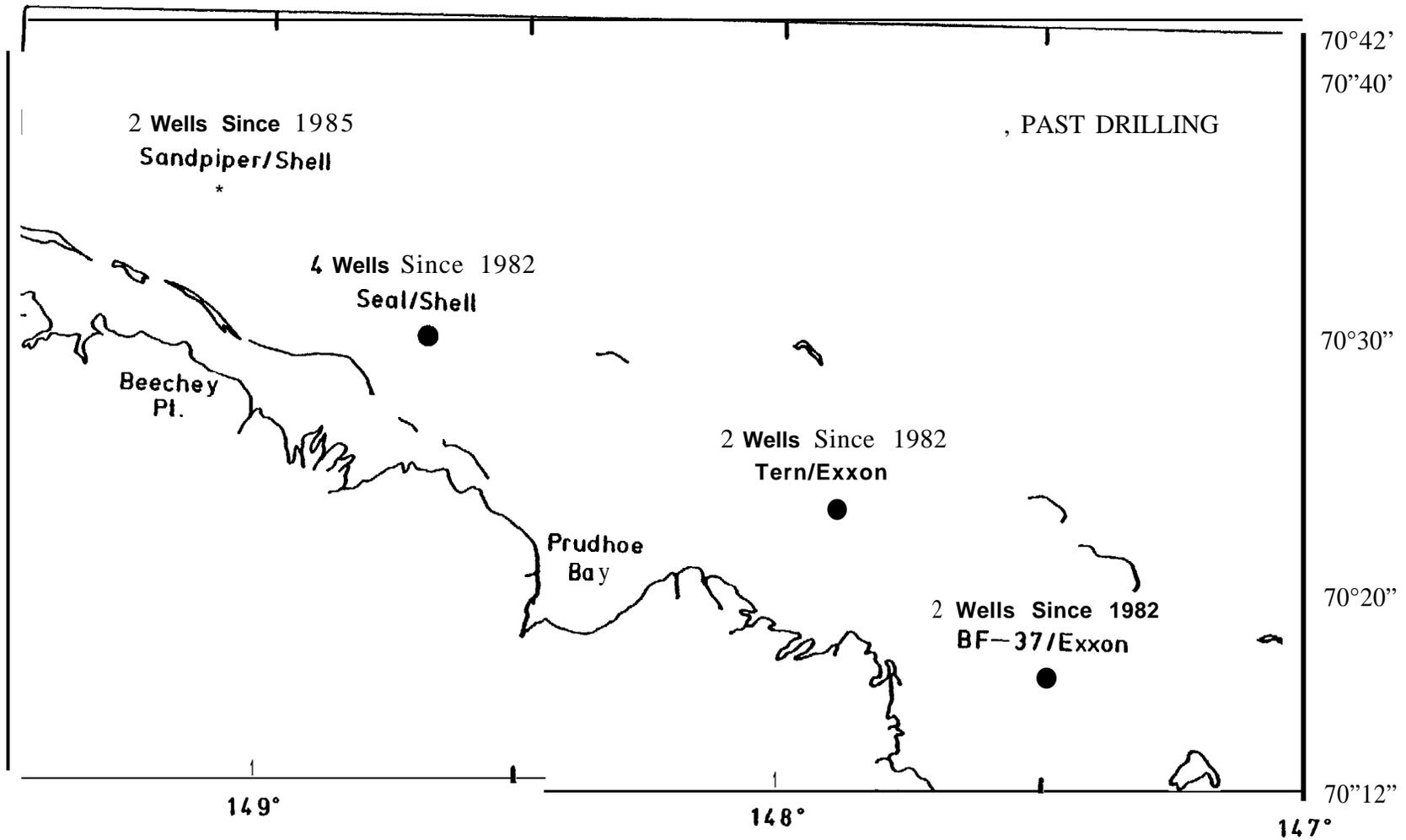


FIGURE 1.2. BEAUFORT SEA OUTER CONTINENTAL SHELF DRILLING LOCATIONS--
CENTRAL STUDY AREA.

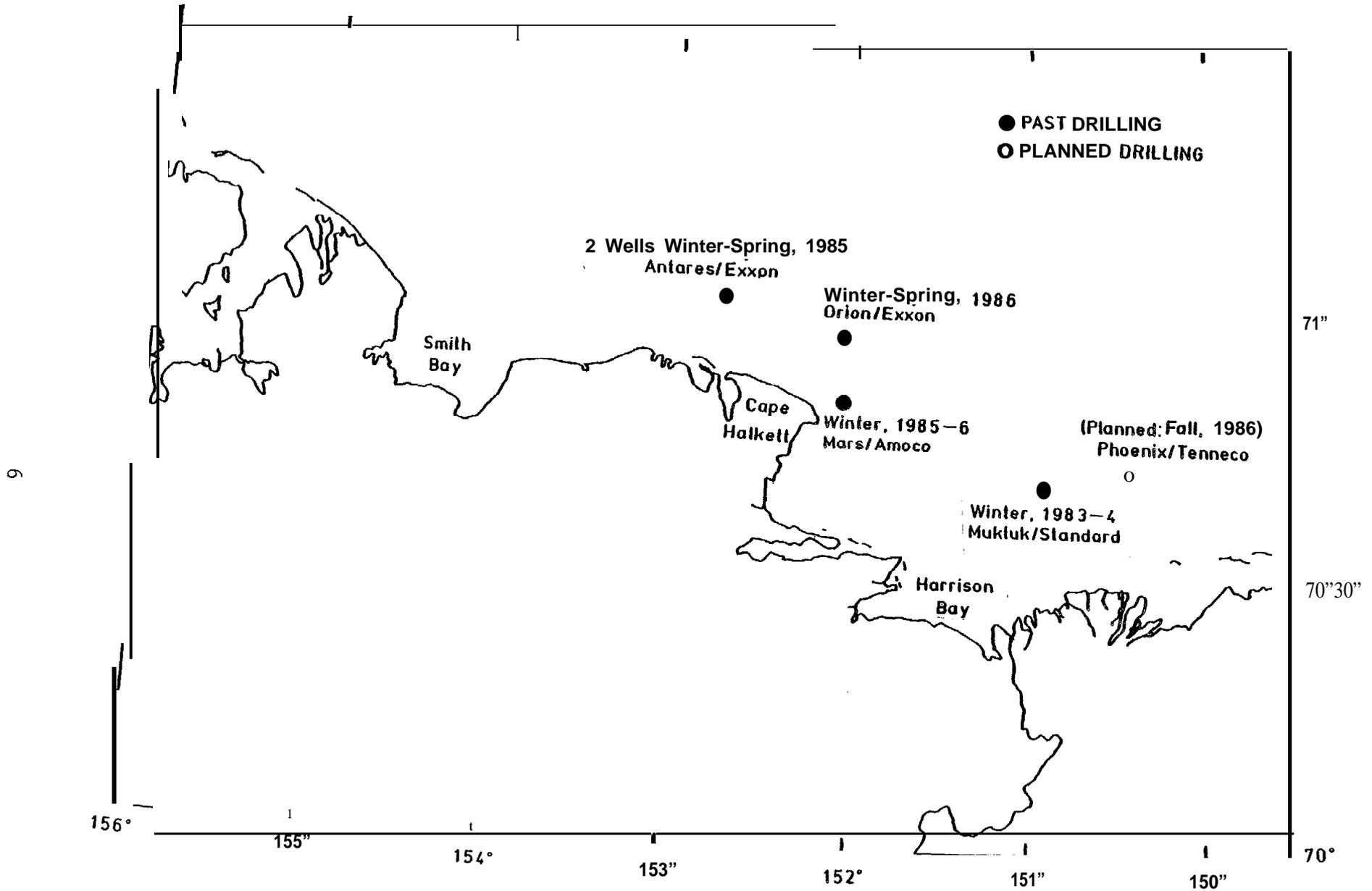


FIGURE 1.3. BEAUFORT SEA OUTER CONTINENTAL SHELF DRILLING LOCATIONS--WESTERN STUDY AREA.

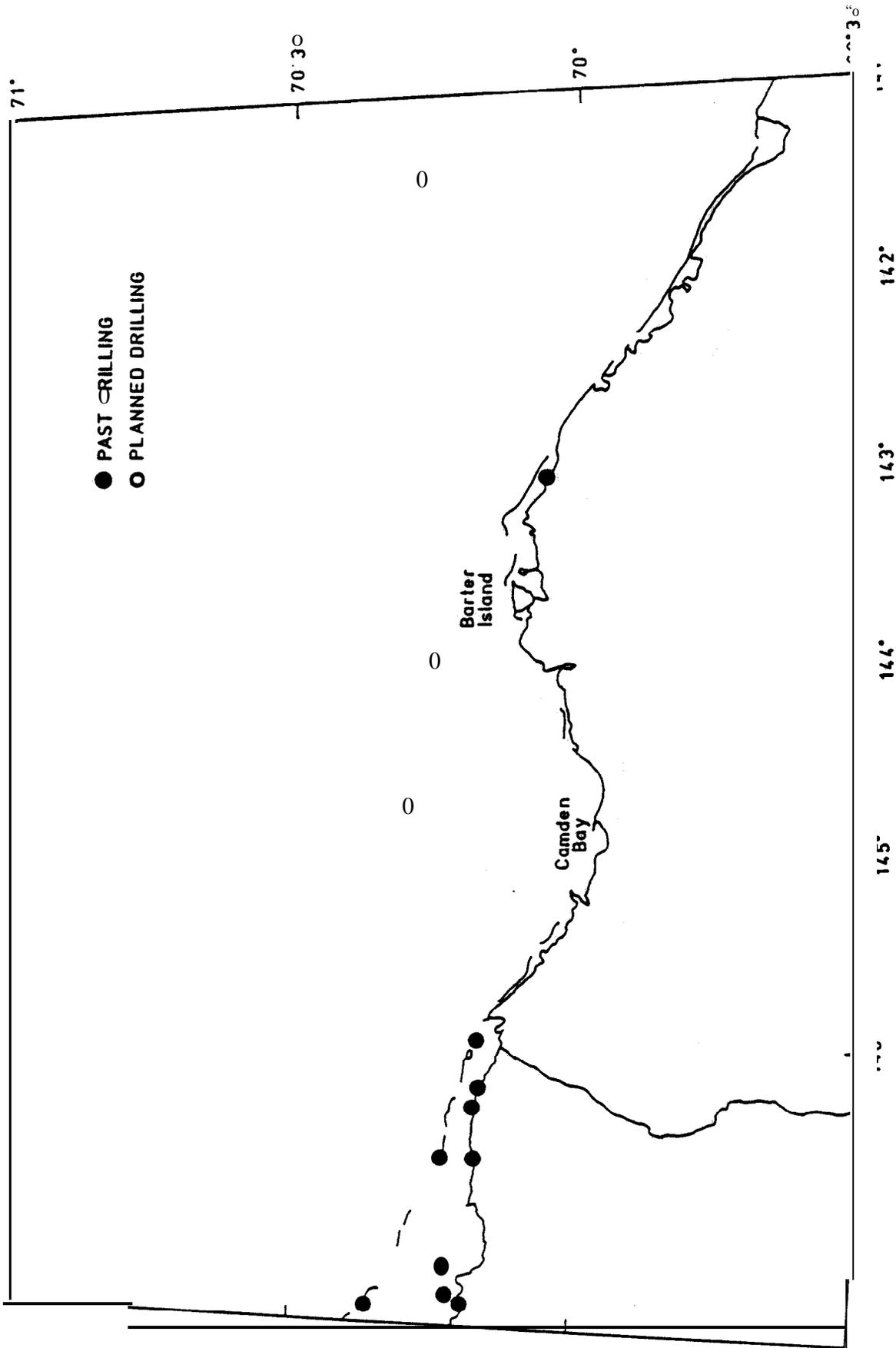


FIGURE 1.4. BEAUFORT SEA DRILLING ACTIVITY ON OUTER AND INNER CONTINENTAL SHELF, BARRIER ISLANDS, RIVER DELTAS, AND COASTLINE—EASTERN STUDY AREA.

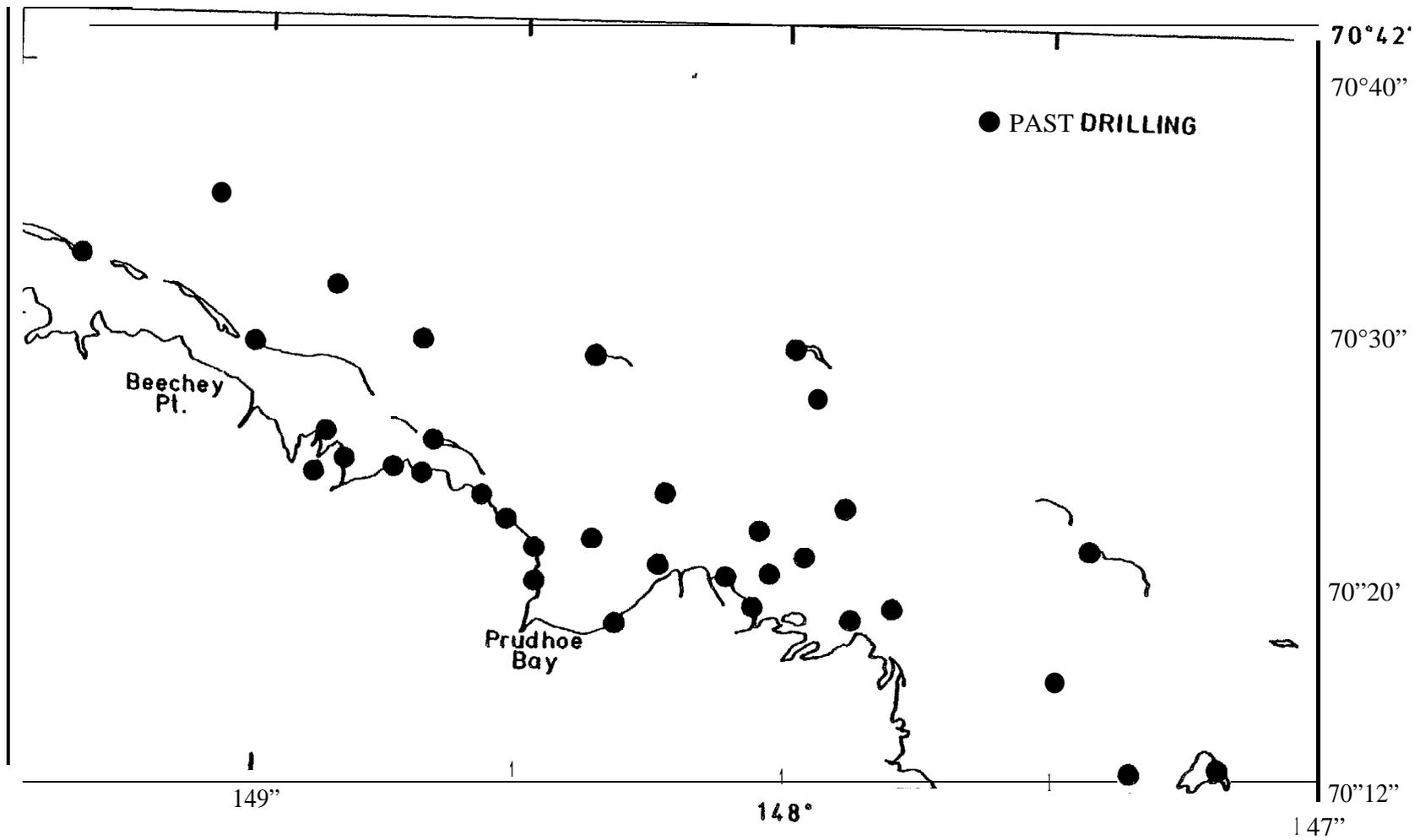


FIGURE 1.5. BEAUFORT SEA DRILLING ACTIVITY ON OUTER AND INNER CONTINENTAL SHELF, BARRIER ISLANDS, RIVER DELTAS, AND COASTLINE-CENTRAL STUDY AREA.

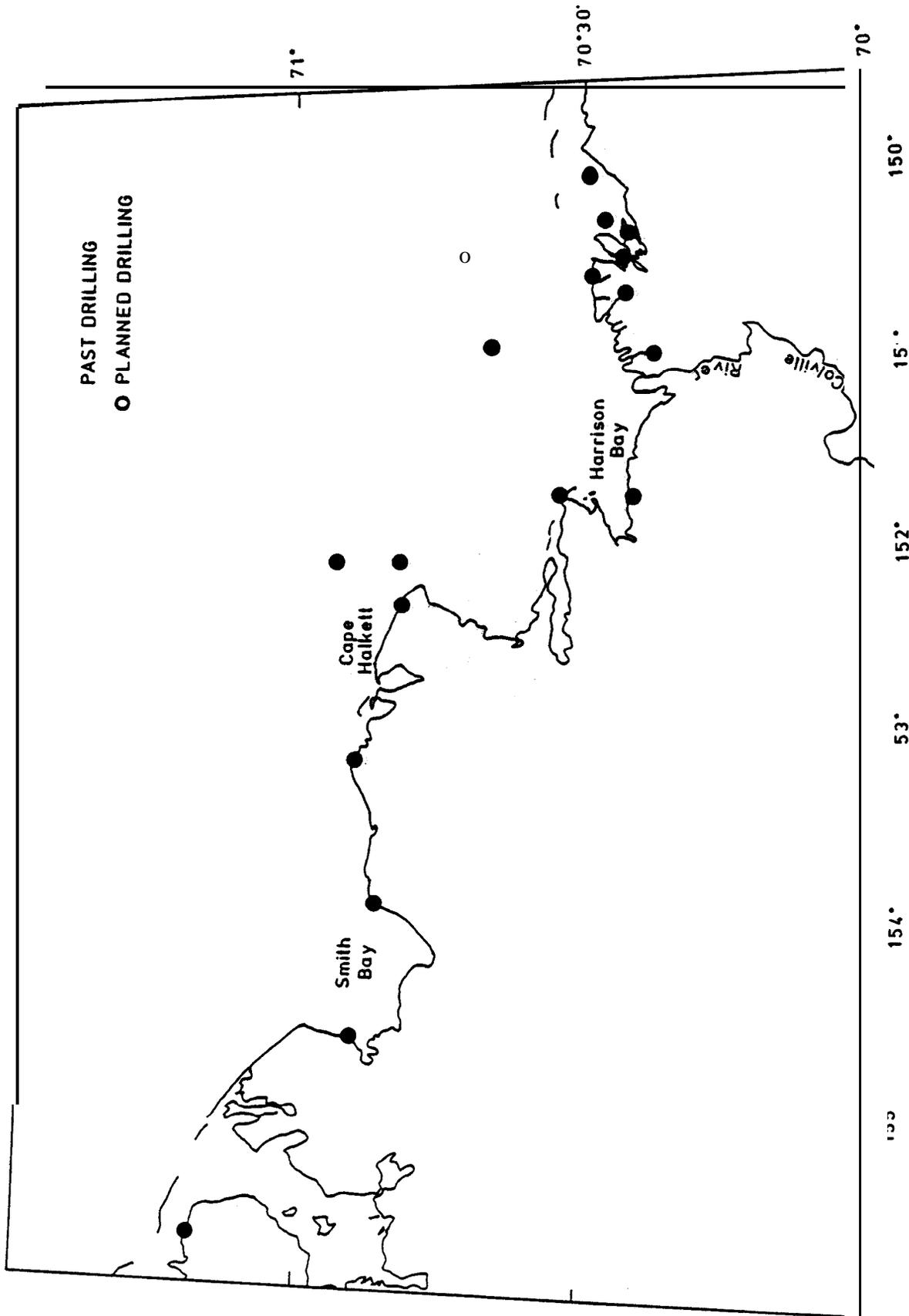


FIGURE 1.6. BEAUFORT SEA DRILLING ACTIVITY ON OUTER AND INNER CONTINENTAL SHELF, BARRIER ISLANDS, RIVER DELTAS, AND COASTLINE--WESTERN STUDY AREA.

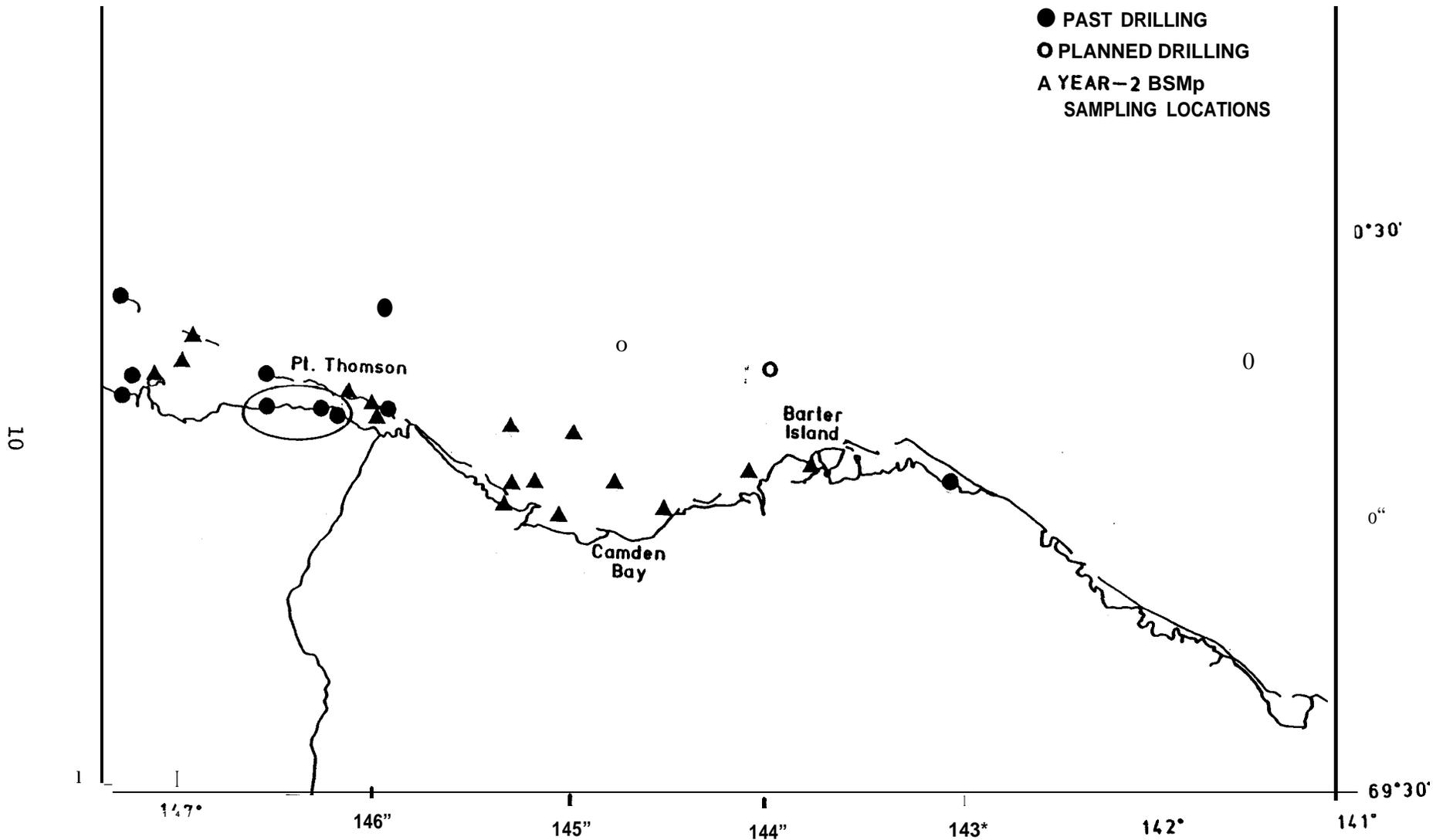


FIGURE 1.7. BEAUFORT SEA OFFSHORE FIELDS WITH TENTATIVE DEVELOPMENT POTENTIAL:-: EASTERN STUDY AREA.

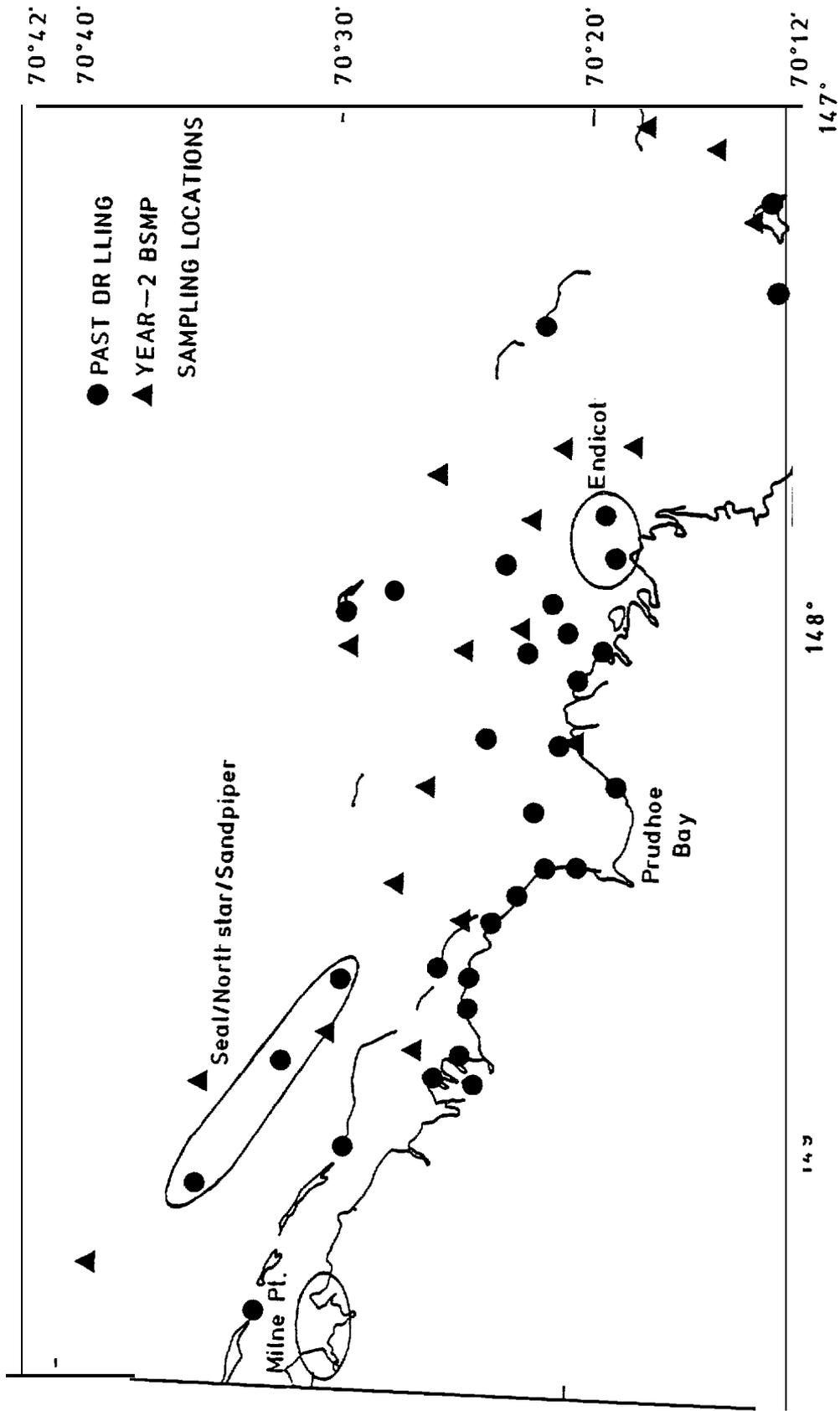


FIGURE 1.8. BEAUFORT SEA OFFSHORE FIELDS WITH TENTATIVE DEVELOPMENT POTENTIAL-- CENTRAL STUDY AREA.

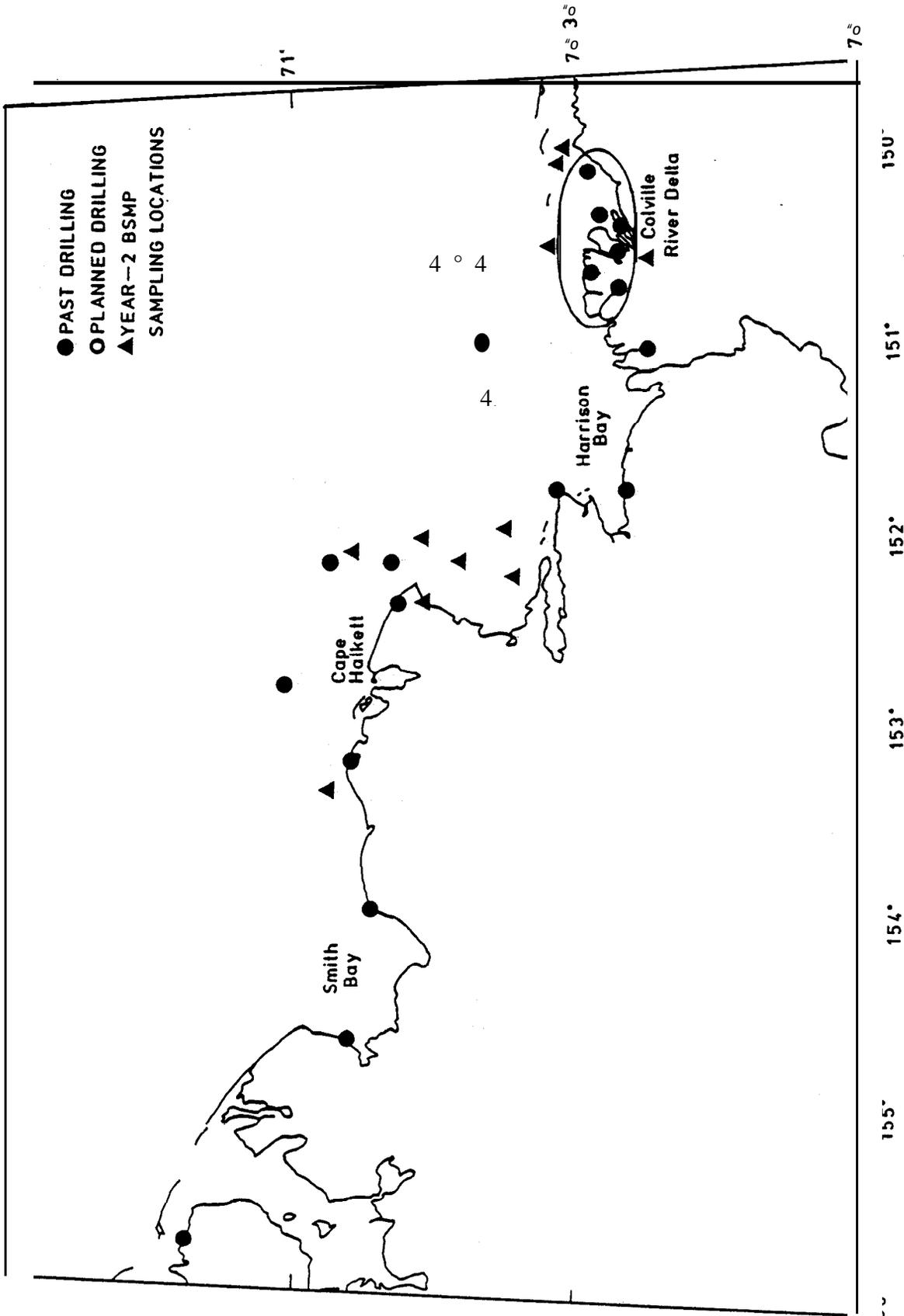


FIGURE 1.9. BEAUFORT SEA OFFSHORE FIELDS WITH TENTATIVE DEVELOPMENT POTENTIAL-- WESTERN STUDY AREA.

TABLE 1.1. 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 mt/Exploration Well, Less for Development Well
 - Drilling Fluids- 900mt/Exploration Well, 25% Less for Development Well
 - Cooling Water, Deck Drainage, Ballast Water- Maybe 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.
-
-

Beaufort Sea prohibit discharge of drilling fluids containing diesel oil, mineral oil, chromates or chlorinated phenol biocides.

Exploration and development drilling will take place from barrier islands, manmade 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 utilization 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 effect-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). Accidents during field development and production may result in oil spills or even blowouts which would represent possible inputs of petroleum to the shallow Beau fort Sea.

Metals which are associated with drilling are listed in Table 1.2. 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.

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 chromate 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 1.2). The metallic impurities in impure barite are associated with highly insoluble sulfide mineral inclusions, particularly 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

TABLE 1.2. CONCENTRATION RANGES OF SEVERAL METALS IN NATURAL MARINE SEDIMENTS AND DRILLING FLUIDS FROM ALASKA^a. CONCENTRATIONS ARE IN mg/kg DRY WT (ppm).

Metal	Alaskan OCS 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	0.015-0.217	NA	NA
Cadmium	<0.02-1.80	NA	NA

^aData from NORTEC, 1981, 1982, 1983; Sharma, 1979; Ecomar, 1983.

^bBarium values obtained by AA and may be low.

NA = Not analyzed.

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

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.

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 downcurrent from the discharge pipe and within 0.1 to 4 h of discharge. Quite frequently, dilutions of 1,000-fold or more are encountered within a short time and distance of discharge.

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 levels 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 (Petrazzuolo, 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 downcurrent of the discharge point.

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; Petrazzuolo, 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.

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 nearshore 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 macroalgae, Eunophyta rubriformis, from the disposal sites contained elevated levels of barium. However, these values were obtained by atomic absorption spectrometry and may not be reliable. The macroalgae 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.

2. SAMPLING METHODS

2.0 INTRODUCTION

Several changes in the sampling methods were made for the Year-2 field program. These included the addition of new sampling locations and the improvement of survey equipment and sampling methods. The Year-2 field program and sampling methods are described in detail in the sections that follow.

2.1 Sampling Locations and Dates

The Year-2 BSMP was designed to obtain complete areal coverage of the Study Area. In order to avoid the nearshore ice, which had precluded sampling in the Camden Bay area during Year-1, the Year-2 field program began a month earlier than in Year-1. Field sampling for the 1985 BSMP was conducted between 7 August and 1 September. Thirty-nine stations were successfully sampled. In addition to reoccupying 26 Year-1 stations, 9 stations that were not sampled due to ice in Year-1 were visited and sampled. One Year-1 station, 5(2), was dropped. Four new near-shore stations, and six river and peat shoreline stations were added to the Year-2 field program.

Table 2.1 compares the Year-1 and Year-2 positions of the 26 stations that were established in Year-1. At most locations, the Year-2 positions were within 0.2' north latitude (0.2 nm) and 0.5' west longitude (0.16 nm) of the Year-1 station coordinates. The survey goals were to attempt reoccupation of the stations to within 0.3 nm of the Year-1 coordinates.

The Beaufort Sea Monitoring Program Study Area with locations of all Year-2 stations, including shoreline and river stations, is presented in Figure 2.1. Sampling dates, station locations and their depths are detailed in Table 2.2, and the river and peat sampling stations are summarized in Table 2.3.

2.2 Logistics and Cruise Narrative

2.2.1 Year-2 Survey Team

The scientific party for the Year-2 field survey was comprised of Year-1 veterans, R. Eugene Ruff and William Steinhauer. Mr. Ruff again 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 formal liaison between the scientific party and Battelle management staff at BNEMRL. He maintained the ship's navigation log and chief scientist's log throughout the survey. Mr. Steinhauer was responsible for the collection and documentation of all field samples, and for the overall integrity of sampling, and sample storage and transfer operations. He maintained the sample cast logs, sediment and tissue sample collection logs, and sample transfer logs.

The 11-m (36-ft) NOAA research vessel No. 1273 was skippered by Mr. George Lapienne and by Lt. Cmdr. Michael Myers of the NOAA Corps. They were assisted by Mr. Russel Gaezel and Mr. Keith Lapienne. Preparation of the NOAA vessel was coordinated by Mr. George Lapienne of the NOAA Anchorage office. Mr. Lapienne and Lt. Cmdr. Myers performed presurvey maintenance, and held a preliminary cruise to assure that the vessel was sea-worthy for the field survey.

2.2.2 Survey Vessel Modifications

Several modifications to the vessel were made prior to the Year-2 field survey. A Tracer Omega-2 navigation system, which was not available for the Year-1

TABLE 2.1. COMPARISON OF 26 STATION LOCATIONS SAMPLED IN YEAR-1 AND YEAR-2.

Station	YEAR-1		YEAR-2	
	Depth (m)	Position	Depth (m)	Position
2E	7.6	70°12.8' 146011.5'	7.0	70°12.8' 146011.7'
2F	1.8	70°10.3' 146001.9'	1.5	70°10.2' 146002.1'
3A	6.1	70°15.3' 147005.6'	6.1	70°15.3' 147005.2'
3B	3.7	70°17.9' 147°02.0'	4.3	70°17.9' 147002.5'
4A	4.3	70°18.4' 147040.0'	4.6	70°18.4' 147039.5'
4B	7.3	70°21.0' 147039.6'	6.4	70°21.1' 147039.7'
4C	9.1	70°26.1' 147042.6'	9.1	70°26.0' 147043.1'
5A	11.6	70°29.9' 148045.8'	11.6	70°29.7' 148°46.0'
5B	16.5	70034.6' 148°54.8'	15.6	70°34.8' 148054.3'
5D	2.0	70°24.3' 148°32.9'	2.0	70°24.7' 148°34.1'
5E	19.2	70°38.9' 149°16.1'	19.2	70°38.9' 149016.3'
5F	1.5	70°26.4' 148049.2'	1.5	70026.51 148049.7'
5G	9.1	70°29.4' 148°02.4'	8.8	70°29.3' 148°02.6'
5(1)	6.4	70°25.1' 148004.9'	5.8	70°24.9' 148003.1'
5(5)	7.0	70°26.0' 148°16.8'	6.4	70°26.2' 148°18.8'
5(10)	8.2	70°27.1' 148030.6'	8.3	70°27.4' 148°30.0'
6A	3.0	70°32.2' 149°56.7'	4.6	70°32.1' 149°57.8'
6B	5.2	70°33.3' 150°24.9'	5.2	70°33.4' 150°24.5'
6C	15.2	70°40.3' 150°32.1'	16.2	7(3040.41 150°32.2'
6D	18.3	70°44.7' 150°29.2'	18.6	70°45.0' 150°28.5'
6F	12.5	70°40.2' 151°12.0'	12.5	70°40.2' 151°12.2'
7A	1.5	70°37.6' 152010.1'	1.5	700370,1 152°09.5'
7B	5.5	70°47.4' 151056.0'	6.1	70°47.4' 151°56.5'
7C	14.3	70°54.8' 152000.7'	13.4	70°54.9' 152°00.4'
7E	2.7	70°43.5' 152°04.2'	3.0	7(3043.41 152°04.3'
7G	3.0	70°39.4' 151053.7'	2.7	70°38.7' 151°53.6'

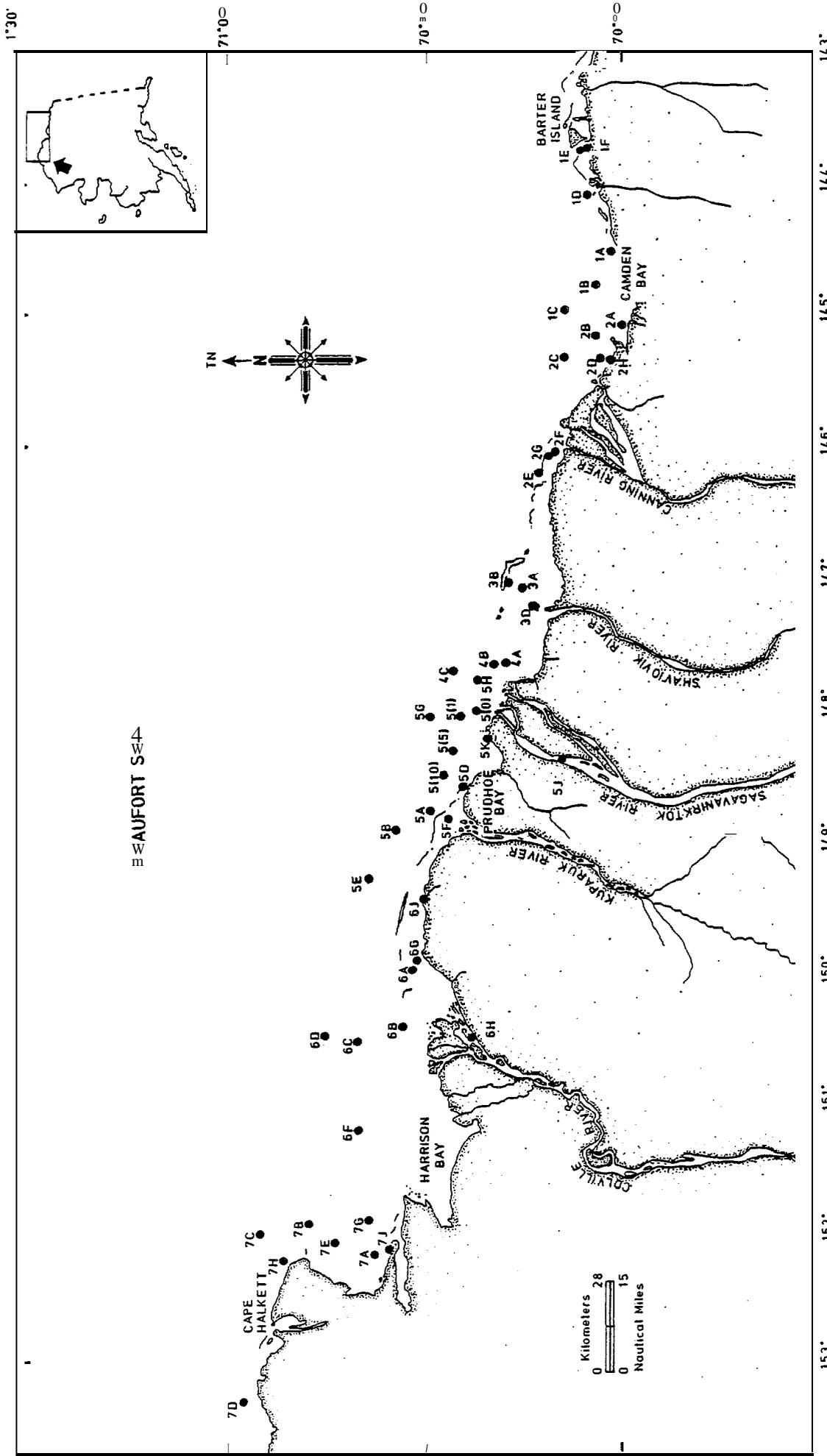


FIGURE 2.1. YEAR-2 BEAUFORT SEA MONITORING PROGRAM STUDY AREA AND STATION LOCATIONS.

TABLE 2.2. STATION LOCATIONS, SAMPLING DATES AND DEPTHS AT STATIONS SAMPLED FOR THE YEAR-2 BEAUFORT SEA MONITORING PROGRAM.

Station Number	Position		Depth (m)	Date Sampled	sample Types Collected
	N. Lat.	W. Long.			
1A	70001.61	144°32.6'	8.2	30 Aug	Marine Sediment, <u>Anonyx, Astarte, Portlandia</u>
1B	70°04.1'	144047.4'	14.0	29 Aug	Marine Sediment, <u>Anonyx, Astarte</u>
1C	70009.1'	145001.5'	25.6	29 Aug	Marine Sediment
1D	7(30)35.5'	144°06.2'	5.8	29 Aug	Marine Sediment
1E	70°06.1'	143046.0'	1.5	29 Aug	Marine Sediment, <u>Anonyx</u>
1F	70°05.5'	143045.3'	N/As	29 Aug	Coastal Peat
2.4	70°00.6'	145005.4'	4.6	30 Aug	Marine Sediment
2B	70004.1'	145012.4'	10.1	30 Aug	Marine Sediment
2C	70009.9'	145020.4'	22.3	29 Aug	Marine Sediment
2D	70°03.7'	145°19.8'	3.2	31 Aug	Marine Sediment
● 2E	70°12.8'	146°11.7'	7.0	31 Aug	Marine Sediment
* 2F	70°10.2'	146°02.1'	1.5	23 Aug	Marine Sediment, <u>Anonyx</u>
2G	70°11.3'	146004.2'	N/A	23 Aug	Coastal Peat
2H	70°01.7'	145022.1'	N/A	31 Aug	Coastal Peat
* 3A	70°15.3'	147005.2'	6.1	22 Aug	Marine Sediment, <u>Anonyx, Astarte</u>
● 3B	70°17.9'	147002.5'	4.3	22 Aug	Marine Sediment
3D	70°13.7'	147013.4'	N/A	22 Aug	Coastal Peat
● 4A	70°13.4'	147039.5'	4.6	21 Aug	Marine Sediment
* 4B	70°21.1'	147039.7'	6.4	21 Aug	Marine Sediment, <u>Anonyx</u>
* 4C	70°26.0'	147043.1'	9.1	1 Sep	Marine Sediment
* 5A	70°29.7'	148046.0'	11.6	10 Aug	Marine Sediment
* 5B	70°34.3'	148054.3'	15.6	10 Aug	Marine Sediment
● 5I3	70024.71	148034.1'	2.0	9 Aug	Marine Sediment
* 5E	70°38.9'	149°16.3'	19.2	10 Aug	Marine Sediment
● 5F	70026.51	148°09.7'	1.5	18 Aug	Marine Sediment, <u>Cyrtodaria</u>
● 5G	7(30)29.3.	148°02.6'	8.8	27 Aug	Marine Sediment
5H	70°22.2'	147047.9'	6.7	1 Sep	Marine Sediment, <u>Anonyx, Astarte</u>
5J	70°07.0'	148°23.3'	N/A	7 Aug	River Sediment
5K	70°20.4'	148°13.3'	N/A	19 Aug	Coastal Peat
5(o)	70°22.6'	148000.5'	5.2	9 Aug	Marine Sediment
● 5(l)	70024.9'	148°03.1'	5.8	9 Aug	Marine Sediment
● 5(s)	70°26.2'	148°18.8'	6.4	9 Aug	Marine Sediment
● 5(10)	70°27.4'	148030.0'	3.3	9 Aug	Marine Sediment
● 6A	70°32.1'	149057.8'	4.6	11 Aug	Marine Sediment
● 6B	70°33.4'	150°24.5'	5.2	11 Aug	Marine Sediment
* 6C	70°40.4'	150°32.2'	16.2	11 Aug	Marine Sediment
● 6D	70°45.0'	150°28.5'	13.6	12 Aug	Marine Sediment, <u>Astarte, Macoma</u>
* 6F	70°40.2'	151°12.2'	12.5	15 Aug	Marine Sediment
6G	70°31.2'	149054.0'	2.1	17 Aug	Marine Sediment, <u>Anonyx, Cyrtodaria</u>
6H	70°23.0'	150030.0'	N/A	14 Aug	River Sediment
6I	70°29.2'	149°26.1'	N/A	13 Aug	Coastal Peat
* 7A	70°37.7'	152°09.5'	1.5	17 Aug	Marine Sediment
* 7B	70°47.4'	151056.5'	6.1	16 Aug	Marine Sediment, <u>Anonyx</u>
● 7C	7(30)54.91	152°00.4'	13.4	16 Aug	Marine Sediment, <u>Anonyx</u>
7D	70°57.6'	153017.4'	7.0	16 Aug	Marine Sediment
* 7E	70°43.4'	152°04.3'	3.0	17 Aug	Marine Sediment, <u>Anonyx</u>
● 7G	70038.71	151°53.6'	2.7	15 Aug	Marine Sediment
7H	70°47.3'	152°16.8'	N/A	16 Aug	Coastal Peat
7I	7(30)35.51	152°08.1'	N/A	17 Aug	Coastal Peat

*Stations sampled in Year-1.

● Shoreline peat or river sediment stations.

TABLE 2.3 SUMMARY OF RIVER AND PEAT SAMPLING STATIONS.

Station	Location	Sample Type
5J	Sagavanirktok River	River Sediment
6H	Colville River	River Sediment
1F	Are y Lagoon	Shoreline Peat
2H	Canning River Lagoon	Shoreline Peat
2G	Flaxman Island	Shoreline Peat
3D	Tigvariak Island	Shoreline Peat
5K	Heald Point	Shoreline Peat
6J	Milne Point	Shoreline Peat
7H	Cape Halkett	Shoreline Peat
7J	Kogru Island	Shoreline Peat

survey, was added to the vessel as a navigational aid for use between satellite fixes. This system, however, did not work well **due** to compass problems and lack of time for adequate calibration. Stations were, therefore, reoccupied by dead-reckoning to the estimated location, waiting for a satellite pass, adjusting accordingly, and then waiting for the next pass.

In order to help reduce exhaust emissions in the sampling area on deck, the exhaust stack was raised approximately 1.2 i-r-r (4 ft) and redirected. Additional scuppers were added on the transom to improve drainage on the work deck. Battelle replaced the existing brass pump/neoprene tubing with an epoxy-coated Jabsco pump/polyethylene tubing system to increase the flow rate of clean wash water for on-board bivalve processing.

With the exception of the Tracer navigation system, all other modifications aided the survey crew in conducting a quality survey as efficiently as possible.

2.2.3 Cruise Narrative

Field operations for Year-2 of the BSMP were resumed early in August 1985. The revised sampling program for Year-2 included reoccupation of the majority of Year-1 stations as well as the addition of stations to the east and west which could not be reached in Year-1. Emphasis was placed on occupying stations inside of the 25-m contour, and on obtaining both bivalve and amphipod samples for tissue analysis. In addition, stations along the shoreline and in the deltas of two major rivers were selected for samples of potential source materials.

The Year-2 sampling program was more ambitious than that attempted during Year-1. The elimination of the hydrographic measurements, however, permitted the survey to be accomplished by two, rather than three, field scientists.

R. Eugene Ruff and William Steinhauer arrived in Prudhoe Bay on the evening of 6 August 1985. The scientific gear was assembled and stowed aboard NOAA launch No. 1273 on 7-8 August, and the cruise got underway on 9 August 1985. The 1985 BSMP field program was essentially accomplished in four cruise legs as follows:

- Leg 1- Western Prudhoe Bay Area: 9-12 August 1985

The first stations occupied were in Prudhoe Bay to ensure that any unforeseen problems requiring shore-based assistance could be quickly remedied. The satellite navigation system was **used** to position the boat within 0.3 nm of the established station positions. Where possible, a surface float tethered to an anchor was deployed at the site and the vessel was permitted to drift in the vicinity. This tactic prevented any stack gases from blowing across the work area. Stations 5(o), 5(1), 5(5), 5(10), 5A, 5B, 5D, 5E, 6A, 6B, and 6C were occupied for sediment chemistry grab samples. In addition, Station 6D was occupied for sediment grabs and for bivalve samples.

The newly constructed road system on the North Slope, to the west of Prudhoe Bay, permitted the boat to be anchored at Oliktok Point rather than having to *steam* back to Prudhoe Bay between legs. This not only saved time, but also meant that the first shore station near Milne Point (Station 6J) could be reached via road. Between cruise Legs 1 and 2, ice conditions in Harrison Bay were reconnoitered from a Cessna equipped with floats. The plane landed 6 miles upstream from the mouth

of the Colville River, where a delta sample was collected (Station 6H).

● Leg 2- Harrison Bay and Points West: 15-18 August 1985

During the second cruise leg, stations 5F, 6F, 6S, 7A, 7S, 7C, 7D, 7E, and 7G were sampled. Bivalves were obtained off Oliktok Point and in Gwydyr Bay. Because molluscs were not located at the proposed 7'H location, this station was not occupied. Shore peat samples near Cape Halkett (Station 7H) and on Kogru Peninsula (Station 73) were obtained from a Zodiac boat because these regions were too shallow for the NOAA boat to land. The amphipod traps were routinely deployed and produced mixed results. At some stations a large number of gammarid amphipods (Anonyx spp.) were captured, while at other locations only a few were obtained. In general, the amphipods were as small or smaller than the meshes (0.5 cm) of the collecting traps and could easily escape when the traps were pulled from the bottom. The traps were subsequently covered with fine nylon mesh (queen-size pantyhose) to help retain the animals. Several different baits were compared and, as past experience had shown, sardines in mustard sauce were greatly preferred by the crustaceans.

The vessel arrived back at Prudhoe Bay for fueling and resupply the evening of 18 August. Between Legs 2 and 3, samples were collected from a shore station on the east side of the bay on Heald Point (Station 5K) and from the Sagavanirktok River delta (Station 53). Both locations were reached via road.

● Leg 3- Eastern Prudhoe Bay Area: 21-23 August 1985

Stations 2F, 3A, 3B, 4A, and 4B were occupied during this leg, and shore samples were collected at Tigvariak and Flaxman Islands (Stations 3D and 2G, respectively). Specimens of the bivalve genus Astarte were obtained at Station 3A. As in Year- 1, molluscs generally occurred in very low numbers. However, the improved bivalve washdown system employed during Year-2 permitted more grab samples to be processed and adequate numbers of bivalves to be obtained. Generally, between 50 and 70 grab samples were processed to obtain a sufficient number of bivalves for a sample.

The weather during Leg 3 was very cold, windy and foggy. Diminished visibility and the presence of ice floes greatly increased the travel time between stations. Many of the stations were sampled at anchor because the boat rolled too heavily while adrift. The northeast wind pushed the ice pack shoreward against the barrier island, preventing access to stations further east. Therefore, the boat was again anchored at Prudhoe Bay to await a shift in the weather pattern.

A break in the weather occurred on Tuesday, 27 August, with clear skies, brilliant sunshine, and a light southeast breeze. Joy Geiselman(COTR) joined the vessel for a day trip to Station 5G

to observe the sampling procedures. With a forecast of continuing southerly winds, preparations were made for a push eastward into Camden Bay and out to Barter Island.

- Leg 4 - Camden Bay and Points East: 28 August-1 September 1985

With the aid of observations made from the air, an easy passage through Mary Sachs Entrance west of Flaxman Island was accomplished.

Stations 1A, 1B, 1C, 1D, 1E, 2A, 2B, 2C, and 2D were successfully occupied in Camden Bay and in the vicinity of Barter Island. Because bivalves could not be located at Station 1E, they were collected nearby at Station 1A. Shore samples were obtained in Arley Lagoon (Station 1F) and near the mouth of the Canning River (Station 2H). No bivalves were found at Station 2G and this station was, therefore, not occupied. Stations 2E and 4C were sampled on the return to Prudhoe, and a final bivalve station was established off the Endicott Causeway. All sampling was completed by late afternoon of 1 September.

Numerous factors contributed to the success of the Year-2 BSMP field effort. Unlike last year, lead time for planning, preparation, and implementation was adequate. Experience gained during the Year-1 cruise was invaluable in anticipating and solving sampling problems. The cruise was scheduled during August to take full advantage of the extended daylight and the short open-water season. The elimination of the hydrographic measurements permitted the reduction in one crew member and resulted in a maximum of four rather than five crew members on board, a much more comfortable number for the size of the boat.

The ice reconnaissance flights were beneficial in planning and executing the short-term cruise goals. Observations made from the air had a direct bearing on the timing and route taken through the barrier islands on the east leg to Camden Bay. In addition, the ability of the plane to land on the Colville River made possible the occupation of the delta station in an otherwise inaccessible area. The expanded North Slope road system was also an asset to the overall sampling program. The fact that several areas could now be reached by truck resulted in more latitude in cruise planning as well as some direct time savings.

Finally, the personnel involved in the operations of NOAA launch No. 1273 were of tremendous help in bringing the Year-2 BSMP survey to a successful conclusion.

2.3 Sampling Methods

2.3.1 Sediment Sampling

As in the Year-1 survey, sediment samples were collected with the 0.1-m² stainless steel Kynar-coated, modified Van Veen grab sampler. Water overlying the

sediment sample was removed with a suction system that facilitated removal of the water before the rolling action of the ship could resuspend the surface sediment. The suction system also aided in achieving 10 grabs/hour, a sampling schedule that had proved difficult to maintain in Year-1.

The Kynar-coated aluminum scoop was redesigned for the Year-2 survey to provide a more accurate template for removal of the 1-cm surface sediment and to permit easier access to the grab sampler. Both the grab sampler and scoops were washed with soap and water, and rinsed with methanol and methylene chloride rinses before use at each station. Between casts at a given station, the grab was rinsed thoroughly with clean seawater provided by the epoxy pump/polyethylene tubing system.

Sediment samples were stored over dry ice (-78°C) in polystyrene shipping containers for field storage and transfer to Battelle New England Marine Research Laboratory (BNEMRL). Some replicates were stored in a chest freezer (-20°C) at the NOAA base camp before shipment to BNEMRL.

As proposed in the field survey manual, one sediment replicate was collected from each side of the grab sampler whenever possible. In most cases, two sediment replicates were collected from each grab. With the addition of the water suction system and the clean water delivery system, the proposed sediment sampling schedule of one replicate every six minutes was easy to maintain.

2.3.2 Peat and River Sample Collection

With the exception of the Heald Point and Milne Point peat samples, which were collected by hiking overland from road access, all coastal peat sample locations were accessed with the Zodiak boat. All peat samples were collected from exposed shoreline peat cliffs. The immediate sampling area was photographically documented. Road access to the Sagavanirktok River facilitated collection of a sediment sample, whereas the Colville River delta station was accessed by float plane.

All peat and river sediment samples were collected with the Kynar-coated aluminum scoop into 250-ml Teflon jars, processed, and stored similarly to sediment samples.

2.3.3 Biota Sampling

Two types of biota samples were collected during the Year-2 survey: nearshore infaunal bivalves and amphipods. Infaunal bivalves were collected with the 0.1-m² Kynar-coated grab. Sediment collected with the grab was placed in a polyethylene barrel and the contents sieved for bivalves through a 5-mm Nytex screen. Seawater for washing the sediment was provided by the Jabsco epoxy/polyethylene pumping system described in Section 2.2.2. An inboard sieve stand was constructed to facilitate the sieving process.

Gammarid amphipods were collected using commercial steel minnow traps that were tethered on a mooring, marked with a small float, approximately 2 m above a small anchor. Whenever possible, the amphipod trap array was deployed at station center upon arrival at station and served to identify the survey area. To minimize contamination originating from the trap, all surfaces of the traps were epoxy-coated. In general, the amphipods collected were much smaller than expected and most were able to escape through the 0.5-cm mesh of the trap during retrieval operations. The traps were, therefore, covered with fine nylon mesh to help retain the animals. A sardine bait contained in a nylon sock was used to attract the amphipods.

The Year-2 biota sampling proceeded generally according to the Year-2 sampling plan. The density of bivalves in sediment samples was low (3-4 bivalves/0.1-m²). However, the sediment samples could be processed with relative ease, allowing bivalve samples to be collected at most designated stations. Upon modification of the amphipod trap to reduce losses of the small animals, amphipod samples were collected at most stations designated for such collections.

2.4 Field Data Management and Sample Handling

2.4.1. Field Logs

Field operations and sample collection, preservation, and transfer were recorded on various log forms:

- Station Logs
- Cast Logs
- Sample Custody and Identification Forms
- Sediment Sample Logs
- Biota Sample Logs
- e Sample Transmittal Forms

Station coordinates, date and length of station occupation, and depth were recorded on the Station Log. Each lowering of the sampling equipment was recorded by station, date and time, and assigned a cast number on the Cast Log. Sampling success and sample numbers were also recorded on the Cast Log.

In addition to the Station and Cast Logs employed during the Year-1 survey, the Sample Custody and Identification Form was also used during the Year-2 survey. Together with the Cast Logs, the Sample Custody and Identification Forms provided the primary documentation for the identification of samples collected in the field. Samples were assigned four-digit alphanumeric sample identification numbers and logged in on these forms according to Battelle Standard Operating Procedure (SOP) No. 6-007-01 (Chemistry Laboratory Sample Custody and Laboratory Sample Identification). Sample types (i.e., sediment chemistry or grain size, biota species) and replicate numbers were also recorded on the Sample Custody and Identification Forms.

Sediment Sample Logs and Biota Sample Logs contained information on the sample type as well as sample replicate numbers. These logs were maintained to track the sampling progress by sample type. Information for these forms was derived from the primary data recorded on the Cast Logs and Sample Custody and Identification Forms.

Each sample collected (sediment chemistry, grain size, biota, and quality control) was confirmed and recorded on a Sample Transmittal Form which accompanied the samples in transit from Deadhorse, AK to BNEML. Upon arrival at BNEML, all samples were checked against the appropriate log forms to validate sample transfer.

2.4.2 Sample Handling

All sediment and biota samples collected for chemical analysis were placed in Teflon jars (250 ml and 500 ml) and immediately transferred to coolers containing dry ice (-78°C). This method of sample preservation worked well because there was ample room for the coolers on the flying bridge and the method of storage required no maintenance. Dry ice was routinely supplied by Ms. Sandra Henry of Anchorage, AK. Before shipment, samples were repacked in small coolers with dry ice and shipped by air courier (DHL) directly to BNEML. Upon arrival at the laboratory, samples were immediately transferred to a commercial freezer (-20°C) for storage.

2.5 Sampling Limitations

Due largely to the perseverance of the scientific party and ship's crew, the Year-2 BSMP field survey accomplished the primary objectives proposed by the SRB committee. All proposed marine sediment stations (39 stations) were successfully occupied and sampled.

Biota samples were not collected in the quantities proposed in the Year-2 sampling plan. However, 11 stations were successfully sampled for infauna or amphipods, and the total numbers of samples from all stations exceeded expectations.

The intercomparison of obtaining sediment samples for trace metal and hydrocarbon chemistry determinations at one station with two different sampling devices (Battelle grab sampler, NOAA box corer) was not accomplished. The NOAA box corer could not be deployed from the NOAA launch without modifications to the vessel. The transom-to-U-frame clearance would have to be increased before the NOAA corer could be deployed from the ship.

3. ANALYTICAL METHODS

3.1 Analytical Rationale

The analytical strategy and specific analytical methods employed in the Year-2 BSMP were structured to meet the overall objectives of the monitoring program stated in Section 1.1 and to incorporate the recommendations made by the Year-1 SRB Committee. The analytical strategy was basically designed to test the four null hypotheses (H_01 through H_04) through appropriate sampling, and analytical and statistical design. The philosophy of the analytical design was that it must result in a set of statistically rigorous measurements rather than merely descriptive information. The Year-1 analytical plan, therefore, was redesigned to enhance statistical treatment of the Year-2 data, and to address the potential contributions of shoreline erosion and riverine inputs to the metal and hydrocarbon budgets of the Study Area.

The analytical plan for Year-2 field samples is presented in Tables 3.1, 3.2, and 3.3 for sediment samples, peat and river samples, and tissue samples, respectively. Laboratory analyses included the determinations of hydrocarbons, metals, grain size, and total organic carbon (TOC) in sediments and peat/river samples, and hydrocarbons and metals in tissue samples.

For sediments and peat/river samples, analyses for trace metals and hydrocarbons were performed on both bulk and mud fractions according to Tables 3.1 and 3.2. In order to reorient the sediment metals program toward examining only the mud fraction, both bulk and mud fractions were analyzed from the 26 Year-1 stations that were resampled in Year-2 to allow for comparisons of Year-1 bulk sediment data with Year-2 bulk data. At the 13 stations that were occupied for the first time in Year-2, metals were determined only on the sediment mud fraction. Complete hydrocarbon analyses (saturates and aromatics) were performed only on bulk sediments from 36 stations. To examine the feasibility of reorienting the hydrocarbon sediment chemistry program towards the mud fraction, hydrocarbons were determined in both bulk sediment and mud fractions from three stations. Eight peat and two river samples were analyzed for metals in the bulk sediment and mud fractions. Hydrocarbons, however, were determined only on the bulk peat and river sediments.

Animal species were collected for tissue analyses at 13 stations. In addition to the four bivalve species obtained in limited numbers in the Year-1 survey, amphipods (*Nonion* spp.) were also collected during the Year-2 survey. As can be noted from Table 3.3, specimens of the same species collected at some stations (e.g., 1A, 1B, 1E, 7B, 7C) were pooled to obtain a sample large enough to permit analyses of four replicates. Four replicates were analyzed for metals for each species collected at each station. The hydrocarbon chemistry program was designed so that four replicate GC and GC/MS analyses could be performed once for each species to determine variability in saturated and aromatic hydrocarbons. Replicates were analyzed by UV/F at all stations. At stations where GC and GC/MS analyses were not replicated, the extracts were pooled to yield a single composite following UV/F analysis.

Frozen replicate samples were returned to the laboratory, homogenized, and carefully split to create "paired analysis" for all chemical parameters measured. Because of different sample storage requirements, grain size samples were not part of the same homogeneous sample split in the laboratory for chemical analysis. Grain size samples were, however, "paired" with the chemistry sample in the sense that they were taken from the same grab as the chemistry sample.

TABLE 3.1. ANALYTICAL PLAN FOR YEAR-2 SEDIMENT SAMPLES.

Type of Analysis	No. of Stations	Replicates Analyzed/Station	Comments
Trace Metals	13	3 composites of 2 replicates each	New Year-2 stations; analysis of mud fraction only .
Trace Metals	26	3 composites of 2 replicates each	Replicated Year-1 stations; analysis of both bulk and mud fraction.
Organics	36	3 composites of 2 replicates each	Stations sampled in Year-2; complete hydrocarbon analysis on bulk sediment.
Organics	3	3 composites of 2 replicates each	Complete hydrocarbon analysis on both bulk and mud fraction.
TOC	39	3 composites of 2 replicates	All stations sampled in Year-2.
Grain Size	39	3 composites of 2 replicates	All stations sampled in Year-2.

TABLE 3.2. ANALYTICAL PLAN FOR YEAR-2 PEAT AND RIVER SAMPLES.

Type of Analysis	No. of Stations	Replicates Analyzed/Station	Comments
Trace Metals	2 River	1 Sample at each station	Analysis of both bulk and mud fraction.
Trace Metals	8 Peat	1 Sample at each station	Analysis of both bulk and mud fraction.
Organics	2 River	1 Sample at each station	Complete hydrocarbon analysis on bulk river sediment.
Organics	8 Peat	1 Sample at each station	Complete hydrocarbon analysis on bulk peat samples.
ToC	2 River	1 Sample at each station	
TOC	8 Peat	1 Sample at each station	
Grain Size	2 River	1 Sample at each station	
Grain Size	8 Peat	1 Sample at each station	

TABLE 3.3. ANALYTICAL PLAN FOR YEAR-2 TISSUE SAMPLES.

Station	Genus	No. of Replicates Collected	Replicates Analyzed			
			UV/F	Organics		Metals
				GC-FID	GC/MS	
1A+1B+1E	<u>Anonyx</u> ^a	4	4	1	4	
1A+1B	<u>Astarte</u> ^b	4	2	1	4	
1A	<u>Portlandia</u> ^b	4	4	4	4	
2F	<u>Anonyx</u>	4			4	
3A	<u>Astarte</u>	4	4	1	4	
	<u>Anonyx</u>	4			4	
4B	<u>Anonyx</u>	4	2	1	4	
5F	<u>Cyrtodaria</u> ^b	4	4	4	4	
5H	<u>Astarte</u>	4	4	4	4	
	<u>Anonyx</u>	4			4	
6D	<u>Macoma</u> ^b	4	2	2	4	
	<u>Astarte</u>	4	2	1	4	
6G	<u>Cyrtodaria</u>	4	4	1	4	
	<u>Anonyx</u>	4	4	4	4	
7B+7C	<u>Anonyx</u>	4	4	1	4	
7E	<u>Anonyx</u>	4	4	1	4	
TOTAL ANALYSES			44	26	64	

^aAmphipod

^bBivalve

3.1.1 Changes in the Analytical Strategy for Year-2

Specific changes in the Year-2 analytical program include the following:

1. Elimination of the hierarchical analytical strategy applied to the Year-1 sediment hydrocarbon analyses. All sediment UV/F analyses in Year-1 revealed a large background of fluorescing material. Although the UV/F method was precise, it was deemed not sufficient] sensitive to potential incremental additions of petroleum compounds. In Year-2, all combined replicates were analyzed for saturate and aromatic hydrocarbons directly, and the UV/F measurement in sediments was eliminated.
2. Increasing the number of replicate samples analyzed for hydrocarbons at each station. In Year-1, lack of GC and GC/ MS replication data at 20 of 27 stations did not allow a valid statistical determination of within-station variability for all hydrocarbon parameters and created some uncertainty as to how the pooled measurements from these stations could be used. In Year-2, determination of within-station variability of saturated and aromatic hydrocarbons was accomplished by analysis of three replicate samples at each station.
3. Incorporation of a limited number of GC/ MS sterane/-triterpane measurements on sediment, and peat and river samples. These biomarkers, which are used to differentiate diagenetic and fossil hydrocarbons, may elucidate the role of shoreline erosion and riverine contributions to the hydrocarbon distribution in the Study Area.

3.1.2 Pooling Strategy

The pooling strategy for Year-2 samples reflects the success of the field sampling effort and the need for the analytical program to include samples from all stations. The statistical design of the analytical program specified some degree of pooling of sediment replicates and biota samples to meet the overall program objectives and specific Year-2 program goals. Specific pooling strategy for sediment replicates and biota samples is discussed in the sections that follow.

3.1.2.1 Sediment Samples. In order to obtain replication data on the maximum number of new stations, or those not replicated in Year-1, 3 sediment samples from each of the 39 stations were analyzed for metals, hydrocarbons, grain size, and TOC. Eight replicates were collected at each station, generally two from each grab sample. Sediment sampling protocol specified that one replicate sample be collected from each side of the grab sam pier.

The sediment pooling scheme is shown in Figure 3.1. As in Year-1, the term replicate has been used to describe each of the subsamples collected from a grab, rather than the grab itself. For analyses, six of the eight station replicates were combined in the laboratory into three pools of two replicates each (e.g., replicates 1+2, 3+4, 5+6). The remaining two replicates (7+8) were archived. Frozen sediment replicates were thawed and homogenized, and equal aliquots (by weight) of each replicate were combined to form the subsamples for each type of analysis (metals, hydrocarbons and TOC). Separation of the mud fraction (silt + clay) of the sediment for metal and hydrocarbon analysis was performed separately on the samples analyzed for metals and for hydrocarbons. Remaining sediment from all replicates was archived separately at BNEMRL.

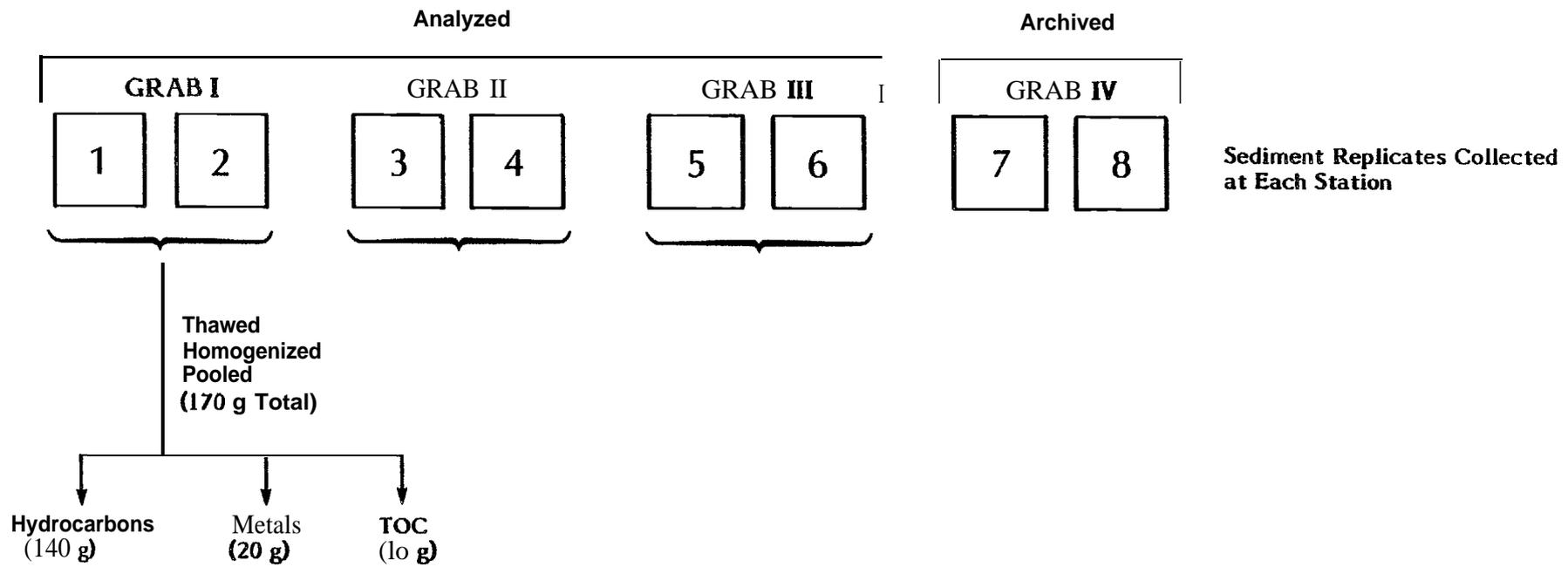


FIGURE 3.1. SEDIMENT **SAMPLE POOLING AND SPLITTING** PROCEDURE

3.1.2.2 Tissue Samples. Biota specimens of the same species, from each station where sampling was successful, were combined in the field to create one sample. The average weight of each individual and approximate numbers of individuals in each sample are listed in Table 3.4. Upon return to the laboratory, this sample was partially thawed, and subsampled for metal and hydrocarbon analyses as shown in Figure 3.2. Generally five times more individuals were required for the hydrocarbon analyses as for metals. The subsamples were subsequently divided into individual replicates for analysis. Subsampling for metals analysis was performed under a laminar flow hood. Generally, four replicates of each sample were analyzed for metals and hydrocarbons. In several locations, the pool of animals collected from a station was not large enough for complete analytical replication. In this case, specimens of the same species from two or three stations within a given geographical area were combined to provide enough tissue for complete analysis and replication. Excess tissue was archived at BNMRL.

3.1.3 Measured Parameters

3.1.3.1 Metals. The seven elements determined in sediments, peat and river samples, and tissues were the same as those analyzed in Year-1. These elements were barium, chromium, vanadium, lead, copper, zinc, and cadmium. The analytical methods employed for the analysis of these elements are listed in Table 3.5 and include flame (FAA) and/or graphite furnace atomic absorption (ZGFAA), inductively-coupled plasma emission spectrophotometry (ICAP), and energy-dispersive x-ray fluorescence (XRF). As a quality control check, some elements were determined by more than one technique. When an initial analysis produced values below detection limits, samples were reanalyzed using a more sensitive technique.

3.1.3.2 Hydrocarbons. The saturated hydrocarbons determined for the Year-2 program (Table 3.6) are identical to those analyzed in Year-1. These hydrocarbons (n-alkanes and isoprenoids) were identified and quantified by high-resolution gas chromatography using flame ionization detection (GC-FID). A set of key diagnostic parameters and ratios (Table 3.7), used to test the null hypotheses (H_01 through H_04), was formulated from the compounds in Table 3.6.

Table 3.8 lists the polynuclear aromatic hydrocarbons (PAHs) determined in sediments and tissues. These compounds were identified and quantified by computer-assisted capillary gas chromatography/mass spectrometry (GC/MS). Tissue samples were additionally analyzed by ultra-violet/fluorescence spectrometry (UV/F) for the determination of total fluorescing material in crude tissue extracts and reported as Prudhoe Bay oil equivalents. Certain saturated hydrocarbon biomarker compounds (steranes, triterpanes) were analyzed by GC/MS. Key aromatic diagnostic parameters and ratios, used to test the null hypotheses, are listed in Table 3.9.

3.1.3.3 Grain Size and Total Organic Carbon. In addition to the metal and hydrocarbon parameters discussed above, each sediment, and peat and river sample was also analyzed for grain size and total organic carbon content.

The grain size samples, although not split from the sediment chemistry samples, were collected from the same grab as the corresponding sediment chemistry samples. Replicates were pooled as described for the chemistry sediment samples (i.e., 1+2, 3+4, 5+6; 7+8 archived). Individual phi categories from -1 to <10 were determined on each of the three pooled replicate samples per station.

Sediment for total organic carbon (TOC) analysis was subsampled from the pooled chemistry replicates. Samples were analyzed for TOC by high temperature combustion.

TABLE 3.4. AVERAGE WET WEIGHTS PER INDIVIDUAL ANIMAL SPECIMENS AND AVERAGE NUMBER OF INDIVIDUALS PER SAMPLE FOR ALL SPECIES COLLECTED.

Genus	Average Wet Weight/Individual	Approximate Number of Individuals/Sam ple
<u>Anonyx</u>	0.2 g	73
<u>Astarte</u>	1.0 g	15
<u>Cyrtodaria</u>	0.2 g	75
<u>Macoma</u>	0.5 g	30
<u>Portlandia</u>	0.2 g	75

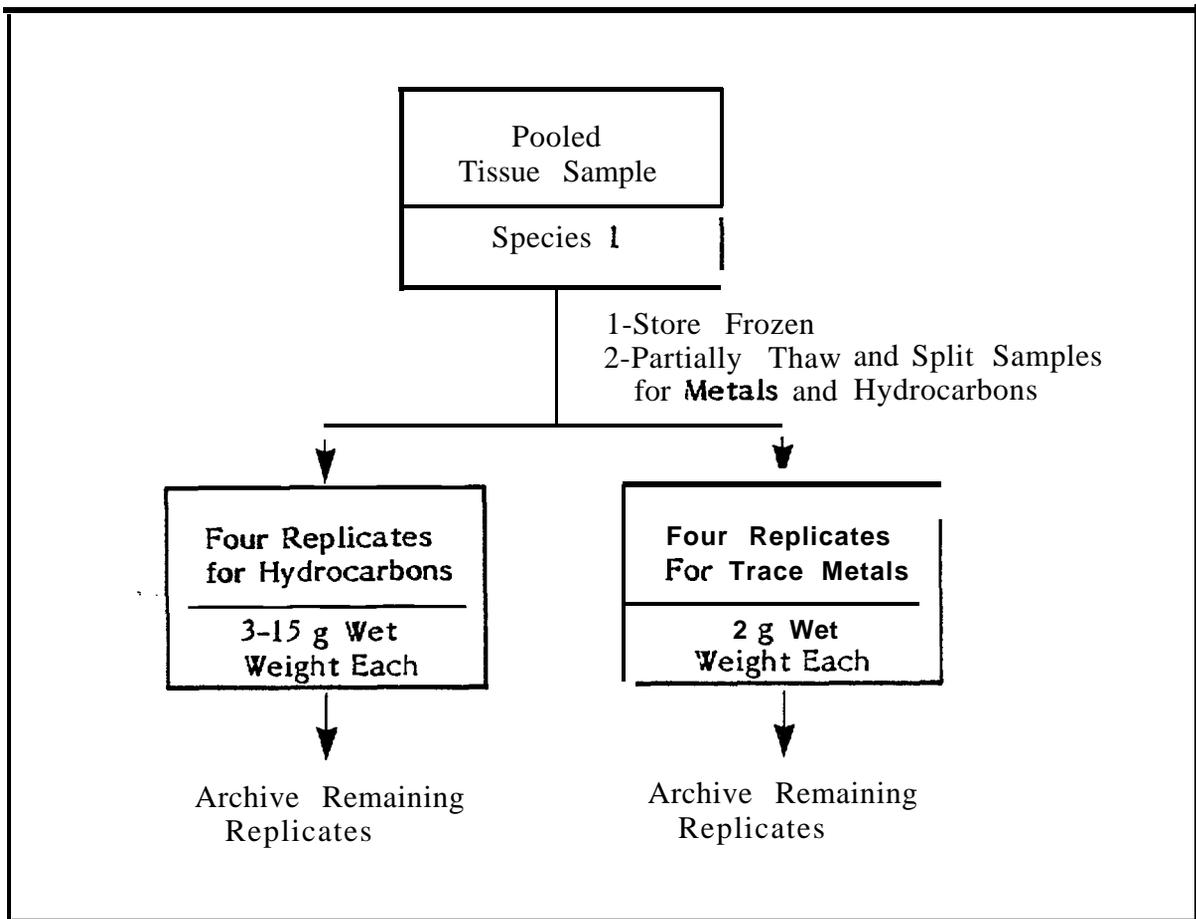


FIGURE 3.2. LABORATORY **SAMPLE** SPLITTING PROCEDURE FOR TISSUES.

TABLE 3.5. ANALYTICAL METHODS USED FOR THE ANALYSIS OF TRACE METALS IN MARINE SEDIMENTS AND TISSUE SAMPLES.

Element	Analytical Method	
	Sediments	Tissues
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

TABLE 3.6. COMPOUNDS DETERMINED BY HIGH-RESOLUTION CAPILLARY GAS CHROMATOGRAPHY USING FLAME IONIZATION DETECTION.

Compound	Relevance
1. <u>Saturated Hydrocarbons</u>	
n-alkanes (n-C ₁₀ to n-C ₃₄)	Weathering and source indicators, especially when ratios are derived.
Isoprenoids (1380;1470;1650;1708; 810) ^a	Weathering indicators (marker compounds in lightly weathered samples).
2. <u>Unresolved Complex Mixture (UCM)</u>	Indicator of weathered petroleum, although microbial activity can also result in formation of these GC/FID unresolved compounds.

^a Where 1300 = retention index of n-C₁₃, 1400 = retention index of n-C₁₄, 1800 = retention index of n-C₁₈.

TABLE 3.7. KEY DIAGNOSTIC PARAMETERS DETERMINED BY HIGH-RESOLUTION CAPILLARY GAS CHROMATOGRAPHY USING FLAME IONIZATION DETECTION.

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 (Pristine)	PRIS	µg/g
Isoprenoid, 1810 (Phytane)	PHY	µg/g
TALK/TOC ^a		µg/mg TOC
TALK/% SILT		
LALK/TALK		
ISO/ALK		

^aTOC = Total Organic Carbon

TABLE 3.8. AROMATIC HYDROCARBONS AND HETEROCYCLICS QUANTIFIED USING HIGH-RESOLUTION CAPILLARY GAS CHROMATOGRAPHY/ MASS SPECTROMETRY.

m/e Ion Search	Compound Identification and Abbreviation
128	Naphthalene (C ₀ N)
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 3.9. KEY DIAGNOSTIC PARAMETERS DETERMINED BY HIGH-RESOLUTION CAPILLARY GAS CHROMATOGRAPHY/MASS SPECTROMETRY.

Variable	Abbreviation	Units
Naphthalene series (C ₀ N + C ₁ N + C ₂ N + C ₃ N + C ₄ N)	N	µg/g
Fluorene series (C ₀ F + C ₁ F + C ₂ F + C ₃ F)	F	µg/g
Phenanthrene series (C ₀ P + C ₁ P + C ₂ P + C ₃ P + C ₄ P)	P	µg/g
Dibenzothiophene series (C ₀ D + C ₁ D + C ₂ D + C ₃ D)	D	µg/g
4- and 5-ringed Polynuclear Aromatic Hydrocarbons (FLAN + PYEN + BAA + CHRY + BFA + BAP + BEP + PERY)	4-, 5-PAH	µg/g
(N+F+P+D) / (N+F+P+D+4-, 5-PAH)	FFPI	

3.2 Analytical Chemistry of Metals

3.2.1 Methods for Sediments

The analyses for trace metals in sediments and tissue samples were conducted using several analytical techniques. Concentrations were determined for barium, cadmium, chromium, copper, lead, vanadium, and zinc. Table 3.10 summarizes the procedures employed in each of the various analytical methods.

Six sediment replicate subsamples from each station were received by the laboratory frozen and were stored frozen at -20°C until analysis. Immediately prior to analysis, each replicate sub sample was sieved through a 2-mm nylon screen to remove gravel. Three replicate composites were created according to the pooling scheme in Figure 3.1. Ten grams from each of the two replicates were combined and freeze dried to a constant weight. For samples for which a separate mud (silt + clay) fraction analysis was required, an aliquot of the bulk sediment was removed and sieved through a 62.5- μm screen. The dry bulk and mud fraction sediments were ground in a Spex ceramic ball mill prior to digestion.

Two digestion procedures were used to totally dissolve the sediment. For ICAP analysis, 0.25 g of dry ground sediment were combined with 2 ml of aqua regia and 6 ml of hydrofluoric acid in a Teflon vial. The vial was sealed with a screw cap and heated at $80-90^{\circ}\text{C}$ for 2 h on a hot plate. The lid was removed and the solution was evaporated to near-dryness to remove the hydrofluoric acid. The residue was dissolved with 0.4N nitric acid.

For analysis by ZGFAA, 0.1 g of sediment was combined with 7 ml of hydrochloric acid in a Teflon vial. The sealed vial was heated in an $80-90^{\circ}\text{C}$ water bath for 1 h. After cooling, 3 ml of nitric acid was added, the vial sealed, and heated again for 1 h in the water bath. After cooling, 0.5 ml of hydrofluoric acid was added to the vial, which was again heated in the water bath for 1 h. When cool, the digestate was transferred to a polystyrene container and diluted with double deionized water to 50 ml.

Approximately 10 percent of the sediments were analyzed by XRF as a cross-check to verify the ICAP results. Some sediment samples were additionally analyzed for copper, lead, and zinc by XRF. Sediments were prepared for XRF by pressing 0.5 g of powdered sediment into a 25-mm-diameter pellet. The analysis was performed on a Kevex spectrometer using a zirconium secondary target for excitation of copper, lead, and zinc. Data reduction methods are described by Nielson (1977).

3.2.2 Methods for Tissue Samples

Biota samples were received frozen and were stored at -20°C until analysis. In preparation for analysis, the organisms were thawed, cleaned of foreign matter using Teflon forceps, and rinsed in double deionized water. Individual bivalves were removed from their shells using Teflon forceps and a titanium knife. A pool of 5-10 individuals of the same species was placed in an acid-cleaned, preweighed plastic jar, the wet weight recorded, and the tissue freeze dried to a constant weight. After recording the dry weight, the tissue was ground to a powder in an all-plastic Spex 8000 ball mill.

Tissues were digested by combining 0.25 g of dry, powdered tissue with 5 ml of nitric acid in a screw-cap Teflon vial, and heating for 8 h at 130°C . After cooling, 1 ml of hydrofluoric acid was added, the vial sealed, and digested for 2 h. After evaporation to near-dryness, the residue was diluted to 25 ml with deionized water followed by acidification with 25 μl nitric acid. Analysis was performed using ZGFAA.

TABLE 3.10. SUMMARY OF ANALYTICAL CONDITIONS FOR METALS IN SEDIMENTS AND TISSUES.

Element	Instrument	Instrument Condition	µg/g (dry weight)	
			Detection Limit	Procedural Blank
Sediment				
Ba	ICAP	493.41 nm 1st order (Forward Power) FP 2.3 Kw observation height 20 mm nebulizer flow 2.5 ml/min	0.4	1.8
Gd	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 µl 228.8 nm, slit 0.7 nm hollow cathode lamp 4 ma gas 50 ml/min 80 & 140°C dry 250 & 300°C ash 1 5009 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 µl 2S3.3 nm, slit 0.7 mm electrodeless discharge lamp 10 W gas 50 ml/min 80 and 140°C dry 250 and 300°C ash 2100°C atomization 2600°C 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 ml/min	6.0	4.8
Zn	XRF	Tungsten tube 40 Kv, 20 ma zirconium secondary source counting time 3000 sec	0.5	0
Tissue				
	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 600C 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 2600°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

3.2.3 Quality Assurance/Quality Control Methods

Quality control activities relating to metals analysis of sediments and tissue included analysis of reagent blanks, procedural blanks, and standard reference materials (SRMs).

Prior to analysis of environmental samples, labware blanks and reagent blanks were analyzed in triplicate for each lot to determine that the blanks were acceptable. Procedural blanks were run through the entire analytical process to check for contamination, to establish a reagent blank to be subtracted from sample results, and to determine detection limits. Five procedural blanks were run with every batch of samples analyzed. 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 environmental samples.

The precision of each analytical instrument for each metal was determined by analysis of five replicates of a certified homogeneous sediment and tissue SRM. Field samples and SRMs were analyzed for barium, copper, lead, and zinc 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 addition was used to evaluate matrix effects for both ICAP and ZGFAA. Ammonium phosphate was used as a matrix modifier in the ZGFAA analysis of cadmium and lead to improve the analytical signal and precision. The Zeeman effect background correction system was used for all ZGFAA analyses.

The results of the quality control procedures are presented and discussed in Section 4.

3.3 Analytical Chemistry of Hydrocarbons

3.3.1 Sediment Preparation

Three surface sediment replicates for each station were analyzed for high molecular-weight hydrocarbons using GC-FID and GC/MS. The extraction methods were based on those of Brown et al. (1979) and Boehm et al. (1982a). The analytical scheme is shown in Figure 3.3. Approximately 70 g of wet sediment from each of the two replicates to be pooled were 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 dried sediment was extracted three times with 100 ml aliquots of dichloromethane:methanol (9:1) by agitating on a platform shaker 4 h for each extraction. All solvent extracts were transferred into a 1-L separator funnel containing 100 ml of Millipore water and 10 g of sodium chloride. The dichloromethane layer was drawn off and the aqueous methanol phase extracted three times with 50-ml aliquots of dichloromethane. The three dichloromethane extracts from each sample were dried, combined, reduced in volume to 1 ml by Kuderna-Danish evaporation, and displaced with hexane. Single aliquots of extracts 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. Column chromatography was performed using a 5% deactivated silica/196 deactivated alumina/activated copper (1:1:2 g) 1 cm id. chromatography column that was wet-packed in methylene chloride

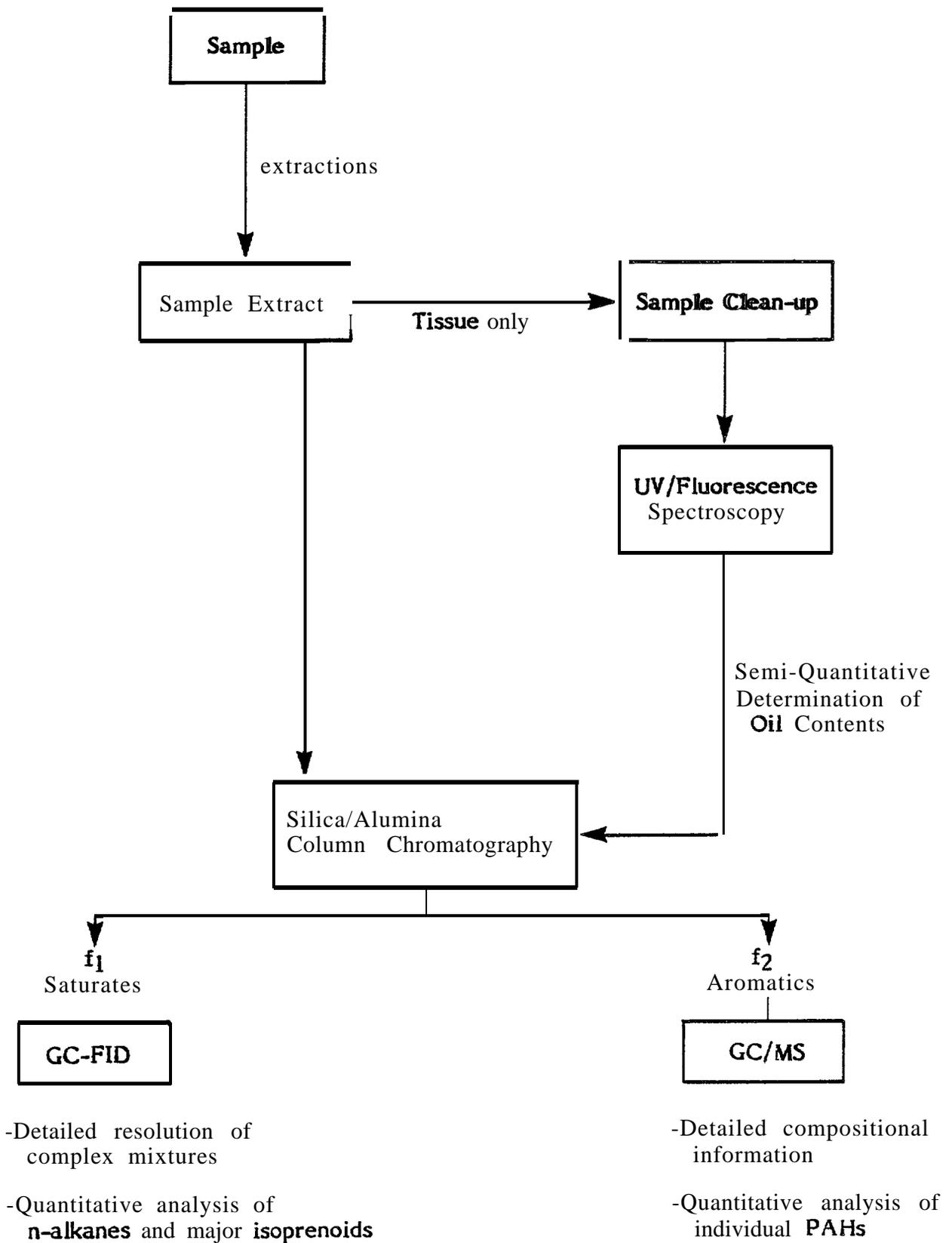


FIGURE 3.3 ANALYTICAL **SCHEME** FOR HYDROCARBONS IN SEDIMENTS AND TISSUES.

and prepared by eluting with 30 ml each of dichloromethane and hexane. The sample extract, which was less than 50 mg extract weight in 0.5 ml hexane, was charged to the column and eluted with 18 ml hexane to isolate the saturated (f₁) hydrocarbons, followed by 21 ml hexane:dichloromethane (1:1) to isolate the unsaturated/aromatic (f₂) hydrocarbons. The f₁ and f₂ fractions were analyzed by GC-FID and GC/MS, respectively.

Sediments were separated into the mud fraction by wet sieving through a 63- μ stainless steel sieve. The washed mud fraction was centrifuged and extracted with methanol/methylene chloride in the centrifuge bottle using the same extraction procedure employed for the bulk sediment. The aqueous supernatant was used for back extraction of the methanolic extract.

3.3.2 Tissue Preparation

Individual replicates of benthic bivalves and amphipods were analyzed by UV/F. Depending on the size of the sample, either individual replicates or pooled samples obtained from individual replicates were analyzed by GC-FID and GC/MS after completion of the UV/F analyses.

Approximately 3-15 g wet weight tissue was extracted and analyzed according to procedures of Boehm et al. (1982b). Bivalve tissues were removed from shells with solvent-rinsed utensils. A wet weight was obtained on a top-loading balance. Whole amphipods and shucked bivalves were digested overnight with 5 N aqueous potassium hydroxide and the digestate was extracted in a centrifuge tube three times with ethyl ether. The extracts were combined, dried with sodium sulfate, and concentrated to 0.5 ml by rotary evaporation. Polar and biogenic compounds, which interfere with UV/F analysis, were removed from the extracts by alumina (6.5 g of 7.5% water-deactivated alumina) column chromatography. The column was eluted with 25 ml of hexane/dichloromethane (9:1) to isolate the saturated, unsaturated/aromatic compounds. The fraction was concentrated and transferred into hexane for UV/F analysis. Individual or pooled extracts were subsequently concentrated by rotary evaporation and displaced with hexane. Total extracts were fractionated into f₁ and f₂ according to procedures described above for sediments. The f₁ saturated and f₂ unsaturated/aromatic fractions were analyzed by GC-FID and GC/MS, respectively.

3.3.3 Analytical Methods

Tissue extracts were analyzed by UV/F for semi-quantitative estimates of aromatic hydrocarbons, and by GC-FID and GC/MS for saturated and unsaturated/aromatic hydrocarbons, respectively.

3.3.3.1 UV/F. 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. (1982c), and Boehm and Fiest (1982).

The tissue sample extract (or a dilution thereof) was dissolved in hexane for analysis by UV/F. The intensity of the fluorescence emission was measured from 250-500 nm, while synchronously scanning the excitation monochromator at 25 nm shorter than the wavelength of the emission monochromator. This technique measured 2- to 5-ringed aromatic hydrocarbons (Lloyd, 1971).

The intensities of the fluorescence spectra were measured at 312, 355, and 425 nm, which correspond to approximate peak maxima of the 2-, 3-, and 4- plus 5-ringed aromatics present in the samples and those present in the Prudhoe Bay crude oil reference standard.

A dilution series of the hexane/crude oil was used to calibrate the method daily. Calibration curves, based on the analysis of Prudhoe Bay crude oil standard, were used to quantify sample extracts. UV/F tissue data are presented in μg Prudhoe Bay crude oil equivalents/g wet weight.

3.3.3.2 GC-FID. GC-FID analysis was used to identify and quantify the saturated petroleum hydrocarbon compounds present in the sample. The concentrations of specific compounds were also used to calculate indicator ratios to test the null hypotheses.

Each extract fraction was analyzed by fused silica capillary gas chromatography on a Hewlett-Packard 5880A gas chromatography equipped with a splitless injection port, a flame ionization detector, and a Shimadzu C-R3A data system. Wall-coated open tubular fused silica columns (0.25 mm x 30 m; J&W Scientific), coated with bonded DB-5 stationary phase, were used to analyze the f₁ saturated hydrocarbon fraction from column chromatography. Instrumental conditions are listed in Table 3.11.

On the Shimadzu C-R3A, hydrocarbon concentrations were calculated using internal standards. 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. 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 complex mixture (UCM) area, adding it to the total resolved integrated area, and calculating a concentration using internal standards. The concentrations of n-alkanes and isoprenoids were determined on a dry-weight basis for sediments and on a wet-weight basis for tissues.

3.3.3.3 GC/MS. The f₂ aromatic hydrocarbon fractions from the adsorption columns were analyzed by GC/MS to determine the composition and concentrations of aromatic hydrocarbons in the samples.

An aliquot of the f₂ fraction was analyzed on a Finnigan 4530 GC/MS equipped with a 0.25-mm id. x 30-m DB-5 fused silica capillary column (J&W Scientific) that was threaded directly into the ion source. Instrumental conditions are listed in Table 3.12. 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 the peaks of the internal standard. Relative response factors for each component were calculated from analyses of analytical standards, if available, or were extrapolated. Compounds detected by GC/MS analyses for this study are listed in Table 3.8.

3.3.4 Quality Assurance/Quality Control Methods

The geochemistry quality assurance program is part of the formal laboratory-wide quality assurance program instituted at Battelle. Specific measures taken before initiation of this study and during the course of the program include

- A rigorous on-the-job training program that included a demonstration of training through analysis of triplicate samples and blanks.
- Adherence to strict sample transfer and custody procedures.
- Laboratory and data book audits.

TABLE 3.11. FUSED SILICA CAPILLARY GAS CHROMATOGRAPHY/FLAME IONIZATION DETECTION ANALYTICAL CONDITIONS.

<u>INSTRUMENT:</u>	Hewlett-Packard 5880A gas chromatography Shimadzu C-R3A integrator/data processor
<u>FEATURES:</u>	Split/splitless capillary inlet system Microprocessor-controlled functions Automatic data reduction/floppy disk data storage
<u>INLET:</u>	Splitless
<u>DETECTOR:</u>	Flame ionization
<u>COLUMN:</u>	
f ₁ :	0.25 mm I.D. x 30 m DB5 fused silica (J&W Scientific)
<u>GASES:</u>	
Carrier:	Helium 2 ml/min
Make-up:	Helium 30 ml/min
Detector:	Air 300 ml/min Hydrogen 30 ml/min
<u>TEMPERATURES:</u>	
Injection port:	250°C
Detector:	300°C
Column oven:	400-2900 3°C/min
<u>DAILY CALIBRATION:</u>	Alkane/mixture
<u>QUANTIFICATION:</u>	Internal standard (F, androstane; cholestane)

TABLE 3.12. GAS CHROMATOGRAPHY/MASS SPECTROMETRY INSTRUMENTAL CONDITIONS.

<u>INSTRUMENT:</u>	Finnegan 4530 gas chromatograph/mass spectrometer
<u>FEATURES:</u>	Data General Nova 4 data system with Incos data system Finnegan MAT 9610
<u>INLET:</u>	Splitless
<u>DETECTOR:</u>	Quadruple mass spectrometer
<u>SCAN RATE:</u>	450 amu/sec (45-450 amu)
<u>IONIZATION VOLTAGE:</u>	70 eV
<u>COLUMN:</u>	0.25 mm i.d. x 30 m DB5 fused silica (J&W Scientific)
<u>INTERFACE:</u>	Direct insertion of column into source
<u>CARRIER GAS:</u>	Helium 2 ml/min
<u>TEMPERATURES:</u>	
Injection Port:	270°C
Separator Oven:	280°C
Source:	250°C
GC Oven:	40-290°C, 10°C/min (temperature program)
<u>DAILY CALIBRATION:</u>	FC43 and aromatic mixture
<u>QUANTIFICATION:</u>	Internal standard (o-terphenyl and D12-chrysene)

- Documented calibration of UV/F, GC-FID, and GC/MS on a daily basis.
- An ongoing analytical quality control program.

The Year-2 analytical quality control program included the following:

- Initial demonstration of laboratory capability through analysis of interim reference material (sediment and mussel tissue) provided by NOAA National Marine Fisheries Laboratory in Seattle.
- Ongoing demonstration of precision and accuracy through analysis of method blanks, spiked blanks, and matrix spike experiments.
- Demonstration of analytical consistency between the Year-1 and Year-2 surveys by reanalysis of samples analyzed in Year-1.

The hydrocarbon chemistry quality control data are presented and discussed in Section 4.

3.4 Auxiliary Parameters

Auxiliary parameters for the Year-2 samples included sediment grain size and TOC. The hydrographic measurements made in Year-1 were eliminated because these data proved to be of little value to the overall objectives of the monitoring program.

3.4.1 Sediment Grain Size

Sediment grain size analyses were performed using sieve and pipet procedures. Division of the sand fraction into phi classes was accomplished by graded sieving according to the methods of Holme and McIntyre (1971). Division of silt and clay into phi categories was based on the pipet method (Folk, 1974).

Three sets of two replicates were composite for each station. A 25 g subsample of homogenized sediment was added to a dispersant solution of aqueous sodium metaphosphate (5 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 followed by shaking for 10 min. The sediment suspension was poured into a 0.063-mm sieve and gently agitated in a basin of water.

The silt and clay fractions (particles <0.063 mm), which passed through the sieve, were resuspended in 1 L of dispersing solution in a graduated cylinder. At specific time intervals, 25-ml aliquots of the suspension were removed, dried at 105°C for 24 h, cooled to room temperature, and weighed to the nearest 0.1 mg to determine the silt and clay phi class intervals.

The sand fraction, which remained on the 0.063 mm sieve, was rinsed into an aluminum weighing pan and dried to constant weight. To divide the sand component into phi intervals, the dried sand was placed in a graduated series of nested sieves (screen sizes of 2 mm, 1 mm, 0.5 mm, 0.25 mm, 0.125 mm, and 0.063 mm) and shaken for 10 min on a Ro-Tap Testing Sieve Shaker.

For the purposes of data reporting and entry into the data base, the -1 to >10 phi classes were recorded separately. They were also combined to generate gravel, sand, silt, and clay sediment size classes for data interpretation.

During the course of analysis, approximately every 10 samples were split and analyzed as duplicates to determine analytical variability. The results of these determinations are presented and discussed in Section 4.

3.4.2 TOC

TOC was determined with a Leco Model WR-12 carbon analyzer. Three sets of two pooled replicates for each station were analyzed. A 150-250 mg homogenized, dried subsample was placed in a ceramic crucible and washed twice with 6N hydrochloric acid to remove carbonate carbon. If reaction was vigorous on the second wash, the sample was washed a third time with hydrochloric acid.

Following decarbonation, the sample was rinsed with distilled water until neutral and then dried at 45°C. Copper and zinc accelerators were added to the sample crucibles prior to combustion in an induction furnace. The evolved carbon dioxide was scrubbed of water, halide, and sulfur before calculation of the percent TOC.

The carbon analyzer was calibrated daily with a series of calibration standards to provide a calibration curve covering the range of interest.

4. PRESENTATION OF RESULTS

4.0 INTRODUCTION

This section presents the data generated from the Year-2 BSMP survey. These data include results of the laboratory analyses for metals and hydrocarbons in marine and riverine sediments, peat samples, and animal tissues. Auxiliary data include grain size and total organic carbon concentrations for sediments and peat samples. Quality control results are also presented and discussed. For Year-1 stations, that were resampled in Year-2, both Year- 1 and Year 2 data are also compared in separate "comparison" tables.

The analytical results are presented in separate subsections for metals, hydrocarbons, and auxiliary measurements. Tabulation of the data has been reduced to only the parameters most relevant to interpretation, similar to the format of the Year-1 report. A complete listing of each data set is stored in our data base management system for transmittal to the National Oceanic Data Center (NODC).

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.

4.1 Metals Data

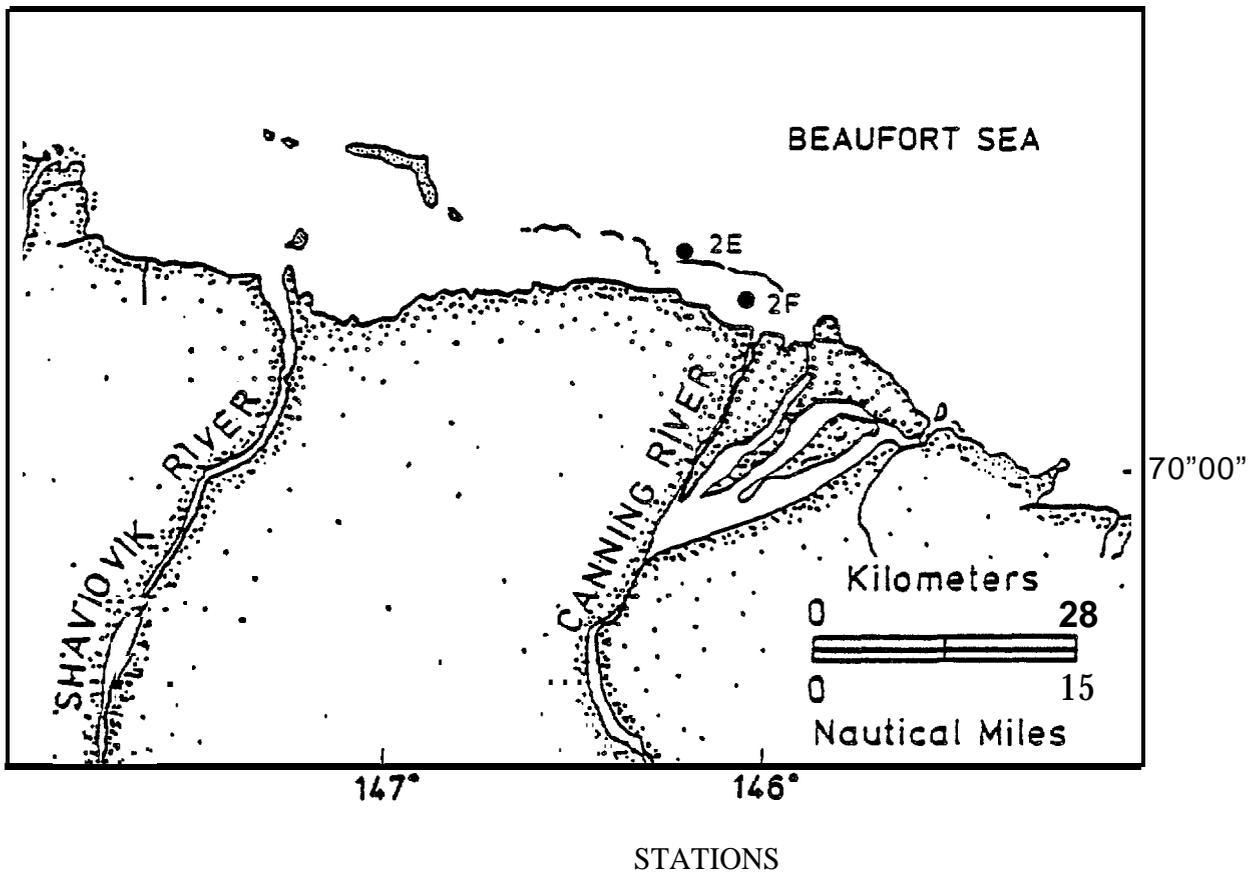
Metals were analyzed in marine and riverine sediments, shoreline peat samples, and tissues. Three samples, each representing two pooled replicates, were analyzed for every station except the peat and river shoreline locations for which single samples were analyzed. Metals were analyzed in the bulk and mud fractions of sediments from stations that were sampled in both Year-1 and Year-2, and from the peat and river stations. Analyses of samples from stations occupied only in Year-2 were restricted to the mud fraction.

All metal concentrations, except for those for peat and river sediments, are reported as the station mean \pm one standard deviation.

4.1.1 Metals in Sediments

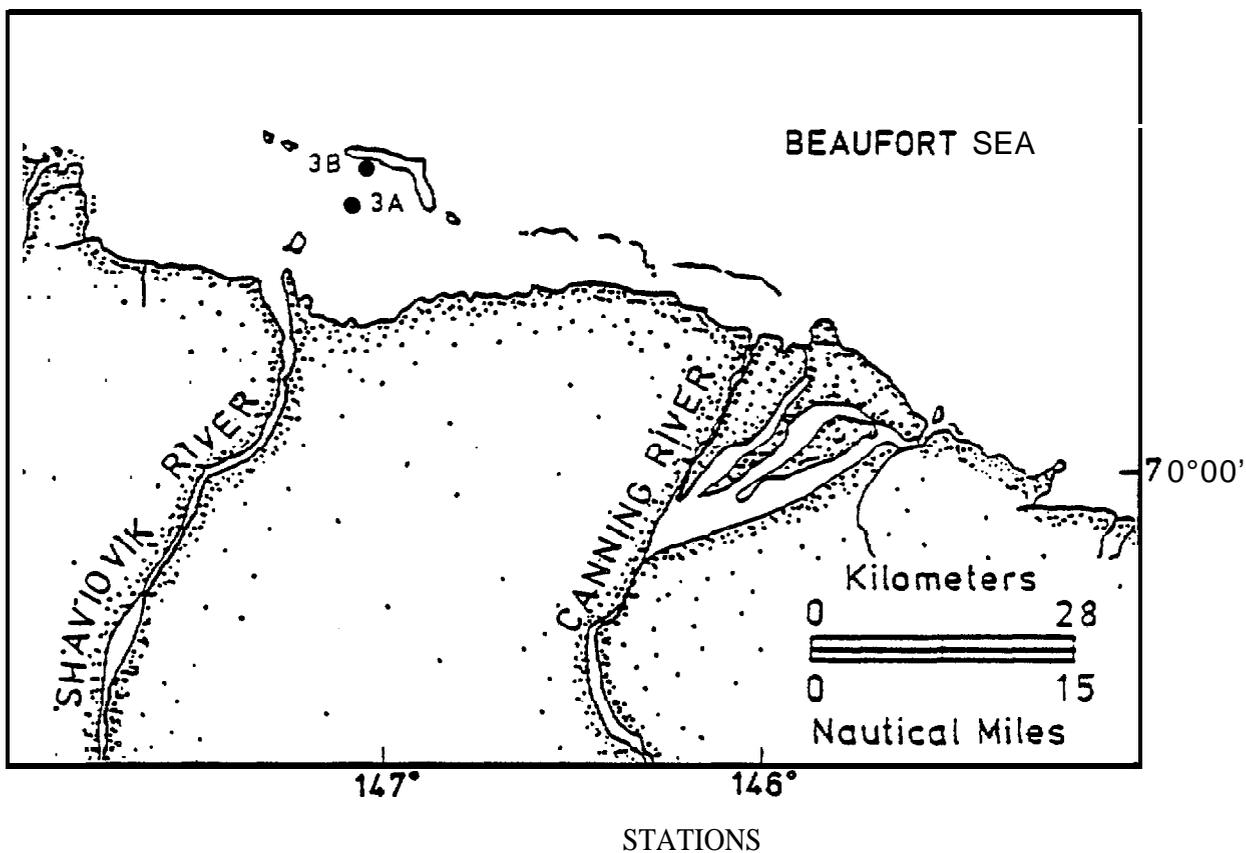
Figures 4.1 through 4.10 present the concentrations of metals in the bulk and mud fraction of sediments from those 26 stations that were sampled in Year- I and resampled in Year-2. Concentrations of metals are generally higher in the mud fraction than in the bulk sediment, although a number of exceptions are noted. Somewhat higher metal concentrations are associated with the bulk sediment from Stations 5B (Figure 4.4) and 7C (Figure 4.9). At Stations 2E (Figure 4.1), 3B (Figure 4.2), and 6A (Figure 4.7), there is only a minimal difference in the concentrations of metals between the bulk sediment and mud fraction. Because the sediment grain sizes at these stations are predominantly silt and clay (see Table 4.1 7), significant differences in the concentrations of metals in bulk and mud are not expected.

Mean concentrations of metals in the mud fraction of sediments from the 13 new Year-2 stations are presented in Figures 4.11 through 4.13. In the Camden Bay area (Figures 4.11 and 4.12), barium means range from 335 to 580 $\mu\text{g/g}$. Lead and copper levels are in the range of 15 to 31 $\mu\text{g/g}$, while chromium, vanadium, and zinc occur between 65 and 143 $\mu\text{g/g}$. Except for lower levels of most metals in Station 1E sediments (Figure 4.1 1), no major trends are obvious in this part of the Study Area. Figure 4.13 presents the concentrations of mud fraction metals in sediments from four stations in the central and western Study Area. The highest concentrations of all metals, except cadmium, were found at Station 7D in Harrison Bay.



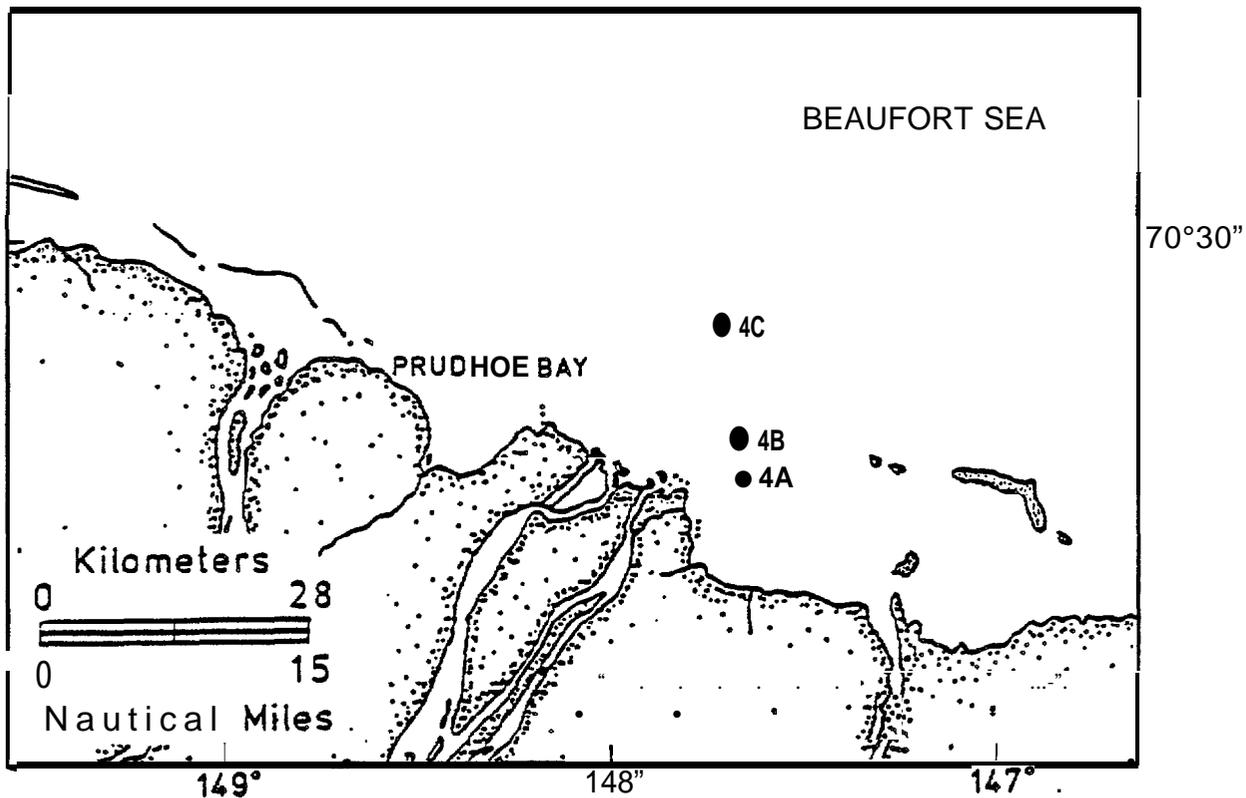
	2E		2F	
	BULK	MUD	BULK	MUD
METALS (ug/g)				
Ba	532 ± 14	549 ± 8	248 ± 11	365 ± 31
Cr	80 ± 3	79 ± 2	37 ± 1	71 ± 6
v	135 ± 3	132 ± 0	62 ± 2	88 ± 3
Pb	18.6 ± 3.4	16.0 ± 1.0	8.1 ± 1.6	10.9 ± 1.0
Cu	30.1 ± 1.7	29.8 ± 0.3	10.2 ± 1.0	20.5 ± 5.2
Zn	116 ± 4	111 ± 2	57 ± 1	76 ± 4
Cd	0.31 ± 0.03	0.29 ± 0.06	0.22 ± 0.00	0.27 ± 0.03

FIGURE 4.1. SUMMARY OF METAL CONCENTRATIONS IN BULK AND MUD FRACTIONS OF SEDIMENTS FROM WEST CAMDEN BAY.



	3A		3B	
	BULK	MUD	BULK	MUD
<u>METALS (µg/g)</u>				
Ba	345 ± 13	453 ± 5	316 ± 26	387 ± 8
Cr	47 ± 2	68 ± 2	57 ± 4	67 ± 2
V	78 ± 4	108 ± 4	101 ± 2	105 ± 4
Pb	10.3 ± 0.7	14.5 ± 3.1	10.5 ± 0.2	11.3 ± 0.2
Cu	16.2 ± 1.8	22.6 ± 2.0	19.8 ± 1.9	19.1 ± 0.4
Zn	64 ± 2	87 ± 4	76 ± 4	80 ± 2
Cd	0.16 ± 0.01	0.15 ± 0.01	0.17 ± 0.02	0.16 ± 0.00

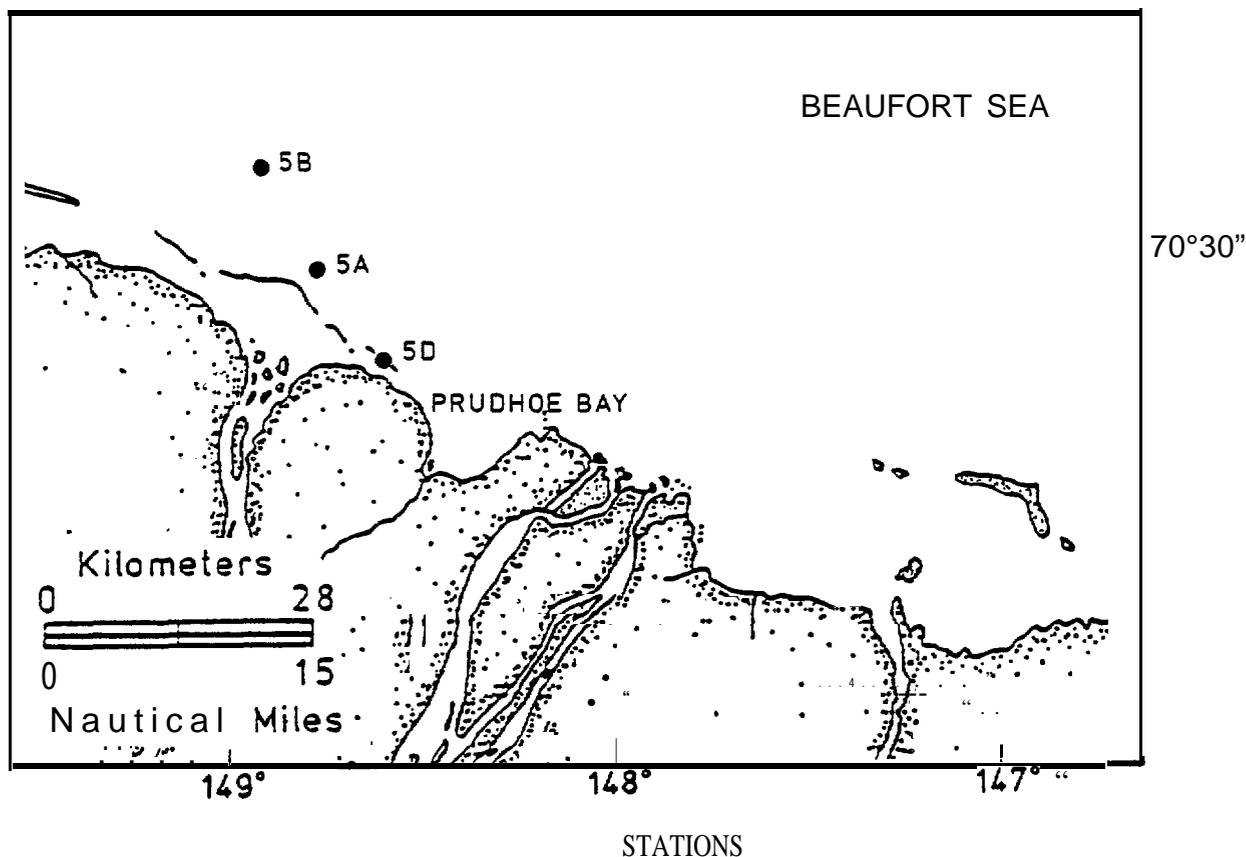
FIGURE 4.2. SUMMARY OF METAL CONCENTRATIONS IN BULK AND MUD FRACTIONS OF SEDIMENTS FROM MIKELSON BAY.



STATIONS

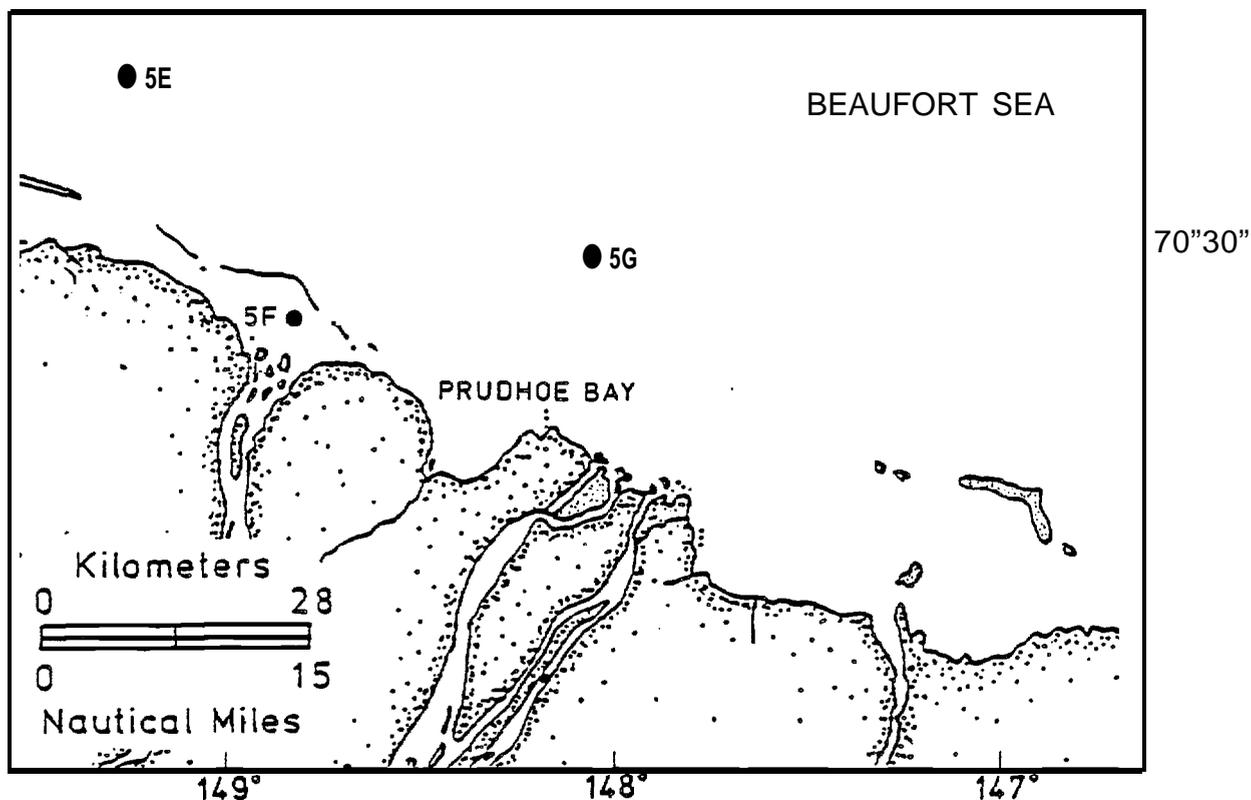
METALS ($\mu\text{g/g}$)	4A		4B		4C	
	BULK	MUD	BULK	MUD	BULK	MUD
Ba	410 \pm 69	511 \pm 35	205 \pm 7	418 \pm 7	266 \pm 18	516 \pm 8
Cr	39 \pm 12	78 \pm 3	29 \pm 3	58 \pm 5	36 \pm 6	78 \pm 4
V	66 \pm 13	129 \pm 4	44 \pm 3	98 \pm 3	63 \pm 6	123 \pm 2
Pb	9.4 \pm 2.3	14.5 \pm 0.2	5.8 \pm 1.2	10.6 \pm 0.4	10.0 \pm 1.0	17.3 \pm 1.8
Cu	14.7 \pm 3.6	27.3 \pm 0.9	8.7 \pm 0.6	19.3 \pm 1.2	11.0 \pm 0.7	23.7 \pm 0.9
Zn	55 \pm 9	104 \pm 2	43 \pm 3	83 : 11	45 \pm 6	94 \pm 4
Cd	0.10 \pm 0.03	0.24 \pm 0.02	0.15 \pm 0.01	0.20 \pm 0.01	0.08 \pm 0.01	0.18 \pm 0.06

FIGURE 4.3. SUMMARY OF METAL CONCENTRATIONS IN BULK AND MUD FRACTION OF SEDIMENTS FROM FOGGY ISLAND BAY AREA.



METALS (ug/g)	5A		5B		5D	
	BULK	MUD	BULK	MUD	BULK	MUD
Ba	314 ± 56	395 ± 87	535 ± 35	579 ± 27	331 ± 25	395 ± 7
Cr	48 ± 3	64 ± 0	87 ± 0	82 ± 0	49 ± 0	62 ± 5
v	73 ± 7	100 ± 5	150 ± 0	141 ± 7	79 ± 3	88 ± 6
Pb	8.4 ± 0.6	11.3 ± 0.7	18.0 ± 0.4	16.5 ± 0.6	7.2 ± 0.5	8.2 ± 0.7
Cu	17.3 ± 3.0	18.9 ± 0.6	31.3 ± 0.5	27.8 ± 0.3	18.0 ± 1.4	17.3 ± 1.1
Zn	60 ± 4	81 ± 4	116 ± 2	104 ± 3	78 ± 5	82 ± 3
Cd	0.21 ± 0.02	0.20 ± 0.03	0.14 ± 0.02	0.13 ± 0.01	0.29 ± 0.00	0.29 ± 0.01

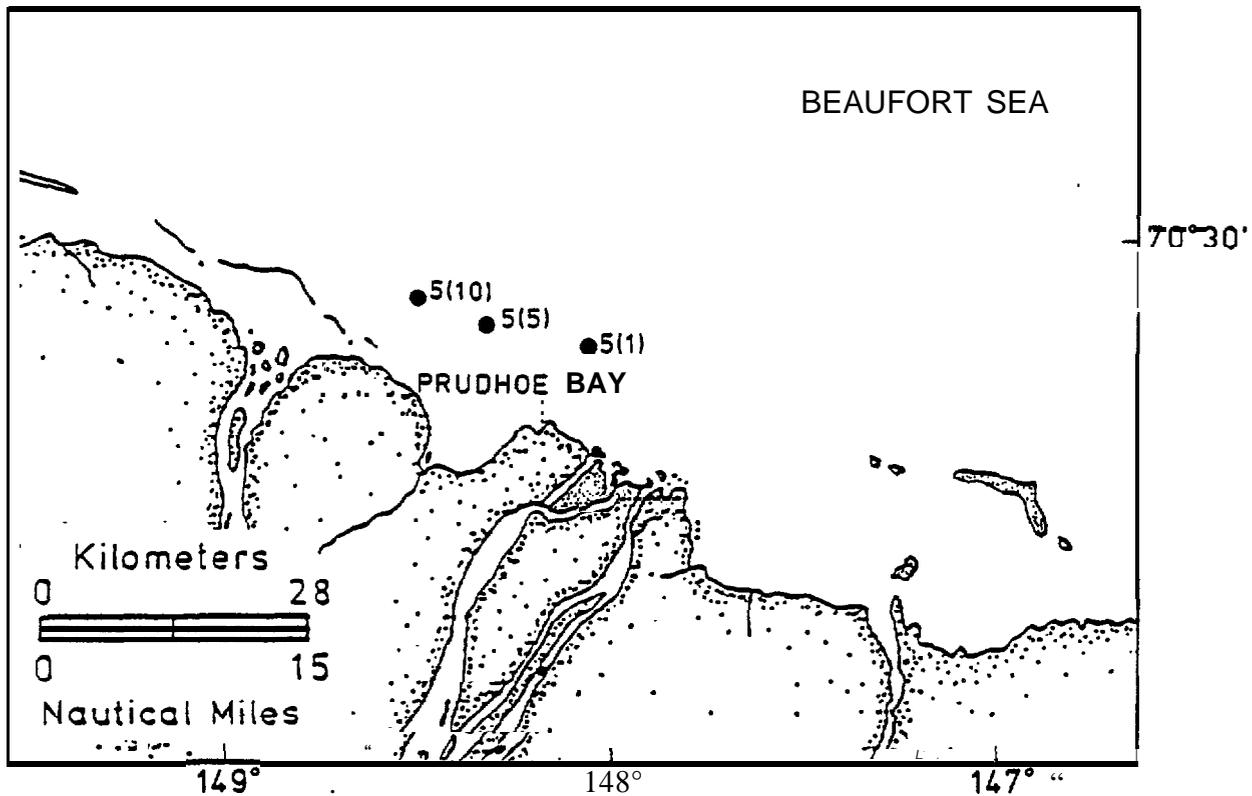
FIGURE 4.4. SUMMARY OF METAL CONCENTRATIONS IN BULK AND MUD FRACTION OF SEDIMENTS FROM PRUDHOE BAY - GWYDYR BAY AREA.



STATIONS

METALS (ug/g)	5E		5F		5G	
	BULK	MUD	BULK	MUD	BULK	MUD
Ba	570 ± 17	565 ± 8	280 ± 11	329 ± 11	259 ± 23	485 ± 73
Cr	83 ± 3	79 ± 3	36 ± 4	56 ± 0	36 ± 2	79 ± 7
v	146 ± 4	145 ± 6	55 ± 4	79 ± 2	62 ± 7	112 ± 4
Pb	17.1 ± 0.9	15.9 ± 0.6	6.7 ± 0.2	6.3 ± 0.8	7.4 ± 1.6	13.8 ± 0.8
Cu	28.4 ± 3.5	29.1 ± 1.8	10.0 ± 1.2	12.3 ± 0.4	11.2 ± 0.9	19.0 ± 0.6
Zn	108 ± 7	102 ± 1	52 ± 4	74 ± 4	47 ± 3	84 ± 7
Cd	0.20 ± 0.00	0.21 ± 0.02	0.15 ± 0.03	0.26 ± 0.04	0.10 ± 0.00	0.15 ± 0.01

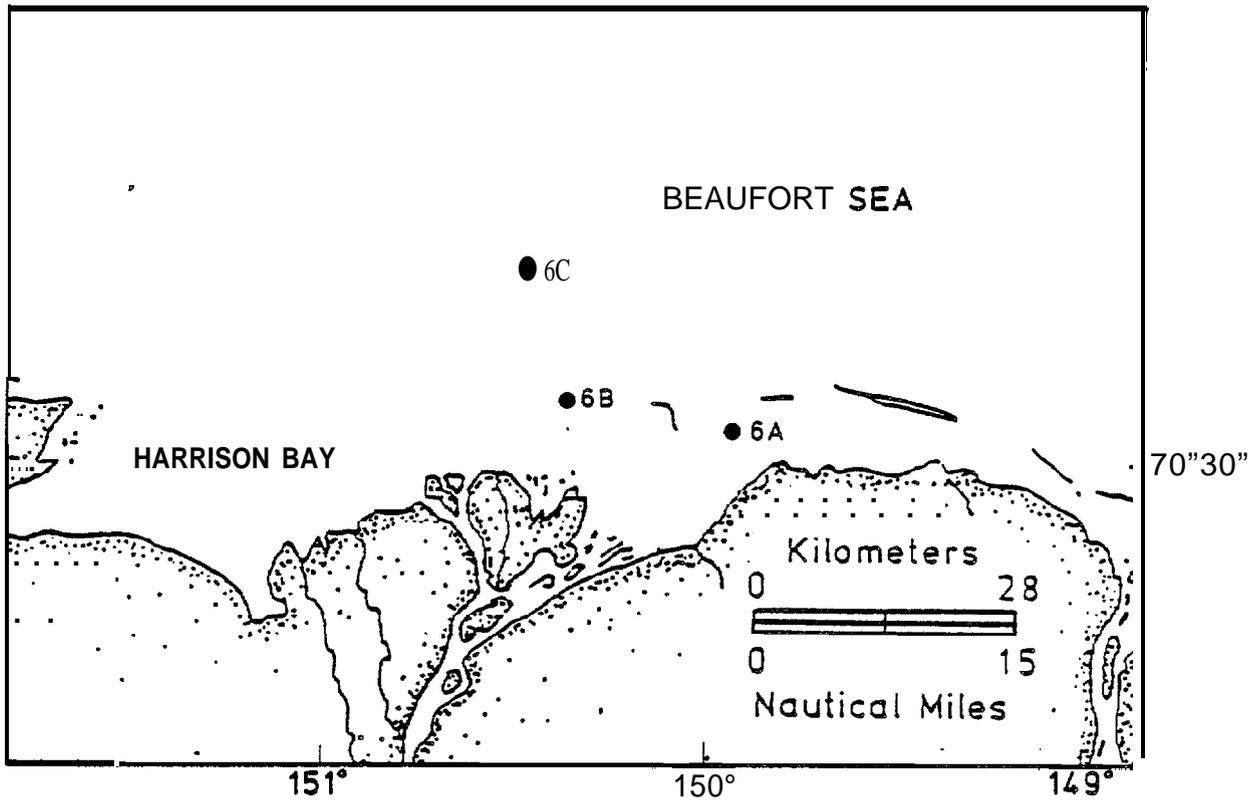
FIGURE 4.5. SUMMARY OF METAL CONCENTRATIONS IN BULK AND MUD FRACTION OF SEDIMENTS FROM PRUDHOE BAY - GWYDYR BAY AREA.



STATIONS

METALS (µg/g)	5(1)		5(5)		5(10)	
	BULK	MUD	BULK	MUD	BULK	MUD
Ba	185 ± 9	273 ± 134	227 ± 36	398 ± 137	262 ± 6	449 ± 3
Cr	21 ± 3	69 ± 3	35 ± 8	70 ± 4	40 ± 2	62 ± 3
V	40 ± 5	78 ± 20	59 ± 9	107 ± 7	62 ± 2	98 ± 5
Pb	8.1 ± 0.5	11.5 ± 2.0	7.0 ± 0.9	11.1 ± 0.7	5.9 ± 0.6	9.9 ± 0.4
Cu	6.3 ± 0.6	16.5 ± 4.7	11.7 ± 2.2	21.2 ± 0.6	11.6 ± 0.3	19.1 ± 1.6
Zn	39 ± 7	66 ± 13	54 ± 13	86 ± 5	58 ± 1	79 ± 1
Cd	0.09 ± 0.02	0.84 ± 1.14	0.15 ± 0.06	0.21 ± 0.01	0.23 ± 0.01	0.21 ± 0.02

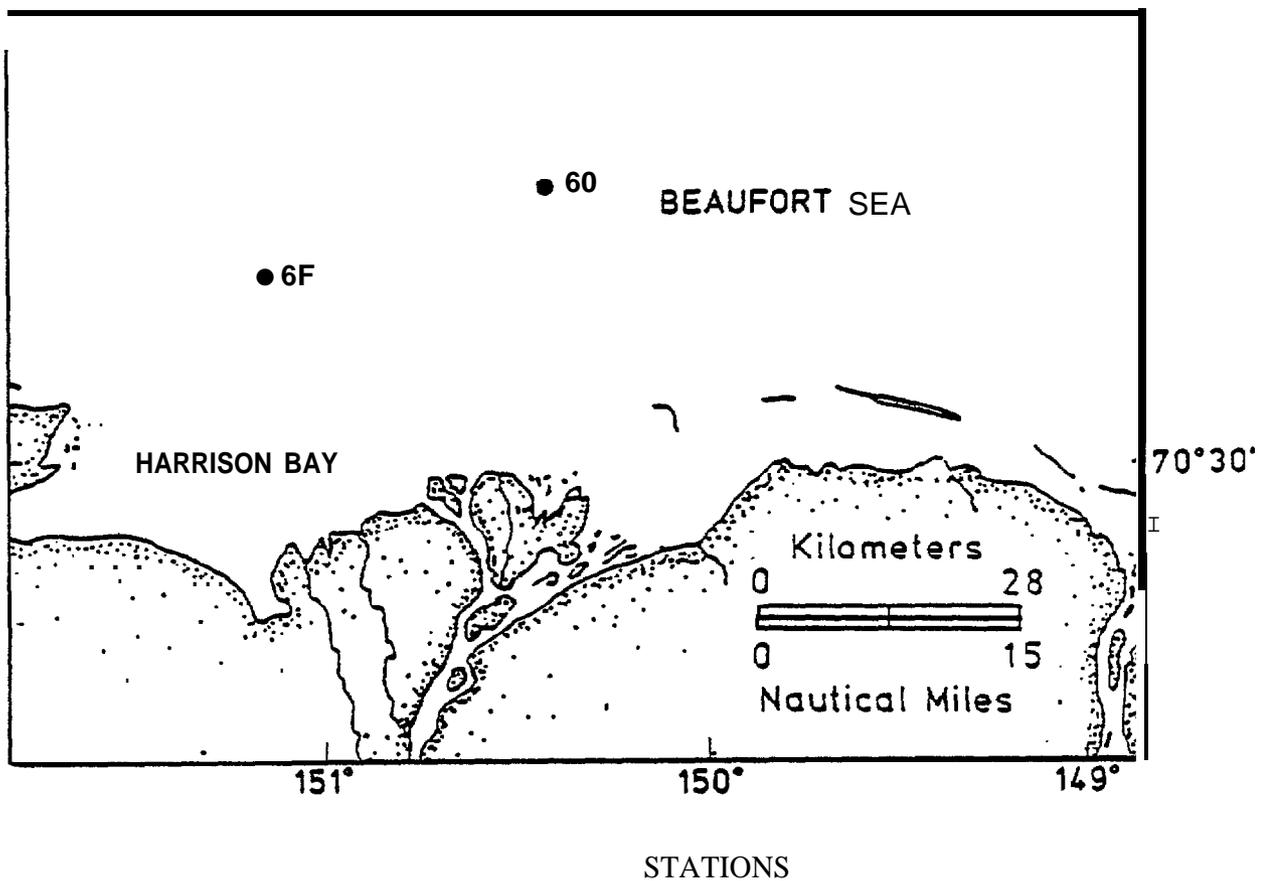
FIGURE 4.6. SUMMARY OF METAL CONCENTRATIONS IN BULK AND MUD FRACTION OF SEDIMENTS FROM ENDICOTT FIELD TRANSECT STATIONS.



STATIONS

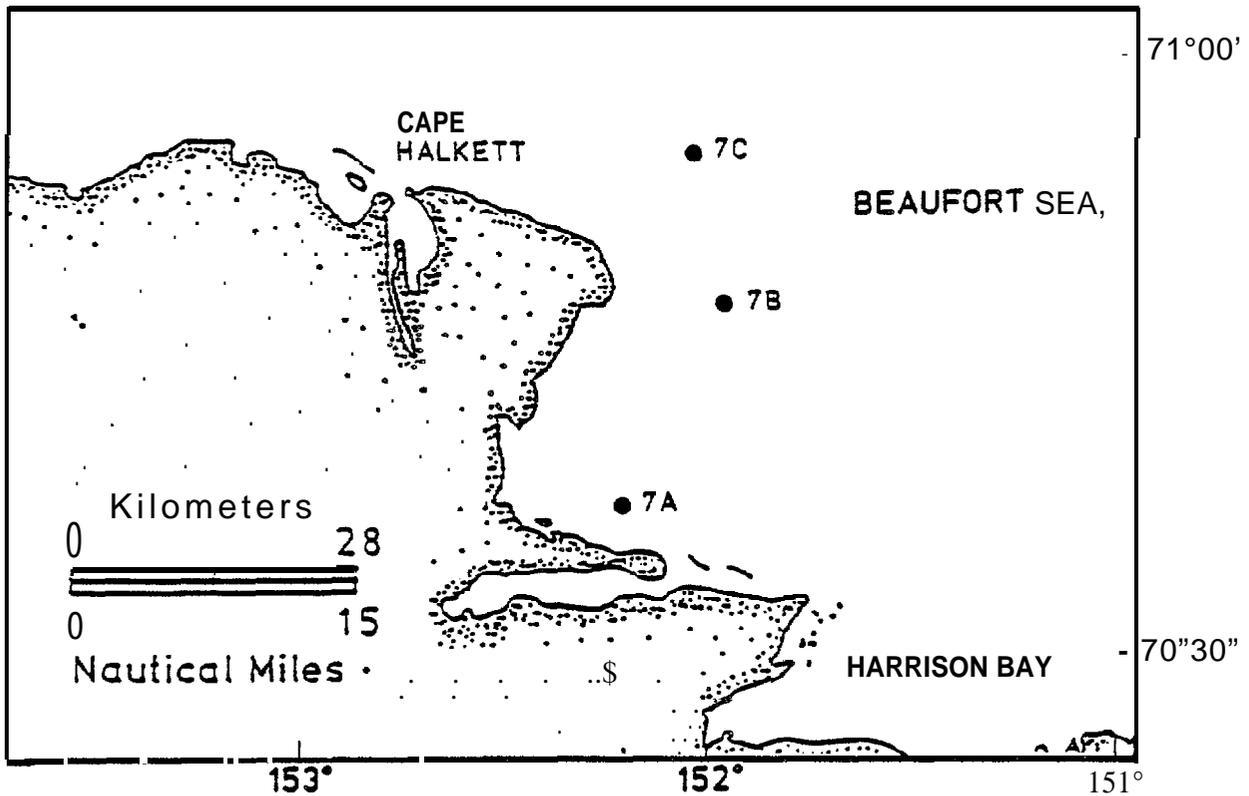
	6A		6B		6C	
	BULK	MUD	BULK	MUD	BULK	MUD
METALS (µg/g)						
Ba	376 ± 26	355 ± 36	502 ± 75	523 ± 43	425 ± 46	436 ± 193
Cr	60 ± 9	76 ± 5	68 ± 5	90 ± 2	67 ± 11	39 ± 9
v	100 ± 11	114 ± 4	108 ± 2	143 ± 6	117 ± 18	151 ± 11
Pb	14.9 ± 2.0	14.4 ± 0.7	12.4 ± 0.6	15.4 ± 1.2	13.1 ± 1.7	16.5 ± 0.6
Cu	22.3 ± 2.4	23.2 ± 2.3	23.3 ± 1.6	31.9 ± 0.4	22.1 ± 4.0	30.6 ± 3.5
Zn	89 ± 10	100 ± 3	87 ± 7	117 ± 2	88 ± 14	113 ± 6
Cd	0.19 ± 0.04	0.17 ± 0.02	0.20 ± 0.01	0.24 ± 0.02	0.13 ± 0.04	0.17 ± 0.02

FIGURE 4.7. SUMMARY OF METAL CONCENTRATIONS IN BULK AND MUD FRACTION OF SEDIMENT FROM STATIONS IN EAST HARRISON BAY.



<u>METALS (µg/g)</u>	613		6F	
	BULK	MUD	BULK	MUD
Ba	288 ± 79	366 ± 73	292 ± 36	568 ± 14
Cr	36 ± 6	80 ± 4	47 ± 3	89 ± 2
V	72 ± 25	134 ± 14	79 ± 3	128 ± 5
Pb	9.4 ± 2.7	14.1 ± 2.0	9.5 ± 3.2	14.2 ± 0.8
Cu	10.8 ± 5.7	24.6 ± 3.6	13.1 ± 0.5	21.6 ± 0.4
Zn	56 ± 16	96 ± 10	60 ± 3	92 ± 0
Cd	0.07 ± 0.03	0.15 ± 0.1	0.12 ± 0.01	0.15 ± 0.01

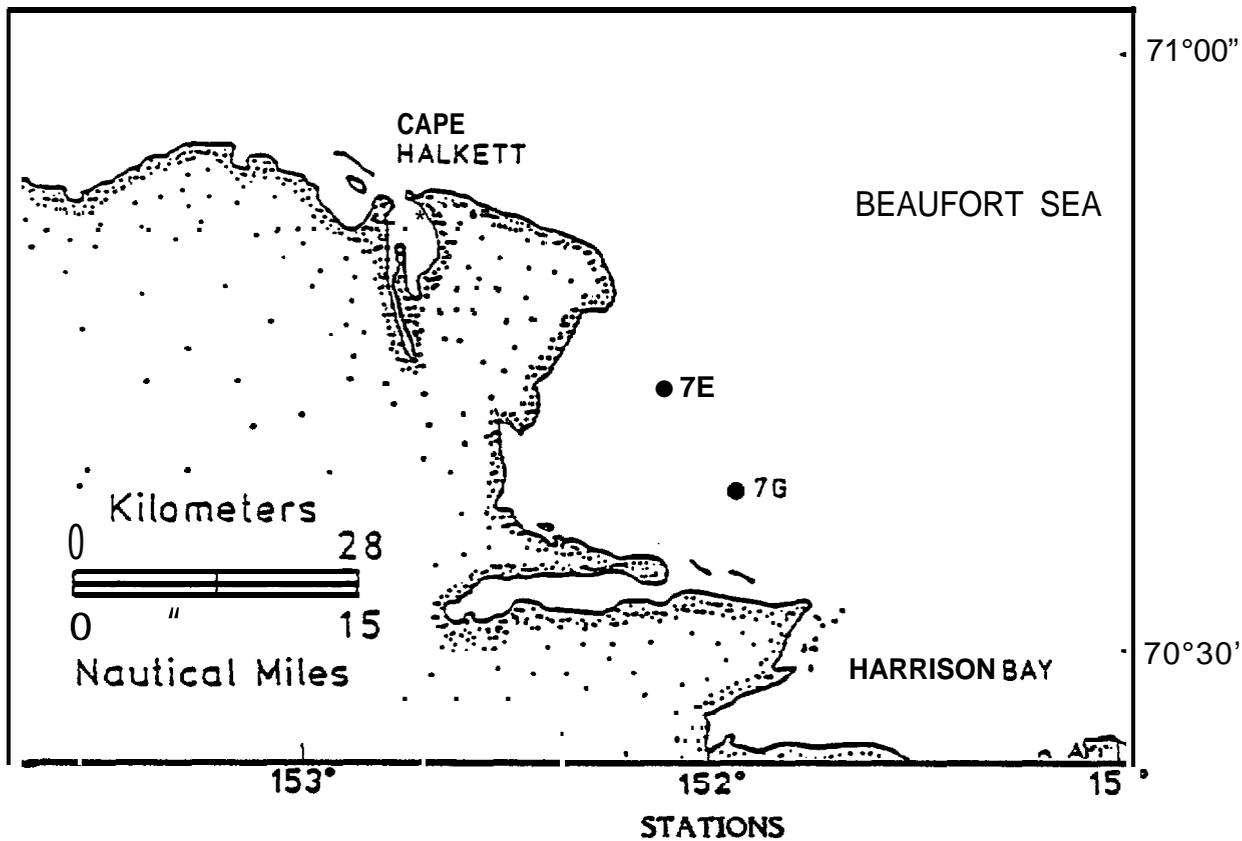
FIGURE 4.8. SUMMARY OF METAL CONCENTRATIONS IN BULK AND MUD FRACTION OF SEDIMENTS FROM STATIONS 613 AND 6F IN EAST HARRISON BAY.



STATIONS

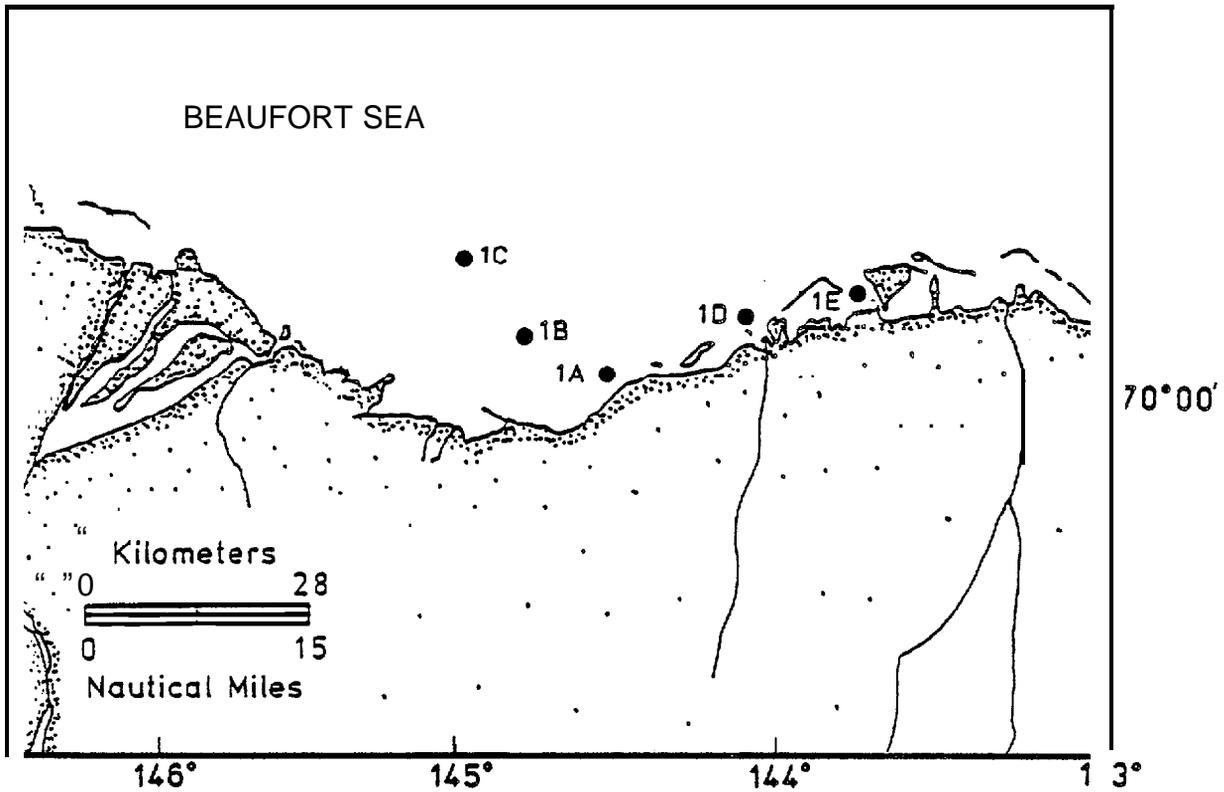
	7A		7B		7C	
	BULK	MUD	BULK	MUD	BULK	MUD
<u>METALS (µg/g)</u>						
Ba	710 ± 28	770 ± 55	484 ± 36	667 ± 222	501 ± 30	489 ± 57
Cr	71 ± 3	90 ± 5	53 ± 4	113 ± 28	85 ± 11	74 ± 14
V	88 ± 3	97 ± 2	58 ± 3	92 ± 8	142 ± 21	126 ± 21
Pb	13.8 ± 1.9	11.6 ± 1.4	10.0 ± 0.6	12.1 ± 0.8	20.5 ± 4.2	16.8 ± 2.6
Cu	14.8 ± 2.8	14.3 ± 1.7	7.2 ± 1.3	14.8 ± 1.3	29.4 ± 5.6	24.9 ± 6.8
Zn	86 ± 2	86 ± 1	50 ± 3	71 ± 9	108 ± 14	95 ± 13
Cd	0.11 ± 0.02	0.11 ± 0.03	0.06 ± 0.03	0.13 ± 0.04	0.16 ± 0.03	0.31 ± 0.28

FIGURE 4.9. SUMMARY OF METAL CONCENTRATIONS IN BULK AND MUD FRACTION OF SEDIMENTS IN WEST HARRISON BAY.



	7E		7G	
	BULK	MUD	BULK	MUD
<u>METALS (µg/g)</u>				
Ba	563 ± 65	785 ± 60	636 ± 26	725 ± 34
Cr	62 ± 5	94 ± 14	45 ± 3	90 ± 8
v	92 ± 4	109 ± 5	68 ± 1	84 ± 4
Pb	13.9 ± 1.1	14.4 ± 1.5	13.9 ± 0.04	10.5 ± 1.9
Cu	18.7 ± 0.8	19.0 ± 2.6	11.8 ± 0.3	14.1 ± 1.5
Zn	76 ± 2	87 ± 2	63 ± 3	72 ± 5
Cd	0.13 ± 0.03	0.14 ± 0.04	0.11 ± 0.04	0.15 ± 0.06

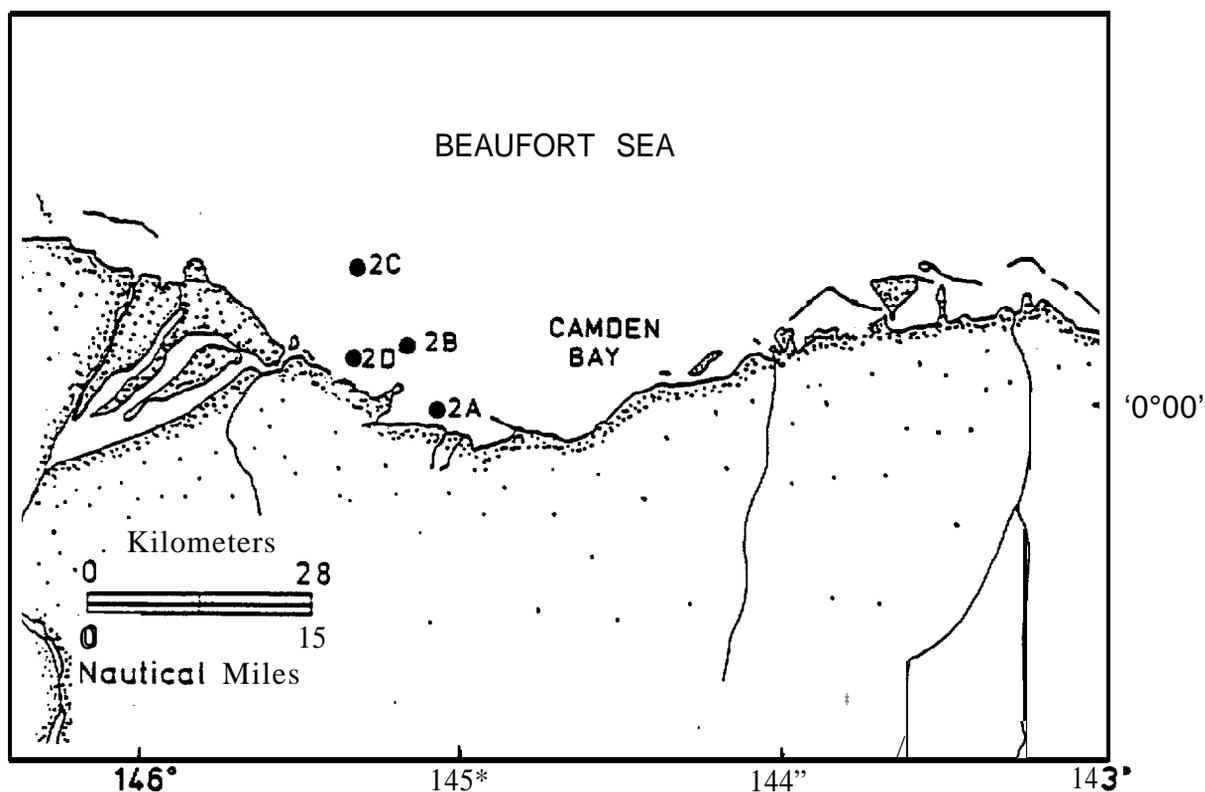
FIGURE 4.10. SUMMARY OF METAL CONCENTRATIONS IN BULK AND MUD FRACTION OF SEDIMENTS FROM STATIONS 7E AND 7G IN WEST HARRISON BAY.



STATIONS

	1A	1B	1C	1D	1E
<u>METALS (µg/g)</u>					
Ba	415 ± 19	580 ± 51	500 ± 40	444 ± 113	485 ± 29
Cr	81 ± 1	79 ± 4	84 ± 8	70 ± 11	65 ± 1
v	123 ± 3	127 ± 8	143 ± 5	105 ± 17	92 ± 1
Pb	19.9 ± 3.0	16.3 ± 1.2	12.4 ± 0.7	15.5 ± 3.3	21.6 ± 1.4
Cu	30.1 ± 1.9	27.9 ± 1.1	25.8 ± 2.1	27.0 ± 7.0	25.3 ± 2.2
Zn	99 ± 5	95 ± 5	106 ± 12	85 ± 15	84 ± 2
Cd	0.22 ± 0.04	0.14 ± 0.03	0.16 ± 0.01	0.20 ± 0.04	0.14 ± 0.01

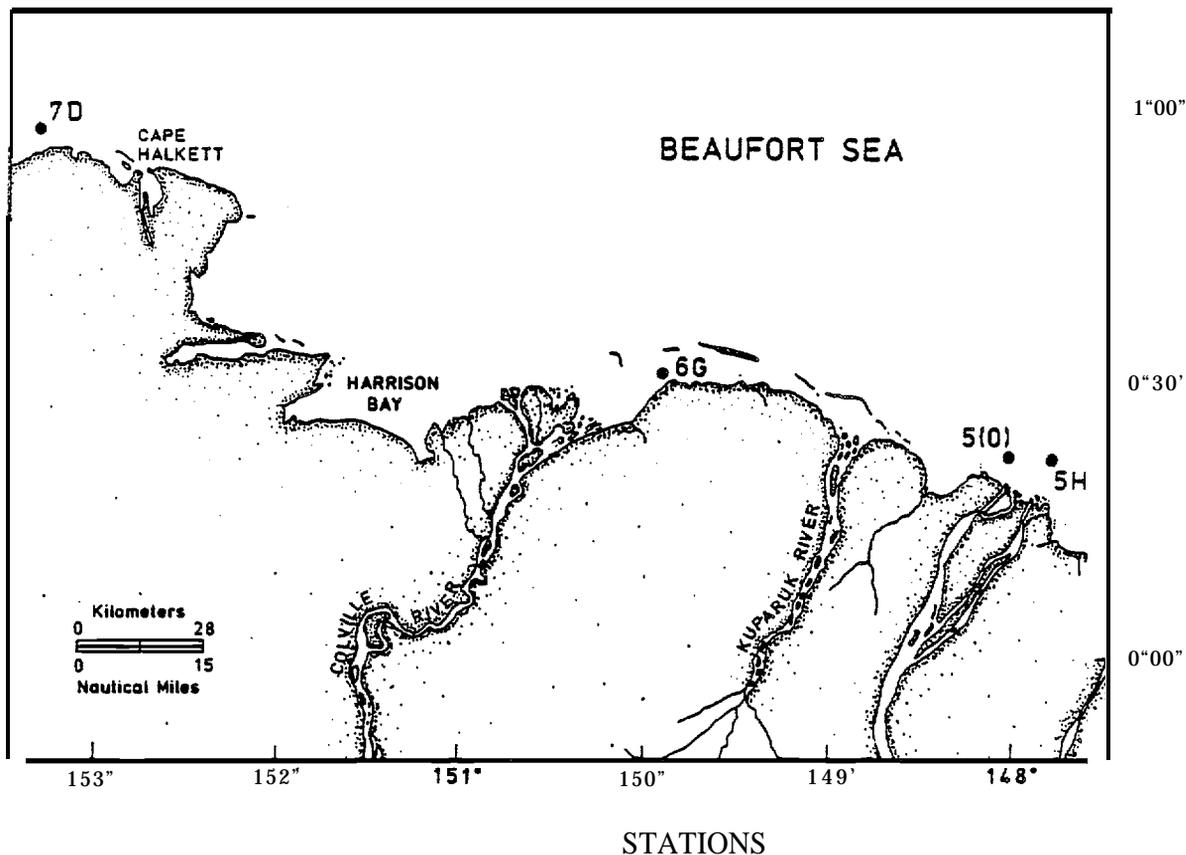
FIGURE 4.11. SUMMARY OF METAL CONCENTRATIONS IN MUD FRACTION OF SEDIMENTS FROM EAST CAMDEN BAY AREA.



STATIONS

	2A	2B	2C	2D
<u>METALS ($\mu\text{g/g}$)</u>				
Ba	486 \pm 46	358 \pm 124	525 \pm 108	335 \pm 80
Cr	72 \pm 9	79 \pm 6	82 \pm 3	80 \pm 10
v	115 \pm 24	127 \pm 13	142 \pm 5	127 \pm 9
Pb	16.5 \pm 3.0	15.9 \pm 1.5	19.2 \pm 1.5	19.3 \pm 4.6
Cu	28.5 \pm 9.5	28.9 \pm 5.4	27.0 \pm 1.6	31.0 \pm 7.0
Zn	95 \pm 15	97 \pm 10	105 \pm 5	109 \pm 15
Cd	0.20 \pm 0.03	0.20 \pm 0.05	0.16 \pm 0.02	0.29 \pm 0.08

FIGURE 4.12. SUMMARY OF METAL CONCENTRATIONS IN MUD FRACTION OF SEDIMENTS FROM WEST CAMDEN BAY AREA.



	<u>5H</u>	<u>5(o)</u>	<u>6G</u>	<u>713</u>
<u>METALS (µg/g)</u>				
Ba	457 ± 12	215 ± 61	419 ± 22	486 ± 47
Cr	63 ± 3	51 ± 3	63 ± 2	83 ± 4
V	109 ± 2	95 ± 3	102 ± 8	126 ± 7
Pb	11*5 ± 0.5	9.4 ± 0.8	11.6 ± 1.8	14.3 ± 0.7
Cu	20.9 ± 0.2	19.0 ± 3.0	19.3 ± 1.3	28.4 ± 2.9
Zn	88 ± 1	78 ± 6	96 ± 9	103 ± 5
Cd	0.22 ± 0.01	0.22 ± 0.03	0.24 ± 0.01	0.16 ± 0.03

FIGURE 4.13. SUMMARY OF METAL CONCENTRATIONS IN MUD FRACTION OF SEDIMENTS FROM THE CENTRAL AND WESTERN STUDY AREA.

Figures 4.14 through 4.22 compare the mean concentrations of metals at the 26 stations sampled in Year-1 and Year-2. Overall, there is relatively good agreement between Year-1 and Year-2 for all metals at most stations. Several exceptions are, however, notable. Stations 2E (Figure 4.14) and 5B (Figure 4.16) Year-2 concentrations are significantly higher than Year-1 levels. It is also noteworthy that, at these stations, a ten-fold increase in the mud content was found between Year-1 and Year-2. Similarly, higher Year-2 metal concentrations are observed at Station 5E (Figure 4.17), but without a proportionate increase in the sediment mud content. Year-2 metal concentrations and mud content at Station 6F (Figure 4.20) are uniformly lower than observed in Year-1.

4.1.2 Metals in River and Peat Samples

A comparison of metals in the bulk and mud fraction of river sediments is shown in Table 4.1. With one exception (Station 6H copper), the concentrations of all metals are higher in the mud fraction than bulk in sediment. The concentrations of all river sediment metals are generally within the same range reported for marine sediments.

Table 4.2 summarizes the concentrations of bulk and mud fraction metals in shoreline peat samples collected throughout the Study Area. The ranges in concentrations are similar to the ranges reported for marine and river sediments. Overall, mud fraction concentrations are generally higher than the corresponding bulk values for most metals. Exceptions are found at Stations 3D and 7H, where the bulk sediments have higher barium concentrations. An unusually low level of barium occurs in the bulk peat from Station 63.

4.1.3 Metals in Tissues

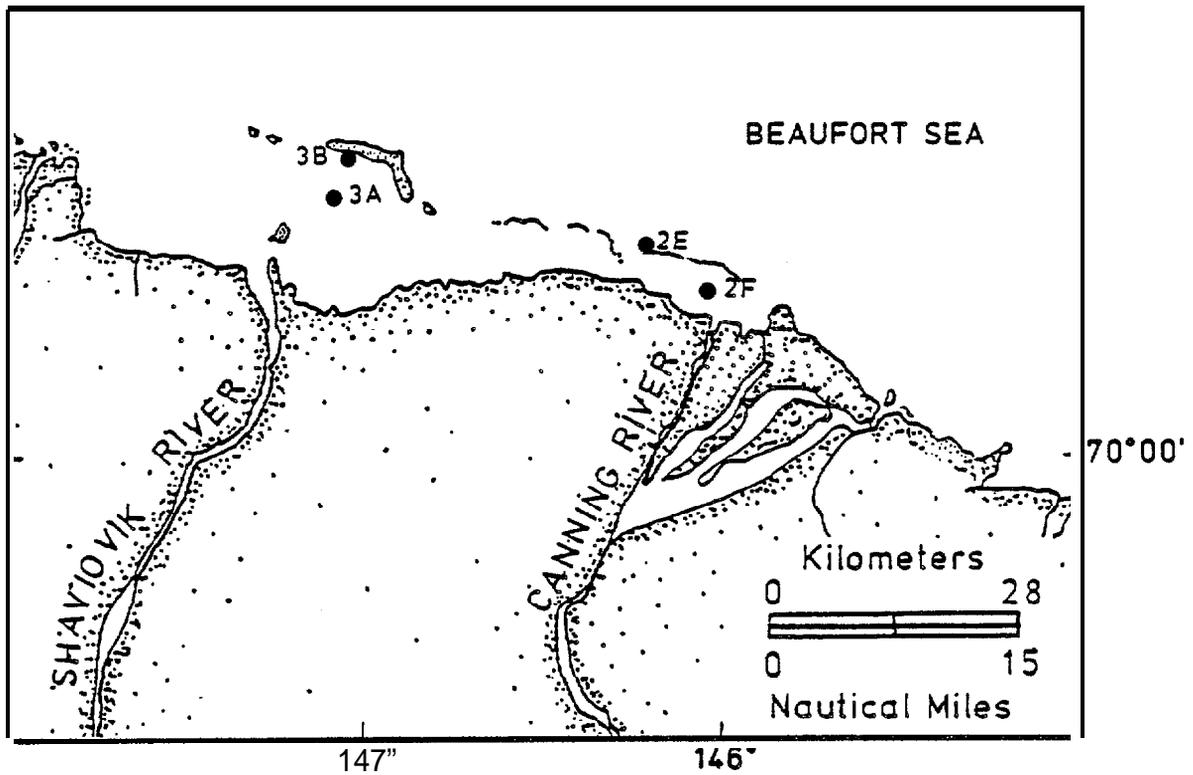
Metals were determined in tissue samples collected from 11 stations. Tables 4.3 and 4.4 present the mean concentrations of metals in all tissue samples collected throughout the Study Area. The range in cadmium concentrations encompasses two orders of magnitude (0.25 -25.5 $\mu\text{g/g}$), while vanadium, lead, and copper values generally range within one order of magnitude. In comparison to sediment metal concentrations in the Study Area, tissue levels of cadmium and copper are about an order of magnitude higher. Barium, chromium, vanadium, and lead, however, are approximately one order of magnitude lower in tissues than in sediments. Zinc levels in both sediments and tissues are generally within the same order of magnitude.

Highest levels of all metals except copper occur in bivalve tissues (e.g., Portlandia, Astarte, and Macoma at Stations 1A, 1 A+1 B, and 6D, respectively). The highest copper concentration (176 $\mu\text{g/g}$) was associated with amphipods from Station 3A. The metal concentrations in Anonyx and Astarte tissues collected throughout the Study Area are summarized in Tables 4.5 and 4.6, respectively. As shown in Table 4.6, lowest concentrations of all metals (except cadmium) in Astarte tissue are associated with Station 5H, while the highest concentrations occur in Station 6D tissues. No trends in the geographical distribution of metals in Anonyx tissue are obvious.

At three stations, bivalves of the same species were collected in both Year-1 and Year-2. Table 4.7 compares the mean Year-1 and Year-2 concentrations of metals in these species. Generally, there is no significant difference in the levels of metals detected in both years. Slightly higher concentrations of vanadium are found in the three Year-2 samples.

4.2 Hydrocarbon Data

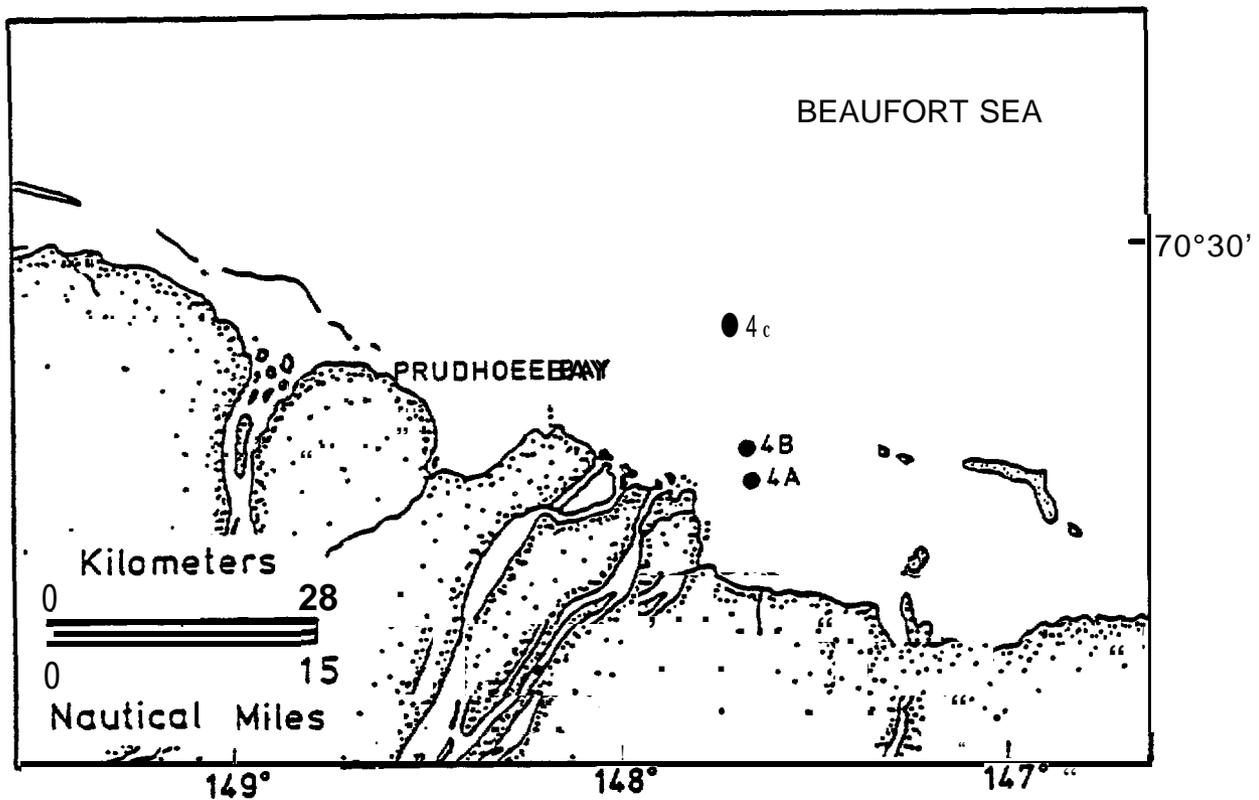
GC-FID analyses for saturated hydrocarbons and GC/MS analyses for aromatics were performed on marine and bulk river sediments, peat samples, and animal tissues. In Year-2, the UV/F scans were eliminated from the sediment analyses and conducted only on tissue samples.



STATIONS

	2E		2F		3A		3B	
	YEAR-1	YEAR-2	YEAR-1	YEAR-2	YEAR-1	YEAR-2	YEAR-1	YEAR-2
METALS (µg/g)								
Ba	193: 10	532 ± 14	261 ± 7	248 ± 11	346 ± 20	345 ± 13	382 ± 15	316 ± 26
Cr	37 ± 3	80 ± 3	46 ± 1	37 ± 0	52 ± 5	47 ± 2	58 ± 2	57 ± 4
v	50 ± 4	135 ± 3	73 ± 3	62 ± 2	88 ± 4	78 ± 4	97 ± 3	101 ± 2
Pb	4.7 ± 0.3	18.6 ± 3.4	6.7 ± 0.3	8.1 ± 1.6	6.1 ± 0.8	10.3 ± 0.7	6.1 ± 2.5	10.5 ± 0.2
Cu	15.3 ± 3.8	30.1 ± 1.7	16.4 ± 1.1	10.2: 1.0	23.0: 1.1	16.2 ± 1.8	29.0 ± 5.5	19.8 ± 1.9
Zn	33 ± 2	116 ± 4	50 ± 9	57 ± 0	58 ± 3	64 ± 2	64 ± 5	76 ± 4
Cd	0.13:0.03	0.31 ± 0.03	0.21 ± 0.02	0.23 ± 0.00	0.16 ± 0.03	0.16 ± 0.01	0.15 ± 0.02	0.17:0.02
% Mud	7.7 ± 1.5	77.6 ± 14.2	15.1 ± 3.6	13.3 :2.4	41.9: 1.8	46.1 ± 0.6	65.2 ± 3.7	74.3 ± 2.9

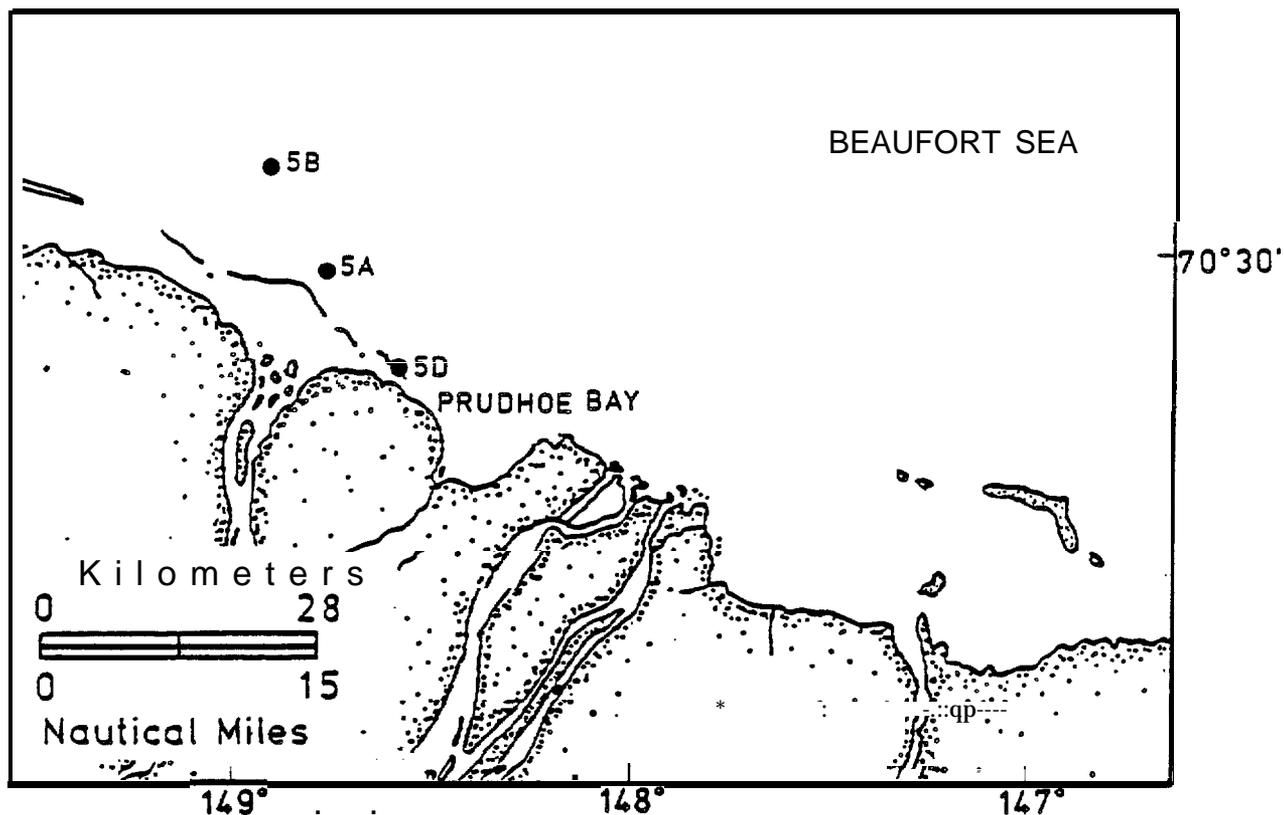
FIGURE 4.14. SUMMARY OF YEAR-1 AND YEAR-2 METAL CONCENTRATIONS AND PERCENT MUD IN WEST CAMDEN BAY - MIKELSONBAY AREA SEDIMENTS.



STATIONS

	4A		4B		4C	
	YEAR-1	YEAR-2	YEAR-1	YEAR-2	YEAR-1	YEAR-2
<u>METALS (µg/g)</u>						
Ba	367 ± 7	410 ± 69	194 ± 11	205 ± 7	254 ± 44	266 ± 18
Cr	52 ± 2	39 ± 12	36 ± 4	29 ± 3	39 ± 6	36 ± 6
V	93 ± 4	66 ± 13	48 ± 6	44 ± 3	57 ± 14	63 ± 6
Pb	8.1 ± 0.8	9.4 ± 2.3	6.1 ± 0.9	5.8 ± 1.2	4.1 ± 1.0	10.0 ± 1.0
Cu	25.0 ± 3.2	14.7 ± 3.6	18.5 ± 3.8	8.7 ± 0.6	18.7 ± 6.2	11.0 ± 0.7
Zn	64 ± 2	55 ± 8	35 ± 5	43 ± 3	33 ± 9	45 ± 6
Cd	0.14 ± 0.03	0.10 ± 0.03	0.18 ± 0.04	0.15 ± 0.01	0.06 ± 0.02	0.08 ± 0.01
<hr/>						
% Mud	33.6 ± 18.8	33.9 ± 10.6	7.6 ± 3.9	6.1 ± 1.7	17.0 ± 17.9	6.3 ± 3.2

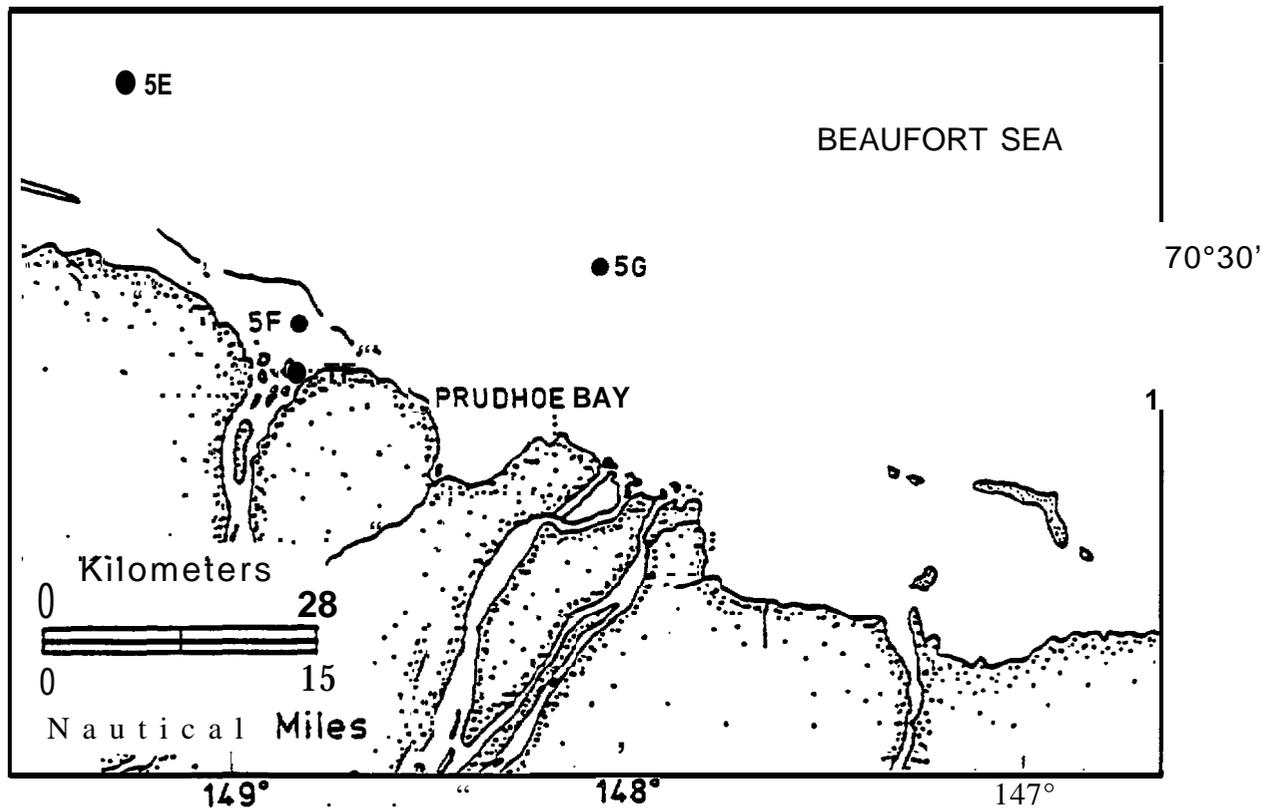
FIGURE 4.15. SUMMARY OF YEAR-1 AND YEAR-2 METAL CONCENTRATIONS AND PERCENT MUD IN FOGGY ISLAND AREA SEDIMENTS.



STATIONS

	5A		5B		5D	
	YEAR-1	YEAR-2	YEAR-1	YEAR-2	YEAR-1	YEAR-2
<u>METALS (µg/g)</u>						
Ba	554 ± 74	314 ± 56	192 ± 6	535 ± 35	373 ± 10	331 ± 25
Cr	55 ± 3	48 ± 3	17 ± 1	87 ± 0	55 ± 2	49 ± 0
v	95 ± 4	73 ± 7	33 ± 2	150 ± 0	92 ± 2	79 ± 3
Pb	9.1 ± 0.9	8.4 ± 0.6	3.9 ± 0.9	18.0 ± 0.4	9.9 ± 0.5	7.2 ± 0.5
Cu	20.6 ± 1.0	17.3 ± 3.0	4.9 ± 0.7	31.3 ± 0.5	24.9 ± 1.2	18.0 ± 1.4
Zn	66 ± 5	60 ± 4	19 ± 3	116 ± 2	76 ± 2	78 ± 5
Cd	0.22 ± 0.03	0.21 ± 0.02	0.04 ± 0	0.14 ± 0.02	0.22 ± 0.01	0.29 ± 0.00
% Mud	72.4 ± 10.0	43.0 ± 7.3	3.1 ± 0.9	77.0 ± 19.3	72.5 ± 2.1	61.6 ± 5.6

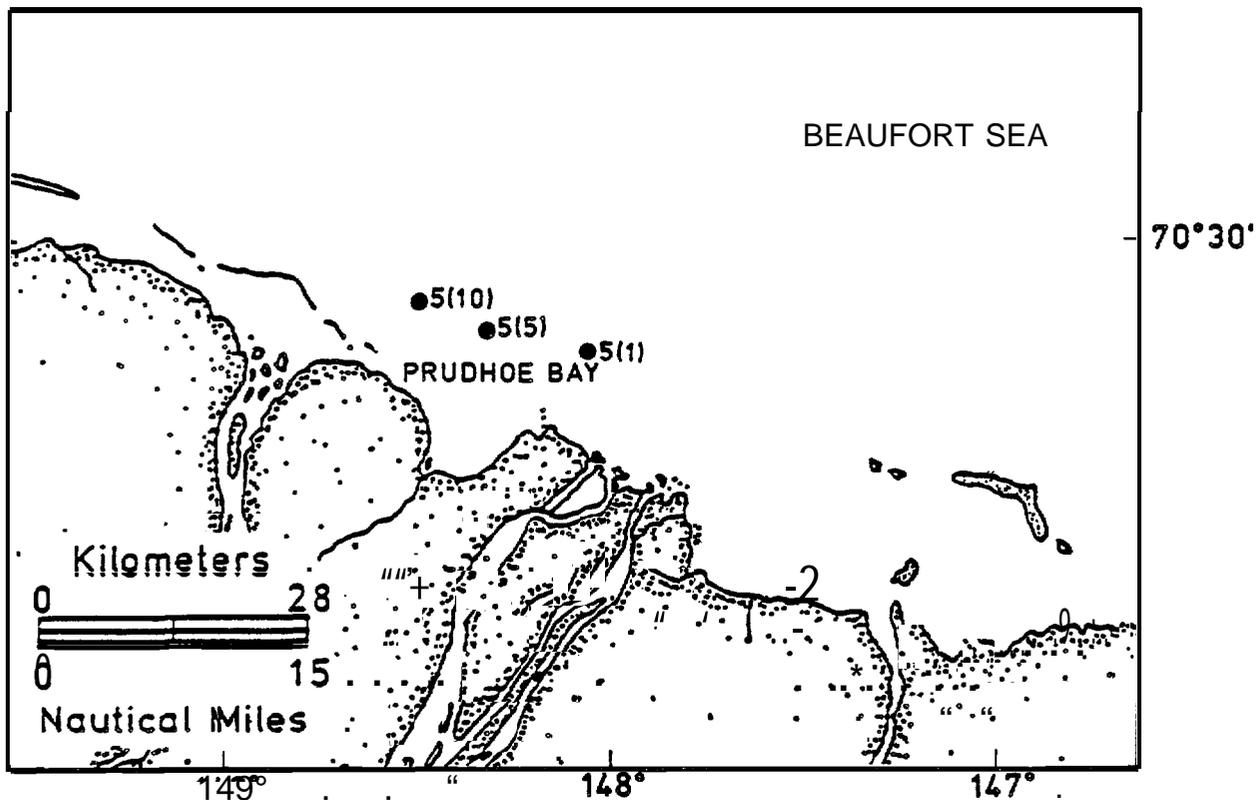
FIGURE 4.16. SUMMARY OF YEAR-I AND YEAR-2 METAL CONCENTRATIONS AND PERCENT MUD IN PRUDHOE BAY - GWYDYR BAY AREA SEDIMENTS.



STATIONS

	SE		SF		5G	
	YEAR-1	YEAR-2	YEAR-1	YEAR-2	YEAR-1	YEAR-2
<u>METALS (µg/g)</u>						
Ba	347 ± 131	570 ± 17	330 ± 12	250 ± 11	286 ± 33	259 ± 23
Cr	36 ± 26	83 ± 3	49 ± 3	36 ± 4	34 ± 4	36 ± 2
v	69 ± 50	146 ± 4	79 ± 2	55 ± 4	62 ± 9	62 ± 7
Pb	6.5 ± 4.9	17.1 ± 0.9	7.8 ± 0.8	6.7 ± 0.2	6.1 ± 0.9	7.4 ± 1.6
Cu	12.8 ± 9.2	28.4 ± 3.5	18.1 ± 0.6	10 ± 1	10.6 ± 1.4	11.2 ± 0.9
Zn	42 ± 34	108 ± 7	64 ± 3	52 ± 4	39 ± 5	47 ± 3
Cd	0.08 ± 0.04	0.20 ± 0.00	0.21 ± 0.03	0.15 ± 0.03	0.11 ± 0.04	0.10 ± 0.00
<hr/>						
% Mud	29.3 ± 36.2	40.3 ± 15.2	61.4 ± 5.2	42.2 ± 2.5	15.3 ± 3.2	11.2 ± 2.5

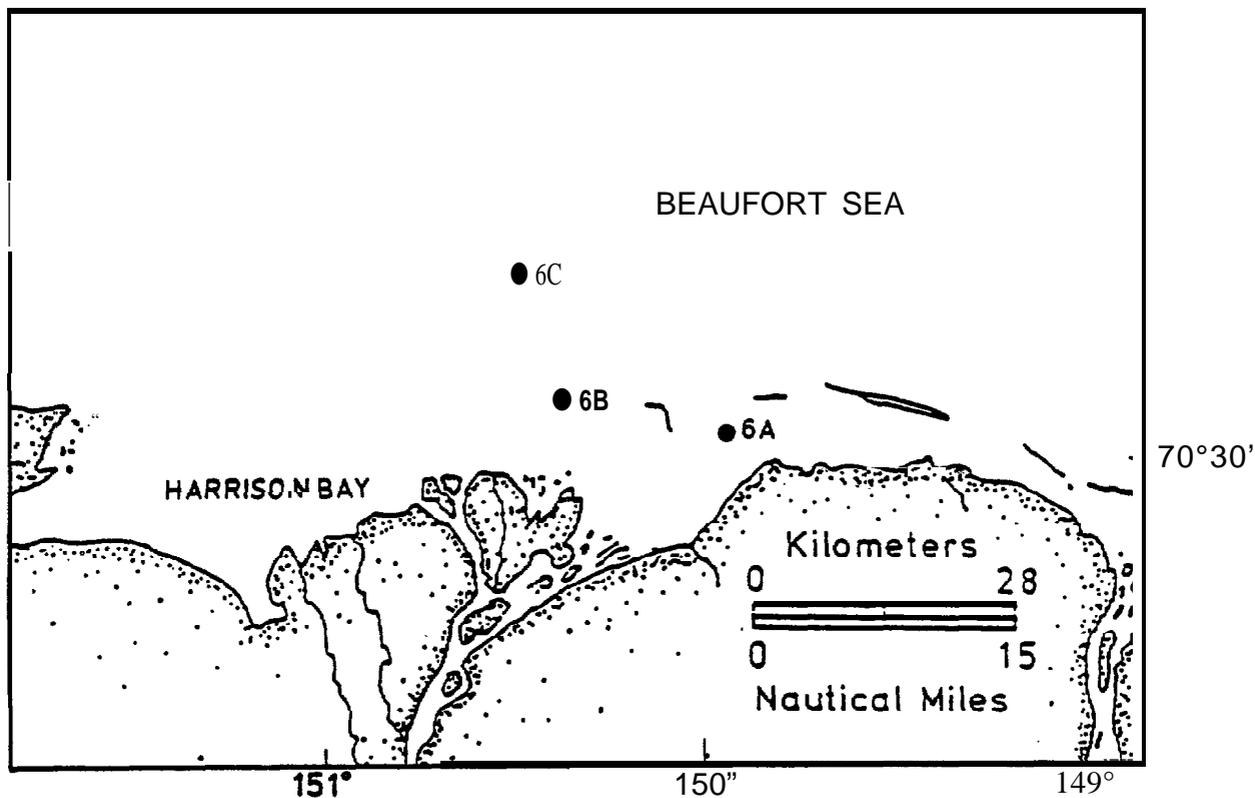
FIGURE 4.17. SUMMARY OF YEAR-1 AND YEAR-2 METAL CONCENTRATIONS AND PERCENT MUD IN PRUDHOE BAY - GWYDYR BAY AREA SEDIMENTS.



STATIONS

	5(1)		5(5)		5(10)	
	YEAR-1	YEAR-2	YEAR-1	YEAR-2	YEAR-1	YEAR-2
<u>METALS (µg/g)</u>						
Ba	236 ± 16	185 ± 10	294 ± 10	227 ± 36	256 ± 6	262 ± 6
Cr	23 ± 6	21 ± 3	40 ± 3	35 ± 8	39 ± 2	40 ± 2
v	45 ± 4	40 ± 5	69 ± 3	59 ± 9	66 ± 3	62 ± 2
Pb	4.9 ± 0.3	8.1 ± 0.5	6.2 ± 0.3	7.0 ± 0.9	5.5 ± 0.5	5.9 ± 0.6
Cu	9.7 ± 2.9	6.3 ± 0.6	15.7 ± 1.2	11.7 ± 2.2	17.3 ± 2.3	11.6 ± 0.3
Zn	35 ± 2	39 ± 6	50 ± 3	54 ± 18	48 ± 1	58 ± 2
Cd	0.15 ± 0.03	0.09 ± 0.02	0.22 ± 0.03	0.15 ± 0.06	0.25 ± 0.03	0.23 ± 0.00
<hr/>						
% Mud	9.6 ± 2.8	1.0 ± 0.2	35.9 ± 2.7	23.5 ± 12.6	34.9 ± 14.7	20.5 ± 3.2

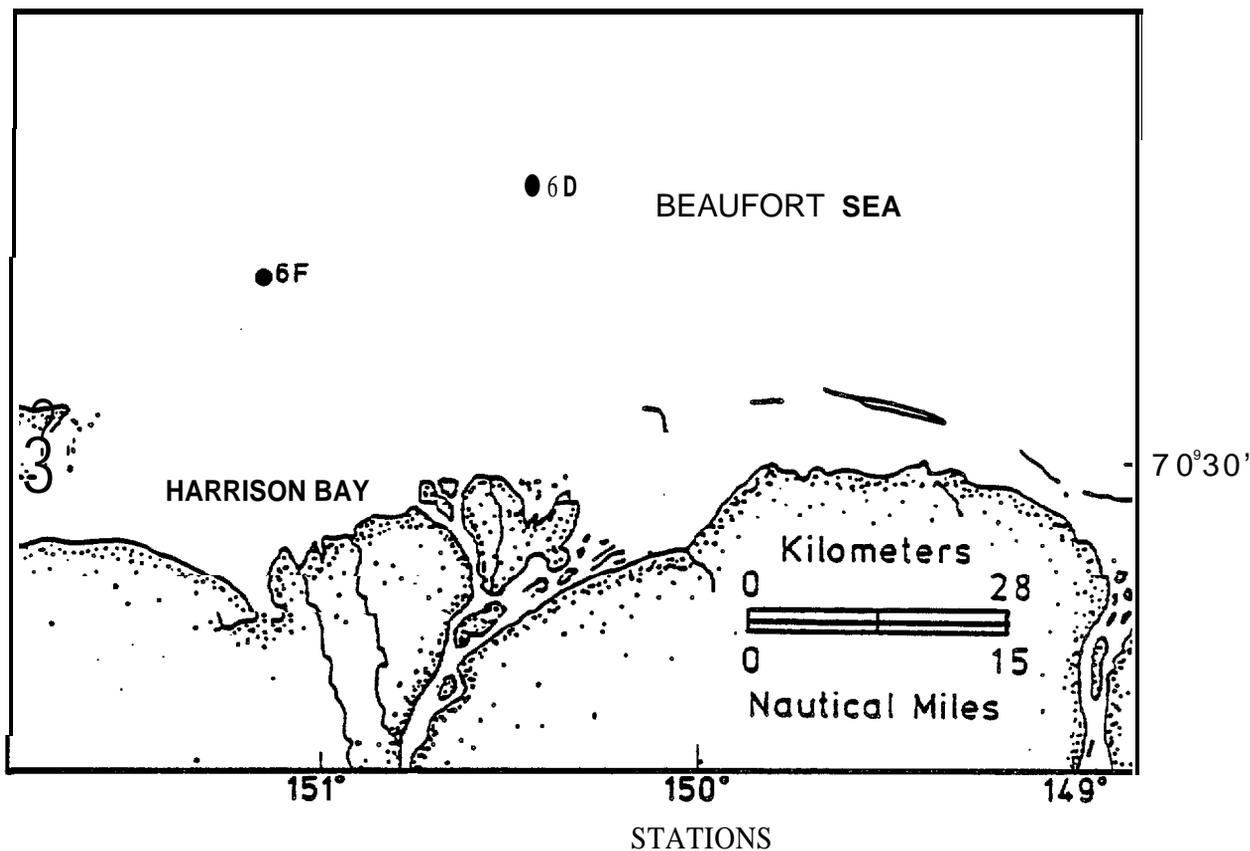
FIGURE 4.18. SUMMARY OF YEAR-1 AND YEAR-2 METAL CONCENTRATIONS AND PERCENT MUD IN EN DICOTT FIELD TRANSECT STATION SEDIMENTS.



STATIONS

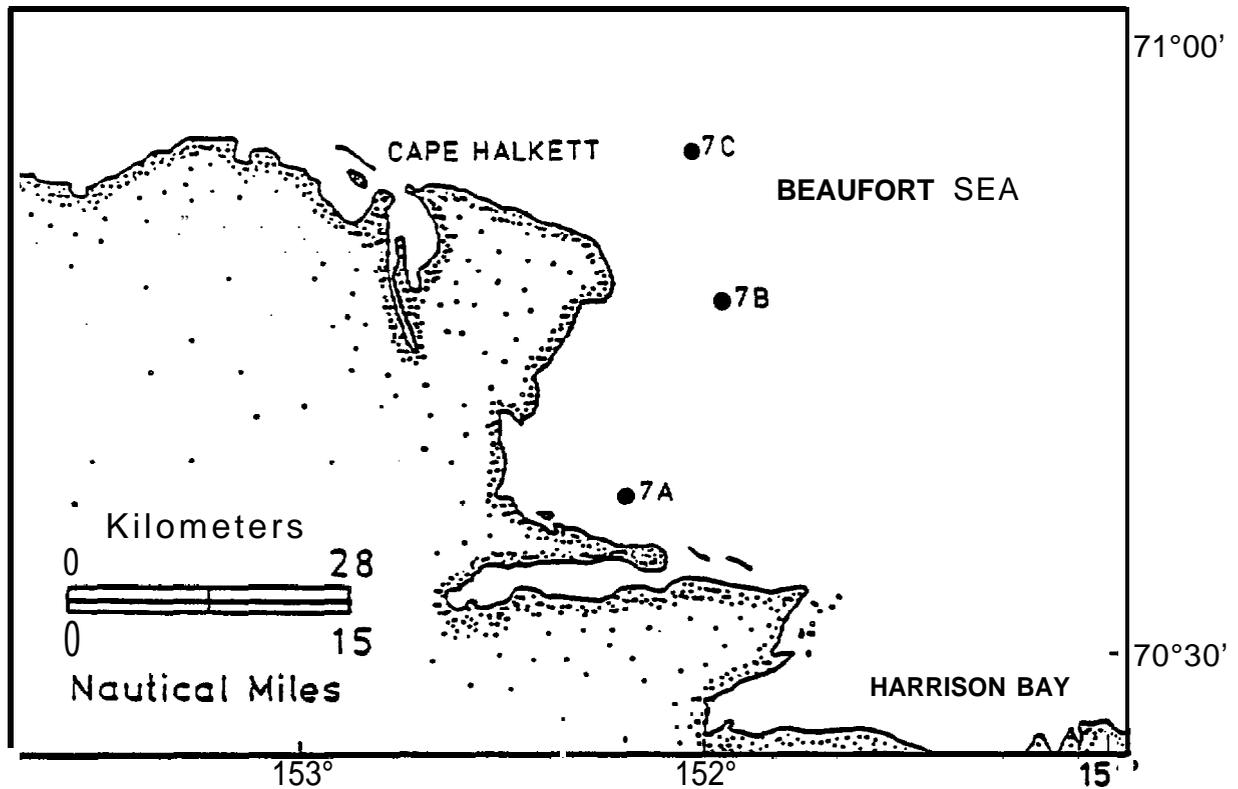
METALS ($\mu\text{g/g}$)	6A		6B		6C	
	YEAR-1	YEAR-2	YEAR-1	YEAR-2	YEAR-1	YEAR-2
8a	385 \pm 11	376 \pm 26	745 \pm 42	502 \pm 75	398 \pm 122	425 \pm 46
Cr	60 \pm 4	60 \pm 9	91 \pm 4	68 \pm 5	65 \pm 18	67 \pm 11
v	91 \pm 4	100 \pm 11	153 \pm 10	108 \pm 2	98 \pm 29	117 \pm 13
Pb	8.7 \pm 1.3	14.9 \pm 2.0	16.7 \pm 1.0	12.4 \pm 0.6	8.4 \pm 2.1	13.1 \pm 1.7
Cu	23.5 \pm 1.4	22.3 \pm 2.4	36.7 \pm 1.6	23.3 \pm 1.6	20.7 \pm 4.2	22.1 \pm 4.0
Zn	70 \pm 2	89 \pm 10	112 \pm 7	87 \pm 7	68 \pm 19	88 \pm 14
Cd	0.13 \pm 0.03	0.19 \pm 0.04	0.29 \pm 0.03	0.20 \pm 0.02	0.06 \pm 0.01	0.13 \pm 0.04
% Mud	66.3 \pm 3.4	81.8 \pm 6.0	88.6 \pm 8.4	83.7 \pm 6.3	30.8 \pm 15.4	49.4 \pm 19.7

FIGURE 4.19. SUMMARY OF YEAR-1 AND YEAR-2 METAL CONCENTRATIONS AND PERCENT MUD IN SEDIMENTS IN EAST HARRISON BAY.



	6D		6F	
	YEAR-1	YEAR-2	YEAR-1	YEAR-2
<u>METALS (µg/g)</u>				
Ba	282 ± 22	288 ± 78	407 ± 141	292 ± 36
Cr	38 ± 4	36 ± 16	63 ± 11	47 ± 3
v	66 ± 7	72 ± 25	109 ± 26	79 ± 3
Pb	7.1 ± 0.6	9.4 ± 2.7	12.5 ± 4.1	9.5 ± 0.3
Cu	9.1 ± 1.7	10.8 ± 5.8	21.2 ± 5.6	13.1 ± 0.6
Zn	45 ± 3	56 ± 16	63 ± 16	60 ± 3
Cd	0.07 ± 0.02	0.07 ± 0.03	0.13 ± 0.04	0.12 ± 0.00
<hr/>				
% Mud	10.8 ± 5.7	17.6 ± 25.0	64.8 ± 26.4	36.3 ± 6.6

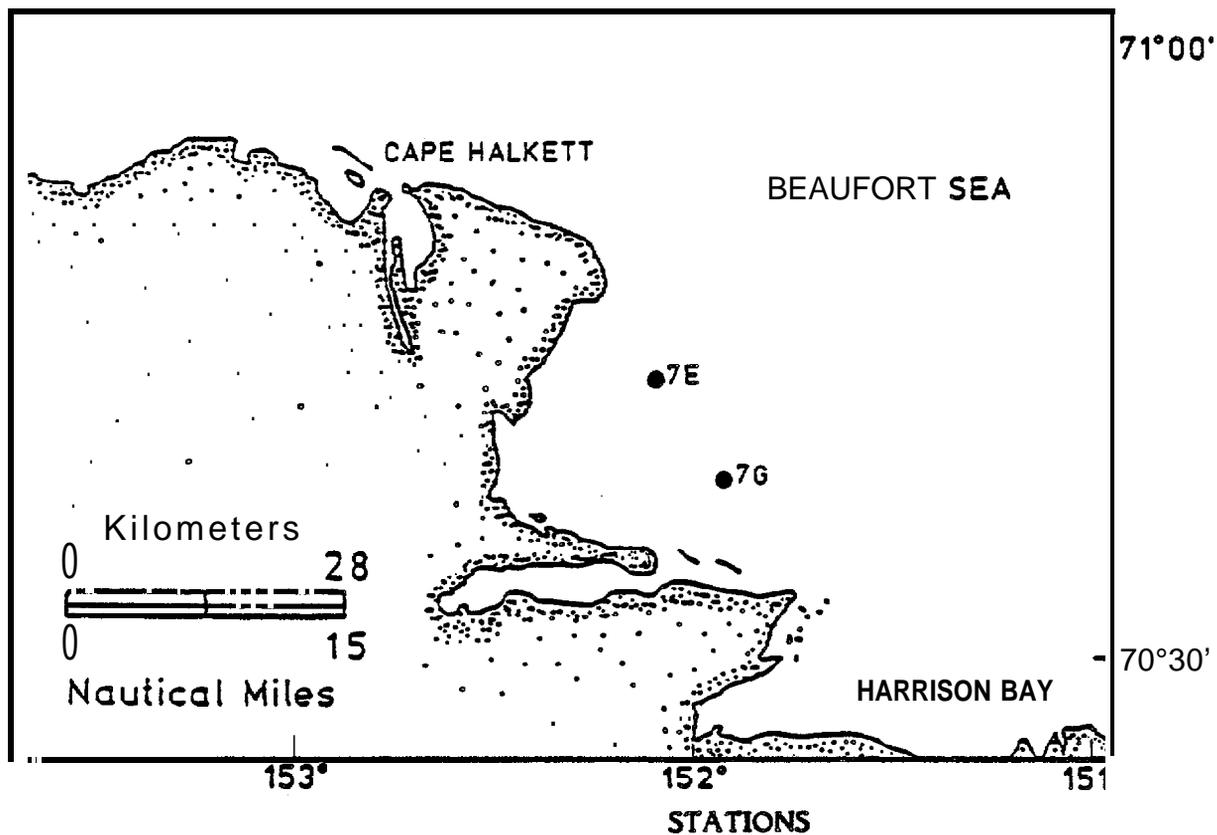
FIGURE 4.20. SUMMARY OF YEAR-1 AND YEAR-2 METAL CONCENTRATIONS AND PERCENT MUD IN SEDIMENTS FROM STATIONS 6D AND 6F IN EAST HARRISON BAY.



STATIONS

	7A		7B		7C	
	YEAR-1	YEAR-2	YEAR-1	YEAR-2	YEAR-1	YEAR-2
METALS (µg/g)						
Ba	698 ± 29	710 ± 28	456 ± 16	484 ± 36	568 ± 9	501 ± 30
Cr	63 ± 4	71 ± 4	49 ± 2	53 ± 4	77 ± 2	85 ± 11
V	87 ± 3	88 ± 3	68 ± 3	58 ± 3	145 ± 4	142 ± 42
Pb	8.5 ± 0.9	13.8 ± 1.9	6.6 ± 0.5	10.0 ± 0.6	14.7 ± 0.9	20.5 ± 4.2
Cu	13.8 ± 2.2	14.8 ± 2.8	9.7 ± 1.0	7.2 ± 1.3	27.0 ± 0.9	29.4 ± 5.6
Zn	75 ± 5	86 ± 2	51 ± 3	50 ± 3	97 ± 1	108 ± 14
Cd	0.10 ± 0.03	0.11 ± 0.02	0.06 ± 0.01	0.06 ± 0.03	0.13 ± 0.02	0.16 ± 0.03
% Mud						
	65.4 ± 5.6	67.4 ± 8.3	13.3 ± 4.5	7.6 ± 2.3	84.6 ± 1.8	88.8 ± 7.3

FIGURE 4.21. SUMMARY OF YEAR-1 AND YEAR-2 METAL CONCENTRATIONS AND PERCENT MUD IN SEDIMENTS IN WEST HARRISON BAY.



	7E		7G	
	YEAR-1	YEAR-2	YEAR-1	YEAR-2
<u>METALS (µg/g)</u>				
Ba	605 ± 13	563 ± 65	607 ± 39	636 ± 26
Cr	62 ± 5	62 ± 5	42 ± 7	45 ± 3
V	92 ± 4	92 ± 2	68 ± 10	68 ± 1
Pb	8.3 ± 0.4	13.9 ± 1.2	11.1 ± 0.6	13.9 ± 0.4
Cu	16.8 ± 1.3	18.7 ± 0.8	11.5 ± 6.6	11.8 ± 0.3
Zn	71 ± 2	76 ± 2	53 ± 2	63 ± 3
Cd	0.15 ± 0.03	0.13 ± 0.03	0.07 ± 0.02	0.11 ± 0.04
<hr/>				
% Mud	68.0 ± 3.6	63.8 ± 10.7	10.6 ± 1.0	27.9 ± 13.3

FIGURE 4.22. SUMMARY OF YEAR-1 AND YEAR-2 METAL CONCENTRATIONS AND PERCENT MUD IN SEDIMENTS FROM STATIONS 7E AND 7G IN WEST HARRISON BAY.

TABLE 4.1. SUMMARY OF METALS IN BULK AND MUD FRACTION OF RIVER SEDIMENT SAMPLES.

	STATIONS			
	5J Sagavanirktok River		6H Colville River	
	BULK	MUD	BULK	MUD
<u>METALS ($\mu\text{g/g}$)</u>				
Ba	102	191	612	953
Cr	41	56	46	101
V	59	84	62	117
Pb	6.2	7.1	8.7	13.1
Cu	15.0	19.4	40.9	24.0
Zn	62	91	60	106
Cd	0.29	0.40	0.15	0.27

TABLE 4.2. SUMMARY OF METAL CONCENTRATIONS IN BULK AND MUD FRACTION OF SHORELINE PEAT SAMPLES COLLECTED THROUGHOUT THE STUDY AREA.

	1F		2H		2G		3D		5K		6J		7H		7J	
	BULK	MUD	BULK	MUD	BULK	MUD	BULK	MUD	BULK	MUD	BULK	MUD	BULK	MUD	BULK	MUD
Ba	471	521	391	491	539	606	526	322	436	513	50	355	593	394	256	383
Cr	65	66	52	61	71	79	15	56	59	72	14	36	31	87	29	64
v	104	103	80	94	109	123	26	67	86	107	20	33	62	134	50	76
Pb	13.8	16.6	10.5	11.2	13.0	9.5	2.0	7.1	7.5	9.3	1.6	2.4	14.4	17.2	14.1	9.7
Cu	24.2	17.6	19.3	20.3	23.6	29.5	9.4	19.5	24.5	24.0	11.2	11.8	17.8	39.1	53.4	21.6
Zn	59	63	67	74	88	99	21	34	97	116	16	23	51	105	60	78
Cd	0.26	0.24	0.20	0.20	0.23	0.24	0.24	0.25	0.24	0.30	0.49	0.36	0.20	0.40	0.34	0.21

TABLE 4.3. SUMMARY OF METAL CONCENTRATIONS IN TISSUE SAMPLES COLLECTED FROM EASTERN STUDY AREA STATIONS.

	STATIONS						
	1A Portlandia ^a	1A+1B+1E Anonyx ^b	1A+1B Astartea	2F Anonyx	Anonyx	3A Astarte	4B Anonyx
<u>METALS</u> ($\mu\text{g/g}$ wet weight)							
Ba	98 \pm 3	39 \pm 3	20 \pm 1	36 \pm 1	22 \pm 1	18 \pm 10	22 \pm 2
Cr	12.52 \pm 0.57	3.39 \pm 0.30	2.54 \pm 0.12	2.05 \pm 0.35	1.13 \pm 0.42	3.03 \pm 1.12	0.39 \pm 0.08
V	22.7 \pm 0.6	4.2 \pm 0.4	2.4 \pm 0.2	1.0 \pm 0.2	0.6 \pm 0.2	5.0 \pm 2.0	<D.L. ^c
Pb	5.57 \pm 0.71	0.67 \pm 0.30	0.32 \pm 0.07	<D.L.	<D.L.	0.45 \pm 0.30	0.13 \pm 0
Cu	35 \pm 1	97 \pm 4	12 \pm 1	77 \pm 2	176 \pm 8	14 \pm 4	131 \pm 7
Zn	179 \pm 8	134 \pm 2	80 \pm 5	107 \pm 4	124 \pm 8	84 \pm 17	105 \pm 3
Cd	7.62 \pm 0.61	0.99 \pm 0.47	25.50 \pm 1.08	0.58 \pm 0.15	1.53 \pm 0	8.16 \pm 1.94	1.03 \pm 0.12

^aBivalve

^bAmphipod

^cDetection Limit

TABLE 4.4. SUMMARY OF METAL CONCENTRATIONS IN TISSUE SAMPLES COLLECTED FROM WESTERN STUDY AREA STATIONS.

	5F Cyrtdariaa	5H Anonyxb	Astartea	6D Macoma ^a	Astarte	6G Anonyx Cyrtdaria	7B+7C Anonyx	7E Anon yx	
<u>METALS</u> ($\mu\text{g/g}$ wet weight)									
Ba	25 \pm 5	23 \pm 5	17 \pm 7	117 \pm 16	30 \pm 12	60 \pm 1	26 \pm 3	27 \pm 3	55 \pm 3
Cr	2.89 \pm 0.65	1.97 \pm 0.89	1.68 \pm 0.36	9.00 \pm 1.55	3.13 \pm 0.86	1.52 \pm 0.05	2.45 \pm 0.73	1.87 \pm 0.56	0.68 \pm 0.07
v	6.5: 1.4	1.6 \pm 0.6	1.2 \pm 0.3	21.2 \pm 2.8	6.8 \pm 3.6	0.7 \pm 0.2	5.5 \pm 0.8	1.6 \pm 0.2	0.4 \pm 0
Pb	0.52 \pm 0.15	<D.L. ^c	0.21 \pm 0.06	3.13 \pm 0.23	0.96 \pm 0.27	0.21 \pm 0.06	0.68 \pm 0.12	<D.L.	<D.L.
Cu	24 \pm 1	129 \pm 2	11 \pm 2	25 \pm 11	23 \pm 10	66 \pm 2	20 \pm 1	154 \pm 7	89 \pm 7
Zn	75 \pm 2	139 \pm 8	65 \pm 5	168 \pm 22	96 \pm 16	72 \pm 2	66 \pm 1	105 \pm 6	85 \pm 1
Cd	1.48 \pm 0.12	1.35 \pm 0.44	11.74 \pm 3.36	4.69 \pm 8.74	11.22 \pm 0.49	0.25 \pm 0.04	1.33 \pm 0.15	0.81 \pm 0.18	0.43 \pm 0.13

^aBivalve

^bAmphipod

^cDetection Limit

TABLE 4.5. SUMMARY OF METAL CONCENTRATIONS IN TISSUES OF THE AMPHIPOD, *Anonyx* sp., COLLECTED FROM STATIONS THROUGHOUT THE STUDY AREA.

	STATIONS							
	1A+1B+1E	2 F	3A	4B	5H	6G	7B+7C	7E
<u>METALS ($\mu\text{g/g}$ wet weight)</u>								
Ba	39	36	22	22	23	60	27	55
Cr	3.39	2.05	1.13	0.39	1.97	1.52	1.87	0.68
V	4.2	1.0	0.6	<D.L. ^a	1.6	0.7	1.6	0.4
Pb	0.67	<D.L.	<D. L.	0.13	<D.L.	0.21	<D.L.	<D.L.
Cu	97	77	176	131	129	66	154	89
Zn	134	107	124	105	139	72	105	85
Cd	0.99	0.58	1.53	1.03	1.35	0.25	0.81	0.43

^aDetection Limit

TABLE 4.6. SUMMARY OF METAL CONCENTRATIONS **IN Astarte** TISSUE SAMPLES COLLECTED FROM STATIONS THROUGHOUT THE STUDY AREA.

	STATIONS			
	1A+1B	3A	5H	6D
<u>METALS</u> <u>($\mu\text{g/g}$ wet weight)</u>				
Ba	20	18	17	30
Cr	2.54	3.03	1.68	3.13
v	2.4	5.0	1.2	6.8
Pb	0.32	0.45	0.21	0.96
Cu	12	14	11	23
Zn	80	84	65	96
Cd	25.5	8.16	11.74	11.22

TABLE 4.7. MEAN CONCENTRATIONS OF METALS IN BIVALVE TISSUES COLLECTED IN YEAR-1 AND YEAR-2.

	3A Astarte		5F Cyrtodaria		6D Astarte	
	YEAR-1	YEAR-2	YEAR-1	YEAR-2	YEAR-1	YEAR-2
<u>METALS ($\mu\text{g/g}$ wet weight)</u>						
Ba	8	19	17	26	30	30
Cd	9.3	8.2	1.4	1.5	11.2	11.2
Cr	2.4	3.0	3.2	2.9	4.5	3.1
Cu	12	15	16	24	28	23
Pb	0.61	0.46	0.48	0.52	0.80	0.97
V	1.9	5.0	3.3	6.5	5.3	6.8
Zn	73	84	68	73	96	97

In contrast to Year-1, in which replicate hydrocarbon analyses were performed on samples from only 7 of the 27 stations, the Year-2 analyses were performed on three pooled replicate samples from each of the 39 stations. One replicate (representing a composite of two samples) was analyzed for each river sediment and shoreline peat station. At three stations, hydrocarbon analyses were performed on both the bulk sediment and mud fraction. Four tissue replicates from each station were scanned by UV/F, and subsequently analyzed by GC-FID and GC/MS when the sample was large enough.

In the tabulation of hydrocarbon data, individual saturated and aromatic compounds are combined and presented as key parameters and ratios, which were determined in Year-1 to be most relevant to the interpretation of the data and testing of the null hypotheses. For the saturated hydrocarbons, these parameters are

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

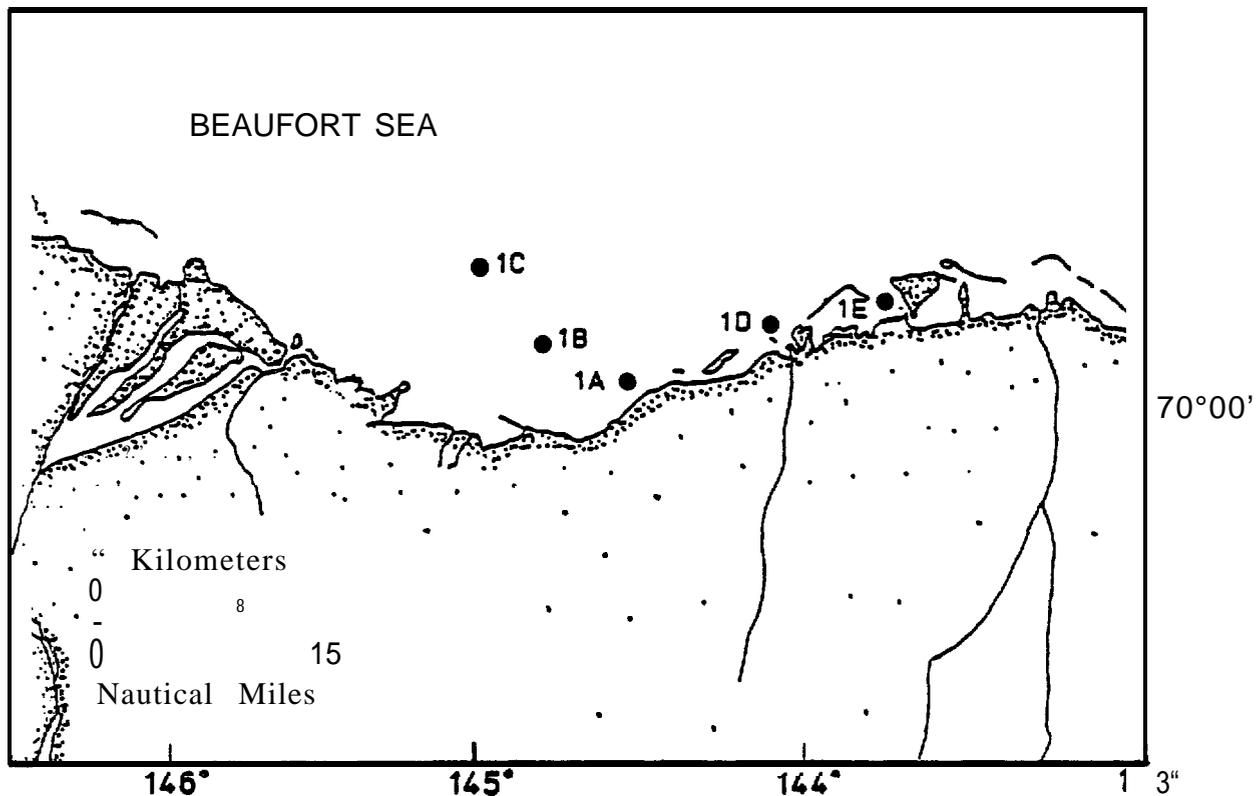
The concentrations of the individual isoprenoids, pristane and phytane, are included in the tabulation of the saturated hydrocarbon data.

Key parameters used to present the aromatic hydrocarbon data are

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

4.2.1 Saturated Hydrocarbons in Sediments

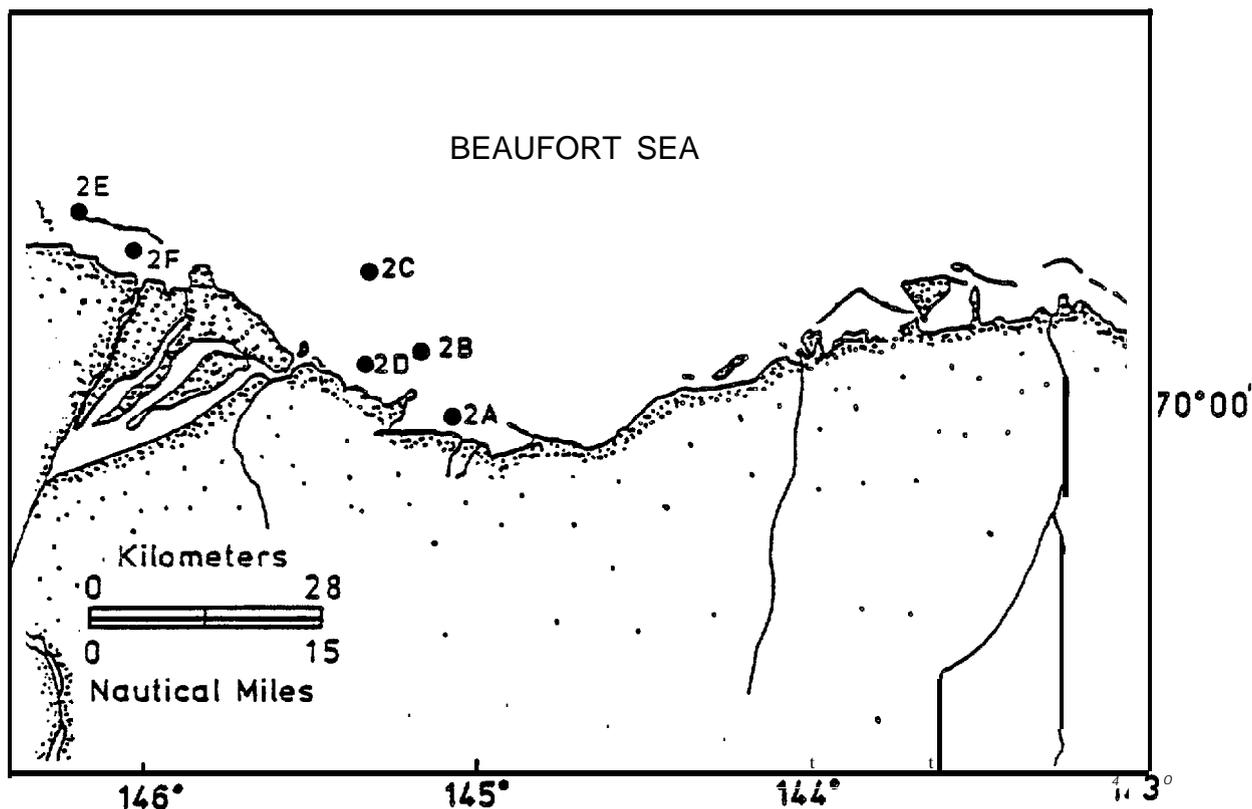
Figures 4.23 through 4.29 present the saturated hydrocarbon parameters for the 39 stations sampled in Year-2. Percent mud (silt + clay) and TOC (mg/g dry weight) are included for comparison on all figures. Total alkanes (TALK), the n-C₁₀ through n-C₃₄ compounds, range from 0.64 to 21.15 µg/g, while the low molecular weight alkanes (LALK), or n-C₁₀ through n-C₂₀ compounds, range from 0.14 to 2.68 µg/g. The lowest sediment concentrations of pristane and phytane are 0.007 to 0.004 µg/g, respectively and the high ends of the ranges are represented by 0.208 and 0.085 µg/g, respectively for pristane and phytane. Total resolved plus unresolved hydrocarbon concentrations (TOT) range from 1.26 to 60.33 µg/g. Percent mud and TOC concentrations vary extensively and are not always in proportion to hydrocarbon concentrations.



STATIONS

	<u>1A</u>	<u>1B</u>	<u>1C</u>	<u>1D</u>	<u>1E</u>
SATURATED HYDROCARBONS (µg/g)					
TALK	7.46 ± 2.73	2.47 ± 0.26	6.70 ± 0.54	3.97 ± 2.91	11.92 ± 0.73
LALK	0.60 ± 0.10	0.38 ± 0.00	1.30 ± 0.16	0.26 ± 0.17	1.09 ± 0.03
Pristane	0.037 ± 0.005	0.029 ± 0.002	0.109 ± 0.007	0.014 ± 0.010	0.026 ± 0.002
Phytane	0.020 ± 0.003	0.016 ± 0.002	0.074 ± 0.006	0.006 ± 0.004	0.014 ± 0.001
TOT	17.37 ± 6.80	4.76 ± 0.48	24.43 ± 2.20	6.83 ± 5.37	22.73 ± 3.32
% Mud	68.7 ± 11.4	14.9 ± 5.4	70.0 ± 3.0	16.9 ± 5.4	92.8 ± 2.7
TOC (mg/g)	11.7 ± 2.0	4.8 ± 3.8	9.6 ± 0.8	7.1 ± 2.9	11.7 ± 1.4

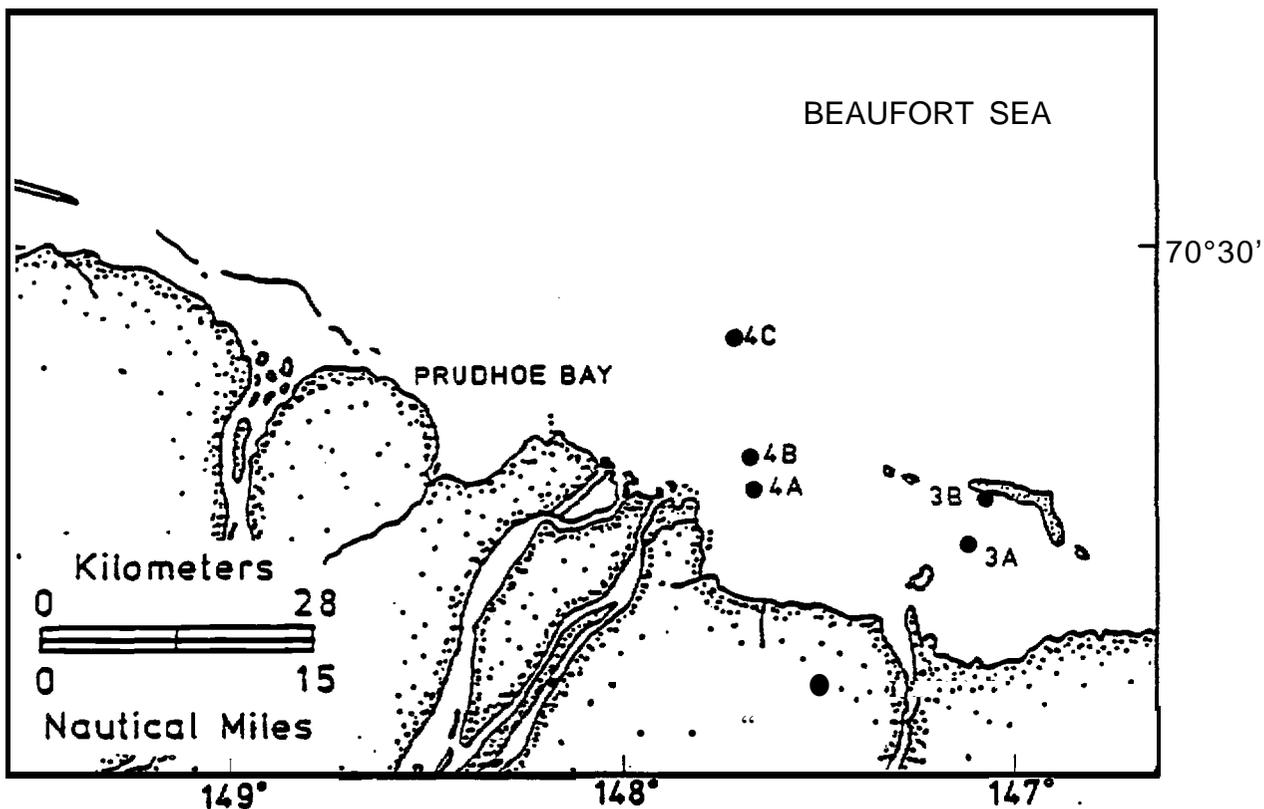
FIGURE 4.23. SUMMARY OF SATURATED HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN EAST CAMDEN BAY AREA SEDIMENTS.



STATIONS

	<u>2A</u>	<u>2B</u>	<u>2C</u>	<u>2D</u>	<u>2E</u>	<u>2F</u>
SATURATED HYDROCARBONS (µg/g)						
TALK	10.61 ± 6.69	4.02 ± 4.07	6.80 ± 0.89	2.78 ± 2.85	6.79 ± 3.40	0.79 ± 0.14
LALK	1.15 ± 0.41	0.51 ± 0.42	1.37 ± 0.24	0.26 ± 0.21	1.08 ± 0.39	0.16 ± 0.02
Pristane	0.093 ± 0.019	0.037 ± 0.031	0.116 ± 0.023	0.019 ± 0.012	0.078 ± 0.026	0.012 ± 0.002
Phytane	0.062 ± 0.011	0.023 ± 0.024	0.079 ± 0.012	0.011 ± 0.006	0.048 ± 0.014	0.006 ± 0.001
TOT	23.10 ± 12.01	9.40 ± 11.43	14.30 ± 1.49	8.22 ± 7.72	23.13 ± 9.85	1.67 ± 0.34
% Mud						
	91.8 ± 1.2	24.4 ± 34.2	71.1 ± 1.2	33.6 ± 43.0	77.6 ± 14.2	13.3 ± 2.4
TOC (mg/g)						
	16.9 ± 5.9	10.2 ± 3.2	7.4 ± 5.8	10.4 ± 7.1	10.6 ± 2.1	4.7 ± 0.6

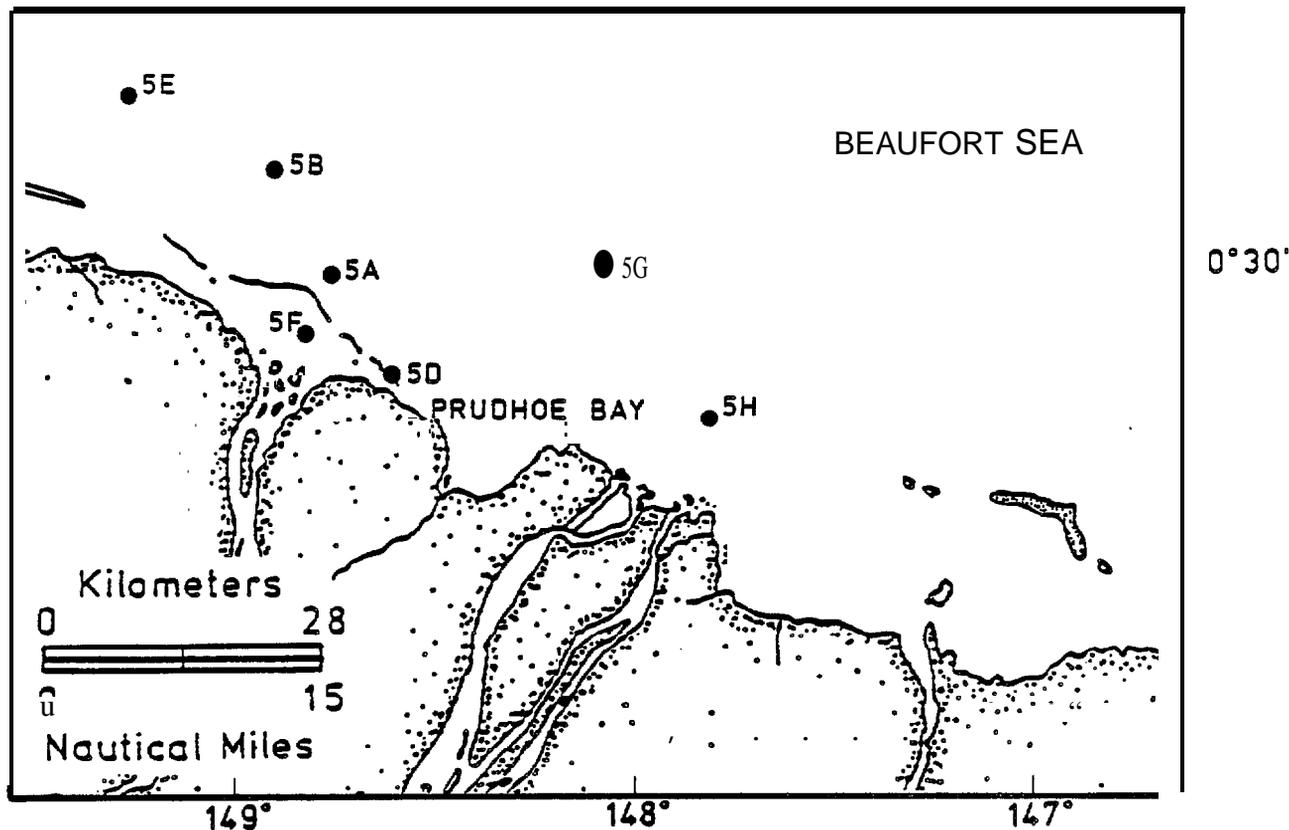
FIGURE 4.24. SUMMARY OF SATURATED HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN WEST CAMDEN BAY AREA SEDIMENTS.



STATCONS

	3A	3B	4A	4B	4C
SATURATED HYDROCARBONS (µg/g)					
TALK	2.52 ± 0.31	6.82 ± 0.30	3.07 ± 0.56	1.45 ± 0.52	2.83 ± 0.84
LALK	0.30 ± 0.03	0.98 ± 0.02	0.44 ± 0.09	0.23 ± 0.05	0.41 ± 0.12
Pristane	0.024 ± 0.002	0.062 ± 0.002	0.028 ± 0.003	0.015 ± 0.003	0.028 ± 0.007
Phytane	0.012 ± 0.001	0.037 ± 0.004	0.017 ± 0.003	0.008 ± 0.002	0.016 ± 0.005
ToT	4.74 ± 0.83	20.80 ± 0.40	9.68 ± 1.86	4.17 ± 1.71	9.13 ± 2.41
% Mud	46.1 ± 0.6	74.3 ± 2.9	33.9 ± 10.6	6.1 ± 1.7	6.3 ± 3.2
TOC (mg/g)	10.8 ± 0.4	7.9 ± 5.9	13.7 ± 4.0	2.3 ± 3.2	10.6 ± 0.8

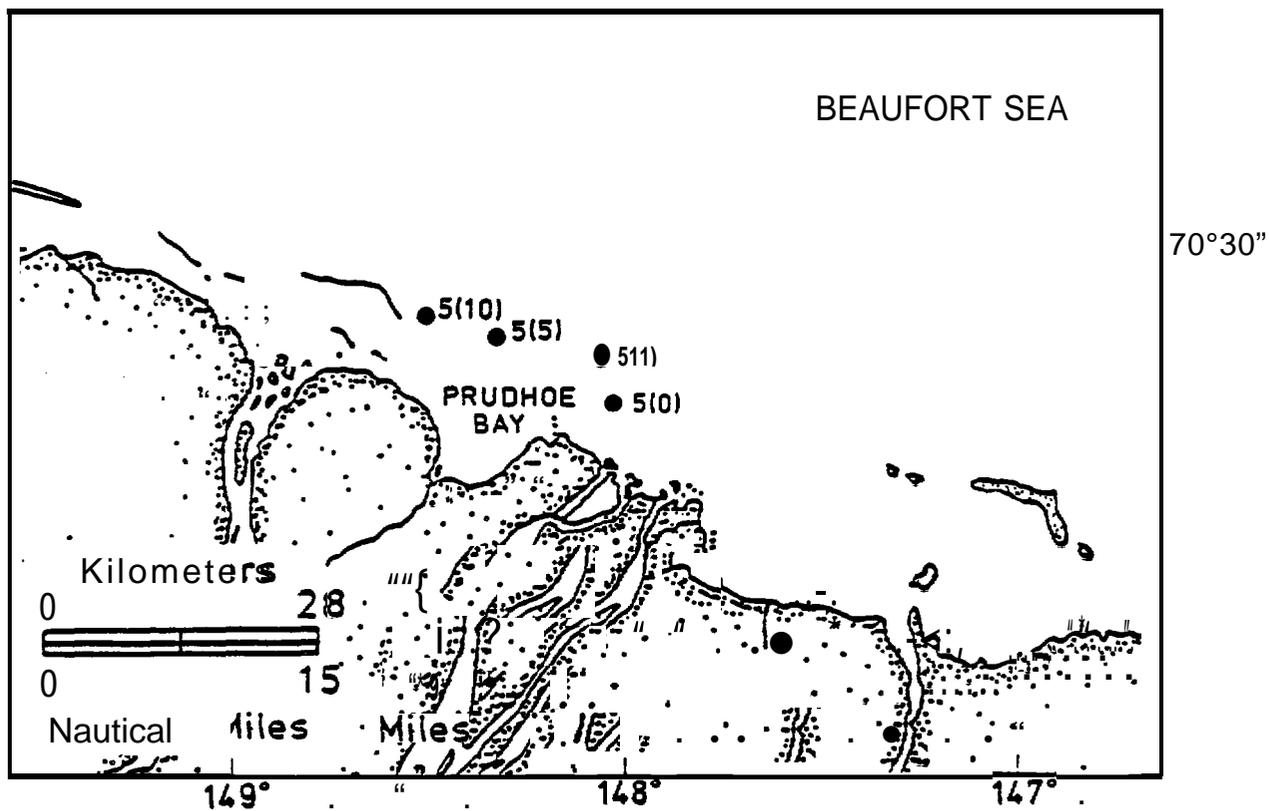
FIGURE 4.25. SUMMARY OF SATURATED HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN MIKELSON BAY - FOGGY ISLAND AREA SEDIMENTS.



STATIONS

	5A	5B	5D	5E	5F	5G	5H
SATURATED HYDROCARBONS (µg/g)							
TALK	4.76 ± 0.15	7.32 ± 0.34	8.43 ± 0.97	8.74 ± 2.87	3.18 ± 0.36	1.97 ± 0.32	3.22 ± 0.75
LALK	0.94 ± 0.10	1.46 ± 0.05	1.05 ± 0.01	1.70 ± 0.31	0.65 ± 0.07	0.36 ± 0.03	0.68 ± 0.16
Pristane	0.050 ± 0.004	0.100 ± 0.004	0.047 ± 0.003	0.119 ± 0.040	0.029 ± 0.002	0.026 ± 0.003	0.030 ± 0.005
Phytane	0.031 ± 0.007	0.085 ± 0.010	0.036 ± 0.008	0.079 ± 0.004	0.019 ± 0.002	0.013 ± 0.002	0.015 ± 0.003
ToT	14.56 ± 5.36	28.70 ± 1.61	27.00 ± 4.30	29.10 ± 5.20	9.88 ± 1.37	5.74 ± 1.26	8.82 ± 1.93
% Mud	43.0 ± 7.3	77.0 ± 19.3	61.6 ± 5.6	40.3 ± 15.2	42.2 ± 2.5	11.2 ± 2.8	15.7 ± 1.9
TOC (mg/g)	13.6 ± 2.8	10.0 ± 0.3	14.6 ± 4.0	9.7 ± 0.6	7.6 ± 1.5	6.6 ± 0.8	16.2 ± 12.3

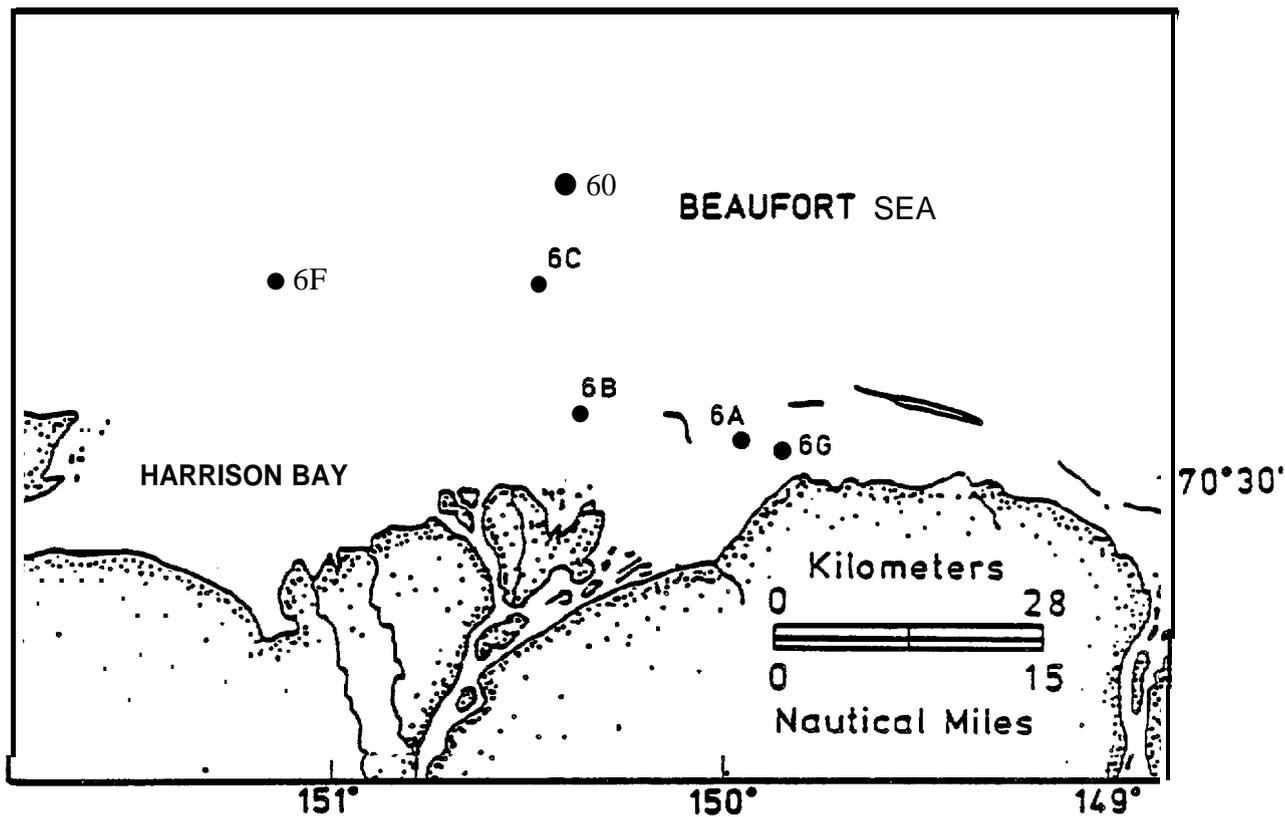
FIGURE 4.26. SUMMARY OF SATURATED HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN PRUDHOE BAY - GWYDYR BAY AREA SEDIMENTS.



STATIONS

	<u>5(0)</u>	<u>5(1)</u>	<u>5(5)</u>	<u>5(10)</u>
SATURATED HYDROCARBONS ($\mu\text{g/g}$)				
TALK	1.41 ± 0.46	0.64 ± 0.48	2.29 ± 0.50	2.86 ± 0.05
LALK	0.30 ± 0.10	0.14 ± 0.10	0.46 ± 0.16	0.56 ± 0.05
Pristane	0.016 ± 0.005	0.007 ± 0.005	0.021 ± 0.007	0.030 ± 0.001
Phytane	0.008 ± 0.003	0.004 ± 0.003	0.011 ± 0.003	0.016 ± 0.000
ToT	3.40 ± 1.70	1.26 ± 0.84	5.30 ± 1.78	7.96 ± 0.43
% Mud	6.3 ± 5.7	5.1 ± 0.2	23.5 ± 12.6	20.5 ± 3.2
Toc (mg/g)	3.9 ± 0.8	2.6 ± 0.7	4.9 ± 2.0	7.0 ± 1.6

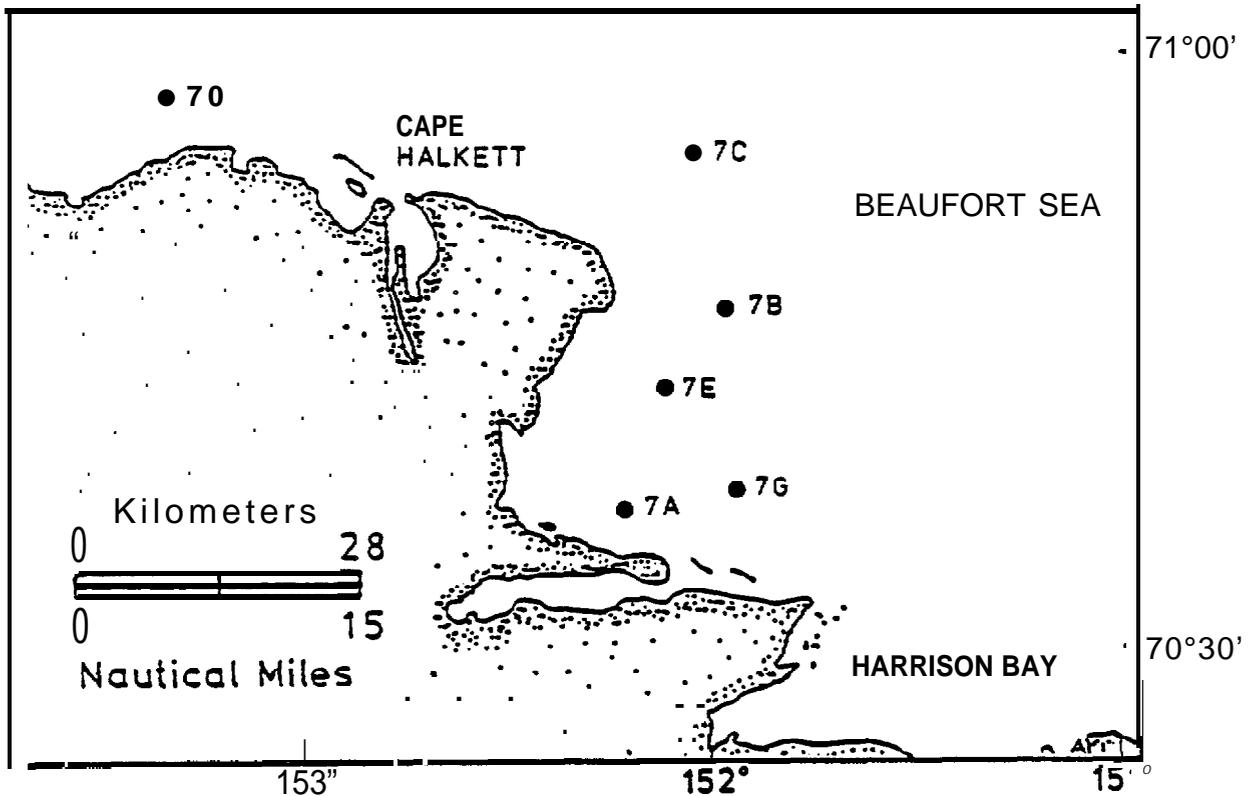
FIGURE 4.27. SUMMARY OF SATURATED HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN ENDICOTT FIELD TRANSECT STATION SEDIMENTS.



STATIONS

	<u>6A</u>	<u>6B</u>	<u>6C</u>	<u>6D</u>	<u>6F</u>	<u>6G</u>
SATURATED HYDROCARBONS (ug/g)						
TALK	11.28 ± 1.05	11.00 ± 2.35	6.76 ± 1.86	2.57 ± 2.16	4.88 ± 0.58	21.15 ± 1.68
LALK	1.31 ± 0.20	1.22 ± 0.06	0.76 ± 0.28	0.32 ± 0.22	0.86 ± 0.13	2.68 ± 0.22
Pristane	0.081 ± 0.010	0.094 ± 0.012	0.065 ± 0.017	0.027 ± 0.022	0.058 ± 0.008	0.124 ± 0.012
Phytane	0.049 ± 0.005	0.050 ± 0.035	0.033 ± 0.024	0.017 ± 0.015	0.031 ± 0.007	0.064 ± 0.005
TOT	29.50 ± 5.94	33.23 ± 6.30	21.27 ± 4.34	7.55 ± 8.04	13.27 ± 1.12	60.33 ± 5.16
<hr/>						
% Mud	81.8 ± 6.0	83.7 ± 6.3	49.4 ± 19.7	17.6 ± 25.0	36.3 ± 6.6	79.1 ± 1.8
<hr/>						
TOC (mg/g)	13.4 ± 2.2	15.9 ± 6.4	8.4 ± 1.5	4.4 ± 1.7	7.6 ± 3.1	18.4 ± 0.7

FIGURE 4.28. SUMMARY OF SATURATED HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN EAST HARRISON BAY SEDIMENTS.



STATIONS

	7A	7B	7C	7D	7E	7G
SATURATED HYDROCARBONS (µg/g)						
TALK	9.25 ± 2.38	3.19 ± 0.30	11.63 ± 2.47	12.77 ± 2.26	11.76 ± 1.07	6.33 ± 1.28
LALK	1.36 ± 0.13	0.60 ± 0.08	1.62 ± 0.31	1.91 ± 0.31	1.90 ± 0.26	1.62 ± 0.44
Pristane	0.103 ± 0.015	0.040 ± 0.004	0.110 ± 0.017	0.136 ± 0.021	0.186 ± 0.040	0.208 ± 0.069
Phytane	0.051 ± 0.008	0.017 ± 0.002	0.051 ± 0.006	0.058 ± 0.013	0.052 ± 0.007	0.047 ± 0.013
TOT	23.13 ± 7.24	6.95 ± 1.30	31.73 ± 5.61	34.47 ± 4.05	33.67 ± 4.13	24.20 ± 6.78
<hr/>						
% Mud	67.4 ± 8.3	7.6 ± 2.3	88.8 ± 7.3	43.5 ± 21.1	63.8 ± 10.7	27.9 ± 13.3
<hr/>						
TOC (mg/g)	10.5 ± 1.6	5.0 ± 0.6	13.2 ± 2.3	9.9 ± 2.0	25.1 ± 10.2	10.5 ± 5.2

FIGURE 4.29. SUMMARY OF SATURATED HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN WEST HARRISON BAY SEDIMENTS.

The data for the East (the "1" stations) and West (the "2" stations) Camden Bay area are presented in Figures 4.23 and 4.24, respectively. The nearshore-to-off shore transect stations (1A, 1 B, and 1C in Figure 4.23, and 2A, 2B, and 2C in Figure 4.24) do not appear to show a gradient for any of the parameters. At these two transects, higher concentrations are generally associated with Stations 1C (offshore) and 2A (nearshore). No significant trends are observed among the other Camden Bay stations.

Figure 4.25 presents data for the Mikelson Bay and Foggy Island Bay areas. In these areas, the highest values for all parameters are observed at Station 3B and the lowest occur at Station 4B. As was found in Year-1, no concentration gradients were associated with the Foggy Island Bay transect stations (4A, 4B, and 4C).

In the central part of the Study Area, the Prudhoe Bay - Gwydyr Bay region includes the "5" stations, which are divided into two station groupings for presentation. In this geographical area, the highest concentrations are found in sediments from Station 5E (Figure 4.26), which is also the furthest offshore station. In contrast to Year-1 data, the higher hydrocarbon concentrations detected in Year-2 are not always associated with nearshore stations (5A, 5D, 5F, and 5I-1).

Data for the Endicott Field transect stations, selected to represent 1-, 5-, and 10-mile distances from the Endicott Field, are presented in Figure 4.27. Saturated hydrocarbon concentrations at these stations do not indicate a gradient away from the proposed area of activity. Instead, higher levels are associated with sediments from Stations 5(5) and 5(10), while lower concentrations are found in Station 5(0) and 5(1) sediments. Percent mud and TOC concentrations follow a similar trend in this area. Lowest sediment saturated hydrocarbon concentrations in the entire Study Area are associated with Station 5(I).

Data for East Harrison Bay (the "6" stations) are displayed in Figure 4.28. As found in Year-1, higher sediment hydrocarbon concentrations are clearly associated with Stations 6A, 6B, and 6G, the stations nearest to the Colville River mouth, while Stations 6C, 6D, and 6F have the lower sediment concentrations. A transect out from the mouth of the Colville River is represented by Stations 6B, 6C, and 6D. Saturated hydrocarbon concentrations, grain size, and TOC concentrations clearly follow the offshore gradient observed in Year-1, with the highest levels occurring at Station 6B and the lowest at Station 6D.

Figure 4.29 presents the data for West Harrison Bay (the "7" stations). In this region, the highest sediment concentrations of saturated hydrocarbons are at Stations 7C and 7D (the westernmost station in the Study Area). As in Year-1, the lowest hydrocarbon, mud, and TOC levels are found in Station 7B sediments.

Year- 1 and Year-2 data, for the seven stations for which a complete set of replicates was analyzed in Year-1, are presented in Table 4.8. No significant increases from Year-1 to Year-2 in any saturated hydrocarbon parameters are noted. At some stations (e.g., 2F, 4A, and 3D) decreases in concentrations are observed in Year-2.

At three stations (1A, 5(5), and 6D), hydrocarbon concentrations were determined in both the bulk and mud fractions of sediments. The saturated hydrocarbon data are presented in Table 4.9. The concentrations in the mud fraction at Station 1 A are approximately two times greater than in the bulk sediment. At Station 5(5), the mud fraction concentrations are 4-6 times higher than in the bulk and at Station 6D, 5-10 times greater than the bulk sediment values.

TABLE 4.8. SUMMARY OF YEAR-1 AND YEAR-2 SATURATED HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN REPLICATED YEAR-1 STATION SEDIMENTS.

SATURATED HYDROCARBONS ($\mu\text{g/g}$)	STATIONS							
	2F		30		4A		5D	
	YEAR-1	YEAR-2	YEAR-1	YEAR-2	YEAR-1	YEAR-2	YEAR-1	YEAR-2
TALK	1.42 \pm 0.26	0.79 \pm 0.14	4.46 \pm 1.19	6.82 \pm 0.30	3.41 \pm 0.33	3.07 \pm 0.56	10.75 \pm 3.60	5.43 \pm 0.97
LALK	0.39 \pm 0.05	0.16 \pm 0.02	0.82 \pm 0.23	0.98 \pm 0.02	0.62 \pm 0.03	0.45 \pm 0.09	1.14 \pm 0.38	1.05 \pm 0.01
Pristane	0.026 \pm 0.001	0.012 \pm 0.002	0.047 \pm 0.013	0.062 \pm 0.002	0.046 \pm 0.004	0.025 \pm 0.003	0.072 \pm 0.023	0.047 \pm 0.003
Phytane	0.010 \pm 0.002	0.006 \pm 0.001	0.023 \pm 0.006	0.037 \pm 0.004	0.019 \pm 0.003	0.017 \pm 0.003	0.034 \pm 0.010	0.036 \pm 0.005
TOT	5.59 \pm 0.78	1.67 \pm 0.34	13.91 \pm 3.34	20.80 \pm 0.40	12.42 \pm 1.69	9.68 \pm 1.86	35.51 \pm 4.36	27.00 \pm 4.30
% Mud	15.1 \pm 3.6	13.3 \pm 2.4	65.2 \pm 3.7	74.3 \pm 2.9	33.6 \pm 18.8	33.9 \pm 10.6	72.5 \pm 2.1	61.6 \pm 5.6
TOC (mg/g)	5.6 \pm 1.0	4.7 \pm 0.6	9.2 \pm 0.5	7.9 \pm 5.9	7.2 \pm 1.0	13.7 \pm 4.0	29.2 \pm 2.1	14.6 \pm 4.0

SATURATED HYDROCARBONS ($\mu\text{g/g}$)	STATIONS					
	6C		SD		7A	
	YEAR-1	YEAR-2	YEAR-1	YEAR-2	YEAR-1	YEAR-2
TALK	3.99 \pm 1.50	6.76 \pm 1.86	2.50 \pm 0.87	2.57 \pm 2.16	5.76 \pm 2.63	9.25 \pm 2.38
LALK	1.21 \pm 0.42	0.76 \pm 0.28	1.27 \pm 0.87	0.32 \pm 0.22	1.33 \pm 0.53	1.36 \pm 0.13
Pristane	0.067 \pm 0.029	0.065 \pm 0.017	0.032 \pm 0.008	0.027 \pm 0.022	0.080 \pm 0.034	0.103 \pm 0.015
Phytane	0.030 \pm 0.017	0.033 \pm 0.024	0.130 \pm 0.003	0.017 \pm 0.015	0.031 \pm 0.011	0.051 \pm 0.008
TOD	15.75 \pm 6.31	21.27 \pm 4.34	7.75 \pm 2.47	7.55 \pm 8.04	21.88 \pm 5.78	23.13 \pm 7.24
% Mud	30.8 \pm 15.4	49.4 \pm 19.7	10.8 \pm 5.7	17.6 \pm 25.0	65.4 \pm 5.6	67.4 \pm 8.3
TOC (mg/g)	6.2 \pm 1.4	8.4 \pm 1.5	3.8 \pm 1.1	4.4 \pm 1.7	11.4 \pm 4.2	10.5 \pm 1.6

TABLE 4.9. SUMMARY OF SATURATED HYDROCARBON **CONCENTRATIONS** IN THE BULK AND MUD FRACTION OF SEDIMENTS FROM SEVERAL STATIONS THROUGHOUT THE STUDY AREA.

	STATIONS					
	1A		5(5)		6D	
	BULK	MUD	BULK	MUD	BULK	MUD
SATURATED HYDROCARBONS (µg/g)						
TALK	7.46 ± 2.73	15.57 ± 6.25	2.29 ± 0.49	12.31 ± 1.99	2.57 ± 2.16	17.16 ± 0.80
LALK	0.60 ± 0.10	1.26 ± 0.14	0.46 ± 0.16	2.20 ± 0.25	0.32 ± 0.22	3.79 ± 0.32
Pristane	0.037 ± 0.005	0.081 ± 0.008	0.021 ± 0.007	0.132 ± 0.016	0.027 ± 0.022	0.258 ± 0.032
Phy tane	0.020 ± 0.003	0.054 ± 0.010	0.011 ± 0.003	0.066 ± 0.005	0.017 ± 0.015	0.141 ± 0.008
TOT	17.37 ± 6.80	27.17 ± 9.08	5.30 ± 1.78	21.13 ± 3.61	7.55 ± 8.04	35.30 ± 8.66

4.2.2 Saturated Hydrocarbons in River and Peat Samples

For the river and peat samples, hydrocarbon concentrations were determined in the bulk samples only. Table 4.10 presents the saturated hydrocarbon concentrations, percent mud, and TOC concentrations in sediments collected from the Sagavanirktok River in the central part of the Study Area and from the Colville River located just east of Harrison Bay. The hydrocarbon concentrations in these river sediments are in the same range as those reported for marine sediments in the same geographic regions.

Concentrations of saturated hydrocarbons in the eight shoreline peat samples collected throughout the Study Area are shown in Table 4.11. Unlike the river samples, the concentrations of saturated hydrocarbons in the peat samples are several orders of magnitude higher than levels observed in marine sediments. The highest concentrations are clearly found at Station 73, which is located on **Kogru** Island in Harrison Bay. TALK concentrations are 10-30 times higher in peat samples than in marine sediments. Total resolved and unresolved hydrocarbons are up to 50 times higher in the peat than in sediments. Peat concentrations of pristane range from 0.015 to 2.65 $\mu\text{g/g}$, or between 2 and 10 times the levels occurring in sediments. Phytane is found in approximately the same concentration ranges in both peat and marine sediments.

4.2.3 Aromatic Hydrocarbons in Sediments

The aromatic hydrocarbon parameters for the 39 stations sampled in Year-2 are presented in Figures 4.30 through 4.36. Percent mud and TOC concentrations are included for comparison. Overall, the highest concentrations of aromatics are observed in the sediments from Station 6B, which is nearest to the mouth of the Colville River. The largest range in concentrations (0.01 -1.05 $\mu\text{g/g}$) is found in the naphthalenes (N). The phenanthrenes (P), dibenzothiophenes (D), and fluorenes (F) range from below detection limit to 0.44, 0.09, and 0.22 $\mu\text{g/g}$, respectively. The polynuclear aromatic hydrocarbons (PAH) were detected between 0.02 and 0.38 $\mu\text{g/g}$.

Data for the Camden Bay area (the "1" and "2" stations) are presented in Figures 4.30 and 4.31. As was found with the saturated hydrocarbon data, no nearshore -to-off shore gradients are detectable in either the Station 1A, 1 B, 1 C, or Station 2A, 2B, 2C transects. Highest sediment aromatics concentrations are associated with the offshore Station 1 C and the nearshore Station 2A.

The Mikelson Bay - Foggy Island Bay areas are represented by the "3" and "4" stations. These data are displayed in Figure 4.32. The trends observed at these stations are similar to trends in the saturated hydrocarbon data. Highest concentrations are associated with Station 3A and 3B sediments, which also have a relatively high mud fraction; lowest levels are found at Station 4B, with correspondingly low mud and TOC concentrations. No concentration gradients were associated with the Foggy Island Bay nearshore-to-of fshore transect (Stations 4A, 4B, and 4C).

Data for the stations ("5") in the general vicinity of Prudhoe Bay are shown in Figure 4.33 and the Endicott Field transect stations are shown separately in Figure 4.34. In contrast to Year-1 observations, in which the highest concentrations occurred at the nearshore Station 5D, the highest Year-2 aromatic hydrocarbon concentrations are found in sediments from offshore Stations 5B and 5E. These stations also have proportionately high sediment mud fractions.

Figure 4.34 presents the data for the Endicott Field transect stations. Although the concentrations of aromatics are generally low with respect to the entire Study Area, the higher concentrations at these transect stations appear to be associated

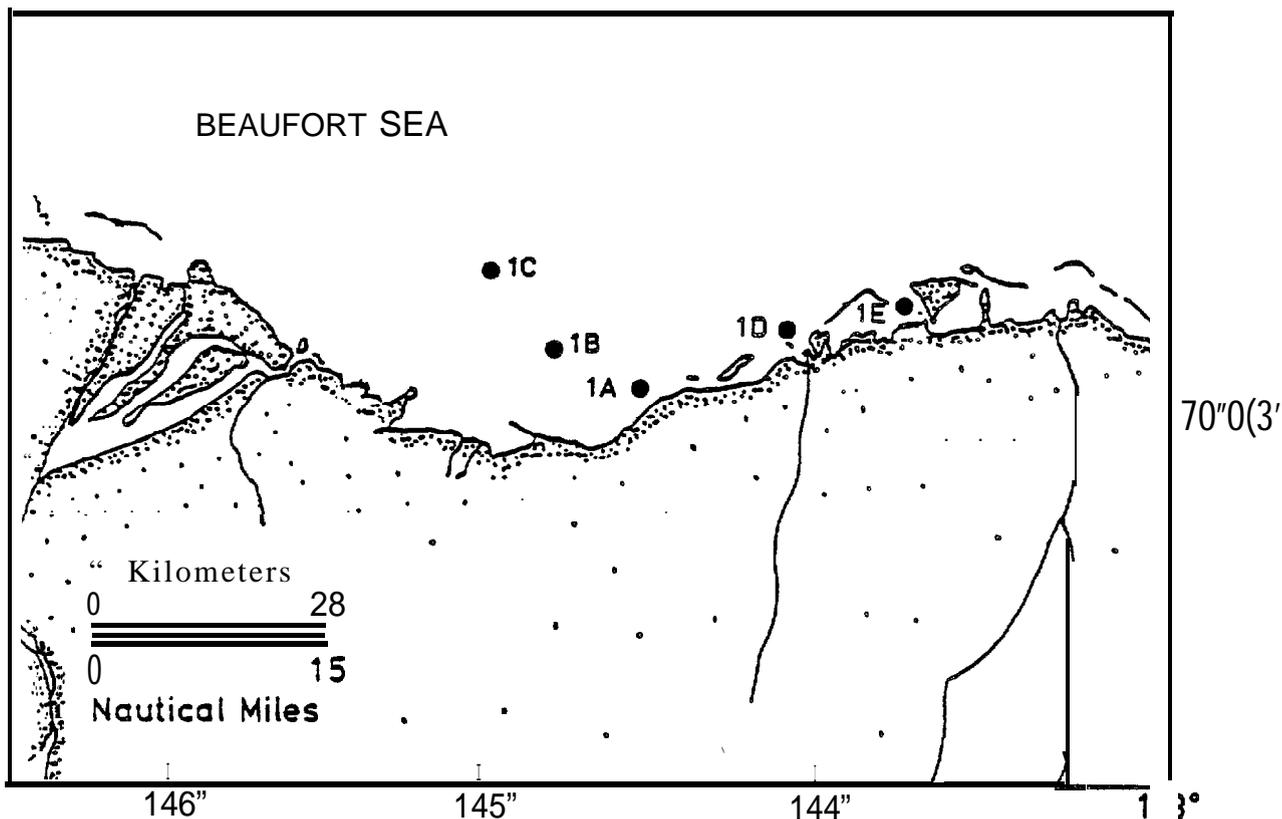
TABLE 4.10. SUMMARY OF SATURATED HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN BULK RIVER SEDIMENTS.

	STATIONS	
	53 Sagavanirktok River	6H Colville River
SATURATED HYDROCARBONS ($\mu\text{g/g}$)		
TALK	8.71	10.64
LALK	1.13	1.24
Pristane	0.025	0.095
Phytane	0.020	0.038
TOT	15.90	25.30
% Mud	15.50	15.44
TOC (mg/g)	12.80	65.50

TABLE 4.11. SUMMARY OF SATURATED HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN BULK SHORELINE PEAT SAMPLES.

	STATIONS							
	1F	2G	2H	3D	5K	63	7H	7J
SATURATED HYDROCARBONS (µg/g)								
TALK	263.6	39.0	83.8	230	82.9	241	41.12	598
LALK	11.60	0.80	2.79	3.54	1.26	5.90	1.72	17.20
Pristane	0.015	0.021	0.066	0.071	0.034	0.026	0.042	2.65
Phytane	c D.L. ^a	0.008	0.043	0.040	0.022	< D.L.	0.023	0.075
TOT	532	49.9	112	388	154	744	50.8	1700
% Mud	87.10	58.30	73.39	44.54	66.20	69.10	7.98	80.50
TOC (mg/g)	95.30	42.20	170.00	228.00	93.40	261.00	22.90	295.00

^aDetection Limit

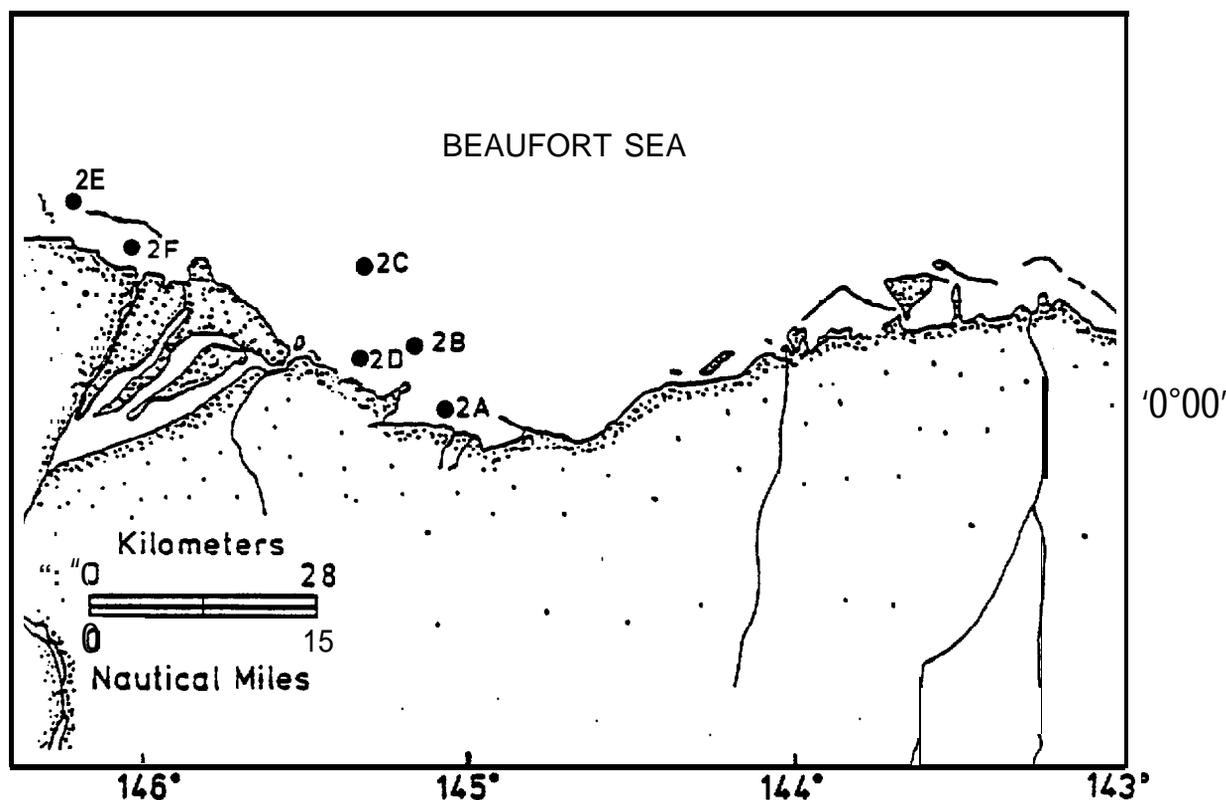


STATIONS

	<u>1A</u>	<u>1B</u>	<u>1C</u>	<u>1D</u>	<u>1E</u>
AROMATIC HYDROCARBONS (µg/g)					
N	0.07 ± 0.00	0.04 ± 0.02	0.22 ± 0.02	0.02 ± 0.02	0.04 ± 0.00
P	0.07 ± 0.01	0.04 ± 0.00	0.18 ± 0.01	0.02 ± 0.01	0.04 ± 0.00
D	0.01 ± 0.00	0.01 ± 0.00	0.04 ± 0.00	< D.L. ^a	< D.L.
F	0.01 ± 0.00	0.01 ± 0.00	0.08 ± 0.01	< D.L.	0.01 ± 0.00
PAH	0.10 ± 0.01	0.04 ± 0.01	0.23 ± 0.02	0.03 ± 0.02	0.04 ± 0.01
% Mud	68.7 ± 11.4	14.9 ± 5.4	70.0 ± 3.0	16.9 ± 5.4	92.8 ± 2.7
ToC (mg/g)	11.7 ± 2.0	4.8 ± 3.8	9.6 ± 0.8	7.1 ± 2.9	11.7 ± 1.4

^aDetection Limit

FIGURE 4.30. SUMMARY OF AROMATIC HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN EAST CAMDEN BAY AREA SEDIMENTS.

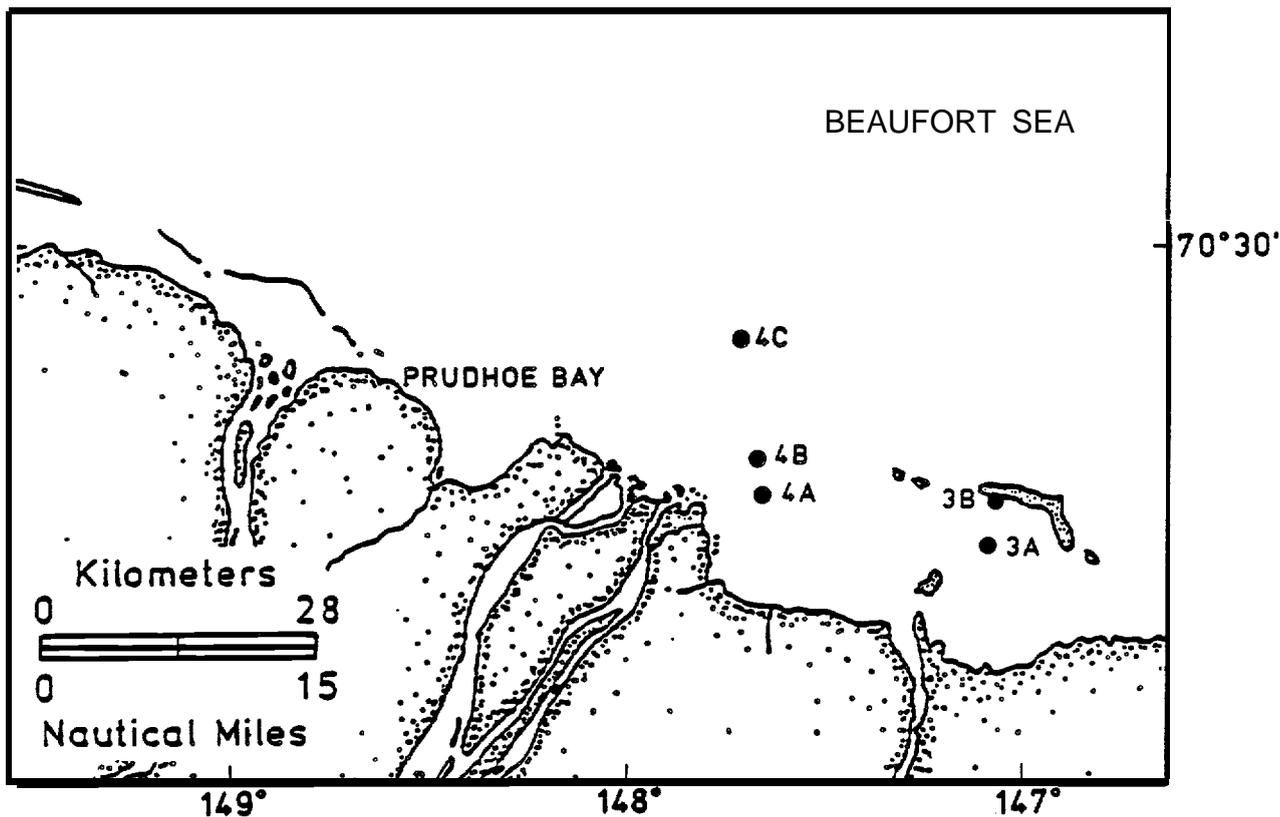


STATIONS

	2A	2B	2C	2D	2E	2F
AROMATIC HYDROCARBONS (µg/g)						
N	0.30 ± 0.03	0.08 ± 0.06	0.24 ± 0.04	0.12 ± 0.11	0.27 ± 0.27	0.05 ± 0.03
P	0.37 ± 0.06	0.07 ± 0.06	0.18 ± 0.02	0.08 ± 0.08	0.17 ± 0.12	0.06 ± 0.01
D	0.04 ± 0.01	0.01 ± 0.01	0.04 ± 0.01	0.01 ± 0.02	0.02 ± 0.01	<D.L. ^a
F	0.10 ± 0.02	0.02 ± 0.02	0.07 ± 0.02	0.02 ± 0.02	0.12 ± 0.05	0.01 ± 0.01
PAH	0.31 ± 0.06	0.08 ± 0.06	0.23 ± 0.00	0.08 ± 0.04	0.15 ± 0.12	0.02 ± 0.01
% Mud	91.8 ± 1.2	24.4 ± 34.2	71.1 ± 1.2	33.6 ± 43.0	77.6 ± 14.2	13.3 ± 2.4
TOC (mg/g)	16.9 ± 5.9	10.2 ± 3.2	7.4 ± 5.8	10.4 ± 7.1	10.6 ± 2.1	4.7 ± 0.6

^aDetection Limit

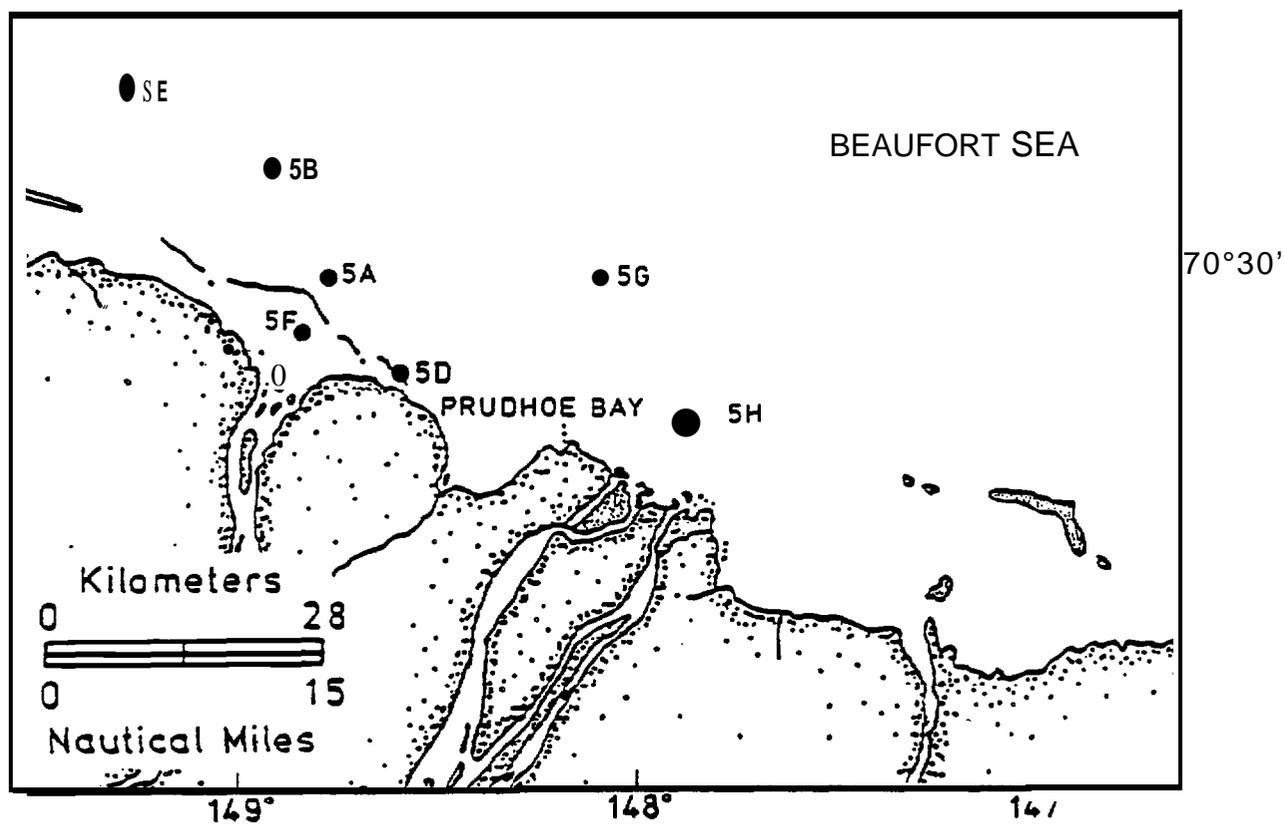
FIGURE 4.31. SUMMARY OF AROMATIC HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN WEST CAMDEN BAY AREA SEDIMENTS.



STATIONS					
	3A	3B	4A	4B	4C
AROMATIC HYDROCARBONS (µg/g)					
N	0.13 ± 0.08	0.09 ± 0.01	0.09 ± 0.01	0.05 ± 0.02	0.10 ± 0.03
P	0.10 ± 0.03	0.16 ± 0.01	0.08 ± 0.01	0.05 ± 0.02	0.09 ± 0.02
D	0.01 ± 0.01	0.02 ± 0.00	0.01 ± 0.00	< D.L. ^a	0.01 ± 0.01
F	0.03 ± 0.01	0.03 ± 0.00	0.01 ± 0.00	0.01 ± 0.01	0.02 ± 0.01
PAH	0.09 ± 0.04	0.08 ± 0.01	0.05 ± 0.02	0.04 ± 0.01	0.08 ± 0.02
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% Mud	46.1 ± 0.6	74.3 ± 2.9	33.9 ± 10.6	6.1 ± 1.7	6.3 ± 3.2
<hr/>					
TOC (mg/g)	10.8 ± 0.4	7.9 ± 5.9	13.7 ± 4.0	2.3 ± 3.2	10.6 ± 0.8

^aDetection Limit

FIGURE 4.32. SUMMARY OF SATURATED HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN THE MIKELSON BAY - FOGGY ISLAND BAY AREA SEDIMENTS.

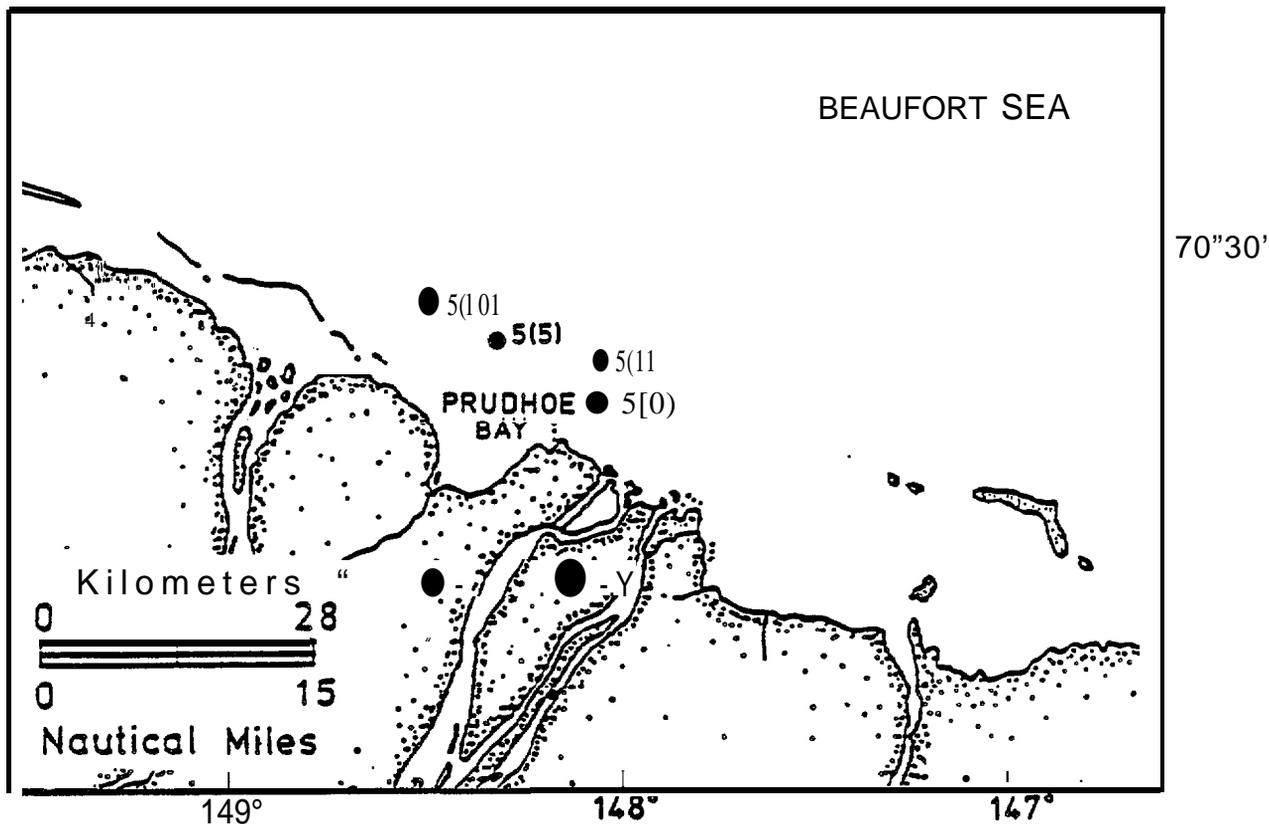


STATIONS

	5A	5B	5D	5E	5F	5G	5H
AROMATIC HYDROCARBONS (ug/g)							
N	0.18 ± 0.04	0.47 ± 0.03	0.20 ± 0.02	0.48 ± 0.02	0.06 ± 0.01	0.08 ± 0.03	0.06 ± 0.01
P	0.11 ± 0.02	0.35 ± 0.01	0.16 ± 0.03	0.32 ± 0.00	0.06 ± 0.01	0.06 ± 0.01	0.06 ± 0.02
D	0.02 ± 0.00	0.06 ± 0.01	0.04 ± 0.01	0.06 ± 0.01	0.02 ± 0.01	< D.L. ^a	0.01 ± 0.00
F	0.02 ± 0.00	0.11 ± 0.02	0.05 ± 0.02	0.08 ± 0.01	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
PAH	0.12 ± 0.02	0.36 ± 0.00	0.16 ± 0.03	0.34 ± 0.01	0.07 ± 0.01	0.06 ± 0.02	0.05 ± 0.02
% Mud	43.0 ± 7.3	77.0 ± 19.3	61.6 ± 5.6	40.3 ± 15.2	42.2 ± 2.5	11.2 ± 2.8	15.7 ± 1.9
TOC (mg/g)	13.6 ± 2.8	10.1 ± 0.3	14.6 ± 4.0	9.7 ± 0.6	7.6 ± 1.4	6.6 ± 0.8	16.2 ± 12.3

^aDetection Limit

FIGURE 4.33. SUMMARY OF AROMATIC HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN PRUDHOE BAY - GWYDYR BAY AREA SEDIMENTS.

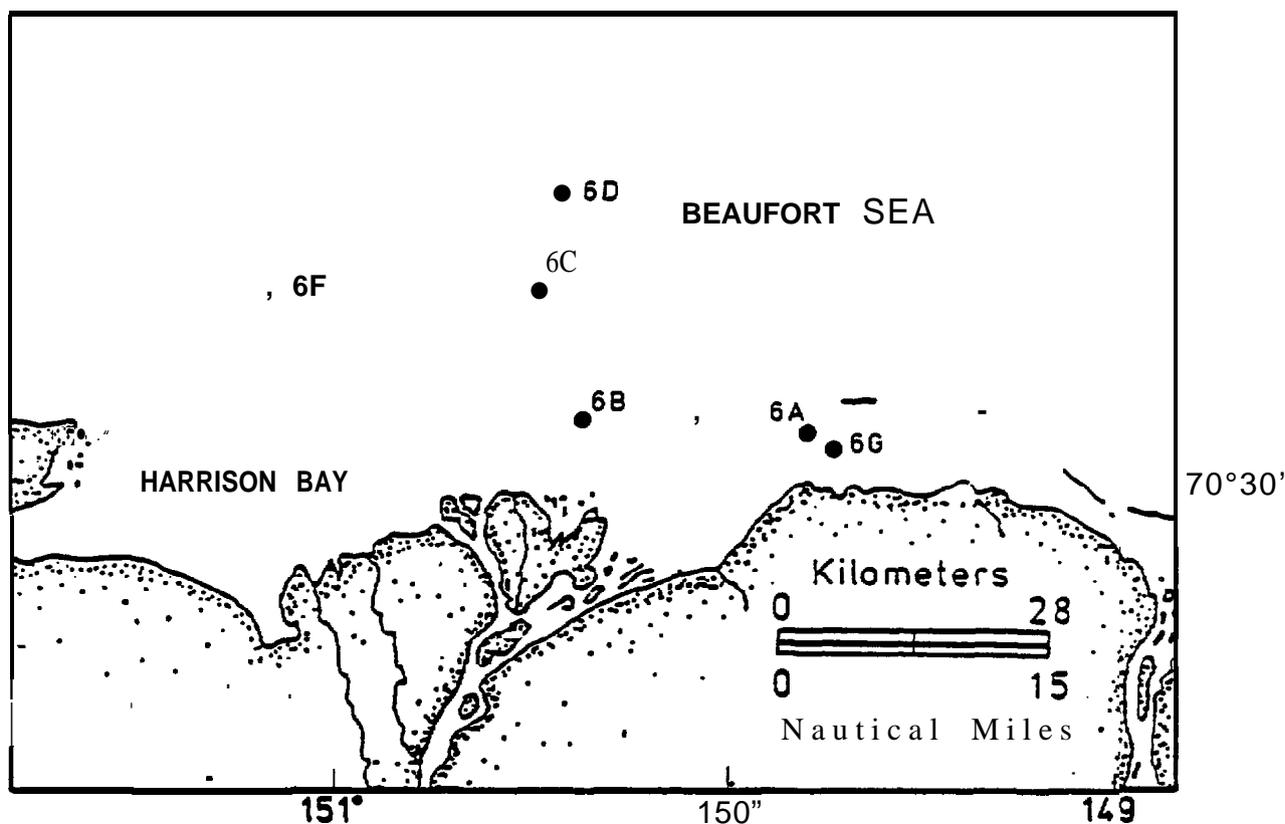


STATIONS

	<u>5(0)</u>	<u>5(1)</u>	<u>5(5)</u>	<u>5(10)</u>
AROMATIC HYDROCARBONS (µg/g)				
N	0.03 ± 0.01	0.02 ± 0.02	0.04 ± 0.04	0.08 ± 0.02
P	0.03 ± 0.01	< D.L. ^a	0.01 ± 0.04	< D.L.
D	< D.L.	0.01 ± 0.00	0.03 ± 0.01	0.02 ± 0.00
F	< D.L.	< D.L.	0.01 ± 0.01	0.03 ± 0.00
PAH	0.04 ± 0.02	0.02 ± 0.01	0.04 ± 0.03	0.06 ± 0.00
<hr/>				
% Mud	6.3 ± 5.9	1.0 ± 0.2	23.5 ± 12.6	20.5 ± 3.2
<hr/>				
TOC (mg/g)	3.9 ± 0.8	2.6 ± 0.7	4.9 ± 2.0	7.0 ± 1.6

^aDetection Limit

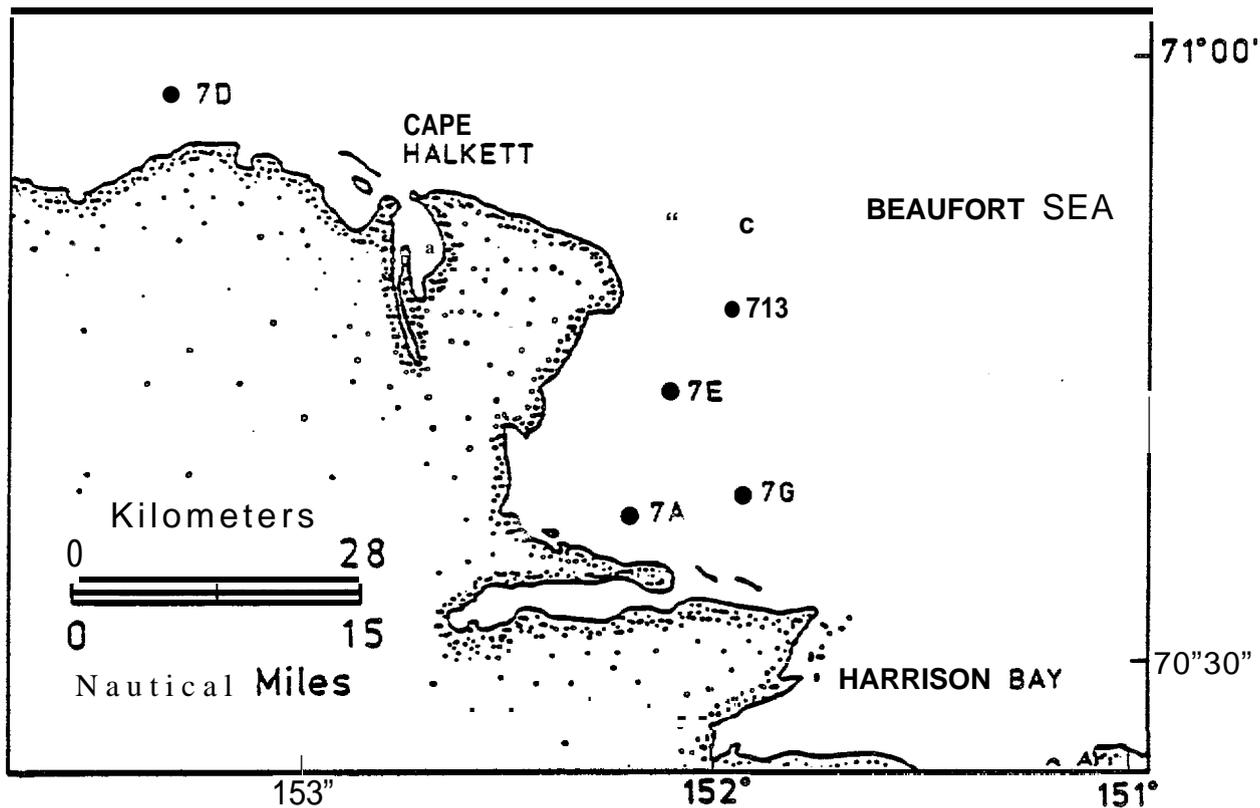
FIGURE 4.34. SUMMARY OF AROMATIC HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN ENDICOTT FIELD TRANSECT STATION SEDIMENTS.



STATIONS

	6A	6B	6C	6D	6F	6G
AROMATIC HYDROCARBONS (µg/g)						
N	0.42 ± 0.05	1.05 ± 0.14	0.37 ± 0.14	0.14 ± 0.16	0.22 ± 0.02	0.48 ± 0.02
P	0.29 ± 0.04	0.44 ± 0.01	0.25 ± 0.09	0.10 ± 0.11	0.14 ± 0.01	0.28 ± 0.01
D	0.06 ± 0.01	0.09 ± 0.01	0.05 ± 0.02	0.02 ± 0.02	0.03 ± 0.00	0.05 ± 0.00
F	0.12 ± 0.02	0.22 ± 0.02	0.11 ± 0.04	0.03 ± 0.04	0.06 ± 0.01	0.08 ± 0.02
PAH	0.26 ± 0.01	0.38 ± 0.02	0.23 ± 0.07	0.10 ± 0.10	0.11 ± 0.01	0.26 ± 0.03
% Mud						
% Mud	81.8 ± 6.0	83.7 ± 6.3	49.4 ± 19.7	17.6 ± 25.0	36.3 ± 6.6	79.1 ± 1.8
TOC (mg/g)						
TOC (mg/g)	13.4 ± 2.2	15.9 ± 6.4	8.4 ± 1.5	4.4 ± 1.7	7.6 ± 3.1	18.4 ± 0.7

FIGURE 4.35. SUMMARY OF AROMATIC HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN EAST HARRISON BAY SEDIMENTS.



STATIONS

	7A	7B	7C	7D	7E	7G
AROMATIC HYDROCARBONS ($\mu\text{g/g}$)						
N	0.46 \pm 0.08	0.01 \pm 0.02	0.66 \pm 0.26	0.18 \pm 0.17	0.74 \pm 0.13	0.19 \pm 0.16
P	0.23 \pm 0.02	0.07 \pm 0.01	0.40 \pm 0.13	0.21 \pm 0.20	0.37 \pm 0.06	0.22 \pm 0.19
D	0.04 \pm 0.00	0.01 \pm 0.00	0.09 \pm 0.04	0.04 \pm 0.04	0.06 \pm 0.02	0.03 \pm 0.02
F	0.07 \pm 0.02	0.02 \pm 0.01	0.10 \pm 0.03	0.05 \pm 0.04	0.10 \pm 0.03	0.02 \pm 0.02
PAH	0.25 \pm 0.03	0.06 \pm 0.00	0.13 \pm 0.11	0.11 \pm 0.10	0.30 \pm 0.06	0.11 \pm 0.10
% Mud	67.4 \pm 8.3	7.6 \pm 2.3	88.8 \pm 7.3	43.8 \pm 21.1	63.8 \pm 10.7	27.9 \pm 13.3
TOC (mg/g)	10.5 \pm 1.6	5.0 \pm 0.6	13.2 \pm 2.3	9.9 \pm 2.0	25.1 \pm 10.2	10.5 \pm 5.2

FIGURE 4.36. SUMMARY OF AROMATIC HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN WEST HARRISON BAY SEDIMENTS.

with Station 5(10). As found in Year-1, as well as for the Year-2 saturated hydrocarbon data, no concentration gradient away from the **Endicott** Field is obvious from the aromatics data.

Aromatics data for the six stations in East Harrison Bay are shown in Figure 4.35. The highest sediment aromatic hydrocarbon concentrations, not only in this region but also the entire **Study** Area, are clearly associated with Station 65. This station is located near the mouth of the **Colville** River. A transect out from the mouth of the river is represented by Stations **6B**, **6C**, and **6D**. As was observed in Year-1, an offshore concentration gradient is clearly indicated in all parameters, with the lowest values occurring at Station **6D**.

Figure 4.36 presents the data for West Harrison Bay (the "7" stations). In this region, high concentrations of aromatic hydrocarbons are found in sediments from Stations **7C** and **7E**. As determined in Year-1, the lowest levels of all aromatic parameters occur in Station **7B** sediments.

A comparison of the Year-1 and Year-2 aromatic hydrocarbon data, for the seven stations for which a complete set of replicates was analyzed in Year-1, is presented in Table 4.12. No significant increases from Year-1 to Year-2 in any parameter are noted. On the contrary, concentrations either similar to those detected in Year-1 or a decrease in Year-2 concentrations are observed.

Hydrocarbon concentrations were determined in both the **bulk** sediment and mud fraction at three stations (**1A**, **5(5)**, and **6D**). The aromatic hydrocarbon data for these stations are presented in Table 4.13. Concentrations for all parameters are approximately 2 to 20 times higher in the mud fraction than in the bulk sediment.

4.2.4 Aromatic Hydrocarbons in River and Peat Samples

Aromatic hydrocarbon concentrations in sediments collected from the **Sagavanirktok** River (Station **53**) in the central **Study** Area and the **Colville** River (Station **6H**) east of Harrison Bay are shown in Table 1.14. **Although** the mud content of the two river sediments is similar, the **Colville** River sediments are two to four times higher in aromatics than sediments from the **Sagavanirktok** River. TOC concentrations are five times higher in the sample from the **Colville** River.

Table 4.15 presents the concentrations of aromatics, percent mud, and TOC in shoreline peat samples collected throughout the **Study** Area. In contrast to the higher levels of saturated hydrocarbons in peat samples than in marine sediments, the concentrations of aromatics in the peat samples are similar to those in marine sediments. **Naphthalenes** (N), **dibenzothiophenes** (D), and **fluorenes** (F) range from less than detection limit to 0.18, 0.13, and 0.33 $\mu\text{g/g}$, respectively. **Phenanthrenes** range between 0.01 and 0.13 $\mu\text{g/g}$. The widest range of concentrations (0.01 -0.41 $\mu\text{g/g}$) occurs within the **PAHs**.

Except for **PAH**, the highest concentrations of aromatics are associated with the sample collected from Station **7H** on **Cape Halkett**. It is interesting to note that both the mud content (**8%**) and TOC concentration (**22.9 mg/g**) of the sample from this location are the lowest for any of the peat samples.

4.2.5 Hydrocarbons in Tissue Samples

Sam. Pies for tissue hydrocarbon analysis were collected from 12 stations throughout the **Study** Area. Four bivalve species (**Portlandia arctica**, **Astarte borealis**, **Cyrtodaria kurriana**, and **Macoma calcareo**) and one amphipod (**Anonyx** sp.) species were

TABLE 4.12. SUMMARY OF YEAR-1 AND YEAR-2 AROMATIC HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN REPLICATED YEAR-1 STATION SEDIMENTS.

	STATIONS					
	2F		3B		4A	
	YEAR-1	YEAR-2	YEAR-1	YEAR-2	YEAR-1	YEAR-2
AROMATIC HYDROCARBONS (ug/g)						
N	0.03 ± 0.01	0.05 ± 0.03	0.15 ± 0.05	0.19 ± 0.01	0.17 ± 0.02	0.09 ± 0.01
P	0.07 ± 0.02	0.06 ± 0.01	0.17 ± 0.05	0.16 ± 0.01	0.19 ± 0.01	0.08 ± 0.01
D	<D.L. ^a	<D.L.	0.02 ± 0.00	0.02 ± 0.00	0.04 ± 0.00	0.01 ± 0.00
F	0.01 ± 0.01	0.01 ± 0.01	0.03 ± 0.01	0.03 ± 0.00	0.04 ± 0.01	0.01 ± 0.00
PAH	0.03 ± 0.01	0.02 ± 0.01	0.08 ± 0.04	0.08 ± 0.01	0.10 ± 0.03	0.05 ± 0.02
% Mud	15.1 ± 3.6	13.3 ± 2.4	62.5 ± 3.7	74.3 ± 2.9	33.6 ± 18.8	33.9 ± 10.6
TOC (mg/g)	5.6 ± 1.0	4.7 ± 0.06	9.2 ± 0.5	7.9 ± 5.9	7.2 ± 1.0	13.7 ± 4.0

3

	STATIONS							
	5D		6C		6D		7A	
	YEAR-1	YEAR-2	YEAR-1	YEAR-2	YEAR-1	YEAR-2	YEAR-1	YEAR-2
AROMATIC HYDROCARBONS (ug/g)								
N	0.36 ± 0.07	0.29 ± 0.02	0.41 ± 0.33	0.37 ± 0.14	0.08 ± 0.03	0.14 ± 0.16	0.96 ± 0.87	0.46 ± 0.08
P	0.40 ± 0.03	0.16 ± 0.03	0.41 ± 0.25	0.25 ± 0.09	0.08 ± 0.03	0.10 ± 0.11	0.76 ± 0.66	0.23 ± 3.02
D	0.07 ± 0.01	0.04 ± 0.01	0.10 ± 0.09	0.25 ± 0.02	0.02 ± 0.00	0.02 ± 0.02	0.14 ± 0.13	0.04 ± 0.00
F	0.25 ± 0.01	0.05 ± 0.02	0.09 ± 0.06	0.11 ± 0.04	0.01 ± 0.01	0.03 ± 0.04	0.12 ± 0.11	0.07 ± 0.02
PAH	0.22 ± 0.08	0.16 ± 0.03	0.16 ± 0.07	0.13 ± 0.07	0.05 ± 0.01	0.10 ± 0.10	0.24 ± 0.13	0.25 ± 0.03
% Mud	72.5 ± 2.1	61.6 ± 5.6	30.5 ± 15.4	49.4 ± 19.7	10.8 ± 5.7	17.6 ± 25.0	65.4 ± 5.6	67.4 ± 8.3
TOC (mg/g)	29.2 ± 22.1	14.6 ± 4.0	6.2 ± 1.4	8.4 ± 1.5	3.8 ± 1.1	4.4 ± 1.7	11.4 ± 4.2	10.5 ± 1.6

^aDetection Limit

TABLE 4.13. SUMMARY OF AROMATIC HYDROCARBON **CONCENTRATIONS** IN THE BULK AND MUD FRACTION OF SEDIMENTS FROM SEVERAL STATIONS THROUGHOUT THE STUDY AREA.

AROMATIC HYDROCARBONS ($\mu\text{g/g}$)	STATIONS					
	1A		5(5)		6D	
	BULK	MUD	BULK	MUD	BULK	MUD
N	0.07 \pm 0.00	0.15 \pm 0.01	0.04 \pm 0.04	0.34 \pm 0.06	0.14 \pm 0.16	0.70 \pm 0.12
P	0.07 \pm 0.01	0.14 \pm 0.01	0.04 \pm 0.03	0.26 \pm 0.05	0.10 \pm 0.11	0.51 \pm 0.12
D	0.01 \pm 0.00	0.02 \pm 0.00	0.01 \pm 0.01	0.03 \pm 0.02	0.02 \pm 0.02	0.08 \pm 0.04
F	0.01 \pm 0.00	0.06 \pm 0.01	0.01 \pm 0.01	0.08 \pm 0.02	0.03 \pm 0.04	0.16 \pm 0.05
PAH	0.01 \pm 0.01	0.23 \pm 0.03	0.04 \pm 0.03	0.32 \pm 0.02	0.10 \pm 0.10	0.61 \pm 0.06

TABLE 4.14. SUMMARY OF AROMATIC HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN BULK RIVER SEDIMENTS.

	STATIONS	
	53 Sagavanirktok River	6H Colville River
AROMATIC HYDROCARBONS ($\mu\text{g/g}$)		
N	0.066	0.257
P	0.065	0.182
D	0.008	0.022
F	0.009	0.019
PAH	0.057	0.216
% Mud	15.50	15.44
TOC (mg/g)	12.80	65.50

TABLE 4.15. SUMMARY OF AROMATIC HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON CONCENTRATIONS IN BULK SHORELINE PEAT SAMPLES.

	STATIONS							
	1F	2G	2H	3D	5K	6J	7H	7J
AROMATIC HYDROCARBONS ($\mu\text{g/g}$)								
N	0.081	0.038	0.087	<D.L. ^a	0.004	0.024	0.182	0.006
P	0.089	0.055	0.078	0.010	0.034	0.013	0.129	0.030
D	0.023	0.011	0.018	0.009	<D.L.	<D.L.	0.032	<D.L.
F	0.015	0.013	0.016	<D.L.	<D.L.	<D.L.	0.329	<D.L.
PAH	0.409	0.051	0.213	0.161	0.015	0.160	0.037	0.010
% Mud	87.10	58.30	73.39	44.54	66.20	69.10	7.98	80.50
TOC (mg/g)	95.30	42.20	170.00	228.00	93.40	261.00	22.90	295.00

^aDetection Limit

obtained for analysis. Four replicates of tissue extract were analyzed by UV/F and, when an adequate amount of extract was available, four GC-FID and GC/MS replicates were also run.

The UV/F, saturated, and aromatic hydrocarbon data for the tissue samples are presented in Table 4.16 for the eastern Study Area stations and in Table 4.17 for the western Study Area stations. UV/F fluorescence at 355 nm was detected in the range of 0.7 to 8.9 $\mu\text{g/g}$ wet weight, where the lower levels are associated with Anonyx sp. and the higher concentrations are found in the bivalve samples. In contrast, the higher concentrations of saturated hydrocarbons occur in the amphipod samples and lower levels are found in the bivalves. Total alkane (TALK) and low molecular-weight alkane (LALK) concentrations range from 1.26 and 0.43 $\mu\text{g/g}$ wet weight to 38.46 and 36.20 $\mu\text{g/g}$ wet weight, respectively. Pristane tissue concentrations vary by three orders of magnitude (0.019-32.2 $\mu\text{g/g}$ wet weight), while phytane concentrations range from less than detection limit to 0.185 $\mu\text{g/g}$ wet weight. The highest tissue concentration of TOT is 78.3 $\mu\text{g/g}$ wet weight in Station 4B Anonyx samples and the lowest levels are 4.36 and 4.0 $\mu\text{g/g}$ wet weight in Astarte tissue.

Relatively lower concentrations of aromatic hydrocarbons were detected in the same tissues. Naphthalenes (N) range from 0.002 to 0.035 $\mu\text{g/g}$ wet weight in bivalves and between 0.004 to 0.015 $\mu\text{g/g}$ wet weight in amphipods. Phenanthrenes (P), dibenzothiophenes (D), fluorenes (F), and PAHs all range between less than detection limit to 0.025 $\mu\text{g/g}$ wet weight for all species.

Tables 4.18 and 4.19 summarize hydrocarbon concentrations in Astarte and Anonyx tissues, respectively. A comparison of Tables 4.18 and 4.19 shows that saturated hydrocarbons are 2 to 10 times higher in Anonyx than in the bivalve Astarte, but that the reverse is true for the aromatics. Astarte collected from Stations 1A+1B (Table 4.18) generally show the highest concentrations of hydrocarbons, while samples from Station 5H have the lowest levels of hydrocarbons in tissues. Table 4.19 shows that, among the Anonyx analyzed, the highest concentrations of saturates occur at stations in West Harrison Bay (Stations 7B, 7C, and 7E). Aromatic hydrocarbons are found in low levels in Anonyx tissues from all stations.

4.3 Auxiliary Parameters

4.3.1 Grain Size

Sediment grain size data for all sediment stations are shown in Table 4.20. Means \pm one standard deviation represent six replicate analyses at each station. Although the analyses determined individual phi size categories for each replicate sample, the data are grouped into gravel, sand, silt, and clay fractions for convenience of interpretation.

Silt and clay fraction means range from less than 1% for each fraction to 40% and 76%, respectively. The widest range, 7%-99%, is observed in the sand fraction, while gravel ranges between 0% and 30%.

As determined in Year-1, sediment textures in the Beau fort Sea are highly variable and few clear trends can be inferred from the data. Based on Year-2 data, sand-dominated sediments in the western Study Area seem to occur more frequently offshore (e.g., Stations 5E, 6D, 6C, and 6F), while sediments high in silt and clay (mud) are generally associated with stations nearer to shore (e.g., Stations 6A, 6B, 6G, 7A, 7E, and 7C). This trend is not obvious in the eastern Study Area. Stations having the highest gravel content (Stations 5(5), 4A, and 4C) occur in the Prudhoe Bay area, where sediments are also primarily sand-textured.

TABLE 4.16. SUMMARY OF HYDROCARBON CONCENTRATIONS IN TISSUE SAMPLES COLLECTED FROM STATIONS IN THE EASTERN STUDY AREA.

	STATIONS				
	<u>1A Portlandia^a</u>	<u>1A+1B Astartea</u>	<u>1A+1B+1E Anonyx^b</u>	<u>3A Astarte</u>	<u>4B Anonyx</u>
SATURATED HYDROCARBONS ($\mu\text{g/g}$ wet weight)					
TALK	6.90 \pm 7.41	5.15	10.91	3.61	10.53
LALK	0.43 \pm 0.31	2.85	3.25	2.18	2.04
Pristane	0.042 \pm 0.029	0.093	1.230	0.086	1.300
Phy tane	0.047 \pm 0.078	0.030	<D.L. ^c	0.024	0.028
TOT	36.17 \pm 55.26	10.30	42.60	7.83	78.30
UV/F (355 nm)	8.9 \pm 0.3	4.0:0.1	1.6 \pm 0.3	3.6 \pm 0.7	1.5 \pm 0.4
AROMATIC HYDROCARBONS ($\mu\text{g/g}$ wet weight)					
N	0.009 \pm 0.001	0.014	0.029	0.003	0.015
P	0.009 \pm 0.003	0.005	<D.L.	0.003	<D.L.
D	0.001 \pm 0.001	0.002	<D.L.	<D.L.	<D.L.
F	0.003 \pm 0.003	0.014	<D.L.	0.002	<D.L.
PAH	0.016 \pm 0.022	0.007	<D.L.	0.001	0.001

^aBivalve

^bAmphipod

^cDetection Limit

TABLE 4.17. SUMMARY OF HYDROCARBON CONCENTRATIONS IN TISSUE SAMPLES COLLECTED FROM STATIONS IN THE WESTERN STUDY AREA.

	STATIONS							
	5F Cyrtodaria ^a	5H Astarte ^a	6D Macoma ^a Astarte		6G Cyrtodaria Anonyx ^b		7B+7C Anonyx	7E Anonyx
SATURATED HYDROCARBONS ($\mu\text{g/g}$ wet weight)								
TALK	3.74 \pm 5.08	2.29 \pm 3.29	13.06 \pm 16.02	1.26	3.62	14.54 \pm 1.03	27.33	38.46
LALK	0.41 \pm 0.03	0.27 \pm 0.04	0.99 \pm 0.85	0.59	1.89	13.67 \pm 0.79	23.80	36.20
Pristane	0.019 \pm 0.015	0.021 \pm 0.021	0.096 \pm 0.074	0.020	0.093	12.02 \pm 1.10	20.70	32.20
Phytane	0.018 \pm 0.021	0.008 \pm 0.001	0.185 \pm 0	0.006	0.052	0.025 \pm 0.001	0.037	0.057
TOT	19.53 \pm 27.86	4.36 \pm 4.69	43.35 \pm 54.80	4.00	19.30	18.30 \pm 2.84	39.80	50.90
UV/F (355 nm)	4.0 \pm 0.4	3.3 \pm 0.2	4.5 \pm 3.2	4.2 \pm 1.0	4.6 \pm 1.0	0.9 \pm 0.3	1.0 \pm 0.4	0.7 \pm 0
AROMATIC HYDROCARBONS ($\mu\text{g/g}$ wet weight)								
N	0.002 \pm 0.001	0.002 \pm 0.002	0.035 \pm 0.041	0.007	0.004	0.009 \pm 0.006	0.004	0.008
P	0.002 \pm 0.001	0.002 \pm 0.002	0.002 \pm 0.003	0.004	0.005	0.001 \pm 0.001	<D.L.	0.001
D	<D.L. ^c	<D.L.	0.001 \pm 0.001	0.002	<D.L.	<D.L.	<D.L.	<D.L.
F	0.001 \pm 0.001	0.002 \pm 0.001	0.025 \pm 0.036	0.002	<D.L.	<D.L.	<D.L.	<D.L.
PAH	0.002 \pm 0.001	0.002 \pm 0.001	0.007 \pm 0.008	0.019	0.005	<D.L.	<D.L.	<D.L.

^aBivalve

^bAmphipod

^cDetection Limit

TABLE 4.18. SLIMMARY OF HYDROCARBON CONCENTRATIONS IN TISSUE OF THE BIVALVE, Astarte sp. COLLECTED THROUGHOUT THE STUDY AREA.

	STATIONS			
	<u>1A+1B</u>	<u>3A</u>	<u>5H</u>	<u>6D</u>
SATURATED HYDROCARBONS (<u>µg/g wet weight</u>)				
TALK	5.15	3.61	2.29 ± 3.29	1.26
LALK	2.85	2.18	0.27 ± 0.04	0.59
Pristane	0.093	0.086	0.021 ± 0.021	0.020
Phytane	0.030	0.024	0.008 ± 0.001	0.006
TOT	10.30	7.83	4.36 ± 4.69	4.00
UV/F	4.0 ± 0.1	3.6 ± 0.7	3.3 ± 0.2	4.2 ± 1.0
AROMATIC HYDROCARBONS (<u>µg/g wet weight</u>)				
N	0.014	0.003	0.002 ± 0.002	0.007
P	0.005	0.003	0.002 ± 0.002	0.004
D	0.002	<D.L. ^a	<D.L.	0.002
F	0.014	0.002	0.002 ± 0	0.002
PAH	0.007	0.001	0.002 ± 0.001	0.019

^aDetection Limit

TABLE 4.19. SUMMARY OF HYDROCARBON CONCENTRATIONS IN TISSUE OF THE AMPHIPOD Anonyx sp. COLLECTED THROUGHOUT THE STUDY AREA.

	STATIONS				
	<u>1A+1B+1E</u>	<u>4B</u>	<u>6G</u>	<u>7B+7C</u>	<u>7E</u>
SATURATED HYDROCARBONS					
<u>($\mu\text{g/g}$ wet weight)</u>					
TALK	10.91	10.53	14.54 + 1.03	27.33	38.46
LALK	3.25	2.04	13.67 + 0.79	23.80	36.20
Pristane	1.230	1.300	12.02 + 1.10	20.70	32.20
Phytane		0.028	0.025	0.037	0.057
TOT	42.60	78.30	18.30 + 2.84	39.80	50.90
UV/F (355 nm)	1.6 \pm 0.3	1.5 \pm 0.4	0.9 \pm 0.3	1.0 \pm 0.4	0.7 \pm 0
AROMATIC HYDROCARBONS					
<u>($\mu\text{g/g}$ wet weight)</u>					
N	0.029	0.015	0.009	0.004	0.008
P	<D.L. ^a	<D.L.	0.001+ 0.001	<D.L.	0.001
D	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.
F	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.
PAH	<D.L.	0.001	<D.L.	<D.L.	<D.L.

^aDetection Limit

TABLE 4.20. SUMMARY OF GRAIN SIZE DATA FOR ALL SEDIMENT STATIONS.

STATION	% GRAVEL	% SAND	% SILT	% CLAY
1A	0.08 ± 0.14	31.22:11.54	47.81 ± 5.69	20.89 ± 5.71
1B	0.38 ± 0.24	84.67 ± 5.15	9.24 ± 3.43	5.70 ± 1.97
1C	0.69 ± 0.12	29.35 ± 3.08	36.71 ± 0.78	33.24 ± 3.48
1D	0.05 ± 0.05	83.02 ± 5.42	13.21 ± 3.53	3.71 ± 1.87
1E	0	7.18 ± 2.67	76.50 ± 2.10	16.32 ± 0.80
2A	0	8.21 ± 1.27	73.82 ± 3.08	17.96 ± 4.10
2B	0.10 ± 0.17	75.58 :34.13	18.82 ± 20.56	10.81 ± 17.02
2C	0.58 ± 0.66	28.30 ± 0.98	34.61 ± 1.39	36.51 ± 0.8S
2D	9.44 ± 11.83	56.94 ± 38.66	21.57 ± 27.98	12.05 ± 2.00
2E	0	22.41 ± 14.20	45.40 ± 7.60	32.19 ± 6.61
2F	0.12 ± 0.10	86.56 ± 2.37	9.58 ± 1.67	3.74 ± 0.88
3A	0.04 ± 0.06	53.88 ± 0.51	33.19 ± 0.81	12.88 ± 0.28
3B	0.18 ± 0.29	25.56 ± 2.70	58.14 ± 1.61	16.13 ± 1.77
4A	30.18 ± 4.89	35.94 ± 5.77	16.81 ± 3.42	17.07 ± 7.19
4B	1.04 ± 1.69	92.81 ± 2.28	4.29 ± 1.23	1.86 ± 0.53
4C	21.22 ± 14.43	72.49 ± 12.45	4.07 ± 2.19	2.23 ± 0.99
5(o)	0	93.67 ± 5.85	5.25 ± 4.81	[.08 ± 1.05
5(1)	0.02 ± 0.03	98.98 ± 0.17	0.63 ± 0.13	0.37 ± 0.12
5(5)	12.78 ± 17.60	63.69 ± 9.37	13.93 ± 6.99	9.59 ± 5.67
5(10)	0.02 ± 0.03	79.50 ± 3.23	17.13 ± 4.43	3.35 ± 2.04
5A	6.16 ± 6.91	50.90 ± 1.41	34.01 ± 8.14	8.93 ± 0.85
5B	1.22 ± 1.98	21.76 ± 17.51	36.69 ± 8.56	40.31 ± 10.79
5I3	0.26 ± 0.45	38.10 ± 5.20	54.52 ± 7.30	7.12 ± 3.23
5E	0.42 ± 0.52	59.33 ± 14.75	17.43 ± 6.00	22.81 ± 9.38
5F	0.90 ± 0.78	56.93 ± 2.88	35.04 ± 2.57	7.12 ± 0.23
5G	0.61 ± 1.06	88.23 ± 3.62	9.11 ± 3.18	2.06 ± 0.43
5H	2.53 ± 3.53	81.78 ± 2.78	12.22 ± 1.66	3.45 ± 0.65
6A	1.02 ± 1.46	17.26 ± 6.34	65.33 ± 5.81	16.39 ± 0.24
6B	0	16.33 ± 6.24	63.12 ± 3.96	20.55 ± 4.00
6C	0.16 ± 0.03	50.40 ± 19.82	24.51 ± 9.85	24.93 ± 10.17
6D	0.03 ± 0.05	32.36 ± 25.06	8.77 ± 12.35	8.54 ± 12.66
6F	0.04 ± 0.03	63.63 ± 6.65	23.22 ± 4.46	13.06 ± 2.40
6G	0.36 ± 0.62	20.56 ± 2.33	65.25 ± 4.59	13.84 ± 3.19
7A	0	32.57 ± 8.34	59.95 ± 8.58	7.47 ± 0.2s
7B	0.07 ± 0.07	92.28 ± 2.32	5.69 ± 1.85	1.97 ± 0.54
7C	0.33 ± 0.39	10.91 ± 7.17	53.40 ± 6.14	35.36 ± 3.46
7D	0.05 ± 0.05	56.11 ± 21.10	27.68 ± 12.72	16.16 ± 8.84
7E	0.07 ± 0.12	36.15 ± 10.59	50.77 ± 10.61	13.01 ± 2.81
7G	0	72.08 ± 13.32	22.63 ± 11.80	5.30 ± 3.78

A comparison of the sediment texture of stations that were sampled in both Year-1 and Year-2 is presented in **Table 4.21**. With the exception of two stations (Station 2E and Station 513), grain size means **generally** do not differ significantly from Year-1 to Year-2. Ranges for each size fraction are very similar in both years.

4.3.2 Total Organic Carbon

TOC data for all Year-2 station sediments are presented in Table 4.22. As found in Year-1, the range in TOC concentrations throughout the Study Area is variable and covers two orders of magnitude (2.6 -25. f **mg/g**). There does not appear to be a regional trend in **TOC** distribution as observed in Year-1 , or correlation with sediment grain size (e.g., Stations 2E and 4C have same TOC concentration but more than a ten-fold difference in sediment mud content).

A comparison of the Year-1 and Year-2 **TOC** concentrations is shown in Table 4.23. At 13 stations, Year-2 **TOC** concentrations are approximately equal to the Year- 1 levels. Concentrations increased at seven stations and decreased at six stations.

4.4 Quality Control Results

4.4.1 Metals

Quality control (**QC**) measures for the metals analyses included analysis of replicate procedural **blanks** and reagent **blanks**, determinations of analytical accuracy and precision, and analysis of metals by more than one technique.

Detection limits were calculated from procedural blanks for sediment and tissue digestion using twice the standard deviation of the mean for replicate blanks. These results are shown in Tables 4.24 and 4.25 for sediments and tissues, respectively. The detection limits are in the range of one-tenth to several **ppm** dry weight. Reagent blanks were determined prior to analysis of the field samples to verify that the detection limits would not be adversely affected by reagents. Data for these analyses are in Tables 4.26 and 4.27 for sediments and tissues, respectively.

Accuracy was determined by analysis of Standard Reference Material (**SR M**) sediment standards MESS-1 and NBS-1 646, and oyster tissue standard NBS- 1566. Results of five replicate analyses of these standards and the certified, or best, value are shown in Tables 4.28 through 4.30. Generally, the range of values obtained overlaps the range of best values, verifying that the methods employed are accurate.

Approximately 10 percent of the sediment samples were analyzed by both XRF and ICAP. The XRF technique does not require sediment dissolution. Comparisons of the data obtained by the two techniques are shown in Table 4.31. The means of triplicate field grab samples are **usually within two standard deviations** for the different techniques.

4.4.2 Hydrocarbons

QC in the hydrocarbon program included initial and ongoing determinations of analytical precision and accuracy through the analysis of **SR Ms**, method blanks, spiked blank samples, and matrix spike sam pies.

Before analysis of the field samples, the laboratory participated in a laboratory **intercalibration** exercise consisting of triplicate analysis of interim reference sediments and mussel homogenate. The **intercalibration** was administered by National Oceanic and Atmospheric Administration National Marine Fisheries Service (NOAA/N MF) Laboratory in Seattle.

TABLE 4.21. COMPARISON OF YEAR-1 AND YEAR-2 SEDIMENT GRAIN SIZE

STATION	% GRAVEL		% SAND		% SILT		% CLAY	
	Year-1	Year-2	Year-1	Year-2	Year-1	Year-2	Year-1	Year-2
2E	0.22 ± 0.20	0	92.00 ± 1.60	22.41 ± 14.20	4.64 ± 0.68	45.60 ± 7.60	2.95 ± 0.80	32.19 ± 6.61
2F	0.04 ± 0.07	0.12 ± 0.10	84.84 ± 3.55	86.56 ± 2.37	10.12 ± 2.99	9.58 ± 1.67	4.58 ± 1.50	3.74 ± 0.88
3A	0.01 ± 0.02	0.04 ± 0.06	58.03 ± 1.79	53.88 ± 0.51	28.18 ± 1.57	33.19 ± 0.81	13.77 ± 1.15	12.88 ± 0.28
3B	0.30 ± 0.59	0.18 ± 0.29	34.46 ± 4.22	25.56 ± 2.70	46.39 ± 3.30	58.14 ± 1.61	18.45 ± 1.22	16.13 ± 1.77
4A	36.44 ± 19.76	30.18 ± 4.89	29.91 ± 8.16	35.94 ± 5.77	16.97 ± 6.71	16.81 ± 3.42	15.80 ± 10.5	17.07 ± 7.19
4B	3.19 ± 6.33	1.04 ± 1.69	89.17 ± 5.89	92.81 ± 2.28	3.48 ± 1.57	4.29 ± 1.23	3.05 ± 2.09	1.86 ± 0.83
4C	26.09 ± 19.05	21.22 ± 14.43	56.88 ± 22.90	72.49 ± 12.45	8.73 ± 3.31	4.07 ± 2.19	7.29 ± 4.01	2.23 ± 0.99
5A	0.05 ± 0.10	6.16 ± 6.91	27.55 ± 9.99	50.90 ± 1.41	51.02 ± 8.84	34.01 ± 8.14	21.72 ± 1.96	8.93 ± 0.81
5B	0.01 ± 0.02	1.22 ± 1.98	96.92 ± 0.95	21.76 ± 17.51	1.72 ± 0.47	36.69 ± 8.56	1.60 ± 0.97	40.31 ± 10.79
5D	1.01 ± 1.33	0.26 ± 0.45	25.70 ± 2.60	38.10 ± 5.20	58.92 ± 3.63	54.52 ± 7.30	13.56 ± 1.26	7.12 ± 3.23
5E	2.18 ± 1.84	0.42 ± 0.52	68.50 ± 36.74	59.33 ± 14.75	9.41 ± 10.53	17.43 ± 6.00	18.96 ± 23.41	22.81 ± 9.38
5F	4.57 ± 5.59	0.90 ± 0.78	34.08 ± 7.43	56.93 ± 2.88	51.00 ± 4.28	35.04 ± 2.57	10.35 ± 2.20	7.12 ± 3.21
5G	0.08 ± 0.16	0.61 ± 1.06	81.58 ± 3.05	88.23 ± 3.62	9.72 ± 1.50	9.11 ± 3.18	7.78 ± 1.56	2.06 ± 0.4
5(I)	1.08 ± 1.62	0.02 ± 0.03	88.01 ± 1.80	98.98 ± 0.17	5.34 ± 1.99	0.63 ± 0.13	4.21 ± 1.27	0.37 ± 0.12
5(S)	0.32 ± 0.28	12.78 ± 17.60	63.77 ± 2.42	63.69 ± 9.37	23.73 ± 2.70	13.93 ± 6.99	12.66 ± 2.14	9.59 ± 5.67
5(10)	0.03 ± 0.06	0.02 ± 0.03	65.07 ± 14.71	79.50 ± 3.23	22.44 ± 8.53	17.13 ± 4.43	11.23 ± 3.36	3.35 ± 2.04
6A	0.24 ± 0.18	1.02 ± 1.46	33.47 ± 3.50	17.26 ± 6.34	48.65 ± 3.02	65.33 ± 5.81	17.85 ± 1.58	16.39 ± 0.24
6B	0	0	11.37 ± 8.48	16.33 ± 6.24	62.80 ± 5.62	63.12 ± 3.96	28.80 ± 1.55	20.55 ± 4.00
6C	0.16 ± 0.16	0.16 ± 0.03	69.00 ± 15.53	50.40 ± 19.82	12.29 ± 7.93	24.51 ± 9.85	16.18 ± 7.27	24.93 ± 10.17
6D	0.10 ± 0.18	0.03 ± 0.05	89.03 ± 5.80	82.36 ± 25.06	4.33 ± 2.25	8.77 ± 12.38	6.54 ± 3.02	8.84 ± 12.66
6F	0.34 ± 0.38	0.04 ± 0.03	34.53 ± 26.53	63.68 ± 6.65	32.86 ± 11.88	23.22 ± 4.46	28.62 ± 13.42	13.06 ± 2.40
7A	0.01 ± 0.03	0	34.58 ± 5.60	32.57 ± 8.34	58.05 ± 4.12	59.95 ± 8.58	7.46 ± 1.80	7.47 ± 0.28
7B	0	0.07 ± 0.07	86.68 ± 4.52	92.28 ± 2.32	8.02 ± 2.83	5.69 ± 1.85	5.30 ± 1.96	1.97 ± 0.54
7C	0.35 ± 0.56	0.33 ± 0.39	15.07 ± 1.79	10.91 ± 7.17	44.42 ± 1.93	53.40 ± 6.14	40.17 ± 2.61	35.36 ± 3.46
7E	0.51 ± 1.01	0.07 ± 0.12	31.72 ± 2.88	36.15 ± 10.59	54.95 ± 4.05	50.77 ± 10.61	13.26 ± 1.55	13.01 ± 2.81
7G	0	0	89.95 ± 1.01	72.08 ± 13.32	8.83 ± 0.57	22.63 ± 11.80	1.24 ± 0.33	5.30 ± 3.78

TABLE 4.22. TOTAL ORGANIC CARBON MEANS AND STANDARD DEVIATIONS, AND PERCENT SILT + CLAY FOR ALL SEDIMENT STATIONS.

STATION	TOC (mg g ⁻¹)	% MUD
1A	11.7 ± 2.0	68.70
1B	6.6 ± 1.4	14.94
1C	9.6 ± 0.8	69.95
1D	7.1 ± 2.9	16.92
1E	11.7 ± 1.5	92.82
2A	16.9 ± 5.9	91.79
2B	10.2 ± 3.2	24.32
2C	10.4 ± 1.6	70.33
2D	10.4 ± 7.1	33.62
2E	10.6 ± 2.1	77.59
2F	4.7 ± 0.6	13.32
3A	10.8 ± 0.4	46.07
3S	11.2 ± 0.3	74.27
464	13.7 ± 4.0	33.88
4B	4.7 ± 1.2	6.14
4C	10.6 ± 0.8	6.31
5A	13.6 ± 2.8	42.94
5B	10.1 ± 0.3	77.00
SD	14.6 ± 4.0	61.64
5E	9.7 ± 0.6	40.24
5F	7.6 ± 1.5	42.16
5G	6.6 ± 0.8	11.17
5H	16.2 ± 12.3	15.67
5(o)	3.9 ± 0.8	6.33
5(1)	2.6 ± 0.7	1.00
5(5)	4.9 ± 2.0	23.52
5(10)	7.0 ± 1.6	20.4s
6A	13.4 ± 2.2	81.71
6B	15.9 ± 6.4	83.66
6C	8.4 ± 1.5	49.43
6D	4.4 ± 1.7	17.61
6F	18.4 ± 0.7	36.28
6G	6.0 ± 0.5	79.09
7A	10.5 ± 1.6	67.44
7B	4.6 ± 0.8	7.65
7C	13.2 ± 2.3	88.76
7D	9.9 ± 2.0	43.84
7E	25.1 ± 10.2	63.78
7G	10.5 ± 5.2	27.92

TABLE 4.23. COMPARISON OF YEAR-1 AND YEAR-2 SEDI-
MENT TOTAL ORGANIC CARBON CONTENT.

STATION	YEAR-1 TOC (mg g ⁻¹)	YEAR-2 TOC (mg g ⁻¹)
2E	2.4 ± 0.2	10.6 ± 2.1
2F	5.6 ± 1.0	4.7 ± 0.6
3A	8.4 ± 0.6	10.8 ± 0.4
3B	9.2 ± 0.5	11.2 ± 0.3
4A	7.2 ± 1.0	13.7 ± 4.0
4B	3.0 ± 0.8	4*7 ± 1.2
4C	3.1 ± 1.6	10.6 ± 0.8
5A	10.1 ± 0.2	13.6 ± 2.8
5B	2.1 ± 0.3	10.1 ± 0.3
5D	29.2 ± 2.1	14.6 ± 4.0
5E	4.5 ± 3.9	9.7 ± 0.6
5F	17.0 ± 2.2	7.6 ± 1.5
5G	6.4 ± 1.8	6.6 ± 0.8
5(1)	4.5 ± 0.9	2.6 ± 0.7
5(5)	9.7 ± 4.6	4.9 ± 2.0
5(10)	12.9 ± 9.2	7.0 ± 1.6
6A	11.5 ± 1.3	13.4 ± 2.2
6B	18.0 ± 0.7	15.9 ± 6.4
6C	6.2 ± 1.4	8.4 ± 1.5
6D	3.8 ± 1.1	4.4 ± 1.7
6F	10.5 ± 3.4	18.4 ± 0.7
7A	11.4 ± 4.2	10.5 ± 1.6
7B	5.6 ± 0.8	4.6 ± 0.8
7C	13.4 ± 0.6	13.2 ± 2.3
7E	17.3 ± 1.8	25.1 ± 10.2
7G	26.3 ± 10.2	10.5 ± 5.2

TABLE 4.24. RESULTS OF FIVE REPLICATE ANALYSES OF PROCEDURAL BLANKS FOR SEDIMENT DIGESTION.

	Metals ($\mu\text{g/g}$ dry weight)						
	Ba	Cd	Cr	Cu	Pb	v	Zn
	0.0	0.02	0.0	0.7	0.42	0.5	1.5
	0.0	0.01	0.0	0.6	0.34	0.0	0.0
	0.0	0.02	0.0	0.0	0.25	0.0	0.0
	0.8	0.01	0.1	0.4	0.43	0.0	1.3
	0.7	0.01	0.1	0.9	0.26	0.0	0.5
Mean	0.3	0.014	0.04	0.52	0.34	0.1	0.46
S.D.	0.4	0.005	0.05	0.31	0.08	0.2	0.55
CV(%)	133	35	122	59	22	200	120
Detection Limit	0.8	0.010	0.10	0.62	0.16	0.4	1.1

TABLE 4.25. RESULTS OF FIVE REPLICATE ANALYSES OF PROCEDURAL BLANKS FOR TISSUE DIGESTION.

	Metals ($\mu\text{g/g}$ dry weight)						
	Ba	Cd	Cr	Cu	Pb	v	Zn
	0.0	0.10	0.60	0.2	0.31	0.2	0.2
	0.0	0.10	0.60	0.0	0.36	0.0	0.1
	0.0	0.10	0.63	0.0	0.30	0.0	0.0
	0.0	0.10	0.58	0.0	0.37	0.0	0.0
	0.0	0.10	0.60	0.1	0.36	0.4	3.2
Mean	0.0	0.10	0.60	0.06	0.34	0.12	0.7
S.D.		0.00	0.02	0.08	0.03	0.16	1.3
Cv (%)		0	3	133	9	133	179
Detection Limit	0.2	0.2	0.04	0.16	0.06	0.32	2.6

TABLE 4.26. RESULTS OF FIVE REPLICATE ANALYSES OF REAGENTS TO ESTABLISH REAGENT BLANK FOR SEDIMENT DIGESTION.

	Metals ($\mu\text{g/g}$ dry weight)						
	Ba	Cd	Cr	Cu	Pb	v	Zn
	0.0	0.02	0.0	0.0	0.43	0.4	0.0
	0.0	0.02	0.0	0.0	0.68	0.2	0.1
	0.0	0.02	0.0	0.0	0.51	0.5	0.0
Mean	0.0	0.02	0.0	0.0	0.54	0.4	0.03
S.D.	0.0	0	0.0	0.0	0.10	0.1	0.05
Cv (%)	0	0	0	0	19	25	157

TABLE 4.27. RESULTS OF FIVE REPLICATE ANALYSES OF REAGENTS TO ESTABLISH REAGENT BLANK FOR TISSUE DIGESTION.

	Metals ($\mu\text{g/g}$ dry weight)						
	Ba	Cd	Cr	Cu	Pb	v	Zn
	0.0	0.09	0.07	0.6	0.27	0.0	0.2
	0.0	0.09	0.23	0.4	0.37	0.0	2.9
	0.0	0.09	0.17	0.2	0.36	0.2	0.0
	0.1	0.09	0.08	0.4	0.33	0.0	1.6
	0.0	0.09	0.10	0.0	0.28	0.0	0.3
Mean	0.02	0.09	0.13	0.32	0.32	0.04	1.0
S. D.	0.04	0.00	0.06	0.20	0.04	0.08	1.1
CV (%)	200	0	47	64	13	200	110

TABLE 4.28. RESULTS OF FIVE REPLICATE ANALYSES OF NBS-1646 STANDARD REFERENCE SEDIMENT.

	Metals ($\mu\text{g/g}$ dry weight)						
	Ba	Cd	Cr	Cu	Pb	v	Zn
	466	0.40	96	26*4	29.8	122	198
	437	0.44	81	22.3	28.9	109	186
	441	0.38	80	20.2	27.9	104	154
	396	0.41	86	21.8	27.9	105	164
	369	0.38	86	20.5	28.9	103	154
Mean	422	0.40	86	22.2	28.7	109	171
S.D.	35	0.02	6	2*2	0.7	7	18
Cv (%)	8	5	7	10	3	6	10
Best Value		0.36	76	18	28.2	94	138
S.D.		0.07	3	3	1.8	1	6

TABLE 4.29. RESULTS OF FIVE REPLICATE ANALYSES OF MESS-1
STANDARD REFERENCE SEDIMENT.

	Metals ($\mu\text{g/g}$ dry weight)						
	Ba	Cd	Cr	Cu	Pb	v	Zn
	287	0.79	59	30.8	35.6	85	229
	296	0.76	62	31.2	36.6	86	222
	283	0.71	60	29.2	37.5	83	206
	272	0.71	63	28.7	37.5	81	208
	312	0.71	60	37.6	35.2	101	250
Mean	290	0.74	61	31.5	36.5	87	223
s. D.	13	0.03	2	3.2	0.9	7	16
Cv (%)	5	4	3	10	3	8	7
Best Value	270	0.59	71	25.1	34.0	72.4	191
S.D.		0.10	11	3.8	6.1	5.3	17

TABLE 4.30. RESULTS OF FIVE REPLICATE ANALYSES OF OYSTER STANDARD 1566 REFERENCE TISSUE.

	Metals ($\mu\text{g/g}$ dry weight)						Zn
	Ba	Cd	Cr	Cu	Pb	v	
	5.4	3.44	0.52	67.7	0.52	2.1	936
	5.5	3.86	0.48	67.2	0.48	2.2	926
	5.6	3.76	0.60	66.4	0.48	2.2	903
	5.3	3.65	0.51	65.5	0.45	2.3	888
	5.2	3.69	0.40	64.8	0.47	2.4	885
Mean	5*4	3.68	0.50	66.3	0.48	2.2	908
S.D.	0.1	0.14	0.06	1.1	0.02	0.1	20
Cv (%)	3	4	13	2	4	5	2
Best Value	N/A	3.5	0.69	63.0	0.48	N/A	852
S*D.		0.4	0.27	3.5	0.04		14

TABLE 4.31. COMPARISON OF THE RESULTS USING DIFFERENT ANALYTICAL TECHNIQUES FOR DETERMINATION OF THE CONCENTRATION OF METALS IN SEDIMENTS.

	Metals ($\mu\text{g/g}$ dry weight)					
	Ba	Cr	Cu	Pb	v	Zn
<u>Station 5A mud fraction (3 replicate composites)</u>						
Mean XRF	641	87	21.8	8.6	87	83
S. D.	17	2	3.0	1.2	10	4
Mean ICAP	419	63	18.6	-	97	78
S. D.	82	1	0.3	-	2	1
Mean ZGFAA				11.3	-	-
S. D.				0.6	-	-
<u>Station 5D mud fraction (3 replicate composites)</u>						
Mean XRF	423	111	18.1	6.7	119	83
S. D.	3	11	1.3	1.1	9	3
Mean ICAP	203	62	17.3	-	88	82
S. D.	150	4	0.9	-	5	2
Mean ZGFAA				3.3	-	-
S. D.				0.6	-	-
<u>Station 6B mud fraction (3 replicate composites)</u>						
Mean XRF	668	113	33.6	14.1	136	113
S. D.	67	12	2.1	1.9	9	7
Mean ICAP	523	90	31.9	-	143	117
S. D.	35	2	0.3	-	5	2
Mean ZGFAA				15.4	-	-
S. D.				1.0	-	-

Results of BNEMRL participation are shown in Tables 4.32 through 4.35. A comparative set of reference data for relatively few **analytes** (PAH only) is presented in Table 4.36. A direct comparison of the parent aromatic hydrocarbon compounds reveals that, although preparation and analysis methods differed considerably from those employed by NOAA, the concentrations of PAH detected by BNEMRL are virtually identical to PAH levels reported by the participating NOAA laboratories. NOAA laboratories utilized **GC-FID** for PAH analysis, a technique that necessitates size-exclusion chromatography for the preparation of sample extracts prior to analysis. This method is useful for the identification of parent 2- to 5-ring compounds. However, for programs such as the **BSMP**, this type of data set is too limited for detailed **geochemical** characterization of the sediment and for determination of petroleum-related additions to sediments and tissues.

Ongoing determinations of precision and accuracy were carried out through the analysis of procedural blanks, spiked blanks, and triplicate analyses of spiked samples. Procedural blank samples were analyzed along with every batch of sediment and tissues processed in the laboratory. A batch of sediment (including peat and mud fractions) generally consisted of 9 to 12 field samples plus the appropriate QC samples. A batch of tissue samples usually included four to six field samples plus the QC samples. The results of these analyses are presented in Tables 4.37 through 4.39. Sediment samples ranged in weight from 53-113 g dry weight, generally exceeding 80 g. The procedural blank data are normalized to 50 g dry weight for direct comparison with the survey data. The wet weight of tissue samples ranged from 3.6-15.3 g and generally exceeded 10 g. Tissue blank data are normalized to 10 g wet weight for direct comparison to the survey data. Method detection limits (**MDL**) determined by the instrument calibration range for the above sample sizes for individual **n-alkanes** are 0.0002 $\mu\text{g/g}$ dry weight and 0.0010 $\mu\text{g/g}$ wet weight for sediment and tissue, respectively. Corresponding MDL for individual PAH are 0.001 $\mu\text{g/g}$ dry weight, and 0.005 $\mu\text{g/g}$ wet weight. Hydrocarbon data that have been reported lower than the MDL represent detectable concentrations, but those for which an acceptable calibration cannot be obtained by present methods.

Procedural blanks analyzed by **GC-FID** revealed hydrocarbon concentrations ranging from 0.06 to 0.60 $\mu\text{g/g}$ dry weight and 0.1 to 1.3 $\mu\text{g/g}$ wet weight for sediment and tissue analyses, respectively. The same samples analyzed by **GC/MS** revealed total PAH concentrations ranging from less than detection limit to 0.064 $\mu\text{g/g}$ dry weight and from 0.001 to 0.041 $\mu\text{g/g}$ wet weight for sediments and tissues, respectively. Except for tissue PAH, all procedural blanks represented less than 10% of the total hydrocarbons (saturates or aromatics) found in the samples accompanying the blanks. Since many tissue PAH levels are extremely low, approaching MDL, levels found in these samples are similar to those found in the blanks. However, tissue PAH levels are reported uncorrected for laboratory background. Analysis of procedural blanks by **GC-FID** revealed the presence of small peaks eluting with undecane (**n-C₁₁**) and near pentacosane (**n-C₂₅**). The potential interferences from peaks at **n-C₂₅** were considered minimal. All field samples were reviewed for the presence of contamination at **n-C₁₁** and corrections made, if necessary, in the calculation of the hydrocarbon parameters containing this peak. PAHs generally present in procedural blanks included **naphthalene**, **phenanthrene**, and **perylene**. However, the concentrations of these compounds were generally low and not considered as interfering in the analysis of any field samples except those tissue samples exhibiting the lowest PAH levels. Tissue samples were additionally analyzed by UV/F spectroscopy. The concentrations of hydrocarbons quantified as Prudhoe Bay Crude Oil equivalents range from less than detection limit to 0.55 $\mu\text{g/g}$ wet weight. Background oil concentrations generally increased with decreasing wavelength.

A series of procedural spiked blanks were processed and analyzed along with the sediment and peat samples. The results of these analyses are presented in Tables 4.40 and 4.41. Recoveries of the **analytes** spiked in the first four samples analyzed by **GC-FID** and in the first three samples analyzed by **GC/MS** tended to be low. Upon investigation, it

TABLE 4.32. SATURATED HYDROCARBON CONCENTRATIONS FOR NOAA TEST SEDIMENTS.

Compound	NOAA-D3 (Jar 1)	NOAA-D3 (Jar 2)	NOAA-D3 (Jar 3)
	Concentration ($\mu\text{g/g}$ dry weight)		
n-C ₁₄	<D.L.	0.03	0.02
n-C ₁₅	0.05	0.04	0.05
n-C ₁₆	0.52	0.05	0.06
Isoprenoid	<D.L.	0.05	0.03
n-C ₁₇	0.06	0.05	0.02
Pristane	0.12	0.14	0.15
n-C ₁₈	0.06	0.10	0.08
Phytane	<D.L.	0.11	0.08
n-C ₁₉	0.06	0.07	0.11
n-C ₂₀	0.12	0.18	0.18
n-C ₂₁	0.08	0.13	0.13
n-C ₂₂	0.09	0.24	0.12
n-C ₂₃	0.07	0.30	0.18
n-C ₂₄	0.10	0.21	0.05
n-C ₂₅	0.19	0.54	0.41
n-C ₂₆	0.17	0.41	0.41
n-C ₂₇	0.50	1.04	1.06
n-C ₂₈	0.41	0.70	0.78
n-C ₂₉	0.83	1.38	1.51
n-C ₃₀	0.27	0.57	0.67
n-C ₃₁	0.94	1.13	1.44
n-C ₃₂	0.27	0.25	0.46
n-C ₃₃	0.19	0.13	0.38
n-C ₃₄	0.16	0.25	0.29
TOTAL RESOLVED CONCENTRATION	22.6	51.6	51.3
TOTAL UNRESOLVED CONCENTRATION	157.9	217.0	199.2

TABLE 4.33. **POLYCYCLIC AROMATIC HYDROCARBON (PAH) CONCENTRATIONS FOR NOAA TEST SEDIMENTS.**

	NOAA-D3 (Jar 1)	NOAA-D3 (Jar 2)	NOAA-D3 (Jar 3)
Compound	Concentration ($\mu\text{g/g}$ dry weight)		
Naphthalene	0.23	0.21	0.19
C ₁ N	0.23	0.23	0.20
C ₂ N	0.36	0.36	0.37
C ₃ N	0.34	0.47	0.43
C ₄ N	0.08	0.09	0.07
Biphenyl	0.07	0.07	0.06
Fluorene	0.36	0.36	0.37
C ₁ F	0.15	0.29	0.29
C ₂ F	0.14	0.32	0.16
C ₃ F	<D.L.	0.44	<D.L.
Phenanthrene	2.34	2.34	2.31
C ₁ P	0.98	1.11	0.96
C ₂ P	0.76	0.74	0.64
C ₃ P	0.31	0.37	0.26
C ₄ P	<D.L.	<D.L.	<D.L.
Dibenzothiophene	0.16	0.16	0.16
C ₁ D	0.10	0.13	0.11
C ₂ D	0.24	0.17	0.21
C ₃ D	<D.L.	0.10	0.09
Fluoranthene	3.74	3.74	3.28
Pyrene	4.14	4.37	3.96
Benanthracene	1.75	1.86	1.68
Chrysene	2.02	2.53	2.45
Benzo(a)fluoranthene	4.11	4.67	4.65
Benzo(e)pyrene	1.65	2.02	1.74
Benzo(a)pyrene	1.70	2.37	2.00
Perylene	0.53	0.86	0.74
TOTAL PAH (Sum of Above Compounds)	26.46	30.39	27.37

TABLE 4.34. SATURATED HYDROCARBON CONCENTRATIONS FOR NOAA TEST TISSUE HOMOGENATE M-2

	Replicate 1	Replicate 2	Replicate 3
	Concentration ($\mu\text{g/g}$ wet weight)		
n-C ₁₄	0.07	0.07	0.09
n-C ₁₅	0.17	0.12	0.15
n-C ₁₆	0.22	0.12	0.14
Isoprenoid	0.11	0.08	0.11
n-C ₁₇	0.30	0.19	0.18
Pristane	0.59	0.37	0.37
n-C ₁₈	0.19	0.11	0.17
Phytane	0.21	0.11	0.11
n-C ₁₉	0.19	0.11	0.11
n-C ₂₀	0.23	0.12	0.11
n-C ₂₁	0.17	0.10	0.09
n-C ₂₂	0.17	0.08	0.08
n-C ₂₃	0.13	0.07	0.06
n-C ₂₄	0.10	0.05	0.05
n-C ₂₅	0.12	0.06	0.05
n-C ₂₆	0.10	0.04	0.03
n-C ₂₇	0.12	0.06	0.05
n-C ₂₈	0.17	0.10	0.08
n-C ₂₉	0.29	0.17	0.14
n-C ₃₀	0.42	0.26	0.20
n-C ₃₁	0.50	0.30	0.23
n-C ₃₂	0.32	0.24	0.15
n-C ₃₃	0.28	0.20	0.13
n-C ₃₄	0.28	0.17	0.12
TOTAL RESOLVED HYDROCARBON CONCENTRATION	14.36	8.00	8.70
TOTAL UNRESOLVED HYDROCARBON CONCENTRATION	15.98	4.09	6.44

TABLE 4.35. **POLYCYCLIC AROMATIC HYDROCARBON (PAH) CONCENTRATIONS FOR NOAA TEST TISSUE HOMOGENATE M-2**

	m/e	Replicate 1	Replicate 2	Replicate 3
Concentration ($\mu\text{g/g}$ wet weight)				
Naphthalene	128	0.04	0.04	0.02
C ₁ N	142	0.44	0.33	0.39
C ₂ N	156	0.85	0.72	0.85
C ₃ N	170	0.56	0.47	0.60
C ₄ N	184	0.07	0.11	0.10
Biphenyl	154	0.07	0.05	0.07
Fluorene	166	0.07	0.07	0.08
C ₁ F	180	0.08	0.06	0.08
C ₂ F	194	0.05	0.03	0.06
C ₃ F	208	0.01	< D.L.	0.02
Phenanthrene	178	0.12	0.11	0.11
C ₁ P	192	0.35	0.27	0.34
C ₂ P	206	0.13	0.10	0.18
C ₃ P	220	0.04	0.03	0.04
C ₄ P	234	< D.L.	< D.L.	0.01
Dibenzothiophene	184	0.05	0.04	0.05
C ₁ D	198	0.07	0.04	0.06
C ₂ D	212	0.03	0.02	0.03
C ₃ D	226	< D.L.	< D.L.	0.01
Fluoranthene	202	0.07	0.06	0.07
Pyrene	202	0.04	0.04	0.04
Benzanthracene	228	0.03	0.03	0.03
Chrysene	228	0.03	0.04	0.04
Benzfluoranthene	252	0.04	0.03	0.04
Benz(e) pyrene	252	0.01	0.01	0.02
Benz(a) pyrene	252	0.01	0.03	0.01
Perylene	252	< D.L.	0.03	0.01
TOTAL PAH (Sum of Above Compounds)		3.17	2.76	3.37

TABLE 4.36. MEAN CONCENTRATIONS OF HYDROCARBONS IN DUWAMISH III REFERENCE SEDIMENT DETERMINED BY THREE NATIONAL MARINE FISHERIES (NMF) LABORATORIES.

HYDROCARBONS	NMF, Seattle		NMF, Gloucester		NMF, Charleston	
	Concentrations (ng/g dry weight) ^a					
Naphthalene	320 (11)	320 (15)	420 (18)	250 (21)	330 (11)	
2-Methylnaphthalene	160 (17)	150 (4)	200 (33)	110 (19)	180 (6)	
1-Methylnaphthalene	120 (16)	110 (5)	150 (32)	80 (16)	150 (8)	
Biphenyl	39 (13)	21 (7)	37 (23)	31 (8)	57 (7)	
2,6-Dimethylnaphthalene	70 (10)	75 (7)	78 (16)	58 (15)	76 (4)	
Acenaphthene	300 (22)	310 (8)	300 (2)	290 (16)	420 (9)	
Fluorene	310 (3)	330 (5)	330 (9)	290 (18)	430 (10)	
Phenanthrene	2300 (8)	2300 (7)	2400 (5)	2200 (9)	3200 (6)	
Anthracene	510 (3)	590 (9)	550 (2)	650 (16)	730 (2)	
1-Methylphenanthrene	220 (11)	220 (7)	220 (5)	410 (52)	320 (10)	
Fluoranthene	3900 (9)	4000 (6)	3900 (4)	3700 (4)	5600 (7)	
Pyrene	4100 (5)	4400 (3)	4200 (4)	3900 (5)	5800 (6)	
Benz(a)anthracene	1500 (7)	1900 (8)	1700 (3)	1400 (5)	2100 (10)	
Chrysene	2600 (7)	3800 (15)	2700 (4)	2100 (7)	3600 (6)	
Benzo(e)pyrene	1600 (4)	2000 (8)	1700 (3)	1400 (5)	2000 (9)	
Benzo(a)pyrene	1800 (3)	2220 (3)	1800 (3)	1700 (7)	2700 (6)	
Perylene	510 (2)	640 (5)	550 (5)	460 (8)	710 (5)	
Dibenz(a,h)anthracene	310 (4)	470 (11)	280 (2)	310 (5)	430 (7)	

^aResults expressed as means (n=3)

Relative standard deviations expressed as a percent of the mean shown in parentheses.

TABLE 4.37. RESULTS OF 12 REPLICATE ANALYSES OF PROCEDURAL BLANKS FOR SEDIMENT HYDROCARBON DETERMINATIONS

	Σ n-alkanes	UCM	Σ PAH
	Hydrocarbons ($\mu\text{g/g}$ dry weight)^a		
	0.11	<D.L.	0.005
	0.06	0.54	<D.L.
	0*33	<D.L.	<D.L.
	0.41	<D.L.	0.001
	0.07	<D.L.	0.013
	0.23	<D.L.	0.011
	0.06	<D.L.	0.001
	0.60	<D.L.	0.003
	0.08	<D.L.	0.003
	0.09	<D.L.	0.064
	0.10	<D.L.	0.007
	0.16	<D.L.	0.007
Mean	0.19		0.010
S.D.	0.17		0.018
Cv	90	-	180
Detection Limits	0.01	0.01	0.001

^a50 g dry weight assumed for computation.

TABLE 4.38. RESULTS OF SIX REPLICATE ANALYSES OF PROCEDURAL BLANKS FOR HYDROCARBON TISSUE DETERMINATION - UV/F DATA.

	312 nm	355 nm	425 nm
Hydrocarbons Concentrations ($\mu\text{g/g wet weight}$) ^a Calculated at 312, 355, and 425 nm			
	0.28	0.07	<D.L.
	0.09	0.03	<D.L.
	<D.L.	<D.L.	<D.L.
	<D.L.	<D.L.	<D.L.
	0.27	0.07	<D.L.
	0.55	0.02	<D.L.
Mean	0.20	0.04	<D.L.
S.D.	0.20	0.03	
Cv	100	75	

^a10 g wet weight assumed for computation
limit of detection 0.01 $\mu\text{g/g wet weight}$.

TABLE 4.39. RESULTS OF 8 REPLICATE ANALYSES OF PROCEDURAL BLANKS FOR HYDROCARBON TISSUE DETERMINATION - GC AND GC/MS DATA.

	Σ n-alkanes	UCM	Σ PAH
	Hydrocarbon Concentration ($\mu\text{g/g}$ wet weight) ^a		
	0.6	<D.L.	0.012
	0.9	<D.L.	0.002
	0.1	<D.L.	0.003
	0.1	<D.L.	0.001
	0.1	<D.L.	0.001
	0.9	<D.L.	0.002
	1.3	<D.L.	0.041
	0.1	<D.L.	0.006
Mean	0.5		0.008
S.D.	0.5		0.014
Cv	100		175
Detection Limits			0.001

^a10 g wet weight assumed for computation.

TABLE 4.40. RESULTS OF 8 REPLICATE ANALYSES OF SPIKED METHOD BLANKS FOR SEDIMENT PROCEDURE - GC-FID DATA.

	n-C ₁₀	n-C ₁₁	n-C ₁₄	n-C ₁₅	n-C ₂₄	n-C ₂₅	n-C ₃₂	n-C ₃₄
	(µg Individual Hydrocarbon)							
	<D.L.	<D.L.	<D.L.	<D.L.	2.11	1.98	1.52	1.53
	2.91	4.74	0.98	0.51	1.64	1.43	1.24	1.32
	2.13	9.11	1.10	1.18	1.58	1.35	1.35	1.44
	0.05	0.13	0.17	0.20	1.75	1.56	1.59	1.67
	1.32	1.86	1.52	1.51	1.76	1.70	2.08	1.81
	0.93	1.42	1.11	1.20	1.46	1.36	1.16	1.34
	1.37	1.90	1.54	1.62	1.97	1.71	1.73	1.78
	0.93	20.46	1.45	0.95	2.38	2.21	1.68	1.78
Mean	1.21	4.95	0.98	0.90	1.83	1.66	1.54	1.58
S.D.	0.98	6.94	0.59	0.60	0.30	0.31	0.30	0.20
Cv	81	140	60	66	17	18	19	13
Amount Spiked (µg)	2.20	2.20	2.20	1.95	2.05	2.05	2.05	2.05
Average Recovery (%)	55	225	45	46	89	81	75	77

TABLE 4.41. RESULTS OF 8 REPLICATE ANALYSES OF SPIKED METHOD BLANKS FOR SEDIMENT PROCEDURE - GC/MS DATA.

			Mean	SD	CV	Amount of Spike (µg)	Average Recovery (%)						
(µg Individual Hydrocarbon)													
Naphthalene	<D.L.	<D.L.	0.02	1.86	1.37	2.00	1.50	2.07	1.11	0.93	84	2.05	54
1-Methyl naphthalene	<D.L.	<D.L.	0.11	1.73	1.39	1.99	1.56	0.97	0.97	0.82	84	2.05	54
2,3-Dimethyl naphthalene	<D.L.	<D.L.	<D.L.	1.91	1.65	2.31	1.99	<D.L.	0.99	1.06	107	2.05	48
Phenanthrene	1.84	1.14	1.85	1.80	1.63	1.97	2.11	1.92	1.78	0.29	16	2.05	87
Dibenzothiophene	1.14	0.76	1.72	1.73	1.58	2.13	2.05	1.91	1.62	0.47	29	2.05	79
Pyrene	0.50	0.77	2.69	2.11	1.97	2.40	2.36	2.43	1.90	0.81	42	2.05	93
Chrysene	1.86	2.81	2.54	2.18	1.71	2.31	2.39	2.13	2.24	0.36	16	2.05	109
Benzo(a)pyrene	<D.L.	2.91	0.20	1.26	1.47	1.11	0.69	0.47	1.01	0.92	91	2.05	45
Perylene	0.30	1.76	1.85	1-36	1.32	1.78	1.81	0.64	1.35	0.59	43	2.05	66

was determined that these samples tended to evaporate to dryness during the routine concentration procedure due to the lack of any extract "matrix." Careful Observation of the sample extracts during the concentration steps remedied this problem and subsequent analyses produced acceptable recoveries. Analysis of the spiked blank samples by GC-FID also revealed the presence of a contaminant coeluting with n-C₁₁. Recoveries presented in Tables 4.40 and 4.41 represent absolute recoveries of analytes determined by a quantification standard placed in the sample immediately before analysis. Field sample analyte concentrations are calculated against an internal standard placed in the sample before analysis and, thus, reported concentrations are always corrected for recovery.

Precision was determined by the analysis of triplicate sediment and tissue samples (UV/F only) spiked with Prudhoe Bay Crude Oil (Tables 4.42 and 4.43), and the analysis of triplicate tissue homogenates (Table 4.44). Results of the sediment analyses indicate very tight analytical precision for the gravimetric data (CV < 1.5), but somewhat less precise chromatographic data. The least precise measurement was the GC-FID calculation of UCM (CV = 35.6). Analysis of the tissue triplicate experiments revealed much higher precision with the spiked sample than with the sample containing hydrocarbons at arctic background concentrations. Recoveries of oil in the spiked tissue samples were 92% and 79% at 312 nm and 425 nm, respectively. Recovery data for the spiked sediment experiment is more difficult to interpret because no analysis of the crude extract was performed. Total saturated and aromatic hydrocarbon weight was 54% of the amount of crude oil spiked into the sample.

4.4.3 Grain Size

Approximately 10 percent of the field samples analyzed were split and analyzed as duplicates. Results of these 12 analyses are presented in Table 4.45. These data indicate that, for the wide range of sediment textures analyzed, reproducibility of the methods employed is acceptable. As can be expected, the greatest variability is observed in the -1 phi category (gravel). Comparison of the results in other phi classes indicates very good analytical precision.

TABLE 4.42. RESULTS OF TRIPPLICATE ANALYSES OF SEDIMENT SAMPLES SPIKED WITH PRUDHOE BAY CRUDE OIL^a

	Replicate 1	Replicate 2	Replicate 3	Mean	S.D.	CV
<u>Concentration (µg ofl-hydrocarbon)</u>						
<u>Gravimetric Data</u>						
Saturated Hydrocarbons	14,674	15,120	14,922	14,905	233	1.5
Aromatic Hydrocarbons	12,396	12,158	12,248	12,251	94	<0.1
Total Hydrocarbons	27,020	27,278	27,170	27,156	129	<0.1
<u>Chromatographic Data</u>						
Resolved Hydrocarbons ^b	3,207	3,201	3,106	3,171	56.6	1.8
Unresolved Complex Mixture ^b	371	790	706	622	222	35.6
Total Hydrocarbons ^b	3,579	3,991	3,812	3,791	206	5.4
Total Aromatic Hydrocarbons	800	825	680	768	78	10.1

^aPre-extracted sediment was dehydrated, spiked with 50 mg Prudhoe Bay Crude Oil (36.3 percent residium; Coleman, 1978), and processed according to sediment procedure used in the BSMP study.

^bSaturated hydrocarbons from n-C₁₀ to n-C₃₄ analyzed by GC-FID.

^cSuite of aromatic analytes analyzed by GC/MS.

TABLE 4.43. RESULTS OF TRIPLICATE ANALYSES OF TISSUE SAMPLES SPIKED WITH PRUDHOE BAY CRUDE OIL - UV/F DATA^a

Wavelength (nm)	Replicate	Replicate	Replicate	Mean	S.D.	CV
	1	2	3			
	(Total Oil in mg)					
312	48.6	42.1	46.9	45.9	3.4	7
355	42.2	38.4	39.5	40.0	2.0	5
425	41.9	38.2	38.6	39.6	2.0	5

^aCommercial clams (Geisha brand) were homogenized and spiked with 50 mg Prudhoe Bay Crude Oil, and processed for UV/F analysis according to tissue procedure.

TABLE 4.44. RESULTS OF TRIPPLICATE ANALYSES OF TISSUE SAMPLES FOR SELECTED HYDROCARBON PARAMETERS (Concentration $\mu\text{g/g}$ Wet Weight).

	Replicate 1	Replicate 2	Replicate 3	Mean	S.D.	CV
<u>Gravimetric Data</u>						
Saturated Hydrocarbons	3.50	4.80	6.4	4.9	1.5	30
Aromatic Hydrocarbons	30.6	123.6	88.2	80.9	46.9	58
Total Hydrocarbons	34.1	128.4	94.7	85.7	48.0	56
<u>Chromatographic Data</u>						
Resolved Hydrocarbons ^a	1.6	3.3	1.6	2.2	1.0	44
Unresolved Complex Mixture ^a	<D.L.	<D.L.	<D.L.	<D.L.		
Total Hydrocarbons ^a	1.6	3.3	1.6	2.2	1.0	44
Total Aromatic Hydrocarbons ^b	7.2	20.0	4.1	10.4	8.4	81
<u>UV/Fluorescence</u>						
312 nm	9.8	9.3	11.0	10.1	0.9	9
355 nm	4.7	4.4	4.9	4.7	0.2	5
425 nm	2.7	2.4	2.6	2.6	0.1	5

^aSaturated hydrocarbons analyzed by GC-FID.

^bAromatic hydrocarbons analyzed by GC-MS.

TABLE 4.45. SUMMARY OF REPLICATE GRAIN SIZE ANALYSES (IN PERCENT).

Phi	STATION 1D		STATION 2B		STATION 2E		STATION 3B	
	A	B	A	B	A	B	A	B
-1	0	0	0	0	0	0	1.27	0.02
0	0	0	0.01	0.02	0	0.01	0.07	0.05
1	0.01	0.01	0.18	0.20	0.05	0.02	0.20	0.17
2	0.24	0.17	0.49	0.45	0.26	0.22	0.59	0.54
3	52.84	52.05	23.56	22.41	5.05	4.80	1.89	1.68
4	35.89	36.39	11.93	11.14	4.54	4.32	22.09	21.45
5	5.29	5.45	3.91	4.17	3.13	2.95	23.68	27.39
6	2.06	2.27	8.17	5.46	13.94	14.40	17.39	16.72
7	1.14	1.19	11.45	11.73	18.45	19.05	9.56	9.39
8	0.76	0.78	9.83	12.91	16.68	16.10	6.37	6.27
9	0.44	0.58	5.92	8.10	10.49	12.45	3.39	4.35
10	0.02	0.05	8.95	6.99	7.16	7.01	2.22	1.72
>10	1.32	1.08	15.59	16.42	20.25	18.66	11.28	10.26

Phi	STATION 5A		STATION 5E		STATION 5K		STATION 5(0)	
	A	B	A	B	A	B	A	B
-1	2.62	4.10	0.17	0.92	4.13	0	0.03	0
0	0.37	0.18	0.30	0.03	0.63	1.13	0.05	0.07
1	0.79	0.65	0.57	0.38	1.88	2.39	0.29	0.30
2	8.88	8.20	6.19	6.42	5.41	7.31	24.53	24.50
3	11.85	11.83	32.54	40.27	9.13	12.01	66.12	65.71
4	32.15	31.52	7.42	7.68	9.63	10.94	5.25	5.37
5	14.99	15.22	0.52	2.39	7.68	9.78	3.13	3.47
6	10.12	10.07	4.75	5.36	20.28	19.88	0	0
7	5.87	5.88	8.39	7.23	20.49	18.51	0	0
8	3.78	3.72	7.83	8.46	6.83	7.21	0	0
9	1.53	2.19	8.95	4.05	1.45	1.27	0.60	0.57
10	2.56	2.19	6.06	5.72	0.83	0.29	0	0
>10	4.49	4.25	16.31	11.07	11.64	9.28	0	0

Phi	STATION 6C		STATION 7A		STATION 7D	
	A	B	A	B	A	B
-1	0.06	0.19	0	0	0	0
0	0.04	0.11	0.03	0	0.02	0
1	0.17	0.15	0.01	0	0.01	0.03
2	0.72	0.74	0.12	0.08	0.10	0.10
3	7.84	7.80	0.46	0.50	7.78	8.06
4	30.52	31.69	27.25	26.12	45.74	45.06
5	5.47	5.70	41.13	43.02	7.17	8.26
6	8.65	7.56	14.57	14.83	5.72	6.09
7	8.76	9.04	6.13	5.63	6.96	6.56
8	8.86	8.62	2.81	2.97	6.86	6.92
9	6.30	5.71	0.88	0.83	5.46	5.80
10	6.66	6.19	0.96	1.00	3.40	3.28
>10	15.95	16.50	5.66	5.01	10.28	9.82

5. ANALYSIS AND INTERPRETATION OF DATA

5.1 Introduction

The analysis of the Year-2 data includes the same approaches as were used in interpreting the Year- 1 data. These approaches include the following:

1. Evaluation of the data from **geochemical** and **biogeochemical** perspectives;
2. Statistical analysis of the data to test program hypotheses.

The first approach concerns the interpretation of the spatial aspects of the data with regard to both the concentrations of target metallic elements and organic compounds, and the compositional aspects of the data. Included are the evaluations of key diagnostic parameters and parameter ratios. In this evaluation, special attention is given to associations of chemical distributions in sediments with possible sources examined directly in the Year-2 program. Coastal peat and riverine inputs of particulate materials, and their associated assemblages of metals and **organics** are discussed in relation to the observed offshore sediment chemical distributions. In the context of evaluating the data for their relevance to monitoring possible contributions from oil and gas exploration and production activities, the importance of background inputs of peat and rivers must be investigated.

The first approach also concerns the evaluation of the association of the metals and **organics** with the mud fraction of the sediment. If potential inputs of anthropogenic metals and **organics** from oil and gas exploration, and production activities are likely to be associated with the fine sediment fraction, then the physical isolation of the fine fraction of the sediments followed by chemical analyses of this fraction can yield important information and can potentially increase the likelihood of detecting small incremental additions of **anthropogenic** materials to the sediments. This line of investigation was introduced to the Year-2 program after analysis of the only bulk sediment in the Year-1 program.

Data from the analyses of **benthic** animals (i.e., bivalve **molluscs** and selected **crustacea**) were also evaluated, both from the aspect of chemical content and composition, and with regard to the relationship of tissue chemical levels to those **chemical** concentrations and compositions in the surrounding sediment. A more extensive collection of animals was made and chemically analyzed in the Year-2 program to examine the usefulness of applying the sentinel organism approach to the **BSMP**.

The second interpretive approach centered on the statistical analyses of the data. This approach included the first opportunity to test the basic hypotheses upon which the monitoring program is based with regard to evaluating temporal changes in chemical concentrations and in key diagnostic parameters.

5.2 Metals Chemistry

During Year-1 of the **BSMP**, the concentrations of 7 metals at 27 sediment stations and 3 bivalve stations were established. In Year-2 of this program, sediments and organisms, shoreline peat samples, and river sediments were collected for analysis. Twenty-six of the original 27 Year-1 sediment stations were resampled to determine annual variability in sediment metals chemistry. Thirteen additional sediment stations were sampled in Year-2 to extend the geographical coverage further to the east and also further offshore. The river sediments and shoreline peat samples were analyzed with the

intent of determining sources of specific metals. Amphipods and benthic bivalves were analyzed from eight stations to determine chemical differences between stations and relate chemical differences to sediment chemistry.

5.2.1 Comparison Between Year-1 and Year-2 Sediment Metals Chemistry

During the Year-2 field program, 26 sediment stations that were sampled in Year-1 were resampled. These 26 sediments were analyzed for metals in both the bulk and mud fractions. In Year-1, only the bulk sediment was analyzed. Metal concentrations in 26 bulk sediments for Years-1 and 2, along with percent mud content of sediments, are presented in Section 4 (Figures 4.14 through 4.22).

Generally, the concentrations of metals and percent mud in Year-2 sediments were identical to those in Year-1 sediments. For the few stations at which metals differed significantly between years, the percent mud usually differed in a corresponding manner. This was the case for Stations 2E, 5B, and 5E, where metals and percent mud appeared to increase from Year-1 to Year-2. At Station 5A, 5F, and 6F, both metals and percent mud decreased. These results indicate that there were significant annual changes in the grain size and metals concentrations at some stations. These annual changes may be due to sediment transport processes or to within-station inhomogeneity, but given the good repositioning precision, the former reason is suspected. The most dramatic changes occurred at Station 5B, where percent mud increased from 3.1% to 77.0% and at Station 2E, where mud increased from 7.7% to 77.696.

The regional mean concentrations of metals, TOC, and percent mud for Year-1 and Year-2 sediments are presented in Table 5.1. It is apparent from the data that very little change occurred within a region during the year. Mean concentrations of metals and TOC generally changed less than ± 20 percent between years, and mud content changed less than ± 10 percent. These results indicate both that the regional sedimentary environment is not greatly changing and that the laboratory analytical techniques used in the two years produce very similar results.

5.2.2 Relationships Between Metals, Sediments, and Source Materials

During the last 20 years there have been several studies that have investigated the sources and movement of sediments to the Beaufort Sea. The major riverine source of sediment is the Colville River which enters eastern Harrison Bay (Carlson, 1976). According to Naidu et al. (1982), most of the river-borne sediments are eventually deposited in deltas or lagoons. Erosion of shoreline peat, estimated at 1-4 m/yr along some regions of the coast, is another major source of sediment to the Beaufort Sea (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.

The results from Year-1 and Year-2 indicate a general relationship between mud concentrations and metals concentrations. A similar correlation was identified between metals, TOC, and mud in Year-1. However, in Year-2 the correlations between metals and TOC for bulk sediments are not as strong as in Year-1.

The correlation coefficients for metals, percent mud, and TOC are presented in Table 5.2. The analytical results are from bulk sediments collected at 26 stations in Year-2. These 26 stations were analyzed for bulk metals in Year-1. The bulk sediments have high positive correlation coefficients (>0.5) among several metals (Pb, Cr, Cu, Zn,

TABLE 1. REGIONAL DIFFERENCES IN THE MEAN CONCENTRATIONS OF METALS IN THE YEAR-1 AND YEAR-2 BULK SEDIMENTS AND THE YEAR-2 MUD FRACTIONS.

	Foggy Island Bay Stations "3" and "4"			Prudhoe Bay Stations "5"			EastHarrisonBay Stations "6"			WestHarrisonBay Stations "7"		
	<u>Year-1</u>	<u>Year-2</u>		<u>Year-1</u>	<u>Year-2</u>		<u>Year-1</u>	<u>Year-2</u>		<u>Year-1</u>	<u>Year-2</u>	
	Bulk	Bulk	Mud	Bulk	Bulk	Mud	Bulk	Bulk	Mud	Bulk	Bulk	Mud
METALS ($\mu\text{g/g}$ Dry Weight)												
Ba	309	308	457	279	329	430	444	376	449	587	578	687
Cd	0.14	0.13	0.19	0.16	0.17	0.28	0.14	0.14	0.18	0.10	0.11	0.17
Cr	47	42	79	37	48	69	64	56	85	58	63	92
Cu	23	14	22	15	16	20	22	13	26	16	16	17
Pb	6.1	9.2	13.5	6.5	9.5	11.6	10.7	11.9	14.9	9.9	14.4	13.1
v	59	70	113	60	81	105	104	95	133	92	90	102
Zn	51	57	89	53	68	84	73	76	103	69	77	82
TOC (% Dry Weight)												
	0.62	0.91	-	0.99	0.85		1.00	0.99		1.48	1.29	-
Mud (% Dry Weight)												
	32	33	-	33	36		51	53		48	51	

TABLE 5.2. PEARSON CORRELATION COEFFICIENTS FOR BULK SEDIMENT METALS, TOTAL ORGANIC CARBON, SILT, AND CLAY. DATA REPRESENT LOG-TRANSFORMED AVERAGES OF 26 STATIONS SAMPLED IN YEAR-1 AND YEAR-2.

	PEARSON CORRELATION COEFFICIENTS / PROB > R UNDER HO:RHO=0 / N = 26									
	LOGCD	LOGPB	LOGBA	LOGCR	LOGCU	LOGZN	LOGV	LOGTOC	SILT	CLAY
LOGCD	1.00000 0.0000	0.07723 0.7077	-0.44489 0.0228	0.36471 0.0670	0.57240 0.0023	0.51694 0.0069	0.40533 0.0399	0.27117 0.1803	0.51132 0.0076	0.33922 0.0900
LOGPB	0.07723 0.7077	1.00000 0.0000	0.62233 0.0007	0.83186 0.0001	0.74956 0.0001	0.82233 0.0001	0.84774 0.0001	0.54724 0.0038	0.50376 0.0087	0.77640 0.0001
LOGBA	-0.44489 0.0228	0.62233 0.0007	1.00000 0.0000	0.44887 0.0214	0.24209 0.2334	0.29041 0.1501	0.37261 0.0608	0.24849 0.2209	0.21806 0.2846	0.31201 0.1207
LOGCR	0.36471 0.0670	0.83186 0.0001	0.44887 0.0214	1.00000 0.0000	0.87593 0.0001	0.94266 0.0001	0.94416 0.0001	0.62310 0.0007	0.67849 0.0001	0.78918 0.0001
LOGCU	0.57240 0.0023	0.74956 0.0001	0.24209 0.2334	0.87593 0.0001	1.00000 0.0000	0.93532 0.0001	0.95178 0.0001	0.64661 0.0004	0.69767 0.0001	0.88080 0.0001
LOGZN	0.51694 0.0069	0.82233 0.0001	0.29041 0.1501	0.94266 0.0001	0.93532 0.0001	1.00000 0.0000	0.96376 0.0001	0.58614 0.0017	0.71745 0.0001	0.85549 0.0001
LOGV	0.40533 0.0399	0.84774 0.0001	0.37261 0.0608	0.94416 0.0001	0.95178 0.0001	0.96376 0.0001	1.00000 0.0000	0.59880 0.0012	0.63218 0.0005	0.88834 0.0001
LOGTOC	0.27117 0.1803	0.54724 0.0038	0.24849 0.2209	0.62310 0.0007	0.64661 0.0004	0.58614 0.0017	0.59880 0.0012	1.00000 0.0000	0.62588 0.0006	0.48553 0.0261
SILT	0.51132 0.0076	0.50376 0.0087	0.21806 0.2846	0.67849 0.0001	0.69767 0.0001	0.71745 0.0001	0.63218 0.0005	0.62588 0.0006	1.00000 0.0000	0.49260 0.0106
CLAY	0.33922 0.0900	0.77640 0.0001	0.31201 0.1207	0.78918 0.0001	0.88080 0.0001	0.85549 0.0001	0.88834 0.0001	0.43553 0.0261	0.49260 0.0106	1.00000 0.0000

and V) and TOC, silt, and clay. Cadmium and barium are weakly correlated (0.2-0.5) with TOC, silt, and clay. The other high positive correlations are among copper, chromium, lead, vanadium, and zinc. There are no strong negative correlations. These correlations support the conclusions of the Year-1 report that grain size and TOC control the distribution of these seven metals in the Beaufort Sea sediments.

The mud fraction of Year-2 sediments was also analyzed for metals in an attempt to normalize for differences in metals due to grain size and TOC. There are no strong correlations between the metals in the mud fraction and TOC. This result is as expected, because the TOC data used for the correlations were for bulk, not mud. The lack of strong correspondence between percent mud and metal content in the bulk fraction indicates that the concentrations of metals do not directly relate to the percent mud in the sediment. In the mud fraction analyzed, the only strong correlations (>0.7) were between lead and copper, lead and vanadium, copper and zinc, copper and vanadium, and zinc and vanadium. These interactions are apparently due to change in grain size or TOC concentration within the mud fraction of these sediments.

Shoreline peat samples were collected, composite, and analyzed for metals in both the bulk and mud fractions. The results are presented in Table 5.3 for mean concentrations in two regions of the Beaufort Sea. These results indicate that peat was not significantly different from sediments in metal content. Also, there was very little difference between the concentration of metals in the bulk or mud fraction of peat. The TOC content of peat was approximately 10 times higher than that in shelf sediments. If the peat samples obtained are representative of Beaufort Sea coastal peat, peat cannot have a major influence on the concentration of metals in sediments, assuming that the TOC concentration of sediment is derived from peat. Because the sediments contain approximately 1% TOC, then the sediment should contain less than 10% peat.

River sediment samples were collected in Year-2 for the purpose of identifying additional potential sources of sediments to the offshore area. The two river sediments collected were very different in barium concentration, grain size, and TOC (Table 5.3). The sample from the Sagavanirktok River was low in barium, TOC, and percent mud. The Colville River sediment was high in barium, TOC, and percent mud, but similar to the Sagavanirktok River and shelf sediment for the other six metals. Although sediments from only two major rivers were analyzed for metals, the data suggest that rivers may be a major source of both sediments and trace metals to the Beaufort Sea. A more extensive river sediment collection is planned for Year-3 of the program and the data from the metal analyses will be important in assessing the significance of rivers as sources of both sediments and trace metals.

5.2.3 Geographical Trends

The data for the concentrations of metals in the mud fraction of sediments collected in Year-2 indicate a lack of strong geographic trends. The Year-1 data also did not detect geographical trends, other than trends that were attributed to regional differences in grain size and TOC. The mud fraction appears to have only a small effect in normalizing the bulk metal concentrations to grain size and TOC.

The mean concentrations of metals in mud samples from five regions of the Beaufort Sea are presented in Table 5.4. Each regional mean was calculated from 5-11 station means. The greatest regional differences were for barium which was about 250 ppm higher in West Harrison Bay than in the other regions. Another regional difference was for chromium, which had a trend similar to barium, with lowest chromium in Prudhoe Bay and highest in West Harrison Bay. The other five metals did not change significantly between regions.

TABLE 5.3. REGIONAL MEAN CONCENTRATIONS OF METALS IN THE BULK AND MUD , FRACTION OF PEAT SAMPLES AND RIVER SEDIMENTS.

	<u>Eastern Study Area (4)</u> <u>Peat Stations "1", "2", "3"</u>		<u>Western Study Area (4)</u> <u>Peat stations "5", "6", "7"</u>		<u>Sagavanirktok River (1)</u>		<u>Colville River (1)</u>	
	Bulk	Mud	Bulk	Mud	Bulk	Mud	Bulk	Mud
METALS ($\mu\text{g/g}$ Dry Weight)								
Ba	482	485	334	411	102	191	612	953
Cd	0.23	0.23	0.32	0.30	0.29	0.40	0.15	0.27
Cr	51	66	33	65	41	56	46	101
Cu	19	22	27	24	15	19	41	24
Pb	9.8	11.1	9.4	9.7	6.3	7. J	8.7	13.1
V	80	97	55	88	59	84	62	117
Zn	59	68	56	81	62	91	60	106
ToC (% Dry Weight)	13.4	-	16.9	-	1.3	-	6.6	
Mud (% Dry Weight)	66	-	56		16		69	

TABLE 5.4. REGIONAL DIFFERENCES **IN THE** MEAN CONCENTRATIONS OF METALS IN THE MUD FRACTION **OF MARINE** SEDIMENTS .

METALS (<u>µg/g</u>)	STUDY REGIONS (NO. OF STATIONS)				
	Camden fky(11) Stations "1" and "2"	Foggy Island (5) Stations "3" and "4"	Prudhoe Bay (11) Stations "5"	East Harrison Bay (6) Stations "6"	West Harrison Bay (6) Stations "7"
Ba	457 ± 117	457 ± 88	430 ± 95	449 ± 117	687 ± 125
Cd	0.21 ± 0.05	0.19 ± 0.03	0.27 ± 19	0.19 ± 0.04	0.17 ± 0.07
Cr	77 ± 6	70 ± 8	67 ± 9	81 ± 10	91 ± 12
Cu	27 ± 3	22 ± 3	20 ± 5	25 ± 5	19 ± 6
Pb	17.2 ± 2.8	13.6 ± 2.4	11.4 ± 2.9	14.4 ± 1.5	13.3 ± 2.1
V	120 ± 18	113 ± 12	105 ± 21	129 ± 16	106 ± 16
Zn	97 ± 11	90 ± 9	84 ± 11	102 ± 9	86 ± 11

A possible explanation for the regional differences in barium and chromium is that different rivers are transporting sediments with different barium and chromium concentrations. In Year-2, two river sediments were sampled, one from the Sagavanirktok River and one from the Colville River. Sediment from the Sagavanirktok River, which enters the Beaufort Sea east of Prudhoe Bay, was low in barium and chromium. However, the Sagavanirktok River sediment was also low in mud content and TOC. Sediment from the Colville River, which enters East Harrison Bay, was high in barium and chromium, as well as mud and TOC (Table 5.3). This relationship between barium and chromium in river sediment and region sediment is interesting, but should be viewed as preliminary, because only one sediment composite was analyzed for each river, and the grain size and TOC differed greatly between rivers. Additional river sediment sample collections are planned during Year-3.

The concentrations of metals in the mud fraction of the shoreline peat samples were similar to the concentrations of metals in mud. The mean concentrations of metals in peat samples from the eastern Beaufort Sea stations ("1", "2", and "3") and from the western Beaufort Sea stations ("Y", "6", and "7") are presented in Table 5.3. There were no significant differences between these regional means, indicating the metals content of peat will not cause regional difference in the concentrations of metals in sediment.

5.2.4 Comparison of Metals Chemistry With Historical Data

The geochemistry of several metals (iron, manganese, copper, cobalt, chromium, nickel, vanadium, and zinc) was examined by Naidu et al. (1981) in four depositional regions of the Beaufort Sea (OCS, Harrison Bay, Simpson and Beaufort Lagoons). Concentrations of all metals in OCS 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 OCS sediments have been conducted by Sweeney (1984) and Robertson and Abel (1979).

The concentrations of metals in sediments which have been reported in Year-1 and Year-2 of the BSMP are generally 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 5.5 due to both variation in sediment texture and possible differences in analytical techniques.

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

5.2.5 Cycling of Metals in Shelf Sediments

The cycling of barium, chromium, vanadium, lead, copper, zinc, and cadmium in shelf sediments has been studied to a limited extent in non-Alaskan marine sediments (Carpenter et al., 1975; Feely et al., 1981; Sholkovitz, 1978; Santschi et al., 1983). The geochemical processes that influence the concentrations of these metals in sediments are not expected to differ greatly in the Beaufort Sea. Barium, chromium, vanadium, and lead, metals primarily associated with crustal minerals, are not readily solubilized or bioaccumulated. The distribution of these crustal elements is controlled by the elemental concentrations in the source materials (e.g., mud, sand) as well as by the degree of physical sorting of grain sizes on the shelf. Biological processes and chemical reactions have virtually no effect on the concentration of crustal elements in sediments.

TABLE 5.5. RANGE OF TOTAL METAL CONCENTRATIONS IN ARCTIC COASTAL SEDIMENTS.

	BSMP (1985, 1986)	Naidu et al. (1982)	Campbell and Loring (1980)
<u>Metal (ppm dry wt.)</u>			
Ba	185-745		
Cd	0.04-0.31		
Cr	17-91	82-97	16-139
Cu	4.9-36.7	0-61	4-42
Pb	3.9-20.5		4-42
v	33-153	25-275	47-156
Zn	19-116	38-130	17-83

Copper, zinc, and cadmium are much more soluble in seawater than crustal elements, and may be more readily released from sediments and available for bioaccumulation. Most of the biogenic cadmium, for example, is released to the water column before the particles are incorporated into the sediments. Copper and zinc, on the other hand, are taken up by suspended particles (e.g., adsorption onto metal oxides or organic matter) or by organisms. As these particles are deposited, only some of the copper and zinc is recycled; the balance is retained in the sediments.

Because much of the particulate cadmium is released to the water column before particles are incorporated into the sediments, the correlations between cadmium and grain size (e.g., $r = 0.3-0.5$), and cadmium and TOC ($r = 0.3$) are weak.

5.2.6 Metals in Tissues

The tissues of amphipods and bivalves were analyzed for metals to determine (1) geographic differences, (2) annual variations in body burdens, (3) relationships between metals in sediment and in tissue of organisms living on or in the sediment, and 4) potential use of sentinel organisms in the BSMP program. Amphipods were collected at nine stations. Each sample was analyzed as four replicate composites of whole animals. Bivalves were collected at 10 stations, several were pooled to form eight samples, and each sample was analyzed as four replicate composites of shucked tissue.

The mean concentrations of metals in amphipod and bivalve tissues are presented in Tables 4.3 and 4.4. The concentration of each metal in the amphipods varied approximately by a factor of three between the lowest and the highest station. There did not appear to be a geographical trend with this limited data set. Although several metals (cadmium, copper, and zinc) appeared to co-vary, there does not appear to be a correlation between the concentrations of metals in tissue and mud from the collection station.

Trace metal data for Alaskan amphipods have been reported in a Nortec (1982) study of the Beaufort Sea Challenge Island drilling fluid disposal site. Table 5.6 compares amphipod tissue trace metal concentrations reported by the Nortec (1982) study with the concentrations found in the Year-2 BSMP. With the exception of lead, the mean tissue trace metal concentrations are similar. The mean lead levels reported by Nortec (1982) are two orders of magnitude higher than the values reported in the present study. We do not have an explanation for this apparent disagreement.

The concentrations of metals in bivalves collected at three stations can be compared for Year-1 and Year-2 (Table 4.7). The data from the two years were similar, indicating very little annual variation had occurred for these species at these stations, and indicating that these animals have great potential for use in detecting changes due to anthropogenic inputs.

The bivalve data set was too limited for each species to determine any meaningful geographic trends. The major differences in the bivalve data set appear to be due to differences between species. The concentration of cadmium in Astarte ranged between 8 and 25 $\mu\text{g/g}$ dry weight. This range is approximately 10 times higher than levels of cadmium found in other bivalve species, including the other filter feeder, Cyrtodaria, and the amphipods. This apparent accumulation of cadmium by Astarte but not by the other filter feeder, Cyrtodaria, is not clear but may be related to physiological properties of the species. As was noted last year, Cyrtodaria contained lower concentrations of cadmium, than other bivalves. The two new species of bivalves analyzed this year (Portlandia and Macoma) contained much higher concentrations of several metals, including barium, chromium, lead, vanadium, and zinc than Astarte and Cyrtodaria. There do not appear to be relationships between body burdens and sediment chemical concentrations. Larger data sets are needed to examine these relationships.

TABLE 5.6. MEAN TRACE **METAL** CONCENTRATIONS IN **ALASKAN AMPHIPOD** TISSUES.

Metals ($\mu\text{g/g}$ wet weight)	Nortec Study (1982)	Year-2 BSMP (1986)
Ba	29 \pm 32	36 \pm 14
Cr	1.8 \pm 0.8	1.6 \pm 0.9
Pb	22.2 \pm 2.2	0.19 \pm 0.19
Cu	83 \pm 26	115 \pm 36
Zn	94 \pm 20	109 \pm 22
Cd	3.8 \pm 0.6	0.87 \pm 0.41

5.3 Hydrocarbon Chemistry

5.3.1 General Interpretational Framework

The data generated as part of the hydrocarbon chemistry task consisted of two types of data: UV/F data that describe gross fluorescence properties of the sample converted to quantitative data based on the arbitrary, but relevant, Prudhoe Bay Crude Oil (PBC) standard; and GC-FID and GC/MS data that yield the concentration of individual saturated (normal and isoprenoid alkanes) and aromatic (2- to 5-ring homologous series) hydrocarbons, respectively. While UV/F data may be precise and informative, in a relative sense, if significant quantities of background fluorescence are present, the gross property data will be insensitive to subtle compositional changes and incremental additions of sub-ppm inputs of "new" material (i.e., pollutants). GC-FID and GC/MS yield accurate and precise data at lower quantitative levels. In addition, key source diagnostic ratios (Tables 5.7 and 5.8) can be calculated and also used, along with quantitative data (Tables 5.9 and 5.10), to address the composition of ambient hydrocarbon concentrations, and to address changes in the composition over time. UV/F data were generated for only animal tissues because it was determined in Year-1 that a large sediment background UV/F signal existed. GC-FID and GC/MS data were generated for all samples.

5.3.2 Review of Historical Data

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 ranged between 0.3 and 20 µg/g dry sediment. The saturated hydrocarbons are dominated by n-alkanes ranging in chain length between 23 and 31 carbon atoms with a strong odd-even preference and no unresolved complex mixture (UCM) 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 alkylhomolog distribution of selected aromatic hydrocarbon series determined by GC/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 (OCS) has been studied by Kaplan and Venkatesan (1981), and Venkatesan and Kaplan (1982). The range of total hydrocarbon concentrations reported was 20 to 50 µg/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 OCS region was not investigated. As with the nearshore sediments, the major source of saturated sedimentary hydrocarbons was found to be higher in plant debris, with no evidence of a UCM 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 OCS sediments examined. The distribution of alkylated homologies determined by GC/MS was found to be characteristic of a pyrogenic origin. The available organic geochemical data for the

TABLE 5.7. SATURATED HYDROCARBON PARAMETER SOURCE RATIOS (GC/FID) USED TO TEST NULL HYPOTHESES H₀₂ (SEDIMENT HYDROCARBON SOURCES) AND H₀₄ (BIVALVE HYDROCARBON SOURCES).

PARAMETER	SIGNIFICANCE
1. LALK/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. IsoprenoidAlkane/Straight Chain Alkane Ratio	This parameter ratio measures the relative abundance of branched, isoprenoidalkanes 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 decreases as oil is added.
4. TOT/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 (µg/g) increase and TOC (mg/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 5.8. PAH SOURCE PARAMETERS (GC/MS) USED TO TEST NULL HYPOTHESES H_{02} (SEDIMENT SOURCES) AND H_{04} (BIVALVE SOURCES).

PARAMETERS	SIGNIFICANCE
1. Fossil Fuel Pollution Index (FFPI) ^a	Pyrogenic or combustion-derived 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 appears to be related to specific sources of PAH (and others).
4. PAH/TOC	Analogous to total hydrocarbon/TOC ratio.

a

$$FFPI = \frac{N + P + F + DB}{\text{Total PAH}} \times 100$$

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

where:

$$\begin{array}{ll}
 N = C_0N + C_1N + C_2N + C_3N + C_4N & \text{(naphthalenes)} \\
 P = C_0P + C_1P + C_2P + C_3P + C_4P & \text{(phenanthrenes)} \\
 F = C_0F + C_1F + C_2F + C_3F & \text{(fluorenes)} \\
 D = C_0D + C_1D + C_2D + C_3D & \text{(dibenzothiophenes)}
 \end{array}$$

$$\text{Total PAH} = N + P + F + D + \text{FLAN} + \text{PYRN} + \text{BAA} + \text{CHRY} + \text{BAP} + \text{BEP} + \text{BFA} + \text{PERY}$$

TABLE 5.9. SATURATED HYDROCARBON QUANTITATIVE PARAMETERS (cc/FID) USED To TEST NULL HYPOTHESES H₀₁ (SEDIMENT CONCENTRATIONS) AND H₀₃ (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 areawide 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 -C ₂₀ (LALK)	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.

TABLE 5.10. PAH QUANTITATIVE Parameters (GC/MS) USED TO TEST NULL HYPOTHESES H_{01} (SEDIMENT CONCENTRATIONS) AND H_{03} (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.

region indicate that hydrocarbons found in nearshore and offshore sediments originate primarily through natural processes, with little evidence of anthropogenic petroleum inputs.

In general, the hydrocarbon concentrations of Beaufort Sea sediments are somewhat elevated over other Outer Continental Shelf sediments. Of more significance, however, is the composition of the hydrocarbons which, because they are largely fossil derived, differ from most other shelf sediments.

5.3.3 Offshore Sediments

5.3.3.1. Overview of Hydrocarbon Data. The analytical results have been summarized in Section 4.2. Total saturated hydrocarbon concentrations in surface sediments ranged from 1.3 to 60 ppm in the Year-2 samples (Figure 5.1). The highest concentrations of saturates were found at stations in the Colville River-Harrison Bay area and in sediments of Stations 5B, 5D, and 5E in deeper waters to the west of the Prudhoe Bay region. These data are certainly consistent with the observations from Year-1. Major differences were found between the Year-1 and Year-2 sediments at Station 2E, where the Year-2 results were a factor of 6 higher than in Year-1 (see Boehm et al., 1985) in spite of a close reoccupation of the station.

Total polynuclear aromatic hydrocarbons (PAH) concentrations ranged from 0.01 to 1.5 ppm. Stations in the Colville River drainage area also contain the highest 2- to 5-ringed PAH concentrations. However, as can be seen from Figure 5.1, there was poor correspondence between the saturated hydrocarbon and PAH compounds. The saturates co-varied strongly with TOC ($r=0.7$), while the PAH compounds are somewhat less strongly correlated (see Table 5.1) ($r=0.6$ to 0.7). A similar trend was noted in the Year-1 samples, perhaps suggesting that the sources of PAH and saturated hydrocarbon compounds may differ.

5.3.3.2. Gas Chromatographic Composition of Saturated Hydrocarbons. The saturated hydrocarbon composition, as determined by GC-FID analysis, is composed of two main features: 1) an n-alkane distribution from n-C₁₀ to n-C₂₀, with no odd-to-even carbon dominance (LALK); and 2) an n-alkane distribution from n-C₂₁ to n-C₃₃, with a distinct odd-carbon preference. As found in the Year-1 program, the total saturated hydrocarbons (TOT) from Year-2 are correlated with both the silt content of the sediment ($r=0.76$) and the TOC content ($r=0.70$). The total alkanes (TALK) are strongly correlated with silt ($r=0.81$) and TOC (0.70), while the LALK compounds are less strongly correlated ($r=0.68$ for silt; $r=0.60$ for TOC).

Sediments from the eastern Camden Bay area (Region 1), sampled for the first time in Year-2, contained lesser relative quantities of LALK compared to the high molecular weight n-alkanes. These high molecular weight alkanes are sourced in terrigenous plant wax material. Several representative GC traces are shown in Figures 5.2 and 5.3. The present understanding of the net transport of sediment in the area is that sediments are transported in a westerly direction. Thus, sediments entering the coastal area from the three major rivers, the Canning, Colville, and Sagavanirktok, would tend to be transported to the west. It appears that the relative paucity of LALK compounds in the sediments from Region 1 to the east of the Canning River (Figure 5.2) may be related to this pattern of transport. Indeed, as described in the next section, the LALK compounds appear to originate mainly in the rivers, possibly due to upstream fossil inputs, while the coastal peat samples, which contribute to the sediments throughout the Study Area, are rich in the higher molecular-weight alkanes, but generally not in the LALK compounds. As the Canning River mouth is approached (Region 2, Figure 5.3), and with increasing distance offshore (Station 1C, Figure 5.2), the LALK compounds appear in greater abundance in the sediment.

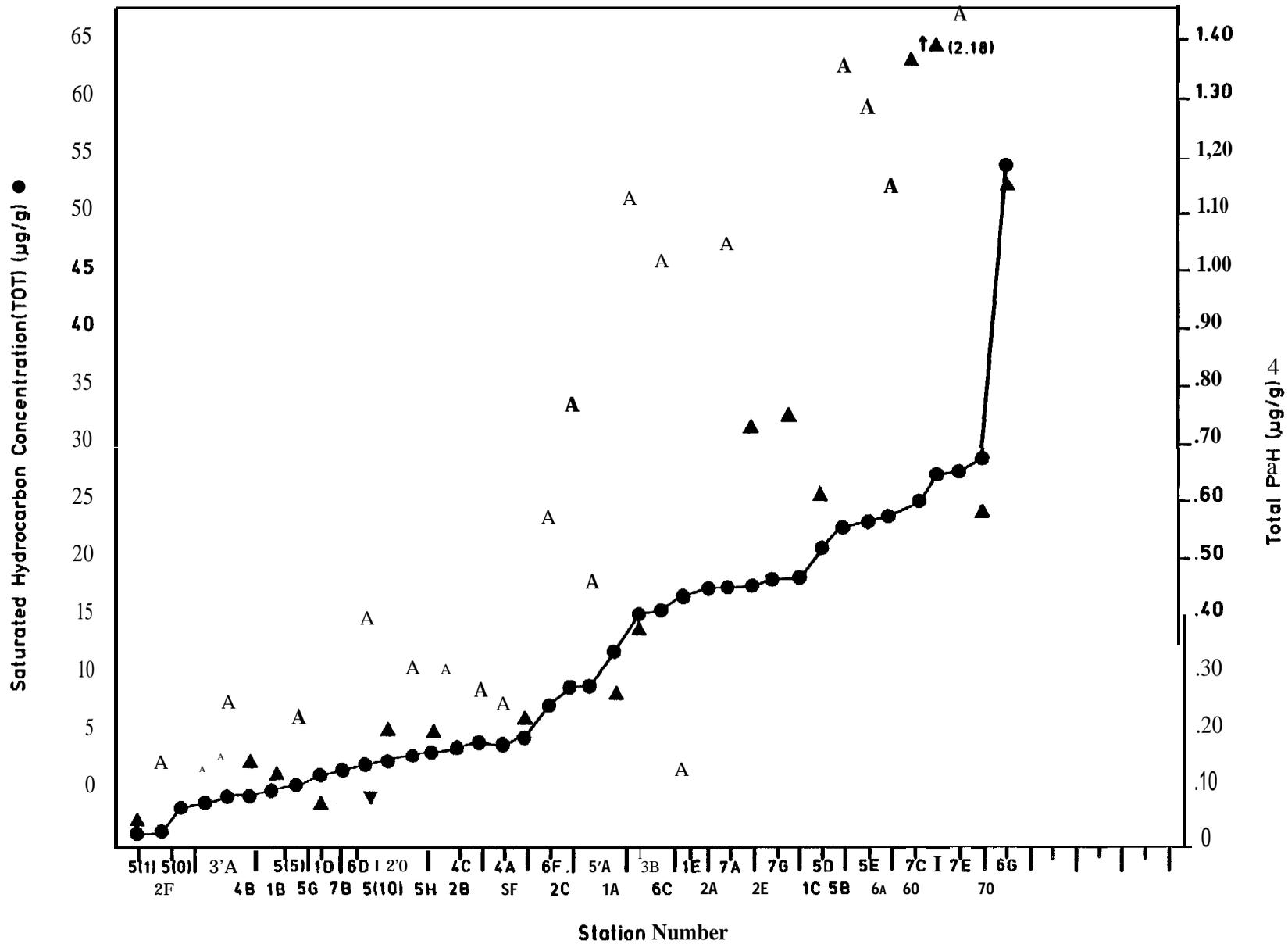


FIGURE 5.1. CONCENTRATIONS OF TOTAL SATURATED HYDROCARBONS (ToT) AND Total PAH ACCORDING TO STATION.

TABLE 5.11. CORRELATION MATRIX OF HYDROCARBON AND RELEVANT AUXILIARY PARAMETERS.

PEARSON CORRELATION COEFFICIENTS / PROB > |R| UNDER H0:RHO=0 / N = 26

	LOEN	LOGF	LOGP	LOGD	LOGPAH	LOGTALK	LOGMLKLOW1708U	IWI810	LOGTOT	LOGTOC	SILT	CLAY	
LOGN	1.00000	0.90084	0.96528	0.92344	0.91520	0.89985	0.82016	0.89629	0.86142	0.87853	0.71168	0.67569	0.60436
	0.0000	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0011
LOGF	0.90084	1.00000	0.89137	0.89642	0.87923	0.87465	0.76180	0.82051	0.82443	0.84536	0.67284	0.073928	0.70215
	0.0001	0.0000	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0002	0.0001	0.0001
LOGP	0.96528	0.89137	1.00000	0.91776	0.89508	0.90931	0.86846	0.92267	0.88760	0.89569	0.68695	0.70670	0.65271
	0.00001	0.0001	0.0000	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003
LOGD	0.92344	0.89642	0.91776	1.00000	0.89411	0.93908	0.82395	0.90235	0.89815	0.93461	0.65412	0.71750	0.62713
	0.0001	0.0001	0.0001	0.0000	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0003	0.0001	0.0006
LOGPAH	0.91520	0.87923	0.89908	0.89411	1.00000	0.86508	0.78426	0.85550	0.86594	0.86903	0.67407	0.65304	0.54843
	0.0001	0.0001	0.0001	0.0001	0.0000	0.0001	0.0001	0.0001	0.0001	0.0001	0.0002	0.0003	0.0037
LOGTALK	0.89995	0.87465	0.90931	0.93908	0.86508	1.00000	0.92587	0.93221	0.93963	0.98609	0.73352	0.80701	0.60635
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0000	0.0000	0.0000	0.0001	0.0001	0.0001	0.0001	0.0010
LOGLALK	0.82016	0.76180	0.86846	0.82395	0.78426	0.92587	1.00000	0.93802	0.93845	0.93087	0.66257	0.69711	0.54474
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0000	0.0001	0.0001	0.0001	0.0002	0.0001	0.0040
LOGV1708	0.89629	0.892051	0.92267	0.90235	0.085550	0.93221	0.93802	1.00000	0.94046	0.093430	0.68845	0.65927	0.55775
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0000	0.0000	0.0001	0.0001	0.0001	0.0002	0.0031
LOGV1810	0.86142	0.82443	0.88760	0.89815	0.86594	0.93963	0.93845	0.94046	1.00000	0.95218	0.68604	0.69552	0.65189
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0000	0.0001	0.0001	0.0001	0.0003
LOGTOT	0.87853	0.84536	0.89569	0.93461	0.86903	0.98609	0.93087	0.93430	0.95218	1.00000	0.71528	0.075139	0.62149
	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0000	0.0001	0.0001	0.0007
LOGTOC	0.71168	0.67284	0.68695	0.65412	0.67407	0.73352	0.66257	0.68845	0.68604	0.71528	1.00000	0.62588	0.43553
	0.0001	0.0002	0.0001	0.0003	0.0002	0.0001	0.0002	0.0001	0.0001	0.0001	0.0000	0.0006	0.0261
SILT	0.67569	0.73928	0.70670	0.71750	0.65304	0.80701	0.69711	0.65927	0.69552	0.75139	0.62588	1.00000	0.49260
	0.0001	0.0001	0.0001	0.0001	0.0003	0.0001	0.0001	0.0002	0.0001	0.0001	0.0006	0.0000	0.0106
CLAY	0.60436	0.70215	0.65271	0.62713	0.54843	0.60635	0.54474	0.55775	0.65189	0.62149	0.43553	0.49260	1.00000
	0.0011	0.00131	0.0003	0.0006	0.0037	0.0010	0.0040	0.0031	0.0003	0.0007	0.0261	0.0106	0.0000

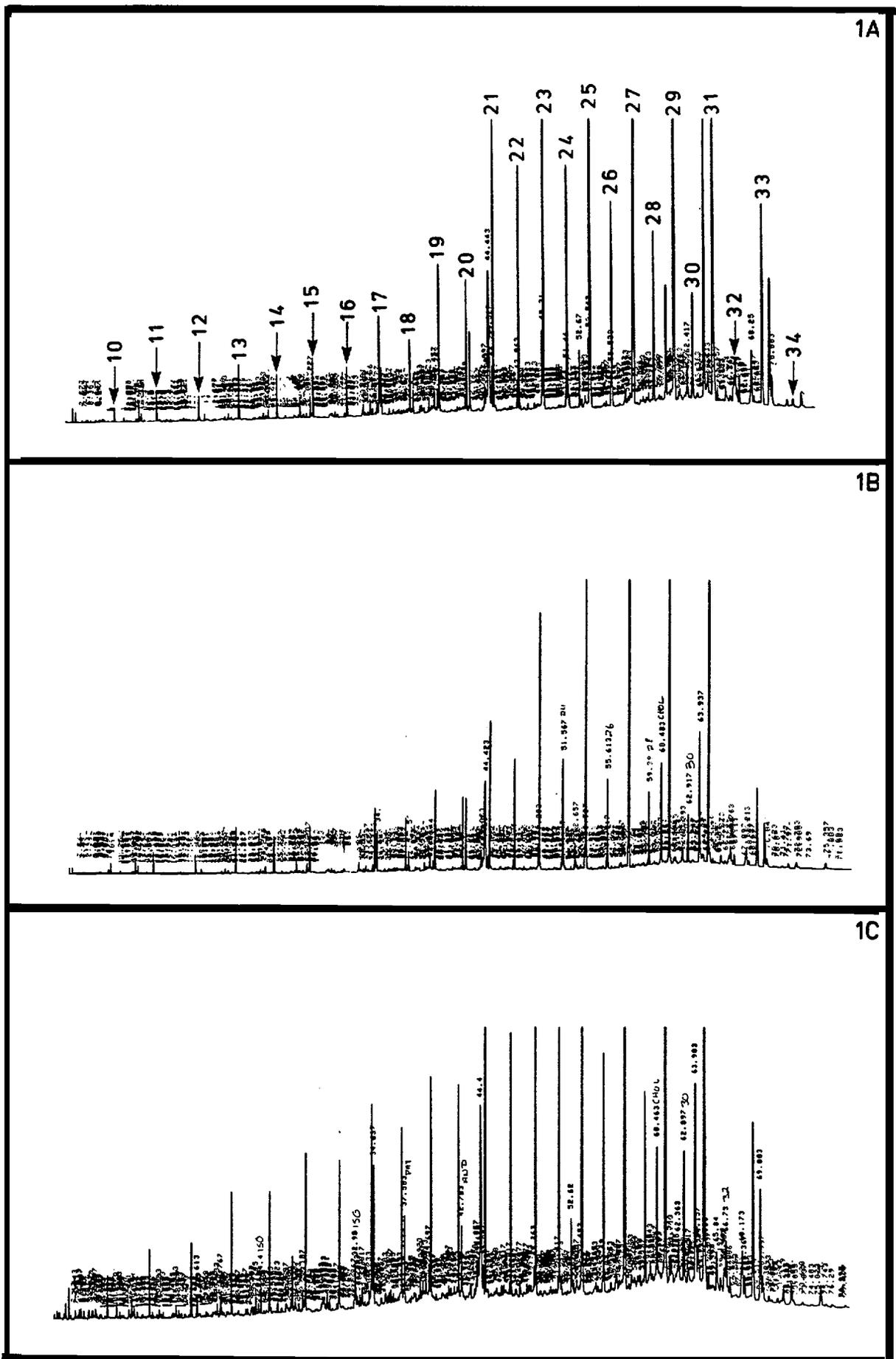


FIGURE 5.2. REPRESENTATIVE SATURATED HYDROCARBON COMPOSITIONS OF SURFACE SEDIMENTS (STATIONS 1A, 1B, 1C).

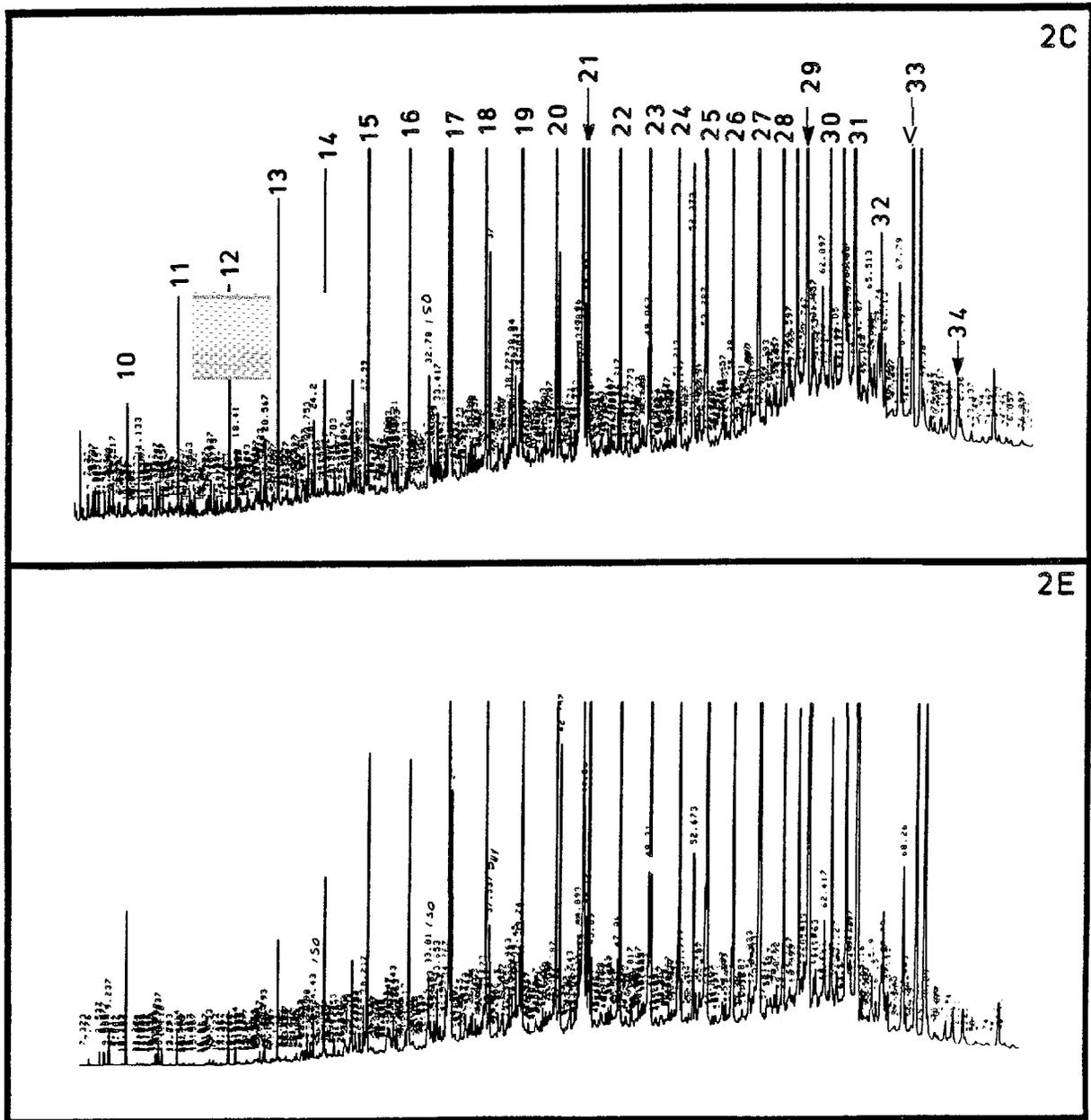


FIGURE 5.3. REPRESENTATIVE SATURATED HYDROCARBON COMPOSITIONS OF SURFACE SEDIMENTS (STATIONS 2C, 2E).

Other GC traces shown in Figure 5.4, from Stations 5G and 6B, represent typical sediments from the region with LALK and the higher molecular-weight alkanes mixed. Several interesting findings were revealed in the GC traces from stations in East Harrison Bay (Region 6). While these sediments contained some of the highest hydrocarbon concentrations, some of the sediments from Region 6 (Figure 5.5, Station 6D) were surprisingly depleted in the LALK compounds in the Year-2 samples. These compounds had been noted as important features of the Year-1 sediments from this region.

A somewhat clearer presentation of the saturated hydrocarbon composition is shown in Table 5.10, in which the key diagnostic saturated hydrocarbon parameters are presented. Although the LALK/TALK ratio appeared to be relatively constant in the entire Year-1 data, one notes a distinct shift in the composition in Region 6 (now comparable to Region 1) due to a "depletion" of the LALK compounds. The source that can be postulated as most responsible for the shift to lower LALK/TALK ratios is coastal peat (see Section 5.2.5). River sediment LALK/TALK ratios were generally higher than those in peat. It is hypothesized that inputs of the two major sources of observed hydrocarbons to the sediment, peat and river sediments, can, by shifts in the yearly relative amounts input to the sediment, also shift the composition of the sediments.

Of the other key saturated hydrocarbon ratios examined and presented in Table 5.12, the ISO/ALK ratio was generally invariant between Years 1 and 2, as was the OEPI, the measure of the odd-carbon predominance. The PRIS/PHY ratio, in general, appeared to decrease slightly throughout the Study Area in Year-2. Note, however, that the significantly elevated PRIS/PHY ratios observed at Stations 7E and 7G in the West Harrison Bay area during Year-1 were again observed in Year-2. Because the peat sample, obtained directly adjacent to these stations, was also enriched in pristane, peat input again appeared to be the dominant source factor to the Harrison Bay area. This hypothesis is further supported by the nature of the GC traces from the sediments of Stations 7E and 7B (Figure 5.6). These chromatograms differed from all others in the Study Area by virtue of the distinct "clusters" of branched alkanes and mono-olefins observed eluting near $n\text{-C}_{11}$, $n\text{-C}_{13}$, $n\text{-C}_{15}$, and $n\text{-C}_{17}$. The peat sample from Kogru Island directly adjacent to these stations contained identical features.

One of the aspects of the Year-2 hydrocarbon study concerned a limited examination of the content and composition of bulk sediment, and the isolated mud fraction of sediments from three stations. These comparisons, shown in Table 5.13, indicate that concentration increased by a factor of 2-10. When the mud fraction was analyzed separately, this increase was directly related to the mud content of the sediment and followed from the strong correlation of saturated hydrocarbon and mud content ($r=0.76$). However, the values of the key diagnostic saturated hydrocarbon parameters were similar in all bulk and mud fraction pairs, as additionally illustrated by the GC traces in Figures 5.5, 5.7, and 5.8.

5.3.3.3. Aromatic Hydrocarbon Composition. The analytical results on the set of aromatic hydrocarbon (AH) determinations have previously been presented in Section 4. As was the case for the Year-1 sediments, the AH composition of the sediments was fairly uniform, with the 2- and 3-ringed naphthalene and phenanthrene series dominant in most of the sediments. Several typical AH compositional plots from the Year-1 sediments (Figures 5.9 and 5.10) represent the range of Al-1 compositions observed in the Year-2 sediments. The quantity of the naphthalene and phenanthrene homologous series greatly exceeded that of the 4- and 5-ringed PAH. As observed in Year-1 sediments, this situation confounds the ability to detect incremental additions of oil-derived PAH to the sediments. As stated last year, this situation is highly unusual for coastal marine sediments. In other continental shelf regions not impacted by petroleum pollutants, the 4- and 5-ringed PAH compounds usually dominate. This dominance results in the FFPI diagnostic ratio being quite low, typically 0.1 to 0.4, in most unimpacted marine

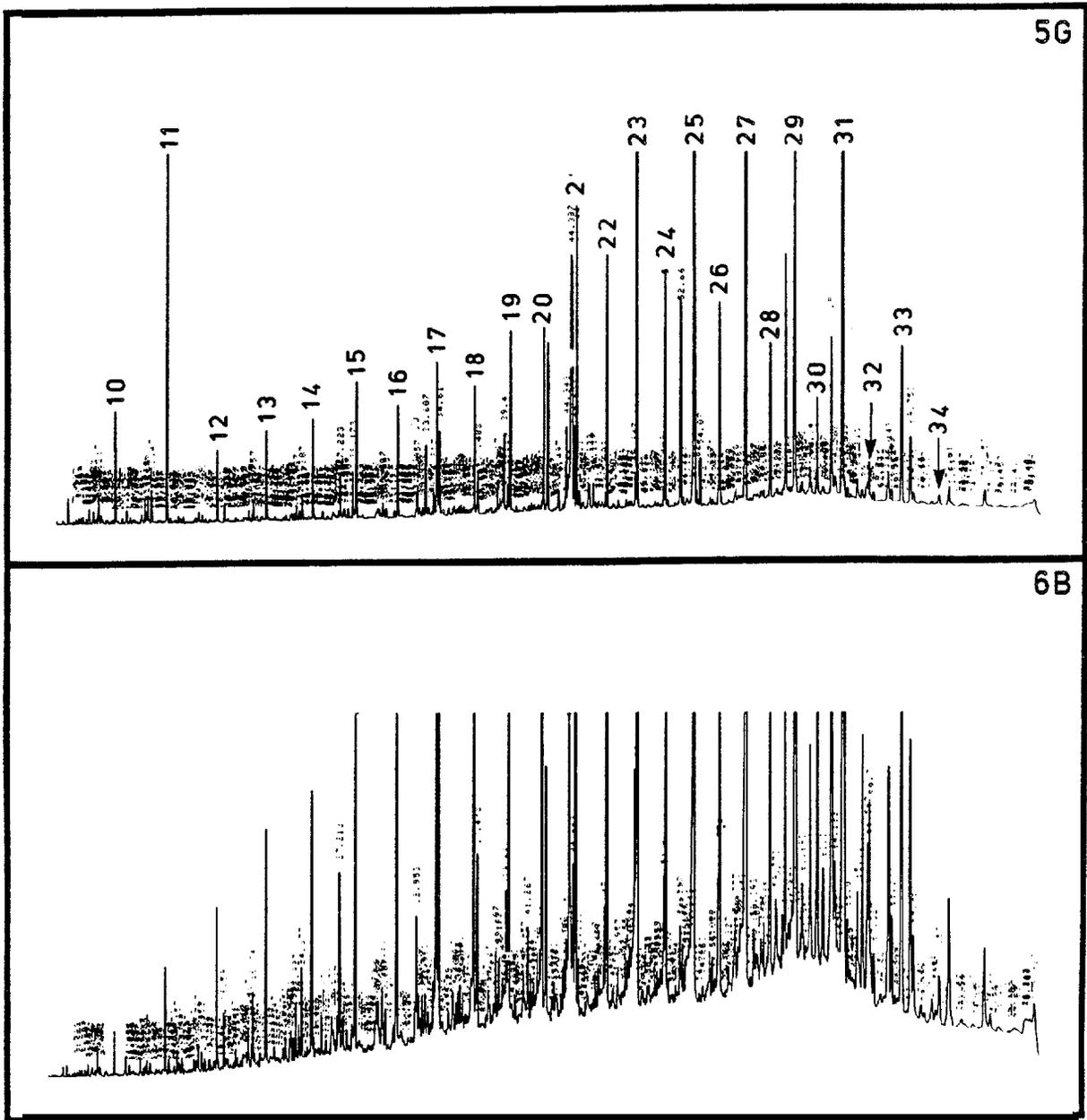


FIGURE 5.4. REPRESENTATIVE SATURATED HYDROCARBON POSITIONS OF SURFACE SEDIMENTS (STATIONS 5G, 6B).

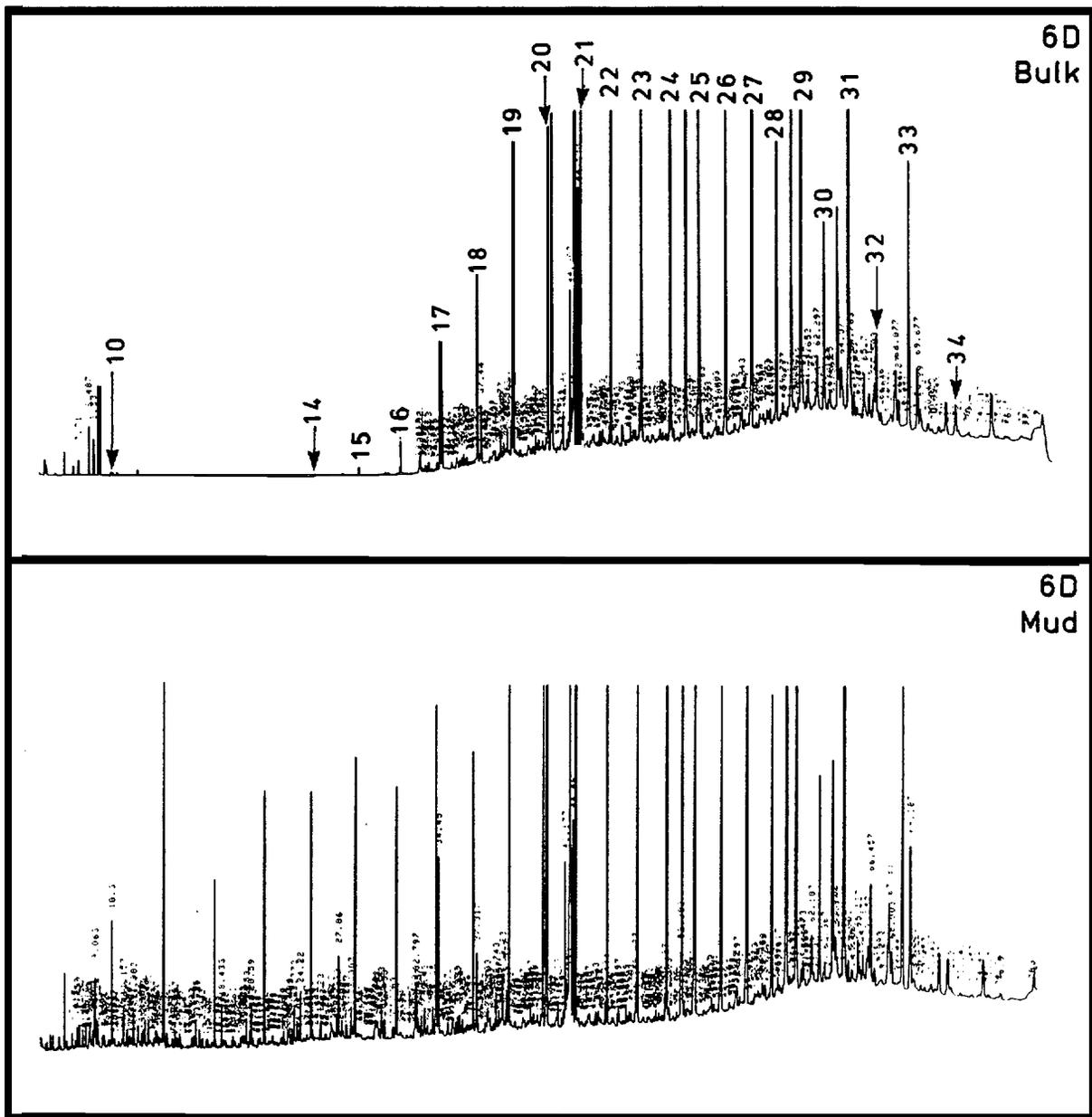


FIGURE 5.5. COMPARISON OF SATURATED HYDROCARBON COMPOSITIONS OF BULK SEDIMENT AND MUD FRACTION FROM STATION 6D.

TABLE 5.12. SUMMARY OF SEVERAL KEY SATURATED HYDROCARBON PARAMETERS AND DIAGNOSTIC RATIOS^a

Station	LALK/TALK		PRIS/PHY		ISO/ALK		OEPI	
	Year- 1	Year-2	Year-1	Year-2	Year-1	Year-2	Year-1	Year-2
1A		0.08		1.8		0.38		7.5
1B		0.15		1.8		0.46		5*9
1C		0.19		1.5		0.55		4.1
1D		0.07		2.3		0.29		8.8
1E		0.09		1.8		0.13		7.1
2A		0.17		1.5		0.43		5.6
2B		0.15		1.8		0.44		5.7
2C		0.20		1.5		0.55		4.4
2D		0.11		1.7		0.38		4.7
2E	0.32	0.17	2.5	1.6	0.44	0.41	6.0	4.3
2F	0.27	0.20	2.6	1.9	0.48	0.44	6.2	4*5
3A	0.18	0.12	2.1	1.9	0.45	0.45	7.0	6.3
30	0.18	0.14	2.0	1.7	0.44	0.42	7.1	5.9
4A	0.18	0.15	2.4	1.6	0.43	0.39	6.2	3.4
40	0.27	0.16	2.3	1.9	0.44	0.42	2.7	3.6
4C	0.27	0.14	2.3	1.7	0.43	0.42	4.9	3.4
5(o)		0.21		2.0		0.41		5.0
5(1)	0.24	0.20	2.3	2.0	0.46	0.35	5.7	4.6
5(5)	0.39	0.24	2.1	1.9	0.52	0.36	5.2	5.3
5(10)	0.19	0.20	2.9	1.8	0.47	0.42	6.5	5.3
5A	0.20	0.20	2.1	1.7	0.52	0.50	6.1	4*9
5B	0.17	0.20	2.5	1.2	0.45	0.61	4.0	3.9
5D	0.36	0.13	2.1	1.4	0.41	0.47	8.1	4.7
5E	0.26	0.20	2.3	1.5	0.45	0.51	4.2	4.3
5F	0.12	0.20	2.3	1.5	0.42	0.44	7.9	4.3
5G	0.25	0.18	2.5	2.0	0.47	0.43	5.5	4.8
5H		0.21		2.0		0.40		5.3
6A	0.29	0.12	2.5	1.7	0.49	0.50	7.0	5.0
6B	0.18	0.11	2.1	1.8	0.51	0.55	5.7	4.1
6C	0.30	0.11	2.2	1.9	0.47	0.51	5.4	4.0
6D	0.48	0.14	2.5	1.6	0.47	0.55	5.2	4.7
6F	0.19	0.18	2.4	1.9	0.46	0.45	7.3	4.6
6G		0.13		2.0		0.39		4.7
7A	0.23	0.15	2.6	2.0	0.55	0.54	6.6	4.9
7B	0.32	0.19	2.7	2.3	0.45	0.43	5.9	4.5
7C	0.23	0.14	2.2	2.1	0.47	0.44	6.2	5.2
7D		0.15		2.4		0.46		5.1
7E	0.22	0.16	3.5	3.6	0.62	0.61	7.1	5.3
7G	0.26	0.25	4.7	4.4	0.92	0.74	3.7	3.8

^aValues represent station means.

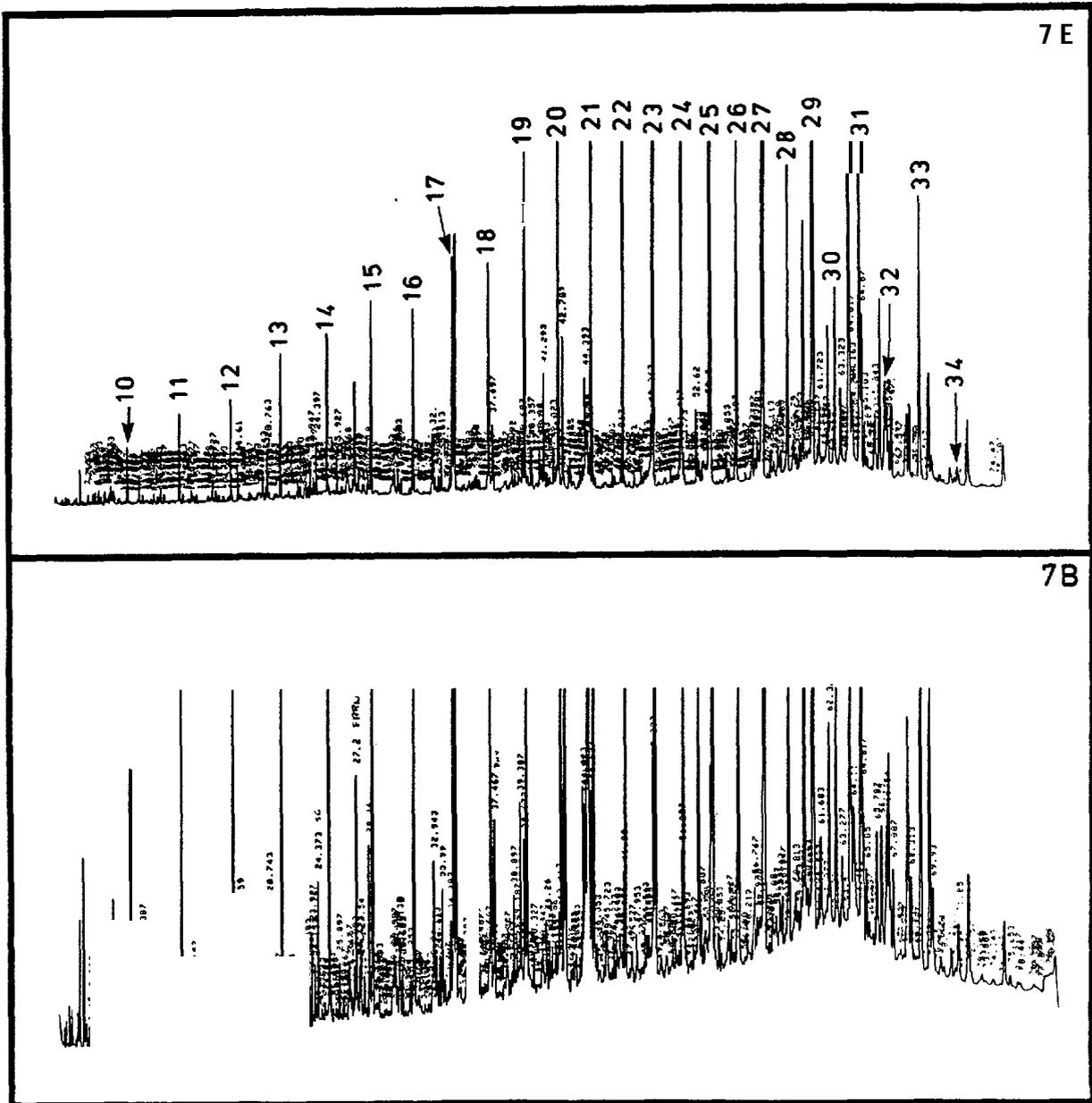


FIGURE 5.6. REPRESENTATIVE SATURATED HYDROCARBON COMPOSITIONS OF SURFACE SEDIMENTS (STATIONS 7E, 7B).

TABLE 5.13. COMPARISON OF BULK SEDIMENT AND MUD FRACTION ANALYTICAL RESULTS FOR SATURATED HYDROCARBONS.

Station	LALK ($\mu\text{g/g}$)	TALK ($\mu\text{g/g}$)	LALK/TALK	PRIS/PHY	ISO/ALK	TOT ($\mu\text{g/g}$)	Mud Content (%)
<u>1A</u>							
Bulk	0.6	7.5	0.08	1.8	0.38	17	68.7
Mud	1.3	15.7	0.09	1.5	0.41	27	
<u>5(5)</u>							
Bulk	0.5	2.3	0.20	1.9	0.36	5.3	23.5
Mud	2.2	12.3	0.18	2.0	0.40	21	
<u>6D</u>							
Bulk	0.3	2.6	0.14	1.6	0.55	7.6	17.6
Mud	3.8	17.1	0.22	1.8	0.45	35	

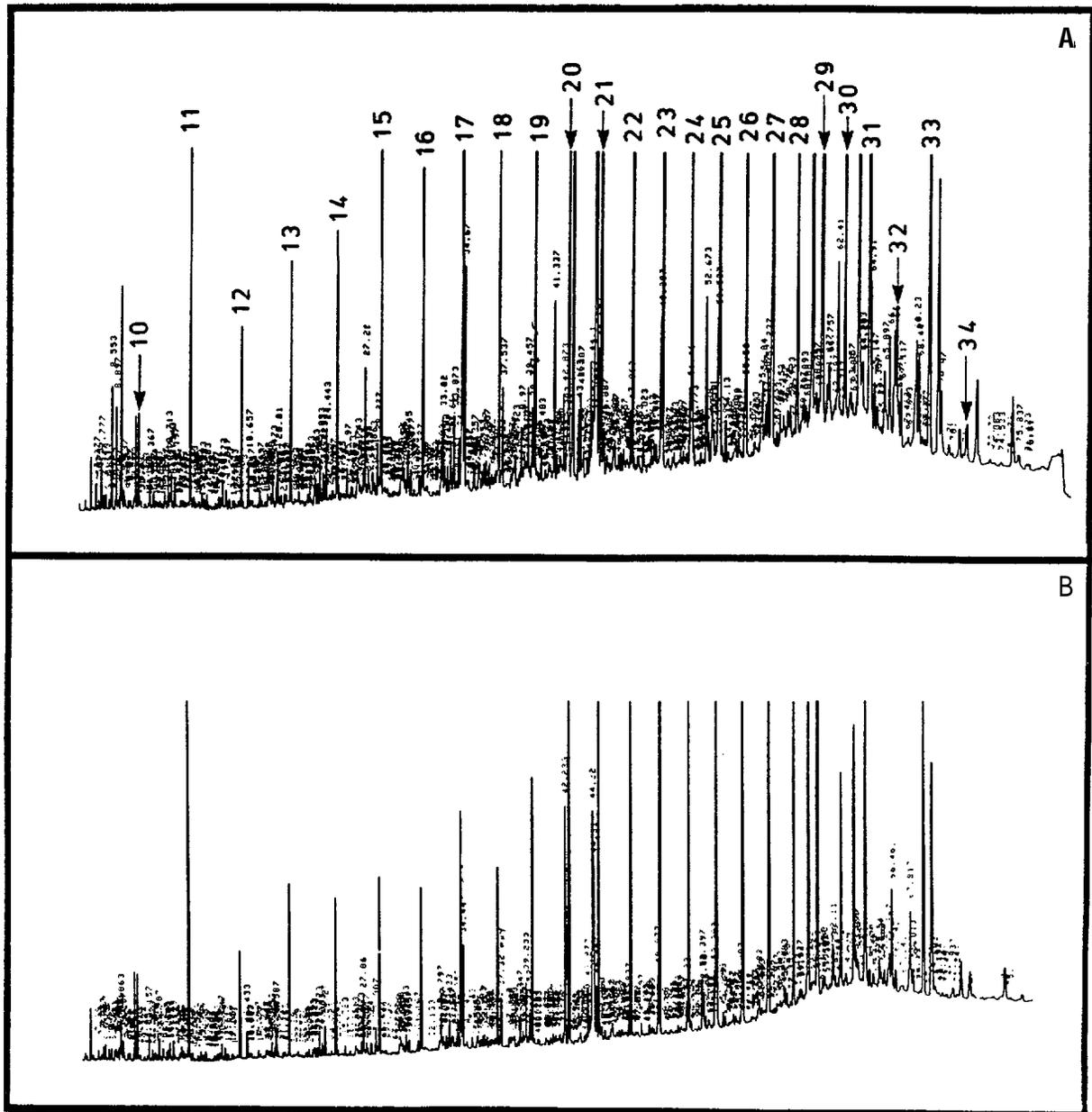


FIGURE 5.7. COMPARISON OF SATURATED HYDROCARBON COMPOSITIONS OF BULK SEDIMENT AND MUD FRACTION FROM STATION 5(5).

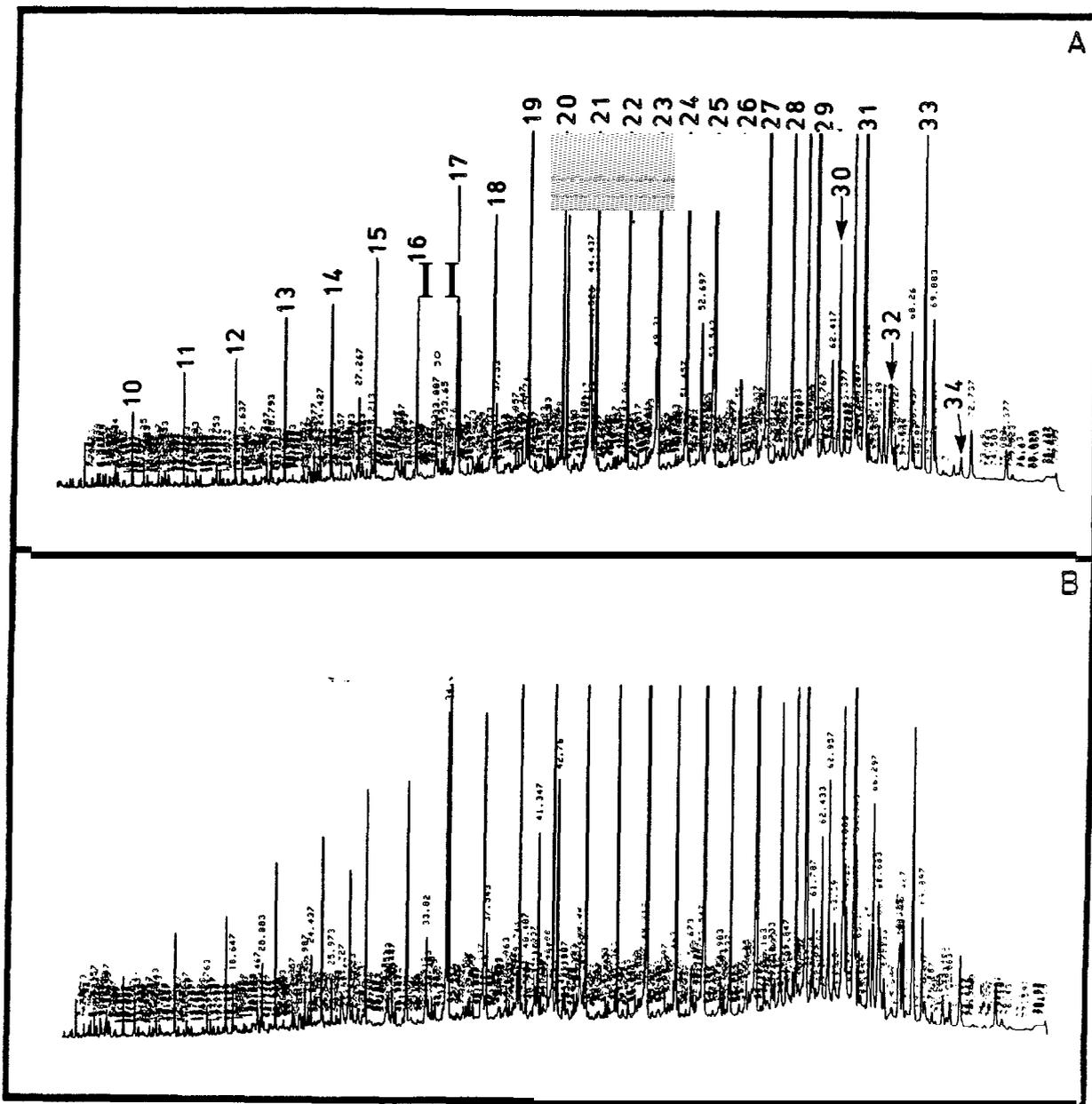


FIGURE 5.8. COMPARISON OF SATURATED HYDROCARBON COMPOSITIONS OF BULK SEDIMENT AND MUD FRACTION FROM STATION 7D.

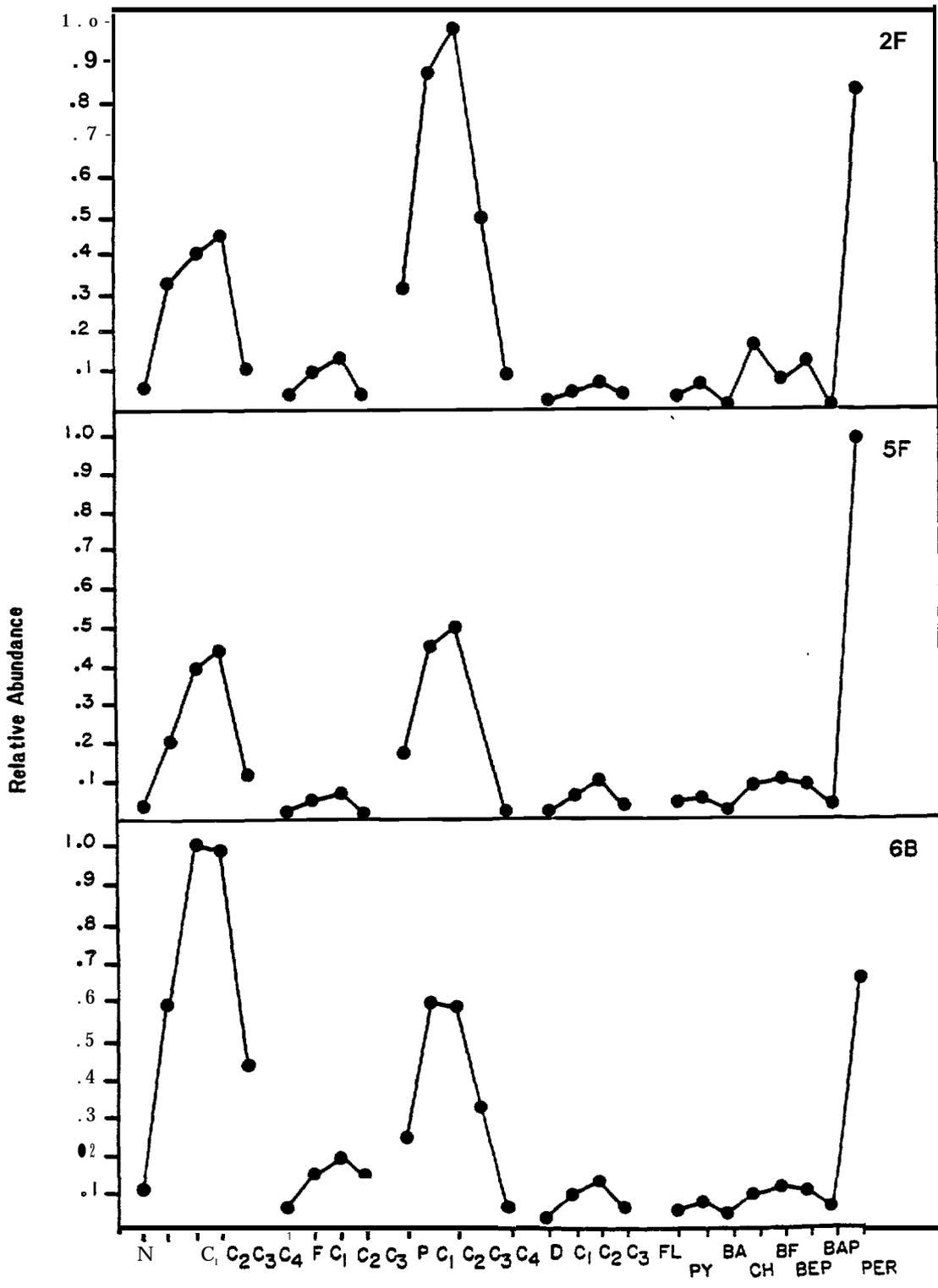


FIGURE 5.9. AROMATIC HYDROCARBON RELATIVE ABUNDANCE PLOTS FROM REPRESENTATIVE SEDIMENT STATIONS.

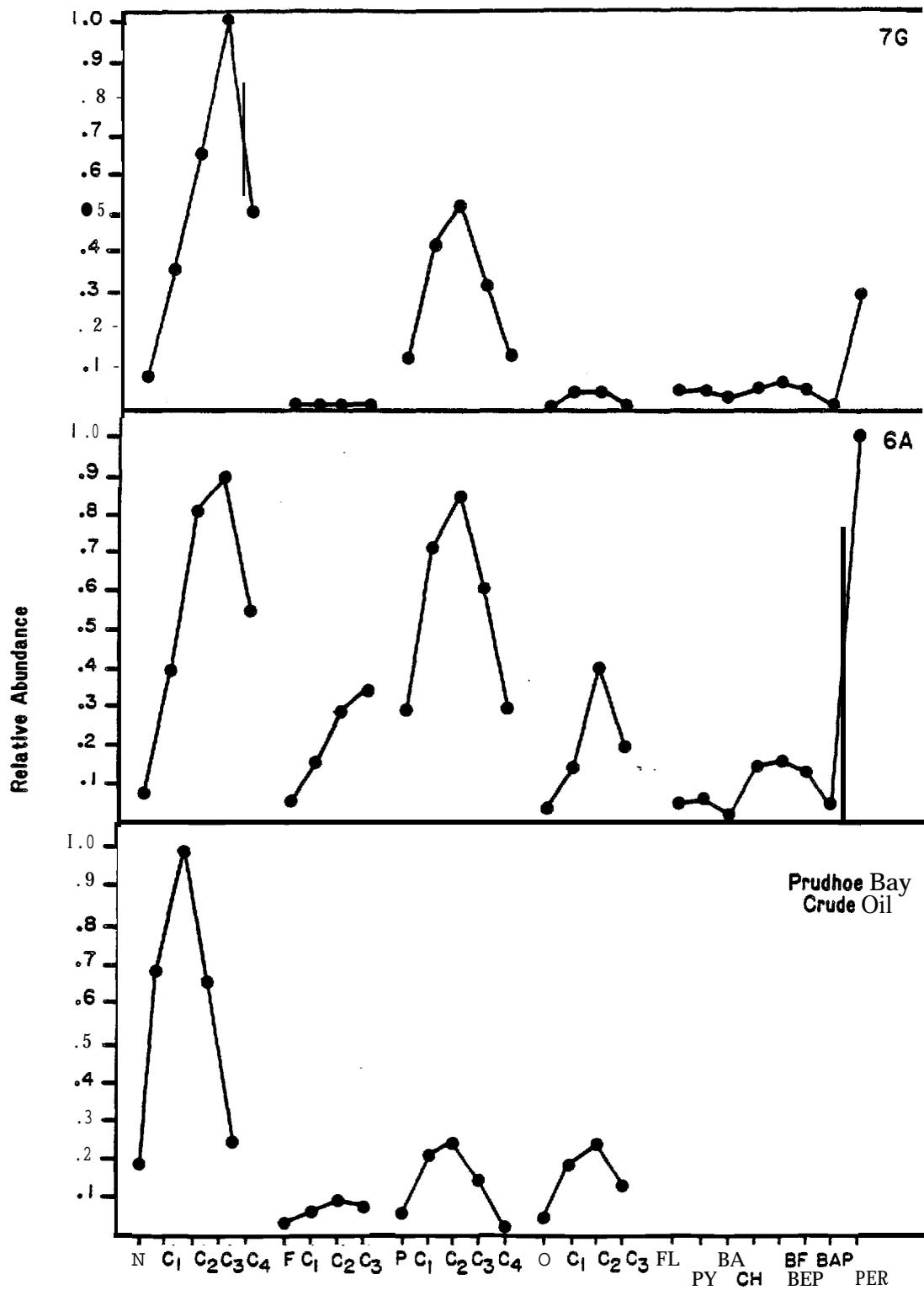


FIGURE 5.10. AROMATIC HYDROCARBON RELATIVE ABUNDANCE PLOTS OF SEDIMENTS AND PRUDHOE BAY CRUDE OIL.

sediments. Thus, with an incremental addition of **petrogenic** AH having an **FFPI** of near unity, the **ratio** increases and petrogenic inputs can be detected. In the Beaufort Sea sediments, the inputs of river sediments appear to contribute to the lower molecular weight AH as they contribute to the LALK compounds previously discussed.

Several diagnostic ratios are presented in Table 5.14. We have previously found in the Year-1 study that the more subtle aspects of the AH composition, namely the N/P and P/D ratios, appear to be potentially more useful than the FFPI or absolute concentration data for monitoring purposes due to the differences between the ratios observed in the Region's sediments and potential sources of crude oil (i.e., Prudhoe Bay Crude). Overall, the Year-2 ratios of N/P are 1.3 ± 0.72 and the P/13 ratios, 7.6 ± 5.6 . The distinct differences between these ratios found in sediment and the corresponding ratios found in a typical crude oil of 4.0 and 1.1, respectively, make these ratios good diagnostics of potential **petrogenic** inputs. The abundance of the **dibenzothiophenes** (D) and, specifically, the ratio of P/D, are excellent potential indicators of petrogenic inputs, with the D compounds present at low absolute and relative quantities in the sediments, and present at larger relative quantities in the crude oil sample.

As with the saturated hydrocarbons, the AH content and composition was explored on bulk sediments and their corresponding mud fractions. The results are summarized in Table 5.15. The key diagnostic parameter ratios of **FFPI**, N/P, and P/D were very similar in the bulk and mud fractions, in spite of large absolute concentration differences in the PAH content.

5.3.3.4. Statistical Correlations. In order to view the individual saturated and aromatic hydrocarbon parameters on a more regional basis, Pearson correlation coefficients were computed for the major parameters. This correlation matrix is presented in Table 5.11.

5.3.3.5. Geographic 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 slopes of the Brooks Range (but not the coastal plain) between 150° and 160°W; the annual flow is 10^{10} 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 (700 18'N, 1510 09'W) slightly west of the Colville and 5 miles from the coast. This lake was named for the natural seep oil that 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 low bluffs that are a common feature on the Beaufort coast. Although these natural sources may account for the PAH found in Harrison Bay sediments, anthropogenic sources associated with river sediments appear to contribute to LALK and the PAH content of the sediment. 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 concentration in Harrison Bay stations which, compared to other stations, are elevated in all saturated and aromatic compounds.

The high mud (silt + clay) content of Harrison Bay sediments, the sediments of Stations 1A, 1C, 1E, 2A, 2C, and 2E of the Camden Bay area and at other stations in the

TABLE 5.14. SUMMARY OF SEVERAL KEY AROMATIC HYDRO-CARBON DIAGNOSTIC RATIOS

Station	FFPI ^a		N/P ^b		P/D ^c	
	Year-1	Year-2	Year-1	Year-2	Year-1	Year-2
1A		0.61		0.99	-	5.9
1B		0.71		1.06		5.8
1C		0.63		1.22	-	4.8
1D		0.61		1.36		13.7
1E		0.71		ion		13.8
2A		0.72		0.81		9.0
2B		0.69		1.04		8.1
2C		0.69		1.29		4.7
2D		0.70		2.83		5.1
2E	0.55	0.79	0.59	1.31	7.9	7.8
2F	0.76	0.82	0.46	0.96	12.7	35.2
3A	0.81	0.75	0.79	1.18	8.6	10.8
30	0.84	0.79	0.92	0.57	8.4	7.1
4A	0.82	0.80	0.93	1.21	4.5	11.5
4B	0.87	0.74	1.0	1.13	3.4	11.4
4C	0.82	0.73	0.74	1.13	4.5	10.0
5(o)		0.65		1.00		8.8
5(1)	0.83	0.69	0.79	0.90	5.1	12.2
5(5)	0.76	0.69	0.74	0.93	5.4	6.2
5(10)	0.83	0.77	0.81	1.32	5.0	3.9
5A	0.81	0.73	1.11	1.71	9.4	6.6
50	0.83	0.73	0.81	1.32	4.0	5.7
5D	0.79	0.74	0.91	1.29	5.8	4.4
5E	0.85	0.73	0.91	1.48	4.6	5.7
5F	0.69	0.68	0.86	1.07	6.7	3.6
5G	0.79	0.71	0.94	1.34	7.5	13.7
5H		0.76	.	1.06	.	8.1
6A	0.83	0.77	0.99	1.48	3.5	5.2
6B	0.85	0.83	1.7	2.35	6.2	5.0
6C	0.83	0.76	0.96	1.51	4.5	4.6
6D	0.79	0.74	1.0	1.35	5.1	4.9
6F	0.82	0.81	1.1	1.58	5.3	5.4
6G		0.78		1.76		5.4
7A	0.83	0.76	1.3	2.02	5.6	5.5
7B	0.80	0.77	1.1	1.70	4.9	4.7
7C	0.93	0.89	1.1	1.70	5.7	4.4
7D	-	0.81		0.86		5.4
7E	0.88	0.81	1.7	2.00	7.4	6.0
7G	0.88	0.80	1.7	0.88	12.1	8.2
Prudhoe Bay Crude Oil		1.00		4.0		1.1

^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).

TABLE 5.15. COMPARISON OF BULK SEDIMENT AND MUD FRACTION ANALYTICAL RESULTS FOR AROMATIC HYDROCARBONS.

Station	Total PAH ($\mu\text{g/g}$)	FFPI	N/P	P/D
1A				
Bulk	0.26	0.61	1.0	5.9
Mud	0.60	0.60	1.1	5.8
5(5)				
Bulk	0.14	0.69	0.9	6.2
Mud	1.00	0.68	1.3	8.3
6D				
B u l k	0.39	0.73	1.4	4.9
Mud	2.10	0.70	1.4	7.0

Study Area (3B, 5B, 5D) suggest that these areas are the most likely depositional areas of fine-grained particles, low density organic detritus and anthropogenic inputs.

Two stations within Harrison Bay, 7E and 7G, exhibited anomalous 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, or may be receiving large quantities of pristane-enriched peat originating from the Kogru Island and adjacent areas.

Marine sediments collected between the mouths of the Colville and Canning Rivers, including the Prudhoe Bay area, showed generally lower total hydrocarbon values than those from Harrison Bay. Higher hydrocarbon concentrations are generally associated with finer-grained (3B, 5B, and 5D) and more organic-rich (4A, 5A, 5D, 5H) stations. There are probably fewer natural petroleum seeps and coal outcrops to the east of the Canning River. The drainage system east of the Colville consists of smaller rivers that discharge material more uniformly along the coast, but nevertheless contain anthropogenic materials as found in the Sagavanirktok River. These factors will lead to greater dispersion and lower concentrations of background hydrocarbon distributions.

5.3.4 River and Peat

Due to the abundance of metal, saturated hydrocarbon, and PAH content observed in the sediments sampled in Year-1, the Year-2 program focused partly on examining possible source materials for observed offshore sediment distributions. Two likely sources are coastal peat, which is widespread along the entire coastline of the Beaufort Sea, and riverine sediments. Eight samples of peat were obtained from Stations 1 F, 2G, 2H, 3D, 5K, 63, 7H, and 73 and two river sediment samples, one each from the Colville and Sagavanirktok Rivers, were analyzed by GC and GC/MS.

The hydrocarbon" results were previously presented in Tables 4.10, 4.11, 4.14, and 4.15. The average values of key saturated hydrocarbon parameters and parameter ratios are presented in Table 5.16. The ratio of total saturates (TOT) to total organic carbon (TOC) in peat averaged 0.027 ± 0.020 over the entire Study Area and ranged from a low of 0.007 at Station 3D (Tigvariak Island) to 0.058 at Station 7J (Kogru Island). The hydrocarbon concentrations in peat were generally much greater than in offshore sediment but the ratio of TOT/TOC was similar in both sample types. The TOT/TOC ratio in offshore sediments averaged 0.017 ± 0.01 and ranged from 0.004 to 0.049.

In examining the data in Table 5.16 for clues as to the relative importance of peat versus river sediment in contributing to the sediment hydrocarbons, one is directed not to the absolute concentration data, but to the diagnostic ratios LALK/TALK, PRIS/PHY, ISO/ALK, and TOT/TOC. The TOT/TOC ratio in peat averaged 0.027, much higher than that in the river sediment (0.00 S); offshore sediments averaged between the two potential source types. However, the ALK/ISO and, especially the LALK/TALK ratios were similar in offshore and river sediments, and quite different from the peat samples. The GC traces of the source types in comparison to each other and to the offshore sediments reveal much about the relative importance of peat and river sediment. Typically, the saturated hydrocarbon distribution in peat is composed of 1) an abundance of terrigenous plant wax n-alkanes (n-C₂₁ to n-C₃₃) with an odd-carbon predominance (OEPI = 7 to 14), and 2) a distinct series of mono-olefins which elute just prior to the corresponding n-alkanes. This mono-olefinic distribution has been reported in lake sediments (Giger et al., 1980) and appears associated with organic matter in a state of early diagenesis. Note that these high molecular weight mono-olefins are absent or found at trace concentrations in the offshore sediments. Note the general absence of the LALK compounds in the GC traces of Figure 5.11, the abundance of higher molecular-weight alkanes and mono-olefins, and the clusters of branched alkanes and mono-olefins eluting

TABLE 5.16. KEY SATURATED HYDROCARBON PARAMETERS AND RATIOS IN COASTAL PEAT AND RIVER SAMPLES.

Station	LALK (µg/g)	TALK (µg/g)	LALK/TALK	Plus (µg/g)	PHY (µg/g)	PRIS/PHY	ISO/ALK	TOT (µg/g)	TOC (mg/g)	TOT/TOC
Peat Stations										
IF	12	260	0.044	0.015	<D.L. ^a		0.022	532	9.5	0.029
2G	0.36	39	0.021	0.021	0.008	2.6	0.20	50	4.2	0.056
2H	2.8	84	0.033	0.066	0.043	1.5	0.12	110	17	0.012
3D	3.7	230	0.015	0.071	0.040	1.3	0.15	390	23	0.007
5K	1.3	83	0.016	0.034	0.022	1.5	0.25	150	9.3	0.017
6J	5.9	240	0.024	0.026	< D.L.		0.032	740	26	0.017
7H	1.7	41	0.042	0.042	0.023	1.8	0.19	51	2.3	0.022
7J	17	600	0.028	2.65	0.075	35	0.43	1700	30	0.053
Average Peat	-	-	0.028 ± 0.01	-	-	-	0.1730.13	-	-	0.027 ± 0.02
River Stations										
5J	1.1	8.7	0.13	0.025	0.020	1.3	0.21	16	1.3	0.012
6H	1.2	10.6	0.12	0.02	0.038	2.5	0.45	25	6.6	0.004
Average River	-	-	0.13 ± 0.01	-	-	1.9	0.33 ± 0.17	-	-	0.008 ± 0.006
Average Offshore Sediments	-	-	0.16 ± 0.04	-	-	2.3	0.43	-	-	0.017 ± 0.01

^aDetection Limit

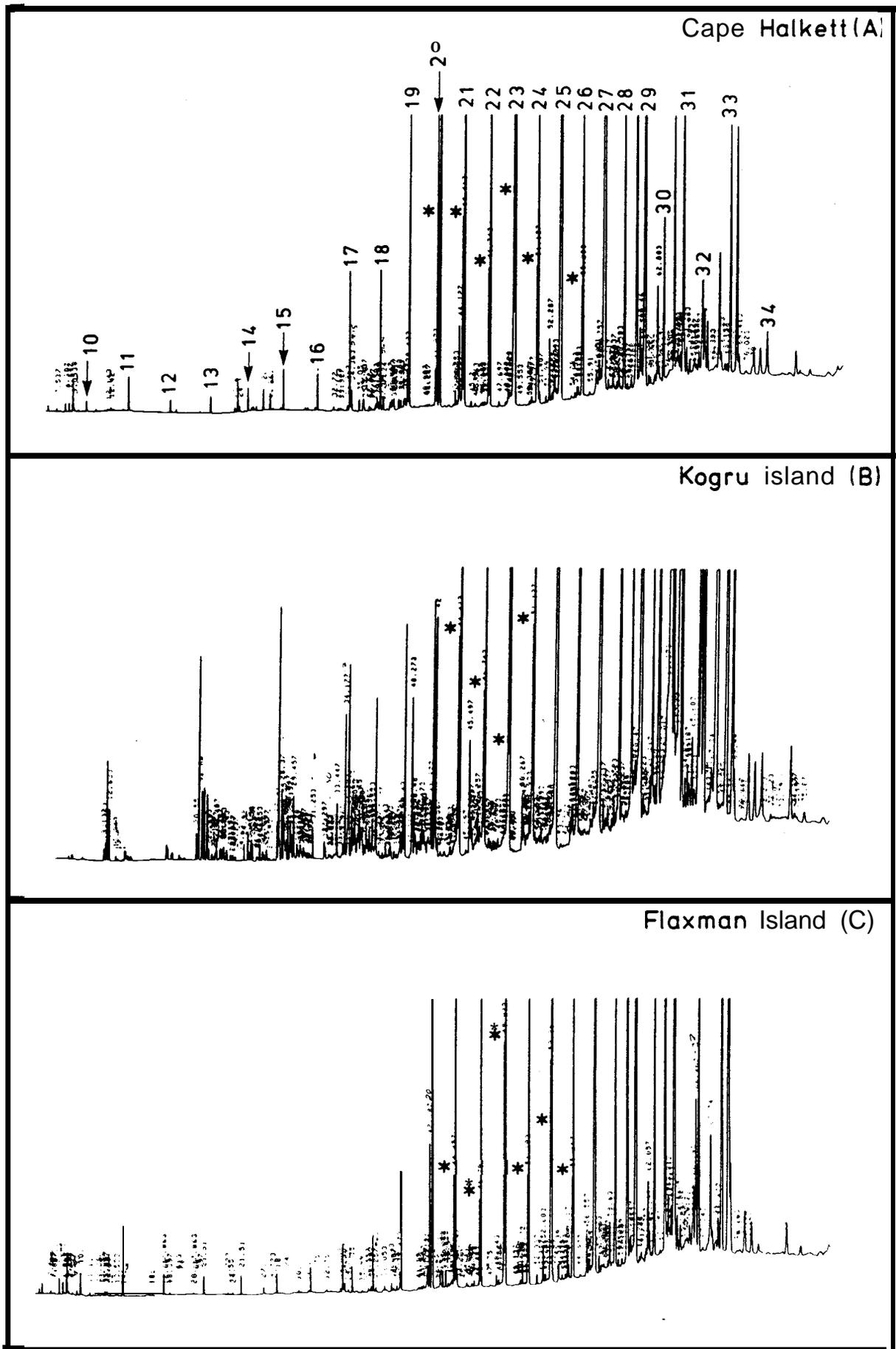


FIGURE 5.11. SATURATED HYDROCARBON COMPOSITION OF COASTAL PEAT. * INDICATES MONO-OLEFIN.

around n-C 13, n-C 15, and n-C 17 in Figure 5.9 (Flaxman Island peat sample). This latter distribution was found in several species of marine animals in the region.

In contrast, the river sediments (Figure 5.12) combined the above-described peat distribution with the abundance of the LALK compounds and with the high molecular weight olefins generally lacking. The result is that the LALK/TALK ratio in the river sediment was quite similar to that found in coastal offshore sediment. Coastal peat along the river banks certainly was an important source of hydrocarbons to the river sediments. However, it is this distribution of LALK compounds that differentiated river sediment from coastal peat and suggested that an upriver source of fossil hydrocarbons (coal and/or oil) combined with peat to form the composition in the river sediments. In turn, it appeared that the river and offshore sediments were quite similar in composition.

The aromatic hydrocarbon distributions of peat and river sediments were also quite instructive. The aromatic content of peat and river sediments was high and it was clear that a combination of these sources contributed to the high PAH content of the offshore sediment. The total PAH content (2-5 rings) of peat averaged 0.3 µg/g and ranged from 0.05 to 0.71 µg/g. The two river sediments averaged 0.45 µg/g and ranged from 0.21 to 0.70 µg/g, while the offshore sediments averaged 0.58 µg/g. On the basis of PAH concentration comparisons, it was clear that the PAH in offshore sediments originated in a combination of peat and river sediments. Key PAH ratios shed more light on the issue. The tabulated average ratios in Table 5.17 indicated the following:

- The N/P ratios of peat, river, and offshore sediments were, on the average, similar.
- The P/D ratios of river and offshore sediments were similar and differed from peat.
- The PAH/TOC ratios in the 39 offshore sediments were similar to the two river samples and quite different from the peat samples.
- The FFPI was similar in river and offshore sediments, both of which were higher than peat. A similarity in offshore and river sediment was apparent and seemed to stem from similarities of the N and P series of aromatics. The lower value of the FFPI in peat indicated that river sediments were the major source of the N and P series. This source of fossil N and P appears to be coincident with the LALK distribution observed for the saturated hydrocarbons.

To further examine the PAH assemblages, alkylhomologue distributions of the river and peat sediment are plotted in Figures 5.13 through 5.15. When viewed in comparison to the offshore sediment similarly plotted in Year-1 (Figures 5.9 and 5.1 O), the similarity of river and offshore sediments was again apparent.

5.3.5 Tissue Hydrocarbons

The tissue hydrocarbon data obtained in the Year-2 program represented a more extensive set of data than was obtained in Year-1 with respect to the numbers of species obtained, the areal coverage, and the quantity of samples obtained for analysis. Thus, the Year-2 data should really be considered as the initial data set to be applied to trend analyses and hypothesis testing. The samples obtained for hydrocarbon analyses were the following:

- Bivalves: Astarte borealis - Stations 1B, 3A, 5H, and 6D
Cyrtodaria kurriana - Stations 5F and 6G

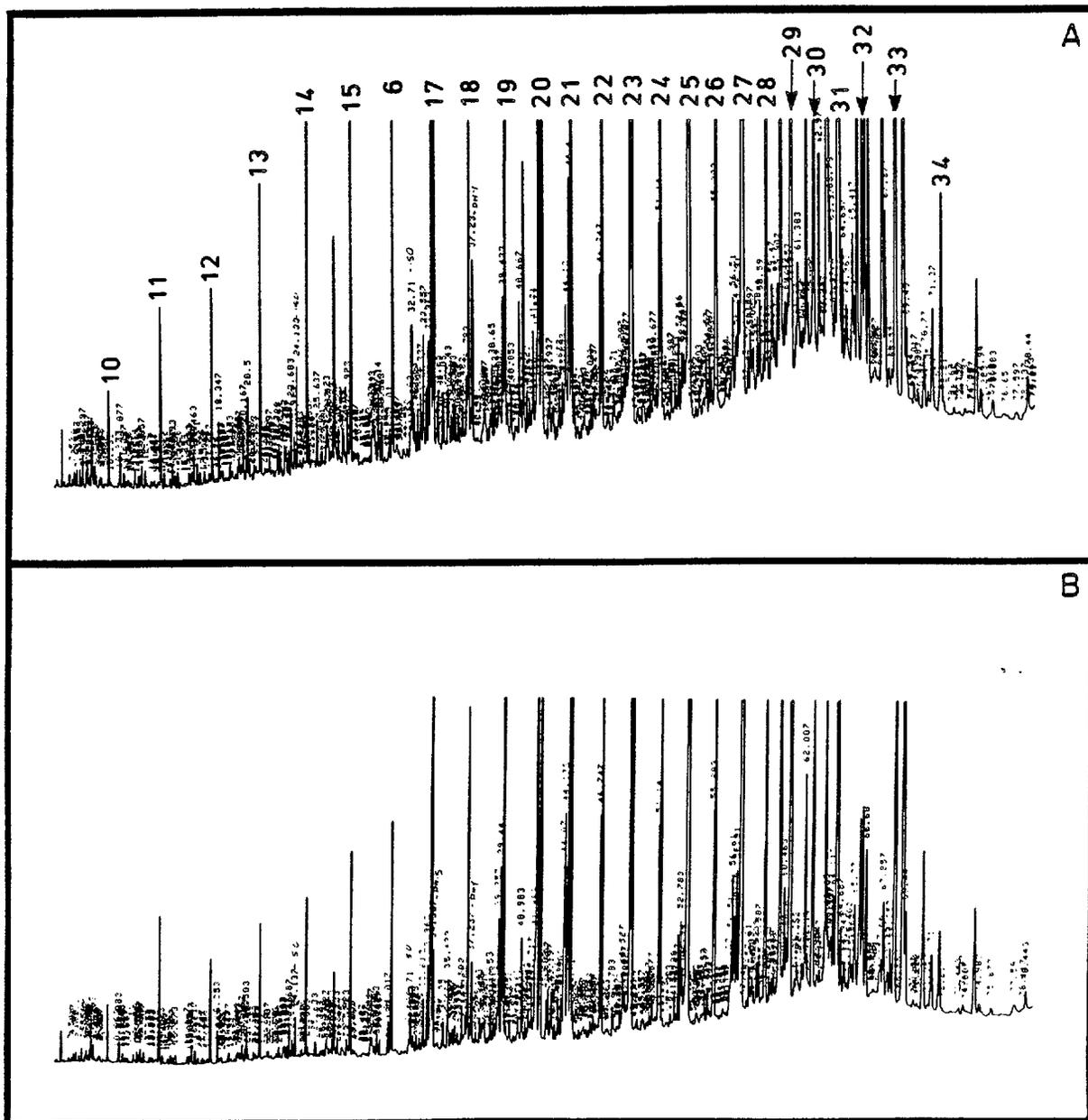


FIGURE 5.12. SATURATED HYDROCARBON COMPOSITION OF RIVER SEDIMENTS. COLVILLE RIVER (A) AND SAGAVANIRK TOK RIVER (B).

TABLE 5.17. KEY AROMATIC HYDROCARBON PARAMETERS AND RATIOS IN COASTAL PEAT AND RIVER SAMPLES.

	Total PAH ($\mu\text{g/g}$)	FFPI	N/P	P/D	Total PAH/TOC (X105)
<u>Peat Stations</u>					
IF	0.62	0.34	0.91	3.9	10
2G	0.17	0.70	0.09	5.0	4
2H	0.41	0.48	1.1	4.3	2.4
3D	0.18	0.10		1.1	0.8
5K	0.05	0.72	0.12		0.6
6J	0.20	0.19	1.8		0.8
7H	0.71	0.95	1.4	4.0	30
7J	0.05	0.78	0.20		0.16
Average Peat	0.30	0.53	1.1	3.7	
<u>River Stations</u>					
5J	0.21	0.72	1.0	8.1	20
6H	0.70	0.70	1.4	8.3	10
Average River	0.45	0.71	1.2	8.2	15
Average Offshore Sediment	0.58	0.73	1.3	7.6	30

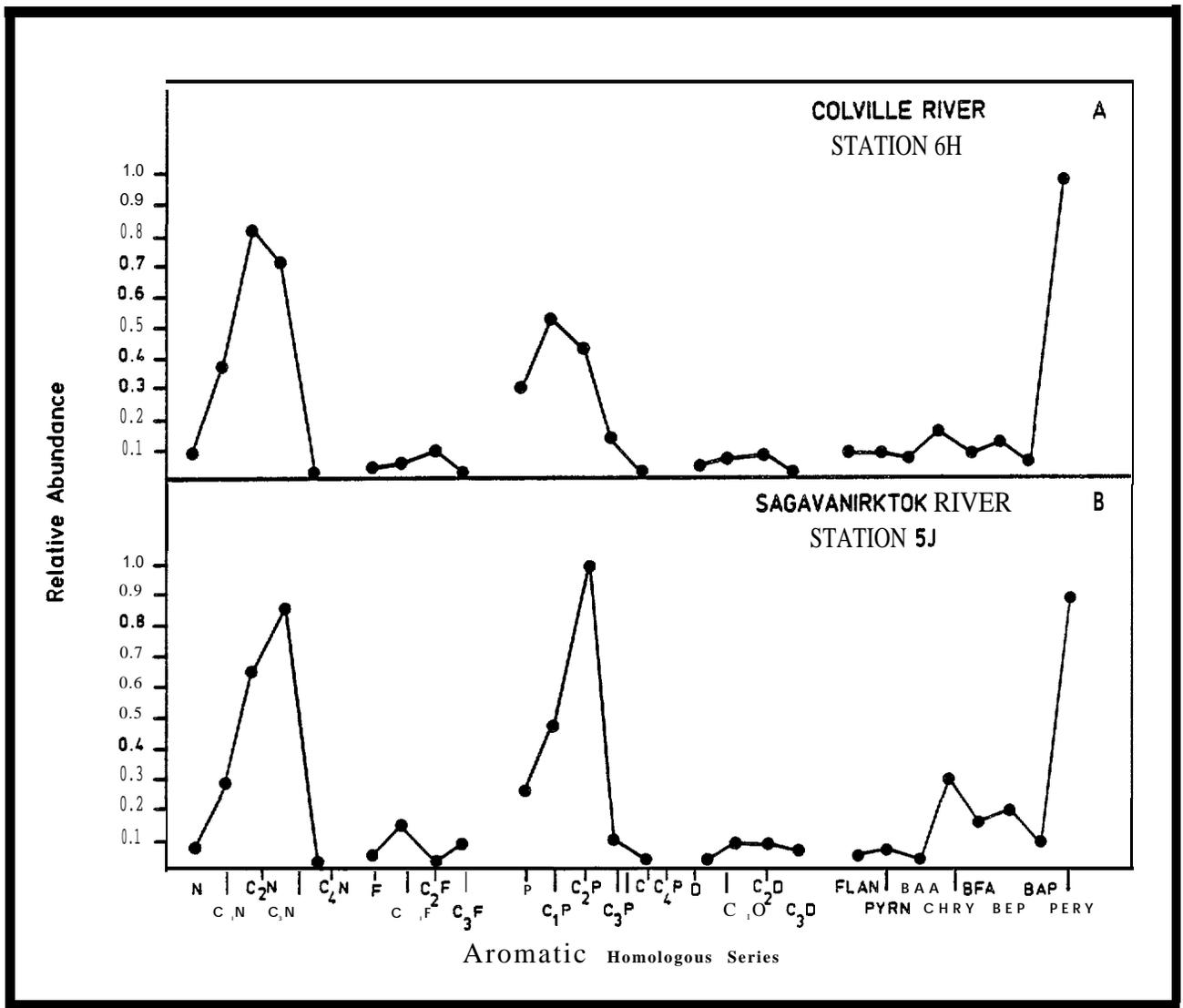


FIGURE 5.13. COMPOSITION OF PAH COMPOUNDS IN RIVER SEDIMENTS.

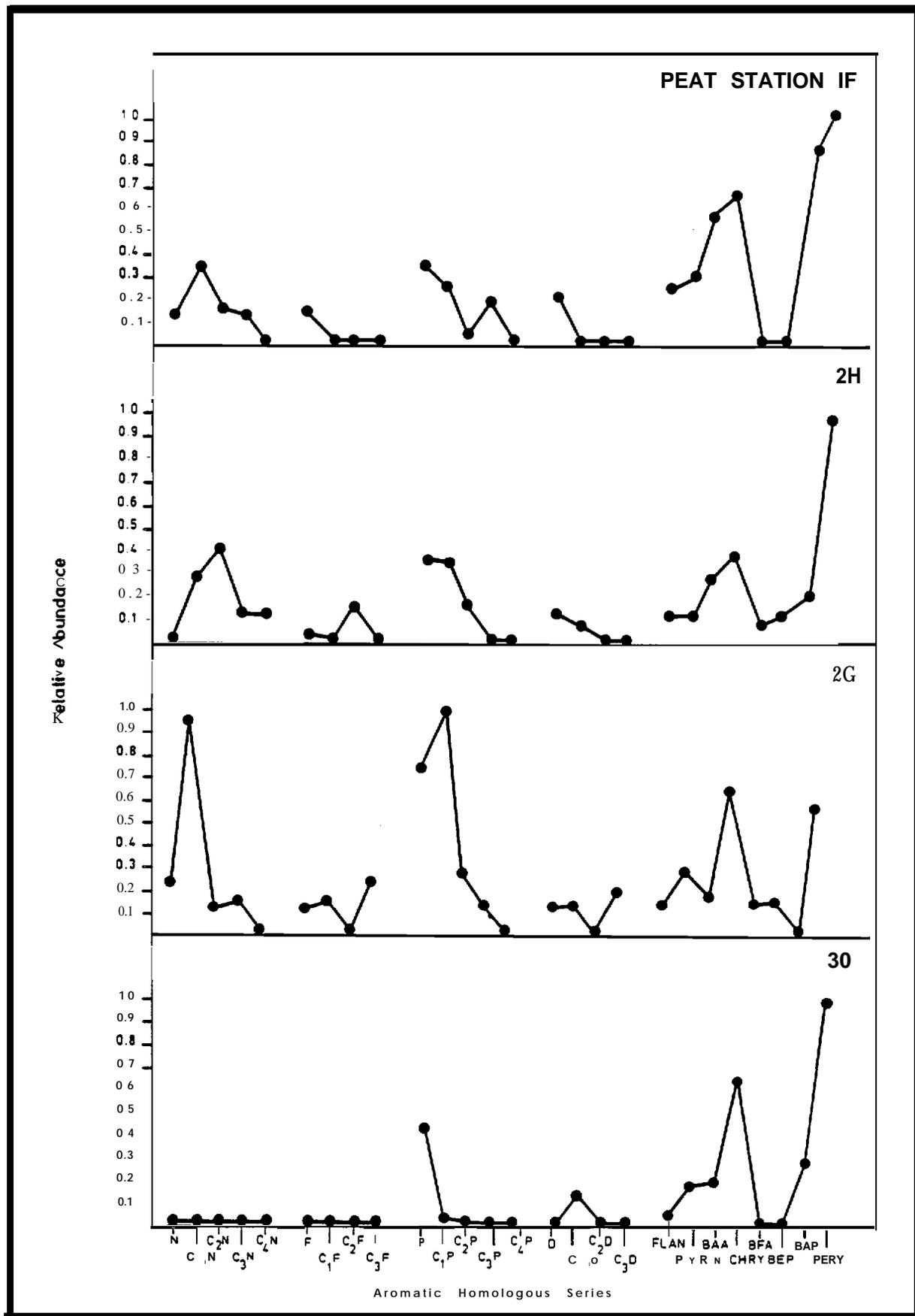


FIGURE 5.14. COMPOSITION OF PAH COMPOUNDS IN COASTAL PEAT SAMPLES.

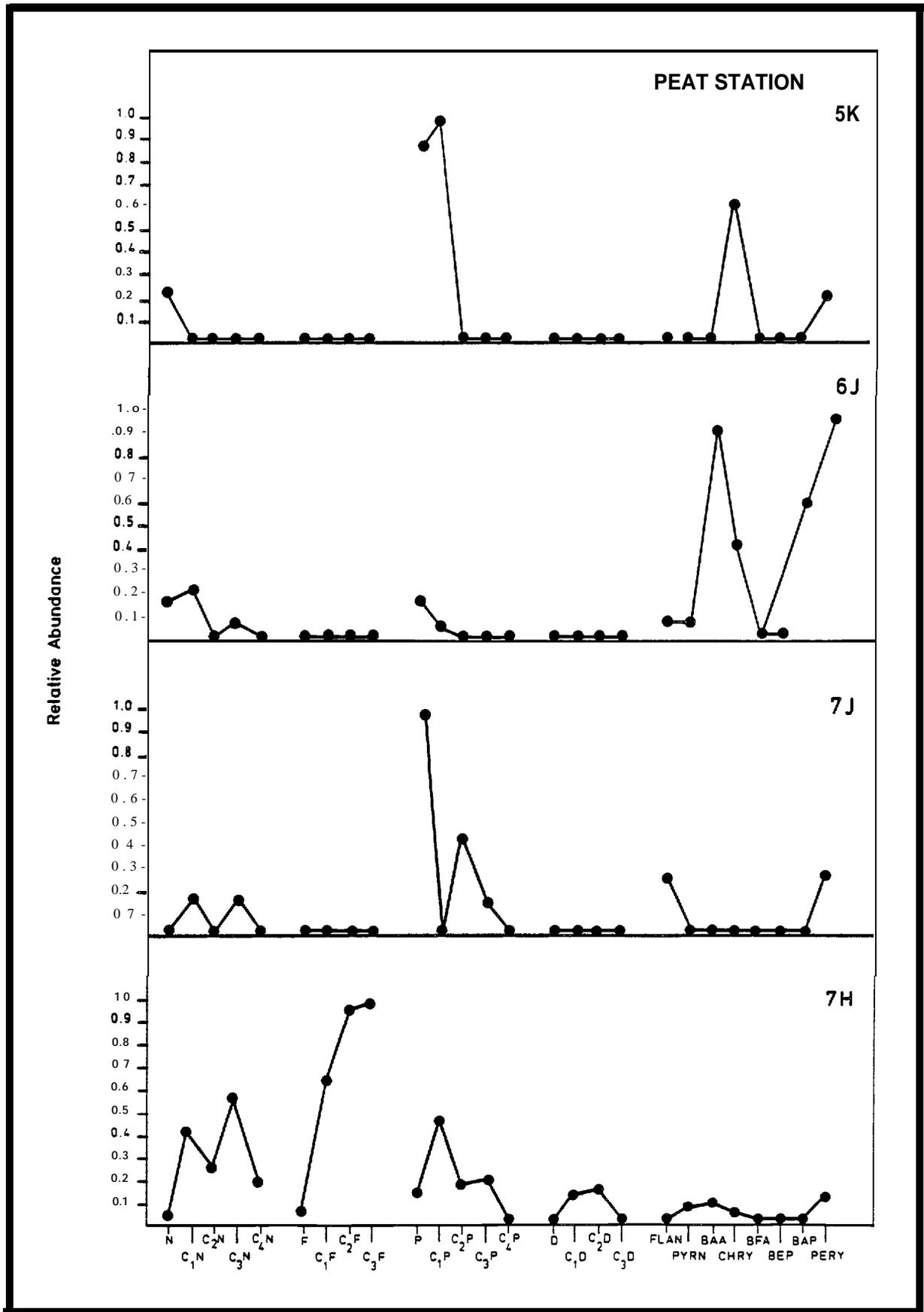


FIGURE 5.15. ADDITIONAL COMPOSITIONS OF PAH COMPOUNDS IN COASTAL PEAT SAMPLES.

Portlandia arctica - Station 1A
Macoma calcaria - Station 6D

- Amphipods: Anonyx sp. - Stations 1A, 1B, 1E, 4B, 5H, 6G, 7B/7C, and 7E.

Amphipod samples from certain stations (1 A/1 B/1 E; 7B/7C) were pooled as indicated to yield a sufficient quantity of sample for the analysis of two to four replicates per pooling. Where sufficient biomass was available from a single station, replicates were obtained from that individual station.

The species collected for tissue analysis represented two basic feeding types: those that filter seawater and potentially acquire **anthropogenic** chemical contaminants from the water column (Astarte, Cyrtodaria), and those that primarily would be expected to acquire such chemicals through processing of detritus at the sediment-water interface (Anonyx, Macoma, Portlandia). Replicate analyses were performed using UV/F, GC, and GC/MS techniques. The results of these analyses are summarized in Section 4.2.5.

The UV/F analyses provided important information on the fluorescent material, presumably aromatic in nature, at each of three wavelengths corresponding to spectral maximum in a standard Prudhoe Bay Crude Oil sample (Figure 5.1 6). Examples of the character of the UV/F spectra for each species are presented in Figures 5.17 and 5.18. Several distinct consistent spectral patterns were revealed. Anonyx samples exhibited a large maximum at approximately 312 nm. This 312-nm maximum was observed for all species examined in this study. Results obtained last year (Boehm et al., 1985) and those obtained in other studies on arctic bivalves (e.g., Boehm et al., 1982b and 1982c) indicate that the 312-nm band is a common background interference, the occurrence of which does not correspond to any aromatic hydrocarbon content as determined by GC/MS analyses. Thus, while the intensity of the 312-nm band varies, and it seemed to vary according to species (Figures 5.17 and 5.18), in contrast, the 355-nm band, corresponding to the 3-ring aromatics (Lloyd, 197 1), appears to be most useful for diagnosing and quantifying petroleum-related inputs to the animals (Boehm et al., 1982b and 1982c). This is why we have chosen in Section 4 to report only the 355-nm band. Anonyx and Macoma both showed low spectral intensities at 355 nm (Figure 5.17). The bivalves Astarte, Portlandia, and Cyrtodaria exhibited UV/F spectra with distinct spectral double bands at 355 nm and 360 nm (Figure 5.18) which resembled the sediment UV/F spectra obtained in the Year-1 program. In addition, the spectral maxima in the region greater than 400 nm indicated that higher molecular weight aromatics (e.g., **perylene**) were found in the animal tissues. Again, sediment inputs were strongly implicated,

Concentrations of Prudhoe Bay oil equivalents (at 355 nm) in the tissues ranged from 0.75 to 8.8 $\mu\text{g/g}$. There appeared to be less variability within each species: Anonyx (0.75 to 1.6 $\mu\text{g/g}$), representing five samples; Astarte (3.3 to 4.0 $\mu\text{g/g}$), representing four samples; and Cyrtodaria (4.0-4.6 $\mu\text{g/g}$), representing two samples. The single sample of Portlandia from Station 1 A in the Camden Bay region exhibited the highest concentration (8.9 $\mu\text{g/g}$). No areal trends were revealed in these data. Thus, it can be inferred that the concentrations of oil equivalents observed represented definitive background concentrations of Prudhoe Bay oil equivalents, the source of this material being from sediment-associated PAH.

GC/MS analyses of these samples focused on PAH content and composition. The results were presented in Tables 4.16 and 4.17 and are reproduced as a summary in Table 5.18. Detectable, but very low concentrations of aromatic hydrocarbons were found in most of the samples. The GC/MS results, which yield concentrations of individual compounds, roughly corresponded to the UV/F results, which examine gross spectral characteristics presumably attributable to aromaticity. For example, all of the species contained background levels of the 3-ringed aromatic series of phenanthrenes at concentrations of less than detection limit (< 0.001) to 0.010 $\mu\text{g/g}$, while the 355 nm UV/F

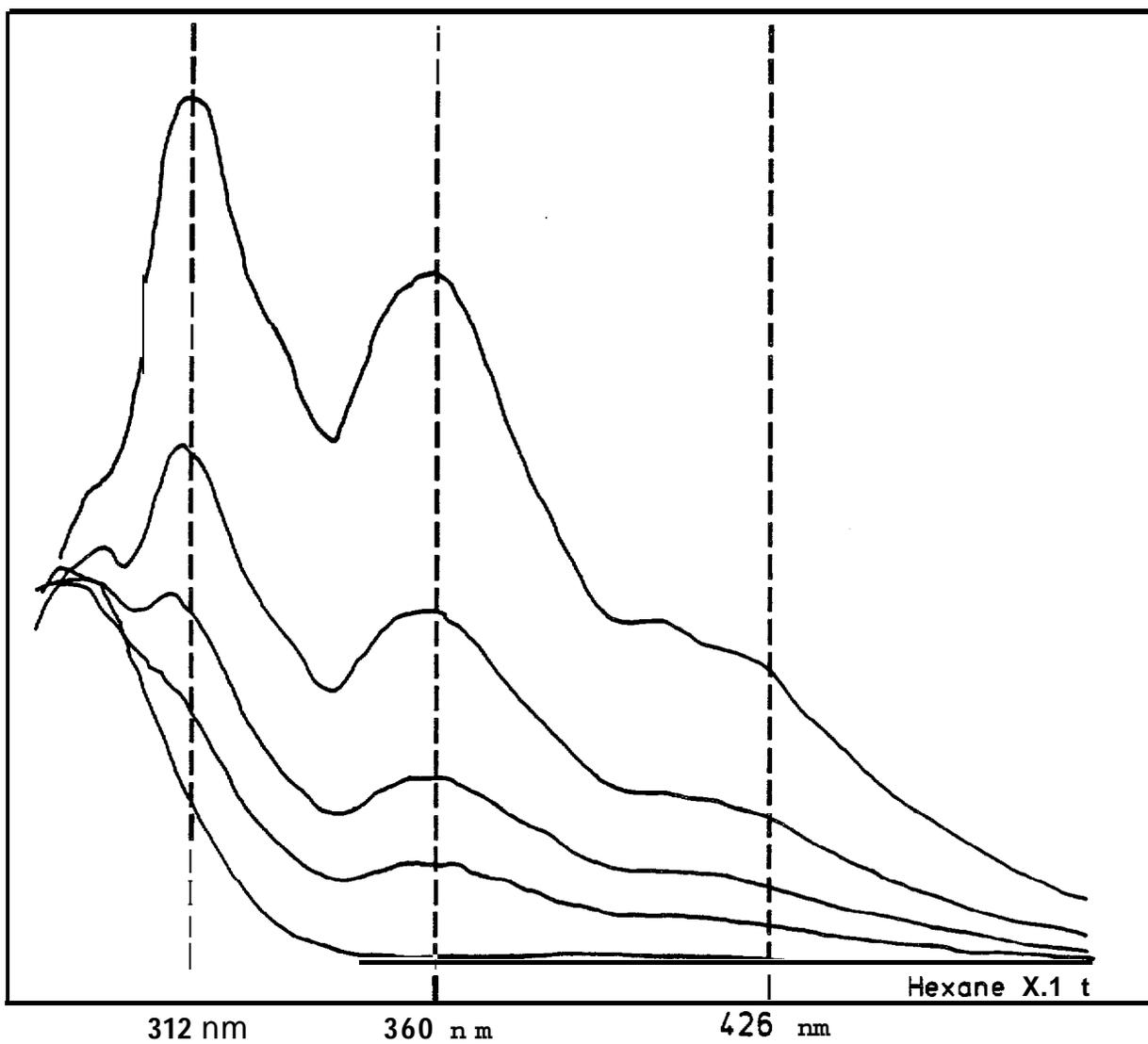


FIGURE 5.16. UV/F SPECTRA OF STANDARD PRUDHOEBAY CRUDE OIL.

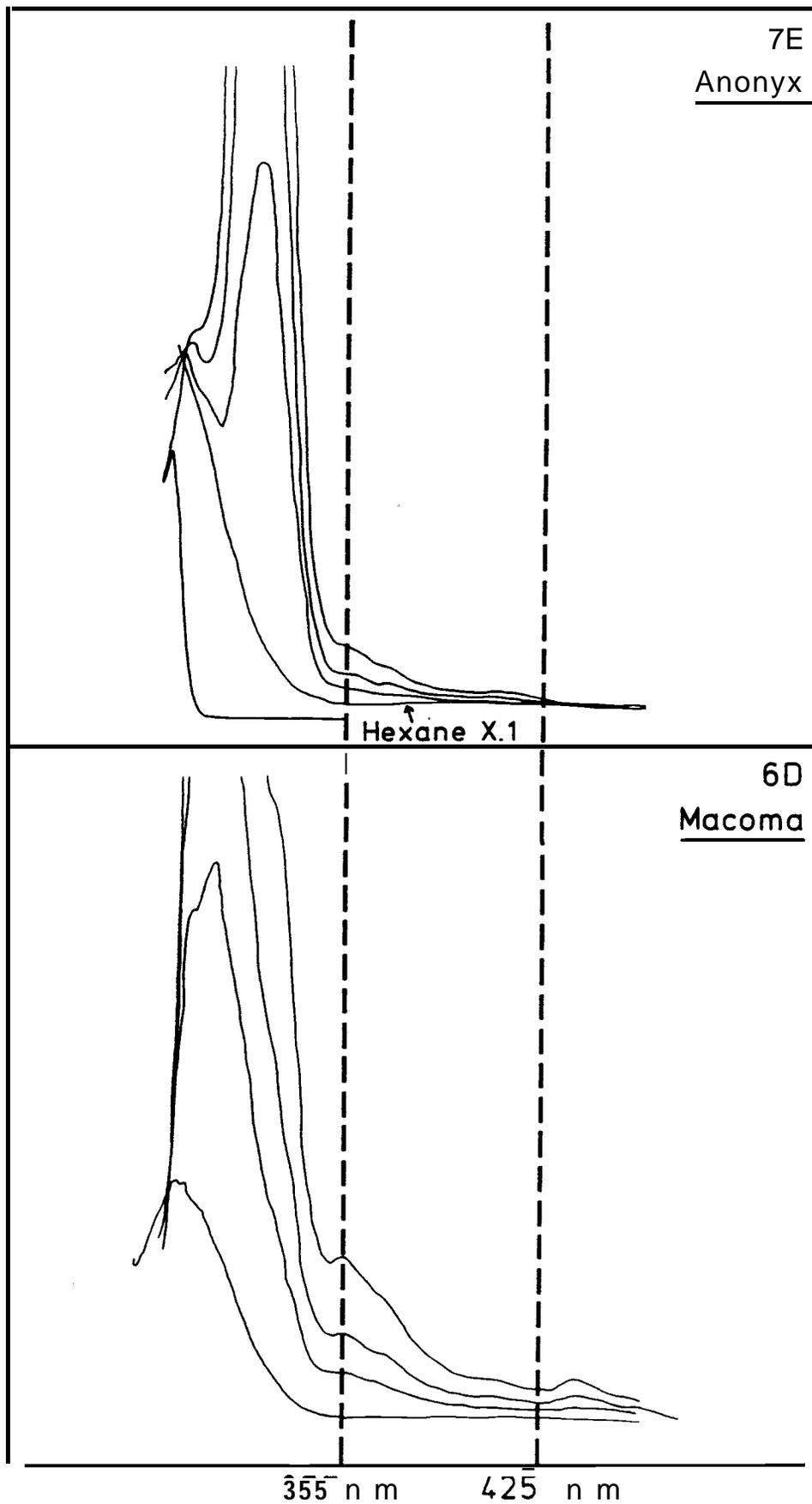


FIGURE 5.17. REPRESENTATIVE UV/F SPECTRA OF SELECTED ANIMAL TISSUE SAMPLES.

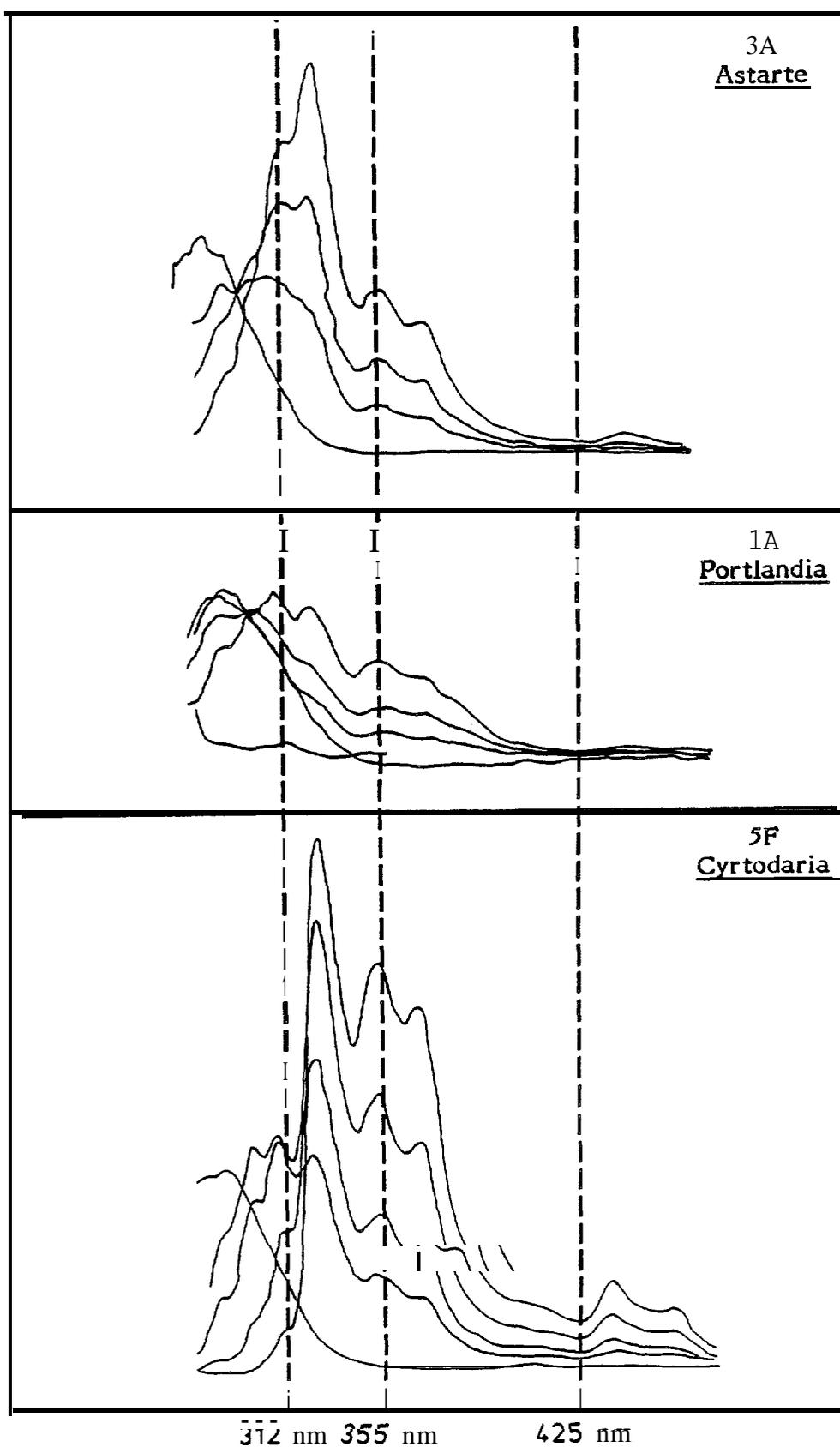


FIGURE 5.18. REPRESENTATIVE UV/F SPECTRA OF SELECTED ANIMAL TISSUE SAMPLES.

TABLE 5.18. AVERAGE CONCENTRATIONS OF SELECTED AROMATIC AND SATURATED HYDROCARBON PARAMETERS IN ANIMAL TISSUES.

	Na	pa	Da	P/D	PAHa	TALKa	LALKa
<u>Anonyx</u>							
1A/B/E	0.029	<D.L. ^b	<D.L.		<D.L.	10.9	0.30
4B	0.015	<D.L.	<D.L.		0.001	10.6	0.20
6G	0.009	<D.L.	<D.L.		<D.L.	14.5	0.94
7B/C	0.004	<D.L.	<D.L.		<D.L.	27.3	0.87
7E	0.008	0.001	<D.L.		<D.L.	38.4	0.94
<u>Astarte</u>							
1A+1B	0.014	0.005	0.002	2.5	0.007	5.1	0.55
3A	0.003	0.003	<D.L.		0.001	3.6	0.60
5H	0.002	0.002	<D.L.		0.002	2.3	0.30
6D	0.007	0.004	0.002	2.0	0.008	1.2	0.46
<u>Cyrtodaria</u>							
5F	0.003	0.002	<D.L.		0.002	3.7	0.29
6G	0.004	0.005	<D.L.		0.005	3.6	0.51
<u>Portlandia</u>							
1A	0.009	0.009	<D.L.		0.016	7.0	0.43
<u>Macoma</u>							
6D	0.035	0.002	0.001	2.0	0.008	13.0	0.14

aConcentrations in µg/g.

N = Naphthalenes (Co-C4)

P = Phenanthrenes (Co-C4)

D = Dibenzothiophenes (Co-C3)

PAH = N+P+D+F

bDetection Limit

band varied from 0.75 to 8.9 µg/g. The Portlandia sample contained the highest UV/F and GC/MS values, Astarte values for both UV/F and GC/MS were intermediate, and values for Anonyx were lowest. Of special interest were the non-detectable to very low levels of the dibenzothiophenes (DBTs) in the animals. These DBT compounds are very important components of Prudhoe Bay crude oil, and presumably other north slope crudes, and the absence of DBT compounds in tissues underlines the usefulness of **DBT and the P/D ratio** in future monitoring of oil and gas inputs to the environment.

The low levels of aromatic hydrocarbons in the tissues, first revealed in Year- 1, was remarkable in view of the large sediment reservoirs of PAH compounds that were apparently not **bioavailable**. There was no relationship of PAH in tissues and sediments of the Beaufort Sea in the range of **animal** species examined.

The saturated hydrocarbon characteristics of the various species examined, as indicated by the CC traces, are presented in Figures 5.19 through 5.21. Two examples of the GC traces from the amphipod Anonyx are shown in Figure 5.19. The chromatogram from Figure 5.1 9A exhibited an abundance of higher molecular weight n-alkanes (see Table 5.1 8) and a **unimodal** unresolved complex mixture (UC M) or "hump." These features can be mistakenly attributed to petroleum inputs. However, the lack of a significant PAH content precluded the assignment of the components observed in Figure 5.19 to petroleum. The UCM may be of microbial origin rather than of petroleum. Not all of the Anonyx samples were similar in composition, with the sample from Station 7E (Figure 5.1 9B) containing the n-alkanes, but little of the UCM distribution. The bivalve Astarte (Figure 5.20) contained saturated hydrocarbon distributions which are similar at all stations (3A, 6D, 1A, and 5H). The distribution shown in Figure 5.20A and expanded in Figure 5.20B was observed at all stations. Prominent were n-alkanes and "clusters" of **mono-olefinic** hydrocarbons surrounding the C₁₃ through C₂₁ alkanes.

Portlandia from Station 1A (Figure 5.21) contained a GC distribution indicative of **biogenic** inputs with sediment hydrocarbon material apparent (n-C₂₅, n-C₂₇, n-C₃₁). The two replicates of Macoma from Station 6D (Figure 5.22) contained markedly different distributions; one indicated very small quantities of hydrocarbons (Figure 5.20A), the other (Figure 5.22B) obviously contained sediment-associated hydrocarbons, as evidenced by the high molecular-weight alkanes and UCM. The two Macoma replicates differed in their PAH content as well; Replicate 1 (Figure 5.22A) contained 0.006 µg/g of naphthalenes, and no phenanthrenes or dibenzothiophenes, while Replicate 2 (Figure 5.22B) contained 0.07 µg/g of naphthalenes, 0.004 µg/g phenanthrenes, and 0.002 µg/g of dibenzothiophenes. These potential differences among replicates must be taken into account when data from later years are interpreted.

Finally, the GC traces of Cyrtodaria from all four replicates at Station 5F and 6G indicated the presence of a **bimodal** UCM and n-alkane feature, which together with the detectable, but very small quantities of PAH, indicated little evidence for petroleum inputs. Ironically, the species with highest PAH content (Table 5.18) was least likely to indicate petrogenic input from the saturated hydrocarbon GC traces.

5.3.5.1 Hydrocarbon Bioavailability Related to Animal Feeding Types.

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 fauna in an oil-impacted area. It appears that filter-feeding bivalves accumulate petroleum

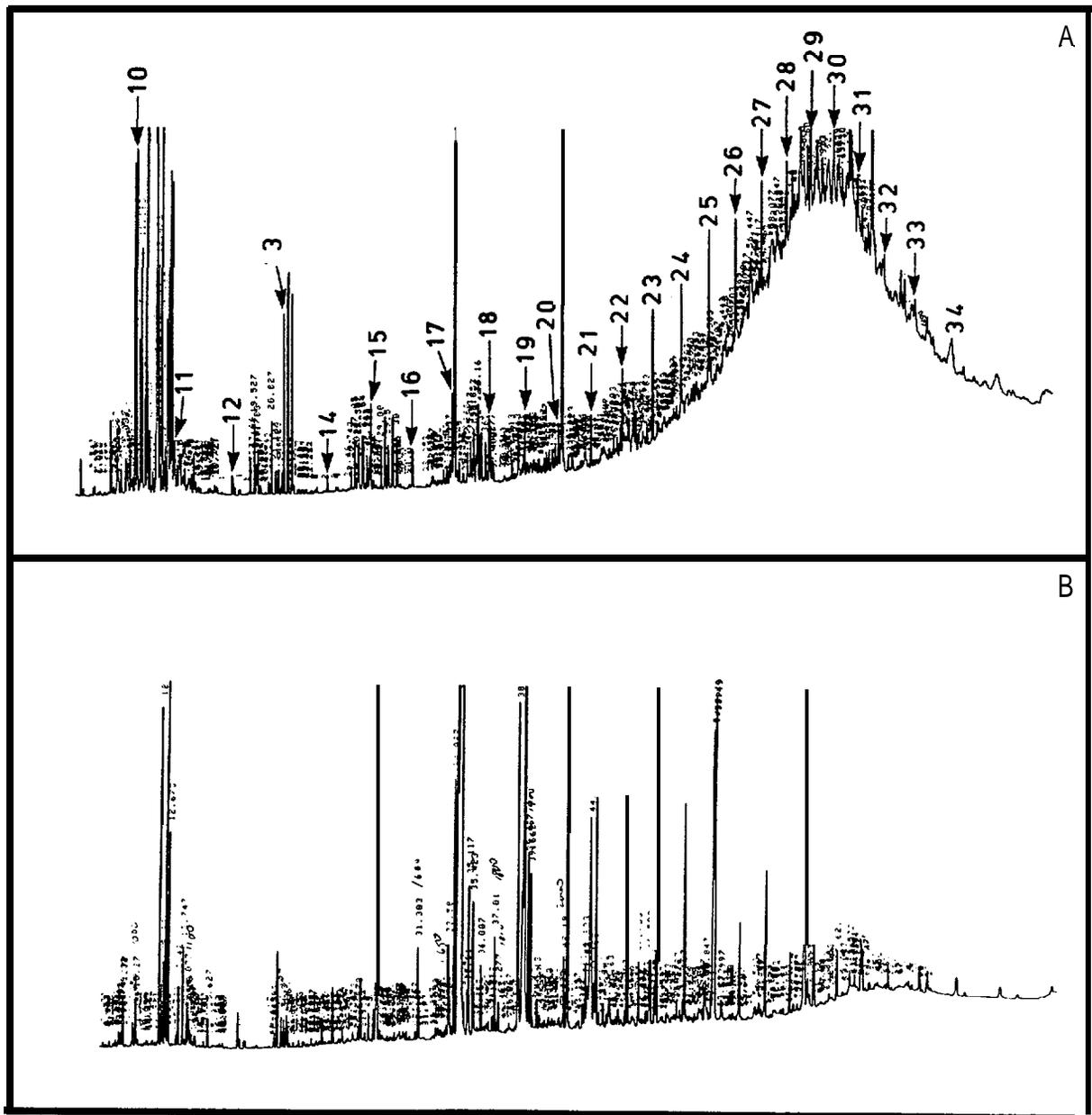


FIGURE 5.19. SATURATED HYDROCARBON COMPOSITION OF MARINE ANIMALS (*Anonyx*).

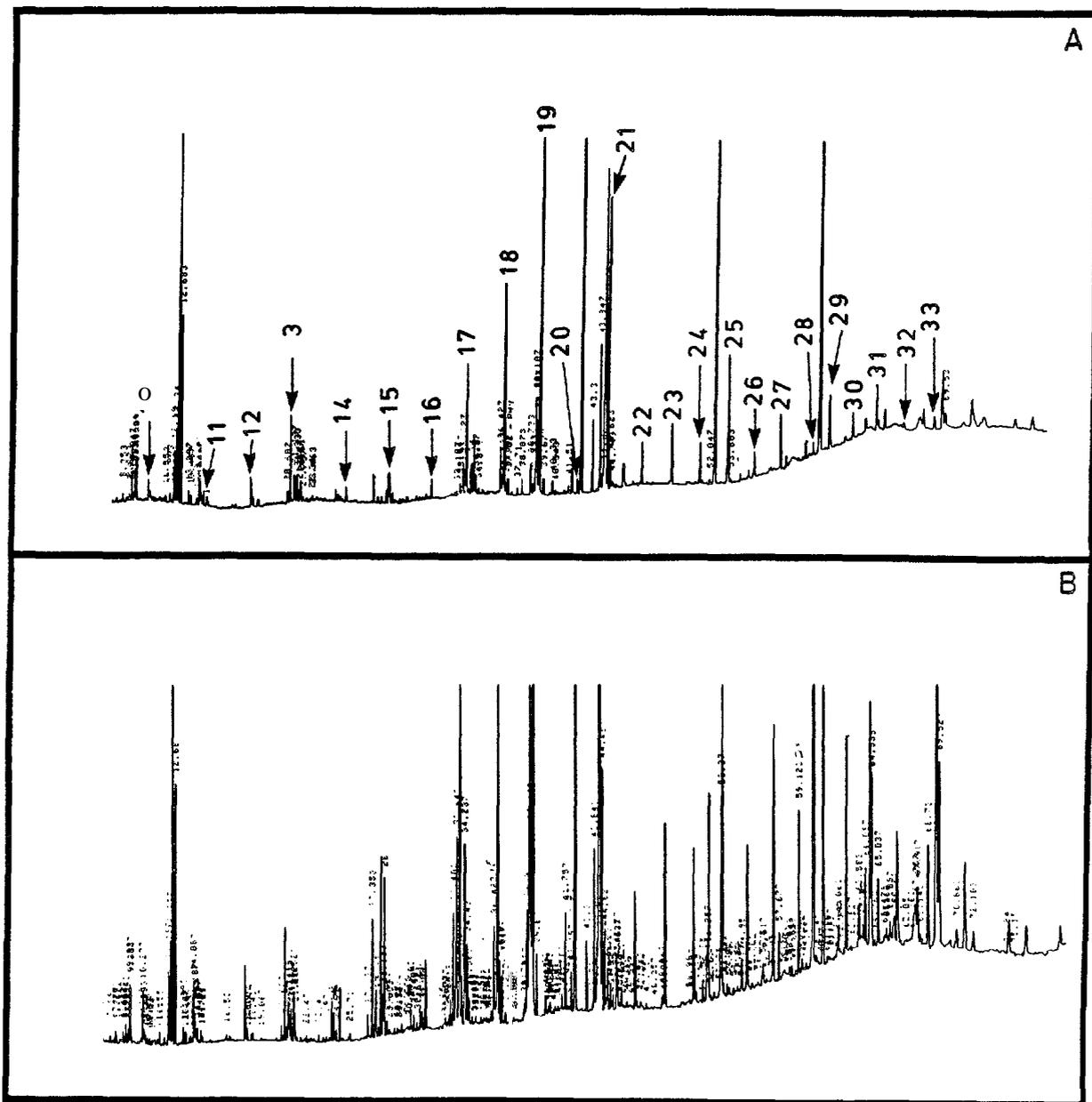


FIGURE 5.20. SATURATED HYDROCARBON COMPOSITION OF MARINE ANIMALS (*Astarte*) ; STATION 6D (A); STATION 3A (B).

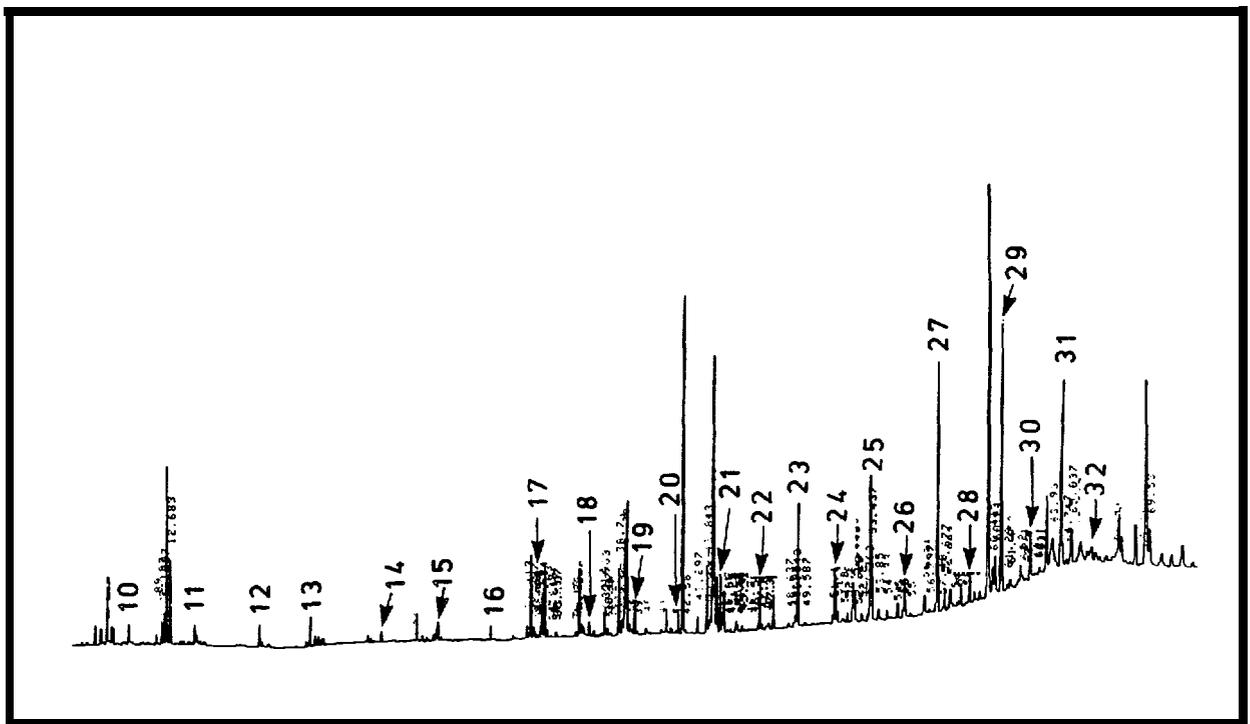


FIGURE 5.21. SATURATED HYDROCARBON COMPOSITIONS OF MARINE ANIMALS (Portlandia).

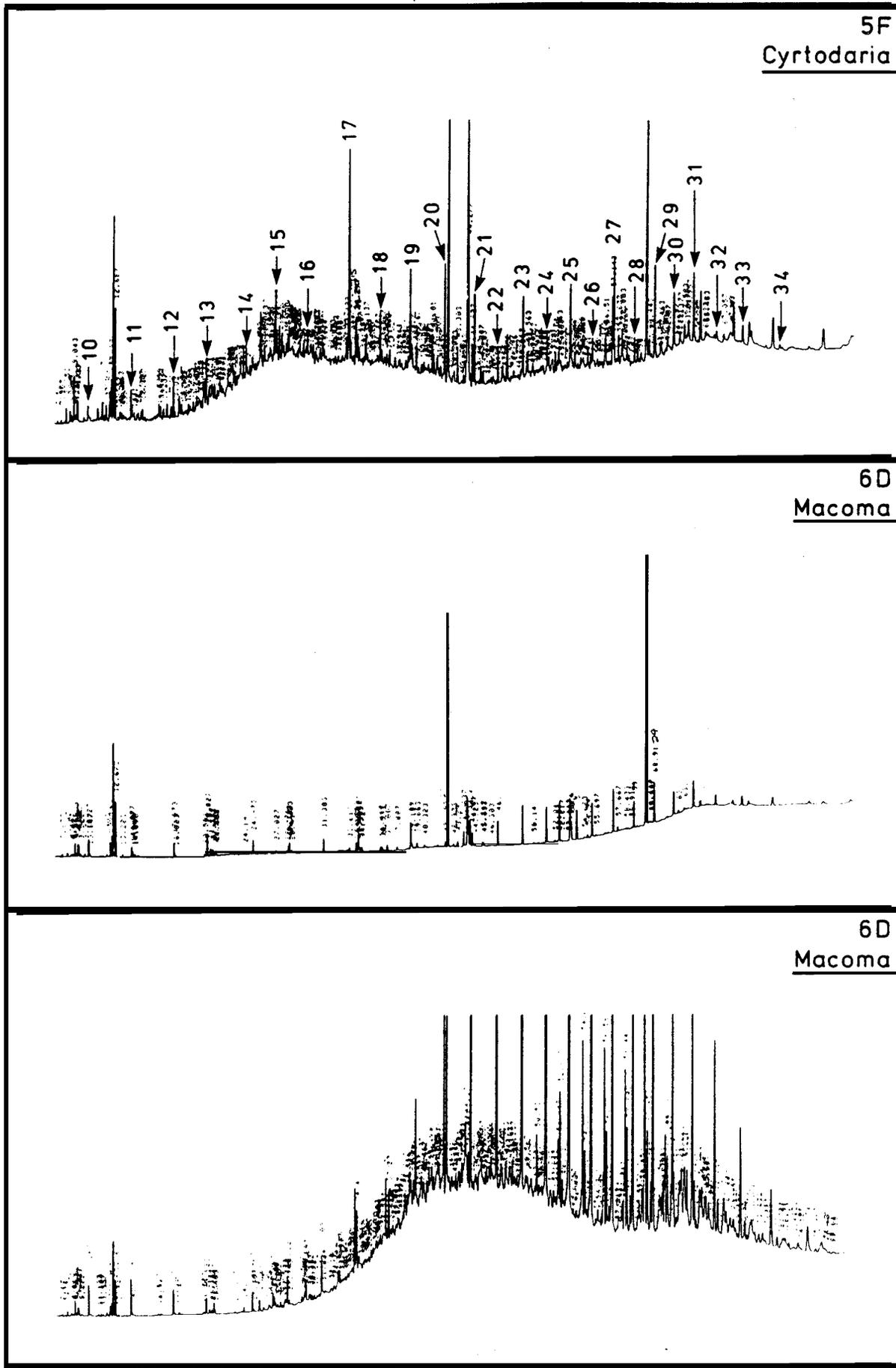


FIGURE 5.22. SATURATED HYDROCARBON COMPOSITION OF MARINE ANIMALS (Cyrtodaria, Macoma).

hydrocarbons primarily from the water column, while deposit-feeding bivalves accumulate hydrocarbons primarily from sediments (Boehm et al., 1982a; Anderson, 1983).

Table 5.19 lists the feeding mechanisms which characterize the animals collected and analyzed in Year-2 of the BSMP. The amphipod, Anonyx, represents a migratory scavenger which feeds primarily on surface detritus. These animals should be considered as integrators of organic material from a region, rather than representative of the station where collected. Astarte and Cyrtodaria are primarily suspension feeders; their tissues are expected to reflect water column (soluble low molecular weight) hydrocarbon contaminants. Portlandia and Macoma are both characterized as surficial deposit feeders. Species utilizing this mode of feeding are expected to accumulate hydrocarbons present in the sediments.

5.4 Statistical Analysis

The statistical analysis for this reporting period focused on two major topics. These are (1) the partial re-analysis of the first year's (1984) data and (2) the assessment of change in the metal and hydrocarbon concentrations between years 1984 and 1985. All statistical analyses reported here used the natural logarithms of the raw data. This was used in the Year-1 data analysis as an effective way to stabilize variance; therefore, it was repeated for consistency in the Year-2 effort.

5.4.1 Partial Re-analysis of Year-i Data

In the first year's data analysis, the effects of normalizing the data with division by percent silt (PSILT), percent clay (PCLAY), and total organic (TOC) carbon did not reduce the within-station variability as expected. As a result, all analyses were based on the unnormalized data.

One of the goals of this year's statistical analysis was to re-examine the normalization issue. A reduction of within-station variability through such normalization would improve the power of the statistical analyses used to test the proposed hypotheses in the Beaufort Sea Monitoring Program. If the variables of interest are highly correlated with another ancillary variable, then normalization (i.e., division) by that ancillary variable may reduce within-station variability.

In the first year's normalization effort, a logarithmic transformation of the variable of interest (e.g., Pb concentration) was compared to the same transformation of the ratio of the variable of interest and one of three ancillary variables, PSILT, PCLAY, or TOC. Since this method was not successful, the following alternative was tried. Regression analyses were performed using the natural log of each variable of interest as the dependent variable and the natural log of each ancillary variable as the independent variable. The estimate of the slope parameter (B), from each of the regression analyses was then used as an exponent for the denominator in the corresponding normalization ratio. The normalization technique previously used forced the slope parameter to be 1.0. This new technique allows the slope parameter to vary.

In addition, it was suspected that the sum of two ancillary variables might also be useful in normalizing the variables of interest. It was determined that PSILT + PCLAY was one sensible combination of ancillary variables.

A one-way ANOVA using stations as the only main effect was conducted by applying the SAS statistical procedure GLM to the log-transformed variables and the log-transformations of the same variables normalized by dividing by either (TOC)**B, (PSILT)**B, (PCLAY)**B, or (PSILT + PCLAY). The root mean square (R MS) of the error term from the above model is a pooled estimate of the within-station standard deviation. These standard deviation estimates for the log-transformed normalized and

TABLE 5.19. MODE OF FEEDING FOR ANIMAL SPECIES COLLECTED AND ANALYZED IN YEAR-2.

Genus	Mode of Feeding
<u>Anonyx</u>	Migratory Surface Scavenger
<u>Astarte</u>	Filter Feeder
<u>Cyrtodaria</u>	Filter Feeder
<u>Macoma</u>	Deposit Feeder
<u>Portlandia</u>	Deposit Feeder

unnormalized variables were compared to determine if a normalization technique was successful at reducing the within-station variability.

Table 5.20 shows that for all variables and for all five normalization techniques, consistent and substantial variance reduction (i.e., a negative percent change in the standard deviation) was not achieved. The 17.9% reduction in variability for vanadium was the largest found and used the **PSILT**B** normalization variable. The **PSILT + PCLAY** normalizing variable actually increased the variability by an average of 73.9% among the metals and 22% among the hydrocarbon variables.

Although the normalization methods that used the regression parameter (B) appeared to be somewhat more successful than the previous year's method, the results were neither dramatic nor consistent, as stated above. Therefore, normalized data were not used for subsequent statistical analyses in this report.

5.4.2 Trend Analysis

5.4.2.1. Variance Estimation in 'Year-1 Data. During the Year- 1 sampling effort, we encountered a potential difficulty with the original sampling design. The grab sampling device used to collect sediment samples sometimes yielded only enough sediment for a single replicate instead of two replicates per grab as called for in the sampling design. In these instances, the second replicate was furnished **using a sediment sample from another grab at the same station.** During the Year-2 effort, both types of replicates (i.e., two from the same grab or two from different grabs) were composite in the field before being shipped for chemical analysis. The practice of compositing replicates from different grabs could have had an effect on the **analysis of trends** from one year to another.

An issue to be addressed in this section is what impact, if any, different sample compositing techniques have on accurately assessing the trends in the metal and hydrocarbon concentrations between Year- 1 and Year-2. The answer rests on having some idea of how uniformly these chemicals are distributed in the sediment samples. A nonuniform distribution could result in substantial differences in the chemical concentrations from one grab location to another within the same station. In this case, **compositing** replicates from different grabs would result in a smaller variance when composite sediment samples were compared.

The statistical tests used to assess the trends are based on a measure of the within-station variability. For the Year-2 data, this is the variance among composite sediment samples. Since this variance could be smaller as stated above, more trends could be declared statistically significant than should be.

It is apparent then, that to assess the impact of the sampling design change, it is necessary to estimate the variability between-grabs. If the between-grab variability is not significantly greater than zero, then different sample compositing techniques can be viewed as having **little** or no effect on the trend analyses.

The SAS procedure PROC NESTED was used to estimate the variance among stations, among grabs, and between replicates. The data were first separated into two subsets, one containing only data in which both replicates came from the same grab and the other containing replicates from different grabs. Since the first **subset** corresponded to the original sample **compositing** design, accurate estimates of the within- and between-grab variability could confidently be produced. These data were analyzed first. If the statistical test showed no significant grab-to-grab variation, then the **compositing** of replicates from different grabs was not considered to be a serious departure from the original sample compositing design. In this case, both subsets of the data were combined

TABLE 5.20. POOLED WITHIN-STATION STANDARD DEVIATION (S.D.) ESTIMATES FOR UNNORMALIZED AND NORMALIZED DATA ON A LOGARITHM (NATURAL) SCALE FOR YEAR-1 (1984) OF THE STUDY.

Metal Parameter	$\ln(x)$	$\ln(x)$ $\ln(\text{TOC})^B$	% Change in S.D.	$\ln(x)$ $\ln(\% \text{ silt})^B$	% Change in S.D.	$\ln(x)$ $\ln(\% \text{ clay})^B$	% Change in S.D.
Cd	0.2536	0.2560	+ 0.9	0.2461	- 3.0	0.2435	- 4.0
Pb	0.1783	0.1810	+ 1.5	0.1633	- 8.4	0.1594	-10.6
Ba	0.1449	0.1416	-2.3	0.1336	- 7.0	0.1286	-11.2
Cu	0.2144	0.2104	- 1.9	0.1987	- 7.3	0.2149	+ 0.2
Cr	0.1637	0.1534	-6.3	0.1385	-15.4	0.1483	- 9.4
Zn	0.2004	0.1915	-4.4	0.1811	- 9.6	0.1822	- 9.1
v	0.1603	0.1420	-11.4	0.1316	-17.9	0.1350	-15.8

Organic Parameter	$\ln(x)$	$\ln(x)$ $\ln(\text{TOC})^B$	% Change in S.D.	$\ln(x)$ $\ln(\% \text{ silt})^B$	% Change in S.D.	$\ln(x)$ $\ln(\% \text{ clay})^B$	% Change in S.D.
N	0.6013	0.5929	- 1.4	0.6515	+ 8.3	0.6479	+ 7.7
F	0.5315	0.5504	+ 3.6	0.5845	+10.0	0.5741	+ 8.0
P	0.5884	0.5686	- 3.4	0.6249	+ 6.2	0.6269	+ 6.5
D	0.5385	0.5523	+ 2.6	0.5838	+ 8.4	0.5850	+ 8.6
PAH	0.8298	0.8481	+ 2.3	0.8360	+ 0.7	0.8593	+ 3.6
TALK	0.3350	0.2907	-13.2	0.3605	+ 7.6	0.3619	+ 8.0
LALK	0.3553	0.3348	-5.8	0.3676	+ 3.5	0.3594	+ 1.2
1708	0.3218	0.2733	-15.1	0.3292	+ 2.3	0.3337	+ 3.7
1810	0.3266	0.2852	-12.7	0.3306	+ 1.2	0.3509	+ 7.4
TOT	0.2710	0.2423	-10.6	0.2725	+ 0.6	0.2698	- 0.4
355	0.3834	0.3476	- 9.3	0.3325	-13.3	0.3480	- 9.2

^B slope parameter of a regression of $\ln(x)$ on either $\ln(\text{TOC})$, $\ln(\% \text{ silt})$ or $\ln(\% \text{ clay})$.

to produce new estimates of station-to-station and replicate-to-replicate (i.e., within station) variances.

In the analysis of the first subset, four of the seven metal concentrations showed no significant ($p > 0.05$) between-grab variability (Table 5.21). The variation within a station for these parameters is composed entirely of replicate-to-replicate variation. In addition, all but three (LALK, P/D, LALK/TALK) of the hydrocarbon parameters showed no significant grab-to-grab variation.

If the between-grab variability was significantly greater than zero, the question might still be raised as to whether this variability should be considered as greater than zero in a practical sense. The last column of Table 5.21 presents the ratio of the between-grab to the within-grab variance. These variance ratios show that Zn, LALK, and LALK/TALK have substantially larger ($> 150\%$) grab-to-grab variation than replicate-to-replicate variation, but for Cr, V, and P/D, the evidence for substantial or practically significant between-grab variability is inconclusive.

To summarize, we cannot say with confidence that compositing replicates from different grabs does not present a potential problem. For most of the variables there was no significant between-grab variability, but for six of them there was. It is recommended that if the scheme of compositing sediment samples before chemical analysis is continued, replicates from the same grab should be combined whenever possible. One statistically sound alternative is to discard the single sediment samples from incomplete grabs.

Furthermore, it is often desirable to attach a more direct interpretation to the individual variance estimates. Each variance estimate is approximately equal to the square of the coefficient of variation on the original scale. This is a well-known interpretation of the variance of lognormally distributed data when the variances on the natural log scale are small. A more detailed explanation of this interpretation is given in the Year-1 Annual Report (Boehm et al., 1985).

5.4.2.2. Trends Within Stations. In order to assess the evidence for year-to-year trends among the concentrations of metals and hydrocarbons in the ocean's sediments, the method of t-tests was used. Specifically, a t-test compares the ratio of the difference in mean chemical concentrations between years and the standard deviation of that difference to a tabled value. This ratio is not expected to be large if, in fact, there is little or no change in the chemical concentrations between years. If the absolute value of this ratio is greater than or equal to the tabled value, then it can be confidently stated that a significant change has occurred. If the difference in mean concentrations is positive, then a decrease occurred in Year-2. If this difference was negative, then an increase occurred.

T-tests were performed for each metal and hydrocarbon variable for a particular station. At 19 of the 26 stations in Year-1, there was only one observation for each hydrocarbon variable. In this case, no estimate of the within-station variance could be calculated. Since the t-test is based on this estimate, it was assumed for the sake of comparing Year-1 and Year-2 hydrocarbon data at all stations, that the Year-2 estimate of the within-station variance was also a reasonable estimate for Year-1.

Table 5.22 shows the results of the two-sample t-tests between Year-1 and Year-2 for each metal and hydrocarbon variable, by station. This table is designed to allow inferences concerning year-to-year changes (or trends) for a specific station. Single asterisks (*) in the last column of Table 5.22 indicate those tests that were significant at the 0.05 probability level of error. That is, for these tests, the probability of incorrectly concluding that a year-to-year change has occurred is less than or equal to 5%. To put it another way, if there was in truth, no change from Year-1 to Year-2, and if 100 such t-

TABLE 5.21. VARIANCE AND VARIANCE RATIO ESTIMATES FOR YEAR-1 ON A LOGARITHMIC (NATURAL) SCALE.

Parameter	Variance Estimates			Variance Ratio (x100) ^a
	Station	Grab	Replicate	
Cd	0.2704	0	0.0672	
Pb	0.1254	0	0.0351	
Ba	0.1573	0	0.0227	
Cu	0.1952	0	0.0485	
Cr	0.1666	0.0071	0.0162	43.83
Zn	0.1538	0.0263	0.0141	186.52
v	0.1424	0.0050	0.0129	38.76
N	0.1673	0	0.0981	
F	0.0026	0	0.0012	
P	0.1022	0	0.0492	
D	0.0035	0	0.0028	
PAH	0.0084	0	0.0038	
LALK	0	0.2304	0.1352	170.41
ISO	0.0030	0.0007	0.0017	
ALK	0.0127	0.0036	0.0074	
V1708	0.0004	0.0001	0.0001	
V1810	0.0001	0.00001	0.0001	
TOT	97.70	15.05	22.76	
FFPI	0.0007	0	0.0034	
TALK	9.318	2.176	1.790	
P/D	2.985	0.3317	0.4533	73.17
LALK/TALK	0.0190	0.0116	0.0012	966.67
ISO/ALK	0.0021	0	0.0004	

^aRatio of the grab to replicate variance estimates. Variance ratios were only computed if the grab-to-grab variability variance estimate was significantly ($p < .05$) greater than zero in the subset free of partial grabs.

TABLE 5.22. GEOMETRIC MEANS AND TWO SAMPLE t-TESTS ON A Logarithmic (NATURAL) SCALE BETWEEN YEAR-1 AND YEAR-2 FOR EACH STATION.

Parameter	Meana Year-1	Meana Year-2	Sig. ^b Prob.
STATION 2E			
Cd	0.1320	0.3058	0.0001**
Pb	4.7347	18.4337	0.0043*
Ba	193.2710	133.5260	0.0009**
Cu	15.0081	30.0662	0.0003**
Cr	37.0436	80.2983	0.0001**
Zn	32.6291	115.9460	0.0001**
V	50.3734	134.9830	0.0001**
N	0.0190	0.1775	0.2503
F	0.0060	0.1147	0.0293*
P	0.0320	0.1451	0.2179
D	0.0040	0.0216	0.0762
PAH	0.0110	0.1321	0.1003
LALK	0.2800	1.2377	0.0836
ISO	0.0244	0.1886	0.0515
ALK	0.0558	0.4619	0.0281*
V1708	0.0095	0.0757	0.0295*
V1810	0.0043	0.0471	0.0184*
TOT	2.9400	21.8984	0.0477*
TOC	2.3736	10.4808	0.0048*
FFPI	0.8472	0.7778	0.5984
TALK	0.8210	6.5290	0.0569
P/D	8.0000	6.7017	0.8355
LALK/TALK	0.3410	0.1895	0.2120
ISO/ALK	0.4372	0.4085	0.7473
STATION 2F			
Cd	0.2099	0.2166	0.4712
Pb	6.6813	7.9804	0.2694
Ba	261.4150	116.9760	0.0530
Cu	15.8902	10.1311	0.0042*
Cr	45.8244	37.3304	0.0001**
Zn	49.3589	57.3314	0.1362

TABLE 5.22. (Continued)

Parameter	Meana Year-1	Meana Year-2	Sig.b Prob.
STATION 21? (Continued)			
V	73.1150	62.3209	0.0003**
N	0.0303	0.0464	0.4517
F	0.0064	0.0112	0.5238
P	0.0660	0.0575	0.4480
D	0.0057	0.0017	0.2668
PAH	0.0347	0.0247	0.1551
LALK	0.4504	0.3924	0.3168
ISO	0.0632	0.0298	0.0031*
ALK	0.1336	0.0679	0.0013**
V1708	0.0258	0.0120	0.0079*
V1810	0.0102	0.0063	0.0017**
TOT	5.5432	1.6504	0.0037*
TOC	5.5015	4.6774	0.1732
FFPI	0.7638	0.8246	0*0155*
TALK	1.4612	1.0179	0.0487*
P/D	13.0122	32.7414	0.2187
LALK/TALK	0.3082	0.3854	0.0051*
ISO/ALK	0.4736	0.4397	0.0419*
STATION 3A			
C d	0.1572	0.1631	0.6585
Pb	6.1063	10.3226	0.0001**
Ba	345.9999	236.9950	0.0740
Cu	22.9776	16.1692	0.0245*
Cr	52.2773	46.6361	0.0535
Zn	58.1146	63.9792	0.0107*
v	88.2670	77.9204	0.0373*
N	0.1430	0.1074	0.7940
F	0.0370	0.0317	0.7454
P	0.1810	0.1019	0.2430
D	0.0210	0.0120	0.5320
PAH	0.0950	0.0907	0.9258
LALK	0.5890	0.3958	0.0820
ISO	0.0938	0.0565	0.0374*
ALK	0.2090	0.1259	0.0215*

TABLE 5.22. (Continued)

Parameter	Mean ^a Year-1	Mean ^a Year-2	Sig. ^b Prob.
STATION 3A (Continued)			
V1708	0.0350	0.0240	0.0692
V1810	0.0169	0.0124	0.0855
TOT	9.9100	4.6940	0.0620
TOC	8.3835	10.7960	0.0002**
FFPI	0.8008	0.7464	0.0777
TALK	2.8790	2.5969	0.5543
P/D	8.6190	8.4384	0.9843
LALK/TALK	0.2045	0.1524	0.0584
ISO/ALK	0.4488	0.4487	0.9922
STATION 3B			
Cd	0.1487	0.1729	0.0983
Pb	6.0667	10.4659	0.0001**
Ba	382.0700	314.9690	0.0455*
Cu	28.2438	19.7081	0.0066*
Cr	58.1424	57.2371	0.7463
Zn	64.3444	73.9148	0.0141*
v	96.7840	100.6590	0.0520
N	0.1463	0.0915	0.0210*
F	0.0283	0.0279	0.9110
P	0.1606	0.1595	0.9678
D	0.0196	0.0224	0.3997
PAH	0.0708	0.0795	0.7471
LALK	0.9211	1.2577	0.0382*
ISO	0.1236	0.1748	0.0208*
ALK	0.2835	0.4119	0.0161*
V1708	0.0460	0.0620	0.0403*
V1810	0.0220	0.0369	0.0036*
TOT	13.5756	20.7974	0.0073*
TOC	9.1702	5.2132	0.5434
FFPI	0.8214	0.7912	0.3019
TALK	4.4546	0.0937	0.0074*
P/D	8.1976	7.1129	0.1970
LALK/TALK	0.2069	0.1773	0.0009**
ISO/ALK	0.4359	0.4244	0.3220

TABLE 5.22. (Continued)

Parameter	Meana Year-1	Meana Year-2	Sig. ^b Prob.
STATION 4A			
Cd	0.1388	0.1002	0.1856
Pb	8.0434	9.2257	0.4121
Ba	366.6050	197.5790	0.4041
Cu	24.8348	14.4234	0.0457*
Cr	51.8068	37.6091	0.1881
Zn	63.9789	54.9167	0.2173
v	93.4197	64.8242	0.0803
N	0.1717	0.0957	0.0049*
F	0.0437	0.0079	0.0045*
P	0.1858	0.0796	0.0035*
D	0.0415	0.0070	0.0105*
PAH	0.1079	0.0476	0.0704
LALK	0.7316	0.5901	0.4058
ISO	0.1163	0.0752	0.0470*
ALK	0.2729	0.1966	0.1317
V1708	0.0462	0.0279	0.0082*
V1810	0.0189	0.0172	0.4471
TOT	12.3398	9.5577	0.1432
TOC	701399	13.3381	0.0504
FFPI	0.8021	0.7945	0.8471
TALK	3.5161	3.2158	0.4322
P/D	4.4724	11.2881	0.0143*
LALK/TALK	0.2081	0.1835	0.6560
ISO/ALK	0.4261	0.3826	0.6560
STATION 4B			
Cd	0.1718	0.1497	0.2947
Pb	6.0232	5.7369	0.7368
Ba	193.8870	175.7820	0.8301
Cu	18.1873	8.6521	0.0001**
Cr	31.9719	28.8962	0.2516
Zn	35.2428	42.5947	0.0274*
v	47.6820	44.2574	0.2982
N	0.0370	0.0488	0.5735
F	0.0100	0.0064	0.8422
P	0.0370	0.0470	0.6230
D	0.0110	0.0047	0.2117
PAH	0.0150	0.0369	0.1023

TABLE 5.22. (Continued)

Parameter	Mean ^a Year-1	Mean ^a Year-2	Sig. ^b Prob.
STATION 45 (Continued)			
LALK	0.2830	0.4681	0.1218
IsO	0.0379	0.0383	0.9619
ALK	0.0857	0.0906	0.8241
V1708	0.0159	0.0146	0.7446
V1810	0.0066	0.0078	0.5595
TOT	3.6200	3.9499	0.8660
TOC	2.8697	0.9865	0.3591
FFPI	0.8636	0.7462	0.1312
TALK	0.9610	1.6351	0.2818
P/D	3.3636	9.8829	0.2978
LALK/TALK	0.2944	0.2862	0.8952
ISO/ALK	0.4422	0.4232	0.1547
STATION 4C			
Cd	0.0559	0.0827	0.1059
Pb	4.0079	9.9159	0.0003*
Ba	251.0840	290.3040	0.1059
Cu	17.8342	10.9523	0.0142*
Cr	39.0611	35.3249	0.4519
Zn	32.2243	44.3979	0.0453*
v	55.3792	62.4598	0.3402
N	0.0660	0.0938	0.4184
F	0.0210	0.0190	0.8415
P	0.0890	0.0853	0.9095
D	0.0200	0.0093	0.4108
PAH	0.0470	0.0737	0.3166
LALK	0.5790	0.6964	0.5986
IsO	0.0732	0.0698	0.8803
ALK	0.1710	0.1695	0.9848
V1708	0.0280	0.0269	0.9034
V1810	0.0123	0.0155	0.5584
TOT	6.8700	8.9383	0.4575
TOC	2.7610	10.5798	0.0008**
FFPI	0.8065	0.7393	0.0042*
TALK	1.9290	3.0584	0.2826
P/D	4.4500	9.1591	0.3444
LALK/TALK	0.3001	0.2276	0.0046*
ISO/ALK	0.4280	0.4118	0.7927

TABLE 5.22. (Continued)

Parameter	Meana Year- 1	Meana Year-2	Sig. ^b Prob.
STATION 5(1)			
Cd	0.1469	0.0840	0.0665
Pb	4.9405	8.0836	0.0002**
Ba	235.8720	184.8350	0.0016**
Cu	9.2218	6.3164	0.0544
Cr	22.5299	20.8201	0.6321
Zn	34.6183	38.6383	0.3746
V	44.8478	39.4851	0.1891
N	0.0440	0.0171	0.5273
F	0.0100	0.0042	0.2689
P	0.0560	0.0225	0.1400
D	0.0110	0.0020	0.1669
PAH	0.0440	0.0204	0.4529
LALK	0.3410	0.1509	0.2919
ISO	0.0401	0.0171	0.3774
ALK	0.0865	0.0488	0.4670
V1708	0.0164	0.0063	0.3464
V1810	0.0073	0.0032	0.4100
TOT	4.6700	1.1004	0.1790
TOC	4.4114	2.5365	0.0470**
FFPI	0.7333	0.6911	0.1550
TALK	1.2750	0.5647	0.3966
P/D	5.0909	11.2557	0.3590
LALK/TALK	0.2674	0.2672	0.9985
ISO/ALK	0.4635	0.3517	0.2215
STATION 5(5)			
Cd	0.2212	0.1446	0.2296
Pb	6.1694	6.9697	0.2519
Ba	294.0140	224.6380	0.1060
Cu	15.6933	11.5871	0.1108
Cr	39.5903	34.0397	0.3898
Zn	50.1063	51.8209	0.8867
V	68.5952	58.1289	0.2304
N	0.1280	0.0223	0.4826
F	0.0320	0.0118	0.0685
P	0.1720	0.0280	0.2614
D	0.0320	0.0047	0.3471

TABLE 5.22. (Continued)

Parameter	Mean ^a Year- 1	Mean ^a Year-2	Sig. ^b Prob.
STATION 5(5) (Continued)			
PAH	0.1280	0.0264	0.3632
LALK	0.8100	0.4540	0.3060
ISO	0.1430	0.0537	0.1397
ALK	0.2740	0.1519	0.4176
V1708	0.0555	0.0201	0.1224
V1810	0.0272	0.0104	0.1226
TOT	13.3000	5.1018	0.1341
TOC	9.0211	4.6182	0.1119
FF PI	0.7398	0.6962	0.4852
TALK	3.6200	2.2609	0.2030
P/D	5.3750	5.9685	0.8225
LALK/TALK	0.2237	0.2008	0.6804
ISO/ALK	0.5218	0.3537	0.3774
STATION 5(10)			
Cd	0.2451	0.2332	0.3988
Pb	5.4810	5.8833	0.3666
Ba	285.7750	68.8551	0.0511
Cu	17.1359	11.5980	0.0007**
Cr	38.1375	39.6308	0.3418
Zn	48.4872	58.3201	0.0006**
v	65.6019	61.9840	0.0648
N	0.1330	0.0820	0.2222
F	0.0360	0.0300	0.4252
P	0.1640	0.0644	0.0175*
D	0.0330	0.0170	0.1321
PAH	0.0800	0.0566	0.0354*
LALK	0.8330	0.5651	0.0075*
ISO	0.1270	0.0817	0.0041*
ALK	0.2690	0.1935	0.0696
V1708	0.0532	0.0294	0.0018**
V1810	0.0183	0.0164	0.0258*
TOT	14.0000	7.9556	0.0118*
TOC	10.4635	6.9194	0.2296

TABLE 5.22. (Continued)

Parameter	Mean ^a Year-1	Mean ^a Year-2	Sig. ^b Prob.
STATKIN 5(10) (Continued)			
FFPI	0.8206	0.7738	0.2516
TALK	3.7230	2.8650	0.0065*
P/D	4.9696	3.7848	0.5309
LALK/TALK	0.2237	0.1972	0.0099*
ISO/ALK	0.4721	0.4222	0.2279
STATION 5A			
Cd	0.2185	0.2123	0.7562
Pb	9.1132	8.3504	0.1653
Ba	550.1920	310.4890	0.0133*
Cu	20.5299	17.1323	0.2068
Cr	54.5911	48.2680	0.0536
Zn	65.5075	60.2393	0.1624
v	95.4137	72.4309	0.0334
N	0.2920	0.1754	0.2146
F	0.0330	0.0228	0.1366
P	0.2640	0.1059	0.0709
D	0.0280	0.0161	0.1341
PAH	0.1580	0.1173	0.2850
LALK	1.2100	1.0752	0.7178
ISO	0.2110	0.1497	0.0557
ALK	0.4080	0.3023	0.0415*
V1708	0.0855	0.0496	0.0253*
V1810	0.0414	0.0302	0.3609
TOT	10.6000	13.7729	0.6502
TOC	10.0469	13.4217	0.0002**
FFPI	0.7961	0.7335	0.0189*
TALK	6.1300	4.9084	0.0844
P/D	9.4285	6.5693	0.0302*
LALK/TALK	0.1974	0.2190	0.6786
ISO/ALK	0.5171	0.4952	0.3978

TABLE 5.22. (Continued)

Parameter	Mean ^a Year-1	Mean ^a Year-2	Sig. ^b Prob.
STATION 5B			
Cd	000400	0.1392	0.0035*
Pb	3.7794	17.9629	0.0001**
13a	192.4110	533.9090	0.0008**
Cu	4.8893	31.2641	0.0001**
Cr	17.1173	87.0000	0.0001**
Zn	18.5074	115.6667	0.0001**
V	32.7968	150.0000	0.0001**
N	0.2190	0.4688	0.0166*
F	0.0850	0.1060	0.4565
P	0.2690	0.3546	0.0079*
D	0.0670	0.0628	0.7416
PAH	0.1510	0.3609	0.0003**
LALK	0.3000	1.4627	0.0006**
1s0	0.0235	0.3490	0.0003**
ALK	0.0527	0.5765	0.0001**
V1708	0.0098	0.0997	0.0003**
V1810	0.0041	0.0851	0.0017**
TOT	2.7800	28.6704	0.0007**
TOC	2.0449	10.0636	0.0001**
FFPI	0.8091	0.7332	0.0605
TALK	0.7900	7.3114	0.0005**
P/D	4.0149	5.6379	0.1462
LALK/TALK	0.3797	0.2000	0*0077*
ISO/ALK	0.4459	0.6054	0.0084*
STATION 5D			
Cd	0.2196	0.2866	0.0001**
Pb	9.8794	7.1753	0.0052*
Ba	372.5590	44.0110	0.0133*
Cu	24.8918	17.9281	0.0104*
Cr	54.9692	49.3311	0.0004**
Zn	76.4785	77.5587	0.7484
v	91.8141	79.2938	0.0141*
N	0.3542	0.1995	0.0010**
F	0.0481	0.0462	0.9081
P	0.3965	0.1545	0.0125
D	0.0677	0.0352	0.0213*

TABLE 5.22. (Continued)

Parameter	Mean ^a Year- 1	Mean ^a Year-2	Sig. ^b Prob.
STATION 5D (Continued)			
PAH	0.2254	0.1538	0.0641
LALK	1.2616	1.0762	0.3961
ISO	0.1864	0.1658	0.5787
ALK	0.4496	0.3532	0.2257
V1708	0.0678	0.0469	0.0882
V1810	0.0326	0.0356	0.6894
TOT	33.5923	26.7677	0.2625
TOC	29.1178	14.2679	0.0383*
FFPI	0.7865	0.7399	0.2196
TALK	10.2785	8.4162	0.3348
P/13	5.8511	4.3948	0.0012**
LALK/TALK	0.1227	0.1278	0.5947
ISO/ALK	0.4145	0.4695	0.3195
STATION 5E			
Cd	0.0705	0.1966	0.0057*
Pb	5.6174	17.1174	0.0036*
Ba	328.7440	470.9880	0.1071
Cu	10.9682	28.2911	0.0083*
Cr	29.9803	82.6244	0.0100*
Zn	33.6655	108.1800	0.0082*
v	57.9227	146.2970	0.0140*
N	0.1650	0.4747	0.0016**
F	0.0450	0.0834	0.206*
P	0.1810	0.3216	0.0013**
D	0.0390	0.0576	0.2167
PAH	0.0830	0.3399	0.0003**
LALK	0.7270	1.7066	0.0567
ISO	0.1120	0.3517	0.0103*
ALK	0.2470	0.6900	0.0289*
V1708	0.0443	0.1145	0.1223
V1810	0.0189	0.0794	0.0014**
TOT	9.0100	28.8058	0.0281*
TOC	5.8404	9.7222	0.4546
FFPI	0.8382	0.7340	0.0078*
TALK	2.4570	8.4796	0.0736
P/D	4.6410	5.5815	0.5224
LALK/TALK	0.2958	0.2012	0.1204
ISO/ALK	0.4534	0.5097	0.3764

TABLE 5.22. (Continued)

Parameter	Mean ^a Year-1	Mean ^a Year-2	Sig. ^b Prob.
STATION 5F			
Cd	0.2051	0.1512	0.1089
Pb	7*7334	6.7215	0.0216
Ba	329.9810	279.5300	0.0036
Cu	18.1093	9.9468	0.0137
Cr	48.9331	35.7993	0.0465*
Zn	63.7647	52.2552	0.0179*
V	79.4837	54.5909	0.0084*
N	0.1960	0.0602	0.0355*
F	0.0240	0.0126	0.3920
P	0.2270	0.0563	0.0130*
D	0.0340	0.0159	0.2171
PAH	0.2300	0.0671	0.0187*
LALK	1.5300	0.6802	0.0213*
ISO	0.2050	0.0883	0*0200*
ALK	0.4950	0.2015	0.0096*
V1708	0.0176	0.0286	0.0086*
V1810	0.0322	0.0191	0.0749
TOT	0.9180	9.8159	0.0046*
TOC	16.8707	7.5374	0.0099*
FFPI	0.6765	0.6805	0.9606
TALK	11.6300	3.2024	0.0099*
P/D	6.6764	3.5333	0.1773
LALK/TALK	0.1315	0.2124	0.0505
ISO/ALK	0.4141	0.4380	0.2368
STATION 5G			
Cd	0.1006	0.0965	0.8011
Pb	6.0736	7.2980	0.2889
Ba	284.6240	257.9350	0.2228
Cu	10.5815	11.1417	0.4830
Cr	34.3395	36.3121	0.2929
Zn	39.2338	46.6008	0.0307*
v	61.3289	61.3877	0.9918
N	0.1270	0.0732	0.4169
F	0.0180	0.0101	0.5055
P	0.1340	0.0556	0.0889
D	0.0180	0.0044	0.2530

TABLE 5.22. (Continued)

Parameter	Mean ^a Year- 1	Mean ^a Year-2	Sig. ^b Prob.
STATION 5G (Continued)			
PAH	0.0880	0.0592	0.3700
LALK	0.8830	0.4369	0.0186*
1s0	0.1310	0.0662	0.0474*
ALK	0.2820	0.1524	0.0728
V1 708	0.0556	0.0256	0.0403*
V1810	0.0224	0.0131	0.0702
TOT	10.9000	5.6458	0.1210
TOC	6.1493	6.5669	0.6517
FFPI	0.7714	0.7069	0.3610
TALK	3.1030	2.0346	0.1454
P/D	7.4444	12.4095	0.5060
LALK/TALK	0.2845	0.2147	0.1360
ISO/ALK	0.4645	0.4346	0.0922
STATION 6A			
Cd	0.1216	0.1875	0.0422*
Pb	8.5969	14.8439	0.0031*
Ba	385.3730	375.0400	0.5831
Cu	23.4674	22.1835	0.4632
Cr	59.5703	59.9240	0.9505
Zn	70.1516	88.3246	0.0638
v	91.4384	99.5930	0.3128
N	0.4450	0.4211	0.7357
F	0.1390	0.1213	0.5734
P	0.4480	0.2849	0.1001
D	0.1290	0.0547	0.0514
PAH	0.2680	0.2602	0.5456
LALK	2.6900	1.2727	0.0494*
1s0	0.2530	0.2243	0.2320
ALK	0.5110	0.4482	0.3625
V1 708	0.0956	0.0809	0.3734
V1810	0.0394	0.0490	0.1866
TOT	25.4000	29.1066	0.6155
TOC	11.4065	13.2891	0.2253

TABLE 5.22. (Continued)

Parameter	Meana Year- 1	Meana Year-2	Sig. ^b Prob.
STATION 6A (Continued)			
FFPI	0.8124	0.7720	0.1662
TALK	8.7300	11.2159	0.1524
P/D	3.4728	5.2040	0.0541
LALK/TALK	0.3081	0.1132	0.0452*
ISO/ALK	0.4951	0.5005	0.8656
STATION 6B			
Cd	0.2872	0.1962	0.0012**
Pb	16.6958	12.4234	0.0008**
Oa	743.6560	498.0080	0.0431*
Cu	36.6366	23.2631	0.0030*
Cr	91.4305	67.5434	0.0123*
Zn	112.1600	86.8065	0.0160*
v	152.7320	107.9880	0.0001**
N	3.5000	1.0413	0.0154*
F	0.6180	0.2231	0.0091*
P	2.0300	0.4456	0.0002**
D	0.3260	0.0889	0.0514
PAH	1.2600	0.3782	0.5456
LALK	4.9400	1.1924	0.0015**
1s0	0.9180	0.2507	0.0087*
ALK	1.8100	0.4620	0.0026*
V1708	0.3050	0.0936	0.0153*
V1810	0.1440	0.0358	0.4057
TOT	68.6000	32.8266	0.0808
TOC	18.0044	15.0909	0.5033
FFPI	0.8370	0.8261	0.5601
TALK	23.6400	10.8077	0.0864
P/D	6.2269	5.0115	0.2011
LALK/TALK	0.2089	0.1103	0.0847
ISO/ALK	0.5071	0.5426	0.7567

TABLE 5.22. (Continued)

Parameter	Meana Year-1	Meana Year-2	Sig.b Prob.
STATION 6C			
Cd	0.0583	0.1263	0.0234*
Pb	8.2072	12.9871	0.0092**
Ba	384.0340	423.2930	0.4893
Cu	20.3252	21.7988	0.6402
Cr	63.1888	66.3208	0.7527
Zn	65.9134	87.2092	0.1107
V	95.2327	116.2960	0.2265
N	0.3349	0.3528	0.8987
F	0.0792	0.1015	0.5457
P	0.3535	0.2337	0.2958
D	0.0799	0.0507	0.2990
PAH	0.1631	0.2255	0.2673
LALK	1.3191	0.7146	0.0974
1s0	0.1606	0.1388	0.6745
ALK	0.3413	0.2752	0.5661
V1708	0.0630	0.0636	0.9635
V1810	0.0271	0.0215	0.7948
TOT	14.9801	20.9457	0.1161
TOC	6.0383	8.3384	0.0720
FFPI	0.8138	0.7633	0.2765
TALK	3.9708	6.5617	0.0769
P/D	4.4218	4.6035	0.7077
LALK/TALK	0.3322	0.1089	0.0038*
ISO/ALK	0.4706	0.5043	0.4602
STATION 6D			
Cd	0.0636	0.0629	0.9733
Pb	7.0008	9.1306	0.2326
Ba	281.5960	28.7810	0.9969
Cu	8.9685	9.8772	0.7715
Cr	38.1906	34.1264	0.6970
Zn	45.4092	54.2703	0.3734
V	65.9854	68.9748	0.8408
N	0.0780	0.0965	0.7678
F	0.0141	0.0168	0.7682
P	0.0787	0.0715	0.8889
D	0.0158	0.0155	0.9812

TABLE 5.22. (Continued)

Parameter	Mean ^a Year-1	Mean ^a Year-2	Sig. ^b Prob.
STATION 6D (Continued)			
PAH	0.0554	0.0707	0.7136
LALK	1.1702	0.2577	0.0622
ISO	0.0769	0.0488	0.4989
ALK	0.1650	0.0892	0.3838
V1708	0.0314	0.0212	0.5401
V1810	0.0125	0.0139	0.8447
TOT	7.7452	5.1454	0.6086
TOC	3.6466	4.1748	0.6034
FFPI	0.7682	0.7378	0.4290
TALK	2.4844	2.0689	0.7278
P/D	4.9782	4.5915	0.7959
LALK/TALK	0.4710	0.1246	0.0256*
ISO/ALK	0.4663	0.5471	0.1777
STATION 6F			
Cd	0.1231	0.1165	0.7203
Pb	11.8009	9.4861	0.2254
Ba	374.7820	290.5610	0.2909
Cu	20.5016	13.1256	0.0116*
Cr	62.7724	47.2666	0.0082*
Zn	67.7646	59.9500	0.2748
v	106.5740	78.6222	0.0322*
N	0.4690	0.2249	0.0132*
F	0.1150	0.0587	0.0727
P	0.4350	0.1420	0.0063*
D	0.0820	0.0263	0.0033*
PAH	0.2650	0.1054	0.0252*
LALK	1.6300	0.8346	0.0630
ISO	0.2350	0.1544	0.2464
ALK	0.5130	0.3439	0.1803
V1708	0.0907	0.0576	0.1258
V1810	0.0375	0.0308	0.5249
TOT	24.2000	13.2345	0.0260*
TOC	9.8215	7.2111	0.3363
FF PI	0.8060	0.8104	0.8508

TABLE 5.22. (Continued)

Parameter	Meana Year- 1	Meana Year-2	Sig. ^b Prob.
STATION 6F (Continued)			
TALK	7.4800	4.8369	0.0923
P/D	5.3048	5.4002	0.5343
LALK/TALK	0.2179	0.1725	0.0410*
ISO/TALK	0.4580	0.4493	0.8637
STATION 7A			
Cd	0.0974	0.1090	0.5305
Pb	8.4258	13.6853	0.0081
Ba	697.4910	709.9720	0.5633
Cu	13.6867	14.5894	0.6466
Cr	62.8813	71.2759	0.0217*
Zn	74.6994	85.9845	0.0024*
V	86.9672	88.2948	0.5706
N	0.5726	0.4597	0.6918
F	0.1642	0.0687	0.0169*
P	0.4477	0.2278	0.2647
D	0.1117	0.0415	0.1188
PAH	0.1333	0.2447	0.4647
LALK	1.4063	1.2959	0.7006
ISO	0.1809	0.2848	0.1010
ALK	0.3322	0.5332	0.0605
V1708	0.0725	0.1019	0.1925
V1810	0.0283	0.0508	0.0339*
TOT	21.2607	22.4199	0.8097
TOC	10.7972	10.4080	0.8386
FFPI	0.7705	0.7645	0.9564
TALK	5.3502	8.9937	0.0927
P/D	5.5216	5.4865	0.9539
LALK/TALK	0.2628	0.1441	0.0149*
ISO/ALK	0.5446	0.5342	0.7927
STATION 7B			
Cd	0.0594	0.0565	0.9105
Pb	6.6390	10.0451	0.0172*
Ba	456.0980	483.8280	0.4626

TABLE 5.22. (Continued)

Parameter	Mean ^a Year-1	Mean ^a Year-2	Sig. ^b Prob.
STATION 7B (Continued)			
Cu	9.6188	7.1435	0.2381
Cr	48.7889	52.9150	0.3814
Zn	50.9202	49.9600	0.7296
v	67.7929	57.9655	0.1090
N	0.1940	0.1162	0.1462
F	0.0420	0.0165	0.1646
P	0.1820	0.0674	0.0312*
D	0.0370	0.0146	0.0033*
PAH	0.1250	0.0631	0.0209*
LALK	1.2800	0.5819	0.0347 *
ISO	0.1090	0.1060	0.8789
ALK	0.2420	0.2447	0.9545
V1708	0.0431	0.0402	0.5721
V1810	0.0161	0.0174	0.5972
TOT	11.4000	6.8735	0.1422
TOC	5.4698	4.9839	0.3709
FFPI	0.7844	0.7707	0.7939
TALK	3.7600	3.1693	0.2573
P/D	4.9189	4.6156	0.8527
LALK/TALK	0.3404	0.1836	0.0105*
ISO/ALK	0.4504	0.4334	0.3287
STATION 7C			
Cd	0.1276	0.1613	0.1598
Pb	14.6573	20.1924	0.1228
Ba	567.6000	500.0660	0.0642
Cu	26.9876	29.9966	0.5941
Cr	77.4815	84.5236	0.3702
Zn	96.9949	107.3510	0.3215
v	145.1270	140.5310	0.7577
N	0.6950	0.6329	0.8466
F	0.1240	0.0953	0.5614
P	0.6140	0.3823	0.3576
D	0.1070	0.0865	0.7247
PAH	0.3620	0.0787	0.4476
LALK	1.9000	1.5564	0.4327
ISO	0.2500	0.2686	0.7340

TABLE 5.22. (Continued)

Parameter	Meana Year-1	Meana Year-2	Sig. ^b Prob.
STATION 7C (Continued)			
ALK	0.5320	0.6139	0.5672
V1708	0.0993	0.1095	0.6244
V1810	0.0450	0.0511	0.4490
TOT	23.7000	31.4221	0.2862
TOC	13.3555	13.1019	0.8654
FFPI	0.8096	0.8887	0.5608
TALK	7.5800	11.4225	0.2198
P/D	5.7383	4.4189	0.1046
LALK/TALK	0.2506	0.1362	0.0021*
ISO/ALK	0.4699	0.4375	0.2091
STATION 7E			
Cd	0.1474	0.1246	0.3280
Pb	8.2992	13.9017	0.0037*
Ba	605.0480	560.6060	0.3795
Cu	16.7900	18.7218	0.0325*
Cr	62.1807	61.8449	0.9321
Zn	70.9724	75.9870	0.0111*
V	92.4287	90.6028	0.7920
N	0.8880	0.7310	0.4480
F	0.0710	0.0998	0.4017
P	0.5110	0.3659	0.2200
D	0.0690	0.0614	0.7669
PAH	0.2340	0.2883	0.4657
LALK	2.0500	1.8448	0.5755
ISO	0.3290	0.3949	0.5027
ALK	0.5330	0.6481	0.2980
V1708	0.1420	0.1829	0.4182
V1810	0.0411	0.0514	0.3078
TOT	2.6000	33.5045	0.2862
TOC	17.1895	23.8109	0.2800
FFPI	0.8680	0.8130	0.1358
TALK	8.2700	11.6787	0.0781
P/D	7.4057	5.9576	0.2926
LALK/TALK	0.2478	0.1579	0.0247*
ISO/ALK	0.6172	0.6093	0.1128

TABLE 5.22. (Continued)

Parameter	Meana Year-1	Meana Year-2	Sig. ^b Prob.
STATION 7G			
Cd	0.0640	0.1085	0.1025
Pb	11.0860	13.8962	0.0001**
Ba	606.1690	635.6490	0.2183
Cu	10.2417	11.8307	0.5146
Cr	41.2003	44.9083	0.3204
Zn	52.9717	62.9378	0.0174*
V	67.9356	67.9951	0.9883
N	0.9880	0.2838	0.0079
F	0.0120	0.0282	0.0510
P	0.5800	0.3242	0.0115*
D	0.0480	0.0393	0.3040
PAH	0.2160	0.1552	0.0804
LALK	1.4800	1.7521	0.6530
Is0	0.4270	0.4025	0.8866
ALK	0.4620	0.5413	0.6353
V1708	0.2140	0.2007	0.8839
V1810	0.0454	0.0459	0.9732
TOT	17.7000	23.5953	0.4580
TOC	24.8718	9.5758	0.0668
FFPI	0.8828	0.8133	0.0026*
TALK	4.4200	6.4044	0.2728
P/D	12.0833	8.2415	0.0431*
LALK/TALK	0.3348	0.2735	0.1206
ISO/ALK	0.9242	0.7436	0.1128

^aGeometric means

^bTwo-tailed test $\alpha=0.05$ on logarithmic scale

* *Significant at Bonferroni criterion ($\alpha/\text{No. of tests}$)

*Significant at the 0.05 probability level.

tests were performed, we would expect to see the t-value as large as the one calculated only 5 times or less.

Normally, the tabulated t-value, used for comparison against a t-value calculated from the data, is chosen to reduce the chances of making an error in declaring mean concentration differences to be significant. The most widely accepted level of error is 5 percent. That is to say, most scientists are willing to take risks in drawing conclusions when they believe that the chance of making an error is approximately 1 in 20. This is, in fact, the level of error associated with a scientific inference if that inference is confined only to one variable (e.g., the change in pb concentration between years). However, when it is of interest to assess the magnitude of change among many variables simultaneously, the risks of making an error are greater than 1 in 20; how much greater depends on the number of variables of interest. The greater the number of t-tests that are performed, the higher the probability of finding one that is significant simply because many have been performed.

The **Bonferroni** method can be used to reduce the chances of making an error in declaring any given t-test, from among many, to be significant. The **Bonferroni** method consists of reducing this overall error rate by dividing the generally accepted level of error in drawing a conclusion by the number of tests that are performed. Since for every station a maximum of 25 variables (chemical concentrations) were compared between years, the **Bonferroni** significance criterion used was $0.05/25$ or 0.002 . Thus, all two-sample t-tests were declared significant according to the **Bonferroni** criterion if $p < 0.002$. These tests are marked by a double asterisk (**) in the last column of Table 5.22.

The major conclusion to be drawn from an inspection of Table 5.22 is that the pattern of change in parameter concentrations among stations is not consistent. For example, there is strong evidence ($p = 0.0001$) from both Stations 2E and 2F for concluding that a significant change has occurred in the concentration of Cr between years. This change was a significant increase at Station 2E but a significant decrease at Station 2F. Furthermore, there is only moderate evidence ($p = 0.0535$) for a change in Cr concentrations between years at Station 3A and absolutely no evidence ($p = 0.7463$) at Station 3B.

It should be pointed out that widely disparate means may not, in fact, be significantly different. This is due to the large variances that may be associated with each sample mean for a particular chemical concentration. Again, since the t-value is a ratio with a variance estimate in the denominator, large variances can produce small t-values and hence insignificant tests.

In addition, Table 5.22 shows that all metal concentrations except Pb were significantly higher, by the **Bonferroni** criterion, at Station 2E in Year-2. Likewise, at Station 5B, all metal concentrations except Cd were significantly higher in Year-2, according to the same **Bonferroni** criterion.

5.4.2.3. Study Region Trends. As a way of summarizing the findings presented in Table 5.22 and of obtaining a grasp on the overall year-to-year trend, regardless of station, a statistical test was performed that allowed every station to contribute information with equal importance to this summarization.

A single (arithmetic average) value for each chemical concentration at each station -was produced from both the Year- 1 and Year-2 data. Since there were 26 stations sampled in Year-1 that were also sampled in Year-2, there were 26 pairs of observations for each chemical concentration. A paired t-test was performed on the natural logarithms of these data.

Table 5.23 shows that only five parameters changed significantly according to the Bonferroni criterion, namely, Pb, P, D, **FFPI**, and LALK/TALK. Of the first four variables (which were not ratios of other variables) only **Pb** showed a significantly larger concentration in Year-2 than in Year-1. Such an evaluation can be performed for any logical grouping of stations. Comparison of all stations grouped together in Year-1 versus all stations in Year-2 may not have any utility for interpreting the monitoring data, but is illustrative of an approach that will be undertaken in Year-3 on a region-by-region basis (i.e., the "1", "2", "3", etc. stations as defined in Section 4).

5.4.3 Variance Estimates for New Stations in Year-2

Thirteen new stations were sampled in Year-2 in addition to 26 others that were also sampled in Year-1. A variance components analysis was performed for these 13 new stations. This **analysis** was similar to that performed for the Year-1 data discussed at the beginning of Section 5.4.2, with two exceptions. Because replicate sediment samples were composite before chemical analysis, the replicate-to-replicate (i.e., within-grab) variance estimate could not be calculated. In addition, beginning in Year-2 chemical analyses of the metal concentrations were conducted on the fine-grained (mud) fraction of the sediment sample, while the hydrocarbon concentrations were determined from the entire (bulk) sediment sample without regard to grain size.

Table 5.24 contains the within-station (grab) and the between-station (station) variability estimates for metal concentrations from the mud fraction of the sediment samples. Associated with each parameter is a statistical test of the hypothesis that there is no between-station variability. For all metal concentrations except Cu and **Zn**, this test was highly significant ($p = 0.001$ or less). That is to say, there is strong evidence that these metal concentrations vary from one station to another.

Table 5.25 contains the within-station and the between-station variance estimates for hydrocarbon concentrations from the bulk sediment samples. With the exception of **TOC**, **FFPI**, and **P/D**, the same statistical tests were all highly significant ($p < 0.0001$). That is, there is strong evidence (approximately 1 in 10,000 chance of error) for concluding that hydrocarbons also vary among stations.

5.4.4 General Approach to Hypothesis Testing and Future Monitoring

The ultimate goal of the BSMP is to test the four null hypotheses, for evaluating environmental effects of **OCS** oil and gas exploration and development activities on the Beaufort Sea, with appropriate statistical analyses:

- 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 the concentration 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 activities.

In Year-1 it was determined that the magnitude of temporal change that could be detected by the monitoring program is a function of both the variability in the measured parameters as well as the number of replicates analyzed each year. Table 5.26,

TABLE 5.23 GEOMETRIC MEANS AND PAIRED T-TEST COMPARISONS ON A LOGARITHMIC (NATURAL) SCALE AMONG METAL AND HYDRO-CARBON PARAMETERS BETWEEN YEAR-1 AND YEAR-2.

Parameter	Year-1a Mean	Year-2a Mean	Sig. ^b Prob.
Cd	0.1257	0.1430	0.1371
Pb	7.2831	10.4636	0.0007**
Ba	350.5440	285.2190	0.0356*
Cu	16.3087	15.0442	0.4283
Cr	45.0832	48.9904	0.4757
Zn	54.3636	67.0205	0.0190*
V	74.7125	79.2912	0.5925
N	0.1844	0.1708	0.1477
F	0.0345	0.0348	0.3403
P	0.1960	0.1286	0.0009**
D	0.0342	0.0199	0.0002**
PAH	0.1078	0.1059	0.4920
LALK	0.9251	0.7943	0.1668
ISO	0.1205	0.1236	0.7312
ALK	0.2528	0.2643	0.8429
V1708	0.0477	0.0464	0.5031
V1810	0.0196	0.0249	0.4967
TOT	8.0765	8.4745	0.4516
TOC	8.0706	8.4745	0.8799
FFPI	0.7996	0.7635	0.0002**
TALK	0.5296	4.3782	0.3864
P/D	5.8573	6.9256	0.2273
LALK/TALK	0.2622	0.1841	0.0003**
ISO/ALK	0.4765	0.4688	0.3159

^aYear 1 and Year 2 geometric means are in original scale.

^bTwo-tailed t-test on a logarithmic scale.

*Significant at 0.05 probability level.

**Significant at Bonferroni criterion ($\alpha/\text{No. of tests}$) = 0.002.

TABLE 5.24. VARIANCE ESTIMATES OF METAL CONCENTRATIONS ON A LOG-ARITHMIC (NATURAL) SCALE FOR 13 NEW STATIONS SAMPLED IN YEAR-2 WITH ASSOCIATED STATISTICAL TESTS.

Parameter	Station	Grab	F-value ^a	Sig. Prob.
Cd	0.038	0.0286	4.90	0.0004
Pb	0.054	0.018	9.81	0.0001
Ba	0.190	0.036	16.59	0.0001
Cu	0.016	0.027	2.79	0.0148
Cr	0.021	0.007	9.43	0.0001
Zn	0.007	0.010	2.88	0.0123
v	0.018	0.009	7.12	0.001

^aF statistics for testing the hypothesis that there is no station-to-station variability.

TABLE 5.25. VARIANCE ESTIMATES OF HYDROCARBON CONCENTRATIONS ON A LOGARITHMIC (NATURAL) SCALE FOR 13 NEW STATIONS SAMPLED IN YEAR-2 WITH ASSOCIATED STATISTICAL TESTS.

Parameter	Station	Grab	F-value ^a	Sig. Prob.
N	0.946	0.373	8.21	<0.0001
F	1.272	0.250	14.65	<0.0001
P	0.962	0.231	12.83	<0.0001
D	1.478	0.248	17.46	<0.0001
PAH	0.780	0.153	15.51	<0.0001
LALK	0.571	0.187	9.92	<0.0001
ISO	0.848	0.179	14.85	<0.0001
ALK	0.688	0.167	13.05	<0.0001
V1708	0.733	0.162	14.22	<0.0001
V1810	0.835	0.194	13.56	<0.0001
TOT	0.711	0.365	6.69	<0.0001
TOC	0.155	0.430	2.05	0.0628
FFPI	0.005	0.006	3.34	0.0058
TALK	0.583	0.293	6.80	<0.0001
P/D	0.082	0.120	2.89	0.0139
LALK/TALK	0.121	0.054	7.55	0.0001
ISO/ALK	0.142	0.006	67.36	<0.0001

^aF statistics for testing the hypothesis that there is no station-to-station variability.

TABLE 5.26. 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		
		4	3	2
Cd	0.18	1.5	1.6	1.7
Pb	0.13	1.4	1.45	1.5
Ba	0.16	1.4	1.5	1.6
Cu	0.21	1.6	1.7	1.8
Cr	0.05	1.1	1.15	1.2
Zn	0.21	1.6	1.7	1.8
V	0.16	1.4	1.5	1.6

Organic Parameter	Pooled Standard Deviation	Second Year Sample Size		
		4	3	2
N	0.60	3.5	4.3	5.2
F	1.24	13.1	21.8	30.6
P	0.60	3.5	4.3	5.2
D	1.01	8.2	12.2	16.3
PAH	0.78	5.1	6.9	8.7
TALK	0.34	2.1	2.35	2.6
LALK	0.37	2.2	2.6	2.8
1708	0.32	2.0	2.25	2.5
1810	0.32	2.0	2.25	2.5
TOT	0.28	1.8	2.0	2.2
UV/F(355)	0.39	2.3	2.65	3.0
FFPI	0.11	1.3	1.35	1.4
P/D	0.60	3.5	4.3	5.2
ISO	0.32	2.0	2.2	2.5
ALK	0.32	2.0	2.2	2.5
LALK/TALK	0.18	1.5	1.6	1.7
ISO/ALK	0.14	1.4	1.45	1.5
TOC	0.30	1.9	2 . 1	2.3

which is based on Year-1 Study Area pooled standard deviations for each parameter, lists the minimum multiplicative changes in concentration which would allow detection of significant changes in Year-2 parameters, based on sample sizes of two, three, and four replicates. The data in this table were used to ascertain that level of significant change in concentrations that could be detected by analysis of three replicates per station in the Year-2 program.

In Year-2, statistical analyses focused on assessing temporal variabilities at each station. The significance of concentration differences between Year-1 and Year-2 for each parameter at each station was determined by two-sample t-tests. These data, which are presented in **Table 5.22** and discussed in Section 5.4.2.2, represent a test of H_{01} . Future approaches to testing the other null hypotheses will rely on data from this type (or similar) analyses. Testing the null hypothesis H_{02} will rely on t-tests of key source parameter ratios.

An approach that can be used to test the null hypotheses H_{01} and H_{02} is outlined in Figure 5.23. The approach to testing H_{03} and H_{04} will be similar when sufficient data on tissues are acquired in Year-3. H_{01} will be accepted if the incremental (e.g., Year-1 to Year-3) change in the mean metal or hydrocarbon concentrations between years is not significant according to the selected variance test. If it is found that the change in the mean concentration is significant (i.e., H_{01} is rejected), according to the criteria of the test, hypothesis H_{02} will be examined. H_{02} considers the source ratios which have been or will be selected to indicate the influence of oil and gas development activity on the observed metal or hydrocarbon concentrations. If H_{02} testing indicates that the observed changes are geochemical in nature (e.g., a change in sediment grain size or TOC, with a corresponding change in a specific metal or hydrocarbon parameter), the corresponding concentration changes may not be indicative of a drilling source. If no corresponding geochemical changes are observed, and significant increases are observed in petroleum source ratios, then such changes may be indirectly related to oil and gas development.

5.4.5 Summary of Statistical Analyses

The efforts to reduce the variance of the chemical concentrations through normalization techniques have not been successful. The Year-1 and Year-2 attempts could not identify a useful function of ancillary variables such as percent silt, percent clay, or total organic carbon, which could be used as a normalization tool. The advantage would have been to increase the power of the statistical tests by using the normalized rather than the original data. It is recommended that no more effort be spent on this issue.

The variance components analysis, which was used to determine the impact of compositing replicate sediment samples before chemical analysis, yielded mixed results. For the most part, chemical concentrations showed no significant between-grab variation; however, 6 of these 25 variables did. It is recommended that replicate sediment samples from the same grab always be composite. In the event that a partial sample (i.e., enough sediment for only one replicate) is obtained, it is recommended that it be discarded.

Because of the large number of statistical tests required to assess the degree of year-to-year change in the chemical concentrations, it is recommended that the Bonferroni significance criterion indicated in Tables 5.22 and 5.23 be used to draw reasonable conclusions. With the exception of two stations, it appears that the pattern of change both in magnitude as well as direction among chemical concentrations within a station and between years, is not clearly discernible. For this reason it seems less useful to draw conclusions regarding the environmental impact of these potential pollutants from summary information across all stations. The summary information (Table 5.23), however, may be useful as a means of identifying directions for future research by identifying those chemical concentrations that show the most difference between years.

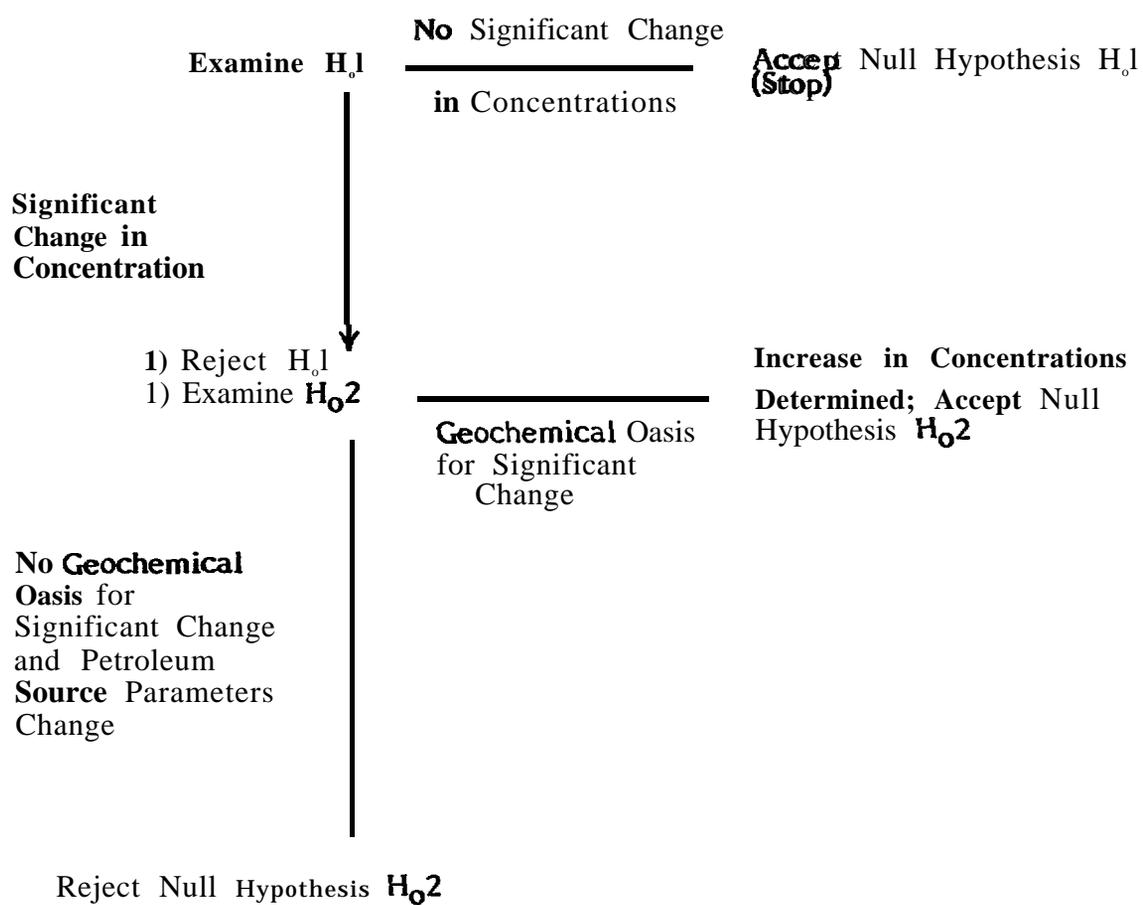


FIGURE 5.23. SCHEMATIC FOR HYPOTHESIS TESTING

Between-station variances that were **not appreciable** (i.e., different from zero) for the new stations in Year-2 could indicate that the corresponding chemical is not an important constituent of the cadre of potential pollutants from off-shore oil drilling.

As a final recommendation, the difficulty and complexity of the effort to compare data from the first two years of the Beaufort Sea Monitoring Program suggests that the replication and **compositing** techniques should be identical from year to year to produce accurate and reliable statistical analyses.

6. STUDY CRITIQUE AND RECOMMENDATIONS FOR YEAR-3

The conduct of the Year-2 study was very successful, and all sampling and analytical objectives were met. Difficulties in sampling of benthic animals during Year-1 were resolved and a very comprehensive collection was obtained in Year-2. Modifications to the NOAA research vessel proved to be worthwhile and contributed to the efficiency and quality of the sampling activity.

Year -2 sampling activities included the complete collection of offshore sediments from the entire Study Area from Barter Island to west of Cape **Halkett**. For those stations **resampled** in the Year-2 program, station reoccupation was accurate to within the required distance from the station center (0.2 rim). In addition, a key collection of shoreline peat samples from the entire Study Area was obtained as part of the examination of the chemical composition of potential source materials. The other part of the source material investigation, the sampling of river sediments, was addressed, but not as extensively as the peat collection. Collection of the **benthic** animals included the following species: *Astarte borealis*, *Macoma* sp., *Portlandia arctica*, *Cyrtodaria kurriana*, and *Anonyx* sp. This collection included different feeding types. The inclusion of different feeding types is of great value to the program because it addresses different pathways by which the benthic population may take up pollutants. It should be stressed that the sampling and chemical analyses of benthic animals performed do not represent an assessment of the condition of the **benthic** population, but instead represent the sentinel organism, or "mussel watch", approach to marine pollution monitoring.

The low levels of metals and diagnostic hydrocarbons observed in the animals make these animals, and the method in general, extremely well-suited for use in a continued monitoring program of the area. These animals potentially represent a very sensitive measure of incremental addition of pollutants to the water column and/or the sediment in which the animals feed. It is not yet clear which species represents the most useful and sensitive choice for this type of monitoring program. The multiple-species approach appears to be the best suited for continued use, given the heterogeneity in animal distributions and the wide coverage of feeding niches and pollutant uptake paths afforded by this approach.

The set of sediments collected and the chemical and statistical analyses performed illustrated the first application of the testing of the program's basic hypotheses. Because the analytical methods and results proved accurate and consistent from Year- 1 to Year-2, the significant changes observed in individual chemical components and component ratios were most likely due to **geochemical** variability caused by annual changes. The sedimentary environment of the Beaufort Sea is very dynamic due to ice scouring in certain areas and to changing shoreline erosional and riverine particulate sedimentation patterns. Changes not attributable to oil and gas exploration and production activities appeared to be detected at several of the stations. The use of the multi-parameter approach to monitoring and the use of diagnostic ratios to examine the hypothesis that "observed changes were due to oil and gas activities" proved to be effective. Although the sediments do contain significant background levels of the metals and hydrocarbons of interest, we remain confident that inputs related to oil and gas activities would be detected and diagnosed by the data analysis and interpretation techniques we employed.

The sampling and analysis of peat and river samples proved to be very important, and should be continued in the future. The reorientation of the metals program to isolate and analyze just the **mud** fraction does reduce the variability in the measurements and will increase the "signal to noise ratios" if oil and gas activities

contribute material to this fraction as expected. The examination of the use of the isolation and analysis of only the mud fraction showed some potential for the hydrocarbon parameters as **well**. **However**, the continued reliance on bulk sediment measurements for the hydrocarbon parameters is recommended.

Specific recommendations for **the** Year-3 study are the following:

1. Sampling and Station Selection

- Resample the **13** stations sampled for the first time in Year-2.
- Obtain a third-year data set from approximately 20 of the 26 stations sampled in Year-1 and Year-2.
- Place a high priority on the **resampling** of bivalves and amphipods from the stations sampled in Year-2. Expand the **animal** sampling program to extend the **areal** coverage.
- Obtain additional samples of river sediment for analysis. Four stations from each of three rivers should be **selected** to obtain a range of grain sizes.

2. Replication

- Obtain three replicates of sediments (**poolings of two**) at all stations sampled. Obtain sufficient biomass for the creation of four replicates of animal tissue at each station.

3. Isolation of Sediment Fine Fraction

- Continue to isolate the mud fraction of sediments for metals analysis.
- Collect only bulk sediment for the organics analyses.

4. Logistics

- Continue to use the techniques employed in the Year-2 (1985) survey.
- Investigate the feasibility of using the Omega-2 navigation system that did not operate well in Year-2.

5. Laboratory Analysis

- Continue **to** use the analytical **plan used** in Year-2.
- Obtain a full set of analytical data (**organics** and metals) for each sample.

The above-listed items **should** be included in the design of the Year-3 Program. All of these items are recommended as necessary to **meet** the overall program objectives.

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