

**ANIMIDA Phase I: Arctic Nearshore
Characterization and Monitoring of the Physical
Environment in the Northstar and Liberty
Development Areas**

Final Report

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**ANIMIDA Phase I: Arctic Nearshore Characterization and
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Northstar and Liberty Development Areas**

Final Report

Dr. Paul D. Boehm, Principal Investigator
Arthur D. Little, Inc.
20 Acorn Park
Cambridge, Massachusetts
02140

Current Address - Battelle
255 Bear Hill Road
Waltham, Massachusetts
02451

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or recommendation for use by the Federal Government.

List of Authors

Mr. John Brown, Battelle

Dr. Paul Boehm, Battelle

Mr. Henry Camp, Arthur D. Little, Inc. (ADL)

Ms. Linda Cook, ADL

Dr. John Trefry, Florida Institute of Technology (FIT)

Mr. Robert P. Trocine, FIT

Mr. Robert D. Rember, FIT

Mr. George Shepard, BBN Technologies (BBNT)

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List of Acronyms and Abbreviations

ADF&G	State of Alaska Department of Fish and Game
ADL	Arthur D. Little, Inc.
AMMTAP	Alaska Marine Mammal Tissue Archival Program
ANIMIDA	Arctic Nearshore Impact Monitoring in the Development Area
ASTM	American Society for Testing and Materials
BBNT	BBN Technologies
BP	British Petroleum
BPXA	British Petroleum Exploration Alaska
BRD	Biological Resource Division
BS	Blank Spike
BSMP	Beaufort Sea Monitoring Program
°C	Degrees Celsius
C	Carbon
CAB	Cellulose-Acetate-Butyrate
CaCl ₂	Calcium Chloride
cm	Centimeter
cm/sec	Centimeters per Second
CMI	Coastal Marine Institute
COC	Chain of Custody
CORIS	Coastal and Offshore Resource Information System
COTR	Contracting Officer's Technical Representative
CPI	Carbon Preference Index
CTD	Conductivity, Temperature, and Depth
CV	Coefficient of Variation
CVAAS	Cold Vapor Atomic Absorption Spectrometry
%D	Percent Difference
DCM	Dichloromethane
DDW	Distilled, Deionized Water
DNA	Deoxyribonucleic Acid
DQO	Data Quality Objectives
DTT	Dithiothreitol
EC&F	Environmental Chemistry and Forensics
EDTA	Ethylene Diamine Triacetic Acid
EIS	Environmental Impact Statement
EPA	U.S. Environmental Protection Agency
ERL	Effects Range-Low
ERM	Effects Range-Medium
FAAS	Flame Atomic Absorption Spectrometry
FID	Flame Ionization Detection
FIT	Florida Institute of Technology
FY	Fiscal Year
g	Gram
GC	Gas Chromatography

List of Acronyms and Abbreviations (continued)

GC/MS	Gas Chromatography/Mass Spectrometry
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
GPC	Gel Permeation Chromatography
GPS	Global Positioning System
H ₂ O	Water
H ₂ O ₂	Hydrogen Peroxide
H ₂ SO ₄	Sulfuric Acid
HCl	Hydrochloric Acid
HClO ₄	Perchloric Acid
HDM	Harvard Design and Mapping
HF	Hydrogen Fluoride
HNO ₃	Nitric Acid
HPLC	High-Performance Liquid Chromatography
ICP/MS	Inductively Coupled Plasma/Mass Spectrometry
ID	Inner Diameter
IRM	Instrument Reference Material
K-D	Kuderna-Danish
Kg	Kilogram
KLI	Kinnetic Laboratories, Inc.
km	Kilometer
ks	Knots
L	Liter
LALK	Lower-Molecular-Weight Alkanes
LCS	Laboratory Control Spike
m	Meter
MDL	Method Detection Limit
mg	Milligram
mL	Milliliter
MMS	Minerals Management Service
MRL	Minimum Reporting Limit
MS	Mass Spectrometry
N	Normal
N/P	Naphthalene/Phenanthrene Ratio
NBS	National Bureau of Standards
NCS	Nitrogen-Carbon-Sulfur Analyzer
NIST	National Institute of Standards and Technology
nm	Nautical Mile
NOAA	National Oceanic and Atmospheric Administration
NODC	National Oceanographic Data Center
NRC	National Research Council of Canada
NSB	North Slope Borough
NTU	Nephelometric Turbidity Units
OCS	Outer Continental Shelf
OCSLA	Outer Continental Shelf Lands Act

List of Acronyms and Abbreviations (continued)

OSI	Organism-Sediment Index
PAH	Polynuclear Aromatic Hydrocarbon
PAR	Photosynthetic Active Radiation
PB	Procedural Blank
PROB	Prudhoe Bay Operations Camp
PCB	Polychlorinated Biphenyl
PDB	Pee Dee Belemnite
PHC	Petroleum Hydrocarbons
POC	Particulate Organic Carbon
POP	Persistent Organic Pollutants
ppb	Parts Per Billion
ppm	Parts Per Million
ppt	Parts Per Trillion
PVC	Polyvinyl Chloride
QA	Quality Assurance
QA/QC	Quality Assurance/Quality Control
QAM	Quality Assurance Manual
QC	Quality Control
%REC	Percent Recovery
R/V	Research Vessel
RF	Response Factor
RFP	Request for Proposal
RL	Reporting Limit
RLU	Relative Light Unit
RPD	Relative Percent Difference
rpm	Revolutions Per Minute
RRF	Relative Response Factor
RSD	Relative Standard Deviation
S/T	Steranes/Triterpanes
SAOB	Sulfide Antioxidant Buffer
SD	Standard Deviation
SDE	Spatial Database Engine
SHC	Saturated Hydrocarbons
SIM	Selected Ion Monitoring
SOP	Standard Operating Procedure
SQL	Structured Query Language
SRB	Scientific Review Board
SRM	Standard Reference Material
STP	Seawater Treatment Plant
TALK	Total Alkanes
TOC	Total Organic Carbon
TPHC	Total Petroleum Hydrocarbons
TSS	Total Suspended Solids
µg	Microgram

List of Acronyms and Abbreviations (continued)

UCM	Unresolved Complex Mixture
URSGWC	URS Greiner Woodward Clyde
USFWS	U.S. Fish and Wildlife Service
USAEDA	U.S. Army Engineering District, Alaska
USDOI	U.S. Department of the Interior
USGS	United States Geological Survey
V/V	Volume to Volume
WBS	Work Breakdown Structure
WWTF	Wastewater Treatment Facility
ZGFAAS	Zeeman Graphite Furnace Atomic Absorption Spectrometry

Executive Summary

Overview

The Arctic Nearshore Impact Monitoring In the Development Area (ANIMIDA) program was conceived and designed to monitor potential factors that might contribute to marine impacts from offshore oil and gas development in the Beaufort Sea. In particular, the focus of this program is British Petroleum's ongoing and planned developments – Northstar and Liberty. The ANIMIDA program is being implemented in phases: Phase I focused on establishing pre-construction/development baselines; Phase II combines the continuation of this baseline survey at Liberty along with initial impact monitoring at Northstar.

In the nearshore Alaskan Beaufort Sea, BP Exploration Alaska, Inc.'s (BPXA) offshore oil development and production activities are underway at the Northstar site and as of November 2001, development is planned at the Liberty site. At each site, the oil field will be developed from a gravel island. A sub-sea pipeline will carry oil shoreward for a land-based connection with existing pipelines. Extensive Environmental Impact Statements (EISs) were prepared for the Northstar area by the U.S. Army Engineering District, Alaska (USAEDA, 1999) and for the Liberty area by the U.S. Department of the Interior (USDOI), Minerals Management Service (MMS).

Over the past three decades, numerous onshore and offshore oil exploration and development projects have been conducted in both the Alaskan and Canadian Beaufort Seas. Discoveries and development include over 20 discoveries in areas such as Endicott (an offshore field in state waters), Sagavanirktok Delta, North, Eider, and Badami. Because of these past activities, the ANIMIDA study area cannot be considered "pristine" from a chemical perspective. Thus, ANIMIDA was designed to both carefully define the "baseline" (pre-development) conditions and to develop sensitive measurement programs that could detect incremental change in these new development areas.

Phase I of ANIMIDA was designed and implemented with a focus on the 1999 late-summer, open-water period and the winter 2000 ice-covered period. The late-summer 1999 sampling represented pre-construction baselines at both the Northstar and Liberty areas. The winter 2000 sampling represented the first construction-monitoring period for Northstar and another pre-construction data acquisition opportunity at Liberty.

Information from this study will be used to 1) establish baseline environmental conditions prior to oil development and production activities, 2) allow for assessment of impacts from oil development and production activities, and 3) provide information needed in post-leasing decisions to help minimize these impacts.

Program Objectives

The primary objectives of the ANIMIDA program are to characterize and monitor the physical environment of the Northstar and Liberty development areas to evaluate potential and actual impacts from these major offshore oil developments.

The overall objectives of Phase I were to implement a measurement and monitoring program focused on those parameters that could be used to determine the existence, extent, and magnitude of environmental effects from the Northstar and Liberty oil development projects. The specific objectives for the Phase I effort are listed below:

- Summarize the existing literature in the study area. This activity was accomplished and findings were presented in Boehm (2000).
- Design and conduct data collection activities to begin to address key study questions and to allow for later hypothesis testing. The specific data collection activities included: collection of surface sediments, bivalves, and amphipods; collection of suspended sediments and regional source samples; and collection of acoustics data and ice cores.
- Develop recommendations for Phase II of the ANIMIDA program. Phase II recommendations were developed based on the results of Phase I.

The plans for Phase II evolved from: a) consideration of the early results from Phase I monitoring; b) reviews of the program by the Scientific Review Board (SRB); and c) public comments received at the first Program Workshop in October 1999 in Anchorage, Alaska. Additional Phase II program objectives and specific study elements are described in Section 5.0 of this report.

The goals of the ANIMIDA program are to address a series of scientific questions concerning the potential impacts of the Northstar and Liberty developments. Each question can then be turned into a testable hypothesis, which guides the design of the technical program. A summary of the five key questions used to formulate the hypotheses for the ANIMIDA program follows.

Question 1. What are the background levels of chemicals of concern (*i.e.*, the organic and trace-metal contaminants) that are known to be associated with oil exploration, development, and production activities, and do the concentrations of these chemicals increase as a result of the developments?

Question 2. If concentrations of organic and/or metal pollutants *do* increase in the environment as a result of the developments, do these increases pose an ecological "threat" or "risk"?

Question 3. Do the Northstar and/or Liberty development activities add significant amounts of sediment particulate material to the waters and ice cover adjacent to the developments?

Question 4. If the levels of suspended particulates/sediments *do* increase as a result of the developments, do these increases pose significant environmental risks to marine plants and animals?

Question 5. Do the construction and operational activities at Northstar and/or Liberty result in noise spectra and/or noise levels that differ from background levels?

The Developments

Northstar

The BPXA Northstar development project is located about 6 miles northeast of Prudhoe Bay. While the Northstar island is in state waters, 6 to 7 wells are or will be in federal waters on the Outer Continental Shelf. The project was approved by the U.S. Army Corps of Engineers in May 1999 and by MMS in September 1999. Northstar is the first offshore oil production facility in the Beaufort Sea without a causeway to shore and with a subsea pipeline system connecting it to onshore processing facilities. Construction of the island was completed by October 2000 and production drilling is underway. First production was initiated in the fourth quarter of 2001. Recoverable reserves are estimated at 175 million barrels of oil. Production is expected to reach a peak rate of 65,000 barrels per day in first quarter 2002.

Liberty

A second BPXA-proposed project is the Liberty Prospect in Foggy Island Bay, east of Prudhoe Bay. It is located about 6 miles east of the Endicott Project. The proposed location is adjacent to Tern Island, which was the site of exploration drilling dating back to 1982. The Minerals Management Service published a draft EIS report for Liberty in early 2001 (USDOL, 2001); the final EIS for Liberty is scheduled to be released in early 2002. Recoverable reserves are estimated at 120 million barrels of oil. Drilling and production will take place on a gravel island with a seabottom footprint of about 18 acres ($\sim 0.073 \text{ km}^2$), and an above-seawater footprint of approximately 9 acres ($\sim 0.037 \text{ km}^2$).

ANIMIDA Study Design

To meet the objectives of the program, the study design focused on measuring those parameters that would be indicators of, or related to, any environmental impacts (i.e., could be used to determine the existence, extent, and magnitude of environmental effects from the Northstar and Liberty oil development projects, and to allow for later hypothesis testing). The elements of primary focus included:

- Hydrocarbons and associated polynuclear aromatic hydrocarbons (PAHs) and metals as primary contaminants of concern
- Sediment contamination
- Bioaccumulation of contaminants
- Suspended sediments – amounts and compositions – in water and in ice cores
- Other natural and anthropogenic sources of contaminants of concern
- Construction and operational noise

The study design for Phase I involved several components:

- Design of a site specific radial array sampling grid around each development centroid
- Selection of area-wide stations that had previously been sampled as part of the MMS Beaufort Sea Monitoring Program (1984-1990)
- Location and sampling of reference stations
- Identification of source samples for collection (e.g., river sediments)

Phase I sampling itself was conducted during an open-water sampling program in the late summer (August/September) of 1999, and a "through-ice" sampling program in April/May 2000. The summer 1999 field and analytical programs were intended to precede any construction and development activities at Northstar and called for a number of field sampling and related laboratory analysis elements:

- Establishing sediment contaminant baselines following site-specific radial designs at Northstar and Liberty areas
- Establishing contaminant baselines along the Northstar pipeline route
- Sampling historical BSMP locations previously sampled in the 1984-1986 and 1989 annual studies, including Boulder Patch and reference locations
- Collecting surface sediments, bivalve molluscs, amphipods, and suspended sediments
- Obtaining current profiles and bathymetric data
- Collecting acoustic measurements
- Obtaining representative samples of sources and natural inputs for the chemicals (organics and metals) of concern
- Analyzing sediment, suspended sediment, and biota samples for a full suite of diagnostic organic and inorganic parameters

The "through-ice" sampling program in April/May 2000 was focused on initial monitoring of Northstar construction activities on the island and pipeline corridors. Specific activities of the "through-ice" data collection activities were to:

- Resample a select subset of the summer 1999 stations
- Obtain current profiles and through-ice photosynthetically active radiation (PAR) measurements
- Conduct acoustic measurements
- Obtain and analyze suspended sediments for inorganic parameters
- Obtain and analyze ice cores for inorganic parameters

Findings

The summer 1999 and winter 2000 field sampling programs successfully obtained samples of surficial sediments, riverine sediments and peat, biota (clams and amphipods), suspended sediments, and ice cores in the ANIMIDA study area. Ancillary data on acoustics, currents, PAR, and conductivity, temperature and depth (CTD) were also collected. Together, these data represent the pre-production baseline for the Northstar and Liberty prospects for the ANIMIDA

Phase I program, and will be used for future comparisons to Phase II measurements (i.e., post-construction monitoring at Northstar and additional pre-production baseline data for Liberty).

Initial interpretations and evaluation of these baseline data have resulted in the following preliminary summary findings:

Sediment Contaminants. Concentrations of hydrocarbons and metals in the sediments adjacent to Northstar and Liberty are generally within the observed historical range for these parameters in the overall study area. Typically PAH profiles indicate significant levels of a fossil fuel-type signature, which appears to be sourced in organic shales brought to the sediments from river runoff and coastal peat. Total natural baseline concentrations of PAHs, a sum of 2- to 6-ringed parent and alkylated PAHs (40+ compounds or isomer groupings) range from <10 parts-per-billion (ppb) to 1,000 ppb. Sediment hydrocarbons, and more specifically PAHs, are highly correlated with the silt+clay content of the sediment. Anomalous PAH concentrations (i.e., levels outside of the 95 percent confidence interval around a PAH/[silt+clay] ratio) were observed at several stations (5D, 5E, and L08). The concentration of PAH at station 5D, near West Dock, was 2,700 ppb. Though anomalous in composition, the PAH concentrations at stations 5E and L08 were within the observed historical range. Further examination of station L08's detailed PAH and saturated hydrocarbon composition revealed a diesel fuel input at this station, the source of which is unknown.

Likewise major- and trace-metal concentrations were observed over a wide range, but the normalization of metals to Al or Fe reduces and explains the variability of trace metals (i.e., potential contaminants from the developments) greatly. Anomalies (i.e., normalized data outside of the 95 percent confidence interval) indicative of current and/or historical anthropogenic inputs, were observed for: Ba at stations 7A, 7B, and 7G; Pb, Cd, and Cu at station 5D; Zn at station 5H; and Pb at station 5(10).

Based on comparisons to sediment quality guidelines introduced by Long et al. (1995), the hydrocarbon and metal concentrations found in the sediments are lower than Effects Range-Low (ERL) benchmarks. Thus, small incremental contaminant additions from development activities are not likely to pose any immediate ecological harm to marine organisms in the study area.

Bioaccumulation. Concentrations of hydrocarbons and metals in the clams and amphipods are within the range of previous studies in the region. Elevated concentrations in sediments, from natural sources, do not appear to be readily bioavailable to marine filter-feeders and deposit feeders.

Suspended Sediments. The concentrations and distributions of suspended sediments during the open-water season appear to be a function of wind and wave conditions, water currents, and depth. In the summer, concentrations of total suspended solids (TSS) and turbidity are at levels of <5 mg/L under relatively calm conditions (wind speeds <5 knots [kts]), but turbidity can exceed 100 mg/L under high wind speeds (>25 kts). Turbidity is about 2 times lower in more offshore waters (water depths >10 m) relative to more nearshore, shallower water, and a near-bottom nepheloid layer with a 50 to 300 percent increase in turbidity was observed at most locations.

Concentrations of trace metals in suspended sediment collected during the open-water period of August 1999 fit the metal-to-Al trends observed for surficial sediments. Results imply that the metals have a similar source in aluminosilicate material that is relatively uniform in composition. For Al versus Cu and most other metals, the data for the source bottom and suspended sediment fit the same trend as the bottom and suspended sediment from the ANIMIDA study area. Thus, the area's rivers are providing no distinguishable tracer among them as far as most trace metals are concerned.

The ice-core data from April 2000 permit calculation of the impact of sediment releases from melting ice on surficial sediment accumulation. Using the worst-case scenario (station LA5), the integrated amount of sediment in the ice core is about 6 mg/cm². As the ice melts and releases this sediment, the impact on the seafloor is accumulation of only about 0.004 cm of sediment per cm². This small impact is consistent for all ice cores collected. The net impact on sediment accumulation would appear to be small in the ANIMIDA study area.

Acoustics. Acoustics measurements from the winter 2000 sampling event indicate that the dominant propagation mode for Northstar Island construction noise (vibrahammer) is through the earth and then locally into the water column. The complete methods, results and discussion of the acoustics program for ANIMIDA are incorporated in a separate report to MMS (Shepard, et al., 2001).

Recommendations

Part of the overall Phase I effort was to rapidly evaluate Phase I preliminary monitoring findings and to develop a set of recommendations for the Phase II program. A suite of ANIMIDA Phase II program objectives were evaluated and subsequently issued as eight separate Task Orders for the Phase II program. Phase II activities are now being implemented, as follows:

- Provide for ANIMIDA Program Coordination: Task Order 001: "The Arctic Nearshore Impact Monitoring In the Development Area (ANIMIDA) Program (Phase II) – Core Contractor Program Management, Logistics, Database, and Reporting"
- Continue Chemical Monitoring Effort: Task Order 002: "Hydrocarbon and Metal Characterization of Sediments, Bivalves, and Amphipods in the ANIMIDA Study Area"
- Continue Acoustic Monitoring Effort (Augment Ongoing Studies – currently under consideration): Task Order 003: "Baseline Acoustic Monitoring: Bowhead Whale Migration Corridor"
- Monitor the Subsistence Whaling Effort: Task Order 004: "Annual Assessment of Subsistence Bowhead Whaling Near Cross Island"
- Examine the Effects of Oil Development on Suspended Particulates: Task Order 005: "Sources, Concentrations, and Dispersion Pathways for Suspended Sediment in Areas of Oil and Gas Development along the Coastal Beaufort Sea"

- Conduct Biological Monitoring of Sensitive Habitats (i.e., the Boulder Patch area): Task Order 006: "Monitoring the 'Boulder Patch' as part of the Arctic Nearshore Impact Monitoring In the Development Area (ANIMIDA) Program (Phase II)"
- Examine Partitioning of Organics and Metals: Task Order 007: "Partitioning of Potential Contaminants between Dissolved and Particulate Phases in Waters of the Coastal Beaufort Sea"
- Evaluate the Levels of Contaminants and Biochemical Indices on Marine Organisms: Task Order 008: "Baseline Characterization of Anthropogenic Contaminants in Biota Associated with the Alaska OCS Liberty and Northstar Oil and Gas Production Units in the Nearshore Beaufort Sea"

MMS added a new objective (with additional funding) for Phase II. This objective is to identify multiple and cumulative exposures to anthropogenic contaminants in the study area per Executive Order 12988 on Environmental Justice. For the Beaufort Sea coastal environment, regionally prioritized contaminants of concern are persistent organic pollutants (POPs) and trace metals.

1.0 Introduction

Under the Outer Continental Shelf Lands Act (OCSLA) (67 Stat. 462) of 1953, the Secretary of the Interior was charged with the responsibility for administering minerals exploration and development of the Outer Continental Shelf (OCS). The OCSLA Amendments of 1978 (92 Stat. 629) established a policy for the management of oil in the OCS and for protection of the marine and coastal environments. The amendments authorize the Secretary of the Interior to conduct studies in areas of offshore oil leasing activities to assess potential impacts on the marine and coastal environments resulting from oil exploration, development, and production activities.

In the nearshore Alaskan Beaufort Sea, offshore oil development and production activities are underway at the Northstar site and development is planned as of November 2001 at the Liberty site, both by British Petroleum Exploration Alaska, Inc. (BPXA). At each site, the oil field will be developed from a gravel island. A sub-sea pipeline will carry oil shoreward for a land-based connection with existing pipelines. Extensive Environmental Impact Statements (EISs) were prepared for the Northstar area by the U.S. Army Engineering District, Alaska (USAEDA, 1999) and for the Liberty area by the U.S. Department of Interior (USDOI), Minerals Management Service (MMS; USDOI, 2001).

In 1998 MMS decided to conduct studies to characterize the pre-development baseline environment and to monitor selected parameters over time as part of a long-term program to assess potential impacts from oil development and production near the Northstar and Liberty sites. Information generated from these studies will be considered in post-leasing decisions to help minimize potential impacts. The program, *Arctic Nearshore Impact Monitoring in the Development Area* (ANIMIDA), was initially designed to carefully monitor perturbations and impacts specifically related to construction activities and oil recovery and transportation via pipeline from the gravel islands to the onshore processing facilities. Thus, the overall rationale of the program was to establish two site-specific baseline and monitoring efforts directed at the Northstar and Liberty developments. Priorities were placed on establishing both a pre-development baseline and a scientific basis for post-construction/development impact monitoring. Elements included contaminants in the sediments and selected marine biota in the area; information on the amount and chemistry of the total suspended matter; information on other natural and anthropogenic sources of contaminants of concern (hydrocarbons and trace metals); and impacts (bioaccumulation) on marine biota.

1.1 Environmental Description

The description of the study area and a summary of the key elements of the physical and biological environments are reviewed briefly in this section.

1.1.1 Study Area

The Alaskan Beaufort Sea comprises the southern part of the Arctic Ocean that lies adjacent to the northern coast of Alaska and extends from the Chukchi Sea at Point Barrow about 370 miles (600 kilometers [km]) east to the Canadian border. The northward extent of the Alaskan Beaufort Sea is about 200 miles (~320 km) to water depths >300 feet (~100 meters [m]) at 73°N. The continental shelf of the Alaskan Beaufort Sea is 37 to 75 miles (60 to 121 km) wide and shallow, with an average water depth of only 120 feet (~37 m) (USAEDA, 1999). Within 1 to 20 miles

(1.6 to 32 km) of the coast, the Beaufort Sea is characterized by numerous narrow and low relief barrier islands.

The Northstar and Liberty project areas are situated in the shallow, coastal waters of the Alaskan Beaufort Sea (Figure 1-1). The Northstar site is seaward of the barrier islands and the Liberty site is landward of several barrier islands. The area of the proposed Northstar development is located about 6 miles (~10 km) offshore of Point Storkersen in the Beaufort Sea in water depths of 30 to 40 feet (~9 to 12 m). The island will be constructed partly on the remains of Seal Island, which was built by Shell Oil Company during the 1980s (USAEDA, 1999).

The Liberty development will be constructed about 6 miles (~10 km) offshore in Foggy Island Bay or 1.5 miles (~2 km) west of Tern Island, where water depths are about 22 feet (~6.7 m) (Figure 1-1). This location is 30 miles (~50 km) southeast of the proposed Northstar development and 7 miles (~12 km) from the Endicott Causeway.

1.1.2 Physical Environment

The complex elements of the Beaufort Sea's physical environment, which have a bearing on oil development and potential impacts, include sea ice, ocean currents, and suspended sediment loads. The regions near the Northstar and Liberty sites are described in detail in the Program Literature Review (Boehm, 2000) and summarized briefly below.

The Beaufort Sea continental shelf is shallow, averaging only 120 feet (~36 meters) in depth, with an average width of 44 miles (~71 km) (Sharma, 1979). Continental shelf waters are ice-covered for about nine months of the year, with open water season generally extending from mid-July until September. Ice cover is a major factor influencing petroleum operations and potential impacts, as it blocks air-sea exchange processes and wind shear, significantly altering circulatory dynamics of coastal waters.

Sea ice is a dominant feature of the Beaufort Sea. Landfast ice extends from shore to water depths of approximately 65 feet (20 m) from at least November through April, with a thickness of 4 to 7 feet (1.2 to 2.1 m) (USAEDA, 1999). In shallow waters, the ice becomes bottomfast. In open water, the polar pack ice is mobile, with ice ridges and open-water leads. Sea ice can cause hazardous conditions or damage in project areas. For example, ice-gouging, caused by the movement of grounded ice keels in response to winds and currents, poses a significant hazard to underwater structures in shallow regions of the Beaufort Sea (USAEDA, 1999). In the landfast sea-ice zone, this occurs most commonly during breakup and freezing. More than four decades of data from the Northstar vicinity indicate that open-water conditions may be expected to exist for 60 to 86 days of the year. The offshore polar pack ice is present within 75 miles (~120 km) of shore, even in summer.

General ocean circulation, wind-generated waves, storm surges, and, to a lesser degree, tides, are the factors that most influence water movement in the Beaufort Sea near the study area coastal zone. Nearshore water currents are primarily wind-driven during the open-water season, aligning with bathymetric contours that parallel the coast in an east-west direction. The net water flow is to the west, as evidenced from previous drifter studies (Figure 1-2). In winter, under-ice currents are under the primary influence of tidal movement and storm surges.

Several major rivers drain into the Beaufort Sea, including the Colville, Sagavanirktok, and Kuparuk rivers. Water flow, along with very high suspended sediment loadings, from the rivers are highly seasonal. Landfast sea ice near river deltas becomes flooded with meltwater from inland drainage and breaks up from late-May to mid-June. Most of the river flow occurs during a four- to six-week period in May to June. Water discharge from the Colville River is about 1×10^{12} ft³/year ($\sim 3 \times 10^{10}$ m³/year) (www.waterdata.usgs.gov). In contrast with the Colville River, water discharge from the Kuparuk and Sagavanirktok Rivers is about 10 times lower at approximately 1×10^{11} ft³/year ($\sim 3 \times 10^9$ m³/year).

Bottom sediments in the Northstar area consist of muddy sand and sandy mud with minor amounts of gravel (USAEDA, 1999). Offshore of the barrier islands, the sediments are stiff silts with scattered gravel. Typical sediment cores show 5 to 25 feet (1.5 to 7.6 m) of fine-grained sand and silt overlying coarser-grained sand and gravel. Concentrations of total organic carbon (TOC) are somewhat variable and generally low with a range of 0.1 to 4.0 percent (Boehm et al., 1990). Sediment grain-size data for the Liberty area show a very patchy distribution in grain size, with surface sediments (top 1 foot) containing 10 to 90 percent silt+clay, and <1 to 30 percent gravel, with the remainder composed of various sand fractions (Montgomery Watson, 1997, 1998). At depths of 8 to 9 feet (~ 2.4 to 2.7 meters), close to the maximum depth of dredging, a very similar and varied distribution of grain size was found.

1.1.3 Biological Environment

The complex biology of the region near the Northstar and Liberty sites is described in detail in the literature review (Boehm, 2000) and summarized briefly below.

Planktonic plants (phytoplankton) and animals (zooplankton) form a major source of food for fishes, birds, and marine mammals in the Beaufort Sea coastal zone. Phytoplankton are the primary source of carbon fixation at the base of the food web. The abundance and distribution of these unicellular algae in the Beaufort Sea coastal zone are dependent upon light intensity, nutrient levels, and oceanographic conditions, including degree of ice cover. Light intensity, in turn, is related to ice cover and to suspended sediment loadings. Primary production is relatively low due primarily to nutrient limitation. Maximum productivity and population levels occur in July and August during the open-water period. Primary productivity is similar between nearshore and offshore waters, ranging from 10 to 15 grams (g) of carbon/square meter annual production. Zooplankton consist of permanent water column residents, as well as larval forms of benthic invertebrates and fishes. Smaller zooplankton include calanoid copepod crustaceans, which are generally dominant in biomass and numbers throughout the year in the Prudhoe region. Meroplanktonic larvae of crabs, worms, and barnacles are prevalent during the summer months. Larger amphipod, mysid, and euphausiid crustacea are major planktonic sources of food for bowhead whale and ringed seal (Lowry, 1993; Frost and Lowry, 1984).

The bottom-dwelling (benthic) invertebrate community consists of animals living within the sediments (infauna) and free-moving or attached animals living on sediments or hard, rocky substrates (epifauna). Beaufort Sea sedimentary invertebrates are significantly affected by the incursion of sea ice, which scours the bottom and eliminates both infaunal and epifaunal organisms for most of the year at depths shallower than 2 to 3 m (~ 6.5 to 9.8 feet) (USDOI,

1990). Much of the shallowest habitat of Prudhoe Bay and Stefansson Sound is protected from extensive ice gouging and reworking of bottom substrates by offshore shoals and barrier islands (Dunton and Schonberg, 1981). In unprotected and deeper areas, a shear zone exists, where ice gouging disturbs the bottom sediments (USDOI, 1990), extending out to a depth of about 20 m (~65 feet). Benthic infaunal populations are relatively limited in this zone, increasing in diversity and biomass in the more-stable sediments at greater depths and distances offshore (Carey, 1978; Carey et al., 1974). The motility of the sedimentary epifauna provides adaptability to the disturbances of the nearshore zone, where they tend to be more diverse and abundant than the infauna. The dominant species are crustaceans (amphipods, isopods, and mysids) that are opportunistic in population development, in accord with seasonality of ice breakup and food inputs in the summer.

Within the Foggy Bay region of Stefansson Sound, a unique biological community is well developed on cobble and boulder substrates. The cobble-boulder field, defined as the Boulder Patch (Figure 1-1), is ideally located - seaward of shallow depths (to 3 m) that are disturbed by ice impingement in winter, and situated inside of the barrier islands and shoals that protect it from extensive ice gouging and reworking of the bottom. The hard substrate, ranging in size from pebbles to boulders exceeding 1 meter in height, provides attachment for the dominant kelp species, *Laminaria solidungula*, and habitat for a large number of invertebrate species, of which sponges, bryozoans, sea-squirts, and cnidarians are prevalent attached forms. Associated motile species include gastropod molluscs, nudibranchs, sea stars, and crabs.

Monitoring of freshwater, marine, and anadromous fishes was an integral part of the Endicott Development program, providing good descriptions of the regional nearshore fauna, their distribution, and seasonality between 1985 and 1994 (Reub et al., 1991; LGL 1994). Seventeen marine, ten anadromous, and six typically freshwater species were collected during this study. The fauna was dominated by marine species (arctic cod and fourhorn sculpin) and anadromous species (arctic cisco and least cisco) (LGL et al., 1998). These types of fish typify nearshore brackish waters, in contrast with the offshore marine ichthyofauna (Craig, 1984). Arctic cod is the dominant species in the Arctic Ocean, serving as an important food source for the large seal populations (Lowry et al., 1980, Frost and Lowry 1984, Burns and Frost, 1979, Nelson et al., 1985).

Eight marine mammal species inhabit coastal and offshore habitats of the Alaskan Beaufort Sea (LGL et al., 1998, USAEDA, 1999). These include the beluga whale (*Delphinapterus leucas*), bowhead whale (*Balaena mysticetus*), gray whale (*Eschrichtius robustus*), ringed seal (*Phoca hispida*), bearded seal (*Erignathus barbatus*), spotted seal (*Phoca largha*), pacific walrus (*Odobenus rosmarus*), and polar bear (*Ursus maritimus*). Marine mammals are a focus of environmental concern for petroleum development impacts, particularly related to construction displacement effects and possible alteration of behavior and distribution in response to acoustical impacts from construction and seismic surveys. Potential oil spill impacts upon marine mammals are discussed in the Northstar EIS (USAEDA, 1999). Ringed seal and polar bear were deemed most susceptible due to their nearshore occurrence.

The nearshore habitats, lagoons, barrier islands, and offshore areas of the Alaskan Beaufort Sea coast are important for the migration, staging, and molting of various species of birds (USDOI,

1990, 1996). An estimated 10 million individual birds representing over 120 species (including terrestrial types) use the Beaufort Sea area from Point Barrow, Alaska to Victoria Island, Canada. Nearly all species are migratory, occurring in the Arctic from May through September (LGL et al., 1998).

1.2 Development History in the Study Area

Over the past three decades, numerous onshore and offshore oil exploration and development projects have been undertaken in both the Alaskan and Canadian Beaufort Seas. Discoveries and development include over 20 discoveries and include areas such as Endicott (an offshore field in state waters), Sagavanirktok Delta, North, Eider, and Badami. Because of this past development, the ANIMIDA study area can not be considered to be "pristine" from a chemical perspective. Operations to the east (i.e., in Canada) may represent a source of contaminants to the Alaskan Beaufort Sea and hence to the Northstar and Liberty study areas. An overview of these developments is presented in Figures 1-3 and 1-4.

Since 1975, seventeen gravel islands have been constructed in waters less than 50 feet (15 meters) deep in the Alaskan Beaufort Sea for exploration drilling. Most of these islands remain in some form, but have been abandoned by removal of all equipment and erosion protection. Two of these gravel islands, Seal and Northstar, are within the Northstar unit. Natural barrier islands have also been used for exploration drilling activities and for staging areas (USAEDA, 1999). Table 1-1 summarizes past oil and gas development and production activities in the Beaufort Sea dating back to 1949.

1.3 Current/Proposed Oil Development

1.3.1 Northstar

The BPXA Northstar development project is located about six miles (~10 km) northeast of Prudhoe Bay. While the Northstar Island is in state waters, six to seven wells are or will be in federal waters on the OCS. The U.S. Army Corps of Engineers approved the project in May 1999 and MMS approval followed in September 1999. Northstar is the first offshore oil production facility in the Beaufort Sea without a causeway to shore and with a subsea pipeline system connecting it to onshore processing facilities. Construction of the island was completed by October 2000 and production drilling is underway. First production was expected in the fourth quarter of 2001. Recoverable reserves are estimated at 175 million barrels of oil. Production is expected to reach a peak rate of 65,000 barrels per day in first quarter 2002. A schematic of the development is shown in Figure 1-5.

Northstar Island was reconstructed from the existing gravel of its predecessor, Seal Island, and from additional gravel hauled to the island from a gravel mine site near the mouth of the Kuparuk River. The island was surrounded by a linked concrete mat armor island slope protection system and the working surface of the island was surrounded by sheet piling. Drilling and production at Northstar has taken place on the gravel island with an above-seawater footprint of about 5 acres (~0.02 km²) (URS Greiner Woodward Clyde [URSGWC], 1998) and a seafloor

footprint designed to be 635 feet by 970 feet (allowing for uncertainties from construction the footprint may be up to 835 feet by 1170 feet).

The summer 1999 sampling in the ANIMIDA Phase I effort represented "pre-development," or baseline, measurements. However, it should be noted that exploration drilling had taken place at Seal Island, dating back to the 1980s.

1.3.2 Liberty

As of November 2001, a second BPXA proposed project is the Liberty Prospect in Foggy Island Bay (Figure 1-1). It is located about six miles east of the Endicott Project. The proposed location is adjacent to Tern Island, which was the site of exploration drilling dating back to 1982. MMS published a draft EIS report for Liberty in early 2001 (USDOl, 2001); the final EIS for Liberty is scheduled to be released in early 2002. Recoverable reserves are estimated at 120 million barrels of oil. Drilling and production will take place on a gravel island with a seabottom footprint of about 18 acres ($\sim 0.073 \text{ km}^2$), and an above-seawater footprint of approximately 9 acres ($\sim 0.037 \text{ km}^2$). Approximately 990,000 cubic yards of gravel would be needed to construct the islands associated with the Liberty project. BPXA proposed mining a new site from an island in the Kadleroshilik River flood plain.

If the proposed project stays on schedule and is approved, construction could start in first quarter 2003, with the first oil production in late 2004, at the earliest. The present work (Phase I) and the future work (Phase II) will all represent pre-development baseline information at Liberty.

1.4 Potential Contaminants and Disturbances of Concern

There are three potential perturbations to the physical environment that may occur due to development activities. These impacts may be a result of: 1) changes to the physical environment from construction (gravel island, causeways, pipeline), 2) associated changes in sediment inputs and resulting sedimentation, and 3) increased availability of chemicals in the environment that may be bioavailable. A fourth potential impact, introduced noise, is addressed in a separate report.

The majority of wastes generated during construction and developmental drilling would consist of drill cuttings and spent muds. Drilling fluids would be disposed of through onsite injection into a permitted disposal well or would be transported offsite to a permitted disposal location. In addition, domestic wastewater, soil waste, and produced waters generated during the project would be injected into the disposal well. Solid wastes, including scrap metal, would be hauled offsite for disposal at an approved facility.

Chronic discharges of contaminants would occur during every breakup from fluids entrained in the ice roads. Entrained contaminants from vehicle exhaust, grease, antifreeze, oil, and other vehicle-related fluids would pass into the Beaufort Sea system at each breakup. These discharges are not expected to be major; however, they would exist over the life of the field.

The greatest effect on water quality from gravel island and pipeline construction would be additional turbidity caused by increases in suspended particles in the water column as a result of island and pipeline construction. Turbidity increases from construction activities generally are temporary and are expected to occur during the winter and end within a few days after construction stops. Trenching for the oil pipeline may also cause resuspension of existing bottom sediments. Both island and pipeline construction may result in incorporation of suspended sediment into sea ice. Construction activities are not expected to introduce or add any chemical pollutants.

1.5 Study Objectives

The primary objectives of the ANIMIDA program are to characterize and monitor the physical environment of the Northstar and Liberty development areas to evaluate potential and actual impacts from these major offshore oil developments.

There is much known about the potential effects of oil developments (USAEDA, 1999; USDO, 2001) and much known about the pre-development baseline in the Beaufort Sea. As part of the ANIMIDA program, a literature review was undertaken to set the stage for further ANIMIDA program elements (Boehm, 2000). Using this information on the Alaskan Beaufort Sea environment together with specific information on the planned developments, a program was designed to monitor the physical environment in the Northstar and Liberty development areas.

The ANIMIDA Program is being implemented in two phases. Phase I was designed and implemented with a focus on the 1999 late-summer, open-water period and the spring 2000 ice-pack-cover period. The late-summer 1999 sampling represented pre-construction baselines at both the Northstar and Liberty locations (see Section 1.1.4). The Spring 2000 sampling represented the first construction-monitoring period for Northstar and another pre-construction data acquisition opportunity at Liberty.

The plans for Phase II evolved from: a) consideration of the early results from Phase I monitoring; b) reviews of the program by the Scientific Review Board (SRB); and c) public comments received at the first Program Workshop in October 1999 in Anchorage, Alaska. Additional Phase II program objectives and specific study elements are described in Section 5.0 of this report.

Phase I Objectives

The overall objectives of Phase I were to implement a measurement/monitoring program focused on those measurements and parameters that could be used to determine the existence, extent, and magnitude of environmental effects from the Northstar and Liberty oil development projects. The specific objectives for the Phase I effort are listed below:

Summarize the existing literature in the study area. This activity was accomplished and findings were presented in Boehm (2000).

Design and conduct data collection activities to begin to address key study questions and to allow for later hypothesis testing. The specific data collection activities included:

a. Designing and conducting an open-water sampling program in the late summer (August/September) of 1999. This aspect of the program was intended to precede any construction activities at Northstar. Specific objectives of the data collection activities were to:

- Implement a site-specific radial monitoring design at Northstar and Liberty locations
- Implement monitoring along the Northstar pipeline route
- Include historical Beaufort Sea Monitoring Program (BSMP) locations previously sampled in the 1984 to 1986 and 1989 annual studies, including Boulder Patch and reference locations
- Collect and analyze surface sediments, bivalve molluscs, benthic amphipods, and suspended sediments
- Obtain current profiles and bathymetric data
- Conduct acoustic measurements
- Obtain representative samples of sources of contaminants and natural inputs for the chemicals (organics and metals) of concern

b. Designing and conducting a "through-ice" sampling program in April/May 2000. This activity was geared towards initial monitoring of Northstar construction activities on the island and pipeline corridors. Specific activities of the "through-ice" data collection activities were to:

- Reoccupy a selected subset of the 1999 summer sampling stations
- Conduct acoustic measurements
- Obtain and analyze suspended sediments
- Obtain and analyze ice cores

Develop recommendations for Phase II of the ANIMIDA program. One of the initial objectives of the Phase I effort was to rapidly evaluate Phase I preliminary monitoring results and to develop a set of recommendations for the Phase II program, which was set to commence in fiscal year (FY) 2000. Phase II program objectives are described in Section 5 of this report.

1.5.1 Research Questions and Hypotheses

The objectives of the ANIMIDA program are to address a series of scientific questions concerning the potential impacts of the Northstar and Liberty developments. Each question can then be turned into a testable hypothesis, which guides the design of the technical program. These pairs of questions (Q) and candidate hypotheses (H) follow.

Q1. What are the background levels of chemicals of concern (i.e., the organic and trace-metal contaminants) that are known to be associated with oil exploration, development, and production activities, and do the concentrations of these chemicals increase as a result of the developments?

H1a. *The concentrations of organic pollutants in sediments do not show any increase as a result of the development of the Northstar and/or Liberty units.*

H1b. *The concentrations of metal pollutants in sediments do not show any increase as a result of the development of the Northstar and/or Liberty units.*

Q2. If concentrations of organic and/or metal pollutants *do* increase in the environment as a result of the developments, do the increased concentrations exceed environmental quality guidelines (e.g., Effects Range-Lows [ERLs])?

H2a. Concentrations of organic pollutants adjacent to the Northstar and/or Liberty developments do not pose an ecological risk to marine organisms as determined by sediment quality benchmarks.

H2b. Concentrations of organic pollutants adjacent to the Northstar and/or Liberty developments do not pose an ecological risk to marine organisms as determined by changes in bioaccumulation by marine animals.

H2c. Concentrations of trace-metal pollutants adjacent to the Northstar and/or Liberty developments do not pose an ecological risk to marine organisms as determined by sediment quality benchmarks.

H2d. Concentrations of trace-metal pollutants adjacent to the Northstar and/or Liberty developments do not pose an ecological risk to marine organisms as determined by changes in bioaccumulation by marine animals.

Q3. Do the Northstar and/or Liberty development activities add significant amounts of sediment particulate material to the waters and ice cover adjacent to the developments?

H3a. The turbidity and suspended sediments in the water column adjacent to Northstar and Liberty are not significantly elevated above naturally occurring, ambient levels.

H3b. The composition of suspended particles is not different than that occurring naturally.

H3c. Suspended sediments from construction on the Northstar and/or Liberty developments are not incorporated into the ice matrix.

Q4. If the levels of suspended particulates/sediments *do* increase as a result of the developments, do these increases pose significant biological risks to marine plants and animals?

H4a. The amounts of suspended sediment in the most ecologically significant locations (e.g., the Boulder Patch community) are within the range of natural background and therefore do not pose a significant risk to plants and animals.

H4b. Suspended sediments occurring in the ice matrix from construction on the Northstar and Liberty developments do not significantly decrease the measurable amount of Photosynthetic Active Radiation (PAR) under the ice and at the seafloor in the Boulder Patch area in late spring.

Q5. Do the construction and operational activities at Northstar and/or Liberty result in noise spectra and/or noise levels that differ from background levels?

H5. Noise levels and related acoustic features in the study area do not differ from background levels as a result of Northstar and/or Liberty construction and operational activities.

1.6 Limitations of this Study

The ANIMIDA study was designed to focus on the most important potential "causative agents" of environmental impacts. Through Phase I of the study, the program has not yet begun to focus on impacts *per se*. It is envisioned that Phase II will include more direct measurements of biological impacts, in terms of sublethal effects on biological enzymatic systems, and direct measurements in the Boulder Patch area. However, Phase I only focuses on contaminants (e.g., metals) and/or perturbations (e.g., suspended sediments) of concern. The results of these pre-development measurements can only serve as a baseline and as a basis for later comparisons as part of the actual monitoring of changes. Thus, Phase I examines potential causative factors in the sediments (polynuclear aromatic hydrocarbons [PAHs] and metals), in animals (bioaccumulated contaminants), and in the water column (suspended sediments and their source[s]). Direct biological measurements will come later.

Phase I is a monitoring, and not impact assessment, study. The basis for the monitoring and later impact studies is only directed at the sediments. Short-term impacts on water quality, which may in turn have a bearing on planktonic populations and primary productivity, will only be inferred from total suspended solids (TSS) measurements and not directly measured.

Because of the known high background levels of hydrocarbons, PAHs, and metals in the area's sediments, and a high variability of the same resulting largely from natural inputs – eroded shales, coals, peat, etc., incremental changes will be difficult to measure. They can only be inferred from a strategy of: 1) low-level sensitive measurements that can detect change; 2) a statistical sampling program that affords enough measurements to detect changes; and 3) a sampling program that includes obtaining representative other sources (natural and anthropogenic) of these chemicals and contaminants, so that sources can be fingerprinted and in turn detected and identified in sediments and in the water column. All of these elements are built into this program. While the program is designed to accomplish this "baselining," it is inherently limited by the large variability and the dynamics of the area, which in turn impose practical limits on the amount of replication that can be accomplished for a given program budget. The bottom line is that changes in measured parameters might only be determined by factors of two or more, which may be the lowest statistically significant change that can be detected in a pre- and post-development monitoring effort.

Table 1-1. Alaska North Slope Oil and Gas Past Development and Production

Name	Location of Field or Pool	Oil or Gas Production	Location of Production Facility	Discovery	Production Began	Category
South Barrow	Onshore	Gas	Onshore	1949	1950	Field
Prudhoe Bay	Onshore	Oil	Onshore	1967	1977	Field
Lisburne	Onshore	Oil	Onshore	1967	1981	Field
Kuparuk	Onshore	Oil	Onshore	1969	1981	Field
East Barrow	Onshore	Gas	Onshore	1974	1981	Field
Milne Point	Onshore	Oil	Onshore	1969	1985	Field
Endicott	Offshore	Oil	Offshore	1978	1986	Field
Sag Delta	Offshore	Oil	Onshore	1976	1989	Field
Sag Delta North	Offshore	Oil	Offshore	1982	1989	Satellite ¹
Schrader Bluff	Onshore	Oil	Onshore	1969	1991	Satellite ²
Walakpa	Onshore	Gas	Onshore	1980	1992	Field
Pt. McIntyre	Offshore	Oil	Onshore	1988	1993	Field
N. Prudhoe Bay	Onshore	Oil	Onshore	1970	1993	Field
Niakuk	Offshore	Oil	Onshore	1985	1994	Field
Sag River	Onshore	Oil	Onshore	1969	1994	Satellite ³
West Beach	Onshore	Oil	Onshore	1976	1994	Field
Cascade	Onshore	Oil	Onshore	1993	1996	Field
West Sak	Onshore	Oil	Onshore	1969	1998	Satellite ²
Badami	Offshore	Oil	Onshore	1990	1998	Field
Eider	Offshore	Oil	Offshore	1998	1998	Satellite ¹
Tarn	Onshore	Oil	Onshore	1991	1999	Field
Tabasco	Onshore	Oil	Onshore	1992	1999	Satellite ²
Midnight Sun/Sambucca	Onshore	Oil	Onshore	1998	1999	Satellite ⁴
Alpine	Onshore	Oil	Onshore	1994	(2000)	Field

Source: USDOl, 2001.

Category Definitions: Field – infrastructure installed to produce one or more pools. Satellite – a pool developed from an existing pad. Pool – petroleum accumulation with defined limits. Prospect – a discovery tested by several wells. Show – a one-well discovery with poorly defined limits and production capacity.

Note ¹ – Satellite associated with Duck Island production unit

Note ² – Satellite associated with Kuparuk River production unit

Note ³ – Satellite associated with Milne Point production unit

Note ⁴ – Satellite associated with Prudhoe Bay production unit

Table 1-2. Alaska North Slope Oil and Gas Reasonably Foreseeable Future Development and Production

Name	Location of Field or Pool	Oil or Gas Production	Location of Production Facility	Discovery	Category
Meltwater	Onshore	Oil	Onshore	2000	Prospect
Nanuk	Onshore	Oil	Onshore	1996	Prospect
Kalubik	Offshore	Oil	Onshore	1992	Prospect
Pete's Wicked	Onshore	Oil	Onshore	1997	Prospect
Sikulik	Onshore	Gas	Onshore	1988	Pool
Thetis Island	Offshore	Oil	Offshore	1993	Prospect
Gwydyr Bay	Offshore	Oil	Onshore	1969	Pool
Mikkelson	Onshore	Oil	Onshore	1978	Prospect
Sandpiper	Offshore	Gas & Oil	Offshore	1986	Pool
Point Thomson	Onshore	Gas & Oil	Onshore	1977	Pools
Sourdough	Onshore	Oil	Onshore	1994	Pool
Yukon Gold	Onshore	Oil	Onshore	1994	Prospect
Flaxman Island	Offshore	Oil	Offshore	1975	Prospect
Stinson	Offshore	Oil	Offshore	1990	Prospect
Hammerhead	Offshore	Oil	Offshore	1985	Pool
Kuvlum	Offshore	Oil	Offshore	1987	Prospect

Source: USDOl, 2001.

Oil and gas developments are listed according to the chance and timing of the development (highest/first to lowest/last).

Category Definitions: Pool – petroleum accumulation with defined limits. Prospect – a discovery tested by several wells.

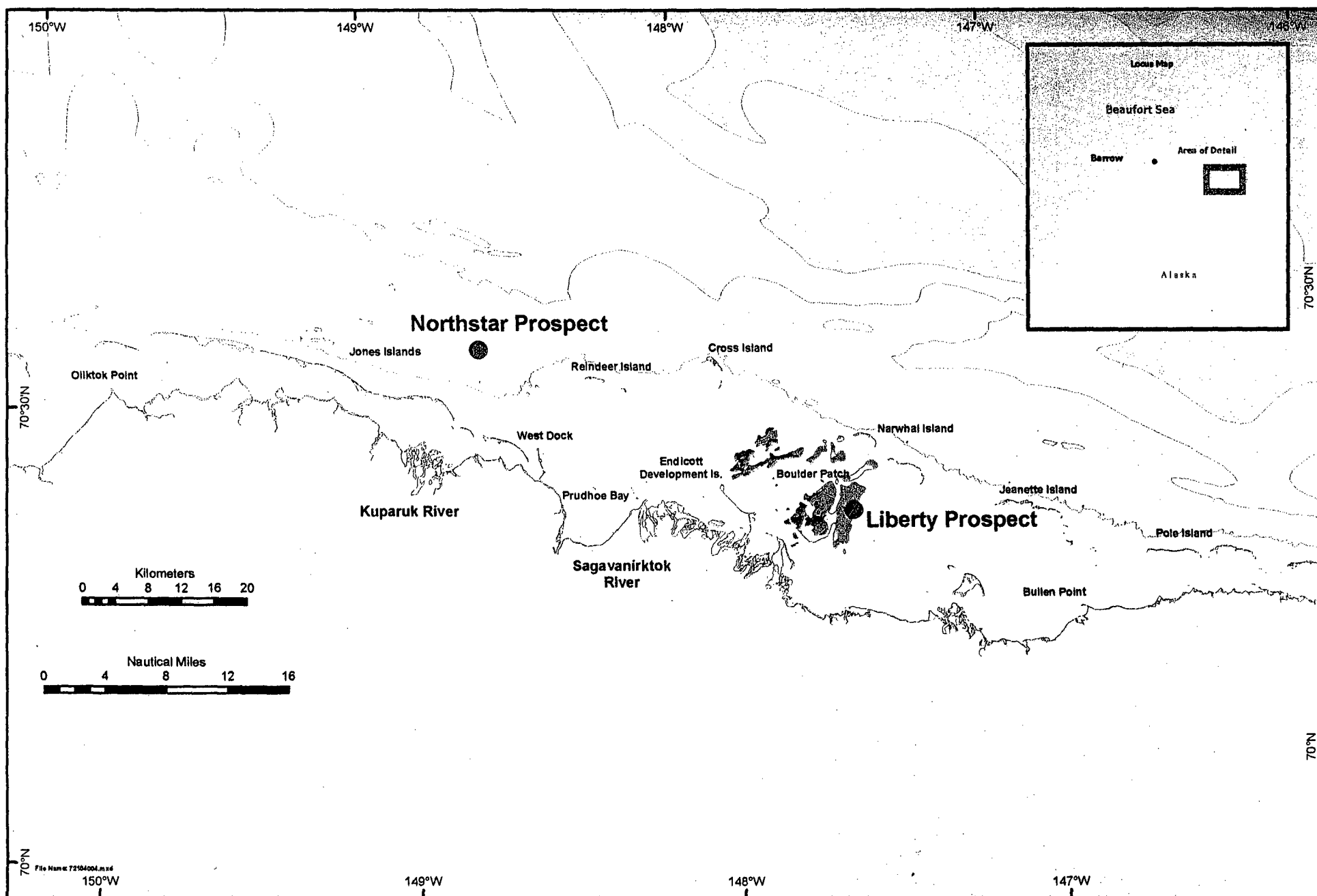


Figure 1-1. Map of the ANIMIDA Phase 1 Study Area

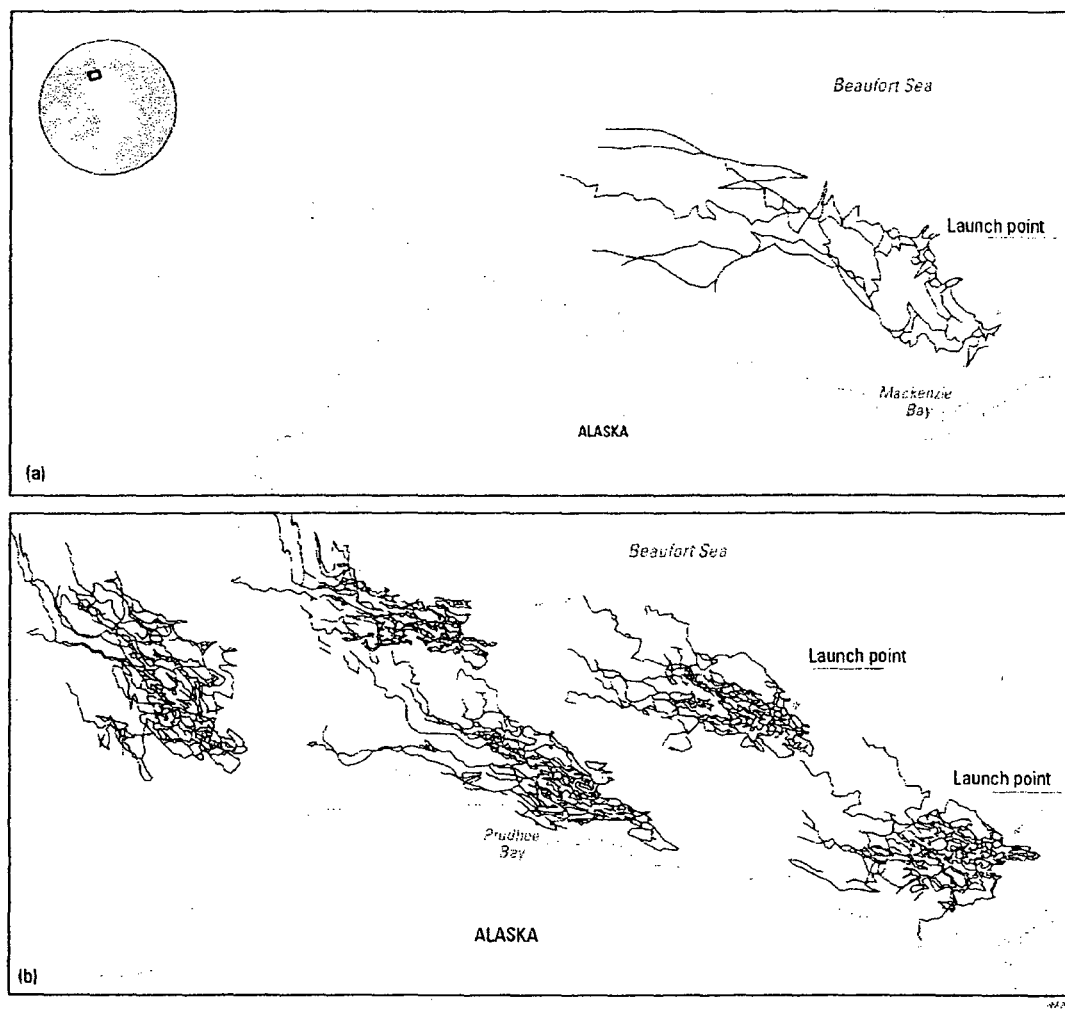


Figure 1-2. Drifter Tracks in the Beaufort Sea

(from www.AMAP.nu.maps-gra/show-figure353)

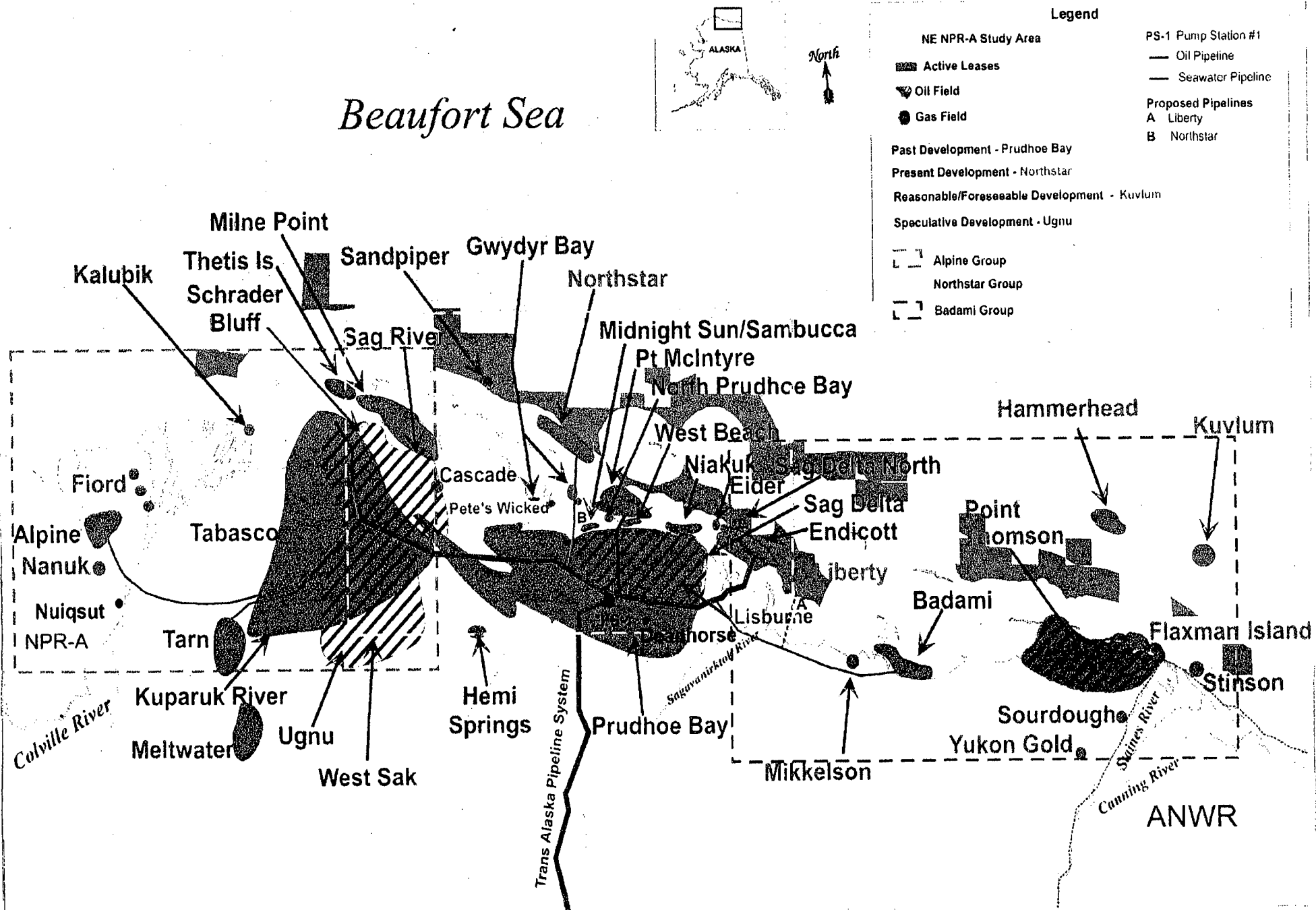


Figure 1-3. General Map of Onshore and Offshore Oil and Gas Development in the Study Areas

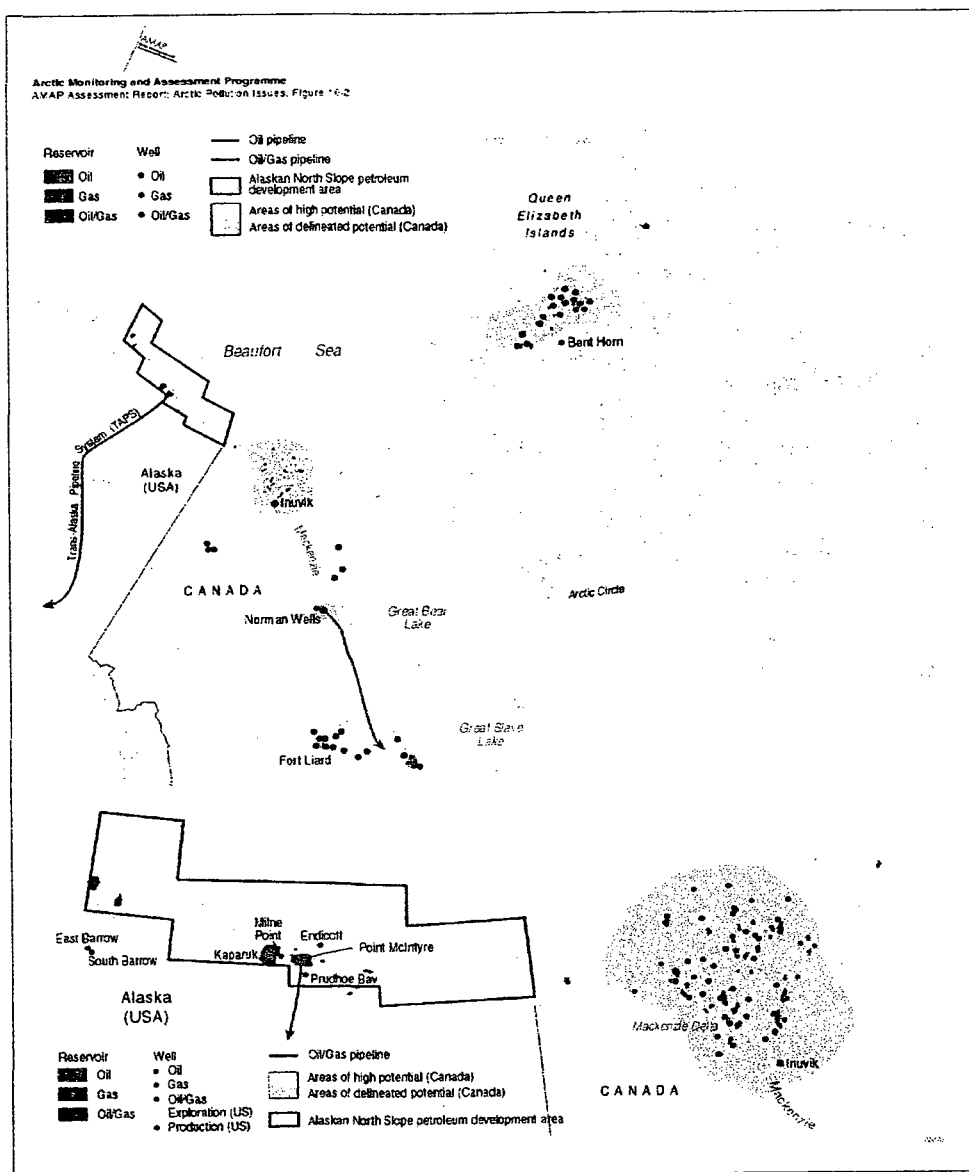


Figure 1-4: Generalized Description of Arctic Oil Developments
 (from <http://www.amap.no/maps-gra/mg-petro.htm>)

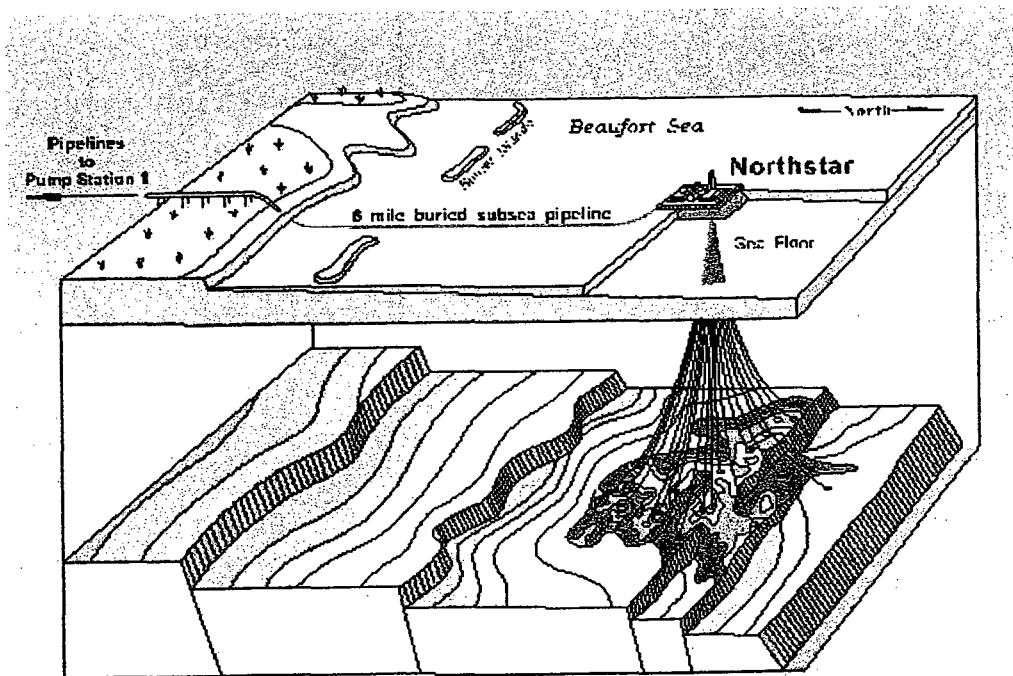


Figure 1-5: Schematic of BP's Northstar Development
 (from: http://www.bp.com/alaska/index_nstar.htm)

2.0 Methods

This section describes the methods used in field sampling, field measurements, and laboratory analyses.

2.1 Field Methods and Study Design

2.1.1 Study Design

The study area for the ANIMIDA program was defined as the nearshore Beaufort Sea bounded by the Stockton Islands to the East, and by the Jones Islands to the West. This area encompassed both the Liberty and Northstar prospect areas, and much of the shoreline where regional Prudhoe Bay oil production activities are occurring. The Phase I ANIMIDA program included two field surveys:

- An open-water survey conducted in August 1999, including sediment, biota, suspended sediment, water column, and acoustics sampling and measurements
- A "through-ice" survey conducted in April 2000 that focused on suspended sediment, ice core, water column, and acoustics sampling and measurements

The overall design of the field program incorporated a sampling program using a combination of site-specific fixed stations around the Liberty and Northstar developments, and regional, historical BSMP stations (Figure 2-1 and Boehm, 1987). The site-specific Liberty and Northstar stations were located in four radial transects centering on the proposed prospect site. The radials were located at 0.5, 1, 2, and 4 kilometer (km) intervals and the transects were oriented approximately North – South and East – West (17 stations per prospect - Figure 2-1). The radial transect orientation enables station comparison spatially away from the development islands, as well as onshore – offshore station comparison, and East – West station comparison to account for the prevailing East – West currents in the region. This design allowed a combination of site-specific stations to be sampled for sediment chemistry, suspended sediment chemistry, and biota (tissue) chemistry, and resulted in four stations being located in the Boulder Patch area.

The acoustics stations were located along two transects centering on each of the Northstar and Liberty prospects. The acoustic transects included stations along a gradient away from the prospects at approximately 0, 5, and 15 Km intervals, running North and East of Northstar, and East and Northwest of Liberty (Figure 2-2). Where possible, the acoustics stations were combined with the sediment chemistry stations to enhance the overall efficiency of the field sampling program.

The summer 1999 field survey included sampling at all stations (Liberty and Northstar stations and BSMP stations), as this survey was to serve as the pre-development baseline for the overall ANIMIDA program. The winter 2000, or "through-ice," sampling program design focused primarily on the Northstar prospect, since construction activities were occurring at that time. The "through-ice" survey included two gradient transects at Northstar and one transect at Liberty, as well as some Northstar activity-specific sampling (Figure 2-2).

Teflon® messenger. After retrieval, the water samples were transferred to acid-washed 5-L plastic containers through a Tygon® tube. The water samples were labeled, sealed in plastic bags, packed in coolers, and taken to on-site laboratory facilities established at ARCO Prudhoe Bay Operations Camp (PBOC). In the lab, the water samples were shaken to resuspend the particulates and the turbidity of each sample was determined using a Hach® Model 2100A turbidimeter that was calibrated with sealed standards. The salinity of each seawater sample also was determined using a Reichert-Jung Model 10419 optical refractometer that was calibrated with standard seawater. Salinity was determined for selected seawater samples by inductive salinometer upon return to FIT to validate the data obtained with the Aanderaa system and the optical refractometer.

In the on-site laboratory, the water samples were vacuum-filtered through polycarbonate filters (Poretics®, 47-mm diameter, 0.4- μ m pore size). Prior to the field effort, the filters were acid-washed in 5N HNO₃, rinsed three times with distilled, deionized water (DDW), dried, and then weighed to the nearest μ g using a Sartorius® Model M3P electronic balance under "clean room" conditions. Vacuum filtration on site was carried out in a Class-100 laminar-flow hood using acid-washed glassware. The particle-bearing filters were then double-bagged in plastic, and stored until dried, and re-weighed in the Marine & Environmental Chemistry Laboratories at FIT.

Surficial Sediment Sampling

Sediment samples were collected using a modified Van-Veen grab sampler. During the collection and handling of sediment samples from the grab sampler, extreme care was taken to avoid contact with metals and hydrocarbon sources. Samples were taken away from the sides of the grab and no metal spatulas were used for the trace metal samples. The grab sampler was protected from stack smoke, grease drips from winches and wire, and other potential airborne contamination during the sampling process.

Sediment samples were collected from the top 1 cm of the grab to represent recent accumulation. Unconsolidated sediment 1 cm deep was removed from the grab with a stainless-steel scoop coated with Kynar. The scoop is 1 cm in depth to facilitate accurate collection depth of the sediment. The top 1 cm was collected by several scoops of the grab, up to the volume required for subsamples, and placed directly in appropriate sample containers. Specific subsamples were collected from each grab into individual containers (using a scoop or a Teflon® spatula) and stored as indicated in Table 2-7.

Suspended Sediment Sampling

Suspended sediments were collected using Niskin bottles at the selected depth(s) (i.e., near-surface, mid-water, and near-bottom) as dictated by the "real-time" CTD, nephelometry, and water current data.

Biota Sampling

Bivalve and amphipod samples were collected at selected stations as part of the sampling survey. A Fish Resource Permit was obtained from the State of Alaska Department of Fish and Game (ADF&G) to allow for the collection of biota samples.

Amphipods (*Anonyx spp.*) were collected using Nitex® mesh-lined, Kynar®-coated minnow traps, baited with sardines. The traps were generally deployed for two to six hours (depending on other sampling activities at adjacent stations) with an anchor and float equipped with a radar reflector to facilitate retrieval of the traps. The sardine bait was placed in an enclosed Nitex® mesh pouch to reduce the possibility of sardine particles becoming entrained with the amphipods. Only five amphipod samples of sufficient size for chemical analysis were collected during the survey. The scarcity of amphipods relative to previous BSMP surveys may have been related to the lack of ice in the nearshore waters. Amphipods are known to occur in areas with ice cover, and the vast stretches of open water encountered during this survey may have restricted the amphipods to areas of denser ice cover, offshore of the survey area. Amphipods were removed from the traps, washed with clean seawater, and placed in a clean sieve for sorting. Any non-*Anonyx spp.* amphipods were removed with clean forceps prior to transfer of the sample into the appropriate sample container.

It was originally intended that bivalves (target species: *Astarte sp.*, *Portlandia sp.*, *Cyrtodaria sp.*, and *Macoma sp.*) would be collected using a modified skip dredge towed behind the boat within the 0.2 nautical mile station radius. In practice, the clam dredge was ineffective in collecting bivalve samples. The dredge was deployed at several stations, but the clayey bottom substrate tended to clog the dredge. No bivalve samples were actually collected with the dredge and instead the grab sampler was used (as in previous BSMP collections). Multiple grabs were collected and sieved through a 1 cm Nitex® screen to isolate target species of bivalves. Target bivalves were then carefully removed to a clean sieve, rinsed with clean seawater, and transferred into the appropriate sample containers using clean forceps or spatulas. Generally, 20 to 40 grabs yielded a sufficient volume of bivalve samples for analysis.

Source Sampling

Source samples were collected in order to compare concentrations and distributions of contaminants in the sediments to potential sources, as well as to determine the potential influence of resuspended river sediment and coastal surficial sediment to the study area.

The source samples collected included water for suspended particulate analysis and sediment for organic and inorganic analysis from the Sagavanirktok, Kuparuk, and Colville Rivers. The Sagavanirktok River source samples were collected south of Deadhorse, near mile 401 on the Dalton Highway. The Kuparuk River source samples were collected ~1/4 mile south of the most southerly access road river crossing. The Colville River samples were collected via helicopter from stations to the North and South of the village of Nuiqsut. A sample of the gravel fill from the Endicott Causeway was also collected. Peat samples were obtained from the banks of the Kuparuk and Colville Rivers.

Water samples were collected from the Sagavanirktok, Colville, and Kuparuk Rivers in 1-L, acid-washed polyethylene bottles. The samples were obtained by wading into the river, waiting until disturbed sediment was washed downstream, and then opening an acid-washed 1-L polyethylene bottle below the surface of the water. When the bottle was full, it was sealed beneath the surface, retrieved, placed in a plastic bag, labeled, and stored in a cooler for return to the on-site laboratory facilities to be filtered.

The river sediment samples for organics analysis were collected from fine-grained surficial sediments (0 to 2 cm) approximately one meter from the shore using a stainless-steel spoon and precleaned glass sample jars. The spoon was rinsed well with alcohol and river water prior to use. The sampling equipment was decontaminated between sample locations by rinsing with distilled water. Metals source samples of riverbank sediment were collected using a plastic scoop and spatula. These sediment samples were placed in plastic bags (for grain size) and 75-milliliter (mL) plastic vials (for trace metals and methyl-mercury) and then stored in coolers. At the on-site lab, sediment samples for trace metal and methyl mercury analyses were frozen and the grain-size samples were refrigerated until transported to FIT. The peat samples, from the river shoreline approximately one meter above water level, were collected in the same manner as the sediments for organics and metals, respectively.

Acoustics Measurements

Measurement of ambient noise levels (*i.e.*, "acoustics sampling") was performed from the MMS *Launch 1273* for the summer 1999 field survey. A separate report was generated for the acoustics portion of the ANIMIDA program based on the nature of the data. This report includes detailed information on the field collection methods for the acoustics data. A copy of the acoustics report is included in Appendix F.

2.1.3 Winter 2000 Field Sampling

The first winter season field survey was conducted from April 24 to May 1, 2000, which coincided with a period of expected favorable weather conditions in the study area, long daylight hours, and activities associated with the Northstar Island and pipeline construction. The scientific crew conducted the field survey from the surface of the shorefast ice and utilized snowmobiles to access each sampling location. Discrete samples and *in situ* measurements were obtained from the program study area. The field sampling methods were conducted in accordance with ADL SOPs. The field sampling and logistics plan (Arthur D. Little, 2000a) prepared for the winter 2000 field survey provides descriptions of the field methods for sample collection and equipment decontamination. Field sampling personnel from Kinetic Laboratories, Inc. (KLI), FIT, and BBNT participated in the survey. The scientific crew conducted the work on a 14- to 16-hour-a-day basis depending on favorable operating conditions. Winter activities were conducted from the surface of the ice with two snowmobiles and freight sleds that were utilized to transport personnel and sampling equipment to each survey location. A detailed description of the activities conducted during the survey, including a log of the daily activities, is included in the field report (Arthur D. Little, 2000b). A summary of the field sampling activities and methods follows in this section.

Samples

The scientific crew collected samples for chemical analyses and recorded acoustic measurements from the program study area. During the 2000 ANIMIDA winter sampling survey, the following components were successfully completed:

- Collected samples at 9 stations
 - 1 historic BSMP station
 - 6 Northstar stations (2 stations associated with trenching operations and 4 at distances of 0.2 km, 1 km, 2 km, and 4 km on a radial from the island)

- 2 Liberty stations (1 in the Boulder Patch and 1 at the location of the proposed Liberty Island)

- Collected 27 water samples (surface, middle, and bottom) at each of the sampling locations to be analyzed for suspended particulates and a subset for chemical constituents
- Collected 9 ice cores for suspended particulate analyses
- Collected 3 source sediment/peat samples (1 gravel borrow pit, 1 Northstar Island, and 1 along pipeline corridor at Stump Island)
- Collected current, turbidity, CTD, and PAR profiles at 9 stations
- Collected acoustic measurements at 8 stations (obtained in the water, ice, and air at each of the sampling sites)

A complete list of the winter 2000 sampling stations that were occupied and sampled in the study area is included in Table 2-2. Table 2-2 also provides station identification, station type, latitude and longitude, depth, date of sampling, and the type of chemical, acoustics, and hydrographic measurements at each location: Figure 2-2, the map of the ANIMIDA study area, shows the locations of the winter 2000 sampling stations. Additional daily survey and sampling station information is included in the 2000 station logs contained in the field report (Arthur D. Little, 2000b).

2.1.3.1 Winter 2000 Through-Ice Field Sampling Procedures

Standard sampling procedures were followed at each sampling station according to the Field Logistics and Sampling Plan for the 2000 MMS Winter Field Survey (Arthur D. Little, 2000a).

Typical sampling procedures included:

- Establish and verify sampling location with a global positioning system (GPS)
- Drill a sampling hole with a gasoline-powered ice auger
- Collect acoustics data and CTD, PAR, and current measurements with an Aandera CTD/doppler current meter and a SeaBird CTD/PAR *in situ* sampler/recorder
- Collect water and ice core samples for analysis of suspended particulates and metals (at selected locations)

Photodocumentation, station logs, and field notes were recorded during the field survey. The station logs for each sampling station are included in the field report (Arthur D. Little, 2000b). Each station log includes a description of the sampling location, observations, number and type(s) of samples collected, and comments.

Water, Suspended Sediment and Ice-Core Measurements

To obtain seawater samples, holes were drilled in the ice using a gasoline-powered drill with a 25-cm-diameter auger. Water samples were collected by lowering a Teflon®-lined Niskin sampler attached to a Kevlar® hydrowire through the ice into the seawater where it was tripped using a Teflon® messenger. After retrieval, the water samples were transferred to acid-washed 5-L plastic containers using a plastic funnel. The sample containers were sealed in plastic bags, labeled, and placed in coolers for transport back to the onshore laboratory facilities. In the lab, the water samples were brought to room temperature to melt any ice that had formed in the sample containers. They were shaken to resuspend the particles and the turbidity of each sample was determined using a Hach® Model 2100A turbidimeter. The salinity of each seawater sample was also determined using a Reichert-Jung Model 10419 optical refractometer.

In the on-site laboratory at the Seawater Treatment Plant (STP), the water samples were vacuum-filtered through polycarbonate filters (Poretics®, 47-mm diameter, 0.4- µm pore size). Prior to the field effort, the filters were acid-washed in 5N HNO₃, rinsed three times with DDW, dried, and then weighed to the nearest µg using a Sartorius® Model M3P electronic balance under "clean room" conditions. Vacuum filtration on site was carried out in a Class 100 laminar-flow hood using acid-washed glassware. The particle-bearing filters were then double-bagged in plastic, and stored until dried, and re-weighed at FIT. *In-situ* profiles of seawater turbidity, CTD, current speed, and direction were obtained by lowering the Aanderaa Instruments system through the borehole in the ice.

Ice cores were collected by attaching a stainless-steel core barrel with serrated teeth to the gasoline-powered drill. The ice core samples were placed in sealed plastic containers, labeled, and stored in coolers for transport to the on-site lab facilities. The ice cores were allowed to melt in the on-site laboratory, after which the samples were shaken to resuspend the particulates and turbidity was determined using a Hach® Model 2100A turbidimeter. The salinity of each seawater sample was also determined using a Reichert-Jung Model 10419 optical refractometer.

Acoustics Measurements

Acoustics sampling was performed in conjunction with the ice core, water column, and suspended sediment sampling during the winter 2000 field survey. A separate report, generated by BBNT for the acoustics portion of the ANIMIDA program, includes detailed information on the field collection methods for the acoustics data (Shepard et al., 2001).

Source, Suspended Sediment, and Gravel Sample Collection

Three source samples (sediment/peat) were collected during the winter 2000 field survey (1 from the gravel borrow pit, 1 from Northstar Island, and 1 along the pipeline corridor at Stump Island). Each gravel/peat sample was collected using a plastic scoop and spatula and was placed in a 75-mL plastic vial (for trace metals and methyl mercury) and then stored in coolers. At the on-site lab, sediment/peat samples for trace metals and methyl mercury analyses were frozen until transported to FIT.

2.2 Analytical Methods

2.2.1 Ancillary Parameters

2.2.1.1 Grain Size

Determination of grain size followed the classic method of Folk (1974) using a combination of wet sieving and pipette techniques. Initially, 10 to 30 grams of wet sediment were placed in a wide-mouth dish using a larger mass for sandy samples and a smaller mass for muddy samples. A small amount of DDW was added to the dish, clay lumps were broken up with a gloved finger, and the wetted sample was poured into a 200-mL glass bottle and shaken vigorously for a few minutes. Then the sample was poured through 2 mm (gravel) and 63 μm (sand) sieves and rinsed until the water was clear. The sediment on each sieve was washed into beakers #1 and #2, respectively, allowed to settle and the overlying, clear water was decanted. The tared beakers were dried at 100 to 110°C and re-weighed.

The glass bottle containing the muddy water (<63 μm) was shaken for about 15 minutes and gently poured into a 1,000-mL cylinder. The cylinder was stirred vigorously with a stirring rod and a timer was started as soon as the rod was removed. No dispersant was needed in these samples of marine sediment as the mud fraction dispersed extremely well. After 20 seconds, 20 mL of sample were withdrawn from a depth of 20 cm using a Class A pipette. The pipette sample was drained into tared beaker #3, dried at 100 to 110°C for 24 hours, and weighed for total silt + clay. After 2 hours and 3 minutes, 20 mL of sample was withdrawn from a depth of 10 cm using a Class A pipette. This pipette sample was drained into tared beaker #4, dried at 100 to 110°C for 24 hours, and weighed for total clay. All masses were determined to the nearest 0.01 g. The total mass of sample was equal to the Sum of masses in beakers 1 + 2 + 3(x 50). The individual percentages were calculated as follows:

- % gravel = (beaker #1 sediment/Sum) x 100%
- % sand = (beaker #2 sediment/Sum) x 100%
- silt = $\{[(50 \times \text{beaker \#3}) - (50 \times \text{beaker \#4})]/\text{Sum}\} \times 100\%$
- % clay = $[(50 \times \text{beaker \#4})/\text{Sum}] \times 100\%$

2.2.1.2 Total Organic Carbon

A 0.5 to 1 gram portion of the freeze-dried sediment was placed in a 10-mL Pyrex® beaker and wetted with 1 mL of DDW followed by the addition of 2 mL of concentrated hydrochloric acid (HCl) to remove any inorganic carbon present. The sediment was dried at 60°C and re-weighed to determine the increase in weight due to the formation of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ as a result of adding HCl. Then, approximately 200 to 400 mg of pre-treated sediment were weighed into ceramic boats and combusted at 900°C in a Shimadzu® TOC-5050A carbon system with SSM-5000A solid sampling module following the manufacturer's instructions. The TOC content of the sediment samples was determined using a four-point calibration curve with pure sucrose as the standard. The TOC concentrations were corrected to account for the increase in sediment mass following the addition of HCl. The calibration curve was checked every 10 samples by analyzing standard reference material (SRM) MESS-2, a marine sediment issued by the National Research Council of Canada (NRC).

2.2.2 Organic Chemical Parameters

Analysis for organic contaminants was conducted by ADL's Environmental Chemistry and Forensics (EC&F) laboratory. The analyses were conducted in accordance with the laboratory's SOPs and generally followed the same procedures used in previous BSMP studies (Boehm et al., 1990). The core organic analyses for the sediment and source samples were:

- Saturated hydrocarbons (SHC) by gas chromatography/flame ionization detection (GC/FID)
- PAH by gas chromatography/mass spectrometry detection (GC/MS)
- Geochemical biomarkers (steranes/triterpanes [S/T]) by GC/MS

Targeted compounds are listed in Tables 2-3, 2-4, and 2-5. This section describes the analytical methods that were used in performing the organic chemical analyses.

2.2.2.1 Sample Preparation

Sediment Samples

The sediment samples were prepared using a procedure based on United States Environmental Protection Agency (EPA) Method 3550A, Ultrasonic Extraction (EPA 1993). The method modifications include orbital shaking of the sample in extraction solvent for 1 hour following the final sonication to enhance recovery of target contaminants. The following is a summary of the method.

Approximately 30 grams (wet weight) of the homogenized sediment were weighed into a Teflon® jar and dried with sodium sulfate. Another 5-gram subsample was placed into an aluminum-weighing pan and heated at 105 °C to a constant weight, for dry weight determination. The sample was serially extracted 3 times with 100 mL of methylene chloride and acetone (1:1, volume to volume [V/V]), each time by sonication. The final sonication was followed by orbital shaking in the extraction solvent for 1 hour.

The surrogates were spiked into the sample after the first addition of solvent and before the first extraction. All sediment samples were spiked with "low-level" surrogates (as defined by the laboratory SOP) because target compound concentrations in the sample were expected to be at trace levels.

The surrogates used were: naphthalene-d8, acenaphthene-d10, phenanthrene-d10, and benzo[a]pyrene-d12 for PAH analysis, 5 α -androsterane and d50-tetracosane for SHC analysis, and 5 β (H)-cholesterol for S/T analysis.

After extraction, samples were concentrated using a Kuderna-Danish (K-D) concentrator on a hot water bath. An extract weight was taken if necessary to determine general organic content levels prior to column cleanup. Extracts were then treated with copper to remove sulfur, and split in half. One-half was archived in a freezer at -20°C and the other half processed through a silica gel column as described in the Extract Fractionation subsection.

Biota Samples

Approximately 20 grams wet weight of tissue (if available) was prepared for extraction. Partially thawed bivalve tissues were removed from the shells with solvent-rinsed stainless-steel utensils and weighed on a top-loading balance. Whole amphipod samples and shucked bivalve samples were completely homogenized using a Tissumizer. An aliquot of each homogenized sample was removed for dry weight determination, and the remaining sample (approximately 10 grams wet weight) was transferred to a clean Teflon® centrifuge tube for digestion. The remainder of the homogenate, if any, was re-labeled and stored frozen as archived samples.

Thirty (30) mL of pre-extracted 6N potassium hydroxide and the surrogates were added to each homogenized tissue sample. The surrogates used were: naphthalene-d8, acenaphthene-d10, phenanthrene-d10, and benzo[a]pyrene-d12 for PAH analysis, 5 α -androstane and d50-tetracosane for SHC analysis, and 5B(H)-cholane and d66-dotriacontane for S/T analysis. Surrogate compounds were spiked into all tissue samples at the low-level because target compound concentrations in the samples were expected to be at trace levels. The container was then flushed with purified nitrogen, sealed, and allowed to digest overnight in a hot water bath at approximately 35°C. After digestion, 30 mL of ethyl ether was added to each sample and the mixture was agitated on an orbital shaker for 5 minutes. The samples were then centrifuged at 2,000 revolutions per minute (rpm) for 5 minutes to facilitate phase separation. The ether layer was removed using a Pasteur pipet and filtered through sodium sulfate into a 250-mL K-D apparatus. The ether extraction of the digest was repeated twice, and the ether extracts combined in the K-D apparatus. The combined ether extract from each sample was reduced in volume to approximately 1 mL by K-D and nitrogen concentration techniques. The extracts were then exchanged to dichloromethane and an aliquot was removed and weighed on an electrobalance for total non-saponifiable lipid weight determinations.

The tissue sample extracts were further processed in order to reduce potential interferences. The extracts were loaded on a 30-cm by 1-cm glass chromatography column filled with 10 gram alumina (activated overnight at 130°C prior to use) and 1 gram anhydrous sodium sulfate. Sample extracts, containing no more than 300 mg of extractable organic material, were loaded onto the alumina column and eluted with 100 mL of methylene chloride. The extracts were concentrated to 5 mL using a K-D concentrator. All extracts were further reduced in volume and exchanged into hexane using nitrogen evaporation. A post-alumina gravimetric weight was recorded prior to further processing using a silica gel column, as described in the Extract Fractionation subsection.

Source Samples

The four source sediment samples [Colville River (2), Sagavanirktok River (1), and Kuparuk River(1)] and the two source peat samples (Colville River and Kuparuk River) were extracted and analyzed using the same procedure as for the other sediment samples.

Field Blanks

One field blank sample consisting of distilled water rinsate of the grab sampler was collected as part of the project quality assurance (QA) program. A "deck" blank, which consisted of an empty sample jar that had been left open on the boat deck during sampling, was also collected. The deck blank was prepared by rinsing the jar three times with approximately 10 mL of

methylene chloride. The methylene chloride rinsates were combined and spiked with low-level SHC, PAH, and S/T surrogates. The field blank was extracted by a liquid-liquid method with methylene chloride. This sample was also spiked with low-level SHC, PAH, and S/T surrogates. The two field blank extracts did not require column cleanup and were prepared for instrumental analysis without further processing.

Extract Fractionation

The sediment and tissue extracts were fractionated in order to remove potential interference and to improve the quality of the analysis at trace levels. The procedure used for fractionation was similar to that used for previous BSMP investigations (Boehm et al., 1990). Prior to fractionation, the sample extracts were exchanged from methylene chloride to hexane under nitrogen.

The fractionation was performed using a 30-cm by 1-cm column that was wet-packed in methylene chloride with 100 percent activated silica gel/5 percent deactivated alumina/activated copper (approximately 11:1:2 g) and preconditioned with 30 mL methylene chloride followed by 30 mL of hexane. The sample extract (which had been verified to be less than 50 mg extractable material per 1 mL) was loaded onto the column. The sample was eluted with 18 mL of hexane and the isolated saturate (f1) fraction was collected. This was followed by 21 mL of hexane:methylene chloride (1:1) to isolate the aromatic (f2) fractions.

Internal Standard Addition

The extracts (or extract fractions) were reduced to a measured final volume under a stream of nitrogen. The final sample extracts were spiked with SHC, PAH, and S/T internal standards, as appropriate for each extract or fraction. In general, the extracts were concentrated to approximately 250 μ L before adding the internal standards in order to lower detection limits. The internal standard compounds used were: chrysene-d12 and fluorene-d10 for PAH; chrysene-d12 for S/T; and d62-triacontane for SHC. The amount of SHC internal standard added to the extracts was adjusted to obtain a target concentration of 50 μ g/mL. The amount of PAH and S/T internal standard added to the extract was adjusted to obtain a target concentration of 1 μ g/mL.

2.2.2.2 Organic Instrumental Analysis

Instrumental analysis of the sediment and tissue samples (including the source samples) included SHC by GC/FID and PAH by GC/MS. In addition, selected samples were analyzed for S/T by GC/MS. The water samples were analyzed for SHC and PAH.

The laboratory SOPs include the acceptability criteria for the calibration, procedural blank, surrogate compound recoveries, and spike recoveries, as well as the corrective action if the criteria are not met, reporting requirements, and method detection limit (MDL) protocols. The data quality objectives (DQO) for these analyses are summarized in Section 2.3.

Saturated Hydrocarbons by Gas Chromatography/Flame Ionization Detection

Analysis for SHCs was performed using a method based on EPA Method 8015 (EPA 1993). Target compounds for the method are SHCs, including normal alkanes from n-C8 through n-C40, pristane, phytane, and selected isoprenoids. Instrument analysis was performed by injection of a portion of the prepared sample extract onto a 30-m long by 0.25-mm inner-diameter (ID)

fused-silica capillary column with DB-5 bonded phase. This column provides baseline resolution of n-alkanes from n-C8 to n-C40 and n-C17/pristane and n-C18/phytane pairs. The injection port is designed for splitless injection and includes a silanized wide-bore glass liner containing a plug of silanized glass wool to reduce high-molecular-weight mass discrimination.

Qualitative identification of target compounds was made by comparison to a standard mixture of calibration standards. Quantitation of the analytes was based on the internal standard compound (d62-triacontane), which was spiked into the sample just prior to analysis. The target compound concentrations were corrected based on surrogate recovery.

Polynuclear Aromatic Hydrocarbons by Gas Chromatography/Mass Spectrometry

Analysis for PAHs was performed using a method based on EPA Method 8270 (EPA 1993). The method modifications include analysis for an expanded list of PAH and operation in the selected ion monitoring (SIM) mode to lower detection limits.

The sample extract was injected onto a 30-m long by 0.25-mm ID fused-silica capillary column with DB-5 bonded phase. This column provides baseline resolution of target PAHs. The injection port is designed for splitless injection and includes a silanized wide-bore glass liner containing a plug of silanized glass wool to reduce high-molecular-weight mass discrimination.

Qualitative identification of target compounds was made by comparison to a standard mixture of target PAHs. Identification of alkyl PAHs was made by comparison to reference oil samples analyzed with each batch of samples. The concentrations of the individual PAHs were calculated relative to one of the two internal standards that were spiked into the sample just prior to instrumental analysis. The target PAH concentrations were quantified using average response factors (RFs) generated from the five-point calibration curve. To quantify the alkyl PAH, homologue groups were assigned the RF of their respective parent PAH compound. Compound concentrations were corrected based on surrogate recoveries.

Steranes and Triterpanes

Only selected sediment and tissue samples were analyzed for S/Ts. Analysis for S/Ts was performed by GC/MS in the selected ion monitoring (SIM) mode using a method similar to that used for PAH analysis. Qualitative identification of the target S/Ts was made by comparison to a reference oil analyzed with each batch.

The concentrations of the identified S/Ts were calculated versus the internal standard chrysene-d12. All target triterpane concentrations were quantified using the average RF of 17(H), 21(H)-hopane (T23) generated from the initial calibration. All target sterane concentrations were quantified using the average RF of cholestane (S17) in the initial calibration. Surrogate recovery of 5b(H)-cholane was calculated relative to the internal standard. Compound concentrations were corrected based on surrogate recovery.

2.2.3 Stable Carbon Isotopes (¹³Carbon)

A portion of the sample treated with HCl for TOC was used for determining values for $\delta^{13}\text{C}$. A weighed portion of the treated and dried sample was processed using a Finnigan-MAT 251 isotope ratio mass spectrometer. The external precision of 0.02 per mil for $\delta^{13}\text{C}$ was determined

by replicate analysis of a laboratory internal standard of calcite. The data were corrected for the usual isobaric interferences using the equations of Craig (1957), as modified for a triple collector mass spectrometer. All isotopic data are reported in per mil units relative to the Pee Dee Belemnite (PDB) reference.

2.2.4 Inorganic Parameters

Analysis for inorganic parameters was conducted by FIT. The analyses were conducted in accordance with FIT's SOPs. The core inorganic analyses for the sediment and source samples were trace and major metals. Targeted analytes and associated MDLs are listed in Table 2-6. This section describes the analytical methods that were used in performing the chemical analyses.

2.2.4.1 Trace and Major Metals Analysis in Suspended and Surficial Sediment

Filters bearing suspended sediment and milligram quantities of SRM #2704, a river sediment SRM issued by the National Institute of Standards and Technology (NIST), were digested in stoppered, 15-mL Teflon® test tubes using Ultrex II® nitric acid (HNO₃), hydrogen fluoride (HF) and HCl. The sealed test tubes were placed in an 80°C water bath where refluxing of the acids completely dissolved the particles on the filters. After digestion, the resultant solutions were transferred to acid-washed, 15-mL polyethylene bottles, diluted to approximately 6 mL with DDW rinses of the Teflon® test tubes, and stored in a plastic bag until analyzed.

Metal concentrations for the dissolved particulate samples, SRMs, and blanks were determined by flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), or inductively coupled plasma/mass spectrometry (ICP/MS) in a manner compatible with EPA Methods Series 7000, 6010A, and 7470 (EPA 1991), respectively.

Particulate Al, Fe, and Zn concentrations were quantified by FAAS using a Perkin-Elmer® Model 4000 AAS (element symbols are defined in Table 2-6). Concentrations of Cd, Cr, Cu, and Pb were quantified by GFAAS using a Perkin-Elmer® Model 4000 AAS equipped with an HGA-400 graphite furnace and AS-40 autosampler. Values for Ba were determined by ICP/MS using a Perkin-Elmer® ELAN 5000 spectrometer. In all cases, the instrument manufacturers' specifications were followed and adherence to quality assurance/quality control (QA/QC) requirements was maintained.

For sediment metal analysis, samples were initially brought to room temperature, then each wet sediment sample was homogenized in the original 75-mL plastic vial using a Teflon® mixing rod. Then, a portion (~2 grams) of each sample was transferred into a pre-weighed plastic vial to determine water content. Once transferred, the wet sediment and the vial were re-weighed. In addition, about 2 to 4 grams of sample were transferred into polypropylene-copolymer centrifuge tubes to determine the Hg content of the sediments. Samples intended for water content measurement were frozen, freeze-dried, and re-weighed to determine the water content. The dried sediment samples were again homogenized using a Teflon® mixing rod.

About 0.45 grams of freeze-dried, homogenized sediment and SRM sediment (BCSS-1) were totally digested in Teflon® beakers using concentrated, high-purity HF-HNO₃-perchloric acid (HClO₄). This method was chosen because it is a total digestion and thus accounts for the entire

amount of metal in the sample. In the digestion process, 1 mL HClO₄, 1 mL HNO₃, and 3 mL HF were added to the sediment in the Teflon® beaker, covered with a Teflon® watch cover, and heated at 50°C until a moist paste formed. The mixture was heated for another 3 hours at 80°C with an additional 2 mL HNO₃ and 3 mL HF before bringing the sample to dryness. Finally, 1 mL HNO₃ and about 30 mL DDW were added to the sample and heated strongly to dissolve perchlorate salts and reduce the volume. The completely dissolved and clear samples were diluted to 20 mL with DDW.

Sediment samples to be analyzed for Hg were digested by heating 2 to 4 grams of wet sediment in acid-washed, polypropylene-copolymer centrifuge tubes with 4 mL HNO₃ and 2 mL sulfuric acid (H₂SO₄). Sample tubes were heated for 1 hour in a 90°C water bath and allowed to cool. Each tube was centrifuged at 2,000 rpm and the supernatant decanted into a 25-mL graduated cylinder. The sediment pellet was rinsed twice with 5 mL DDW, centrifuged, and decanted into the graduated cylinder before diluting to a final volume of 20 mL with DDW.

Labware used in the digestion process was acid-washed with hot 8N HNO₃ and rinsed three times with DDW. Two procedural blanks, two duplicate samples, and two SRMs were prepared with each set of 40 samples. SRM BCSS-1 (trace metals except Hg) and MESS-2 (Hg), sediment samples issued by the NRC, were used.

Sediment samples, SRMs, and procedural and reagent blanks were analyzed by FAAS, GFAAS (Zeeman or Continuum background correction), cold vapor atomic absorption spectrometry (CVAAS) or ICP/MS. Mercury concentrations were measured by CVAAS using a Laboratory Data Control Model 1235 Mercury Monitor. The method used for each element and the corresponding MDLs are presented in Table 2-6. All analytical techniques followed manufacturers' specifications, laboratory SOPs, and the details provided in Section 2.3 below. These methods are based on EPA methods described for Series 7000 (FAAS and GFAAS), Series 7470 (CVAAS), and Series 6010A (ICP/MS) (EPA 1991).

2.2.4.2 Methyl Mercury Analysis in Sediment

Concentrations of methyl mercury were determined Dr. Y. Cai at Florida International University using GC with atomic fluorescence spectrometry following aqueous derivatization with sodium tetraphenylborate as described in Cai, et al. (2000).

2.2.4.3 Trace and Major Metals Analysis in Organism Tissue

Prior to acid digestion, the homogenized tissue samples received from ADL were thawed and re-mixed with a Teflon® stirring rod. The samples were then split into two portions, one subsample to be digested wet for Hg and the other to be freeze-dried and digested for determination of the remaining trace metals. The freeze-dried subsamples also provided the percent water content data needed to convert the Hg results from a wet-weight to dry-weight basis.

The concentrations of all metals (except Hg) were determined using 4 to 6 grams of wet-weight tissue weighed into 100-mL glass digestion flasks. These subsamples were freeze-dried, reweighed for percent water content, and then digested by the sequential addition of

concentrated, high-purity HNO_3 , hydrogen peroxide (H_2O_2), and HCl with gentle refluxing. Aliquots of tissue SRMs were digested along with the experimental samples. Once the tissue samples and SRMs were completely dissolved, the clear solutions were transferred to graduated cylinders, diluted to 20 mL with DDW rinses of the digestion flasks, and then stored in labeled 30-mL polyethylene screw-cap bottles for trace metal analysis.

Mercury determinations were carried out using 0.4 to 0.7 grams of wet tissue and dry SRMs weighed into 50-mL glass digestion tubes. These subsamples were digested by the addition of concentrated, high-purity HNO_3 and H_2SO_4 and refluxing at 90°C for 1 hour in the sealed tubes. The dissolved samples were transferred to graduated cylinders, diluted to 20 mL with DDW rinses of the digestion tubes, and then stored in labeled 30-mL polyethylene screw-cap bottles for Hg analysis.

Metal concentrations in the digested tissue samples, SRMs, and blanks were determined by FAAS, GFAAS (Zeeman or Continuum background correction), CVAAS, or ICP/MS. The method used for each element and the corresponding MDLs are given in Table 2-6. All analytical techniques followed manufacturers' specifications, SOPs on file at FIT, and the details provided in Section 2.3 below. These methods are based on EPA methods described for Series 7000 (FAAS and GFAAS), Series 7470 (CVAAS), and Series 6010A (ICP/MS) (EPA 1991).

2.3 Quality Assurance/Quality Control

A QA plan, which included quality control (QC) measures, was employed for the program. This section presents the key elements of the plan.

2.3.1 Quality Assurance

2.3.1.1 Documentation

The procedures for monitoring the activities of key staff, meeting contract requirements, submission of all deliverables, budget control, and communications are detailed in the various documents that together compose the project management plan:

- A detailed work breakdown structure (WBS) for all tasks, designating primary task leader and responsibilities for key personnel and staff;
- A field sampling and logistics plan for field operations, including scheduling, staffing, training, QC sample collection and analysis procedures, sample chain-of-custody specifications, and sample shipping; and
- A laboratory work plan for laboratory analysis, including laboratory procedures, analytical DQOs, QC procedures, corrective action criteria, and data entry/data management.

The supporting quality assurance documentation includes the general company policies and procedures (hiring practices, performance evaluations, program management and control tools, and technical review procedures), the Quality Assurance Manual (QAM) for the respective laboratories, and SOPs for field and laboratory operations.

2.3.1.2 Quality Management

Program

As the ADL Program Manager, Dr. Paul Boehm was the primary contact with MMS for the program and was responsible for the communication, coordination, and scheduling of all tasks, subtasks, meetings, and deliverables. The Program QA/QC Officer, Dr. Judi Harris, was responsible for the overall QA/QC activities of the project, including oversight of the record keeping for the program. The Program Manager was kept apprised of the program's status by the Field Sampling and Analytical Laboratory Leaders.

Field

Mr. John Brown served as the Field Team Leader for the sediment and benthic tissue collection surveys and, as such, was responsible for completion of all field activities in accordance with the field sampling and logistics plans and communication with the Program Manager and the field team. He was also responsible for implementing field QC, including issuance and tracking of measurement and test equipment; proper labeling, handling, storage, and shipping of samples; chain-of-custody procedures; and control and collection of all field documentation.

The field sampling team was provided a briefing of QA measures prior to beginning field sampling. The field personnel were briefed on the potential for contamination and cross-contamination of samples and given guidance on techniques to minimize such problems. In general, this included training on the use of pre-cleaned sample containers; use of clean sampling equipment; use of the decontamination protocols; and good handling practices. It also included training on the specified sampling procedures and protocols in accordance with SOPs.

Laboratory

As organic chemistry task leader, Mr. John Brown was responsible for oversight of the organics analyses performed by ADL's EC&F laboratory. Dr. John Trefry was the inorganic chemistry task leader and was responsible for oversight of the inorganic analyses performed by FIT.

Laboratory analyses were performed in accordance with the laboratories' QAMs and the project-specific laboratory workplan. Oversight of the laboratory QA program was the responsibility of the laboratory's QA manager. Implementation of quality practices was the responsibility of the laboratory manager, who had specific responsibilities for:

- Implementing and adhering to the QA and corporate policies and procedures within the laboratory
- Approving SOPs
- Maintaining adequate staffing
- Implementing internal/external audit findings corrective actions

Prior to the start of laboratory analyses, the laboratory staff were provided project-specific training, which included a discussion of the project background and objectives; project organization; sample preparation and instrumental analysis procedures; data quality objectives; QC procedures; and reporting instructions. The task leaders provided this training.

2.3.1.3 Sample Custody, Preservation, and Tracking

The following section describes the procedures that were employed to ensure the integrity of the samples, including prevention of contamination in the field, ensuring safe transport, and documenting sample custody and transfer.

Sample Handling

All field sampling equipment was decontaminated prior to use at each sampling station. The equipment was:

- scrubbed with brushes and liquid soap-and-water mixture to remove any accumulated sediment
- wiped clean with a sorbent pad, paper towel, or rag (if necessary)
- rinsed with seawater (from hose or buckets, as appropriate)
- rinsed with distilled water
- rinsed with isopropanol solvent
- rinsed with deionized water (optional)

The clean equipment was prevented from recontamination prior to sampling by either decontamination immediately prior to use or protection by wrapping securely in aluminum foil that had been decontaminated. Precautions were taken to ensure that clean equipment did not contact anything other than the sample, air, or other clean equipment. Clean equipment was prevented from contact with the ground (except for the immediate sampling area), hands, clothing, plastic bags, buckets, trays, etc.

At all times after collection, sample integrity and custody were maintained. Chain-of-custody (COC) procedures are specified in formal SOPs and are followed for all sample storage and shipment activities. Chain-of-custody seals and sample labels were applied to each sample container, ensuring sample integrity. All field samples were unambiguously labeled in waterproof ink with the following information:

- Sample site
- Unique field sample number
- Date and time of sample collection
- Details of preservation used

The type of sample containers used and the sample storage methods are provided in Table 2-7. Pre-cleaned sample containers that had been certified as such by the vendor were used for the program.

In the field, sediment, biota, and QC samples for chemical analysis were immediately inventoried and stored in a secure area after collection. Inventory included counting of all the samples to ensure that all samples were collected and safely returned to the custody area on board, documenting all samples in field logs, and preparing the chain-of-custody form.

Sample Shipment

Following completion of the cruise, samples were packed in coolers for overnight shipment from the PBOC in Deadhorse using Federal Express airfreight courier. The samples were frozen prior to transportation and shipped to the appropriate analytical laboratories (Table 2-7), either frozen packed on dry ice or refrigerated packed with frozen blue ice via overnight service. Custody seals were used on all shipping coolers to maintain custodial security while the samples were in the possession of a third party (i.e., airfreight courier).

Receipt at ADL

Quality assurance practices were applied at the moment samples were received at the laboratory. The laboratory sample custodian received all samples. Prior to opening the cooler, the cooler was checked for the presence of intact custody seals. The cooler was then opened and the temperature of the samples was measured by measuring the temperature of a representative sample. Each sample was carefully checked for identification, which was then cross-referenced against the COC records. Samples were logged in and a unique laboratory identification number was assigned to each sample. Problems or discrepancies with the coolers, samples, or documentation were documented and the project manager was notified immediately so that issues could be resolved.

After samples were received into the laboratory and a unique identification number assigned, the samples were placed in a secure, uniquely identified storage area until extraction. As is the practice by the laboratory, temperatures of all of the refrigerators and freezers were monitored and recorded daily. Samples were removed and thawed for sample preparation and then returned to frozen storage, where they will be stored for a period of at least two years.

Documentation tracking sample possession from the time it is collected (including equipment and container preparation) to the point at which the samples and extracts are discarded is necessary to ensure the credibility and validity of field and laboratory results. For this program, documentation was accomplished through initiating a COC record for each sample at the time of its collection and carrying the required paperwork through the final reporting of results, and to the final program files.

A COC form accompanied the samples as they were delivered from the field to the laboratory. Upon receipt, the document was signed by the laboratory's sample custodian, and dated as acknowledgement of receipt of the samples. Thereafter, the laboratory internal COC protocols, described in the individual laboratory QA program plans or similar documentation, were utilized.

Receipt at FIT

Each sediment, suspended solids, tissue, and source sample received by the Marine & Environmental Chemistry Laboratories at FIT was carefully inspected to ensure that it was intact and that the identification number on the sample container matched that found on the custody sheet. All sediment and source samples were kept refrigerated ($4^{\circ}\text{C} \pm 2^{\circ}\text{C}$) and all tissue samples were kept frozen ($\sim 20^{\circ}\text{C}$) until processed for analysis. Suspended solids samples were dried under cleanroom conditions and stored at room temperature until analysis.

2.3.2 Field Quality Control

2.3.2.1 Sample Handling

Equipment decontamination procedures were strictly followed during the sampling. The decontamination included a physical scrub with soap and water, rinses with seawater and distilled water, and a rinse with isopropanol.

2.3.2.2 Quality Control Samples

As part of the QA program, several types of field QC samples were collected during the survey.

Blanks

Blank samples were collected to characterize potential influences from equipment and the sampling activities.

One field (deck) blank was collected during sediment sampling. To collect the field blank, a clean, prelabeled sample jar of the same batch used for sample collection was carried into the working area, opened during the collection of one sample, and returned to the laboratory with the field samples. One container was collected each for organics and metals. The field blank was stored under the same conditions as the associated field samples.

An equipment blank was collected from rinsate of the sediment sampling equipment. The procedure for collecting the equipment blank followed these steps:

- The equipment was decontaminated according to the SOP
- The equipment was rinsed with high-purity, deionized water and the rinsate collected directly into two clean, prelabeled water sample containers (one container each for organics and metals)
- A precleaned stainless-steel funnel was used to assist in the collection
- The equipment blank was stored under the same conditions as the associated field samples

A sample of diesel fuel typical of that used in marine vessels in the Arctic was taken during a previous field survey and was available at ADL. The purpose of this sample was to, if necessary, be able to characterize any potential sample contamination believed to originate from the shipboard diesel fuel (e.g., exhaust and surface sheen).

Field Replicates

As a QC measure, replicate samples were collected as part of the field sampling design at sample stations 5(1) and L11. At these locations, sediment samples were collected in triplicate so that the reproducibility and range of results could be evaluated.

Turbidimeter Calibration

The Hach turbidimeter was calibrated prior to each use with the standards provided by the manufacturer. The instrumental blank was determined using a glass cuvette filled with DDW. The Aanderaa turbidity sensor was calibrated by the manufacturer prior to delivery and checked in air (zero turbidity) and with the sensor blocked (full-scale turbidity) prior to use.

Salinity Calibration

The Reichert-Jung Model 10419 optical refractometer was calibrated prior to each use with Standard Seawater (Ocean Scientific International, salinity = 34.998) and DDW. The Aanderaa conductivity sensor was calibrated by the manufacturer prior to delivery and checked against DDW and samples of known salinity prior to use. Salinity samples were also collected in the field and shipped to the Marine & Environmental Chemistry Laboratories at FIT, where their salinities were determined using a PortaSal® Model 8410 salinometer as a cross-check on the field instruments.

2.3.2.3 Documentation

Throughout the field surveys, field notes were maintained by the scientists in log books and in a station log. Biota (bivalve and amphipod) sampling information was also recorded on log forms. Exceptions to procedures specified in the sampling and analysis plans, if any, were recorded on the forms.

Film and digital media were used to photo-document the surveys. This documentation recorded specific samples, sampling procedures, and unusual sediment types.

2.3.3 Organic Chemistry Laboratory Quality Control

2.3.3.1 Data Quality Objectives and Quality Control Samples

A set of DQOs was established for the program to ensure that the analytical data would be of the quality necessary to achieve the project objectives. The DQOs were also designed to enhance the ability of the methods to identify and accurately quantify source-specific oils. The DQOs were adapted from the specific laboratory analytical SOPs and were included in the laboratory workplan specific for the program. They are included here as Tables 2-8 and 2-9.

For processing, samples were grouped together in batches of 20 field samples, plus associated QC samples. In general, the QC samples processed along with the sediment samples included one procedural blank, one blank spike, and one SRM (Sediment SRM 1941a) per batch. The blank spike sample was fortified with PAH matrix spike solution and SHC matrix spike solution. The QC samples processed with each batch of tissue samples included one procedural blank, one blank spike, one SRM (Tissue SRM 1974a), and one duplicate analysis. The blank spike sample was fortified with PAH and SHC matrix spike solutions.

There were a number of additional measures added to the processing of the samples to monitor QC and to aid in the assessment of the data's usability with respect to the program objectives. An important part of this is the evaluation of specific QC samples for accuracy, precision, and potential contamination. The following is a general description of some elements.

Solvent and Standard Checks

Prior to sample analysis, every lot of solvent used in the analytical process was analyzed in duplicate to verify that it was free of contamination and acceptable for use. Likewise, prior to spiking the samples with surrogates and internal standards, all standard preparation records were checked. No standards were used for an analysis unless they had been approved for use.

Instrument Calibration

Before instrumental analysis of sample extracts, a multi-level calibration was analyzed and the linearity of the analyte response factors was evaluated. A continuing calibration standard was analyzed regularly to check the stability of the instrument response. If the relative standard deviations (RSDs) for the initial calibration or the percent difference of the daily calibration did not meet the criteria set in the SOP, a new calibration was run and the affected samples re-analyzed.

Reference Samples

For PAHs, to assess the accuracy of the mixture used to calibrate the method, an independently verified instrument reference material (IRM) was analyzed against the calibration standard. The values of the analytes had to be within 15 percent of the target value for the calibration solution to be valid.

In addition, a solution of an assayed crude oil was analyzed with each initial calibration sequence and the results were compared to a laboratory-established mean to assess method accuracy. The solution was also used to provide petroleum pattern information and aid in qualitative identification of target compounds.

Procedural Blank

A procedural blank was processed and analyzed with each analytical batch in order to monitor potential contamination resulting from laboratory solvents, reagents, glassware, and processing procedures.

Blank Spike

A blank matrix was spiked with representative target compounds prior to extraction to assess the effect of the sample processing procedure independent of sample matrix effects.

Laboratory Duplicate

A field sample was analyzed in duplicate to assess the precision of the method in the target matrix.

Standard Reference Materials

A Standard Reference Material of a well-characterized sample of known concentration was processed through sample preparation and instrumental analysis with each batch of samples. The results were compared to externally certified values to assess method accuracy. This program used SRM samples provided by NIST: SRM 1944 for sediment samples and SRM 1974a for tissue samples.

2.3.3.2 Laboratory Records

The laboratory maintained detailed records throughout the processing of the samples. All raw instrumental data were archived electronically. Completed records or copies of forms were collated into a binder for final archive storage. The final laboratory data package contains

sufficient detail so that an external audit could be performed. The documentation in the final data package includes:

- Lot numbers, vendor, and preparation records for reagents and standards
- Sample preparation records
- Analytical procedures used that are not documented in laboratory SOPs
- Instrument analysis records
- Instrument raw data hardcopy
- Documentation of observations or deviations encountered

2.3.3.3 Laboratory Data Review

The following describes the process of data reporting and review by the laboratory. The chemistry data for each analysis were reduced and reviewed by the laboratory staff and then assembled into the final data package. The assembled package was peer reviewed and checked to ensure that the DQOs were met, that the analyses met the program objectives, and that the data were traceable and defensible. The data were also reviewed for compliance with the documented procedures and quality objectives in the work plan. Data were also reviewed for internal consistency and against expected or known values.

After the final laboratory data package review, it was subjected to a formal audit. The audit process is coordinated by the QA Manager and follows the procedure outlined in the ADL Data Review SOP. The formal audit process included a 100-percent review of all hand-calculated values and a 20-percent review of computer-generated results. The process also checked the traceability of a final result through the instrument calibration and to the sample preparation steps. A formal report was issued to the facility supervisors at the completion of the audit for response. Upon completion of the responses, the auditor released the results to the Program Manager for review and reporting. The final laboratory data package and the audit report are maintained in the laboratory files.

2.3.4 Metals Chemistry Laboratory Quality Control

Quality Control Measurements for Analysis

For this project, QC measures included balance calibration, instrument calibration (FAAS, GFAAS, Zeeman Graphite Furnace Atomic Absorption Spectrometry [ZGFAAS], CVAAS, ICP/MS, TOC analyzer, turbidimeters, and *in-situ* instrument sensors), matrix spike analysis for each metal, duplicate sample analysis, SRM analysis, procedural blank analysis and standard checks. With each batch of up to 40 samples, 2 procedural blanks, 2 SRMs, 2 duplicate samples and 2 matrix-spiked samples were analyzed. Data Quality Objectives for these QC measurements are provided in Table 2-10.

Instrument Calibration

Electronic balances used for weighing samples and reagents were calibrated prior to each use with certified (National Bureau of Standards [NBS]-traceable) standard weights. All pipets (electronic or manual) were calibrated prior to use. Each of the spectrometers used for metals analysis was initially standardized with a three- to five-point calibration with a linear correlation coefficient of $r \geq 0.999$ required before experimental samples could be analyzed. Analysis of complete three- to five-point calibrations and/or single standard checks alternated every 5 to 10

samples until all of the analyses were complete. The RSD between complete calibration and standard check was required to be <15 percent or recalibration and reanalysis of the affected samples was performed.

Matrix Spike Analysis

Matrix spikes were prepared for a minimum of 5 percent of the total number of samples analyzed and included each metal to be determined. Results from matrix spike analysis using the method of standard additions provide information on the extent of any signal suppression or enhancement due to the sample matrix. If necessary (i.e., spike results outside 80 to 120 percent limit), spiking frequency was increased to 20 percent and a correction applied to the metal concentrations of the experimental samples.

Duplicate Sample Analysis

Duplicate samples from homogenized field samples (as distinct from field replicates) were prepared in the laboratory for a minimum of 5 percent of the total samples. These laboratory duplicates were included as part of each set of sample digestions and analyses and provided a measure of analytical precision.

Procedural Blank Analysis

Two procedural blanks were prepared with each set of 40 samples to monitor potential contamination resulting from laboratory reagents, glassware, and processing procedures. These blanks were processed using the same analytical scheme, reagents, and handling techniques as used for the experimental samples.

SRM Analysis

A common method used to evaluate the accuracy of environmental data is to analyze SRMs, samples for which consensus or "accepted" analyte concentrations exist. The following SRMs were used: Marine Sediments BCSS-1 and MESS-2 (NRC); Buffalo River Sediment 2704 (NIST); Mussel Tissue 2976 (NIST); Dogfish Muscle DORM-2 (NRC); and Trace Elements in Water 1643d (NIST). Metal concentrations obtained for the SRMs were required to be within ± 20 percent of accepted values for >85 percent of other certified analyses. When no certified values existed for a metal, matrix spikes were used to evaluate analytical accuracy.

Filter Weighing

All weighing-related manipulation of the filters used for suspended particulate quantification took place under cleanroom conditions, including controlled temperature and relative humidity. Each filter was weighed twice in random order, with a minimum of 5 percent of the filters being weighed in triplicate. Static effects during filter weighing were controlled by placement of two ^{210}Po anti-static devices near the weighing pan within the balance. The standard deviation for the mass of each filter was required to be <2 μg for the value to be accepted.

2.4 Database Management

As part of the ANIMIDA program, MMS requested that the ANIMIDA data be incorporated into the MMS Coastal and Offshore Resource Information System (CORIS) database. This required database design and development to include the various data types generated by the ANIMIDA program into CORIS. Harvard Design and Mapping (HDM – Cambridge, MA) is subcontracted to ADL for completing the database design and data submission. Thus far, a study of the CORIS database design and structure has been performed. The CORIS structure has been expanded to include data for acoustics, water, sediments, peat, particles, and tissue chemistry. These data have been separated into tables with both field definitions and names that follow the existing CORIS structure. CORIS's metadata tables are being added to the metadata information from this environmental survey. An Entity Relationship diagram is being created to show how the environmental chemistry and acoustics data relate to each other and can be related to the metadata tables in CORIS. Spatial Database Engine (SDE) layers and scripts have been created for acoustics, water chemistry, and dry chemistry data. We will work closely with MMS to finalize our database design. Once the database design and structure are finalized, tables will be created using Oracle Structured Query Language (SQL) scripts. In addition, primary keys, foreign keys, sequence numbers, indices, and a data dictionary will be created prior to CORIS database submission of all ANIMIDA data. All final ANIMIDA data will be archived in the MMS CORIS database.

Table 2-2. Winter 2000 MMS ANIMIDA Stations Sampled.

Station ID	Station Type	Latitude	Longitude	Depth (m)	Ice Depth (m)	Date	Samples/Measurements			
							Suspended Particulates	Current, CTD, & PAR	Ice Core	Acoustics
5(5)	BSMP	70° 26.108	148° 18.090	6.5	1.6	4/27/00	1	1	1	1
LA2	Liberty	70° 18.970	147° 37.928	6.0	1.6	4/28/00	1	1	1	1
LA3	Liberty	70° 16.778	147° 33.529	6.1	1.6	4/28/00	1	1	1	1
NS-Trench1	Northstar	70° 28.806	148° 41.607	9.7	1.6	4/25/00	1	1	1	1
NS-Trench2	Northstar	70° 29.144	148° 42.197	10.4	1.6	4/25/00	1	1	1	
NA2	Northstar	70° 30.817	148° 36.351	10.8	1.7	4/26/00	1	1	1	1
NA3	Northstar	70° 29.569	148° 41.460	11.5	2.4	4/26/00	1	1	1	1
NA5	Northstar	70° 29.889	148° 40.734	11.8	1.8	4/29/00	1	1	1	1
NA6	Northstar	70° 30.372	148° 39.911	12.4	1.8	4/29/00	1	1	1	1

Note: All latitudes and longitudes in NAD83 datum.

Table 2-3. Saturated Hydrocarbons Target List

Compound	Reporting Code	Internal Standard/ Surrogate Reference	Compound	Reporting Code	Internal Standard/ Surrogate Reference
n-Octane (optional)	C8	A/1	n-Hexacosane	C26	A/1
n-Nonane	C9	A/1	n-Heptacosane	C27	A/1
n-Decane	C10	A/1	n-Octacosane	C28	A/1
n-Undecane	C11	A/1	n-Nonacosane	C29	A/1
n-Dodecane	C12	A/1	n-Triacontane	C30	A/1
n-Tridecane	C13	A/1	n-Hentriacontane	C31	A/1
Isoprenoid RRT 1380	1380	A/1	n-Dotriacontane	C32	A/1
n-Tetradecane	C14	A/1	n-Tritriacontane	C33	A/1
Isoprenoid RRT 1470	1470	A/1	n-Tetracontane	C34	A/1
n-Pentadecane	C15	A/1	n-Pentatriacontane	C35	A/1
Isoprenoid RRT 1650	1650	A/1	n-Hexatriacontane	C36	A/1
n-Hexadecane	C16	A/1	n-Heptatriacontane	C37	A/1
n-Heptadecane	C17	A/1	n-Octatriacontane	C38	A/1
Pristane	PRIS	A/1	n-Nonatriacontane	C39	A/1
n-Octadecane	C18	A/1	n-Tetracontane	C40	A/1
Phytane	PHYT	A/1			
n-Nonadecane	C19	A/1	<u>Surrogate Compounds</u>		
n-Eicosane	C20	A/1	Tetracosane-d ₃₀	D50T	A/1
n-Heneicosane	C21	A/1	5a-Androstane	5AA	B/1
n-Docosane	C22	A/1			
n-Tricosane	C23	A/1	<u>Internal Standard</u>		
n-Tetracosane	C24	A/1	triacontane-d ₃₀	D62T	1
n-Pentacosane	C25	A/1			

Internal Standard/Surrogate Reference indicates internal standard used for quantitation and surrogate compound used to correct analytical results

Also used in reporting:

TOTRES: Total of resolved compounds in sample extract

TPHC: Total of resolved and unresolved compounds in sample extract

Table 2-4. Polynuclear Aromatic Hydrocarbon and Alkyl Polynuclear Aromatic Hydrocarbon Target List

Compound	Reporting Code	Internal Standard/Surrogate Reference	Compound	Reporting Code	Internal Standard/Surrogate Reference
Naphthalene	C0N	A/1	Benzo[a]anthracene	BAA	B/3
C1-Naphthalenes	C1N	A/2			
C ₂ -Naphthalenes	C2N	A/2	Chrysene	C0C	B/3
C ₃ -Naphthalenes	C3N	A/2	C ₁ -Chrysenes	C1C	B/3
C ₄ -Naphthalenes	C4N	A/2	C ₂ -Chrysenes	C2C	B/3
			C ₃ -Chrysenes	C3C	B/3
			C ₄ -Chrysenes	C4C	B/3
Acenaphthylene	ACEY	A/2			
Acenaphthene	ACE	A/2			
Biphenyl	BIP	A/2			
			Benzo[b]fluoranthene	BBF	B/4
Fluorene	C0F	A/2	Benzo[k]fluoranthene	BKF	B/4
C ₁ -Fluorenes	C1F	A/2	Benzo[e]pyrene	BEP	B/4
C ₂ -Fluorenes	C2F	A/2	Benzo[a]pyrene	BAP	B/4
C ₃ -Fluorenes	C3F	A/2	Perylene	PER	B/4
			Indeno[1,2,3-c,d]pyrene	IND	B/4
Anthracene	C0A	A/3	Dibenzo[a,h]anthracene	DAH	B/4
Phenanthrene	C0P	A/3	Benzo[g,h,i]perylene	BGP	B/4
C ₁ -Phenanthrenes/Anthracenes	C1P/A	A/3			
C ₂ -Phenanthrenes/Anthracenes	C2P/A	A/3			
C ₃ -Phenanthrenes/Anthracenes	C3P/A	A/3			
C ₄ -Phenanthrenes/Anthracenes	C4P/A	A/3			
Dibenzothiophene	C0D	A/3			
C ₁ -Dibenzothiophenes	C1D	A/3	<u>Surrogate Compounds</u>		
C ₂ -Dibenzothiophenes	C2D	A/3	Naphthalene-d ₈	D8N	A/1
C ₃ -Dibenzothiophenes	C3D	A/3	Acenaphthene-d ₁₀	D10ACE	A/2
			Phenanthrene-d ₁₀	D10PH	A/3
Fluoranthene	FLANT	A/3	Benzo[a]pyrene-d ₁₂	D12BAP	B/4
Pyrene	PYR	A/3			
C ₁ -Fluoranthenes/Pyrenes	C1F/P	A/3	<u>Internal Standard</u>		
C ₂ -Fluoranthenes/Pyrenes	C2F/P	A/3	Fluorene-d ₁₀	D10F	A
C ₃ -Fluoranthenes/Pyrenes	C3F/P	A/3	Chrysene-d ₁₂	D12C	B

Internal Standard/Surrogate Reference indicates internal standard used for quantitation and surrogate compound used to correct analytical results.

2-ring PAHs include: naphthalenes, acenaphthylene, acenaphthene, biphenyl, and fluorenes

3-ring PAHs include: anthracenes, and phenanthrenes

4-ring PAHs include: fluoranthenes, pyrenes, benzo(a)anthracene, chrysenes, benzo(b)fluoranthene, and benzo(k)fluoranthene

5-ring PAHs include: benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(1,2,3-cd)pyrene, and dibenz(a,h)anthracene

Benzo(g,h,i)perylene is a 6-ring PAH

Table 2-5: Sterane and Triterpane Target List

Compound	Reporting Code	Internal Standard/ Surrogate Reference	Compound	Reporting Code	Internal Standard/ Surrogate Reference
C ₂₇ Diterpane	T4	A/1	Surrogate Compounds		
13b,17a-diacholestane(20S)	S4	A/1	n-Dotriacontane-d ₃₆	D66	1
13b,17a-diacholestane(20R)	S5	A/1	5b(H)-cholane	5B	2
C ₃₀ Tricyclictriterpane	T9	A/1			
C ₃₀ Tricyclictriterpane	T10	A/1	Internal Standards		
## 5a,14a,17a-cholestane(20R)	S17	A/1	Chrysene-d ₁₂	D12C	A
18a(H)-22,29,30-trisnorhopane(TS)	T11	A/1			
17a(H)-22,29,30-trisnorhopane(TM)	T12	A/1			
5a,14a,17a,24-methylcholestane(20R)	S24	A/1			
5a,14a,17a,24-ethylcholestane(20S)	S25	A/1			
5a,14a,17a,24-ethylcholestane(20R)	S28	A/1			
17a(H),21b(H)-30-norhopane	T15	A/1			
18a(H)-oleanane	T18	A/1			
17a(H),21b(H)-hopane	T19	A/1			
22S-17a(H),21b(H)-30-homohopane	T21	A/1			
22R-17a(H),21b(H)-30-homohopane	T22	A/1			
## 17b(H),21b(H)-hopane	T23	A/1			

Internal Standard/Surrogate Reference indicates internal standard used for quantitation and surrogate compound used to correct analytical results

Compound used in calibration, but not reported

Table 2-6: Summary of Instrumental Methods and Method Detection Limits for Metal Analysis of Sediment and Organisms

Metal	Sediments		Organisms	
	Method	MDLs ($\mu\text{g metal/g}$ dry sediment)	Method	MDLs ($\mu\text{g metal/g}$ tissue dry weight)
Ag – silver	ZGFAAS	0.01	ZGFAAS	0.004
Al – aluminum	FAAS	10	FAAS	2.3
As – arsenic	ZGFAAS	0.2	ZGFAAS	0.03
Ba – barium	ICP-MS	1	ICP-MS	0.01
Be – beryllium	ICP-MS	0.1	ZGFAAS	0.002
Cd – cadmium	ICP-MS	0.02	GFAAS	0.001
Co – cobalt	ICP-MS	0.5	GFAAS	0.3
Cr – chromium	FAAS	1	GFAAS	0.01
Cu – copper	FAAS	2	FAAS	0.7
Fe – iron	FAAS	10	FAAS	2.5
Hg – mercury	CVAAS	0.001	CVAAS	0.001
Mn – manganese	FAAS	3	FAAS	1.1
Ni – nickel	ICP-MS	0.5	GFAAS	0.01
Pb – lead	ICP-MS	0.2	ICP-MS	0.003
Sb – antimony	ICP-MS	0.1	ICP-MS	0.001
Tl – thallium	ICP-MS	0.05	ICP-MS	0.001
V – vanadium	FAAS	10	GFAAS	0.01
Zn – zinc	FAAS	2	FAAS	0.4
Other Parameters				
Grain Size	Sieve and Pipet	---		
TOC	Shimadzu Carbon System	0.1		

Notes:

CVAAS = Cold Vapor Atomic Absorption Spectrometry

FAAS = Flame Atomic Absorption Spectrometry

GFAAS = Graphite Furnace Atomic Absorption Spectrometry

ICP/MS = Inductively Coupled Plasma/Mass Spectrometry

MDL = Method Detection Limit

ZGFAAS = Zeeman Graphite Furnace Atomic Absorption Spectrometry

Table 2-7. Sample Containers, Preservation, and Laboratory List

Sample Type	Analysis	Precleaned Container	Storage/Preservative	Analytical Laboratory
Sediment	SHC, PAH, S/T	250 mL glass	Frozen -20°C	Arthur D. Little
Sediment	Metals, TOC, Grain Size	Plastic jar	Frozen -20°C	Florida Institute of Technology
Sediment	Grain Size	Plastic bag	Frozen -20°C	Florida Institute of Technology
Suspended Sediment (aqueous phase)	Metals	Plastic jar	Acidified	Florida Institute of Technology
Suspended Sediment (filtrate)	Metals	Plastic container	None	Florida Institute of Technology
Biota (Clams and Amphipods)	SHC, PAH, S/T, metals	250 mL glass	Frozen -20°C	Arthur D. Little (homogenate was sent to FIT for metals)
Source Samples – Sediment, Gravel, Peat	SHC, PAH, S/T	250 mL glass	Frozen -20°C	Arthur D. Little
Source Samples – Sediment, Gravel, Peat	Metals	Plastic jar	Frozen -20°C	Florida Institute of Technology
Source Samples – Sediment, Gravel, Peat	Grain Size	Plastic bag	Frozen -20°C	Florida Institute of Technology
Source Sample – Suspended Sediment (aqueous phase)	Metals	Plastic jar	Acidified	Florida Institute of Technology
Source Sample – Suspended Sediment (filtrate)	Metals	Plastic container	None	Florida Institute of Technology
Equipment Blank	SHC, PAH	250 mL glass	Frozen -20°C	Arthur D. Little
Equipment Blank	Metals	Plastic jar	Frozen -20°C	Florida Institute of Technology

Table 2-8. Data Quality Objectives for Saturated Hydrocarbon and Polynuclear Aromatic Hydrocarbon Analyses

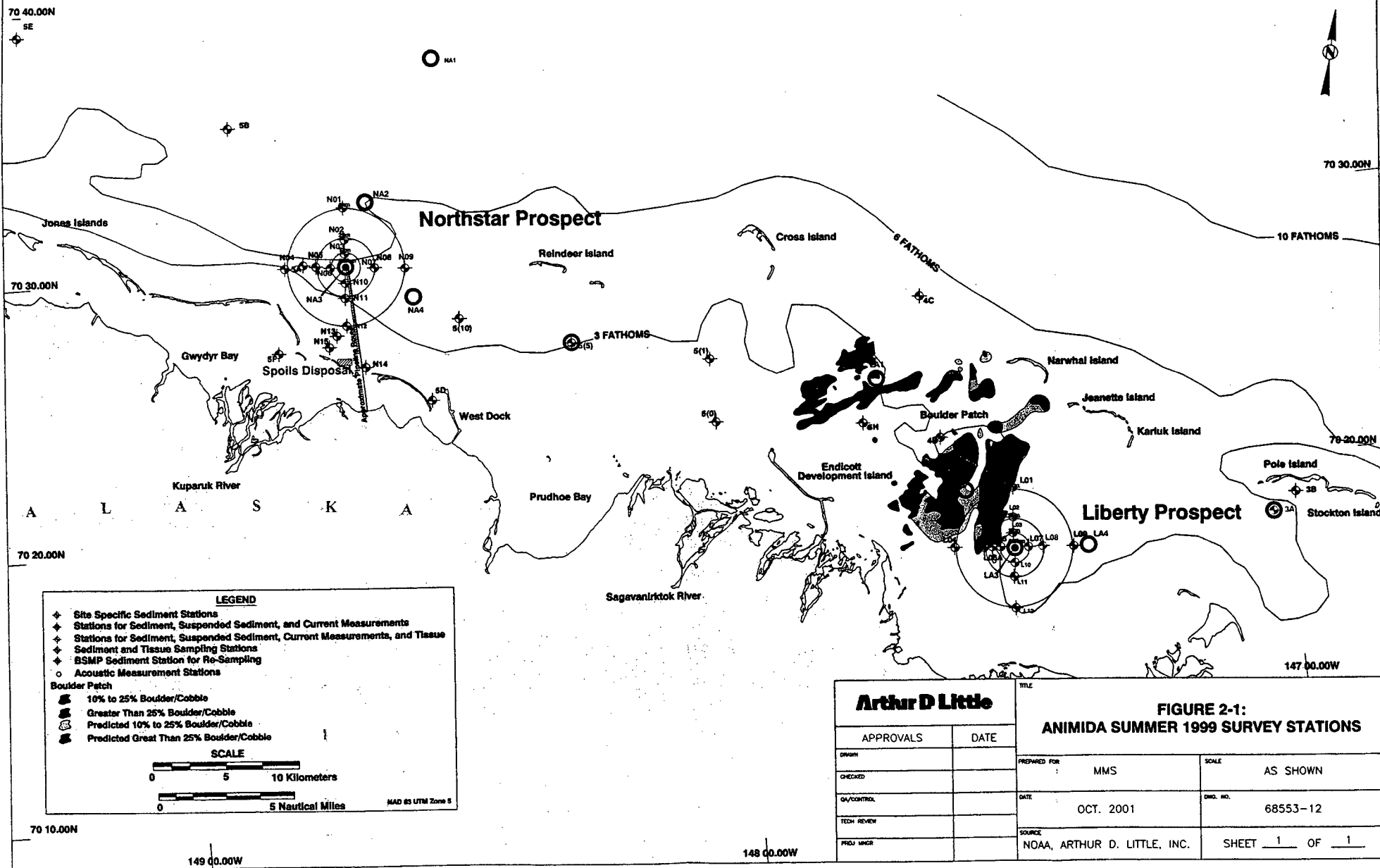
Element or Sample Type	Minimum Frequency	DQO/Acceptance Criteria
Initial Calibration	Prior to every instrument sequence for PAH analysis and as needed for SHC analysis	5-point curve, %RSD < 35% for all target analytes; 90% must be < 25%
Continuing Calibration	After every 12 samples or 16 hours, whichever is more frequent, and at end of instrument sequence	%D < 35% for all target analytes; 90% must be < 25%
Oil Reference Standard (North Slope Crude)	One with each instrument sequence (North Slope Crude)	%D < 35% from laboratory mean for target compounds (use surrogate-corrected values) except for compounds below the reporting limit
Procedural Blank	One per batch	No analyte to exceed 5 times the MDL unless sample amount is > 10 times blank amount
Blank Spike	One per batch	Recovery between 35 and 125% for PAH, and 45 to 125% for SHC
Instrument SRM (1491)	One per instrument sequence (PAH only)	Values must be <15% difference of true value for all certified analytes
Sediment SRM (1941a)/Tissue SRM (1974a)	One per batch as appropriate (PAH only)	Values must be within 30% of the true value on average for all analytes, not to exceed 35% of true value for more than 30% of the analytes
Laboratory Duplicate	One per 40 field samples	RPD < 30% for all analytes >10 times the MDL; Mean RPD <30%
Surrogate Recovery	Every sample	Recovery between 45 and 125% (35% for d8-naphthalene)

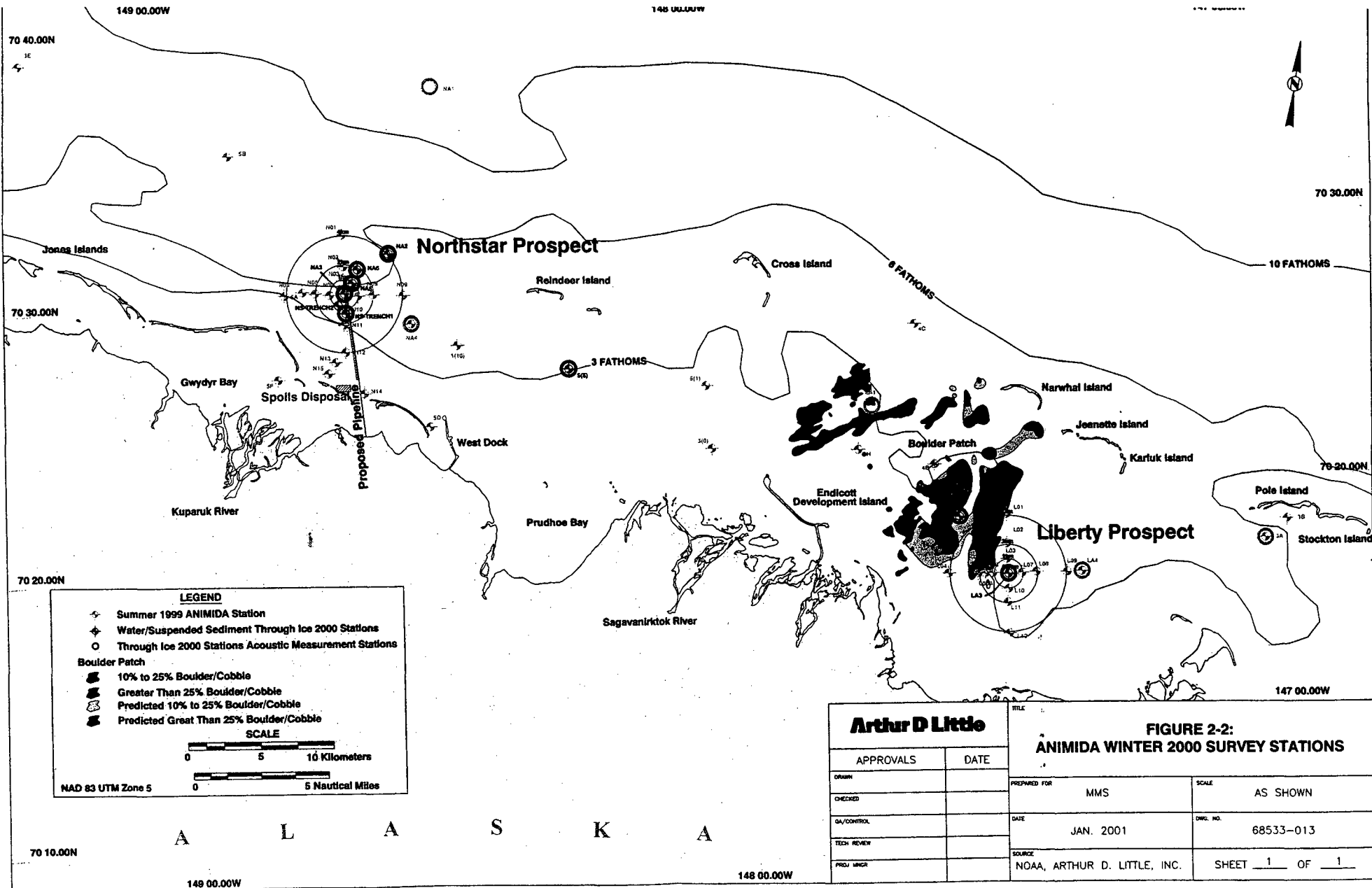
Table 2-9. Data Quality Objectives for Sterane and Triterpane Analyses

Element or Sample Type	Minimum Frequency	DQO/Acceptance Criteria
Initial Calibration	Prior to every instrument sequence	4-point curve, %RSD < 25% for all target analytes
Continuing Calibration	After every 12 samples or 16 hours, whichever is more frequent, and at end of instrument sequence	%D < 25% for all analytes
Oil Reference Standard (North Slope Crude)	One with each instrument sequence (North Slope Crude)	%D < 35% from laboratory mean for target compounds (use surrogate-corrected values) except for compounds below the reporting limit
Procedural Blank	One per batch	No analyte to exceed 5 times the MDL unless sample amount is > 10 times blank amount
Surrogate Recovery	Every sample	Recovery between 45 and 125%

Table 2-10. Data Quality Objectives and Criteria for Metals Analyses

Element or Sample Type	Minimum Frequency	DQO/Acceptance Criteria
Initial Calibration	Prior to every batch of samples	3- to 5-point curve depending on the element and a blank. Standard Curve correlation coefficient $r^2 \geq 0.999$ for all analytes
Continuing Calibration	Must end every analytical sequence; for flame, repeat all standards every 5 samples; for graphite furnace and ICP/MS recheck standard after every 8 to 10 samples	%RSD <15% for all analytes
Standard Reference Materials	One per batch of 20 samples	Values must be within 20% of accepted values for >85% of the certified analytes and within 25% for Hg.
Method Blank	One per batch of 20 samples	No more than 2 analytes to exceed 5 times MDL unless analyte not detected in associated samples
Matrix Spike and Spike Method Blank	One per batch of 20 samples	%RSD 80 to 120%
Laboratory Duplicate	One per batch of 20 samples	RSD <25% for 65% of the analytes





3.0 Results

This section presents the results for the general chemistry, organic, and inorganic analyses for the surficial sediment, suspended sediment, and ice core samples collected from the ANIMIDA study area in August 1999 and April 2000.

3.1 Surficial Sediments (0-1 cm)

The results and general trends in the TOC, grain-size, organic, and inorganic data from the surficial sediment samples collected during the summer 1999 ANIMIDA field survey are presented in this subsection. Results from the organic analyses of the river source samples are also discussed.

3.1.1 General Chemical and Physical Measurements

3.1.1.1 Total Organic Carbon and Grain Size

Surficial sediments from each station were analyzed for TOC and grain-size (percent gravel, sand, silt, and clay). The TOC values for surficial sediment samples range from 0.01 percent in the sandy sediment at station N01 to 3.42 percent in a mud-rich sample from station L06a (Table 3-1 and Appendix A). The mean value for TOC of 0.62 percent more closely represents the overall data set as most TOC values are <1 percent and only one value is >2 percent (Table 3-1). Considerable patchiness is found for TOC values across the study area, partly in response to similar patchiness in the occurrence of fine-grained sediment, as described below. Overall, the TOC concentrations are typical of values reported for Arctic shelf sediments. For example, Carsola (1954) reported a range of TOC values from 0.2 to 1.2 percent for Beaufort Sea sediments.

The grain-size results show similar variability to that described above for TOC. Gravel content (>2 mm) ranges from 0 percent at 30 locations to 46.9 percent at nearshore station N13 (Appendix A). Likewise, the clay content (<0.062 mm) varies from about 1 percent at several locations to 53.7 percent at station N06. Sediment resuspension, along with across- and along-shelf transport, are dynamic components of the inner shelf of the Beaufort Sea that certainly contribute to observed variations in grain-size distribution in the top 1 cm of sediment.

Based on the 1999 grain-size data, a few general trends can be observed. In the western portion of the study area, gravel was found at five locations, three of which (N12, N13, and N14) are just seaward of Gwydyr Bay and close to the inner line of islands (Figure 3-1). Most of the shallow-water, nearshore stations west of Endicott are dominated by sand, with little or no silt or clay (Figure 3-1). These locations are characterized by grounded ice during the winter and/or very active flushing during spring runoff. In the immediate area of the Northstar Prospect, just seaward of the stations with sand and gravel, the sediment is predominantly silt and clay (Figure 3-1). This area most likely represents at least a temporary depositional area for finer-grained sediments introduced during river runoff. At more-offshore stations such as N01, 5B, and 5E, the surficial sediment is again dominated by sand.

The trends in the area of the Liberty Prospect are more complex (Figure 3-2); however, several of the same general features can be observed. Gravel was collected at nearshore stations 4A and L12 and more sand was found nearer to shore than in the immediate area of the Liberty Prospect. A patch of mostly silt and clay was found near and to the east of the proposed site for the Liberty

Prospect (Figure 3-2). Once again, sediment from the more-offshore locations (e.g., 4C, 4B, and L01) contained predominantly sand. These trends will help focus future sampling efforts for both surficial and suspended sediment.

A good, positive relationship was found for TOC versus silt + clay as higher surface area sediment can adsorb larger amounts of organic matter (Figure 3-3). This trend is consistent with similar patchiness in the distribution of both grain-size and TOC. At silt + clay levels >80 percent, a wider range in concentrations of TOC is observed, effectively from about 0.7 to 2 percent, plus the one higher value at 3.4 percent. Variability in TOC levels and grain-size distribution throughout the area is certainly consistent with similar variability in the presence and abundance of benthic organisms such as amphipods and clams.

3.1.2 Organics

Organic parameter results for the surficial sediment samples are summarized in Tables 3-2 through 3-4. The summary results include total PAH (PAH – which includes the sum of all parent and alkyl PAHs), total petroleum hydrocarbons (TPHC – the sum of the resolved and unresolved saturated hydrocarbons n-C9 through n-C40), and total steranes and triterpanes (Total S/T – the sum of the sterane and triterpane target compounds). The data for each of these summary parameters are presented on a dry-weight sediment basis and results for field replicates are presented as the mean value with the standard deviation in parentheses. The results are separated into three regional groupings: BSMP stations (Table 3-2), Northstar stations (Table 3-3), and Liberty stations (Table 3-4). Within the BSMP station results, regional means for three historical BSMP-defined regions (Foggy Island, Endicott Field, and Kuparuk River) are provided for comparison to historical data. In addition, river and peat source sample summary data are included. Descriptions of key diagnostic parameters, which are useful in describing the overall organics dataset and will be used for comparisons to historical data and future ANIMIDA program data, are provided in Table 3-5. The complete organics data, including concentrations for individual PAH, SHC, and S/T target compounds, are included in Appendix B.

3.1.2.1 Saturated Hydrocarbons

Concentrations of TPHC in surficial sediments from the offshore study ranged from 0.21 to 50 mg/Kg. The TPHC concentrations were generally at low levels for most stations, with two notable exceptions: station 5D at 50 mg/Kg, and station L08 at 17 mg/Kg. The TPHC levels across the study area regions (Northstar, Liberty, and the three BSMP regions) are similar (mean TPHC concentrations of 2.3 to 7.1 mg/Kg), with the exception of the Kuparuk River BSMP region, which had a mean concentration of 15 mg/Kg (Tables 3-2 through 3-4). The mean TPHC was elevated in the Kuparuk River region relative to the other regions due to the higher concentration found at station 5D, which substantially raised the regional mean. The river sediment and peat samples were found to have TPHC levels substantially higher than the surficial sediments (Table 3-2). The high TPHC levels (ranging from 5.8 to 36 mg/Kg for all the river and peat samples) are likely due to the higher organic material content in these samples, as supported by the higher TOC values for these samples. Nonetheless, the composition of SHCs in the river sediment and peat samples was similar to the surficial sediments, indicating a common TPHC source relationship between the river sediments and the nearshore surficial sediments. For example, similar patterns are noted in the GC/FID chromatograms and PAH distribution

histograms for the Colville River (Figure 4-10), Northstar Station 6 (Figure 4-11), Liberty Station 6 (Figure 4-12), and BSMP Station 3A (Figure 4-13).

3.1.2.2 Polynuclear Aromatic Hydrocarbons

In general, low to moderate levels of PAH were encountered across the study area. The mean Total PAH concentrations at both the Liberty and Northstar regions were comparable and are considered in the low range for marine sediments (330 $\mu\text{g/Kg}$ and 380 $\mu\text{g/Kg}$, respectively; Boehm *et al.*, 1998). The Total PAH concentrations measured at the BSMP stations were generally within the same range, with means of 290 $\mu\text{g/Kg}$ and 340 $\mu\text{g/Kg}$ for the Foggy Island and Endicott Regions, respectively. When compared to the other BSMP regions, the Kuparuk River Bay region had an elevated mean Total PAH concentration (760 $\mu\text{g/Kg}$) due to the high PAH compound concentrations at station 5D. Station 5D had a total PAH concentration (2,700 $\mu\text{g/Kg}$) nearly an order of magnitude higher than the means for the other regions. When the results for Station 5D are excluded, the regional mean Total PAH concentration for the Kuparuk River Bay region is 270 $\mu\text{g/Kg}$. (Station 5D also had high Total PHC and SHC results.) This result suggests that there may be PAH contamination at this station, which is adjacent to an area of high construction and development activity (*i.e.*, West Dock). Overall, the levels of PAH measured are well within the range of values reported from previous studies of the region and other Alaskan coastal areas (Table 3-6).

The total PAH concentrations in the Colville River sediment and peat samples are also nearly an order of magnitude higher than those for the Northstar, Liberty, and BSMP regional means (Tables 3-2 through 3-4). Similar to the SHCs, the enrichment in PAHs is associated with the higher organic material content in these samples as supported by the higher TOC values. The exceptions to this trend are the Kuparuk River sediment and peat samples and the Sagavanirktok River sediment sample, which have lower total PAH concentrations with a corresponding high organic carbon content.

3.1.2.3 Steranes and Triterpanes

Biomarker analyses were only performed on a selected subset of samples, so no regional means have been generated for comparisons; however, the S/T concentrations in the surficial sediment samples are quite low. The total S/T concentrations range from 6.5 $\mu\text{g/Kg}$ at station N14 to 490 $\mu\text{g/Kg}$ at station 5D. With the exception of station 5D, total S/T concentrations were less than 100 $\mu\text{g/Kg}$ for all analyzed samples. The total S/T concentrations in the river and peat are somewhat higher, but are at levels expected to correspond to the other measured organic parameters.

3.1.3 Metals

All surficial sediments, (top 1 cm) were analyzed for total concentrations of Ag, Al, As, Ba, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Sn, Tl, V, and Zn (Table 3-1 and Appendix C). The resulting data show that average concentrations for each metal in sediment from throughout the study area are similar to or less than values for average continental crust, except for Ag, Cd, and Sb, with concentrations that are enriched by a factor of 1.5 to 2 (Table 3-1). These apparent enrichments appear to be natural for the area and are discussed in Section 4.

Concentrations of metals show a similar degree of patchiness throughout the study area to that shown above for TOC and grain-size (Tables 3-1, 3-7, 3-8, and 3-9). One way to demonstrate this variability is to compare calculated values of [maximum/minimum] for each metal for all sediment samples from throughout the study area. For Ba, the value for [maximum/minimum] is lowest at ~5 (753/155), whereas for Cd, the value for [maximum/minimum] is greatest at ~16 (0.79/0.05). Overall, for all 18 metals studied during 1999 in sediment from the ANIMIDA study area, the average value for [maximum/minimum] is ~8. This average of an 8-fold range for metals values in sediments shows the large variation in absolute concentrations for metals in sediment. Fortunately, metal concentrations vary in response to variations in grain-size and TOC; thus a predictable normalization process can be developed to simplify comparisons among samples. This process will be discussed in Section 4.1.

Within the data set, the highest concentrations of Cd, Hg, and Pb were found at station 5D near West Dock (Table 3-7). The highest concentrations of Ag, As, Co, Cu, and Ni in sediments also were found at station 5D (see Appendix C). Nearby at station 5(10), the highest concentrations of Ba and an elevated level of Pb were determined (Table 3-7). Station 5A was also characterized by higher concentrations of Hg and Pb (Table 3-7). The area around West Dock was certainly active during 1999 and this area may warrant more detailed monitoring during future efforts.

In the area of the Northstar Prospect, the lowest metal concentrations were found in the sandy, nearshore sediment at stations N12, N13, N14, and N15 (Table 3-8). In accordance with the grain-size distribution, the highest levels of metals occurred in a cluster of stations (N03, N04, N05, and N06) with silty sediment (Table 3-8). In the immediate area of Liberty Prospect, no clear trends in grain-size or metal distribution were observed. The highest metal levels were found at stations L02, L03, and L06 and the lowest metal values were observed at nearby station L04 (Table 3-9).

Some variability is also observed in metal concentrations for sediment samples collected from the same location during separate deployments of the grab sampler. Triplicate grab samples were collected from stations 5(1) and L11 during 1999. At station 5(1) in 1999, concentrations of Al were very uniform with a coefficient of variation (CV = [standard deviation/mean] x 100 percent) of only 2.4 percent (Table 3-1a). In contrast with station 5(1), concentrations of Al at station L11 were more variable (Table 3-1a). The observed variability among samples from the same station is related to variations in sediment grain-size. As described below, and in more detail in Section 4, these variations can be normalized. Direct comparisons of absolute concentrations of metals in sediments should be avoided in preference for normalized values (metals ratioed to Al).

The patchwork of metal concentrations throughout the study area can be unified by normalizing metal values to either Al or Fe and thereby removing variations in metal concentrations that result from differences in grain-size, TOC, and/or mineralogy. For example, Figure 3-4 shows a strong, positive relationship between Al and grain-size, expressed either as percent silt + clay or just percent clay. The finer-grained material is richer in Al-bearing clays, whereas the coarser-grained sediment contains Al-poor quartz sands and carbonate shell fragments. The TOC data

also correlate relatively well with grain-size (Figure 3-3) and Al, thereby supporting the utility of Al as a normalizing element.

Iron concentrations correlated extremely well ($r = 0.97$) with Al levels (Figure 3-5). Thus, either element can be used to normalize the other metal concentrations. One example of a metal/Al plot is given for V (Figure 3-5b) to show the effectiveness of the normalization process. Even though individual metal concentrations are extremely variable from station to station, these differences can be explained by variations in grain-size, TOC, and/or mineralogy when normalized to Al. Concentrations of V and other metals follow Al in that higher levels are found in aluminosilicate clays and lower levels are found in quartz and carbonate sands. Thus, plots such as shown in Figure 3-5 show the natural trend (*i.e.*, V/Al ratio) for area sediments. Positive deviations from a prediction interval constructed around the regression line can often be related to anthropogenic inputs of that metal. This concept is developed in detail in Section 4.

Concentrations of methyl Hg were determined for a subset of 30 sediment samples. Mean concentrations of methyl Hg were 0.37 ± 0.36 ng/g with a range of <0.01-1.41 ng/g (Appendix C). The percent of total Hg that was methyl Hg averaged 0.7 ± 0.4 percent with most sediments having <1 percent of the total Hg present as methyl Hg (Figure 3-6).

3.2 Suspended Sediments

3.2.1 Physical Measurements

3.2.1.1 Turbidity and Total Suspended Solids – August 1999

Concentrations of suspended particles in the water column were determined during open-water (August 1999) and under-ice (April 2000) conditions by the following three methods: vertical profiles of *in situ* turbidity (nephelometric), laboratory analysis of turbidity using discrete samples, and filtration of water for TSS (Appendices D and E). Interrelationships among the three techniques were good. Values for laboratory turbidity (in nephelometric turbidity units, or NTU) correlated well with values for TSS (Figure 3-7); both measurements were made using the same discrete sample. For ease of comparison, values for TSS in mg/L are approximately equal to twice the turbidity in NTU (Figure 3-7). Direct comparison of laboratory turbidity with *in situ* turbidity is more complicated because of the greater sample depth (z) integrated by the water bottle (about 1 m) versus the vertical path width of the *in situ* turbidimeter (<1 cm). However, the *in situ* and laboratory turbidity values compare well at levels <50 NTU (Figure 3-8). Only two data points at high turbidity levels show an inconsistency with the linear trend. Additional data are needed at these higher levels to expand the trend presently identified in Figure 3-8. Overall, each of the three independent measures of water clarity can be calculated from one of the other measurements.

Turbidity (laboratory) and TSS during the open-water period of August 1999 ranged from 1.8 to 75 NTU and 2.9 to 119 mg/L, respectively, with the large variations due mostly to changes in wind conditions. The overall variation in turbidity is best explained using *in situ* data from station N13 for three different dates (Figure 3-9). During the first sampling at station N13 on August 18, 1999, the wind was almost calm (<5 knots) and there was a sizeable amount of nearshore floating ice. Turbidity (*in situ*) levels during these calm conditions were about 2 to 3 NTU at stations N13 (Figure 3-9) and N14, the only two locations to be sampled before 6 days of

>25 knot (kt) winds from the northeast. Immediately after the storm subsided, *in situ* turbidity levels on August 25 were as high as 80 NTU, decreasing to about 40 NTU two days later on August 27 (Figure 3-9). Thus, the maximum and minimum turbidity and TSS levels were recorded at the same station, one week apart. Under relatively calm winds (<5 kts) during late summer, turbidity levels are likely to be <3 NTU (TSS <5 mg/L) and under high winds (>25 kts), turbidity may be in excess of 80 NTU.

One spatial view of turbidity in the area of the Northstar Prospect is obtained using the data from August 25, 1999 (Figure 3-10). At stations N05 and N08, where water depths are about 11 m, the vertical profiles for *in situ* turbidity are very similar with a gradual increase from about 10 NTU at the surface to about 20 NTU near the bottom (Figure 3-10). In somewhat shallower water, about 2 km closer to shore, the turbidity in the surface water is closer to 20 NTU, increasing to 50 NTU near bottom (7.5 m). Finally, at station N13 (water depth ~4 m), the turbidity was markedly higher.

Shifts in turbidity are clearly related to wind and water current velocities. Recent data from Dr. Tom Weingartner's (University of Alaska at Fairbanks) year-long deployment of a current meter and transmissometer arrays will help to develop a clearer seasonal picture relating turbidity with water movement. Our single-point-in-time measurements at station N13 show a current velocity of 20 cm/sec and less on August 18, 1999, just prior to the storm (Figure 3-11). Following the storm, after the wind speed and wave height had already decreased greatly, current velocities still approached 40 cm/sec (Figure 3-12). In each case, water flow was parallel to the adjacent barrier islands. The infusion of colder, offshore water during the storm also was evident in the August 25 profiles (Figure 3-12). During the upcoming year, we will collaborate with Dr. Tom Weingartner to fill in the details on current velocities and link his transmissometer data with our nephelometer and TSS results.

Hydrography data for station N05 (Figure 3-13) show that current velocities of 10 to 20 cm/sec are coincident with *in situ* turbidity values of 12 to 21 NTU. Similar water conditions were observed at stations N08 and N11. Data for TSS also are available for these stations, with concentrations of about 20 to 30 mg/L at most depths, excluding a TSS level of 56 mg/L in a near-bottom nepheloid layer at station N11.

Vertical profiles for *in situ* turbidity in the area of the Liberty Prospect (L05, L08 and L11) were similar, with levels of 5 to 10 NTU throughout most of the water column and increasing to about 20 NTU on approach to the water-sediment interface (Figure 3-14). Current velocities at these three stations ranged from 5 to 15 cm/sec. Turbidity levels at 4B were significantly greater than at the other stations, most likely in response to greater current velocities of 30 to 40 cm/sec. Station 3A, in the lee of Pole Island, had turbidity levels similar to those near Liberty Prospect and lower than the open waters at station 4B.

3.2.1.2 Turbidity and Total Suspended Solids - April 2000

Turbidity (laboratory) and TSS during the ice-covered period of April 2000 ranged from 0.15 to 1.35 NTU and 0.14 to 2.0 mg/L, respectively. These levels are 10 to >100 times lower than values obtained during the open-water period of August 1999 and provide a good overview of turbidity and TSS under the 1.6- to 2.4-m-thick layers of sea ice (Table 3-10). The lowest levels of turbidity and TSS were observed at the more-offshore stations of NA2, 5(5), and LA2 (Table

3-10), where the overall average value for TSS was 0.25 ± 0.06 mg/L. The vertical profiles for transmissivity show >80 percent light transmittance, consistent with low and relatively uniform turbidity throughout the water column (Figure 3-15).

Temperatures were very uniform and near freezing at -1.8°C at each station, except in the slightly more-saline water at station LA2 (Figures 3-16 and 3-17). Likewise, salinity values were relatively uniform from station to station, excluding the more-saline water at station LA3 and somewhat lower salinity at station 5(5). A minor increase in salinity was observed at total depths (ice+water) >11 meters (m) at stations NA5 and NA6. Current movement was at 1 to 4 cm/sec, and generally from the northwest or southeast. Under-ice currents tend to be tidally influenced and follow the contours of the adjacent islands with diurnal shifts in direction. No simple relationship was observed between turbidity and current speed at the low levels of both parameters.

Backfilling of the pipeline trench from Northstar to the mainland was ongoing during the April 2000 sampling trip. Although the winter sampling plan was designed to determine background levels of turbidity and TSS under ice, water sampling was carried out at 5 locations in the Northstar area to investigate the influence of the backfilling process on turbidity. Station NT1 was about 200 meters east and downstream of the backfilling operation. The transmissivity data show a marked decrease in light transmission at total depths >8 m (Figure 3-18). Turbidity in the sample collected at 9 m (ice + water) was 1.35 NTU, about 3 to 4 times greater than found at more distant areas. Concentrations of TSS were 2.0 and 1.5 mg/L at a total depth of 9 m at station NT1, about 5 to 8 times greater than apparent background levels. Due to a minor instrument malfunction, the transmissometer data shown were collected on the day following water column sampling. At station NT2, about 300+ m northwest of the backfilling operation, transmissivity was lower than background levels, but rather uniform between 3 and 10 m. Values for TSS were elevated at 0.5 mg/L at a total depth of 3 m, but somewhat higher than background levels of 0.25 mg/L, at 6 m (0.38 mg/L), and 9 m (0.35 mg/L). Current velocities at stations NT1 and NT2 averaged about 2 cm/sec.

At increased distances from Northstar Island (NA3, ~500m; NA5, ~1 km; and NA6, ~2 km), values for TSS averaged 0.32 ± 0.15 mg/L and were comparable with background levels. The transmissivity profiles show uniform and high transmissivity throughout most of the water column with a small, apparent near-bottom nepheloid layer that is possibly an artifact of sampling. However, bottom currents were as high as 4.6 cm/sec. In addition, reduced transmissivity was also observed at a total depth of about 4 m at station NA3.

3.2.1.3 Particulate Organic Carbon – August 1999

Concentrations of particulate organic carbon (POC) averaged 2.4 ± 0.9 percent of the TSS throughout the study area, with a range of 1.2 to 4.8 percent. Although all POC values >4 percent were obtained for surface water samples, the overall average of surface samples versus subsurface samples was only 2.6 percent relative to 2.2 percent. Average organic carbon values for these suspended sediments are about 4 times greater than the mean level of 0.6 percent in surficial sediments from the area. Higher organic carbon levels in suspended sediment are most likely the combined result of the presence of plankton in the water column and resuspension of finer-grained, more organic-rich sediments. When the POC values are expressed in $\mu\text{g/L}$, they

average 580 ± 420 $\mu\text{g/L}$, ranging from 130 $\mu\text{g/L}$ in the calm waters of station N13 on August 18 to 1,300 $\mu\text{g/L}$ in a near-bottom sample from N11 after the storm.

3.2.1.4 Particulate Organic Carbon – April 2000

Concentrations of POC averaged 10 ± 3 percent of the TSS throughout the study area with a range of about 8 to 14 percent. Average organic carbon values for these suspended sediments from under the ice are about 4 times greater than the mean level for the suspended sediment during August 1999 and about 16 times greater than values of 0.6 percent in surficial sediments from the area. When the POC values are expressed in $\mu\text{g/L}$, they average about 80 ± 50 $\mu\text{g/L}$, ranging from 24 $\mu\text{g/L}$ at station NA6 to 164 $\mu\text{g/L}$ at station NT1. These levels are about 5 to 50 times lower than determined during August 1999. Thus, the particles under the ice are somewhat more organic-rich, but far less abundant.

3.2.2 Metals

3.2.2.1 August 1999

Concentrations of metals in suspended sediment samples collected during August 1999 were very uniform throughout the area, with the values for the RSD [(standard deviation/mean)*100%] for the complete data set less than or equal to 10 percent for Al, Ba, Cr, Fe, and Zn (Table 3-11). Somewhat higher values for the RSD for Cd (45 percent), Cu (19 percent), and Pb (24 percent) result from one or more anomalous values, as discussed below. The spatial uniformity in metal concentrations is further demonstrated in Table 3-11 with separate summary data for the BSMP, Northstar, and Liberty stations.

When compared with values for surficial sediment, metal concentrations in suspended particles are 2.0 ± 0.2 times higher, with the exception of Cd with levels that are 3 times higher in suspended sediment (Table 3-11) than surficial sediment (Table 3-1). Despite these higher absolute values for metals in suspended sediments, the ratios of the various metals to Al are consistent with the previously discussed results for surficial sediments (Figure 3-19). All of the data for Fe, Ba, Cr, and Zn plot within the 99 percent prediction intervals established for these metals versus Al from the sediment results (Table 3-11). However, these data are all skewed toward high Al and metal levels because fine-grained clays that are naturally rich in Al and trace metals dominate the suspended sediment.

Two suspended sediment data points for Cu (stations N13 and N14) plot above the upper-prediction interval in the Al versus Cu plot (Figure 3-19c). Surficial sediment from these stations was not enriched with Cu; however, sediment from nearby station 5D did have high Cu levels. The same sample of suspended sediment from station N14 that was enriched with Cu also contained high levels of Pb, at 43 $\mu\text{g/g}$.

The most distinct behavior for metals in suspended sediment was found for Cd, with concentrations that ranged from 0.3 to 1.4 $\mu\text{g/g}$ in suspended sediment relative to 0.05 to 0.8 in surficial sediment. Cadmium is often taken up at high levels naturally in plankton. This process and other scenarios are discussed later in Section 4.

3.2.2.2 April 2000

Concentrations of metals were determined in some suspended sediment samples collected during April 2000, even though the levels of TSS were extremely low. The Fe and Al concentrations of

the suspended sediment under the ice averaged 4.07 ± 0.76 percent and 4.45 ± 1.09 percent, respectively. The mean Fe content of the particles collected under ice was almost the same as the mean Fe level of 3.92 percent found during the open-water period. However, the Al content of the under-ice particles was about 40 percent lower than the mean value of 7.48 percent Al during the open-water period. The decrease in the Al content of the particles collected under ice is partially explained by dilution of aluminosilicate material with organic matter because the concentration of particulate organic matter (~3 times the organic carbon level) increased from ~7 percent to ~30 percent. At the same time, the Fe content of the particles remained the same. Assuming that the Fe levels were not impacted by contamination during sampling, the data suggest that a separate, more Fe-rich phase was associated with the under-ice particles. When the Fe/Al ratios for particles collected under ice are compared with data from the open-water samples (Figure 3-20), the under-ice particles contain Fe at levels that are 1.5 to 2.5 percent (of TSS mass) higher than the open-water samples. Adsorption of iron hydrous oxides on these fine-grained particles may account for the observed shift in the Fe/Al ratio (Figure 3-20). Furthermore, organic-rich (12.5 percent organic carbon) suspended sediment from the Kuparuk River, collected during August 1999, was enriched with Fe, as shown with the two inverted, orange triangles in Figure 3-20.

Concentrations of Ba in the suspended sediment collected under the ice also show enrichment relative to Al, as shown for Fe (Figure 3-20). The organic-rich samples from the Kuparuk River also show this trend. One possible explanation for this trend is that a fine-grained, almost colloidal Fe fraction is present in the water column at all times, and can only be easily discriminated at very low levels of TSS. Concentrations of the other trace metals are more variable; however, the same general trend of higher levels of Cd, Cu and Pb are observed relative to Al in the under-ice samples. In some cases where TSS levels were low (<0.2 mg/L), some concern for sample contamination exists. For example, dissolved Pb levels were determined for 4 samples, to help assess the possibility for sample contamination due to a gas-powered auger and the difficulties of collecting and transferring samples out on the ice. In two cases, dissolved Pb levels were $0.009 \mu\text{g/L}$ and seem reasonable; the suspended sediment samples also contained plausible levels of Pb at 36 and $56 \mu\text{g/g}$. In the other two instances, the dissolved Pb levels were 0.049 and $0.084 \mu\text{g/L}$ and the particles contained Pb at 184 and $297 \mu\text{g/g}$. Considering that previously, no data were available for TSS under the ice, a solid increase in knowledge has occurred. However, these data indicate that as Phase II evolves, extreme caution needs to be exercised in the field and the field laboratory to minimize contamination. Furthermore, concentrations of dissolved metal levels should be made in tandem with particle metal determinations to help to better assess data quality.

3.2.3 Stable Carbon Isotopes (δC^{13})

The $^{13}\text{C}/^{12}\text{C}$ ratio was determined for samples of surficial sediment, suspended sediment, and source material from throughout the study area. The results are expressed as δC^{13} , where

$$\delta\text{C}^{13} = \{ [(^{13}\text{C}/^{12}\text{C})_{\text{sample}} / (^{13}\text{C}/^{12}\text{C})_{\text{PDB standard}}] - 1 \} \times 1000$$

and the standard is PDB. Values for δC^{13} in surficial sediment average about -23 per mil (Table 3-12) for all three areas (BSMP, Northstar, and Liberty). Relative to the surficial sediment, the δC^{13} in samples of suspended sediment were more negative (richer in ^{12}C relative to ^{13}C than the

surficial sediment) at about -28 to -31 per mil (Table 3-12). The river suspended sediment had δC^{13} values closer to the values for suspended sediment from the coastal Beaufort Sea, whereas the river sediment had δC^{13} values closer to those for surficial sediment from the coastal Beaufort Sea (Table 3-12).

The carbon isotope data can be used to help identify the sources of organic carbon to surficial and suspended sediments in the area. The potential sources include terrigenous and marine materials (Table 3-13). The terrigenous component can be characterized isotopically using peat and grass ($\delta C^{13} = -28.5 \pm 1.3$ per mil) and river suspended sediment ($\delta C^{13} = -30.3 \pm 0.5$ per mil) and the marine component can be defined using amphipods ($\delta C^{13} = -19.1 \pm 0.6$ per mil) and plankton ($\delta C^{13} = -22 \pm 2$ per mil). The δC^{13} data for peat, grass and plankton are taken from earlier work by Schell (1983) and therefore may not be exactly comparable with the new values reported here. Collection of peat and plankton samples is planned for the ANIMIDA study to ensure an internally consistent data set. The suspended sediment collected from the study area during August 1999, with a $\delta C^{13} = -29.2 \pm 4.5$ per mil, seems to have a predominantly terrigenous source, with δC^{13} values that are more in line with river suspended sediment, peat, and grass. In contrast, surficial sediment from the study area has a carbon isotope signature that is much closer to values found for marine amphipods and plankton than terrigenous peat and grass (Table 3-13). This information will be used to discuss the overall cycling of sediment, metals, and carbon later in the discussion section.

3.2.4 Ice Cores

Ice cores were collected at all nine stations during the April 2000 sampling expedition. As specified in the sampling plan, each core was subdivided into 2 to 3 sections. Each core was thawed upon return to the field laboratory, the volume measured, and the particles in the core obtained by filtration. Concentrations of particles in the ice cores were highly variable, ranging from 1.2 to 248 mg/L. In general, concentrations of particles were lowest in the deeper portions of each core. At depths >100 cm in the cores, the mean concentration of particles was 4.2 mg/L, with only one value >3 mg/L. In contrast, the mean value for particles in the upper 100 cm of the cores was 54 mg/L. At station LA2, for example, the values for sediment in the ice cores were as follows: 205 mg/L (0 to 55 cm), 2.6 mg/L (55 to 95 cm) and 1.8 mg/L (95 to 155 cm). Even at a more-offshore station (NA2), the same trend was observed with 11 mg/L (0 to 35 cm), 3.6 mg/L (35 to 70 cm) and 1.8 mg/L (70 to 150 cm).

The distribution of sediment in the ice cores is consistent with the pattern of formation of this sea ice. The top layer (as sampled) forms first and freezes the suspended sediment in the ambient water into the ice matrix. Storms during the fall seasons can keep the TSS at levels of >10 to 100 mg/L. Some time after the top layer of ice forms, the energy of the underlying water is dramatically decreased and suspended particles slowly settle out such that the later ice that forms from the water below contains considerably lower levels of sediment.

Data for Fe and Al in sediment from the ice cores provide some additional insight into differences between the composition of particles during the open-water and under-ice seasons (Figure 3-21). The blue hexagons in Figure 3-21 are for samples from the top layers of the ice cores, where sediment loading was higher and where ice had frozen with ambient particles suspended during late summer and fall. The Fe/Al ratios for these sediments recovered from the

ice cores are consistent with the composition of suspended particles collected from the open water during August 1999. The green hexagons (Figure 3-21) are mainly for samples collected from the lower layers of the ice cores, where suspended sediment was derived from the under-ice environment. Sediment from deeper in the ice cores has a Fe/Al ratio that is consistent with the under-ice suspended particles (gray circles in Figure 3-21). These results strengthen the argument that the under-ice particles are more Fe-rich. Particles coated with iron hydrous oxides can adsorb very large quantities of various metals, such as Pb and Cd, among others. Such under-ice geochemical processes provide an interesting scenario for overall cycling of metals in the coastal Beaufort Sea that will be discussed briefly in Section 4 and studied in more detail during Phase II using scanning electron microscopy, energy-dispersive x-ray analysis, and more samples of water and suspended particles.

3.3 Tissues

3.3.1 Organics

SHC and PAH measurements were made in pooled samples of amphipods (*Anonyx spp.*), and clams (*Astarte* and *Cyrtodaria*) at stations where sufficient organisms could be collected. Sterane and triterpane measurements were also determined for four of the biota tissue samples. The concentrations of Total PAH, Total PHC, and Total S/T are presented in Table 3-14 (wet-weight basis). In general, the concentrations of all organic target compounds in the tissue of all species were quite low. Total PAH concentrations range from 13 to 80 µg/Kg, Total PHC values were measured between 1 and 18 mg/Kg, and the Total S/T concentrations in the four samples analyzed ranged from 5.5 to 18 µg/Kg.

3.3.2 Metals

Concentrations of Ag, Al, As, Ba, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Sn, Tl, V and Zn were determined for samples of amphipods (*Anonyx*) and clams (*Astarte* and *Cyrtodaria*) at stations where they could be found. Concentrations of selected metals are presented on a dry-weight basis for pooled samples in Tables 3-15 and 3-16. Data for water content are included with the complete dataset in Appendix C so that metal concentrations can also be calculated on a wet-weight basis.

Metal concentrations in the three pooled samples of amphipods (*Anonyx sp. small*) from the Northstar and Liberty areas were very similar (Tables 3-15 and 3-16 and Appendix C) with values for the RSD values that were <10 percent for Ag, Cu, Mn, Tl, V, and Zn and <25 percent for As, Ba, Be, Cd, Co, Fe, Hg, Ni, Pb and Sb. In contrast, the larger amphipods (*Anonyx sp. large*) from offshore station 5B had 2 to 3 times lower levels of Ag, Ba, Co, Cu, Fe, Mn, Pb, and V, yet 2 to 3 times higher levels of As, Cd, Cr, Hg, and Zn (Tables 3-15 and 3-16). Station 5B is in deeper water (~15 m) on the open shelf relative to the other stations at water depths <8 m. With only a single sample of the larger *Anonyx*, attempts at explaining observed differences in metal levels would be premature.

Metal concentrations in the four pooled samples of clams (*Astarte*) from the Northstar and Liberty areas also were relatively similar among samples (Tables 3-15 and 3-16, and Appendix C), with values for the coefficient of variation ([standard deviation/mean] x 100%) that were <15 percent for As, Ba, Hg, Pb, Tl, V, and Zn and <25 percent for Ag, Cd, Fe, Mn, and Sb. The

second clam species (*Cyrtodaria*) was analyzed as a lab duplicate with precision better than 10 percent (as a coefficient of variation [CV]) for each element.

3.4 Quality Control Results

This section provides an evaluation of the quality and usability of the environmental data based on the results for the field and laboratory QC samples collected and analyzed during this program. Tables 3-17 through 3-19 summarize the organic field and laboratory QC results. Tables 3-20 through 3-23 summarize the inorganic field and laboratory QC results.

In general, no serious data quality issues were noted that would adversely affect the quality or use of the organic or inorganic data. All reported data are usable for project objectives.

3.4.1 Field Quality Control

Field QC samples were collected to assess overall precision, accuracy, and representativeness of the sampling and analytical efforts. The results for the field QC sample analyses are presented in Appendices A through E, along with the associated environmental samples. Discussion and interpretation of the results are provided in the following sections.

Equipment and field blanks were collected to assess potential sample contamination introduced from sample collection and handling procedures. Replicate field samples were collected to assess sample representativeness and precision relative to sample collection procedures and sample matrix.

Field QC also included the verification of field instrument calibrations prior to use as described in Section 2.3. All field instruments passed their calibration and QC checks.

3.4.1.1 Equipment Blanks

One equipment blank was collected and submitted for analysis during the sediment sampling event. This sample was collected from a rinse of the grab sampling equipment at station N15, after decontamination of the equipment. PAH, SHC, and metals analyses were performed on this equipment blank. The equipment blank results were evaluated to assess the potential for cross-contamination of samples due to inadequate sampling equipment decontamination.

Two PAH compounds, naphthalenes and biphenyl, were detected at very low concentrations in the equipment blank. Both of these compounds were detected at concentrations below the reporting limit (RL) and less than 5 times the MDL; the total PAH concentration in this blank was 0.16 µg/L. Trace concentrations of several straight-chain alkanes (*i.e.*, n-C26, n-C27, n-C28, and n-C36) were detected in the equipment blank. These compounds were detected at concentrations less than 1/10 the RL and less than 5 times the MDL; the total SHC concentration in this blank was 99 µg/L, less than ¼ the RL. Concentrations of all metal analytes in the equipment blank were less than 5 times the MDL.

These results indicate that the decontamination procedures used on the sediment sampling equipment were adequate and would have minimized the potential for sample cross-contamination.

3.4.1.2 Field Blanks

One field (deck) blank sample was taken during the collection of sediment samples. PAH, SHC, and metals analyses were performed on this field blank. The field blank results were evaluated to assess the potential for atmospheric or other contamination that the field samples may have been subject to during sample collection.

The concentrations of all metal analytes were less than 5 times the MDL and no PAHs or SHCs were detected in the field blank, indicating that samples were not subject to atmospheric or other contamination during sample collection.

3.4.1.3 Field Replicates

Two sets of field replicate samples were generated during the collection of the sediment samples in the form of triplicate samples collected at sampling stations 5(1) and L11. The field replicate results were evaluated to assess analytical precision relative to sample collection procedures and sample matrix.

For the triplicate samples collected at sampling station 5(1), the majority of the PAH and SHC results were detected at concentrations near or below the sample-specific RL and no PAH or SHC results were reported at concentrations greater than 5 times the RL. There is increased uncertainty in the quantitation of results that are reported at concentrations near the RL. Relative standard deviations are typically calculated to assess field replicate precision; however, due to the low reported concentrations and the increased variability of quantitation at concentrations near the RL, the RSD values are not an accurate measure of analytical precision. Instead, the absolute standard deviation of the triplicate measurements was used to assess comparability of the field replicate results. The absolute standard deviations for the PAH analyses ranged from 0 to 1.45 µg/Kg and the absolute standard deviations for the SHC analyses ranged from 0 to 0.039 mg/Kg for the n-alkanes and was 0.006 mg/Kg for the total PHC. These absolute standard deviations are less than 2 times the reported RLs and are within the accepted margin of error of the analytical methods. Thus, acceptable precision was achieved for the PAH and SHC analyses of the field replicate samples collected at sampling station 5(1).

For the triplicate samples collected at sampling station L11, the majority of the SHC results were detected at concentrations near or below the sample-specific RL and no SHC results were reported at concentrations greater than 5 times the RL. Due to the low reported concentrations, the absolute standard deviation of the triplicate measurements was used to assess comparability of the field replicate results. The absolute standard deviations for the SHC analyses ranged from 0 to 0.07 mg/Kg for the n-alkanes and was 2.02 mg/Kg for the total PHC. These absolute standard deviations are less than 2 times the reported RLs and are within the accepted margin of error of the analytical method. Thus, acceptable precision was achieved for the SHC analyses of the field replicate samples collected at sampling station L11.

For the triplicate PAH analyses at sampling station L11, the RSD was used to assess field replicate precision when 2 of the 3 measurements were at or above 5 times the RL. If 2 or more of the measurements were below 5 times the RL, the absolute standard deviation was used to assess precision. The RSD values ranged from 30.3 percent to 45.6 percent and are within the accepted field replicate precision criteria of 50 percent RSD for sediments. The absolute standard deviations for the PAH analyses (with 2 or more concentrations below 5 times the RL)

ranged from 0.02 to 2.17 µg/Kg. These absolute standard deviations are less than or equal to 2 times the reported RLs and are within the accepted margin of error of the analytical method. Thus, acceptable precision was achieved for the PAH analyses of the field replicate samples collected at sampling station L11.

No field replicate analyses were performed for the S/T analyses since only a limited number of samples were selected for S/T analysis.

Field triplicates were collected and analyzed for surficial sediment (2 sets) and suspended sediment (1 set). The average relative standard deviation ($RSD = [(std. deviation/mean) \times 100 \text{ percent}]$) for the sediment samples was 18.3 percent for sample L11 and 14.8 percent for sample 5(1) for the 18 metals studied. These values are larger than the RSD results for laboratory duplicates presented below because the sediments are quite patchy with respect to grain-size and metal composition at many stations. However, by ratioing trace metal concentrations to Al, as described previously, this variability is normalized and the resulting ratios are considerably more uniform than the absolute values. In this manner, concern for variability introduced by variations in grain-size is minimized. The RSD for the field triplicate for suspended sediment was 6.6 percent for the 8 metals studied. This value is more in line with the laboratory RSD presented below because the particles in suspension are more uniformly mixed in the water column.

3.4.2 Organics Quality Control

Laboratory QC samples were analyzed to assess precision and accuracy of the sample preparation and analytical procedures. The number and type of laboratory QC samples was based on the total number of field samples and as specified in ADL SOPs and the Field Sampling and Logistics Plans (Arthur D. Little 1999a, and Arthur D. Little 2000a). For this program, the following laboratory QC samples and measures were used to evaluate accuracy and precision of the analytical data: surrogate recoveries, procedural blanks, blank spike samples, laboratory duplicates, standard reference materials, and oil reference standards. The results for the organic QC samples and measures are presented in Appendix B, along with the results for the associated environmental samples. Discussion and interpretation of the results are provided in the following sections.

In addition to the program-specific QC, ADL participated in the National Oceanic & Atmospheric Administration/National Institute of Standards & Technology (NOAA/NIST) intercalibration exercises for organics in 1998, 1999, and 2000. Triplicate analyses of marine sediment and mussel tissue were analyzed for organics, including PAHs, as part of these exercises. The results of the ADL analyses were within the top 10 percent of the more than 30 laboratories participating in the exercises.

3.4.2.1 Surrogate Results

Surrogate compounds were added to all environmental and QC samples prior to sample preparation. These compounds were added to determine the efficiency of the sample extraction and analysis procedures. Surrogate recoveries were evaluated to assess analytical method accuracy relative to sample matrix and laboratory performance.

For the PAH analyses, all of the environmental and QC sample surrogate recoveries were within the recovery acceptance limits, with one exception. The method blank associated with the tissue samples had two of the four surrogates with low recoveries. The blank spike associated with this method blank had acceptable surrogate and spike recoveries and all of the associated samples had acceptable surrogate recoveries. Thus, these low surrogate recoveries in the method blank do not adversely affect the quality or usability of the associated environmental sample data.

For the SHC and S/T analyses, all of the environmental and QC sample surrogate recoveries were within the recovery acceptance limits without exception.

3.4.2.2 Procedural Blanks

A laboratory procedural blank (PB) was prepared with each sample preparation batch by extracting a blank sample matrix (sodium sulfate) as if it were one of the environmental samples. Procedural blanks are used to assess the potential of contamination introduced during sample preparation and analysis. For this project, two PBs were prepared and analyzed with the tissue samples and three PBs were prepared and analyzed with the sediment samples. PAH and SHC analyses were performed on each PB. S/T analyses were not performed on the PBs.

PAH target compounds were detected at trace concentrations less than the RL in all of the tissue and sediment PBs. Between 5 and 18 PAH target compounds were detected in each of the PBs. Naphthalene was identified in all the blanks and is a common contaminant associated with the solvents used during sample preparation. Several SHC target compounds ranging from n-C16 to n-C34 were detected at trace concentrations less than 1/2 the RL in the tissue and sediment PBs. Environmental sample results that were within 5 times the associated PB concentration were qualified with a "B" to indicate that the compound was also present in the blank. Of the results that were qualified with a "B", none of these results were at concentrations greater than 5 times the sample-specific RL.

Overall, the PB results met the DQOs specified in the laboratory QA plan for the program, and do not indicate concentrations of laboratory contamination that would adversely affect the quality or usability of the associated sample data. Results that were qualified with a "B" may be biased high or may be false positives.

3.4.2.3 Blank Spike Sample Recoveries

A blank spike sample (BS) was prepared with each sample preparation batch by spiking a blank sample matrix with known concentrations of a subset of the target compounds. BSs are used to assess the accuracy of the sample preparation and analysis procedures independent of sample matrix effects. For this project, one BS was prepared and analyzed with the tissue samples and three BSs were prepared and analyzed with the sediment samples. PAH and SHC analyses were performed on each BS. S/T analyses were not performed on the BSs.

For the PAHs analyses, all of the tissue BS recoveries were within the recovery acceptance limits. For sediments, the recoveries of several compounds - benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene - exceeded the acceptance limits. The recoveries for these compounds were raised apparently due to the low response of the associated internal standard (d₁₂-benzo[a]pyrene) in the BS analyses. This QC issue does not adversely affect the quality or usability of the associated

sample data since the response for internal standard d₁₂-benzo(a)pyrene was significantly greater and within acceptance limits in the associated samples. The internal standard response for d₁₂-benzo(a)pyrene ranged from 77 to 123 percent of the daily calibration response in the associated environmental samples, while the responses in the BS analyses were 49 percent, 49 percent, and 60 percent.

For the SHC analyses, all of the tissue and sediment BS recoveries were within the recovery acceptance limits, with two exceptions. Decane (nC10) recovered below the acceptance limits in two of the sediment BSs, indicating that the n-C10 results in the associated environmental samples may be biased low. Overall, this data quality issue has a negligible impact on data quality and usability since n-C10 is not a key compound in data evaluation and decane contributes only a small amount to the total PHC concentration.

3.4.2.4 Laboratory Duplicates

Laboratory duplicates were prepared with several sample preparation batches by extracting a second separate aliquot of an environmental sample. Laboratory duplicates were evaluated to assess analytical precision related to laboratory performance and sample matrix. For this project, one laboratory duplicate (99-5F-01-PHC-CY) was prepared and analyzed with the tissue samples and two laboratory duplicates were prepared and analyzed with the sediment samples (99-DUP-01-PHC-S and 99-L05-01-PHC-S). PAH and SHC analyses were performed on each laboratory duplicate. S/T analyses were not performed on the laboratory duplicates.

For the sediment and tissue PAH analyses, good laboratory duplicate precision was noted, with RPDs less than 30 percent for the majority of the compounds, including compounds detected at concentrations below the RL. The mean RPD for each laboratory duplicate pair was less than 30 percent. Of the four compounds that had RPDs greater than 30 percent, all of the concentrations were less than 10 times the associated MDL. The laboratory duplicate precision criterion does not apply to compounds detected at concentrations less than 10 times the MDL due to increased variability at low concentrations. (RPD was calculated as the absolute difference between the two measurements divided by the mean of the two measurements.)

For the sediment SHC analyses, good laboratory duplicate precision was noted, with RPDs less than 30 percent for the majority of the compounds, including compounds detected below the RL. The mean RPD for each laboratory duplicate pair was less than 30 percent. Of the two compounds that had RPDs greater than 30 percent, all of the concentrations were less than 10 times the associated MDL.

For the tissue SHC analyses, all of the compound concentrations were less than 10 times the associated MDL. RPDs are typically calculated to assess laboratory duplicate precision; however, due to the low reported concentrations and the increased variability of quantitation at concentrations near the RL, the RPDs would not be an accurate measure of analytical precision for this laboratory duplicate evaluation. Instead, the absolute difference of the duplicate measurements was used to assess analytical precision. These absolute differences were all less than the RLs and were within the accepted margin of error of the analytical method.

Overall, the laboratory duplicate results met the DQOs specified in the laboratory QA plan for the program.

3.4.2.5 Standard Reference Materials

Instrument SRMs were analyzed with each instrumental analytical sequence to assess accuracy of the instrument calibration (PAH only). A matrix-specific SRM was prepared and analyzed with each sample preparation batch to assess accuracy of the analytical method relative to sample preparation and analysis procedures. PAH analyses were performed on each SRM. SHC and S/T analyses were not performed on the SRMs since there are no certified values for these compounds.

Instrument SRM. SRM 1491 (a solution of parent PAHs in solvent with certified concentrations) was analyzed prior to each PAH analytical sequence. The percent differences (%Ds) of the measured values versus the certified values were within 15 percent for all instrument SRMs, as required in the laboratory QA plan, indicating that the instrument calibrations were acceptable.

Sediment SRM. Three SRMs (SRM 1941a – a freeze-dried marine sediment with certified concentrations for PAHs) were prepared and analyzed for PAHs along with the sediment samples. The %Ds of the measured values versus the certified values for the PAH compounds were within the acceptance criteria of 30 percent on average per SRM and 35 percent for the individual compounds, with a few exceptions. The response for naphthalene in all three SRMs was more than 30 percent lower than the certified value (-39% D, -36% D, and -54% D). These results indicate that the measurement of naphthalene in the sediment samples may be biased low by approximately 40 percent, possibly due to loss of this more-volatile PAH during sample preparation. Responses greater than 30 percent higher than the certified values were noted for dibenzo(a,h)anthracene in two SRMs and for benzo(b)fluoranthene in one SRM. The results for these compounds in the associated sediment sample may be biased high. These QC issues have a minor impact on the quality and usability of the associated sample data since the exceedances were not extreme and did not result in any data being considered unusable.

Tissue SRM. One SRM (NIST SRM 1974a - certified for PAHs) was prepared and analyzed for PAHs along with the tissue samples. All of the compound concentrations were within 35 percent of the certified values, with one exception. Anthracene's concentration was 130 percent greater than the certified value. The high recovery of anthracene is consistent with the results obtained for this compound in multiple (more than 20 samples) analyses of SRM 1974a over the last four years by ADL. This QC issue does not impact the quality or usability of the associated sample data since acceptable recoveries for anthracene were noted in the BS and instrument SRM analyses, and since it appears that the certified value for anthracene in NIST SRM 1974a is incorrect.

3.4.2.6 Control Oil Analyses

A North Slope Crude oil sample was analyzed prior to each analytical sequence for PAH, SHC, and S/T analysis. The results of the North Slope Crude oil analyses were used to evaluate accuracy of the analytical methods, provide a chromatographic pattern for comparisons with samples, and provide an independent check of the quantitation for alkyl PAHs, S/Ts, and SHCs. Results of the control oil analyses were compared to laboratory mean values generated from multiple analyses of the oils. For the PAH, SHC, and S/T analyses, all of the results were within the acceptance limits.

3.4.3 Metals Laboratory Quality Control

Laboratory QC samples were analyzed to assess precision and accuracy of the sample preparation and analytical procedures. For this program, the following laboratory QC samples and measures were used to evaluate accuracy and precision of the analytical data: procedural blanks, matrix spike samples, laboratory duplicates, and standard reference materials. The results for the inorganic QC samples and measures are presented in Tables 3-20 through 3-23 and Appendices A and C, along with the results for the associated environmental samples. Discussion and interpretation of the results are provided in the following sections.

3.4.3.1 Procedural Blanks

Two method blanks were processed and analyzed with each batch of samples to monitor potential contamination resulting from laboratory reagents, glassware, and processing procedures. No contamination from any of these sources was noted and concentrations of analytes in the blanks do not exceed 5 times the MDL.

3.4.3.2 Matrix Spike Sample

Matrix spike samples were analyzed with each batch of sediment, organism, and suspended solids samples using the method of standard additions. Results from these analyses provide information on the extent of any signal suppression or enhancement due to the matrix. Spike results for the sediment, organism, and suspended solids samples are shown in Tables 3-21 through 3-23, and are within the 80 to 120 percent range specified in the DQOs (Table 2-10), except for sediment Ag and V, and organism Co and Hg. In response, the spiking frequency was increased for these four metals in their respective matrices and a spike correction applied to the sample metal concentrations.

3.4.3.3 Laboratory Duplicates

Duplicate subsamples taken from individual sediment and water samples in the laboratory were analyzed to estimate analytical precision. Analytical precision for sediment metal analyses ($n = 4$ pair of duplicate samples) ranged from 0.5 percent RSD for Cu to 7.7 percent RSD for Ag. For organism tissue samples ($n = 1$), precision of duplicate sample analysis ranged from 0 percent RSD for Co to 15.7 percent RSD for Tl. In the case of Tl, the high percent RSD is due to the very low concentrations of Tl present (0.012 and 0.015 $\mu\text{g/g}$ dry weight in the duplicate samples). The percent RSD for duplicate TSS concentrations averaged 1.9 percent RSD in the summer sampling ($n = 7$). In the winter sampling only one duplicate was obtained: the TSS RSD from this duplicate sample was 28.6 percent RSD, (which results from the very low TSS concentrations found under the ice). The percent RSD in suspended solids metal concentrations ranged from 0.4 percent (Al) to 6.2 percent (Pb) for the summer sampling ($n = 1$), and 0 percent (Fe) to 6.1 percent (Cd) during the winter sampling ($n = 1$). Analytical precision of particulate TOC analyses averaged 12.4 percent for both sampling periods ($n = 6$).

3.4.3.4 Standard Reference Materials

SRMs were processed and analyzed for trace metals along with the experimental samples as described in the Methods section (Section 2). The results of these analyses are shown in Tables 3-21 (sediment analysis), 3-22 (organism analysis), and 3-23 (suspended solids analysis). The metal concentrations determined for each SRM, were all within the range of certified values or within the DQO limits of the reference values provided by the certifying agencies.

For TOC analyses, the marine sediment SRM MESS-2 was used as a QA sample. This SRM is certified for total carbon content (inorganic plus organic); therefore, the TOC values in Tables 3-21 and 3-23 are slightly below the certified total carbon value. Nevertheless, the TOC values determined for MESS-2 were consistently reproducible with percent RSD of ~ 1 percent.

Table 3-1. Summary Data by Region for Metals, Total Organic Carbon, and Grain Size

	Region	Ag (µg/g)	Al (%)	As (µg/g)	Ba (µg/g)	Be (µg/g)	Cd (µg/g)	Co (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)
Mean Std. Dev. Range	Beaufort Sea Monitoring Program (BSMP)	0.11 ±0.09 0.06-0.44	3.41 ±1.74 1.33-6.43	11.7 ±6.2 5.2-27.3	360 ±177 155-753	1.24 ±0.60 0.40-2.30	0.24 ±0.19 0.05-0.79	7.6 ±4.6 2.20-18.3	49.0 ±26.9 15.1-91.1	17.4 ±12.9 4.0-46.9	2.06 ±0.96 0.72-3.47
Mean Std. Dev. Range	Northstar Prospect	0.12 ±0.07 0.04-0.13	3.68 ±2.10 1.13-7.26	11.9 ±5.8 4.2-22.7	448 ±169 164-712	1.25 ±0.61 0.60-2.30	0.22 ±0.11 0.07-0.43	7.1 ±3.6 2.70-13.1	53.6 ±29.9 12.7-104.3	17.3 ±12.5 12.5-37.6	2.07 ±1.14 0.74-3.89
Mean Std. Dev. Range	Liberty Prospect	0.10 ±0.03 0.03-0.16	3.76 ±1.27 2.36-6.32	11.1 ±3.3 6.8-17.3	418 ±124 289-674	1.13 ±0.38 0.50-2.00	0.18 ±0.10 0.07-0.37	6.9 ±2.0 4.50-11.4	54.2 ±19.0 27.8-86.5	16.2 ±7.9 7.4-30.9	1.98 ±0.67 0.72-3.47
Mean Std. Dev. Range	Average of BSMP, Northstar and Liberty	0.11 ±0.07 0.03-0.44	3.61 ±1.71 1.13-7.26	11.5 ±5.2 4.2-27.3	407 ±160 155-753	1.23 ±0.60 0.40-2.30	0.21 ±0.14 0.05-0.79	7.6 ±4.6 2.2-18.3	52.1 ±25.3 12.7-104.3	17.0 ±11.2 4.0-46.9	2.03 ±0.93 0.72-3.89
Average Continental Crust (Wedepohl, 1995)		0.07	7.96	1.7	584	2.4	0.1	24	126	25	4.32

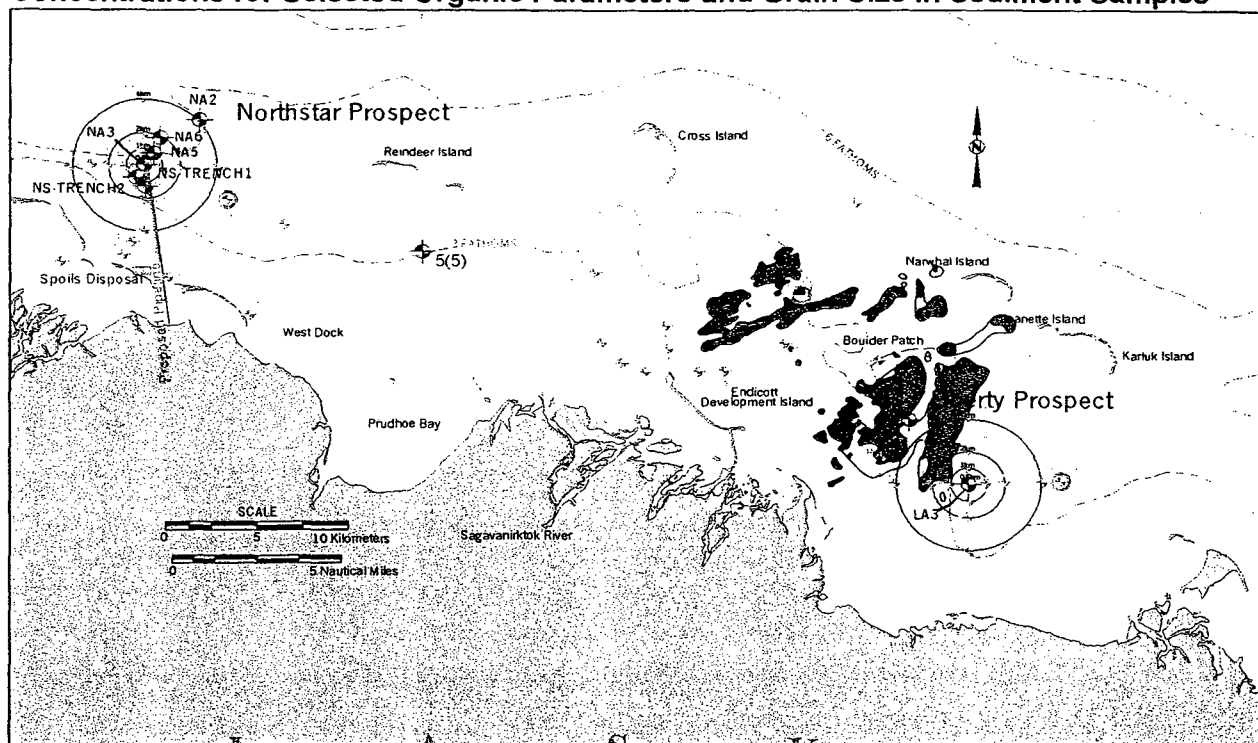
	Region	Hg (µg/g)	Mn (µg/g)	Ni (µg/g)	Pb (µg/g)	Sb (µg/g)	Tl (µg/g)	V (µg/g)	Zn (µg/g)	TOC (%)	Silt + Clay (%)
Mean Std. Dev. Range	Beaufort Sea Monitoring Program (BSMP)	0.04 ±0.05 0.003-0.20	287 ±144 89.8-545	22.0 ±13.5 6.0-48.4	9.8 ±6.1 3.2-22.3	0.50 ±0.30 0.15-1.14	0.36 ±0.22 0.12-0.92	82.1 ±45.0 26.9-153	63.0 ±39.2 14.8-124	0.41 ±0.38 0.05-1.3	35.2 ±35.1 1.7-98.7
Mean Std. Dev. Range	Northstar Prospect	0.04 ±0.03 0.008-0.09	272 ±167 62.4-606	22.5 ±12.6 7.1-43.0	9.7 ±6.4 3.2-20.3	0.44 ±0.23 0.22-0.84	0.37 ±0.21 0.15-0.75	88.9 ±55.1 28.1-173	63.9 ±41.8 16.7-131	0.70 ±0.66 0.01-1.93	44.6 ±40.6 1.0-98.8
Mean Std. Dev. Range	Liberty Prospect	0.03 ±0.02 0.01-0.07	245 ±70 170-397	22.2 ±8.0 12.4-39.3	10.0 ±3.6 6.40-18.2	0.52 ±0.18 0.33-1.01	0.41 ±0.14 0.29-0.81	83.8 ±28.0 51.0-133	63.8 ±24.9 34.0-108	0.79 ±0.76 0.27-3.42	50.7 ±26.5 2.1-93.3
Mean Std. Dev. Range	Average of BSMP, Northstar and Liberty	0.04 ±0.04 0.003-0.02	269 ±133 62-606	22.2 ±11.5 6.0-48.4	9.9 ±5.4 3.2-22.3	0.49 ±0.24 0.15-1.14	0.38 ±0.19 0.12-0.92	84.8 ±43.4 26.9-173	63.5 ±35.5 14.8-131	0.62 ±0.62 0.01-3.42	43.1 ±34.4 1.0-98.0
Average Continental Crust (Wedepohl, 1995)		0.04	716	56	14.8	0.30	0.52	98	65	-	-

Table 3-1a. Summary Data Showing Within-Site Variability for Concentrations of Metals in Sediment Samples

	Sample	Al (%)	Ba (µg/g)	Cr (µg/g)	Hg (µg/g)	Pb (µg/g)	Zn (µg/g)
Replicates	99-5(1)-01	1.81	232	17.6	0.005	5.8	27.3
	99-5(1)-02	1.82	237	18.1	0.005	5.8	23.0
	99-5(1)-03	1.89	247	29.7	0.0004	5.9	26.9
CV (%)		2.4	3.2	31.4	12.3	1.0	31.4
Replicates	99-L11-01	2.36	289	32.0	0.024	6.4	34.0
	99-L11-02	3.31	355	46.1	0.028	8.9	50.6
	99-L11-03	2.61	307	32.4	0.018	7.4	38.2
CV (%)		17.8	10.8	21.8	21.6	16.6	21.1

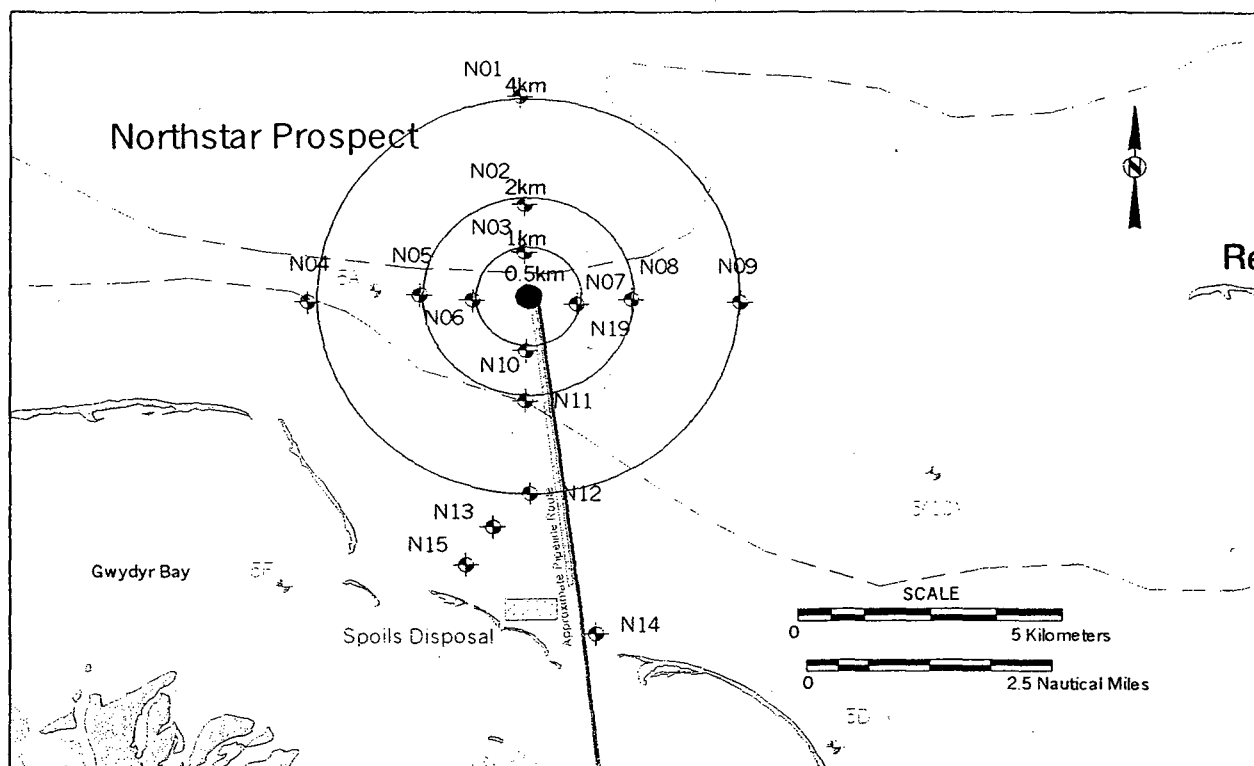
Coefficient of variation (CV) = [standard deviation/mean] x 100%.

Table 3-2. Map Showing Beaufort Sea Monitoring Program Sampling Stations and Table of Concentrations for Selected Organic Parameters and Grain Size in Sediment Samples



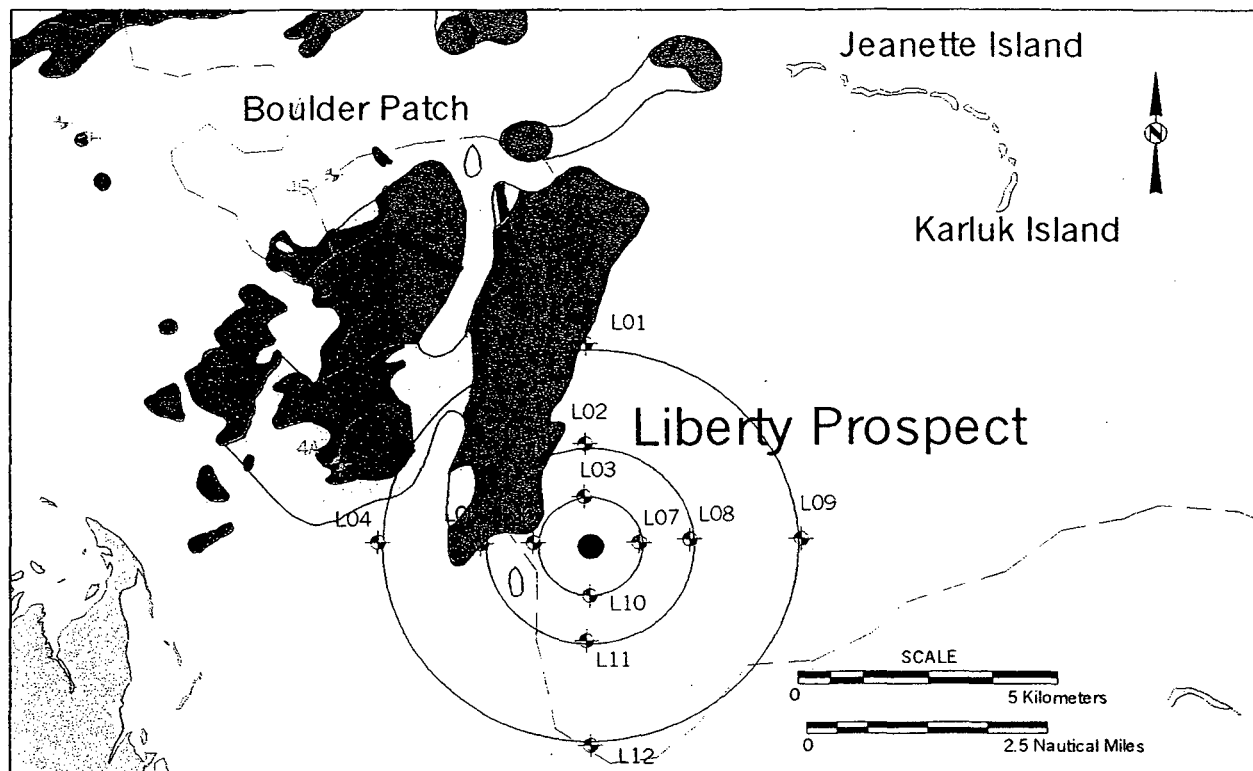
Station	Total PAH ($\mu\text{g/Kg}$)	Total PHC (mg/Kg)	Total S/T ($\mu\text{g/Kg}$)	TOC(%)	Silt+Clay(%)
Foggy Island					
3A	480	7.6	49	1.0	90
3B	470	7.9		0.90	84
4A	410	5.3		0.54	33
4B	110	0.90	9.0	0.12	14
4C	21	0.40		0.10	1.8
5H	270	4.8		0.49	31
Mean (SD)	290 (190)	4.5 (3.2)		0.53 (0.38)	42 (37)
Endicott Field					
5(0)	440	6.4		0.58	39
5(1)	27 (16)	0.52 (0.01)		0.093 (0.031)	2.2 (0.17)
5(5)	170	1.4	21	0.30	22
5(10)	710	12		1.3	88
Mean (SD)	340 (300)	5.1 (5.3)		0.57 (0.53)	38 (37)
Kuparuk River Bay					
5A	700	11		Not analyzed	99
5B	24	0.25		0.050	1.7
5D	2,700	50	490	0.16	58
5E	170	11	26	0.45	18
5F	180	1.9		0.24	12
Mean (SD)	760 (1,100)	15 (20)		0.22 (0.17)	38 (40)
River Sources					
Colville (1)	2,600	36	340	1.6	
Colville (2)	2,200	31		2.4	
Kuparuk	100	11	72	4.7	
Sagavanirktok	320	5.8	25	2.0	
Colville Peat	1,900	32	180	13	
Kuparuk Peat	110	21	61	27	

Table 3-3. Map Showing Northstar Sampling Stations and Table of Concentrations for Selected Organic Parameters and Grain Size in Sediment Samples



Station	Total PAH ($\mu\text{g/Kg}$)	Total PHC (mg/Kg)	Total S/T ($\mu\text{g/Kg}$)	TOC(%)	Silt+Clay(%)
Northstar					
N01	8.6	0.21	1.2	0.01	1.0
N02	470	6.2	—	0.48	63
N03	680	11	—	1.5	90
N04	590	9.8	—	1.9	90
N05	600	7.8	—	0.90	94
N06	960	13	82	1.5	97
N07	57	0.45	—	0.09	12
N08	100	0.74	—	0.50	17
N09	370	6.0	—	0.44	59
N10	720	11	—	1.5	99
N11	17	0.26	—	0.09	2.1
N12	150	2.6	—	0.30	21
N13	160	3.5	16	0.51	15
N14	47	0.63	6.5	0.27	6.8
N15	6.8	0.21	—	0.05	1.9
Mean (SD)	330 (320)	4.9 (4.7)	—	0.67 (0.64)	45 (41)

Table 3-4. Map Showing Liberty Sampling Stations and Table of Concentrations for Selected Organic Parameters and Grain Size in Sediment Samples



Station	Total PAH ($\mu\text{g/Kg}$)	Total PHC (mg/Kg)	Total S/T ($\mu\text{g/Kg}$)	TOC(%)	Silt+Clay(%)
Liberty					
L01	360	5.0	33	0.45	2.1
L02	490	7.5	—	0.78	86
L03	860	16	—	1.1	93
L04	400	5.7	—	0.45	50
L05	130	1.8	—	0.48	32
L06	450	8.6	45	0.93	69
L07	450	6.9	—	0.52	54
L08	300	17	53	0.44	68
L09	260	4.7	33	0.50	36
L10	340	5.2	—	0.63	60
L11	230	2.6 (2.0)	—	0.54 (0.28)	31 (8.4)
L12	260	3.8	—	0.49	31
Mean (SD)	380 (180)	7.1 (4.8)	—	0.61 (0.21)	51 (26)

Table 3-5. Diagnostic Ratios and Parameters of Saturated Hydrocarbons, Polynuclear Aromatic Hydrocarbons, and Steranes and Triterpanes

Parameter	Relevance in Environmental Samples
Saturated Hydrocarbons (SHC)	
Isoprenoids	The sum of selected branched isoprenoid alkanes including: phytane, pristane, farnesane [1470], and unidentified isoprenoids at relative retention indices 1380 and 1650. Isoprenoids are abundant in petroleum and are resistant to degradation relative to the corresponding n-alkanes.
LALK	The sum of lower-molecular-weight n-alkanes (n-C ₉ to n-C ₂₀) generally associated with "fresh" petroleum inputs.
TALK	The sum of total alkanes, which includes those of biogenic and petrogenic origin (n-C ₉ to n-C ₄₀).
LALK/TALK	Diagnostic alkane compositional ratio used to determine the relative abundance of lower-molecular-weight alkanes, which includes those of biogenic origin.
PHY/PRIS	Source of phytane (PHY) is mainly petroleum, whereas pristane (PRIS) is derived from both biological matter and oil. In "clean" environmental samples, this ratio is very low and increases as oil is added.
n-C ₁₆ /(n-C ₁₅ + n-C ₁₇)	The ratio of n-alkane hexadecane (n-C ₁₆) over pentadecane (n-C ₁₅) and heptadecane (n-C ₁₇). At "background" levels of total hydrocarbons n-C ₁₅ and n-C ₁₇ can be used as indicators of plankton (algal) hydrocarbon inputs. As plankton productivity increases, the ratio decreases.
CPI	Carbon Preference Index. Describes the relative amounts of odd- and even-chain alkanes within a specific alkane boiling range [$CPI = (n-C_{27} + n-C_{29} + n-C_{31}) / (n-C_{26} + n-C_{28} + n-C_{30})$]. CPI of 2 - 4 indicates terrestrial plants; as oil additions increase, the CPI is lowered to near 1.0.
TPHC	Total Saturated Hydrocarbons. The sum of the resolved plus unresolved saturated hydrocarbons.
Polynuclear Aromatic Hydrocarbons (PAH)	
N/P	The naphthalenes (N) to phenanthrenes/anthracenes (P) ratio is diagnostic for inputs of fresh petroleum, and as a weathering indicator. Naphthalenes are characteristic of fresh crude oil; the ratio decreases with increased weathering. (N= Naphthalene series [C0N + C1N + C2N + C3N + C4N]; P= Phenanthrene/Anthracene Series [C0P/A + C1P/A + C2P/A + C3P/A + C4P/A]).
C2D/C2P	Ratio of C2 alkyl dibenzothiophenes (D) and C2 alkyl phenanthrenes (P) is a useful diagnostic source ratio for petroleum.
C3D/C3P	Ratio of C3 alkyl dibenzothiophenes (D) and C3 alkyl phenanthrenes (P) is a useful diagnostic source ratio for petroleum.
Perylene	A biogenic PAH formed during the early diagenesis in marine and lacustrine sediments; may be associated with terrestrial plant source precursors.
Total PAH	The sum of all PAH target analytes; includes 2- through 6-ring parent PAH and C1 - C4 alkyl-substituted PAH.
Pyrogenic PAH	The sum of combustion PAH compounds (4-, 5-, and 6-ring PAH: fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene, and indeno[1,2,3-c,d]pyrene.
Petrogenic PAH	The sum of petrogenic PAH compounds (2-, 3-, and 4-ring PAH: naphthalenes [C0 - C4], acenaphthene, acenaphthylene, fluorene [C0 - C3], phenanthrenes [C0 - C4], dibenzothiophenes [C0 - C3], chrysenes [C1 - C4], and fluoranthenes/pyrenes [C1 - C3]).
Pyrogenic/Petrogenic	The ratio of pyrogenic PAH compounds to petrogenic PAH compounds is useful for determining the relative contribution of pyrogenic and petrogenic hydrocarbons and in differentiating hydrocarbon sources.

Table 3-5 cont. Diagnostic Ratios and Parameters of Saturated Hydrocarbons, Polynuclear Aromatic Hydrocarbons, and Steranes and Triterpanes

Parameter	Relevance in Environmental Samples
Steranes/Triterpanes (S/T)	
Total S/T	The sum of all sterane and triterpane biomarker target analytes.
T21/T22	The ratio of C31-homohopane (22S) (T21) to C31-homohopane (22R) (T22); useful for determining the contribution of recent biogenic material.
Hopane	C30-Hopane (T19), commonly one of the most abundant triterpanes in petroleum.
Ts/(Ts + Tm)	Ratio of C27-trisnorhopane (Ts) to C27-trisnorhopane (Tm); used as a maturity indicator for petroleum and also as a source ratio for different crude oils.
Oleanane/Hopane	The ratio of C30-oleanane (T18) to C30-hopane (T19); indicates the relative amounts of oleanane, which is a marker of angiosperm (post-Cretaceous) contribution to petroleum diagenesis.

CPI – Carbon Preference Index

LALK – Low-molecular-weight n-alkanes

LALK/TALK – LALK:TALK ratio

PHY/PRIS – Phytane:pristane ratio

TALK – Total n-alkanes

Table 3-6. Average Total Organic Carbon in Surficial Sediments from ANIMIDA Study Area, Alaska Marine Sediments, and Cook Inlet and Shelikof Strait Sediments

Organic Parameter	Average (Range) Concentrations for ANIMIDA Study Area Surficial Sediments ($\mu\text{g/g}$)	Concentrations in Alaska Marine Sediments ($\mu\text{g/g}$) ^a	Concentrations in Cook Inlet and Shelikof Strait Sediments ($\mu\text{g/g}$) ^b
Total PAH	0.39 (0.007 – 2.7)	0.016 - 2.4	0.001 – 1.080
Total PHC ^c	6.6 (0.21 – 50)	0.47 - 38	0.9 - 69.0
Total S/T	0.029 (0.001 – 0.081)	NA	0.009 – 0.087

^a Prince William Sound subtidal and Beaufort Sea (Bence, *et al.*, 1996; Boehm *et al.*, 1991).

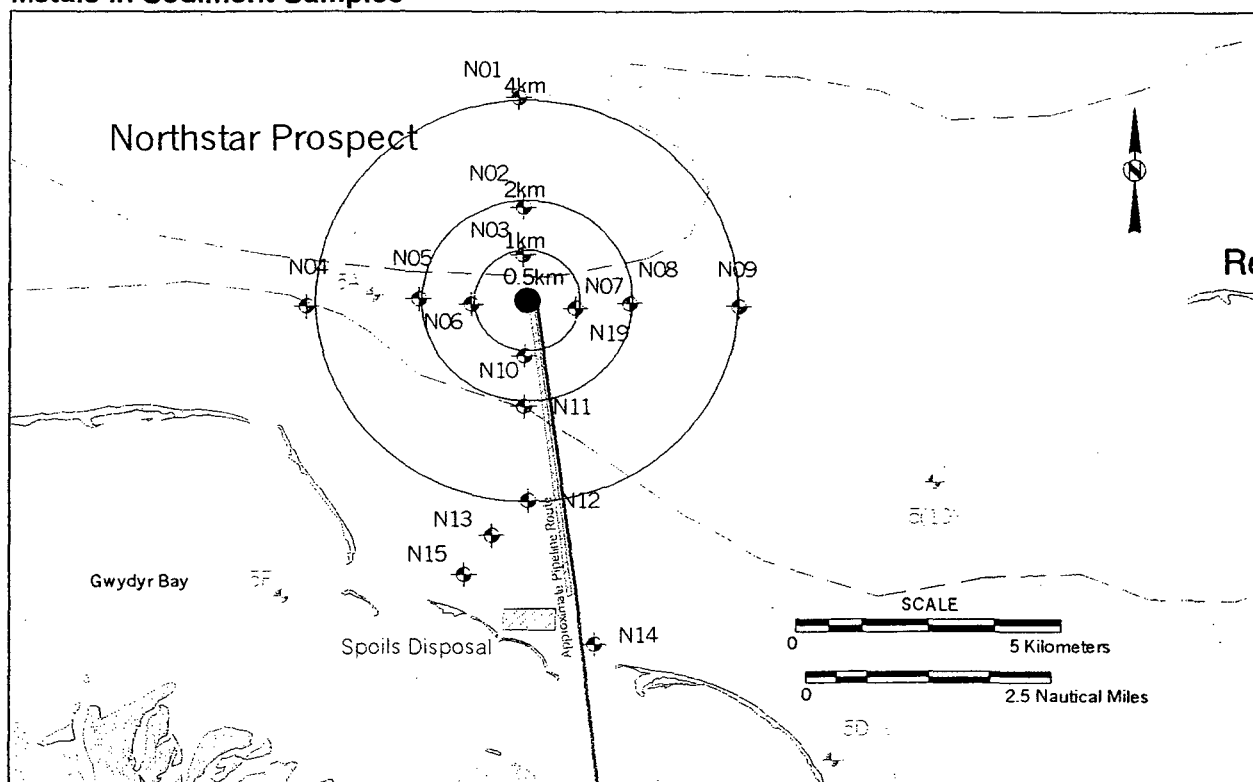
^b ENRI - UAA, 1995, Hyland, *et al.*, 1995; ADL, 1996; KLI, 1996; KLI, 1997; Boehm *et al.*, 1999).

^c Total PHC concentrations for the ANIMIDA study included saturated hydrocarbons only, while Total PHC concentrations for the other studies included saturated and aromatic hydrocarbons.

NA – not applicable.

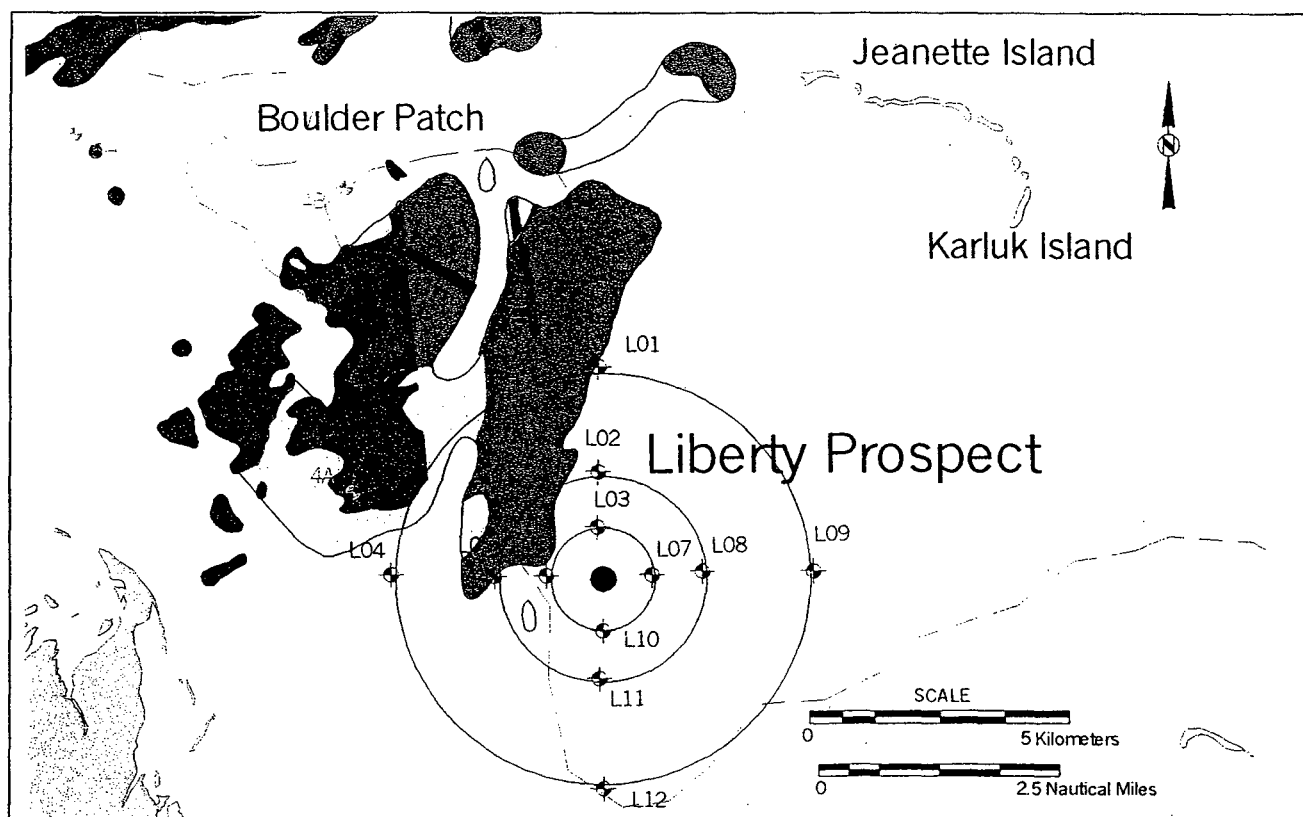
Highlighted numbers are maximum values found during the 1999 sampling period.

Table 3-8. Map of Northstar Sampling Stations and Table of Concentrations for Selected Metals in Sediment Samples



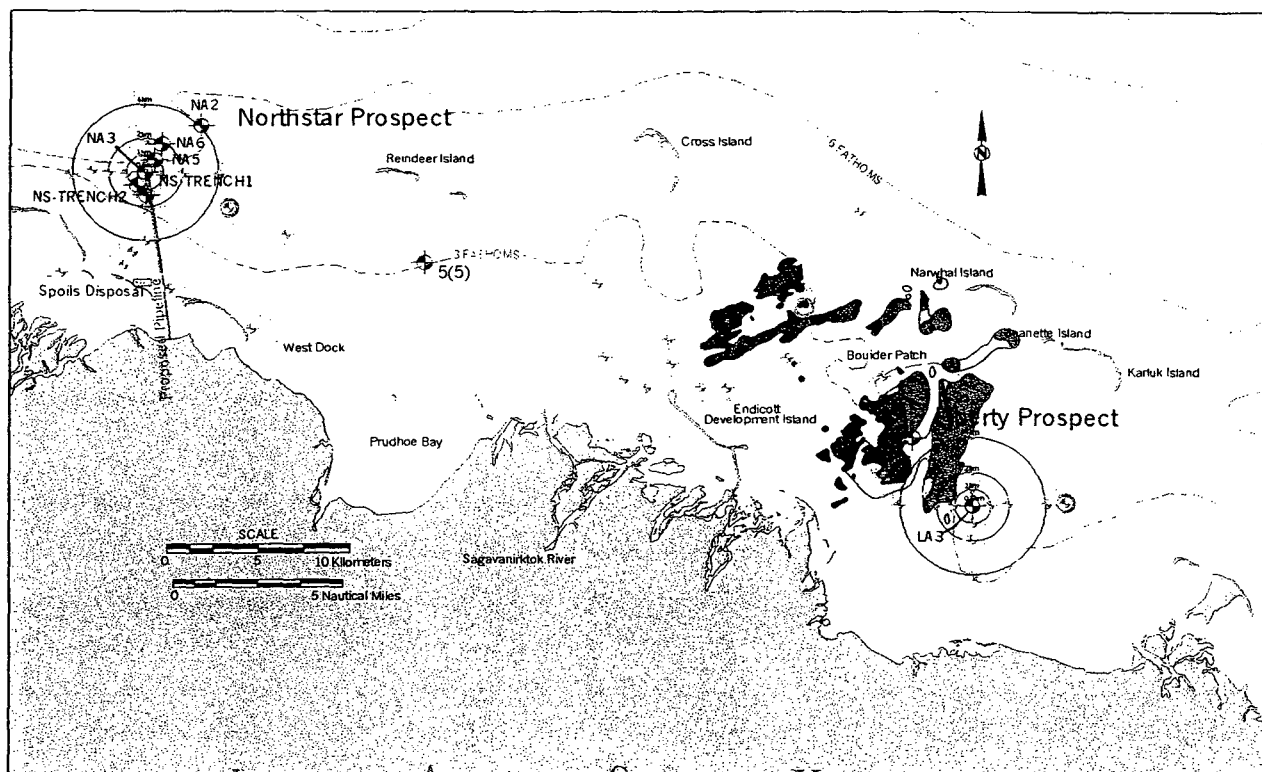
Station	Al (%)	Ba (µg/g)	Hg (µg/g)	Pb (µg/g)	Cd (µg/g)
N01	1.43	253	0.008	4.7	N.D.
N02	4.29	425	0.035	9.8	0.20
N03	5.70	577	0.073	16.2	0.30
N04	5.73	601	0.085	18.1	0.32
N05	5.82	612	0.054	16.0	0.31
N06	7.26	712	0.077	20.3	0.43
N07	2.47	269	0.023	4.0	0.14
N08	2.38	247	0.019	3.8	0.15
N09	4.76	452	0.037	11.0	0.26
N10	6.59	683	0.082	19.9	0.29
N11	1.54	164	0.010	3.2	0.07
N12	2.12	486	0.013	5.6	0.08
N13	2.06	458	0.010	5.0	0.08
N14	1.35	519	0.009	4.3	N.D.
N15	1.13	284	0.008	3.7	N.D.

Table 3-9. Map of Liberty Sampling Stations and Table of Concentrations of Selected Metals in Sediment Samples



Station	Al (%)	Ba ($\mu\text{g/g}$)	Hg ($\mu\text{g/g}$)	Pb ($\mu\text{g/g}$)	Cd ($\mu\text{g/g}$)
L01	4.01	388	0.028	8.6	0.17
L02	6.32	674	0.052	18.2	0.37
L03	5.82	554	0.053	14.7	0.26
L04	3.13	307	0.022	8.8	0.12
L05	2.51	315	0.010	6.8	0.08
L06	5.10	538	0.060	14.2	0.34
L07	3.82	419	0.042	8.6	0.21
L08	2.83	564	0.023	8.3	0.15
L09	3.26	341	0.035	10.0	0.16
L10	3.91	437	0.037	8.5	0.21
L11	2.36	289	0.024	6.4	0.07
L12	3.03	335	0.021	9.0	0.15

Table 3-10. Map of Stations Sampled During April 2000 for Total Suspended Sediment and Laboratory Turbidity and Table of Results



Location	NA2	NA3	NA5	NA6	5(5)	LA2	LA3	NT1	NT2
TSS (mg/L)	0.25 ±0.04	0.35 ±0.14	0.28 ±0.18	-	0.23 ±0.05	0.26 ±0.11	0.44 ±0.23	1.2 ±0.5	0.41 ±0.08
Lab Turbidity (NTU)	0.4 ±0.2	0.4 ±0.2	0.4 ±0.1	0.3 ±0.1	0.3 ±0.05	0.4 ±0.3	0.4 ±0.1	0.8 ±0.6	0.2 ±0.05

Table 3-11. Summary Data by Region for Metals in Suspended Sediment Samples

	Region	Al (%)	Ba (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Pb (µg/g)	Zn (µg/g)
Mean Std. Dev.	Beaufort Sea Monitoring Program (BSMP)	7.28 ±0.38	700 ±35	0.44 ±0.11	87.2 ±11.2	35.8 ±2.6	3.81 ±0.22	19.7 ±3.5	123 ±10
Mean Std. Dev.	Northstar Prospect	7.42 ±0.44	700 ±43	0.72 ±0.33	92.6 ±8.4	41.3 ±9.3	3.94 ±0.23	21.9 ±6.6	137 ±11
Mean Std. Dev.	Liberty Prospect	7.85 ±0.29	738 ±28	0.67 ±0.23	97.4 ±5.0	37.6 ±2.9	3.98 ±0.09	21.5 ±2.3	143 ±14
Mean Std. Dev. Range	Average of BSMP, Northstar and Liberty	7.48 ±0.44	708 ±41	0.64 ±0.29	92.2 ±9.1	39.1 ±7.4	3.92 ±0.21	21.3 ±5.2	135 ±14
Surface Sediment Average for ANIMIDA Std. Dev.		3.61 ±1.71	407 ±160	0.21 ±0.14	52.1 ±25.3	17.0 ±11.2	2.03 ±0.93	9.9 ±5.4	63.5 ±35.5
Average Continental Crust (Wedepohl, 1995)		7.96	584	0.1	126	25	4.32	14.8	65

Table 3-12. Results for δC^{13} in Surface and Suspended Sediment Samples from the Beaufort Sea Monitoring Program, Northstar, and Liberty Areas and from Local Rivers

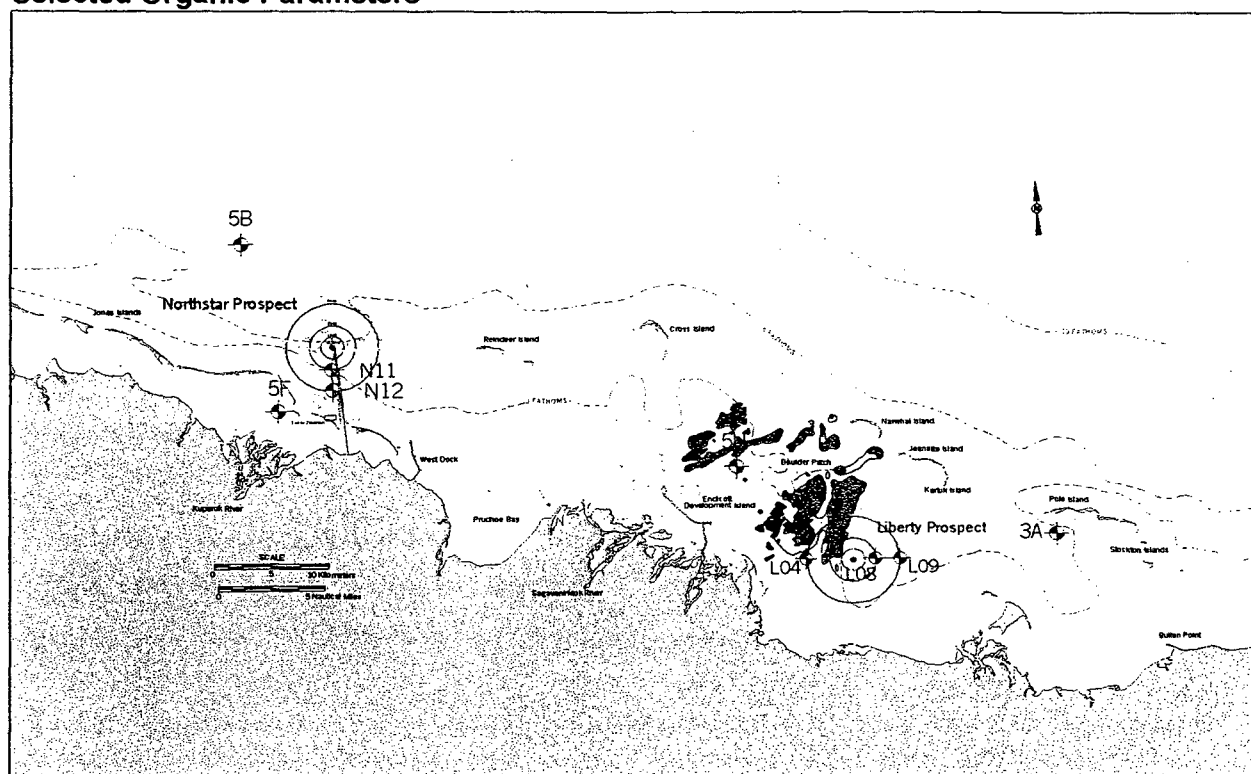
Sample Type	Location	δC^{13} (per mil)
Surface Sediment	BSMP	-23.1 ± 2.0
Surface Sediment	Northstar	-23.5 ± 1.1
Surface Sediment	Liberty	-23.2 ± 2.8
Suspended Sediment	BSMP	-30.8 ± 2.5
Suspended Sediment	Northstar	-29.0 ± 5.0
Suspended Sediment	Liberty	-27.9 ± 4.3
River Sediment	Colville, Kuparuk, and Sagavanirktok Rivers	-24.5 ± 0.4
River Suspended Sediment	Colville, Kuparuk, and Sagavanirktok Rivers	-30.3 ± 0.5

Table 3-13. Summary Results for δC^{13} in Surface Sediment, Suspended Sediment, and Source Material Samples from the Study Area

Sample Type	Location	δC^{13} (per mil)
Surface Sediment	BSMP, Northstar, and Liberty	-23.3 ± 2.5
Suspended Sediment	BSMP, Northstar, and Liberty	-29.2 ± 4.5
River Sediment	Colville, Kuparuk, and Sagavanirktok Rivers	-24.5 ± 0.4
River Suspended Sediment	Colville, Kuparuk, and Sagavanirktok Rivers	-30.3 ± 0.5
Peat and Grass	Coastal Beaufort Sea	$-28.5 \pm 1.3^*$
Amphipods	Coastal Beaufort Sea	$-19.1 \pm 0.6^*$
Plankton	Coastal Beaufort Sea	$-22 \pm 2^*$

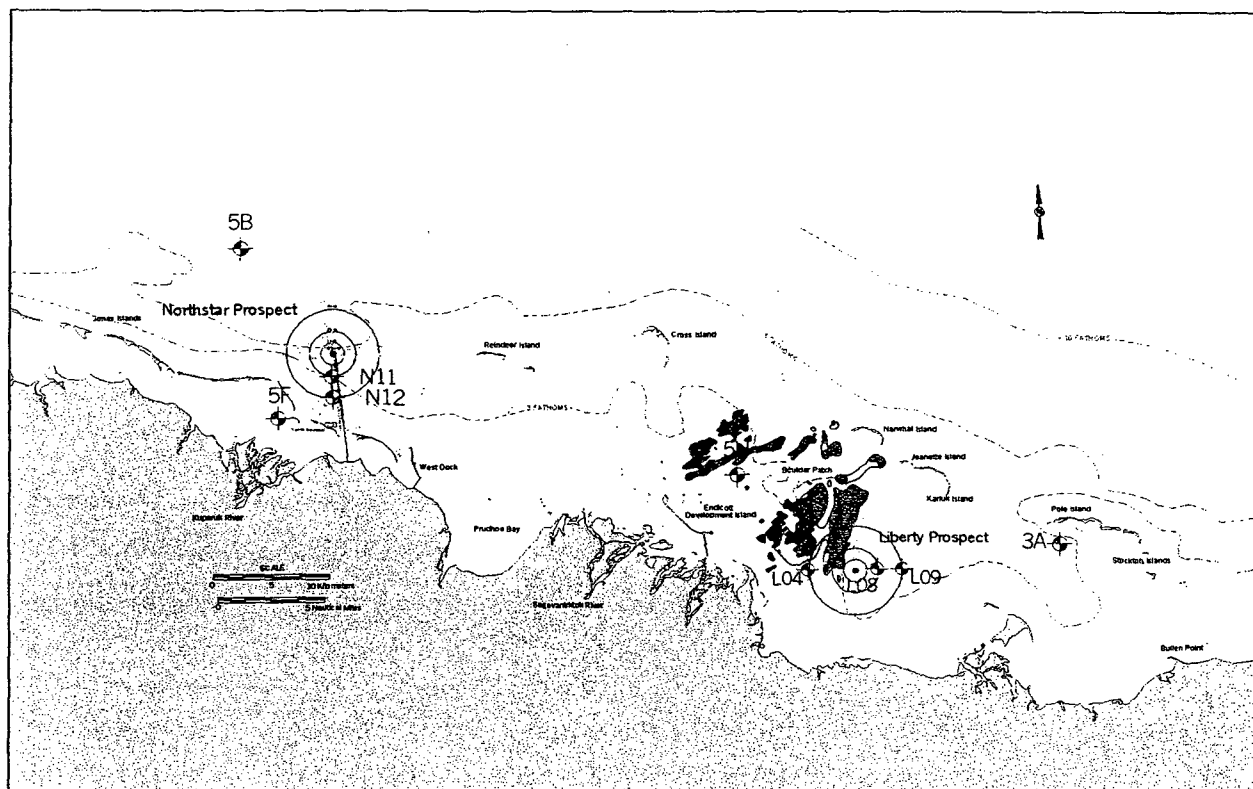
* Schell (1983)

Table 3-14. Map of Sampling Stations for Organisms with Table of Concentrations for Selected Organic Parameters



Station	Species	Total PAH ($\mu\text{g/Kg}$ wet weight)	Total PHC (mg/Kg wet weight)	Total S/T ($\mu\text{g/Kg}$ wet weight)
3A	<i>Astarte</i>	13	1.0	18
5H	<i>Astarte</i>	17	1.2	
5B	<i>Anonyx</i>	19	18	
5F	<i>Cyrtodaria</i>	36	1.4	5.6
L04	<i>Anonyx</i>	80	8.7	
L08	<i>Astarte</i>	15	1.1	9.0
L09	<i>Astarte</i>	20	9.6	
N11	<i>Anonyx</i>	15	3.2	
N12	<i>Anonyx</i>	15	2.0	5.5

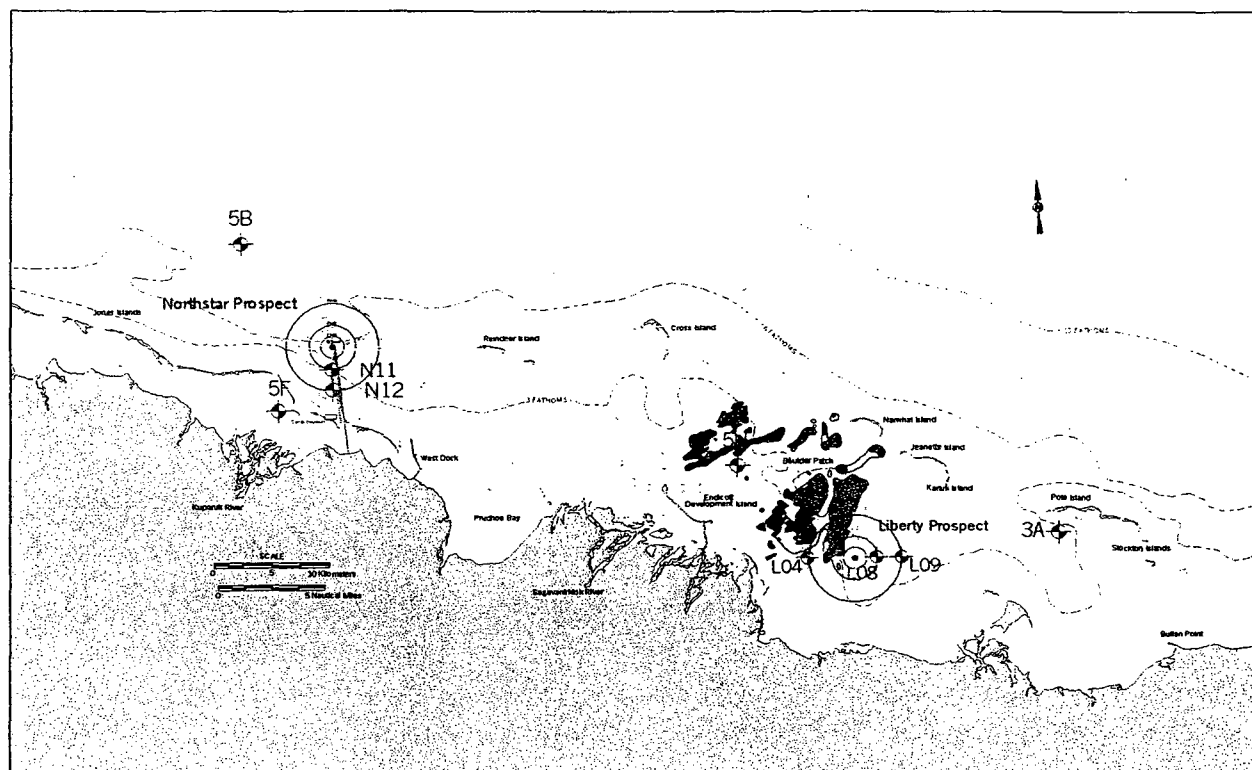
Table 3-15. Map of Sampling Stations for Organisms and Table of Concentrations for Selected Metals (Cd, Cu, Hg, and Pb)



Station	Organism	Cd ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Hg ($\mu\text{g/g}$)	Pb ($\mu\text{g/g}$)
N11	<i>Anonyx</i> , small	0.40	128	0.045	0.25
N12	<i>Anonyx</i> , small	0.45	120	0.045	0.29
L04	<i>Anonyx</i> , small	0.63	134	0.056	0.37
5B	<i>Anonyx</i> , large	1.3	51.5	0.085	0.13
L08	<i>Astarte</i>	6.8	15.5	0.065	0.76
L09	<i>Astarte</i>	7.2	13.1	0.056	0.71
3A	<i>Astarte</i>	9.8	11.5	0.059	0.69
5H	<i>Astarte</i>	8.9	23.9	0.052	0.62
5F	<i>Cyrtodaria</i>	1.3	26.0	0.043	0.62

Anonyx (an amphipod), *Astarte* (a clam), *Cyrtodaria* (a clam).

Table 3-16. Map of Sampling Stations for Organisms with Table of Concentrations for Selected Metals (As, Ba, V, and Zn)



Station	Organism	As ($\mu\text{g/g}$)	Ba ($\mu\text{g/g}$)	V ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)
N11	<i>Anonyx</i> , small	7.0	18.9	1.6	93.0
N12	<i>Anonyx</i> , small	6.0	20.2	1.5	92.9
L04	<i>Anonyx</i> , small	7.8	25.1	1.7	91.2
5B	<i>Anonyx</i> , large	14.9	7.4	1.1	215
L08	<i>Astarte</i>	11.6	16.0	2.8	82.6
L09	<i>Astarte</i>	9.2	16.1	3.8	68.8
3A	<i>Astarte</i>	11.0	14.0	3.7	70.0
5H	<i>Astarte</i>	9.7	19.8	3.5	82.8
5F	<i>Cyrtodaria</i>	6.6	9.1	2.5	68.0

Anonyx (an amphipod), *Astarte* (a clam), *Cyrtodaria* (a clam).

Table 3-17. Organic Quality Control Result Summary – Polynuclear Aromatic Hydrocarbon Analyses

QC Sample or Measurement Type	Acceptance Criteria	Quality Control Result Summary	Impact to Data Quality and Usability
Equipment Blank	No compound to exceed 5 times the MDL	All criteria were met.	None
Field Blank	No compound to exceed 5 times the MDL	All criteria were met.	None
Field Replicate	RSD < 50% for all compounds >5 times the RL	All criteria were met.	None
Initial Calibration	%RSD <25% for all compounds (up to 10% of compounds can be >25%, but <35%)	All criteria were met.	None
Continuing Calibration	%D <25% for all compounds (up to 10% of compounds can be >25%, but <35%)	All criteria were met.	None
Surrogate Recoveries	45 to 125% recovery (35 – 125% for d8-naphthalene)	All criteria were met, with the exception of two low recoveries in a procedural blank.	None. Surrogate recoveries were acceptable in the associated samples.
Procedural Blank	No compound to exceed 5 times the MDL unless sample amount is >10 times blank amount	All criteria were met. Several PAHs were detected at trace concentrations, but less than 5 times the MDL.	Minor. Results within 5 times the blank result were qualified "B" and may be biased high or false positives.
Blank Spike Sample Recoveries	35 to 125% recovery for spiked compounds	All criteria were met for the tissue BS. Several PAHs were recovered at >125% in the sediment BSs due to low response of the associated internal standard.	None. The IS responses in the samples were all significantly greater than the BS; thus, the quantitation of the sample results was not impacted.
Laboratory Duplicate	RPD <30% for all compounds >10 times the MDL; mean RPD <30%	All criteria were met.	None
Instrument SRM (1491)	Measured values must be within 15% of true value for all certified compounds	All criteria were met.	None
Sediment SRM (1941a)	Measured values must be within 30% of the true value on average for all compounds, not to exceed 35% of true value for more than 30% of the compounds	All criteria were met for the sediment SRMs, with the exception of low responses for naphthalene.	Minor. The naphthalene results in the sediment samples may be biased low by approximately 40%.
Tissue SRM (1974a)	Measured values must be within 30% of the true value on average for all compounds, not to exceed 35% of true value for more than 30% of the compounds	All criteria were met for the tissue SRM, with the exception of a high response for anthracene.	None. The certified value for anthracene in SRM 1974a appears to be incorrect based on consistently high anthracene results in repeated analyses over the past four years.
Oil Reference Standard (North Slope Crude)	%D <35% for compounds above the RL	All criteria were met.	None

Table 3-18. Organic Quality Control Result Summary – Saturated Hydrocarbon Analyses

QC Sample or Measurement Type	Acceptance Criteria	Quality Control Result Summary	Impact to Data Quality and Usability
Equipment Blank	No compound to exceed 5 times the MDL	All criteria were met.	None
Field Blank	No compound to exceed 5 times the MDL	All criteria were met.	None
Field Replicate	RSD < 50% for all compounds >5 times the RL	All criteria were met.	None
Initial Calibration	%RSD <25% for all compounds (up to 10% of compounds can be >25%, but <35%)	All criteria were met.	None
Continuing Calibration	%D <25% for all compounds (up to 10% of compounds can be >25%, but <35%)	All criteria were met.	None
Surrogate Recoveries	45 to 125% recovery	All criteria were met.	None
Procedural Blank	No compound to exceed 5 times the MDL unless sample amount is >10 times blank amount	All criteria were met. Several SHCs were detected at trace concentrations less than 5 times the MDL.	Minor. Results within 5 times the associated blank result were qualified with a "B" and may be biased high or may be false positives. All qualified results were less than 2 times the reporting limit.
Blank Spike Sample Recoveries	35 to 125% recovery for spiked compounds	All criteria were met for the tissue BS. Decane was recovered at less than 35% in two sediment BSs.	Minor. The decane results in the associated samples may be biased low.
Laboratory Duplicate	RPD <30% for all compounds >10 times the MDL; mean RPD <30%	All criteria were met.	None
Oil Reference Standard (North Slope Crude)	%D <35% for compounds above the RL	All criteria were met.	None

Table 3-19. Organic Quality Control Result Summary – Sterane and Triterpane Analyses

QC Sample or Measurement Type	Acceptance Criteria	Quality Control Result Summary	Impact to Data Quality and Usability
Equipment Blank	No compound to exceed 5 times the MDL	An equipment blank was not analyzed with the associated samples.	
Field Blank	No compound to exceed 5 times the MDL	A field blank was not analyzed with the associated samples.	
Field Replicate	RSD < 50% for all compounds >5 times the RL	Field replicates were not analyzed with the associated samples.	
Initial Calibration	%RSD <25% for all compounds	All criteria were met.	None
Continuing Calibration	%D <25% for all compounds	All criteria were met.	None
Surrogate Standards	45 to 125% recovery	All criteria were met.	None
Procedural Blank	No compound to exceed 5 times the MDL unless sample amount is >10 times blank amount	A procedural blank was not analyzed with the associated samples.	
Oil Reference Standard (North Slope Crude)	%D <35% for compounds above the RL	All criteria were met.	None

Table 3-20. Inorganic Quality Control Result Summary – Trace-Metal Analyses

QC Sample or Measurement Type	Acceptance Criteria	Quality Control Result Summary	Impact to Data Quality and Usability
Equipment Blanks	No trace-metal concentration to exceed 5 times the MDL	All criteria were met.	None
Field Blanks	No trace-metal concentration to exceed 5 times the MDL	All criteria were met.	None
Field Replicates	RSD <50% for all trace metal concentrations >5 times the MDL	All criteria were met.	None
Initial Calibration	Standard Curve, correlation coefficient $r \geq 0.999$ for a 3 to 5 point curve for all trace metals	All criteria were met.	None
Continuing Calibration	%D <15% for all trace metals or repeat Initial Calibration and sample analyses	All criteria were met.	None
Matrix Spike Recoveries	60 to 125% recovery for all trace metals	All criteria were met.	None
Procedural Blanks	No trace metal concentration to exceed 5 times the MDL unless the sample amount is >10 times the blank concentration	All criteria were met.	None
Laboratory Duplicates	RSD <25% for all trace metal concentrations >10 times the MDL; mean RSD <25%	All criteria were met.	None
Sediment SRMs (MESS-2, 2704, 1643d)	Measured values must be within 20% of the certified or reference values for >85% of the SRM analyses.	All criteria were met.	None
Tissue SRMs (DORM-2, 2976, 1643d)	Measured values must be within 20% of the certified or reference values for >85% of the SRM analyses.	All criteria were met.	None
Dissolved SRMs (CASS-3)	Measured values must be within 20% of the certified or reference values for >85% of the SRM analyses.	All criteria were met.	None

Table 3-21. SRM Results for BCSS-1 and MESS-2

Sample ID	Ag ($\mu\text{g/g}$)	Al (%)	As ($\mu\text{g/g}$)	Ba ($\mu\text{g/g}$)	Be ($\mu\text{g/g}$)	Cd ($\mu\text{g/g}$)	Co ($\mu\text{g/g}$)	Cr ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Fe (%)
SRM-BCSS-1 This Study, 1999 (n = 2)	0.09 ± 0.0	6.13 ± 0.12	12.1 ± 0.5	317 ± 11	1.5 ± 0.2	0.25 ± 0.01	11.1 ± 0.4	111 ± 0	18.1 ± 0.6	3.21 ± 0.01
SRM BCSS-1 NRC Certified	0.11 ± 0.03	6.26 ± 0.22	11.1 ± 1.4	(330)	1.3 ± 0.3	0.25 ± 0.04	11.4 ± 2.1	123 ± 14	18.5 ± 2.7	3.29 ± 0.10
SRM MESS-2 This Study, 1999 (n = 4)	--	--	--	--	--	--	--	--	--	--
SRM MESS-2 NRC Certified	--	--	--	--	--	--	--	--	--	--
Spike Recovery (%) 1999	68.0 ± 6.1	106.0 ± 2.1	99.6 ± 8.4	106.3 --	96.7 --	109.2 --	100.6 --	100.0 ± 4.2	109 ± 0	99.0 ± 7.1

Sample ID	Hg ($\mu\text{g/g}$)	Mn ($\mu\text{g/g}$)	Ni ($\mu\text{g/g}$)	Pb ($\mu\text{g/g}$)	Sb ($\mu\text{g/g}$)	Ti ($\mu\text{g/g}$)	V ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)	TOC (%)
SRM-BCSS-1 This Study, 1999 (n = 2)	--	226 ± 4	52.1 ± 2.0	22.8 ± 0.4	0.65 ± 0.02	0.53 ± 0.01	97.1 ± 2.1	111 ± 1	--
SRM BCSS-1 NRC Certified	--	229 ± 15	55.3 ± 3.6	22.7 ± 3.4	0.59 ± 0.06	(0.6)	93.4 ± 4.9	119 ± 12	2.19 ± 0.09
SRM MESS-2 This Study, 1999 (n = 4)	0.092 ± 0.004	--	--	--	--	--	--	--	--
SRM MESS-2 NRC Certified	0.092 ± 0.009	--	--	--	--	--	--	--	2.14 ± 0.03
Spike Recovery (%) 1999	85.9 ± 6.6	99.5 ± 6.4	91.4 --	95.7 --	108.6 --	109.2 --	124 ± 4.7	94.5 ± 0.6	NA

Notes: Values in parenthesis are for reference only; SRM not certified by the NRC.
Mean results \pm standard deviation are presented.
Marine sediment SRMs issued by NRC.

Table 3-22. SRM Results for Trace Metals in Mussel Tissue, Dogfish Muscle, and Water

Standard Reference Material	Ag ($\mu\text{g/g}$)	Al ($\mu\text{g/g}$)	As ($\mu\text{g/g}$)	Ba ($\mu\text{g/g}$)	Be ($\mu\text{g/g}$)	Cd ($\mu\text{g/g}$)	Co ($\mu\text{g/g}$)	Cr ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)
SRM 2976 This Study, 1999 (n = 1)	0.008	150	13.1	0.63	0.009	0.81	0.63	0.63	3.95
SRM 2976 NIST Certified	(0.011) (± 0.005)	(134) (± 34)	13.3 ± 1.8	--	--	0.82 ± 0.16	(0.61) (± 0.02)	(0.50) (± 0.16)	4.02 ± 0.33
SRM DORM-2 This Study, 1999 (n = 1)	0.040	9.5	17.8	2.24	0.007	0.047	0.189	30.9	2.43
SRM DORM-2 NRC Certified	0.041 ± 0.013	10.9 ± 1.7	18.0 ± 1.1	--	--	0.043 ± 0.008	0.182 ± 0.031	34.7 ± 5.5	2.34 ± 0.16
SRM 1643d This Study, 1999 (n = 1)	--	--	--	509.3 $\mu\text{g/L}$	12.50 $\mu\text{g/L}$	--	--	--	--
SRM 1643d NIST Certified	--	--	--	506.5 $\mu\text{g/L}$ ± 8.9	12.53 $\mu\text{g/L}$ ± 0.28	--	--	--	--
Spike Recovery (%) 1999 (Tissue)	92.3 --	96.6 --	92.6 --	101.6 --	100.4 --	103.7 --	130.0 --	91.7 --	101.5 --

Notes: Values in parenthesis are for reference only; SRM not certified by the NRC. Mean results \pm standard deviation are presented.

SRM 2976 – Mussel tissue issued by NIST; SRM DORM-2 – Dogfish Muscle certified by NRC; SRM 1643d – Trace Metals in Waters issued by NIST

Table 3-22 (continued). SRM Results for Trace Metals in Mussel Tissue, Dogfish Muscle, and Water

Standard Reference Material	Fe ($\mu\text{g/g}$)	Hg ($\mu\text{g/g}$)	Mn ($\mu\text{g/g}$)	Ni ($\mu\text{g/g}$)	Pb ($\mu\text{g/g}$)	Sb ($\mu\text{g/g}$)	Ti ($\mu\text{g/g}$)	V ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)
SRM 2976 This Study, 1999 (n = 1/2)	172	0.063 ± 0.001	34.5	0.95	1.09	0.012	0.003	0.82	144
SRM 2976 NIST Certified	171.0 ± 4.9	0.061 ± 0.0036	(33) (± 2)	(0.93) (± 0.12)	1.19 ± 0.18	--	(0.001)	--	137 ± 13
SRM DORM-2 This Study, 1999 (n = 1)	137	--	3.77	17.4	0.071	0.026	0.005	0.25	24.3
SRM DORM-2 NRC Certified	142 ± 10	4.64 ± 0.26	3.66 ± 0.34	19.4 ± 3.1	0.065 ± 0.007	--	(0.004)	--	25.6 ± 2.3
SRM 1643d This Study, 1999 (n = 1)	--	--	--	--	--	54.6 $\mu\text{g/L}$	7.45 $\mu\text{g/L}$	34.2 $\mu\text{g/L}$	--
SRM 1643d NIST Certified	--	--	--	--	--	54.1 $\mu\text{g/L}$ ± 1.1	7.28 $\mu\text{g/L}$ ± 0.25	35.1 $\mu\text{g/L}$ ± 1.4	--
Spike Recovery (%) 1999 (Tissue)	104.9 --	62.3 ± 2.9	97.7 --	95.8 --	91.3 --	99.4 --	100.5 --	91.9 --	100.1 --

Notes: Values in parenthesis are for reference only; SRM not certified by the NRC or NIST.

Table 3-23. SRM Results for Trace Metals in River and Marine Sediment

Standard Reference Material	Al (%)	Ba (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Pb (µg/g)	Zn (µg/g)	TOC (%)
SRM 2704 This Study, 1999 (n = 4)	6.19 ±0.07	421 ±7	3.45 ±0.15	132 ±1	101 ±1.7	4.15 ±0.07	161 ±4	443 ±4	--
SRM 2704 NIST Certified	6.11 ±0.16	414 ±12	3.45 ±0.22	135 ±5	98.6 ±5.0	3.45 ±0.22	161 ±17	438 ±12	--
SRM MESS-2 This Study, 1999 (n = 8)	--	--	--	--	--	--	--	--	1.95 ±0.02
SRM MESS-2 NRC Certified	--	--	--	--	--	--	--	--	2.14* ±0.03
Spike Recovery (%) 1999	101.0 ±5.2	100.1 ±0.9	97.1 ±7.3	93.2 ±1.1	105.2 ±3.8	100.3 ±2.4	97.2 ±3.2	96.9 ±1.8	101.0 ±1.2

Notes: Values in parenthesis are for reference only; SRM not certified by NIST.

*Total Carbon (organic plus inorganic).

Mean results + standard deviation are presented.

SRM 2704 – River Sediment issued by NIST; SRM MESS-2 – Marine Sediment certified by NRC

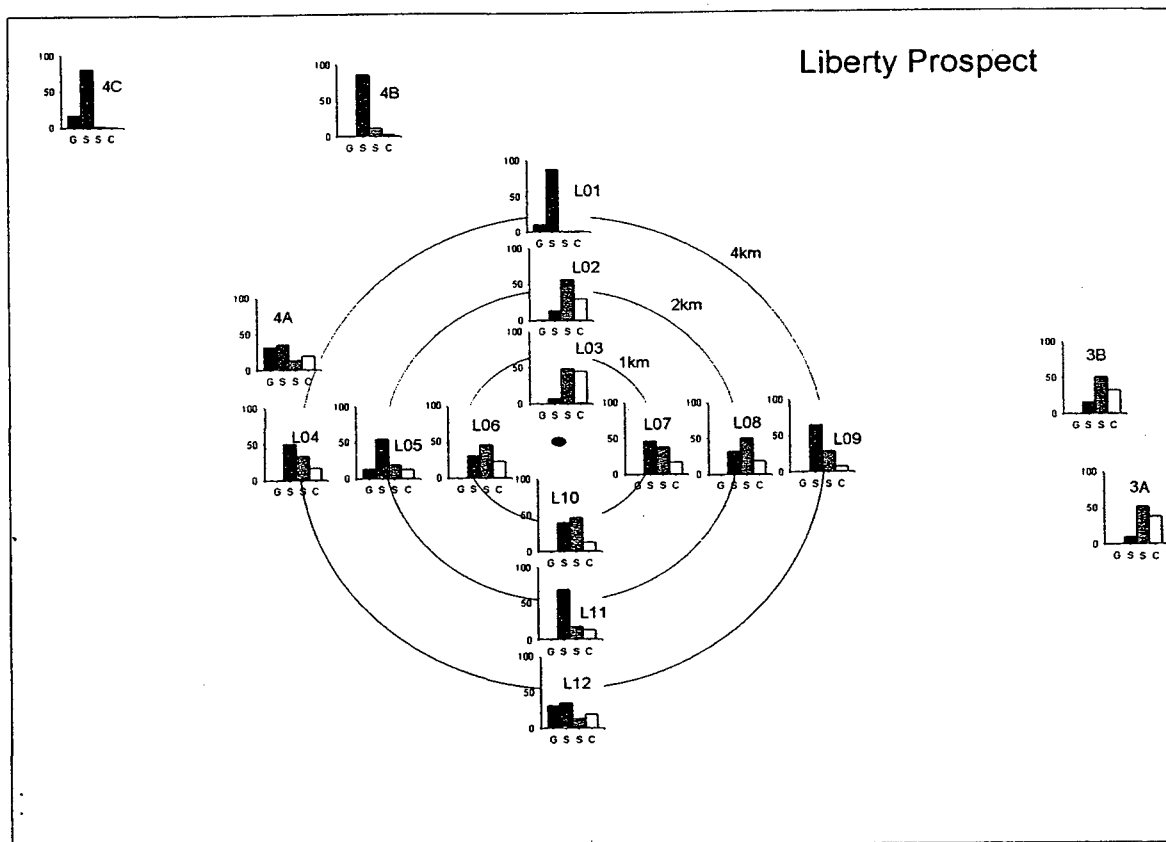
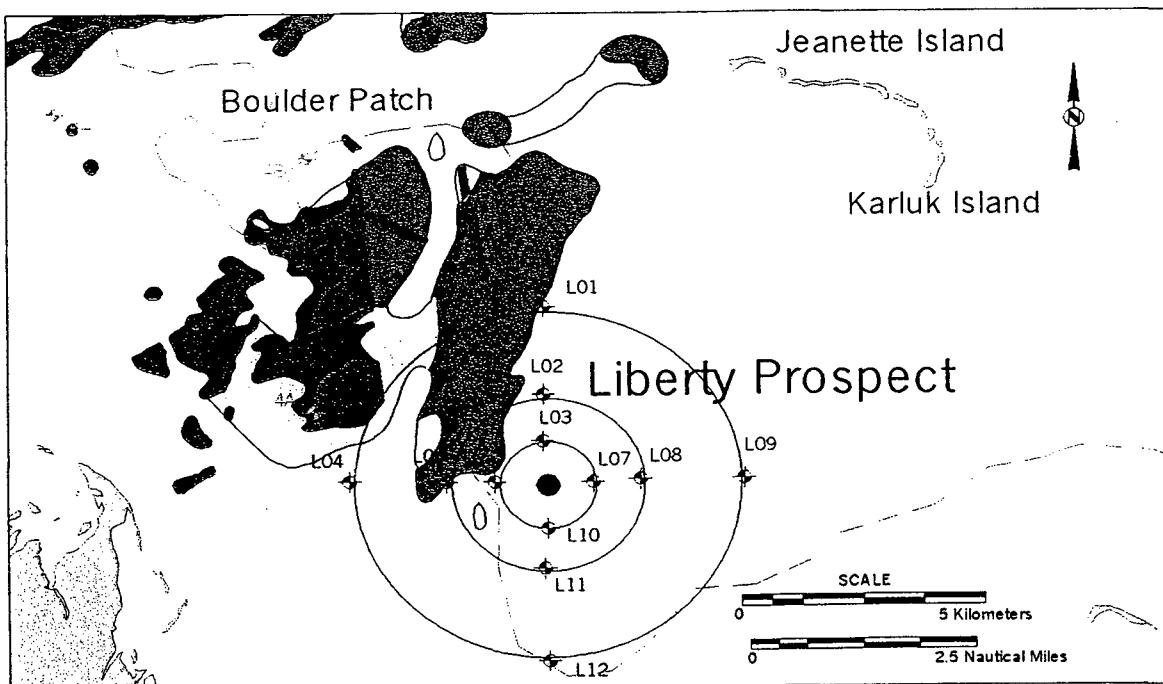


Figure 3-2. Map of Liberty Sampling Stations and Grain-Size Histograms

Histograms show grain-size distribution as percent gravel (black bar), sand (red bar), silt (green bar), and clay (yellow bar).

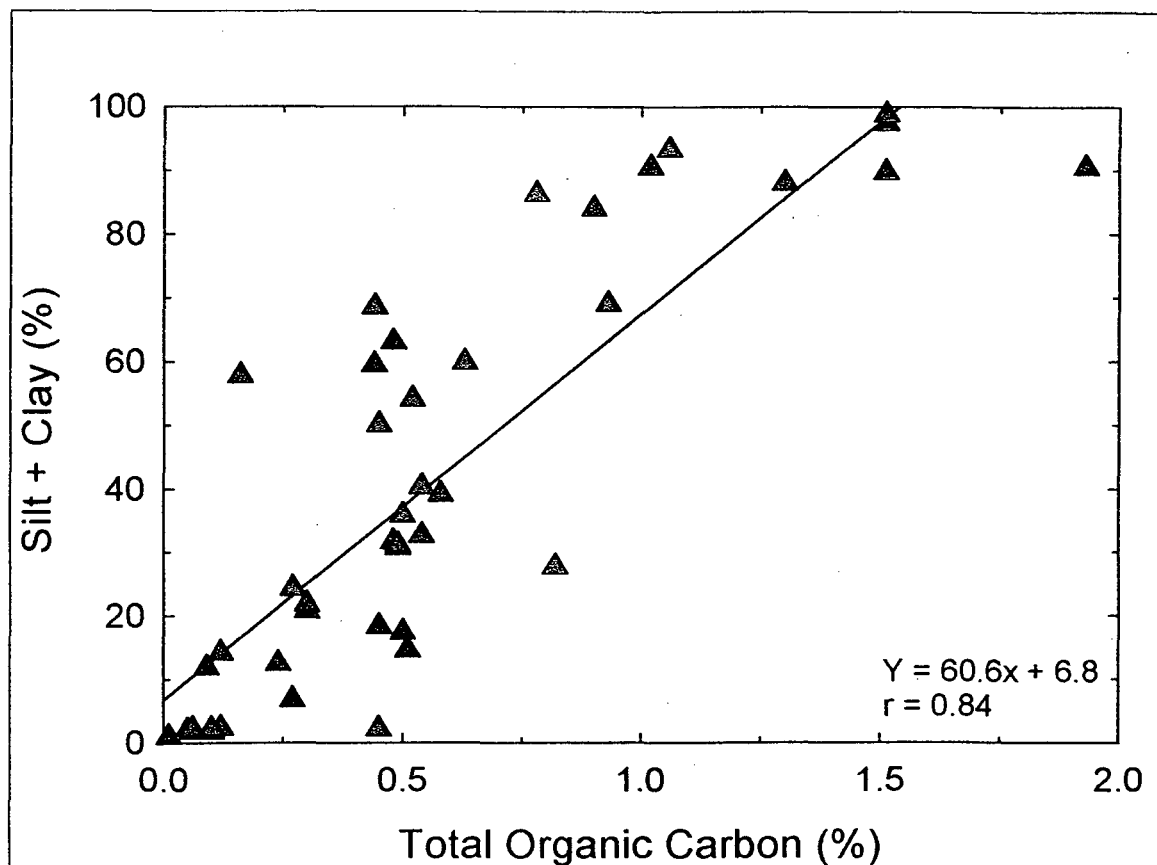


Figure 3-3. Total Organic Carbon versus Silt + Clay for Surficial Sediment Samples from Beaufort Sea Monitoring Program, Northstar, and Liberty Stations

1999 BSMP samples (blue triangles), Northstar samples (red triangles), and Liberty samples (green triangles)

The line, equation, and correlation coefficient (r) are from a linear regression calculation. The maximum value of 3.42% TOC at [silt + clay] = 87% is not shown on the figure or included in the regression calculation because it is presently treated as an anomalous point.

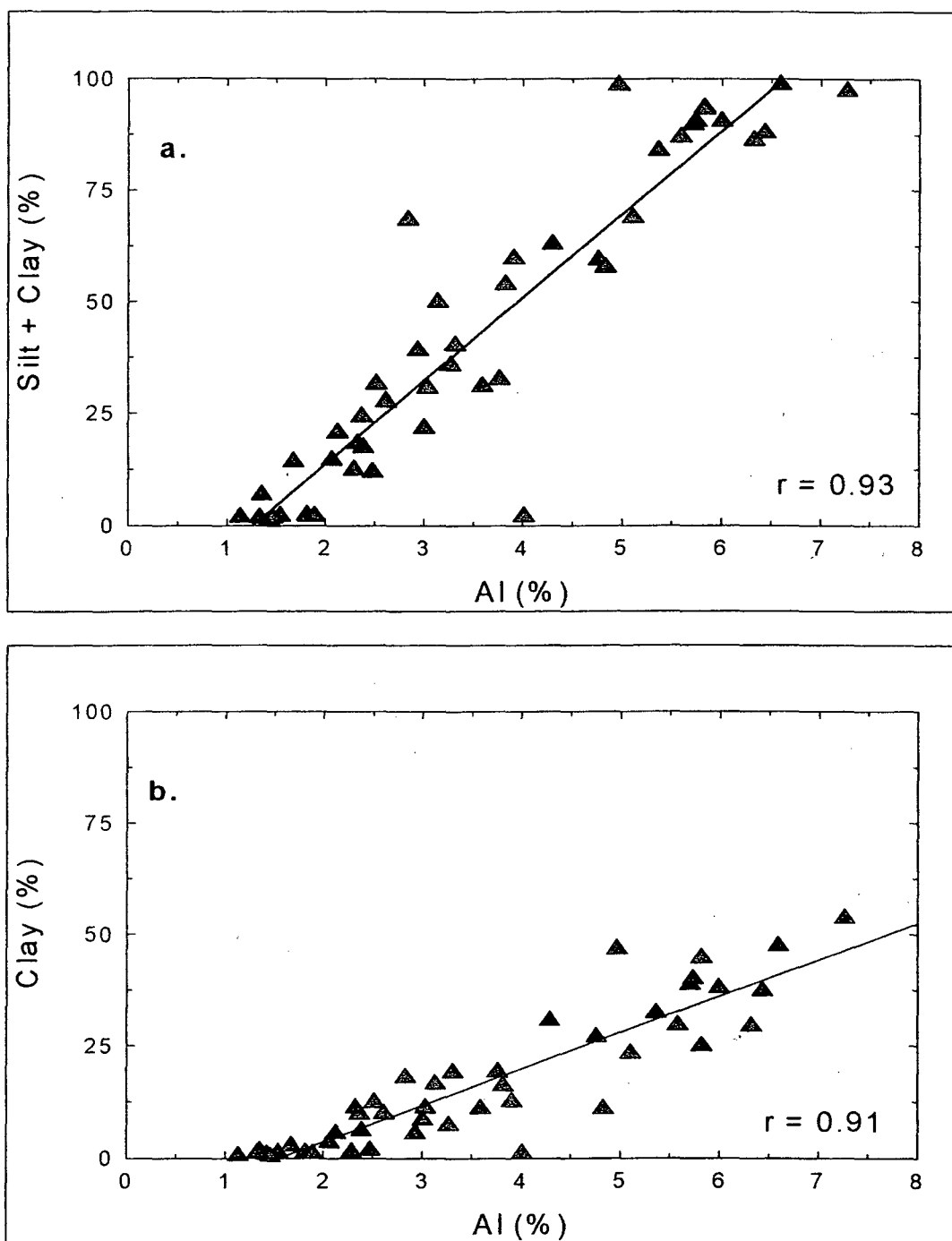


Figure 3-4. Concentrations of Al versus (a) Silt + Clay and (b) Clay for Surficial Sediment Samples from Beaufort Sea Monitoring Program, Northstar, and Liberty Stations

BSMP samples (blue triangles), Northstar samples (red triangles), and Liberty samples (green triangles)

The line and correlation coefficient (r) are from linear regression calculations.

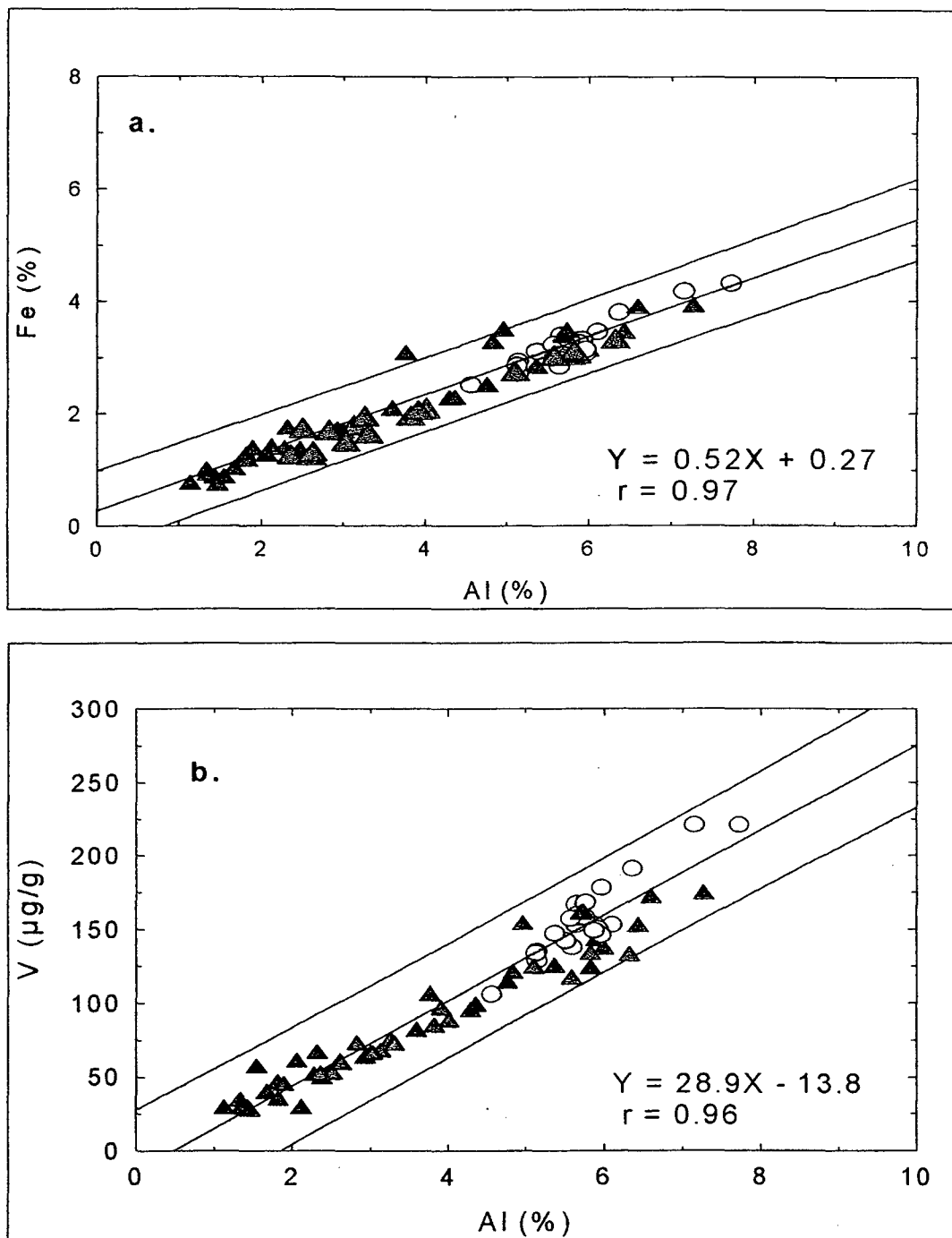


Figure 3-5. Concentrations of Al versus (a) Fe and (b) V for Surficial Sediment Samples from Beaufort Sea Monitoring Program, Northstar, and Liberty Stations

1989 BSMP samples (yellow circles), 1999 BSMP samples (blue triangles), Northstar samples (red triangles), and Liberty samples (green triangles)

The lines, equations, correlation coefficients (r) and 99% prediction intervals are from linear regression and related statistical calculations.

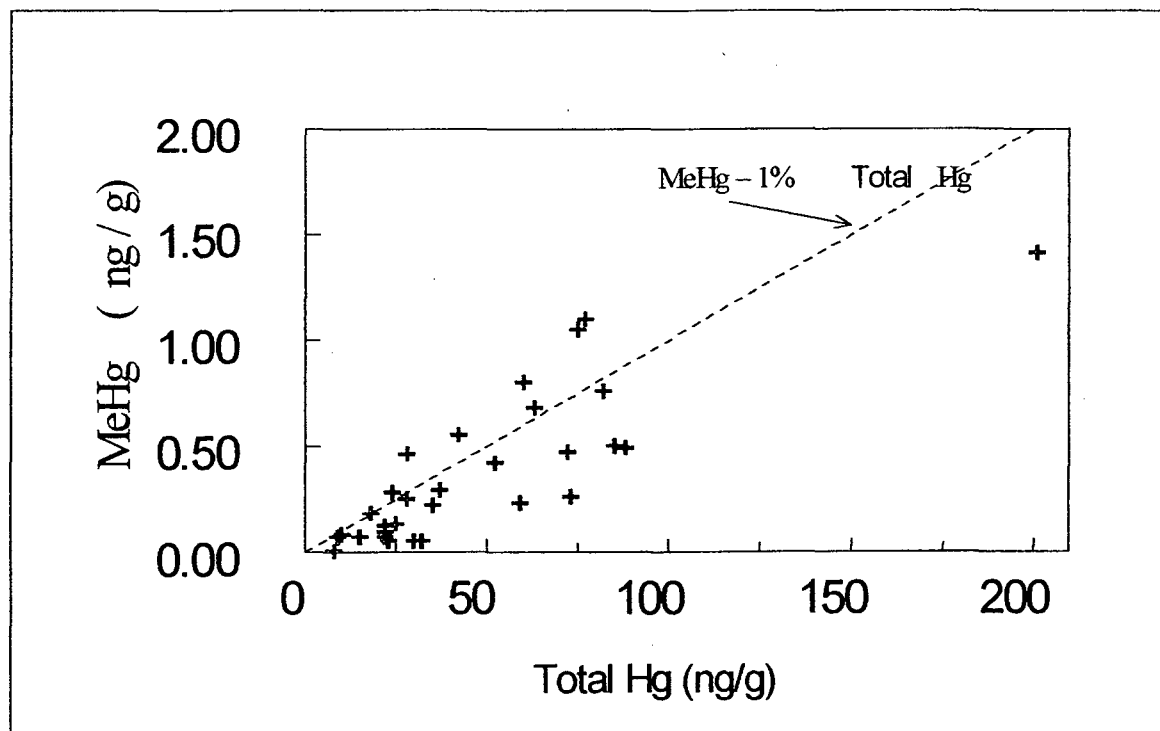


Figure 3-6. Concentrations of Total Hg versus Methyl Hg for Surficial Sediment Samples from 1999 ANIMIDA Study Area

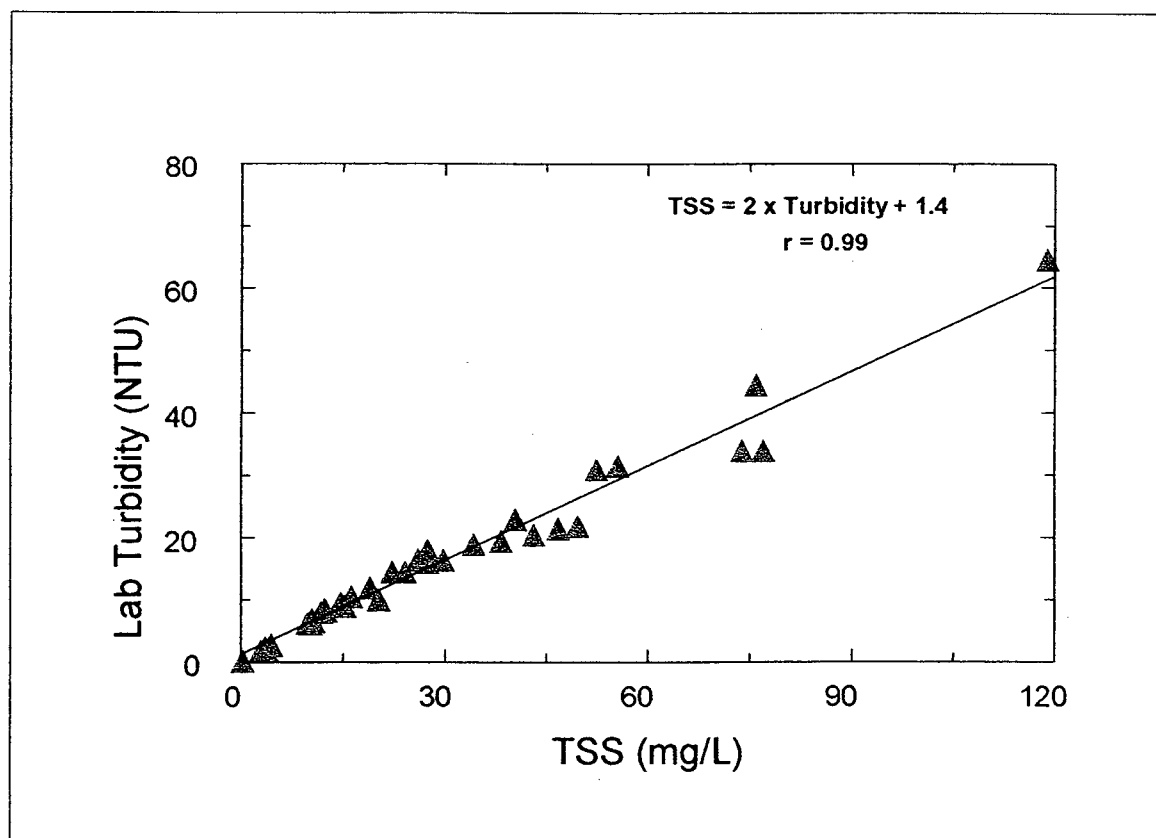


Figure 3-7. Total Suspended Solids versus Laboratory Turbidity for 1999 ANIMIDA Study Area Samples

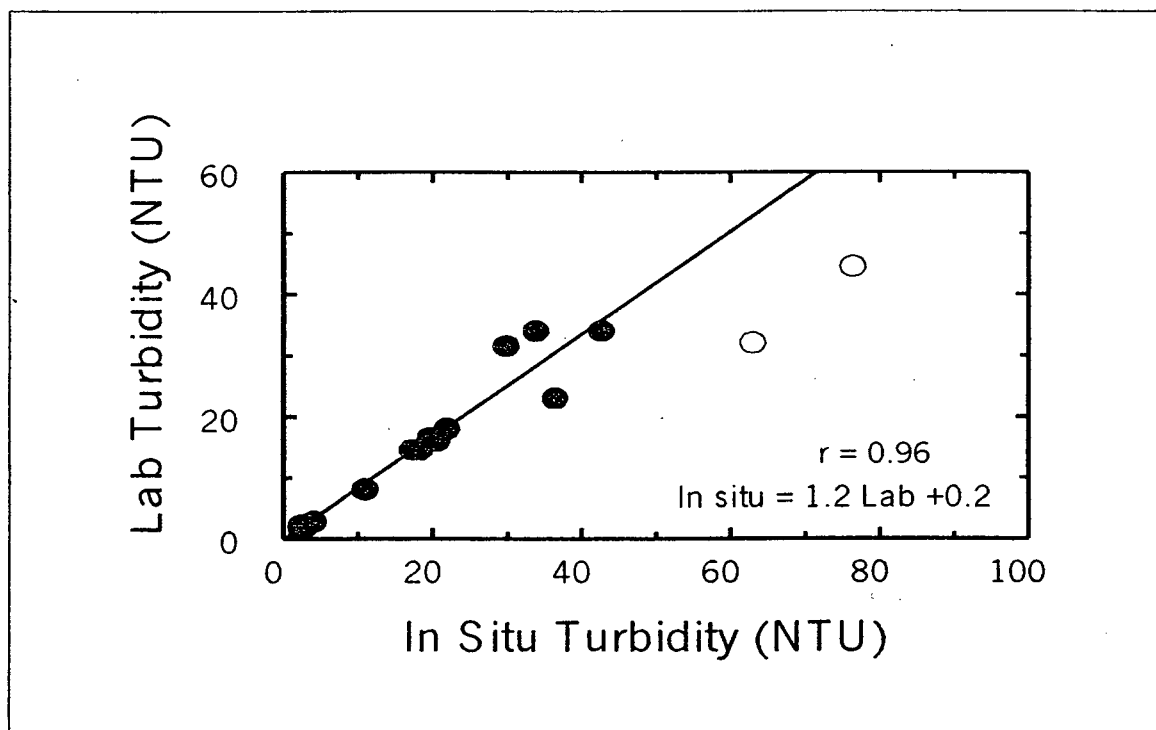


Figure 3-8. *In situ* Turbidity versus Laboratory Turbidity for 1999 ANIMIDA Study Area Samples

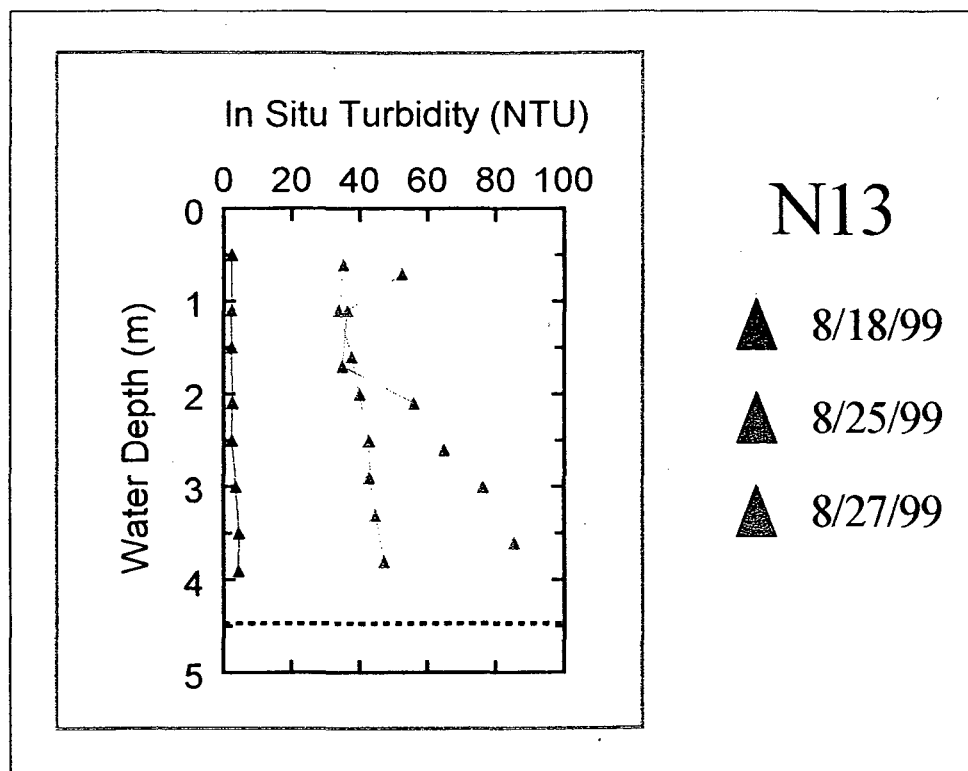


Figure 3-9. Vertical Profiles for *In situ* Turbidity for Station N13 Sampled on Three Different Dates

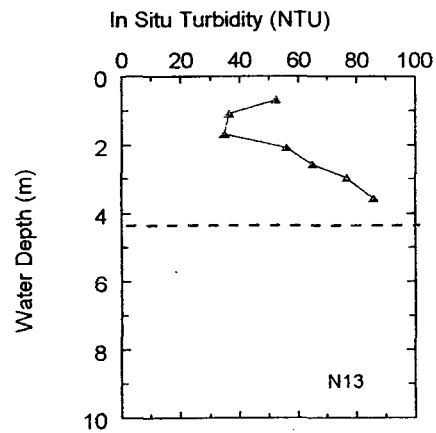
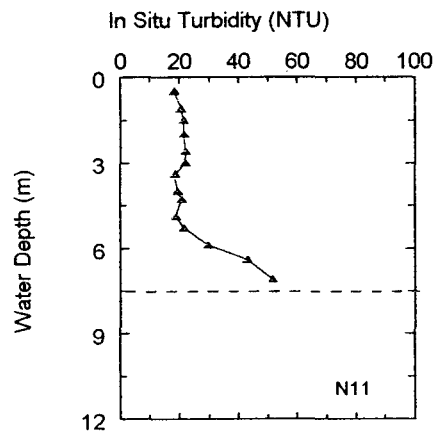
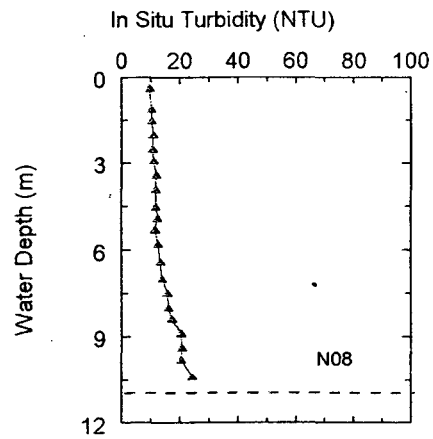
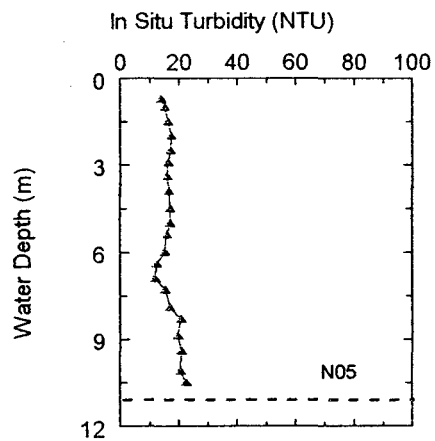


Figure 3-10. Vertical Profiles for *In situ* Turbidity for Stations N05, N08, N11, and N13 Sampled on August 25, 1999

Station N13, August 18, 1999

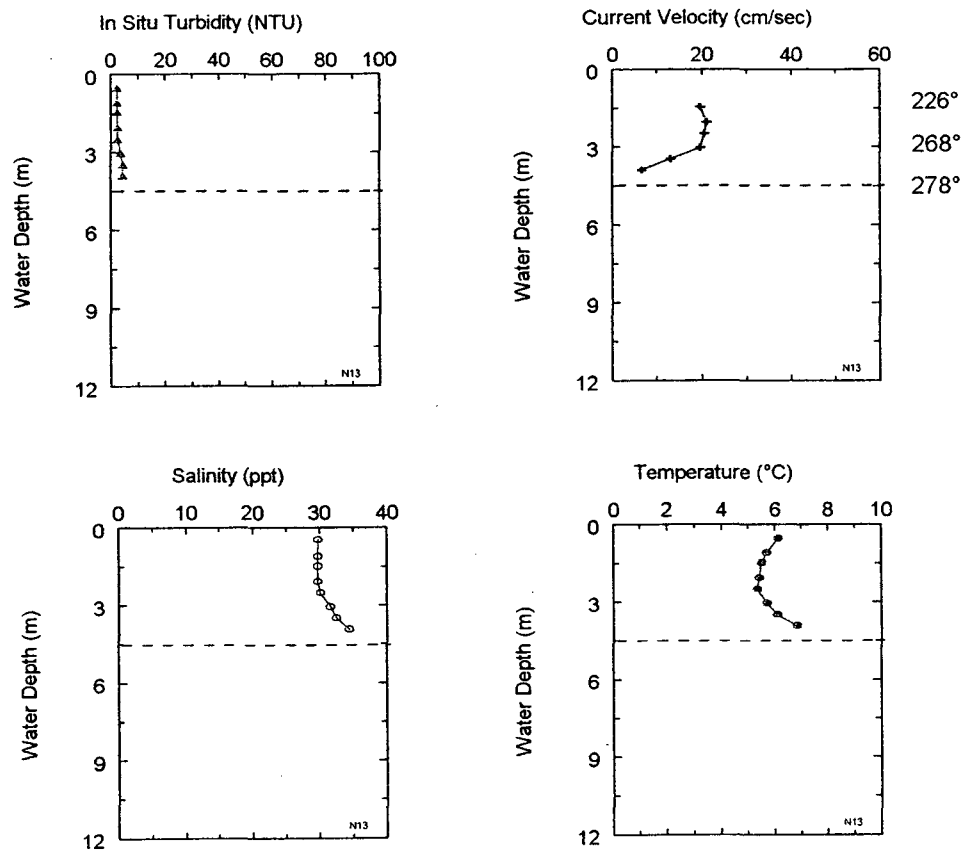


Figure 3-11. Vertical Profiles for *In situ* Turbidity, Current Velocity and Direction, Salinity, and Temperature for Station N13 Sampled August 18, 1999

Station N13, August 25, 1999

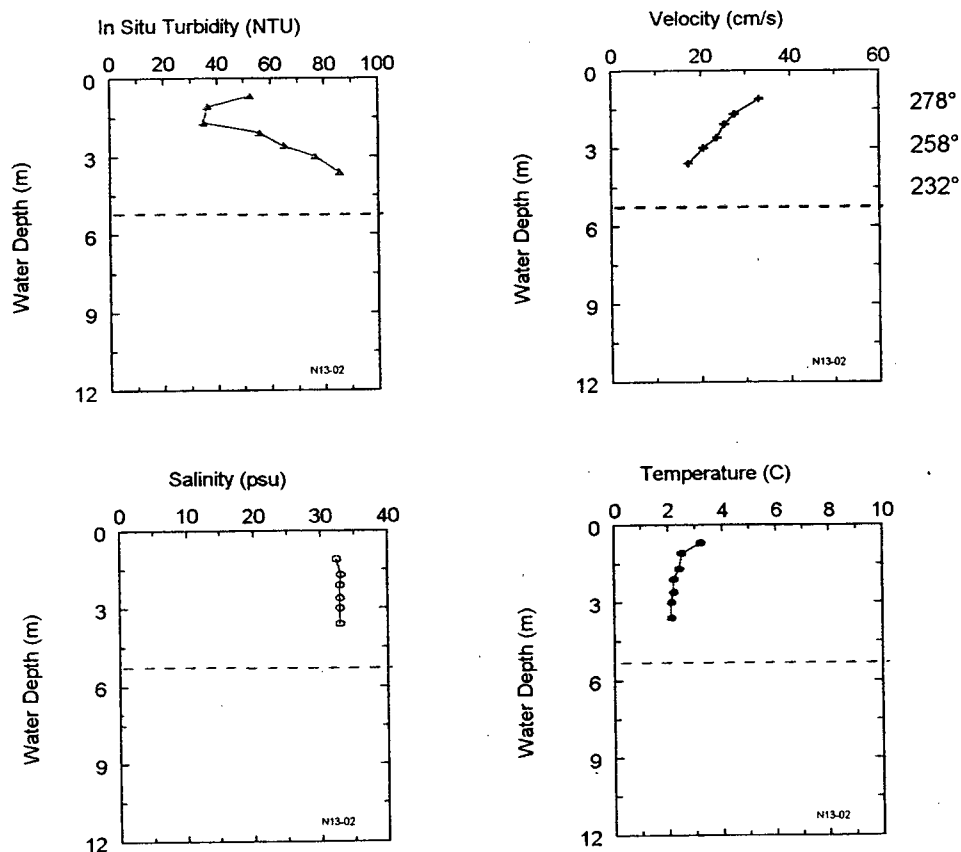


Figure 3-12. Vertical Profiles for *In situ* Turbidity, Current Velocity and Direction, Salinity, and Temperature for Station N13 Sampled August 25, 1999

Station N05, August 26, 1999

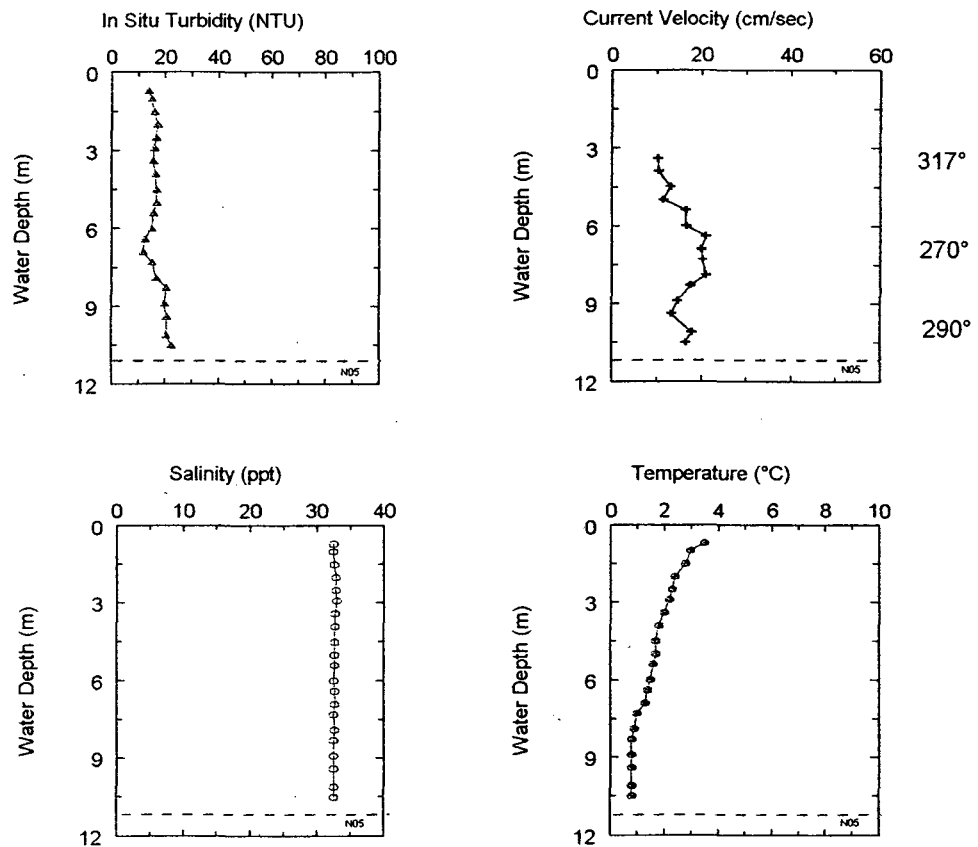


Figure 3-13. Vertical Profiles for *In situ* Turbidity, Current Velocity and Direction, Salinity, and Temperature for Station N05 Sampled August 26, 1999

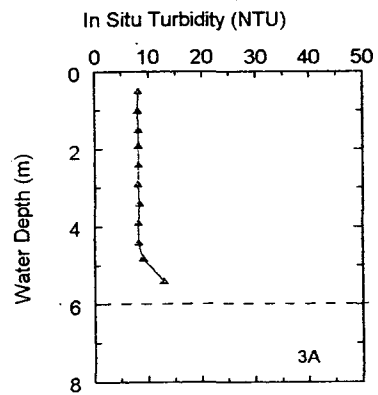
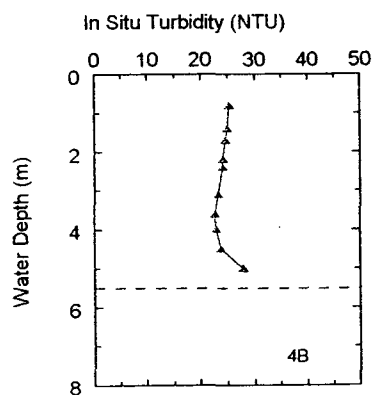
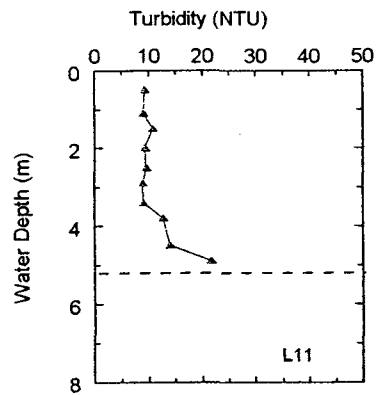
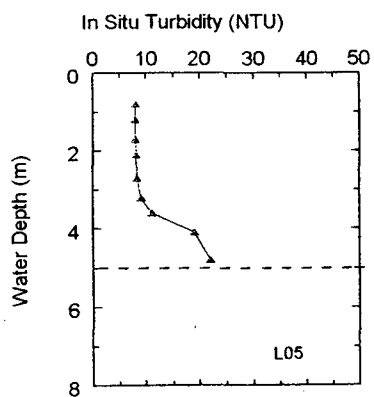


Figure 3-14. Vertical Profiles for *In situ* Turbidity for Stations L05, L11, 4B, and 3A Sampled August 28-29, 1999

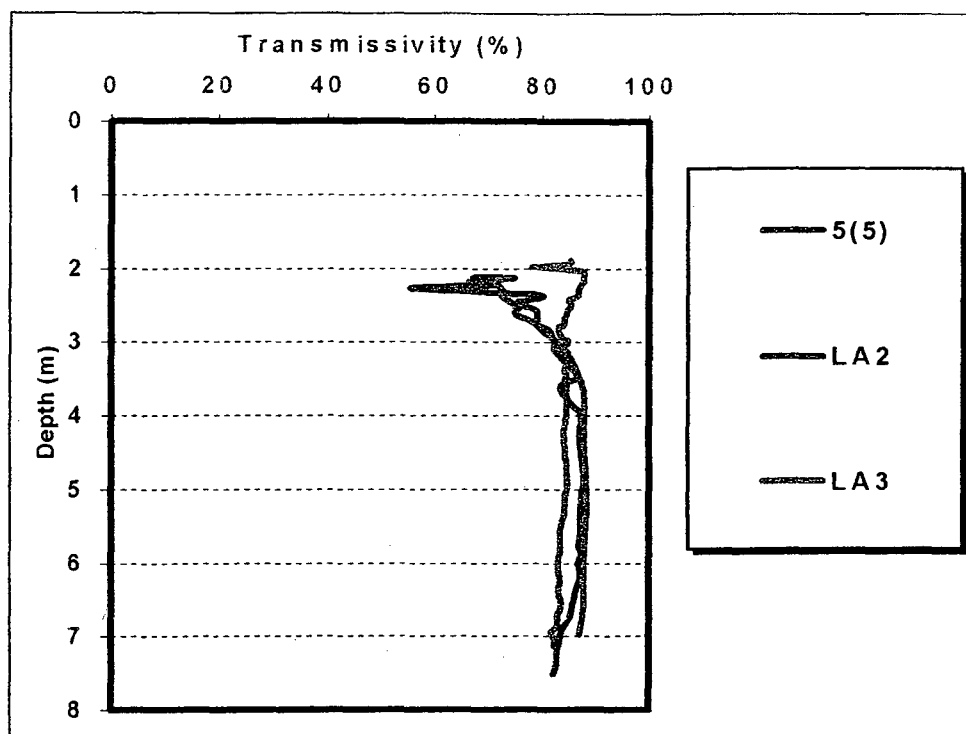


Figure 3-15. Vertical Profiles of Transmissivity for Stations 5(5), LA2, and LA3 Sampled During April 2000 (Top 2 m were a layer of ice.)

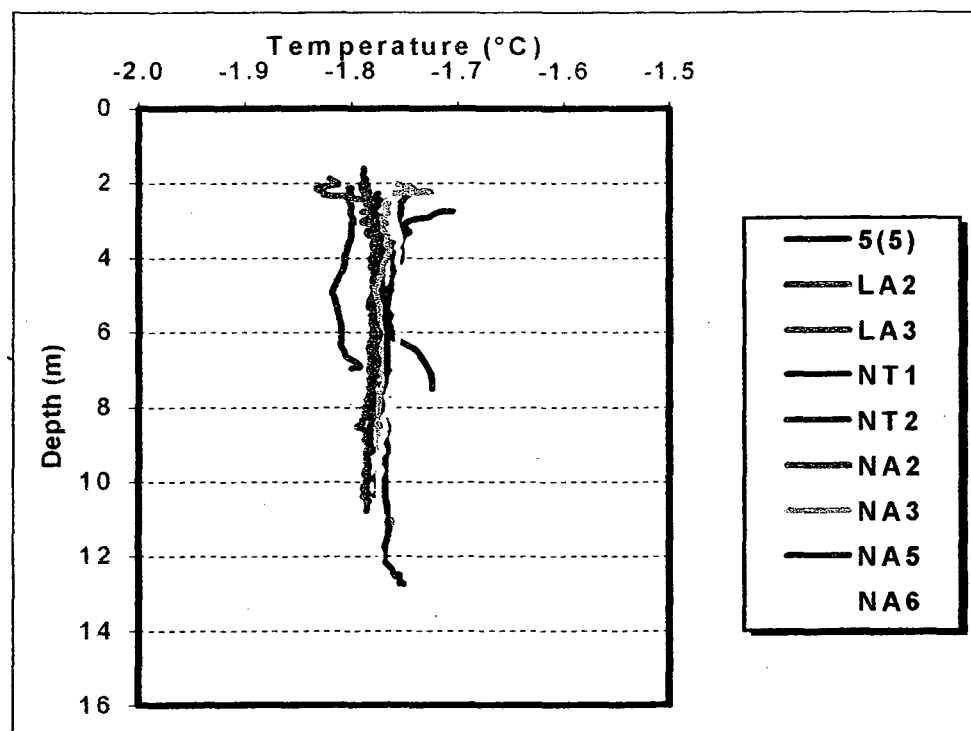


Figure 3-16. Vertical Profiles for Temperature at Stations Sampled During April 2000

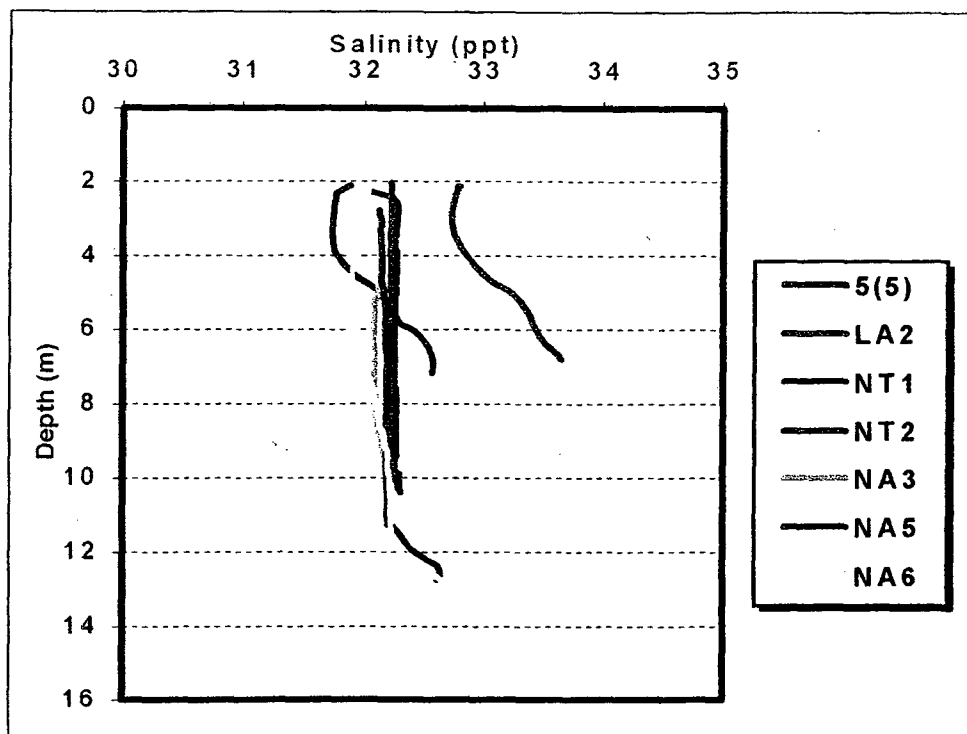


Figure 3-17. Vertical Profiles for Salinity at Stations Sampled During April 2000

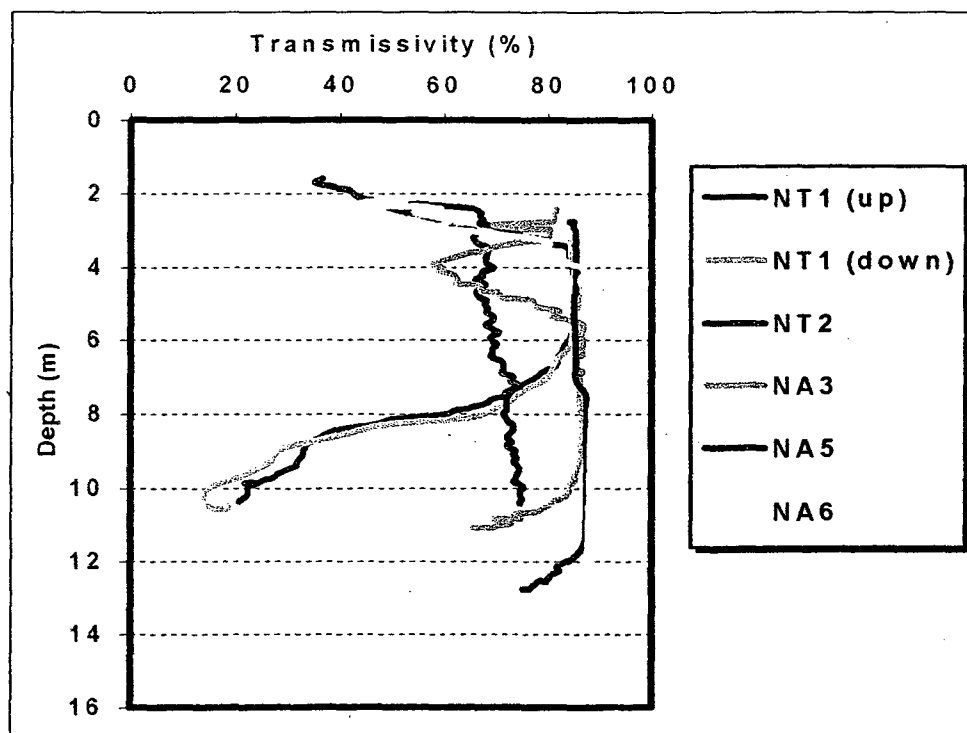


Figure 3-18. Vertical Profiles of Transmissivity for Stations Sampled Near Northstar During April 2000

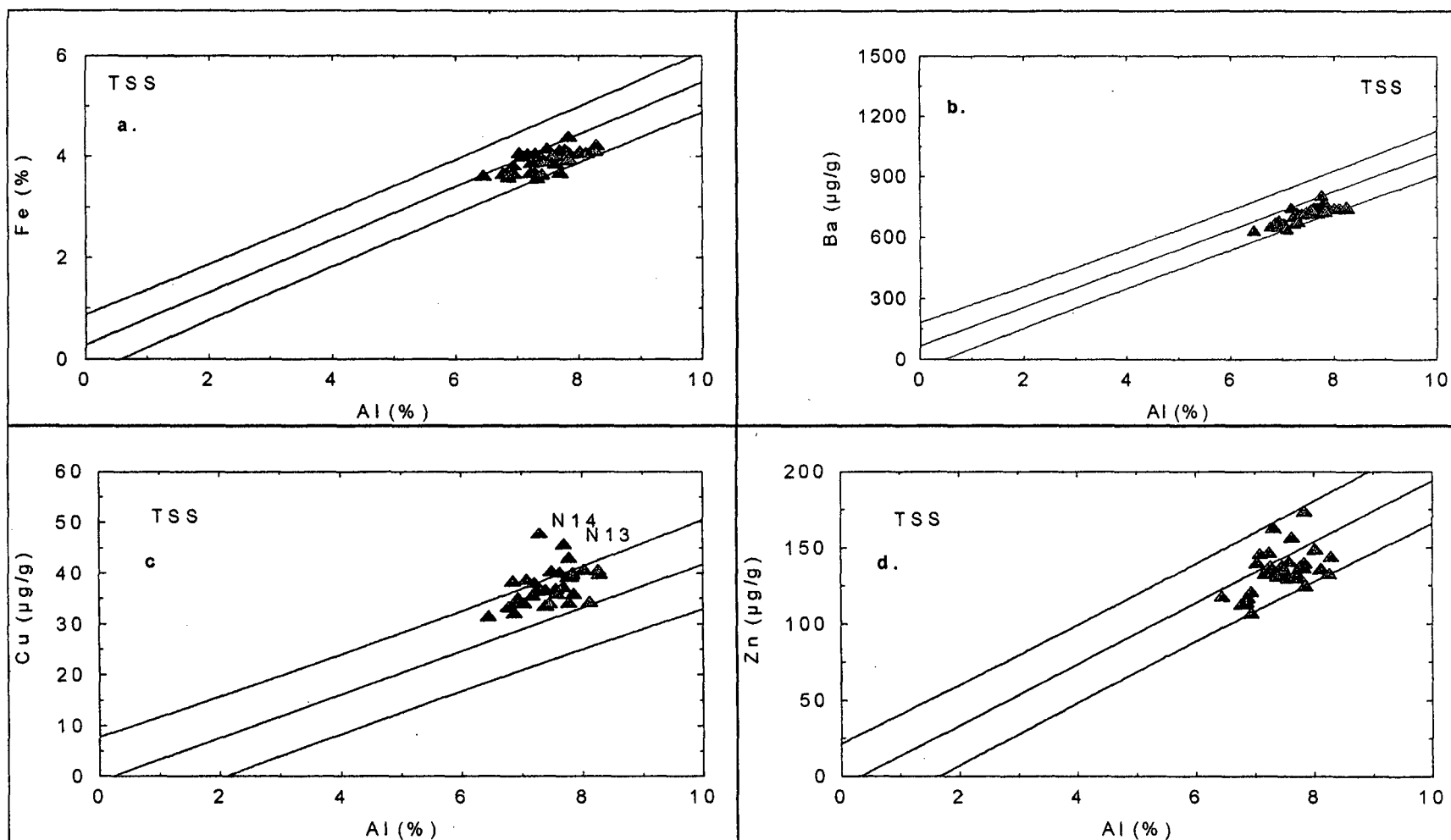


Figure 3-19. Concentrations of Al versus (a) Fe, (b) Ba, (c) Cu, and (d) Zn for Total Suspended Solid Samples

Samples collected during August 1999 from the BSMP stations (blue triangles), Northstar stations (red triangles), and Liberty stations (green triangles). Lines show linear regression fit to sediment data with 99% prediction intervals.

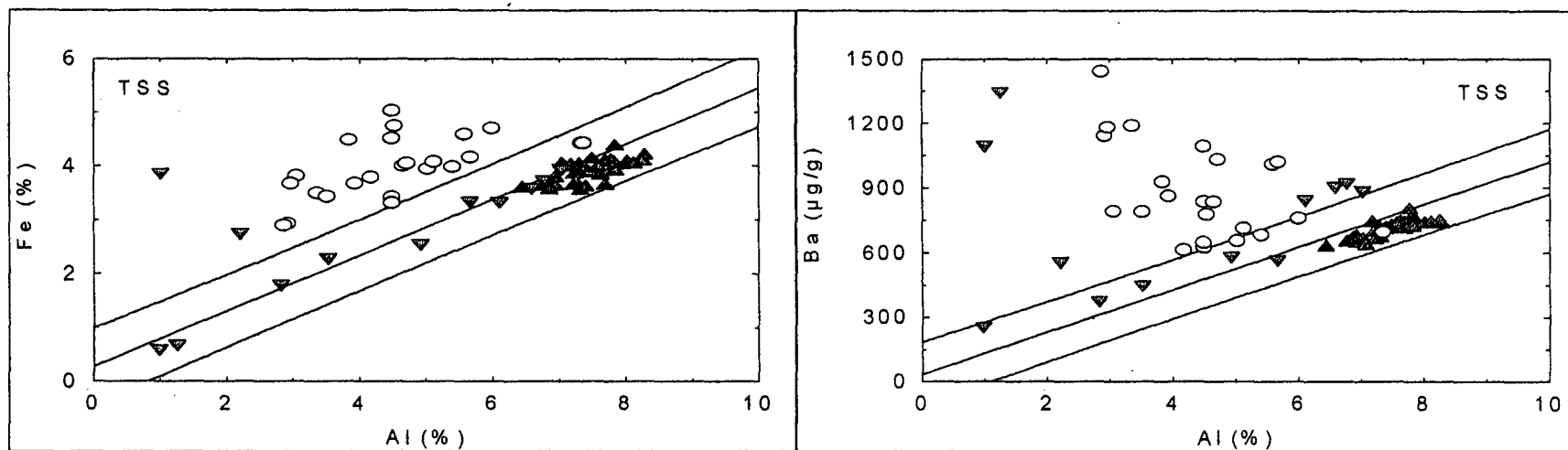


Figure 3-20. Concentrations of Al versus (a) Fe and (b) Ba for Total Suspended Solid and Source Material Samples

Samples collected during April 2000 (gray circles) and August 1999 (Northstar-red, Liberty-green and BSMP-blue triangles). Source material collected during August 1999 (inverted orange triangles). Lines show linear regression fit to sediment data with 99% prediction intervals.

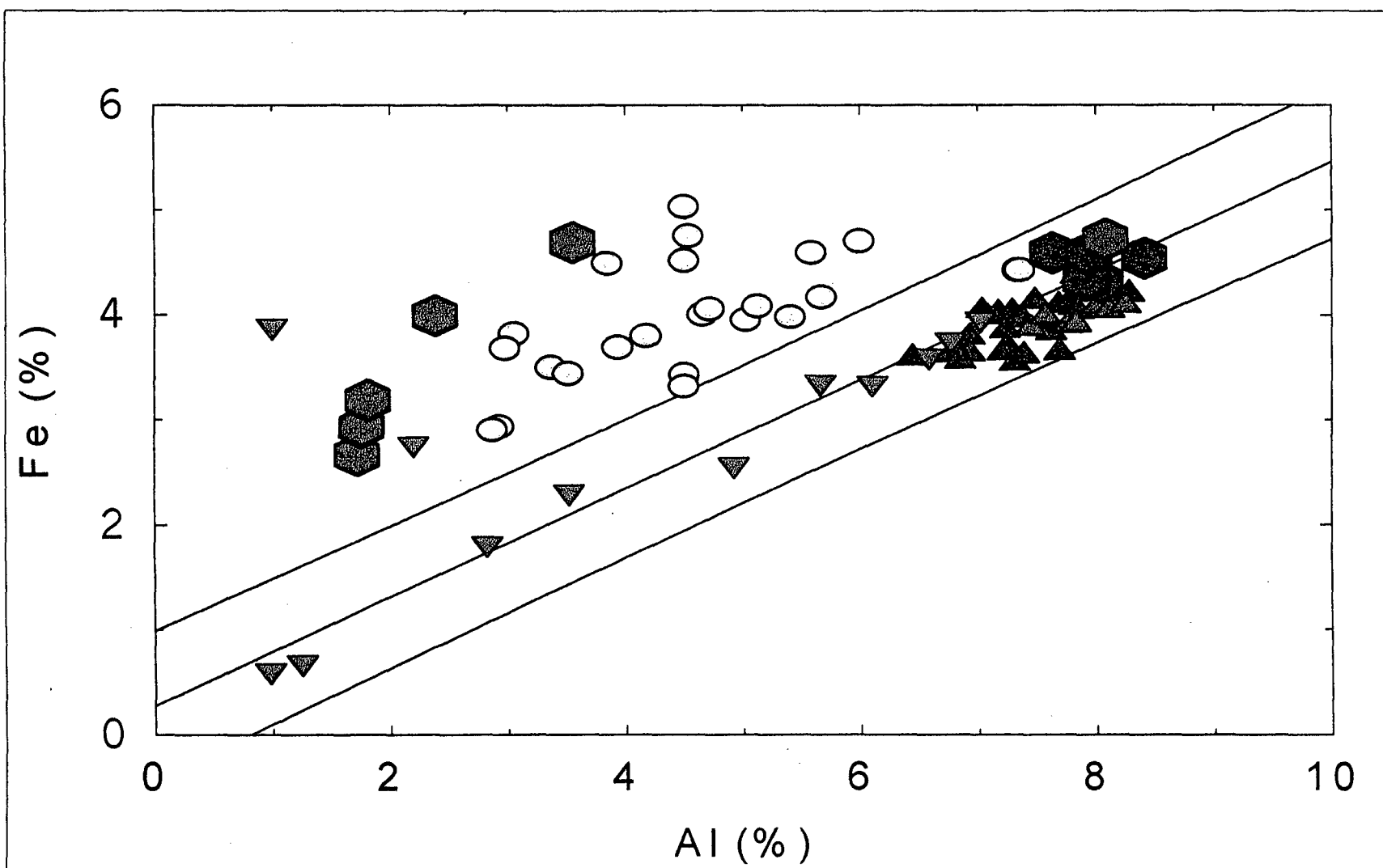


Figure 3-21. Concentrations of Al versus Fe for Ice Core Sediment, Total Suspended Solid, and Source Material Samples

Samples collected during April 2000 (gray circles) and August 1999 (Northstar-red, Liberty-green and BSMP-blue triangles). Source material collected during August 1999 (inverted orange triangles). Lines show linear regression fit to sediment data with 99% prediction intervals.

4.0 Discussion

The Summer 1999 and Winter 2000 field sampling programs successfully obtained data on surficial sediments, riverine sediments and peat, biota (clams and amphipods), suspended sediments, and ice cores in the ANIMIDA study area. Ancillary data on currents, PAR, and CTD were also collected. Together, these data represent the pre-production baseline for the Northstar and Liberty prospects for the ANIMIDA Phase I program, and will be used for future comparisons to Phase II (post-production) measurements. In this section of the report the results will be further evaluated for general trends and relationships, and comparison to previous BSMP studies. Statistical comparisons of the data for the purpose of hypothesis testing will be performed as part of the ANIMIDA Phase II program, once post-development data are collected.

4.1 Surficial Sediments (0-1 cm)

4.1.1 Metals

4.1.1.1 BSMP Elements

Concentrations of Al, Ba, Cd, Cr, Cu, Fe, Pb, V, and Zn were also determined during the 1989 BSMP supported by MMS. The earlier data are combined here with the 1999 results to introduce a series of templates for identification and future tracking of possible metal contamination. The proposed normalization process is first introduced here in some detail using data for Ba. Then, the proposed approach is applied to the other metals.

In each case, concentrations of the trace metal of interest are plotted versus Al, as shown for Ba in Figure 4-1. The naturally occurring levels of trace metals can vary as a function of sediment grain size, organic carbon content, and mineralogy. For example, most trace metals, and the major metal Al, are present at very low levels in quartz sand or carbonate. In contrast, concentrations of most trace metals and Al are much higher in fine-grained aluminosilicates. Aluminum is rarely introduced by anthropogenic processes and is present at percent levels in most sediment relative to parts-per-million (ppm) levels for trace metals. Thus, Al often provides a valuable normalization tool that can incorporate the metal-controlling variables of grain size, organic carbon content, and mineralogy. In the ideal case (Figure 4-1), a good linear correlation is observed between concentrations of a trace metal and Al. At low levels of Al and Ba, the sediment is rich in quartz sand. At higher levels of Al and Ba, the sediment is clay-rich.

A 99 percent prediction interval has been drawn on Figure 4-1 for the line determined from linear regression. Natural sediment from the Beaufort Sea is thus predicted to follow the trend presented in Figure 4-1. Any positive deviations in Ba levels, above the upper prediction limit, will suggest the presence of anthropogenic inputs of Ba such as might occur from the discharge of drilling mud containing barite. The trends in Figure 4-1 support the conclusion that no discernible anthropogenic inputs of Ba can be detected in sediment from the BSMP stations in the Prudhoe Bay area during 1989 and 1999. The value for Ba in average continental crust is slightly below the lower 99 percent confidence interval developed from the BSMP data (Figure 4-1); however, this crustal value is a grand average with a relatively large standard deviation. Recent studies in the Shelikof Strait, Alaska, found background levels of Ba (pre-1900 from sediment in cores) at comparable Al levels to be about 800 $\mu\text{g/g}$ (Boehm et al., 2001). Future efforts in the Beaufort Sea will use sediment cores to determine if metal values for pre-development sediment fit the "modern" prediction interval.

To demonstrate how normalization to Al can be used to identify sediment metal contamination, the 1989 data from the western portion of Harrison Bay, where some drilling mud has been discharged in the past, are added to the previous plot (Figure 4-2a). Concentrations of Ba are clearly above the upper 99 percent prediction interval for 3 samples from stations 7A, 7B, and 7G, but not for samples from the other two stations (7C and 7E). Based on the strong linear relationship for sediment from other locations, the evidence supports an anthropogenic source for some of the Ba in the samples identified as anomalous in Figure 4-2a. The sensitivity of this approach is amplified by realizing that the excess Ba in the most anomalous sample point in Figure 4-2a ($1,100 \mu\text{g/g} - 700 \mu\text{g/g} = 400 \mu\text{g/g}$) can be explained by the presence of barite at only 0.07 percent of the total sediment mass (pure barite contains Ba at $588,000 \mu\text{g/g}$).

To complete this initial overview, the sediment data for the new stations in the Northstar and Liberty areas were added to the Al versus Ba plot (Figure 4-2b). Four points plotted slightly above the 99 percent prediction interval (Figure 4-2b). These deviations are smaller than those previously shown for Harrison Bay (Figure 4-2a) and three of them (from stations N12, N13, and N14) plot in a manner similar to that found for the nearby Kuparuk River, a minor complexity in the Ba data that is discussed in a later section on source sediment.

This approach of normalizing metal concentrations to Al or Fe has been used successfully in a number of other environments to identify sediment metal contamination (e.g., Trefry and Presley, 1976; Schropp et al., 1990). Metal concentrations in sediments from the coastal Beaufort Sea may also be normalized using Fe based on the very good relationship for Al versus Fe ($r = 0.96$ for the BSMP stations; Figure 4-3). When the 1999 data for the Northstar and Liberty areas are added to the Al versus Fe plot for the BSMP stations, all of the additional points plot within the 99 percent prediction interval. Concentrations of neither Al nor Fe were determined in sediments collected for the 1986 MMS study and thus the 1986 data are not used in this initial evaluation of potential contamination. However, Crecelius et al. (1991) did normalize metal concentrations to V for the 1986 data, thereby providing a possible link with the 1989 and 1999 results, a link that will be investigated during the upcoming Phase II study.

The metal/Al approach for identifying sediment with potential anthropogenic inputs was applied to each of the other metals studied by first evaluating those elements for which data from 1989 are available. For Cr and V (Figure 4-4), the linear regression equations and the 99 percent prediction intervals were determined using the 1989 and 1999 data from the BSMP stations and then validated by adding the 1999 data from the Northstar and Liberty areas. All points plot within the 99 percent prediction interval, thereby showing the potential utility of these templates for identifying natural sediment levels of Cr and V. The cumulative results also support the absence of any discernible anthropogenic inputs of Cr or V to area sediments. The average crustal abundance values for Cr (Figure 4-4a) and Fe (Figure 4-3a) from Wedepohl (1995) fit the Beaufort Sea sediments; however, the crustal value for V is considerably lower than that found in area sediments. Background levels of V in sediment from Shelikof Strait with comparable Al concentrations are about 140 to $150 \mu\text{g/g}$ and closer to values from the Beaufort Sea. Once again, a historical perspective for trace metals using sediment cores should be checked during Phase II of the ANIMIDA program.

Sediment quality "guidelines" for Cr also have been added to Figure 4-4b. Such criteria have been used extensively worldwide as an initial assessment of possible adverse biological effects from trace metals and PAH in sediments. One set of criteria introduced by Long et al. (1995) uses an Effects Range-Low (ERL) and Effects Range-Medium (ERM). These guidelines are based on field, laboratory, and modeling studies conducted in the United States that coupled concentrations of contaminants in sediments with adverse biological effects (e.g., Long and Morgan, 1990). The ERM is defined as the concentration of a substance in the sediment that results in an adverse biological effect in about 50 percent of the test organisms. The ERL is defined as the concentration of a substance that affects 10 percent of the test organisms. For general application, the criteria have been applied as follows: adverse biological effects are "rarely" observed when metal or PAH levels are <ERL, "occasionally" observed when contaminants are present at levels between the ERL and ERM, and "frequently" observed when concentrations are >ERM. Nine of the 17 metals investigated during this study have been assigned ERL and ERM concentrations by Long et al. (1995). Concentrations of Cr in quite a few sediment samples and in average continental crust exceed the value for the ERL (Figures 4-4a and 4-4b). Similar observations are regularly made for Cr, most likely because the database compiled by Long et al. (1995) used Cr concentrations from an acid leach of the sediment rather than a total digestion. Only a small fraction (<25 percent) of the total Cr is removed by a strong acid leach (Trefry and Presley, 1976; Sinex et al., 1980). Thus, a leachable Cr value equal to the ERL level of 82 µg/g is more likely comparable with a total Cr level of >200 µg/g, a value considerably higher than Cr values for continental crust or any samples from this study. The ERL and ERM values for Cr may need to be revised in the second iteration of these sediment quality criteria. No data points exceed the established ERM for Cr.

Concentrations of Cu and Zn also follow a strong linear relationship versus Al for the BSMP stations sampled during 1989 and 1999 (Figures 4-5a and 4-5c). As the template for each metal was being developed, one point on each plot was clearly above any 99 percent prediction interval that was constructed and therefore one point from each of the template plots using the BSMP data was rejected from the linear regression and prediction interval calculations. The anomalous Cu and Zn values were for stations 5D (near West Dock) and 5H (near Endicott), respectively. To validate each template, the 1999 data for the Northstar and Liberty areas were plotted in Figures 4-5b and 4-5d. One or two points (e.g., N04 for Cu) are just slightly above the upper limit of the 99 percent prediction interval. Similar to the results for Cr, several points on the Al versus Cu plot exceed the present ERL; however, the ERL is very close to the average crustal abundance and below natural levels for many sediments. In contrast, all data points from this study fall below the ERL for Zn (Figure 4-5d). Zinc is more easily leached from sediments with strong acid and thus the resulting ERL values may be more applicable. In summary, a reasonable predictive tool appears to be available for Cu and Zn and, at present, one station has an elevated level of Cu (5D) and one station has an elevated level of Zn (5H). No values exceed the ERL or ERM for Zn and no values exceed the ERM for Cu. The ERL for Cu needs to be reevaluated for application to total Cu concentrations.

Plots of Al versus Pb and Cd using the 1989 and 1999 BSMP data do not show the strong linear relationships found for Cr, V, Cu, and Zn, as discussed above (Figures 4-6a and 4-6c). Some of the discrepancy results from very low concentrations for each metal and some from scatter in the 1989 data. To construct a template for future use, the point for sample 5D was rejected from

both data sets and the point for sample 5(10) was rejected from the Pb data set because these points far exceeded any 99 percent prediction level that was constructed. The resulting linear regression lines have broad 99 percent prediction intervals and show that station 5D for Pb and Cd and station 5(10) for Pb exceed the upper limit. Values for average continental crust plot within the prediction interval for each metal (Figures 4-6a and 4-6c).

If the 1999 data for sediment from the Northstar and Liberty areas are added to the Pb and Cd plots, and the 1989 BSMP data are removed, the correlation coefficients are greatly increased and the width of the 99 percent prediction interval is narrowed considerably (Figures 4-6b and 4-6d). The 1989 and 1999 data were produced by the same laboratory (Florida Institute of Technology); however, analysis for Pb and Cd in 1989 was carried out by GFAAS, whereas ICP/MS was used in 1999. The ICP/MS data seem to be more precise at low levels for these two metals.

With either template, concentrations of both Pb and Cd are above the 99 percent prediction interval at station 5D. No data points for either Pb or Cd exceed the ERL or the ERM. Overall, the sediments of the area appear to have low and natural levels of both metals, with one exception. A final choice of templates for Pb and Cd will be made following analysis of the 2000 samples and some pre-development samples from sediment cores.

4.1.1.2 New ANIMIDA Metals

Concentrations of the remaining nine metals (Ag, As, Be, Co, Hg, Mn, Ni, Sb, and Tl) were determined only for the 1999 samples. Sediment quality criteria are presently available for four (Ag, As, Hg, and Ni) of these nine metals. Concentrations of Ag are low and somewhat variable, with most values $<0.1 \mu\text{g/g}$ and in close agreement with the value for average continental crust (Figure 4-7a). The resulting template for the Al versus Ag plot has a relatively wide prediction interval (Figure 4-7a), with one data point for station 5D exceeding the upper interval and no Ag values above the ERL or ERM. The Al versus As and Hg plots (Figures 4-7b and 4-7c) provide good templates for future assessments, with each graph identifying one point, for station 5D, as possibly having a small anthropogenic contribution of As and Hg. No points exceed or are close to the ERL for As; however, the Hg value for station 5D is about double the expected levels and exceeds the ERL, but not the ERM. Similar to results for Cr and Cu, many points on the Al versus Ni plot exceed the present ERL; however, the ERL is less than the average crustal abundance and below natural levels for many sediments. One station (5D) has an elevated level of Ni and the ERL and ERM for Ni need to be reevaluated.

Concentrations of Be, Co, Sb, and Tl correlated well with Al (Figure 4-8). The linear regression equations and the prediction intervals for these metals were obtained using the complete 1999 data set. The data for average continental crust fit within the prediction intervals for Be and Tl; however, the crustal value is lower for Sb and higher for Co relative to Beaufort Sea sediments. Overall, the results show slightly elevated values for Co and Sb at station 5D and for Co at station 4A.

In summary, a series of Al versus metal plots have been developed and fit with linear regression equations and 99 percent prediction intervals. Each plot serves as a template for monitoring future trends in sediment metal concentrations in the study area. Where possible, the plots were

developed with the 1989 and 1999 data from the BSMP and then validated with data from the 1999 surveys of the Northstar and Liberty stations. Region-wide, the sediments contain natural levels of the 16 metals studied (Ag, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Tl, V, and Zn), with only minor exceptions. These exceptions, identified by positive anomalies on the metal/Al plots, are extremely limited and include the following: station 4A (Co), station 5D (Ag, As, Cd, Co, Cu, Hg, Pb, and Sb), and station 5H (Zn). The strong correlation coefficients for the metal/Al graphs show that natural levels of metals can be predicted with good reliability and therefore the outlook for identifying inputs of contaminant metals to sediments during future years is good.

4.1.2 Hydrocarbons

The hydrocarbon dataset for surficial sediments includes SHC, PAH, and S/T data. These data are analyzed in part using a suite of diagnostic parameters and ratios (Table 3-5). Some of the general trends observed in these data for several areas of interest are evaluated in this section. These areas include: 1) sources of hydrocarbons, 2) spatial variability, or comparisons between stations, 3) temporal variability, or comparisons between years, and 4) comparisons to sediment quality benchmarks or "guidelines." The results of these data evaluations will be used as the foundation for future statistical applications of the data to test hypotheses after the development of the Northstar and Liberty prospects during Phase II of the program.

To facilitate the presentation and discussion of the organics data, GC/FID chromatograms from the SHC analysis, PAH distribution plots, and triterpane extracted ion chromatogram profiles for representative samples throughout the study area were selected and are presented in Figures 4-9 through 4-15. The samples selected for presentation are as follows:

- North Slope Crude Oil – composite pipeline sample (Figure 4-9)
- Colville River sediment (Figure 4-10)
- Station N06 – Northstar sediment (Figure 4-11)
- Station L06 – Liberty sediment (Figure 4-12)
- Station 3A – BSMP sediment station near Stockton Islands (Figure 4-13)
- Station L08 – Liberty sediment (Figure 4-14)
- Station 5D – BSMP sediment station near Stump Island/West Dock (Figure 4-15)

4.1.2.1 Hydrocarbon Sources

Saturated Hydrocarbons

In general, the surficial sediments (GC/FID chromatograms in Figures 4-10 through 4-15) exhibit a mixture of primarily terrestrial biogenic hydrocarbons and lower levels of petroleum hydrocarbons (Figure 4-9 shows a North Slope Crude Oil reference). This assemblage is clearly dominated by plant wax normal (i.e., straight-chain) alkanes in the n-C27 through n-C33 carbon range. This is further demonstrated by carbon preference index (CPI) values that range from two to seven for most samples (Figure 4-16), which is characteristic of sediments influenced by terrigenous plant inputs (Wakeham and Carpenter, 1976; Boehm, 1984). Four samples have CPI ratios of less than two (5B, 5E, N01, and N15). With the exception of 5E, the lower CPI ratios at these stations are due to the fact that the SHC concentrations are very low (i.e., trace levels), with corresponding low TOC and high sand content, factors which all contribute to CPI ratio

uncertainty and potential inaccuracy. However, the CPI ratio of 1.25 at station 5E, with a corresponding TPHC concentration of 11 mg/Kg, is characteristic of a petroleum component present in this sample.

Traces of lower-molecular-weight alkanes (LALK – n-C9 through n-C20 alkanes), indicative of a petroleum source, are visible as more minor components relative to the plant wax alkanes in the sediment and river samples (Figures 4-10 through 4-15). This clearly visible petroleum alkane signature in the sediments has been well documented by previous studies in the region (Boehm, et al., 1987; Steinhauer and Boehm, 1992; and Boehm et al., 1990). The clear exception to this trend is station L08 (Figure 4-14), which has a GC/FID chromatogram with a distinct unresolved complex mixture (UCM) or “hump” in the n-C10 through n-C24 carbon range. The GC/FID pattern observed in this sample is characteristic of a diesel fuel hydrocarbon source. The diesel fuel pattern is slightly weathered, indicating a recent source of diesel fuel contamination at this station. The absence of any similar diesel fuel signatures in adjacent samples suggests a very limited or patchy area of sediment contamination. This result clearly warrants further evaluation of the sediments from this station in future field surveys.

Polynuclear Aromatic Hydrocarbons

The PAH distributions for most of the surficial sediments show that the PAHs are primarily of a combined fossil fuel origin (i.e., petroleum and coal) with a somewhat variable biogenic component (perylene), and lesser contributions of pyrogenic or combustion-related compounds (e.g., 4-, 5-, and 6-ring PAHs). The petrogenic PAHs account for approximately 90 percent of the Total PAH less perylene throughout the study area. Perylene was abundant in surficial sediments, often the most abundant single PAH compound in the overall PAH distribution (Figures 4-10 through 4-15). Perylene is a naturally occurring PAH formed during early diagenesis in sediments from biological source precursors (Wakeham and Farrington, 1980; Wakeham, et al., 1980). It may also be found in crude oil at very trace concentrations. In past studies, perylene was found at comparable concentrations in the BSMP sediments (Boehm et al., 1990).

The variations in PAH composition of representative surficial sediments from the region are shown in the PAH distribution plots in Figures 4-10 through 4-15. For comparison, the PAH distribution plot of a North Slope Crude oil is shown in Figure 4-9. The PAH distributions are generally similar throughout all the regions of the study area and are characterized by the presence of a full suite of relatively “unweathered” petroleum PAHs (i.e., naphthalenes \geq phenanthrenes) similar to the PAH distribution seen in the North Slope Crude oil. As noted previously, perylene dominates the overall PAH distribution as one of the most abundant individual PAHs in the samples. Perylene is found at equal or greater relative abundance in the river sediments and peat (Figure 4-10), which suggests the relationship of the rivers as a source of the hydrocarbons in the nearshore sediments, as noted previously for the SHCs.

Low levels of 4-, 5-, and 6-ring combustion PAHs are also present, but are generally only a minor component of the overall PAH composition in the sediments. The 4-, 5-, and 6-ring combustion PAHs appear slightly enriched in the peat samples relative to the sediments, but are still a minor contributor to the overall PAH composition.

The PAH distribution in station L08 sediment (Figure 4-14) shows a clear increase in the abundance of 2- and 3-ring petroleum PAHs, particularly with the naphthalenes, relative to the other sediment samples. This further supports the GC/FID evidence of diesel fuel contamination in this sample. The other two samples that were identified as being enriched in petroleum based on SHC results (5D and 5E) do not show evidence of a corresponding enrichment in PAH or change in PAH distribution. This result suggests that the source of the hydrocarbon enrichment may be depleted in PAH versus SHC, relative to the regional petroleum hydrocarbon background already present in the sediments (e.g., coal and lubricating oil-range products).

Triterpanes

In general, the triterpane distributions in the sediment samples are indicative of a petroleum pattern (Figures 4-10 through 4-15), with varying abundances of a suite of recent organic material triterpane markers. For example, a characteristic petroleum triterpane pattern dominated by norhopane (T15) and C30-hopane (T19) is shown in Figure 4-9 for the North Slope Crude oil. The triterpane distributions for most sediment samples comprise a mixture of these characteristic petroleum triterpanes, along with recent organic or biogenic markers such as diploptene (the large peak to the left of the T21 and T22 doublet - Figure 4-11) and other unnamed triterpanes (the large peaks which elute prior to T15 and in the 45- to 47-minute range - Peters and Moldowan, 1993). In addition, the relative abundance of T22 at much greater levels than T21 in some samples provides further evidence of substantial recent organic matter inputs to the surficial sediments. Many of the sediment samples contain trace levels of oleanane (T18), indicating the presence of a non-North Slope Crude, post-Cretaceous/Tertiary petroleum source; i.e., T18 is absent in bulk North Slope Crude oil (Bence et al., 1996). The origin of this petroleum signal is unknown, but it is likely from regional background inputs. Seep oils from from Kavik and Angun may have trace oleananes, as part of their biodegraded biomarker signature. The presence of oleanane has also been reported in Canadian McKenzie Delta crude oils far to the west of the study area (Banet, 1995).

The triterpane distributions of the Colville River sediments and peat (Figure 4-10) have the same mixture of recent organic matter and petroleum hydrocarbon patterns as observed in many of the sediment samples (for example, station N06 - Figure 4-11). This similarity suggests that there is a strong link between Colville River hydrocarbon sources - mostly erosional inputs of coal shale, peat, etc. (i.e., natural background) and the sediments. However, given the documented current transport regime of East to West in the study area, it is likely that the surficial sediments are also influenced by rivers to the East, as well as the Colville River.

The Kuparuk and Sagavanirktok River sediments contain many of the same recent organic matter triterpane markers, but generally have different distributions than the Colville River sediments. In particular, the ratio of T21/T22, where T22 is an order of magnitude higher than T21, is characteristic of an immature or recent hydrocarbon source, possibly indicative of coal. This predominant T22 pattern is also found in three of the surficial sediment samples - 5(5) to the West of the Sagavanirktok River delta, and N14 and 5D near the mouth of the Kuparuk River - indicating the influence of these rivers to the deposition of surficial sediments at these stations. The presence of the predominant T22 pattern at station 5D (Figure 4-15) is of particular interest, since the SHC and PAH data show evidence of petroleum hydrocarbon contamination at this

station. The observed T22 pattern indicates that coal particles, possibly from the Kuparuk River, may be one of the sources of the hydrocarbon enrichment.

Two other surficial sediment samples have distinctly different triterpane distributions. Both 5E and L08 (Figure 4-14) have triterpane distributions more characteristic of a petroleum source, i.e., a predominance of hopanes (T15 and T19). In the case of L08, this is not surprising since other organic data clearly indicate diesel fuel contamination. However, the abundance of petroleum triterpanes also indicates a petroleum product "heavier" than diesel, as triterpanes are typically removed from diesel-range fuels during the distillation process. This result indicates that the observed petroleum contamination at L08 is a complex mixture of hydrocarbons including diesel and heavier hydrocarbons such as No. 6 fuel oil or crude oil. This could be the result of drilling mud/cutting residues from historical adjacent exploratory drilling (i.e., Tern Island), as the standard practice at the time allowed disposal of used drill muds on the ice during winter drilling. This is further supported by the elevated barium levels (when normalized to Al) observed in the sediment from L08. The petroleum triterpanes in the surficial sediment at 5E further confirm the presence of low levels of a "heavy" petroleum hydrocarbon source shown by the SHC and PAH results, but the specific origins of these "contaminants" are not known.

4.1.2.2 Spatial Variability

In examining the spatial variability, or variability between stations, one useful technique involves examining the relationship between the organic parameter of interest and TOC content or alternatively, the percent silt + clay. The natural background concentrations of organics will often vary as a function of fine-grained sediment (silt + clay) and TOC. Thus, samples enriched in organics from anthropogenic sources can be identified by normalizing the target organic parameter and generating a linear regression line and prediction interval on a cross-plot.

Two plots of total PAH minus perylene versus TOC and silt + clay are shown in Figure 4-17. The Total PAH less perylene is used to reduce variability introduced to the Total PAH by perylene and can vary by sediment type. Total PAH less perylene has been used in other studies in evaluating sediment PAH in Cook Inlet (Hyland, et al., 1995; Boehm et al., 2001). In both plots, a good linear correlation is established between concentrations of PAH and both TOC and silt + clay ($R^2 = 0.76$ and 0.83 , respectively – 5D was determined to be a statistical outlier and was not included in the regression calculation). This regression defines the natural geological/geochemical background. In both cases, the data point from station 5D is clearly well outside the calculated 99 percent prediction interval of the regression line. This result indicates that 5D sediment is enriched in Total PAH relative to the expected background for the region. As noted previously, station 5D sediments were identified as being contaminated with hydrocarbons, although the source of this contamination is still unclear (i.e., coal versus petroleum) and will need to be examined more closely in Phase II work.

Similar plots for TPHC versus TOC and silt + clay (Figure 4-18) result in a slightly lower regression correlation coefficient than for the Total PAH graphs ($R^2 = 0.53$ and 0.69 , respectively – once again calculated without the 5D outlier). However, the same trend is observed, with sediment from 5D showing a clear enrichment of TPHC relative to the regional background (99 percent prediction interval), further supporting the previously noted hydrocarbon contamination. In the TPHC plots two other samples, L08 and 5E, were found to slightly exceed the upper limit

of the 99 percent prediction interval (L08 only versus TOC, and L08 and 5E for silt + clay). Based on the analytical data, these two samples were also previously identified as being enriched in petroleum hydrocarbons. Diesel contamination with possible crude oil was identified in L08 and a "heavy" hydrocarbon product depleted in PAH was identified in 5E.

Another approach in identifying potential anthropogenic inputs to the sediments involves examining the relationship of TPHC versus Total PAH (Figure 4-19). In this plot, a linear regression and 99 percent prediction intervals are calculated without sample 5D, since the vast separation of 5D from the main cluster of samples can be misleading when determining linear relationships. However, in the plot the calculated regression is high even without 5D ($R^2 = 0.71$ and 0.72 , respectively, for Total PAH and Total PAH less perylene versus TPHC). Two of the samples that previously showed enrichment in petroleum hydrocarbons by the other techniques (L08 and 5E) also fall above the 99 percent prediction interval in these plots, further corroborating the presence of hydrocarbon contaminants. Of particular interest is that station 5D falls within the expected range of Total PAH versus Total PHC for the regional hydrocarbon background. This could indicate a coal source, as suggested earlier, but does not rule out a mixed petroleum source with a saturate to aromatic ratio similar to the sediments.

Overall, these techniques provide a sensitive baseline process to measure anthropogenic inputs into the system from Northstar and Liberty activities, given radial sampling design around the prospects and regional BSMP station coverage.

4.1.2.3 Temporal Variability

Comparisons of the 1999 sediment data to 1989 and earlier BSMP and earlier data are limited to SHC and PAH parameters, as samples were not analyzed for S/Ts before 1999. Additionally, only generalized comparisons of Northstar and Liberty regional data can be made to historical sediment data since these stations were not sampled in previous studies. A comparison of the total PAH concentrations in sediments between 1999 and the 1984 – 1986 and 1989 BSMP data is shown in Figure 4-20. Regional means are provided for Foggy Island, Kuparuk River, Endicott, Northstar, and Liberty. The 1989 West Camden Bay regional mean is also included for comparison as a background or reference region. The 1999 regional mean Total PAH concentrations are within the same range measured in the earlier BSMP programs. The 95 percent confidence intervals for the regional means overlap between years within each region (performed on log-transformed data), indicating no significant temporal trends in Total PAH. It should be noted that the 1999 mean for the Kuparuk River region is strongly influenced by the high Total PAH concentration from station 5D; the mean is a factor of two lower when 5D is not included. The Northstar and Liberty regional means for Total PAH fall within the range measured for the three other BSMP regions and both are less than the 1989 West Camden Bay reference value.

The comparison of the ANIMIDA 1999 Total PHC regional means versus the BSMP total PHC means is shown in Figure 4-21. As observed for PAH, the 1999 Total PHC means are within the same range as previous BSMP values. However, there is greater variability between years than observed for the PAH data. This is likely an artifact of changes in the GC/FID analytical techniques used to measure SHCs, and the same trend was documented for the 1989 sediments (Boehm et al., 1990). The mean Total PHC concentration for Northstar is less than the 1989

West Camden Bay reference value (4.89 mg/Kg versus 5.39 mg/Kg, respectively) while Mean Total PHC for Liberty is somewhat higher (7.06 mg/Kg). However, the 95 percent confidence intervals for the regional means substantially overlap between years, within each region, suggesting there are no temporal differences in Total PHC (performed on log-transformed data).

Although no temporal trends were observed in the Total PAH, substantial differences in the ratio of pyrogenic to petrogenic PAH were observed for the 1999 and 1989 BSMP sediment data (Figure 4-22). The calculated ratios in 1999 are higher than in 1989 (mean ratios of 0.096 and 0.038, respectively) at all possible stations. The ratio could not be determined for station 5E in 1989 due to non-detected pyrogenic PAH in that year. Reanalysis of several 1989 archived sediment samples according to the current analytical protocols indicates that this shift in the pyrogenic/petrogenic ratio may be related entirely to differences in the 1989 vs. 1999 analytical methods. Specifically, the shift is likely due to a difference in quantitating the alkyl PAHs. The pyrogenic/petrogenic ratios of the three recently analyzed 1989 archived sediment samples showed a significant increase in the ratios. (The reanalysis of the 1989 sediments will be presented with the Phase II analytical results.) The impact of this finding will be evaluated in Phase II of the ANIMIDA program.

4.1.2.4 Sediment Quality Guidelines

Sediment quality criteria have been developed to assess possible adverse biological effects from metals, polychlorinated biphenyls (PCBs), pesticides, and PAH. The commonly utilized criteria are the ERL and ERM presented by Long et al. (1995). The general applications of the guidelines have been to state that adverse biological effects are "rarely" observed when PAH levels are less than the ERL, "occasionally" observed when contaminants are present at levels between the ERL and ERM, and "frequently" observed when concentrations exceed the ERM.

ERL and ERM values have been developed for 13 individual PAH compounds and three classes of PAH (low- and high-molecular-weight PAH, and Total PAH). A comparison of the Total PAH from all ANIMIDA sediments by study region to the ERL and ERM criteria is shown in Figure 4-23. None of the Total PAH concentrations determined in this study exceed the ERL. Station 5D, which had the highest measured Total PAH at 2,700 µg/Kg, was still well below the ERL value of 4,022 µg/Kg. The mean Total PAH values from each study region were generally an order of magnitude lower than the ERL. Similarly, the individual PAH concentrations did not exceed the ERL for the 13 PAHs listed, which could be compared directly. The sum of the two methyl naphthalene isomers at station 5D (130 µg/Kg – the sum of two isomers) was higher than the ERL value listed for the single 2-methyl naphthalene isomer (70 µg/Kg). However, the value would be less than the ERL using an estimate of 50 percent contribution of 2-methyl naphthalene to the sum of the methyl naphthalene isomers. In summary, based on sediment quality criteria, the concentrations of PAH found in the study area sediments are not likely to pose immediate ecological risk to marine organisms in the area.

4.2 Organisms

4.2.1 Metals

Data from 1986, 1989 and 1999 are available for Ba, Cd, Cr, Cu, Fe, Pb, V, and Zn in clams (*Astarte*) and amphipods (*Anonyx*) from four stations in the area of the BSMP that is being studied during the ANIMIDA program. These results provide a temporal perspective for monitoring trends in body burdens of selected metals over time. During 1999, concentrations of ten additional metals (Ag, Al, As, Be, Co, Hg, Mn, Ni, Sb, and Tl) were determined in the same three species of organisms to broaden the spectrum of analytes.

Mean concentrations of Ba, Cu, Pb, V, and Zn in clams sampled during 1986, 1989, and 1999 are remarkably uniform among years (Figure 4-24). Such uniformity is encouraging with respect to using body burdens for metals as a long-term indicator of metal availability. This uniformity also could be used to state that no detectable shifts in metal levels in *Astarte* have occurred between 1986 and 1999. However, the standard deviation for a given metal in an individual year is sometimes large. Such variability limits statistical discrimination of changes in metal concentrations. For example, the RSD for the six pooled samples of *Astarte* for 1989 was ~50 percent for Ba and Pb and 75 percent for Cd. In contrast, the RSDs for the four pooled samples of *Astarte* from 1999 were 15 percent for Ba, 9 percent for Pb, and 17 percent for Cd. Some anomalous points that led to high values for the RSD can be partially explained, whereas others may be due to natural variability, as described below. In any case, some additional effort will need to be devoted to the organism portion of the monitoring effort to increase its future utility.

One factor that introduces variability into concentrations of some elements in clams is the amount of sediment contained in the gut. Because sediment in the gut may be passed up to the next trophic level, it is not usually an issue in risk analysis; however, variable amounts of sediment can contribute to some of the higher values observed for the RSD in the clam data. For example, the large RSD for Ba in the 1989 data for *Astarte* (Figure 4-24) is partly due to a Ba level of 40.4 $\mu\text{g/g}$ (overall mean was 24 $\mu\text{g Ba/g}$) in one sample from station 6D, where the Fe concentration was 80 percent higher than the average for the other samples. If half of this Fe in the *Astarte* is due to sediment in the gut, then Ba associated with sediment can account for >40 percent of the Ba in the clam. The same sample from station 6D also contained V at levels almost double those in the other five samples and this excess V is most likely bound to sediment. The elements influenced by excess loading of sediment are those that are present at very low levels in the organism relative to the sediment. In this study, the metals most affected by sediment are Ba, Be, Co, Pb, Sb, Tl, and V. For most of the remaining elements (Ag, As, Cd, Cu, Hg, Mn, and Zn), natural metal levels in the clam are high enough to minimize the influence of excess amounts of sediment. The sediment/clam issue will be further addressed during Phase II in order to maximize the screening capabilities of the clam data.

Comparison of the 1986, 1989 and 1999 data for metals in clams also may be limited by geographical differences in sample location because *Astarte* were collected at only two common stations during 1989 and 1999 (stations 3A and 5H). Finally, the small numbers of pools of samples also limits the statistical power of the data. All of these factors that influence the utility of using the data for metals in *Astarte* will be more rigorously evaluated during Phase II of the ANIMIDA program. More-detailed discussion of the 10 new metals in the study also will be

reserved until the samples collected during August 2000 are analyzed. However, the RSDs for the new elements for 1999 are generally encouraging: Ag (17%), Al (13%), As (11%), Be (9%), Co (35%), Hg (9%), Mn (24%), Ni (30%), Sb (19%), and Tl (7%).

Average concentrations of metals in the amphipod *Anonyx* are more variable from year to year than observed for the clam *Astarte* (Figure 4-25). In the case of the amphipods, excess sediment is not an important issue because Fe levels are low, at 200 to 400 $\mu\text{g/g}$ relative to 1,000 to 2,000 $\mu\text{g/g}$ in the clam. Furthermore, the values for the RSD in the 1999 data are quite low, with many metals having RSDs <15 percent, as previously described. Only one of the seven stations where amphipods were collected in 1989 was also occupied in 1999. The amphipod data for the ten new metals are also quite encouraging, with the following values for the RSD in the small *Anonyx*: Ag (2%), Al (26%), As (13%), Be (16%), Co (16%), Hg (13%), Mn (6%), Ni (14%), Sb (15%), and Tl (8%). When the 1999 data for clams and amphipods are combined with results from samples collected at the same stations during August 2000, a more valid and useful framework for using these organisms as sentinels of possible future metal contamination can be proposed and tested.

Hydrocarbons

The GC/FID chromatogram, PAH distribution plot, and triterpane extracted ion chromatogram profile of a representative tissue sample (station 3A *Astarte*) are shown in Figure 4-26.

The GC/FID results show trace levels of terrigenous plant wax hydrocarbons in the n-C24 through n-C32 range, a pattern similar to the surficial sediments. The PAH distributions show trace levels of a mixture of petrogenic PAHs (e.g., 2- and 3-ring PAH and alkyl PAH) and pyrogenic PAHs (e.g., 4-, 5-, and 6-ring PAH), and perylene. The low levels of PAH found in the tissue samples result in "truncated" PAH patterns, where alkyl PAH compounds are below the detection limit of the analytical method. Nonetheless, the pattern of PAHs in the tissues is generally similar to the surficial sediments when the influence of detection limits is accounted for. The one sample with the highest Total PAH concentration (L04 - *Anonyx* at 80 $\mu\text{g/Kg}$) shows a predominance of several pyrogenic PAHs (i.e., phenanthrene, fluoranthene, and pyrene) that was not observed in any of the other tissue samples.

The S/Ts in the tissue samples were near the detection levels in most samples, making interpretation of the patterns more difficult. In some samples, the presence of interferences from the natural fats and oils of the tissue matrix were also encountered. Nevertheless, the triterpane distributions in the tissue samples generally corresponded to the patterns observed in the sediments, with a predominance of both biogenic and recent organic matter triterpane markers. Overall, the organic data set for the tissue samples reveals the presence of trace levels of hydrocarbons, generally similar in distribution to the sediments, indicating a positive relationship between the background sediment hydrocarbons and the body burdens of the clams and amphipods.

The limited overlap stations for tissue samples collected in both 1999 and 1989 enable only precursory evaluation of temporal data trends. A comparison of the PAH data in the 1989 and 1999 tissues, where stations and organism type coincide, shows a trend of lower Total PAH less perylene concentrations in 1999 than in 1989 (Figure 4-27). A similar trend is observed for the

Total PHC concentrations, with the exception of the *Anonyx* at station 5B, where the Total PHC concentration was approximately four times higher in 1999 than in 1989 (Figure 4-28). The observed higher value may be due to natural fat or oil interferences in this sample or could be related to the different species of *Anonyx* comprising sample (station 5B *Anonyx* were noted as being the "large" variety in the field records). Differences for certain metal analytes were also noted in the 5B *Anonyx* sample relative to the samples composed of small individuals, suggesting the size of the organisms may be the source of the observed differences. Additional tissue data corresponding to the 1999 sampling locations are clearly necessary to further evaluate the hydrocarbon relationships in the bivalves and amphipods, and their possible use as sentinel organisms for bioaccumulation of hydrocarbon contaminants.

4.3 Suspended Sediment in Water and Ice

4.3.1 Physical Considerations

After the spring runoff from rivers subsides, the concentrations and distribution of suspended sediment during the open-water season in the ANIMIDA study area appear to be a function of wind conditions, water currents, and water depth. Data have been collected and evaluated for only one open-water period thus far in the ANIMIDA program (August 1999). The database will be expanded during Phase II of the study. Results obtained before and after the August 1999 storm (Figure 4-29) helped to establish the overview described in Section 3.2. In summary, a preliminary descriptive picture for mid-summer is as follows: 1) concentrations of TSS and turbidity are at levels of <3 NTU (<5 mg/L) under relatively calm conditions (wind speeds <5 kts), 2) concentrations of TSS and turbidity can exceed 80 NTU (and 100 mg/L) under high wind speeds (>25 kts), 3) turbidity may be about two times lower in more-offshore waters (water depths >10 m) relative to more-nearshore, shallower water, and 4) a near-bottom nepheloid layer with a 50 to 300 percent increase in turbidity may be observed at most locations. The TSS data also can be used to integrate the total mass of suspended sediment in the water column (in g/m²), as shown for station N13 in Figure 4-29 as follows:

$$\text{Integrated TSS (g/m}^2\text{)} = \text{Integrated } [(TSS \text{ in g/m}^3) \times (\text{water column depth in m})]$$

$$\text{where TSS (g/m}^3\text{)} = TSS \text{ (mg/L)} \times (1 \text{ g/1000 mg}) \times (1000\text{L/m}^3)$$

$$\text{or Integrated TSS (g/cm}^2\text{)} = \text{Integrated TSS (g/m}^2\text{)}/10,000.$$

The integrated amounts of suspended sediment in the water column can be converted to a layer thickness of surficial sediment that, if resuspended, would produce the observed TSS levels in the water column as follows:

$$\text{Resuspended sediment layer (cm)} = \text{Integrated TSS (g/cm}^2\text{)} \times (1 \text{ cm}^3/1.6 \text{ g wet sediment})$$

and thus

$$\text{Resuspended sediment layer (N13, 8/18/99)} = (0.003 \text{ g/cm}^2) \times (0.625 \text{ cm}^3/\text{g}) = 0.002 \text{ cm}$$

The calculations show that a layer of fine-grained sediment equal to only 0.002 cm would need to be resuspended to provide enough suspended sediment to produce the background conditions observed at station N13 on August 18, 1999. In the post-storm water column, the thickness of the layer of sediment that would need to be resuspended at N13 increases to 0.03 cm. These results show how sensitive these shallow waters are to resuspension events and infer that very high TSS levels may be observed during storm conditions. Current velocities typically ranged from about 5 to >40 cm/sec during the August 1999 sampling trip.

The under-ice data for suspended sediment also provide a valuable and previously unavailable baseline for identifying potential impacts during winter construction activities. The lowest levels of turbidity and TSS were observed at the more-offshore stations of NA2, 5(5), and LA2, where the overall average value for TSS was 0.25 ± 0.06 mg/L, about 10 to >100 times lower than values obtained during the open-water period of August 1999. The transmissivity data suggest that a small nepheloid layer is present at each station.

Although the winter sampling plan was originally designed only to determine background levels of turbidity and TSS under ice, water sampling was carried out at 5 locations in the Northstar area to investigate the influence of the backfilling process on turbidity. The previously described results show that about 200 m downstream of the backfilling operation, transmissivity decreased at depths >8 m. Concentrations of TSS were 2.0 and 1.5 mg/L at a water depth of 9 m at station NT1, about 5 to 8 times greater than apparent background levels. Just upstream of the backfilling operation, transmissivity was lower than background levels, but rather uniform between 3 and 10 m. Current velocities near the backfilling operation averaged about 2 cm/sec. At increased distances from Northstar Island (NA3, ~0.5 km; NA5, ~1 km; and NA6, ~2 km), values for TSS averaged 0.32 ± 0.15 mg/L and were comparable with background levels. Collectively, the turbidity and TSS data from open-water and under-ice conditions have greatly enhanced our understanding of the concentrations and distributions of suspended sediment in the ANIMIDA area.

The complementary ice-core data for suspended sediment may possibly be used to 1) show a record of whether the ice formed under turbid- or clear-water conditions and 2) determine the amount of sediment that will be released to the water column when the ice melts. The distribution of sediment in the ice cores is consistent with the pattern of formation of this sea ice. The top layer (as sampled) forms first and freezes in the suspended sediment in the ambient water (Figure 4-30). Storms during the fall seasons can keep the TSS at levels of >10 to 100 mg/L. Some time after the top layer of ice forms, the energy of the underlying water is dramatically decreased and suspended particles slowly settle out such that the later ice that forms from below contains considerably lower levels of sediment (Figure 4-30). The actual patterns of sediment distribution in the ice cores may be more complex than the simple picture described above, depending on ice rafting and other processes. More detailed sub-sampling of the ice cores may improve the record of events recorded in the ice.

The ice-core data from April 2000 does permit calculation of the impact of sediment releases from melting ice on surficial sediment accumulation. Using the worst-case scenario (station LA5), the integrated amount of sediment in the ice core is about 6 mg/cm^2 (Figure 4-31). As the ice melts and releases this sediment, the impact on the seafloor is an accumulation of only about

0.004 cm of sediment per cm^2 (Figure 4-31). This small impact is consistent for all ice cores collected. Certainly, increased loading may be possible at some locations; however, the net impact on sediment accumulation would appear to be small in the ANIMIDA study area.

4.3.2 Chemical Considerations

Concentrations of trace metals in suspended sediment collected during the open-water period of August 1999 fit the metal-to-Al trends observed for surficial sediments (Figure 4-32). However, most points on the metal/Al graphs for suspended sediment plot at higher levels of each metal because the suspended sediment is richer in fine-grained aluminosilicates and contains little or no carbonate or quartz. These results imply that the metals have a similar source in aluminosilicate material that is relatively uniform in composition. For Al versus Cu and most other metals (Figure 4-32), the data for the source bottom and suspended sediment fit the same trend as the bottom and suspended sediment from the ANIMIDA study area. Thus, the area rivers are providing no distinguishable tracer among them as far as most trace metals are concerned. Values for Fe, Ba, and Cr were elevated, relative to Al, for the Kuparuk River (positive anomalies shown with inverted orange triangles on Figure 4-32b). The Kuparuk River sample was taken at a time of low TSS and may be relatively richer in a fine-grained iron oxide phase than the other samples, similar to observations made in samples collected from under the ice. Overall, no distinct elemental signature for different sources of sediment to the ANIMIDA study area has yet been identified.

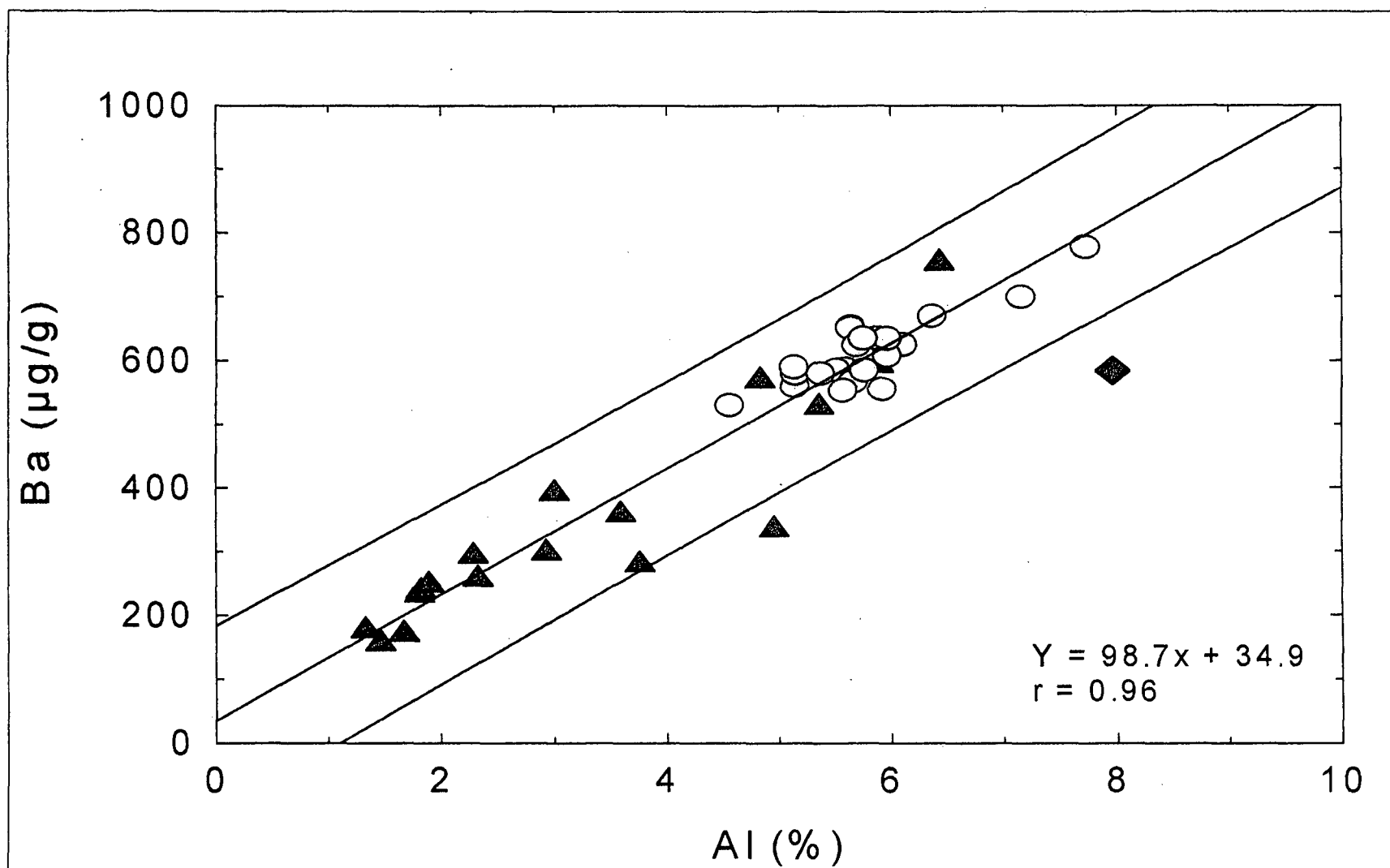


Figure 4-1. Concentrations of Al versus Ba in Surficial Sediment Samples from Beaufort Sea Monitoring Program Stations

BSMP stations [3A, 3B, 4A-C, 5A, 5B, 5D-H, and 5(0, 1, 5, 10)] from 1989 (yellow circles) and from 1999 (blue triangles) and average continental crust (brown diamond, from Wedepohl, 1995).

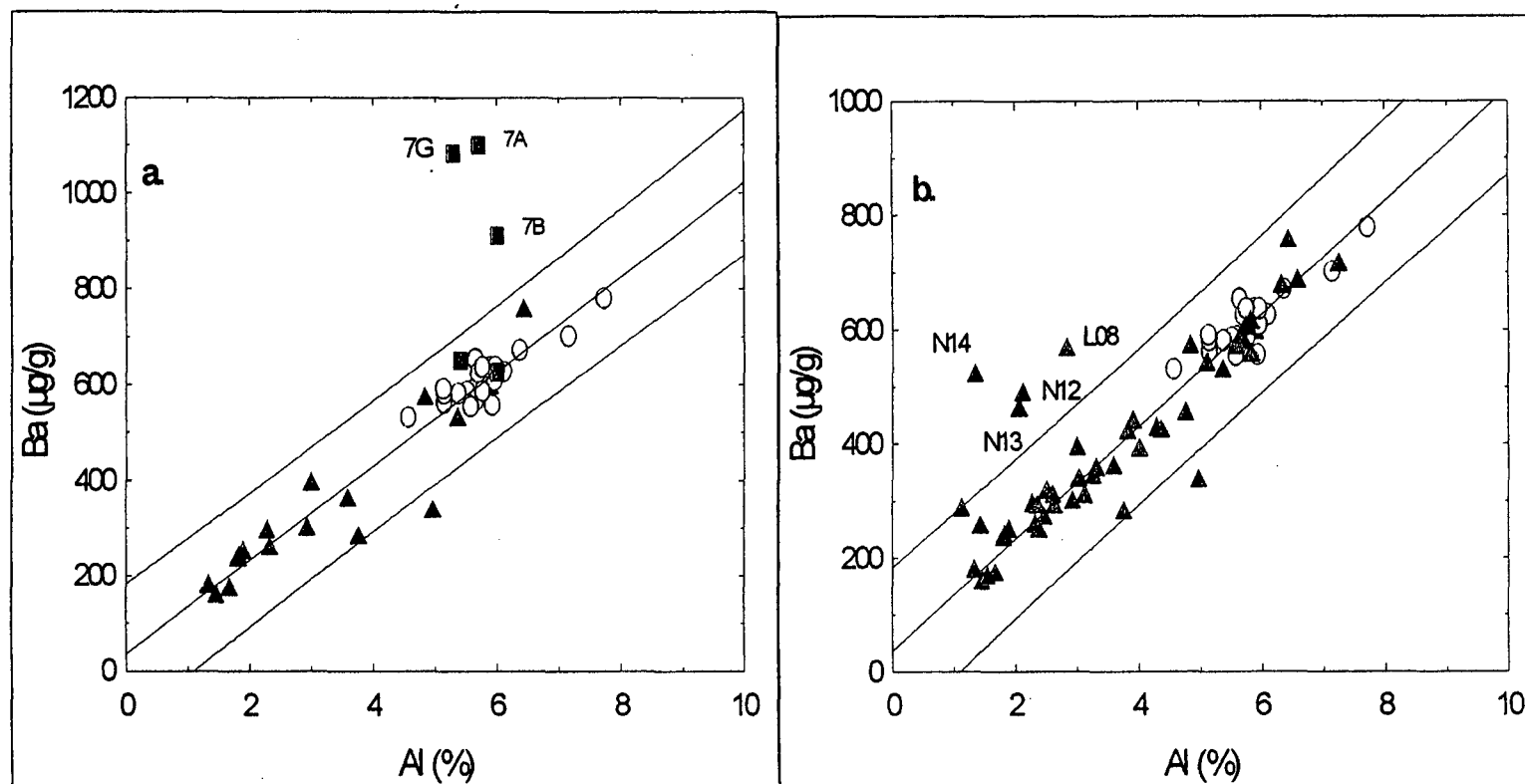


Figure 4-2. Concentrations of Al versus Ba in Sediment Samples from (a) Beaufort Sea Monitoring Program and Harrison Bay Stations and (b) Beaufort Sea Monitoring Program, Northstar, and Liberty Stations

BSMP stations (yellow circles for 1989, blue triangles for 1999), 1989 Harrison Bay stations (red squares), Northstar stations (red triangles), and Liberty stations (green triangles).

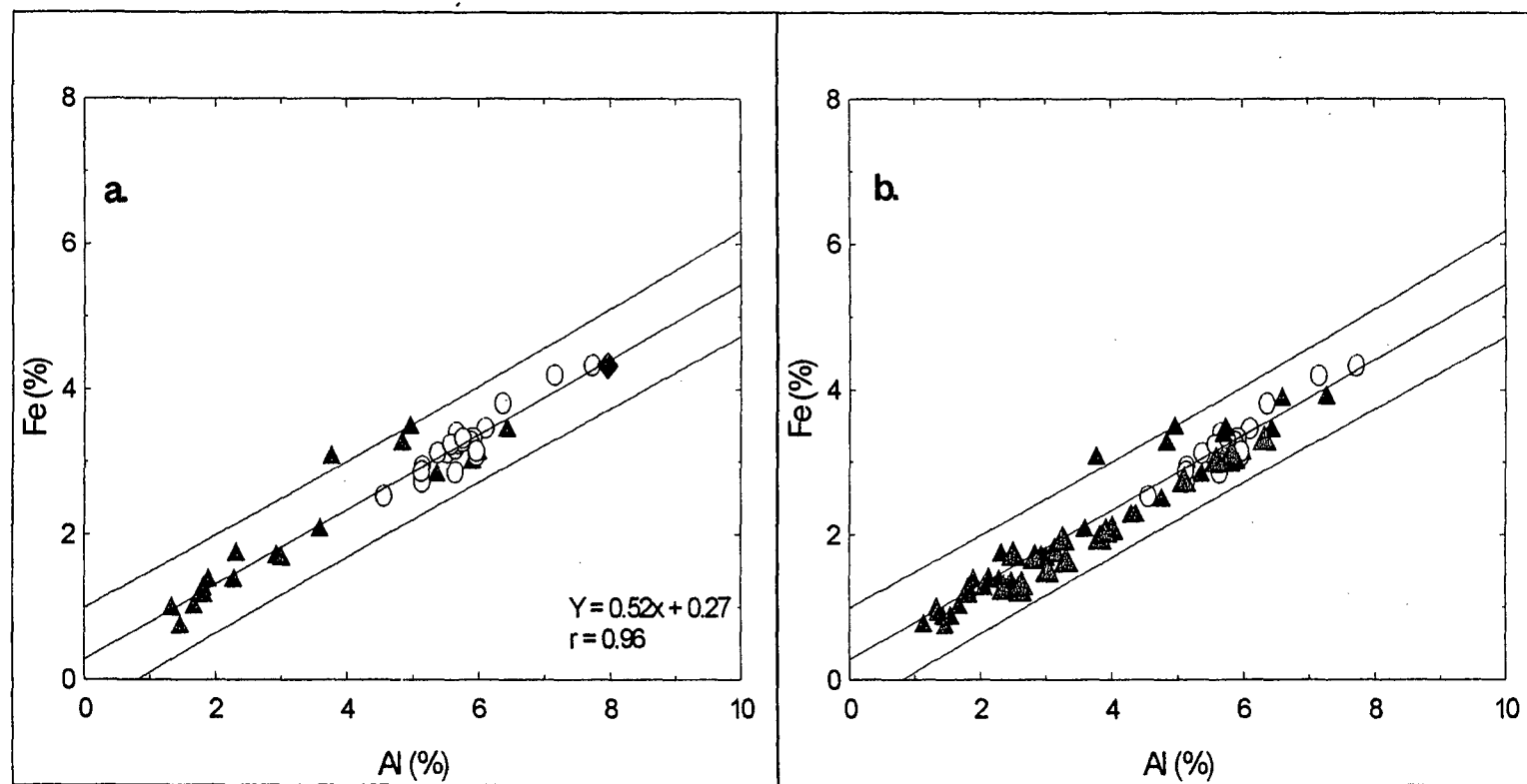


Figure 4-3. Concentrations of Al versus Fe for Sediment Samples from (a) Beaufort Sea Monitoring Program Stations and (b) Beaufort Sea Monitoring Program, Northstar, and Liberty Stations

BSMP stations (yellow circles for 1989, blue triangles for 1999), Northstar stations (red triangles), and Liberty stations (green triangles). Brown diamond shows value for average continental crust (from Wedepohl, 1995). Linear regression lines, equations, and 99% prediction intervals displayed.

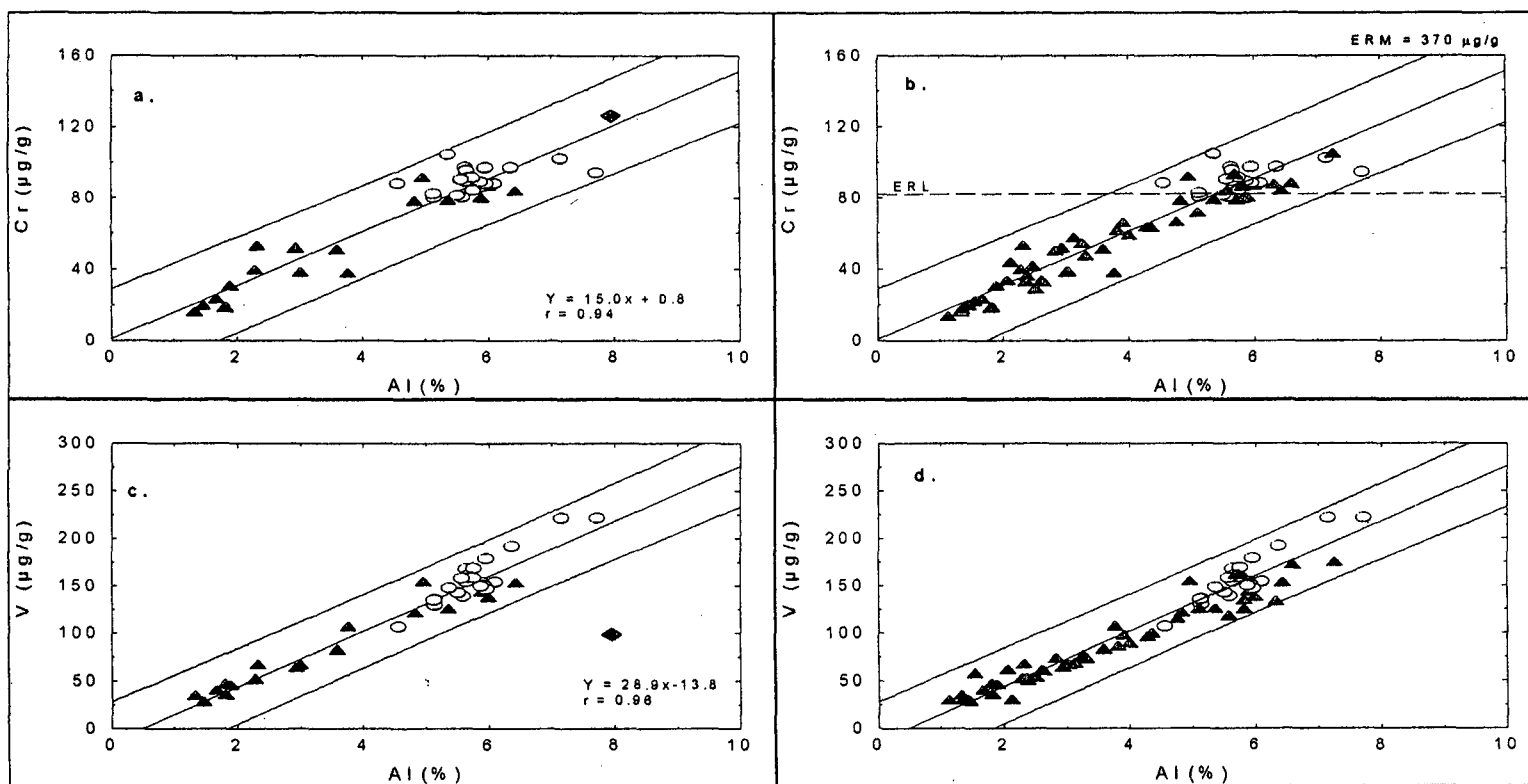


Figure 4-4. Concentrations of Al versus Cr for Sediment Samples from (a) Beaufort Sea Monitoring Program Stations and (b) Beaufort Sea Monitoring Program, Northstar, and Liberty Stations. Concentrations of Al versus V for Sediment Samples from (c) Beaufort Sea Monitoring Program Stations and (d) Beaufort Sea Monitoring Program, Northstar, and Liberty Stations

BSMP stations (yellow circles for 1989, blue triangles for 1999), Northstar stations (red triangles), and Liberty stations (green triangles). Brown diamond shows value for average continental crust (from Wedepohl, 1995). Linear regression lines, equations, 99% prediction intervals, and ERL and ERM values displayed.

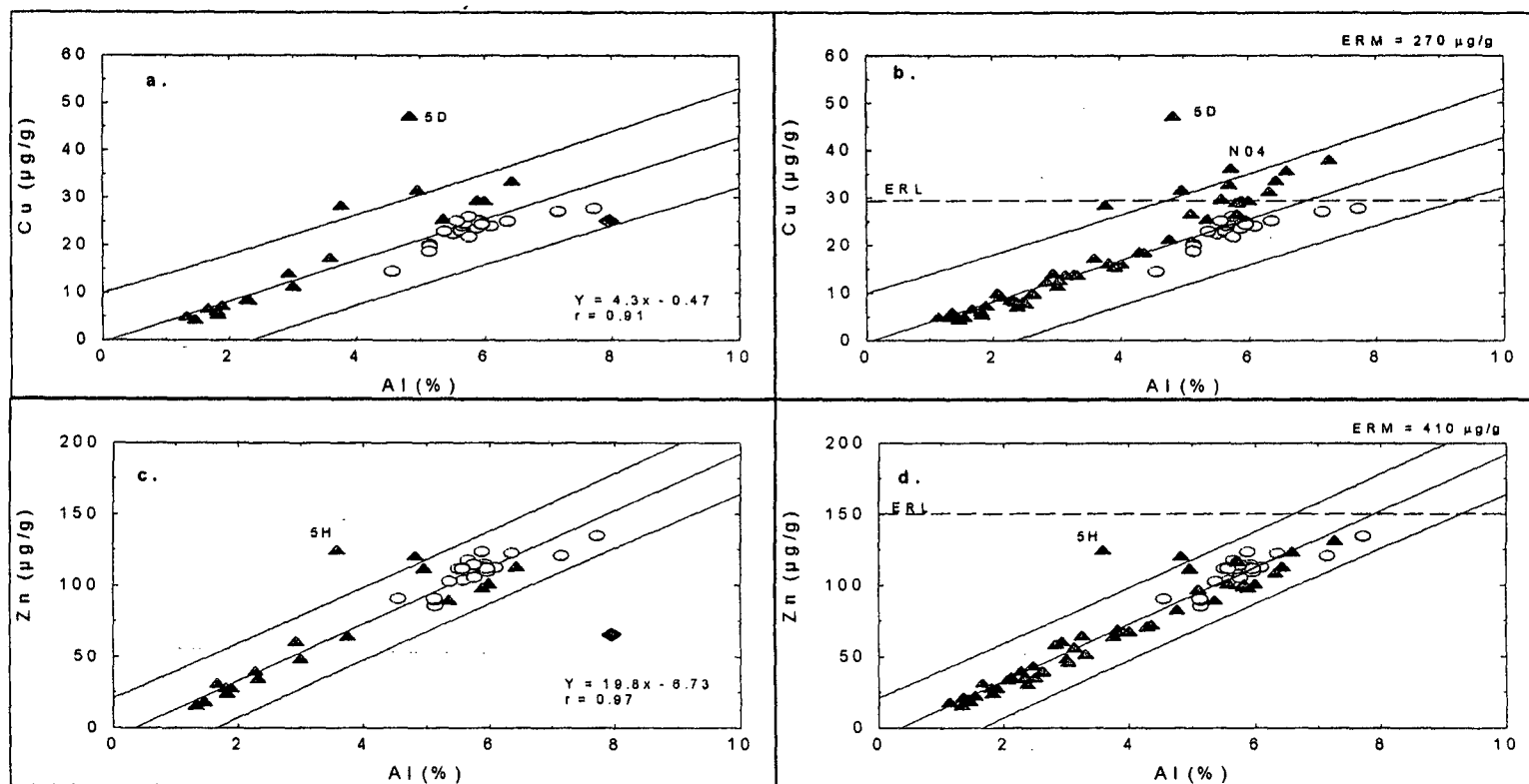


Figure 4-5. Concentrations of Al versus Cu for Sediment Samples from (a) Beaufort Sea Monitoring Program Stations and (b) Beaufort Sea Monitoring Program, Northstar, and Liberty Stations. Concentrations of Al versus Zn for Sediment Samples from (c) Beaufort Sea Monitoring Program Stations and (d) Beaufort Sea Monitoring Program, Northstar, and Liberty Stations

BSMP stations (yellow circles for 1989, blue triangles for 1999), Northstar stations (red triangles), and Liberty stations (green triangles). Brown diamond shows value for average continental crust (from Wedepohl, 1995). Linear regression lines, equations, 99% prediction intervals, and ERL and ERM values displayed.

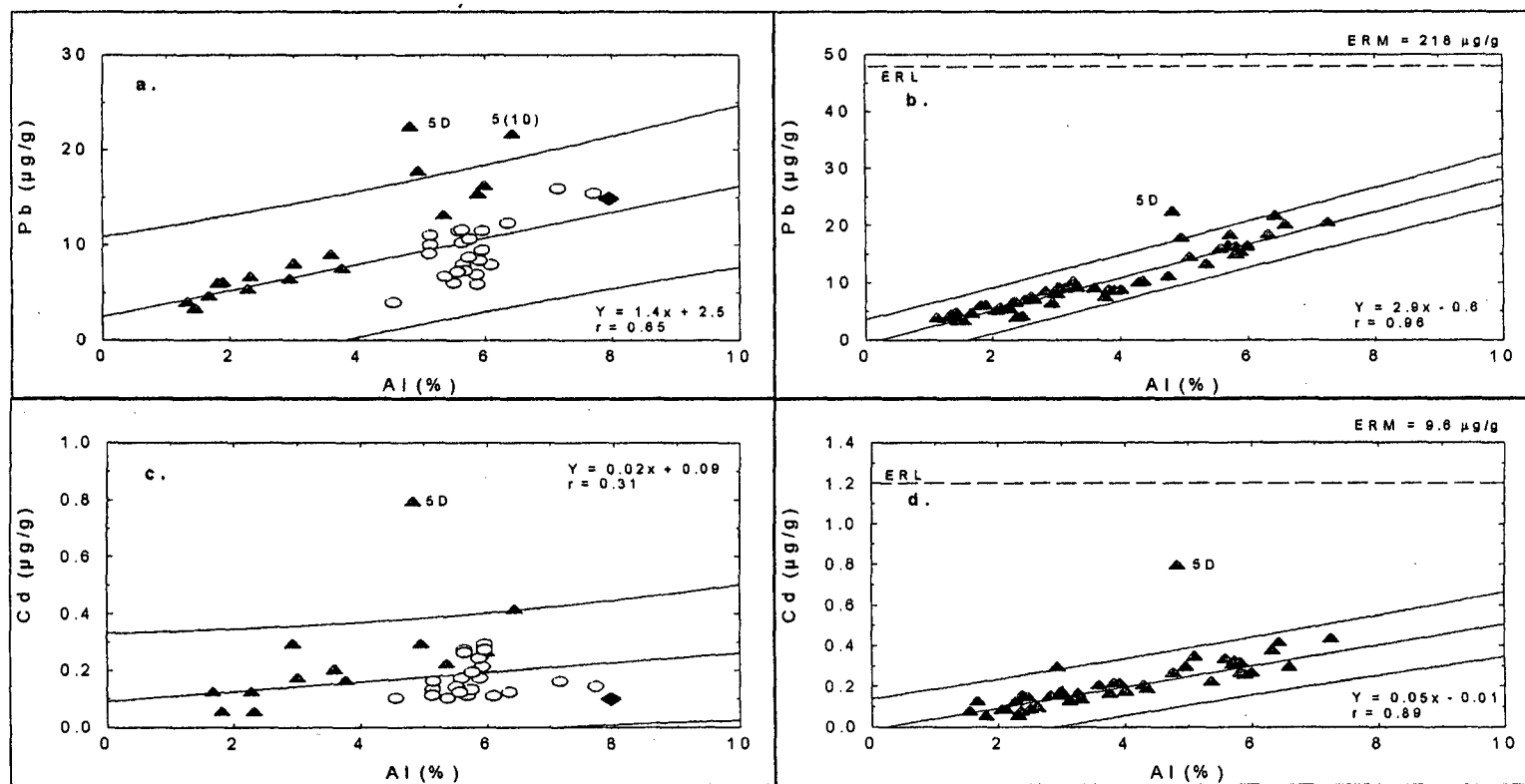


Figure 4-6. Concentrations of Al versus Pb for Sediment Samples from (a) Beaufort Sea Monitoring Program Stations and (b) Beaufort Sea Monitoring Program, Northstar, and Liberty Stations. Concentrations of Al versus Cd for Sediment Samples from (c) Beaufort Sea Monitoring Program Stations and (d) Beaufort Sea Monitoring Program, Northstar, and Liberty Stations

BSMP stations (yellow circles for 1989, blue triangles for 1999), Northstar stations (red triangles), and Liberty stations (green triangles). Brown diamond shows value for average continental crust (from Wedepohl, 1995). Linear regression lines, equations, 99% prediction intervals, and ERL and ERM values displayed.

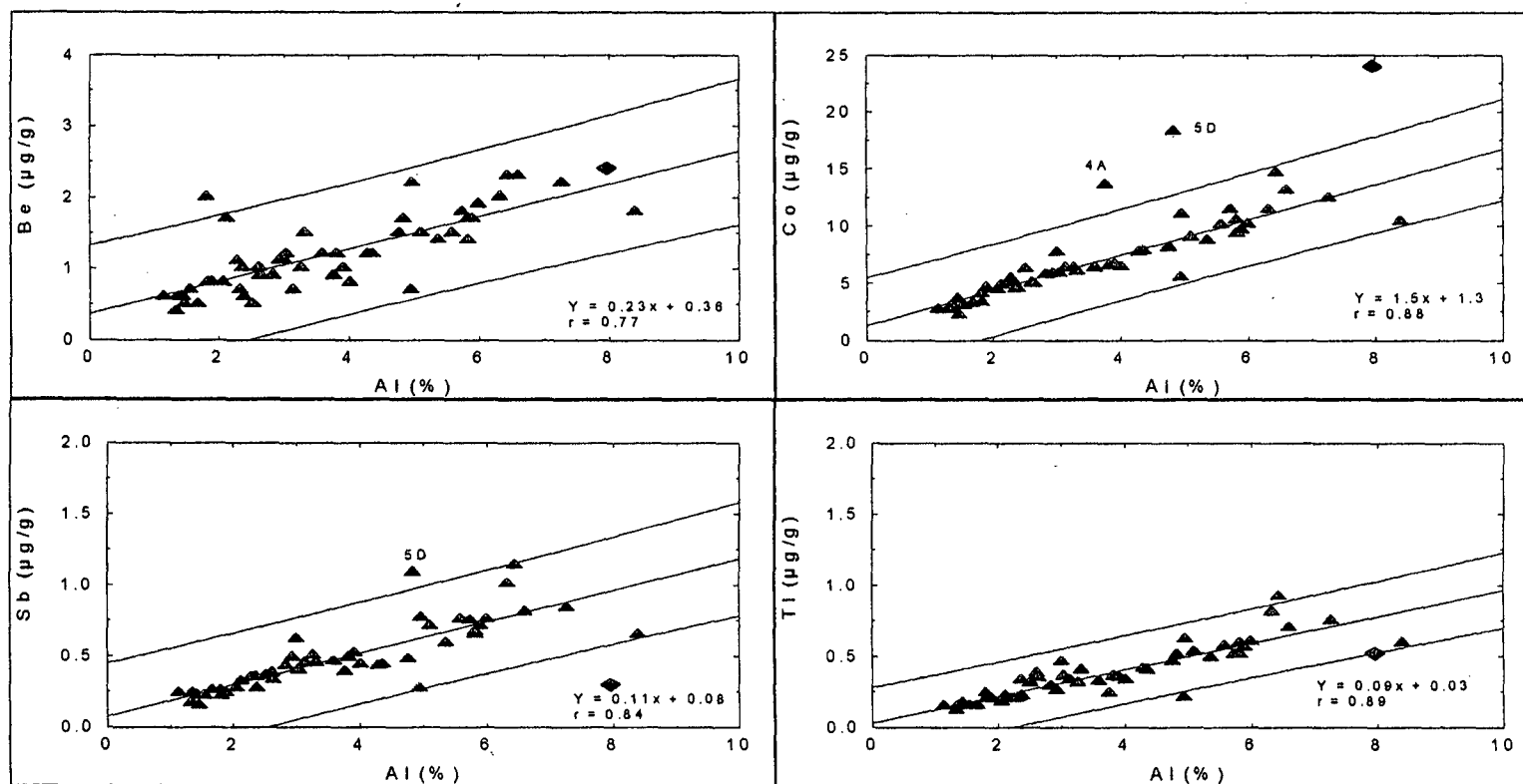
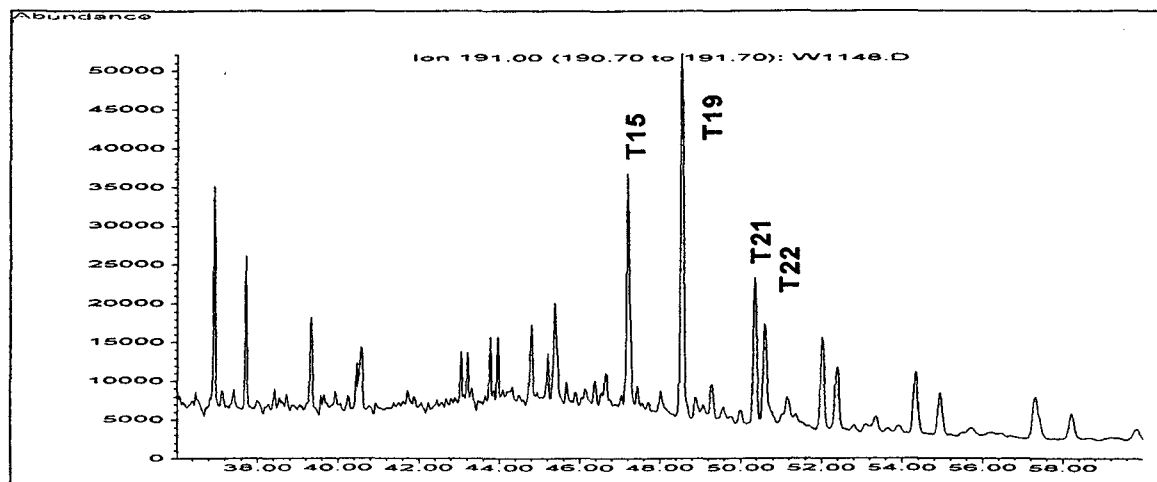
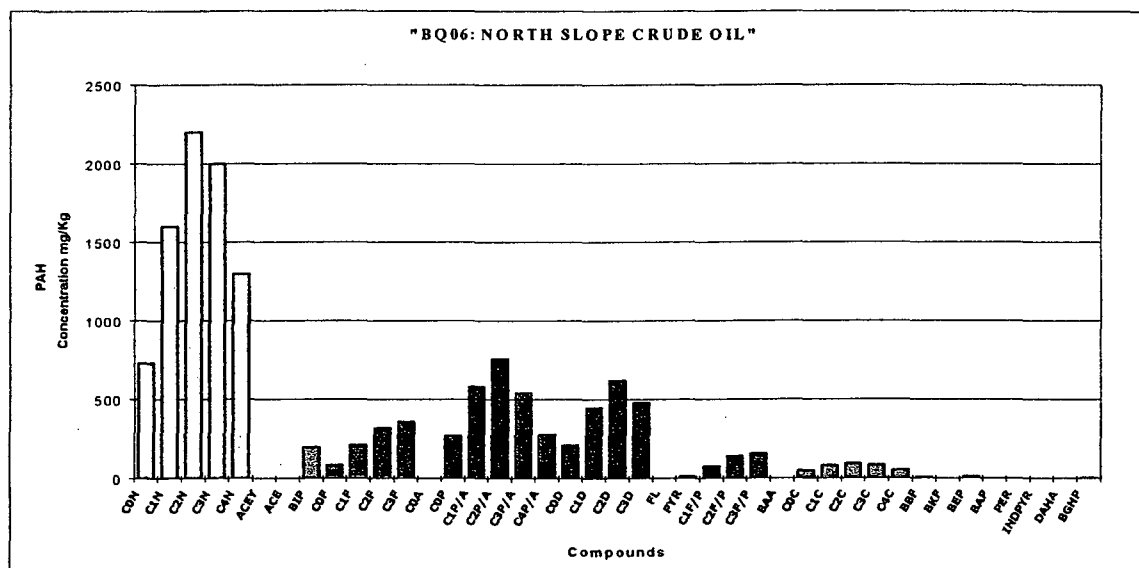
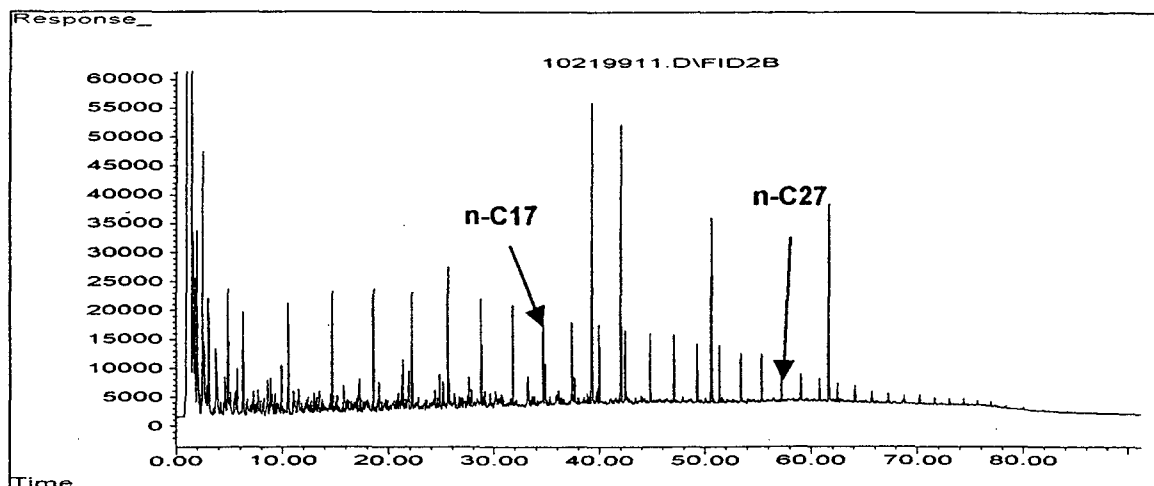


Figure 4-8. Concentrations of Al versus (a) Be, (b) Co, (c) Sb, and (d) Ti for Beaufort Sea Monitoring Program, Northstar, and Liberty Sediment Samples

BSMP stations (blue triangles for 1999), Northstar stations (red triangles), and Liberty stations (green triangles). Brown diamond shows value for average continental crust (from Wedepohl, 1995). Linear regression lines, equations, and 99% prediction intervals displayed.

Figure 4-9. North Slope Crude Oil – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)



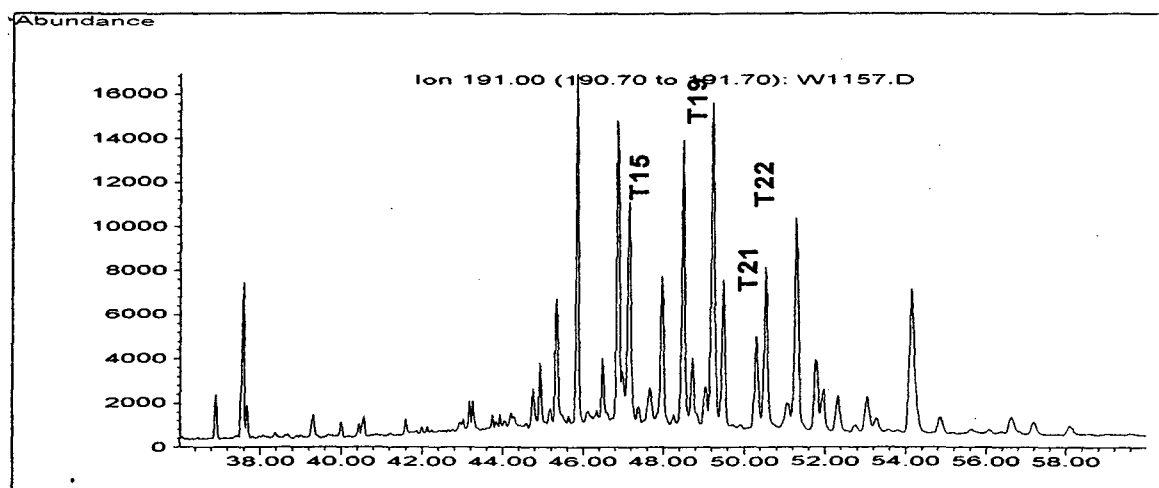


Figure 4-12. Liberty Station 6 Sediment – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

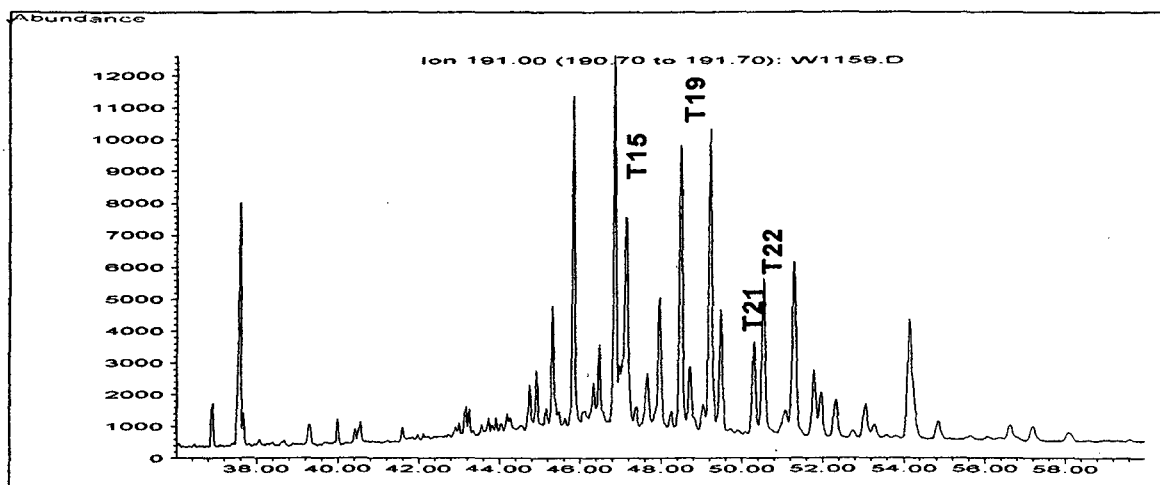
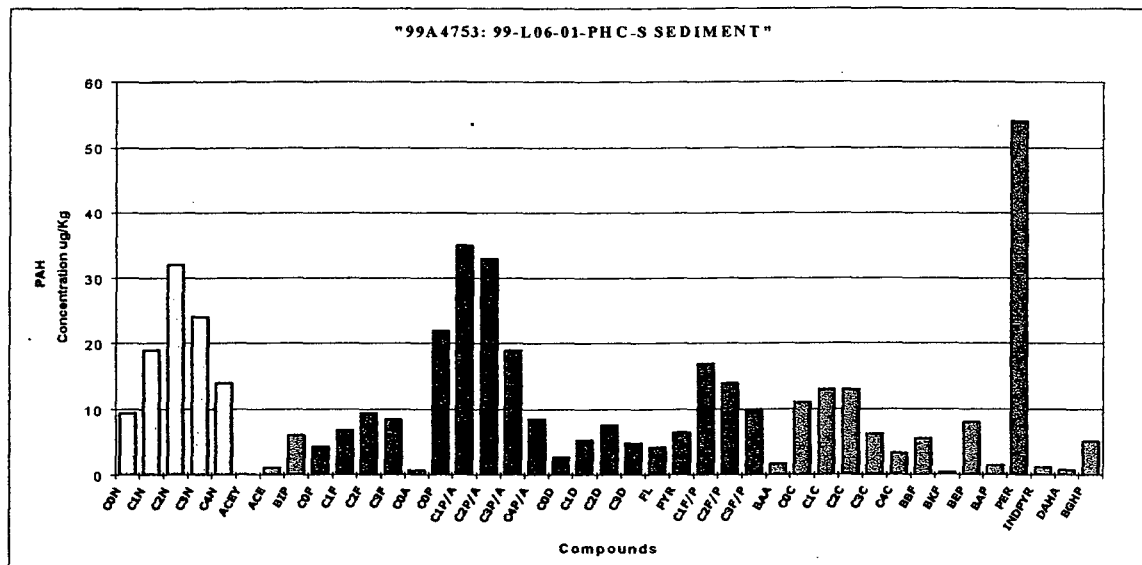
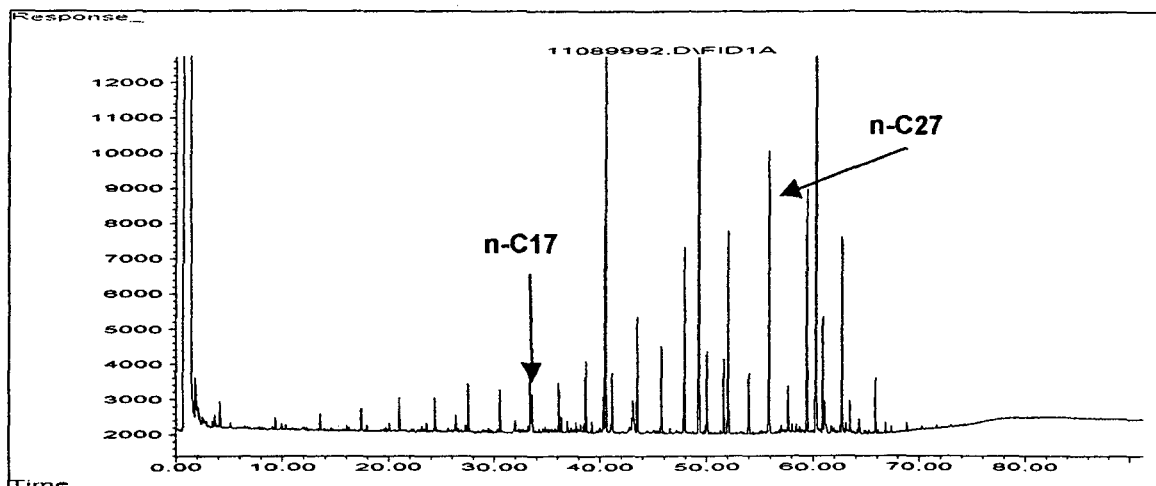
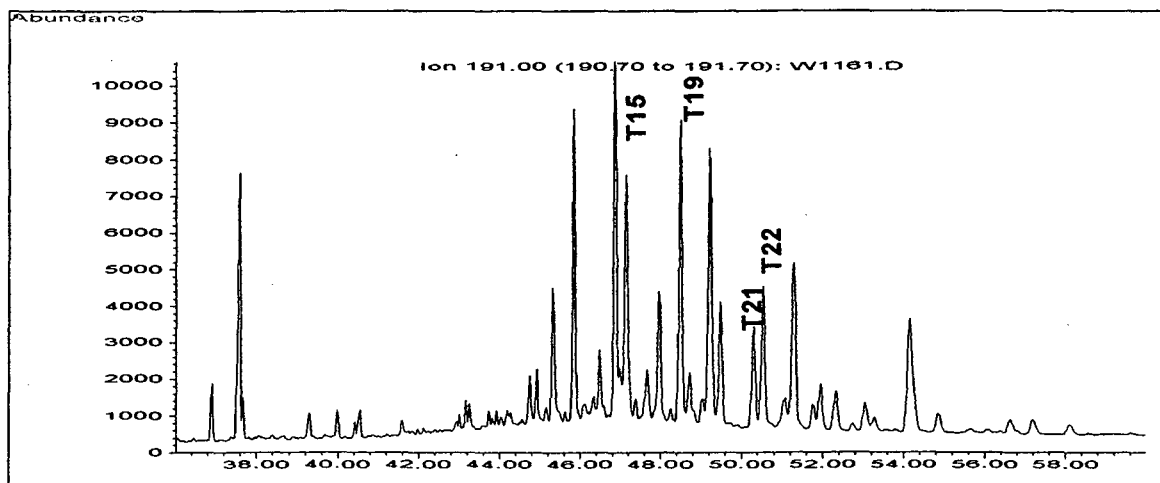
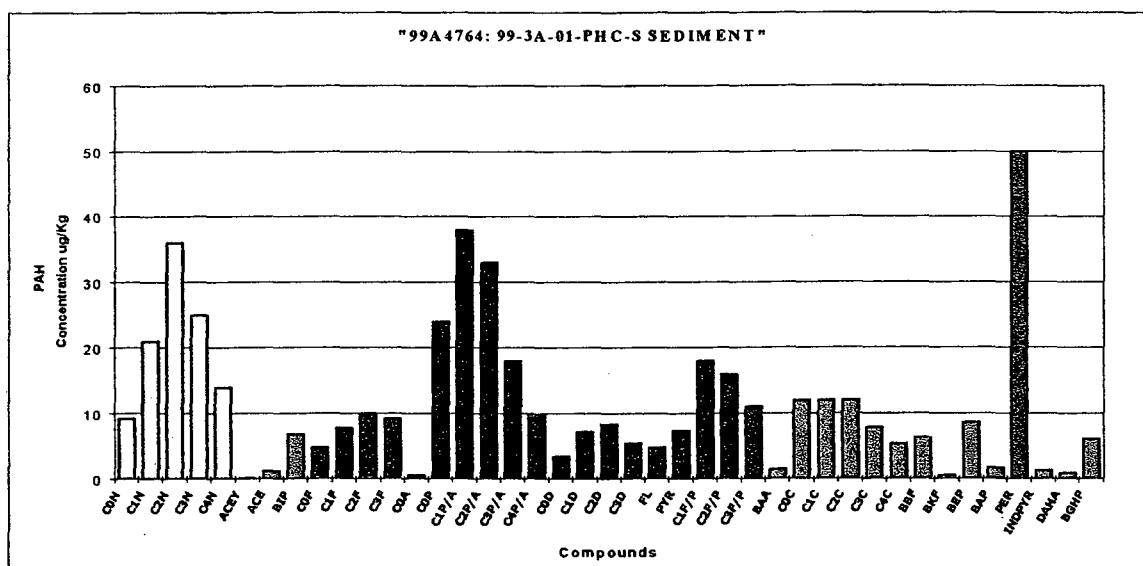
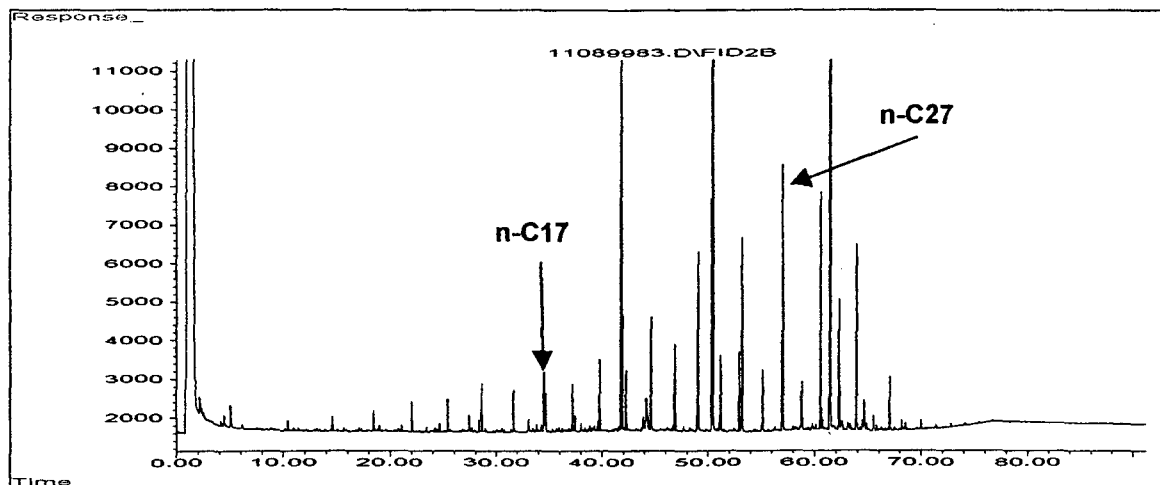


Figure 4-13. Station 3A Sediment – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)



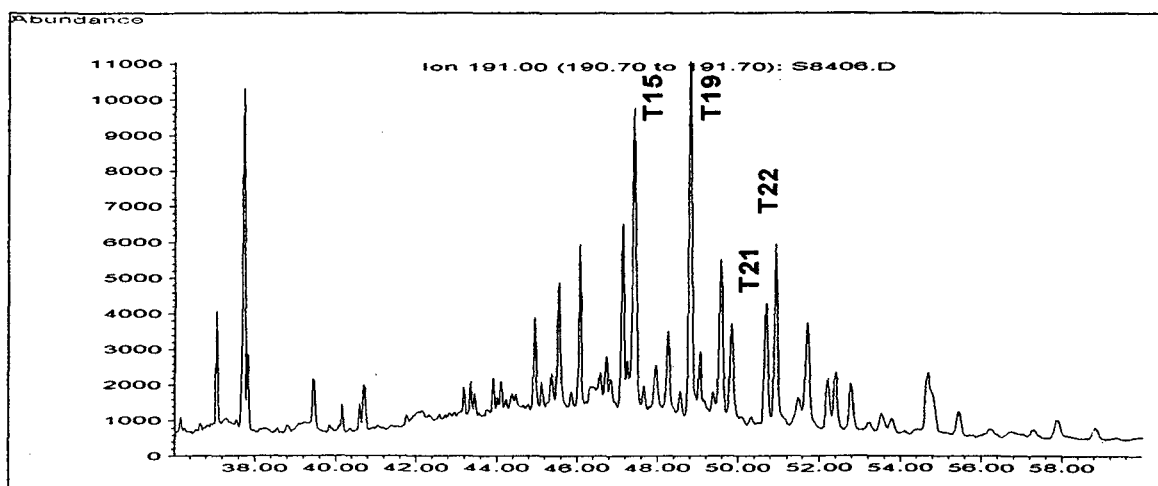
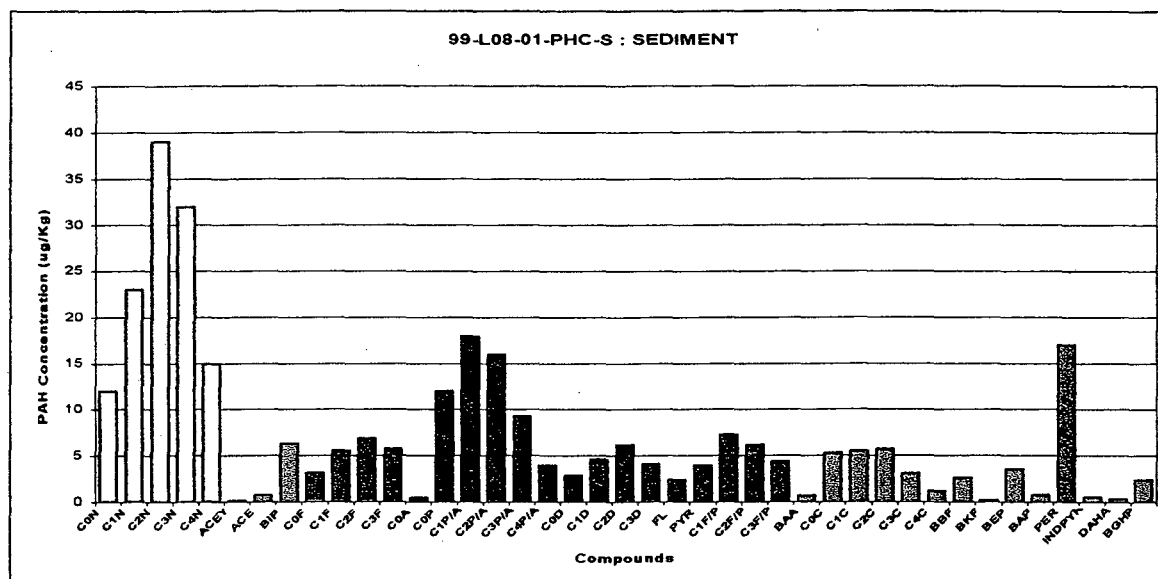
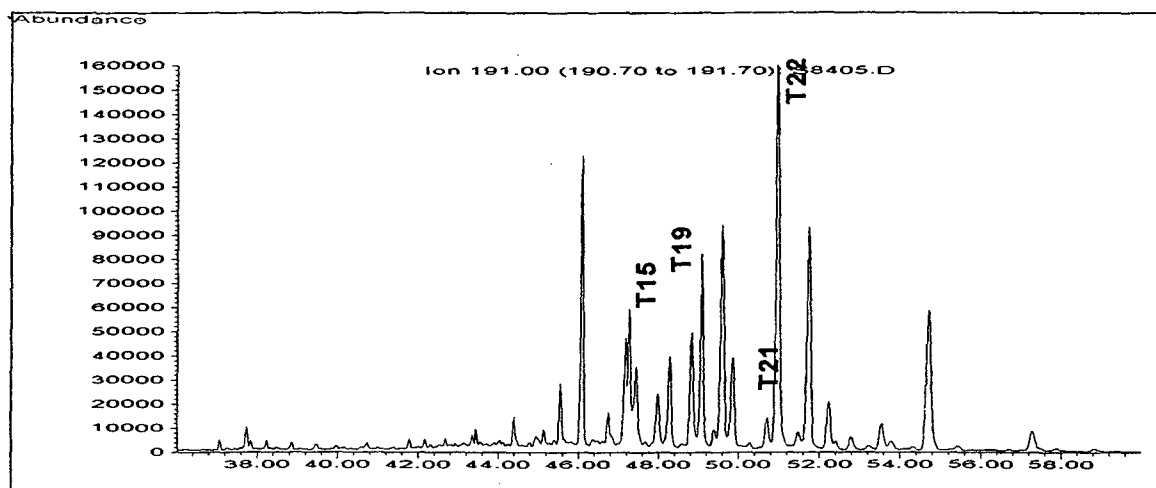
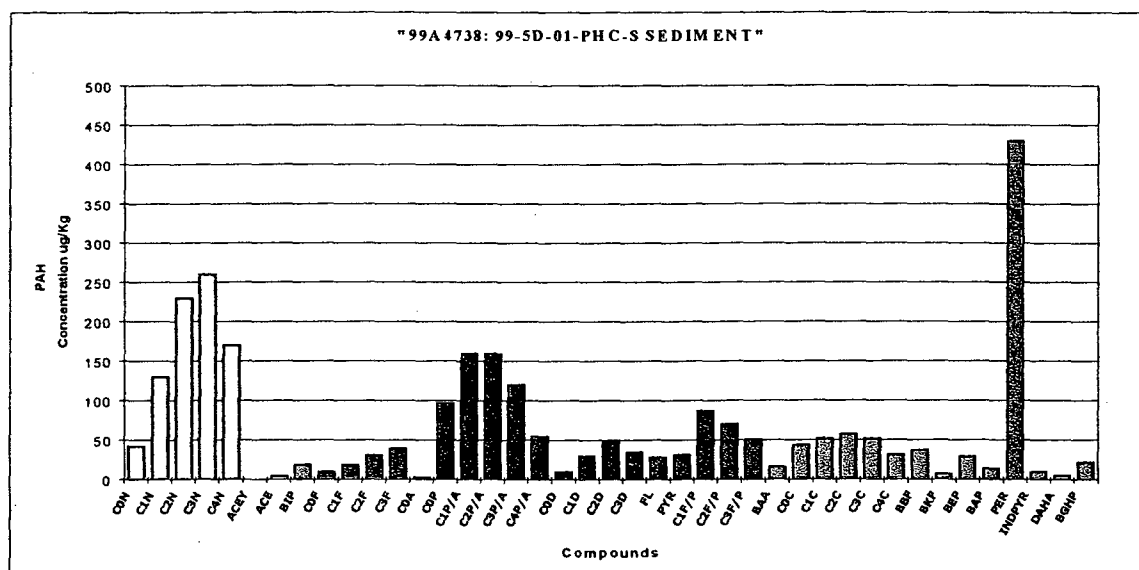
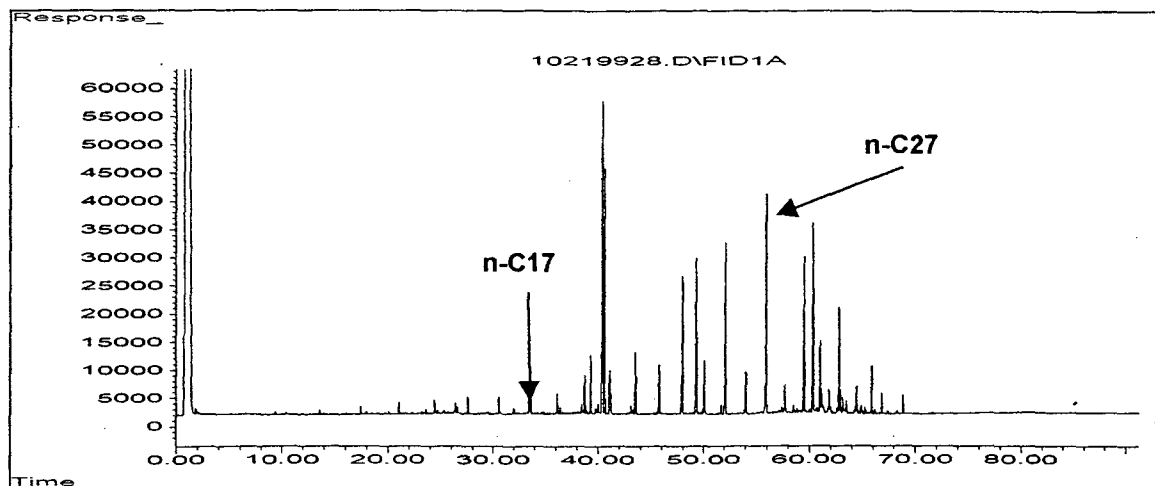


Figure 4-15. Station 5D Sediment – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)



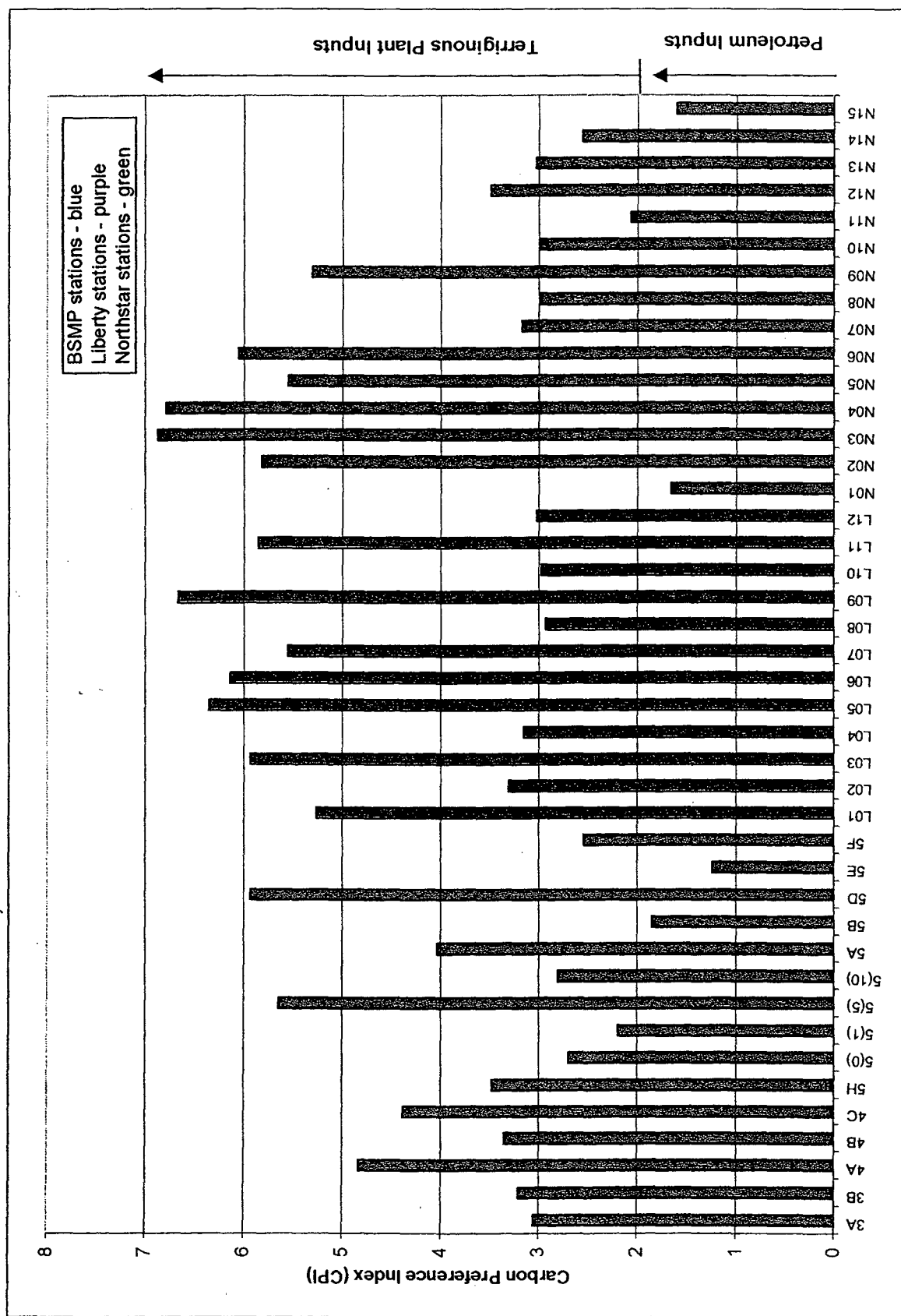


Figure 4-16. Carbon Preference Index Plot of the Beaufort Sea Monitoring Program, Liberty, and Northstar Sediment Samples

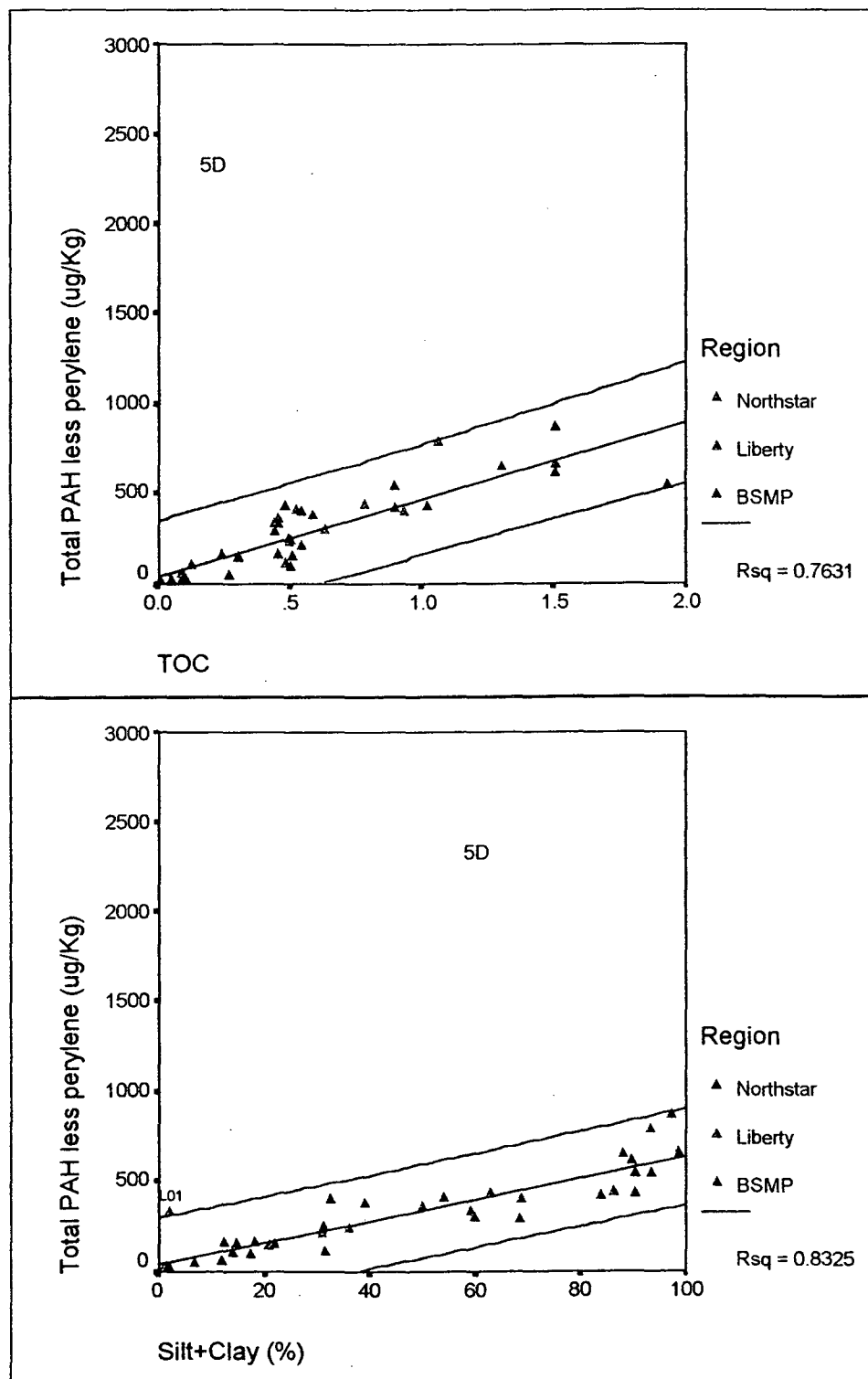


Figure 4-17. Scatterplot of Total Organic Carbon and Silt + Clay Results versus Total Polynuclear Aromatic Hydrocarbons Less Perylene Concentrations for Beaufort Sea Monitoring Program, Northstar, and Liberty Surficial Sediment Samples

The lines, Rsq, and 99% prediction intervals are from linear regression and related statistical calculations and exclude station 5D. The location of the station 5D data point is annotated with a text label.

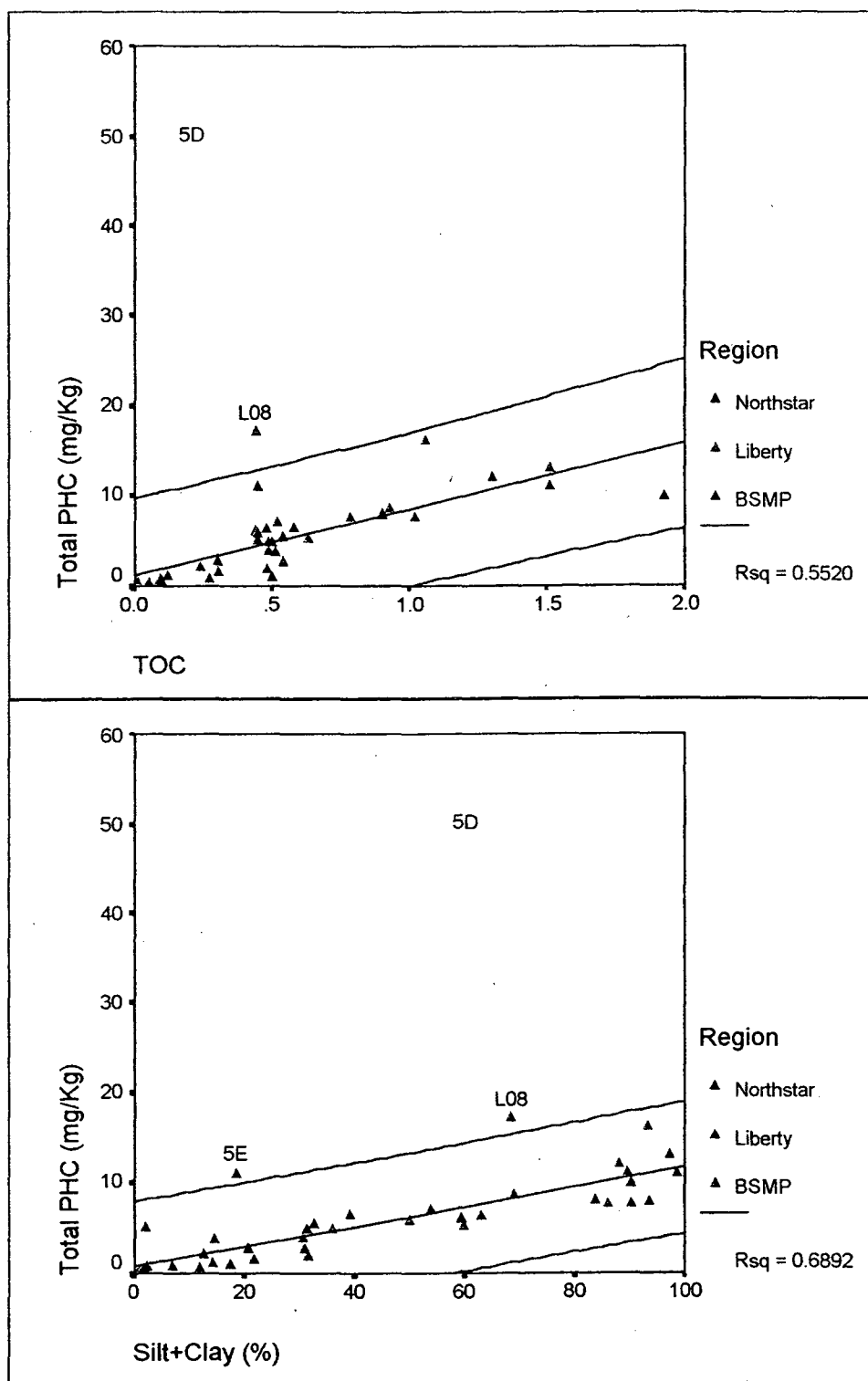


Figure 4-18. Scatterplot of Total Organic Carbon and Silt + Clay Results versus Total Petroleum Hydrocarbon Concentrations for Beaufort Sea Monitoring Program, Northstar, and Liberty Surficial Sediment Samples

The lines, Rsq, and 99% prediction intervals are from linear regression and related statistical calculations and exclude station 5D. The location of the station 5D data point is annotated with a text label.

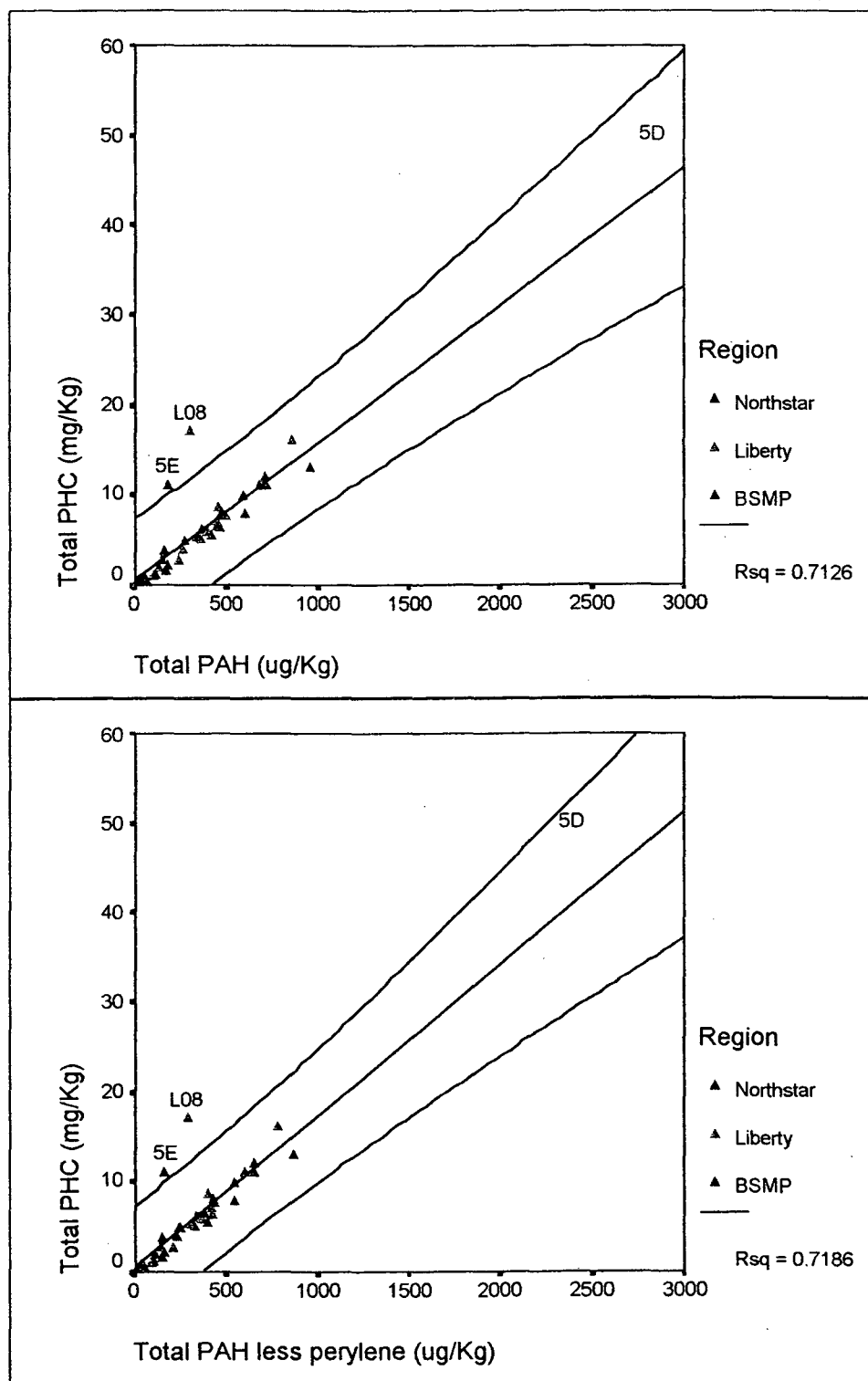


Figure 4-19. Scatterplot of Total Organic Carbon and Silt + Clay Results versus Total Petroleum Hydrocarbon and Total PAH Less Perylene Concentrations for Beaufort Sea Monitoring Program, Northstar, and Liberty Surficial Sediment Samples

The lines, Rsq, and 99% prediction intervals are from linear regression and related statistical calculations and exclude station 5D. The location of the station 5D data point is annotated with a text label.

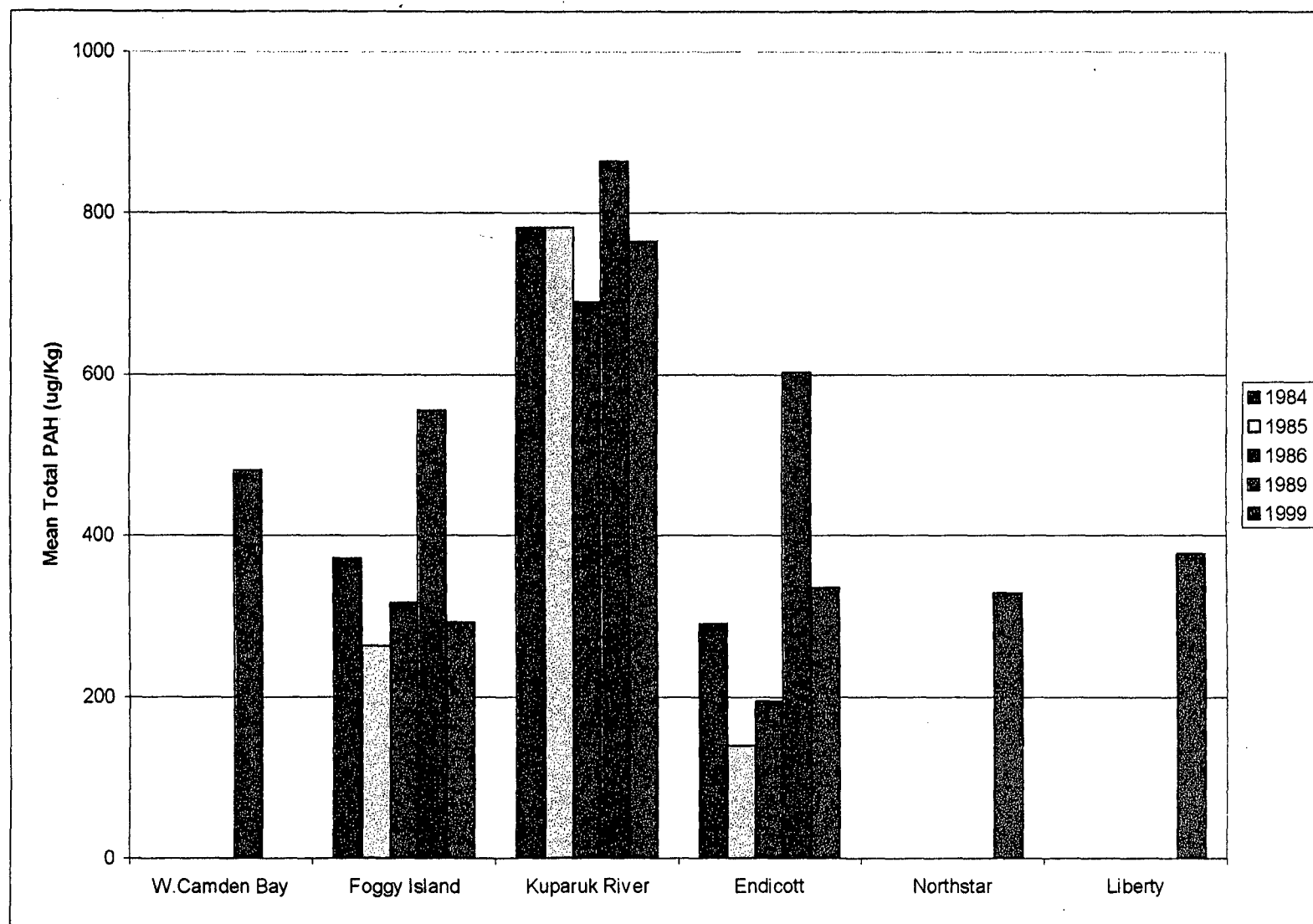


Figure 4-20. Regional Mean Total Polynuclear Aromatic Hydrocarbon Concentrations of Surficial Sediment Samples for 1984, 1985, 1986, 1989, and 1999

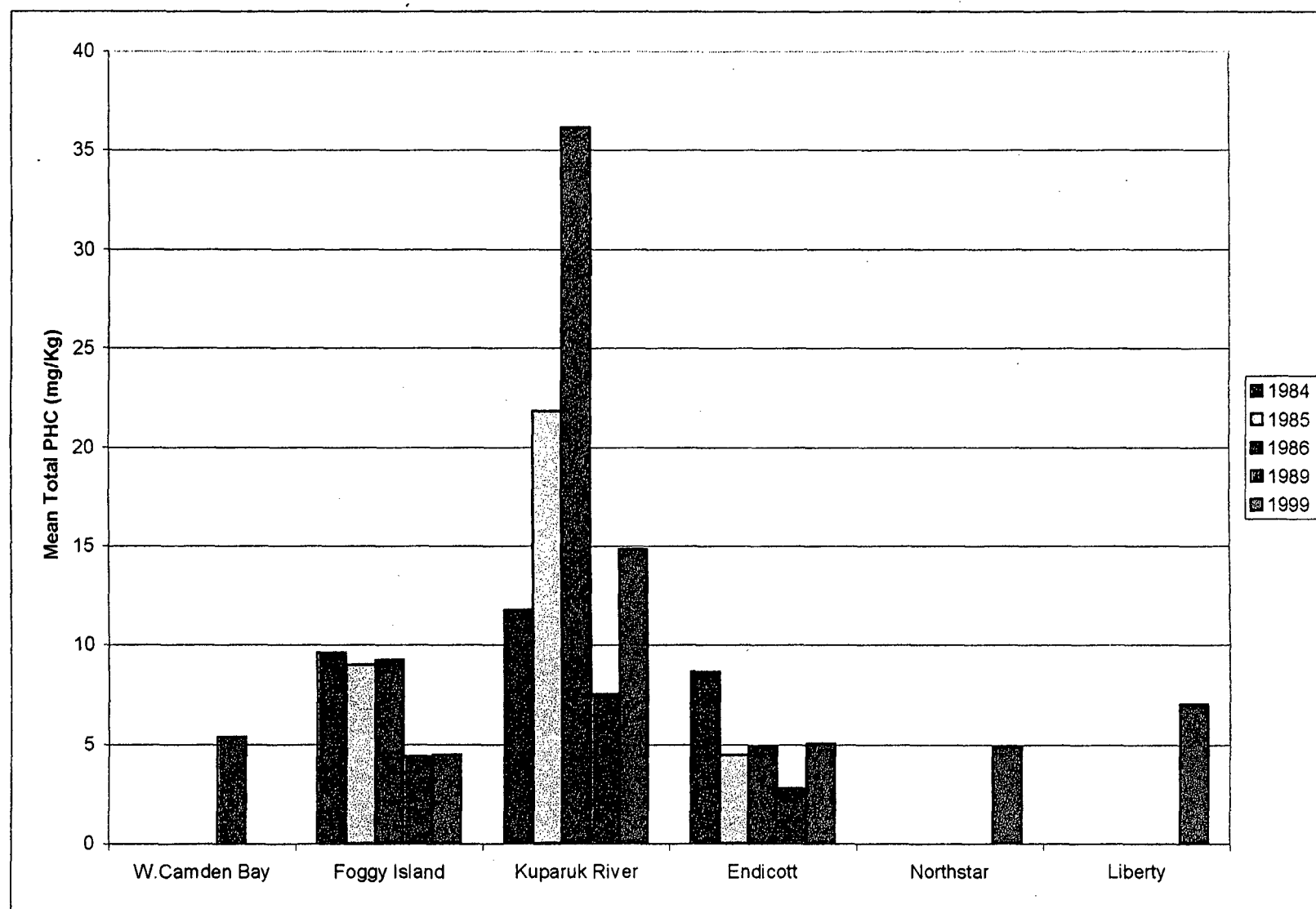


Figure 4-21. Regional Mean Total Petroleum Hydrocarbon Concentrations of Surficial Sediment Samples for 1984, 1985, 1986, 1989, and 1999

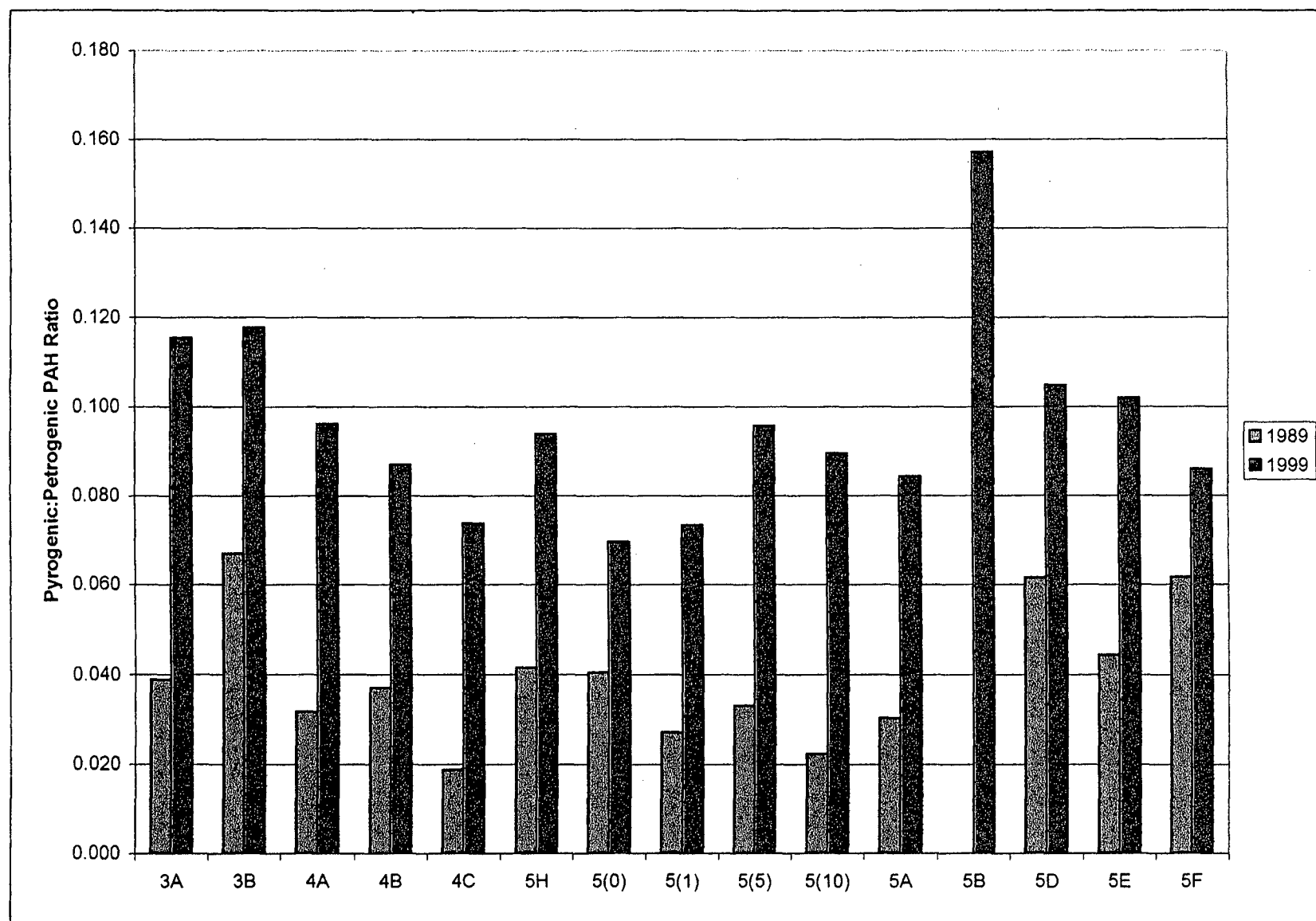


Figure 4-22. Pyrogenic:Petrogenic Ratios of Beaufort Sea Monitoring Program Surficial Sediment Samples for 1989 and 1999

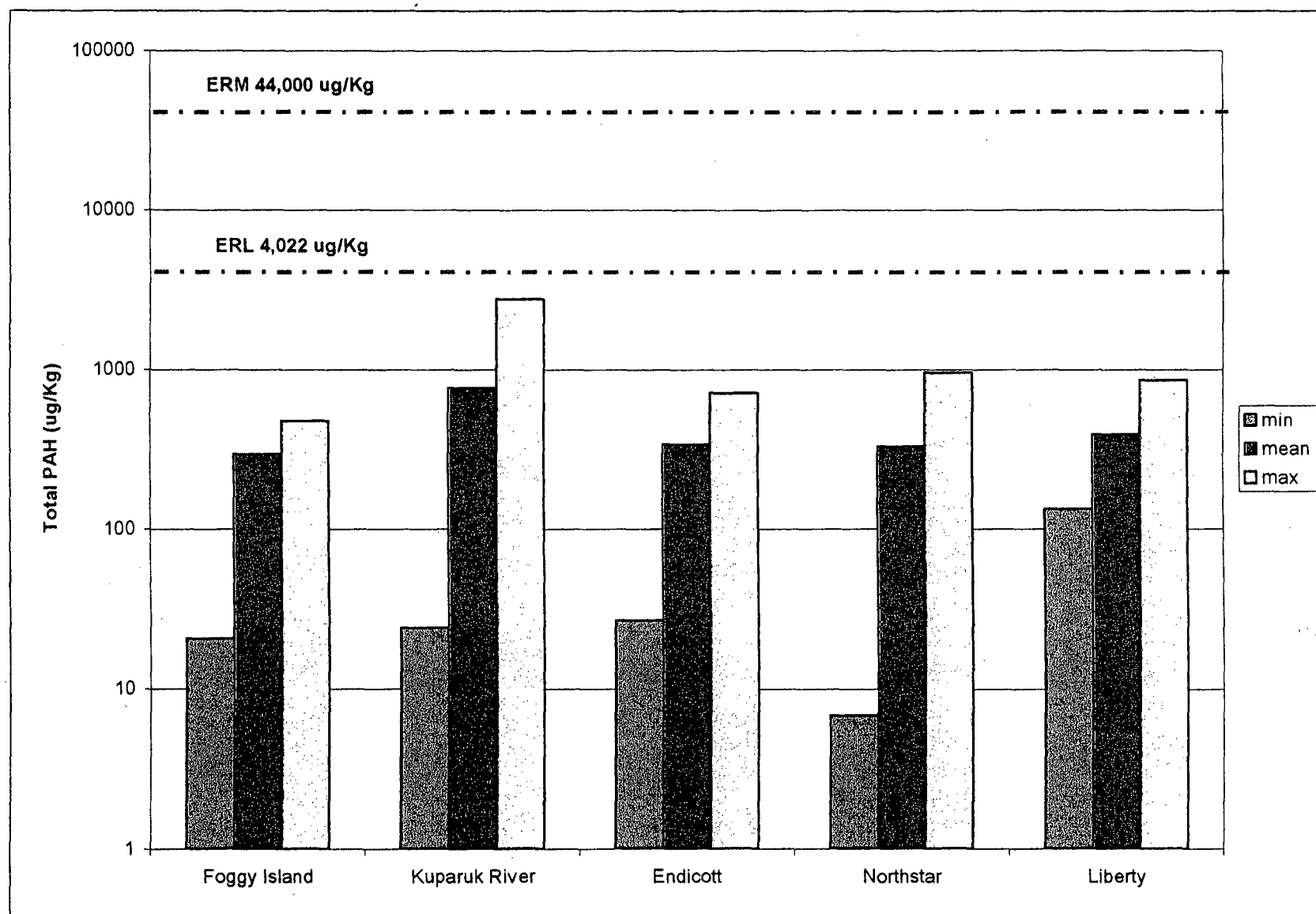


Figure 4-23. Comparison of Regional Mean Total Polynuclear Aromatic Hydrocarbon Concentrations to Sediment Quality Criteria Effects Range-Low and Effects Range-Medium Values (Long et al., 1995) Note: y-axis is present on a logarithmic scale.

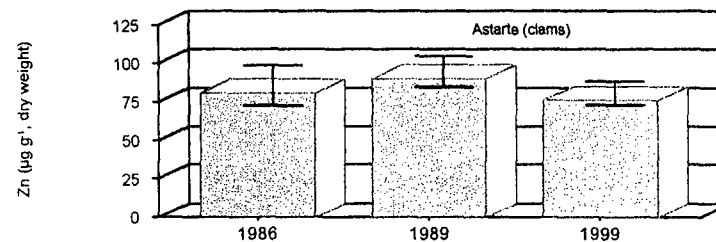
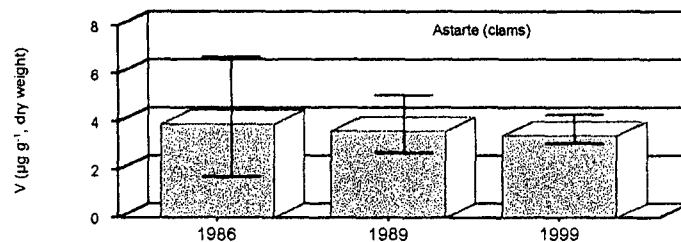
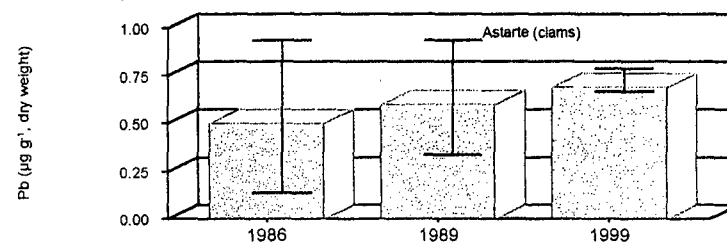
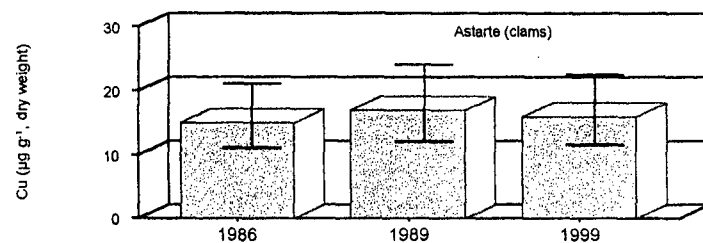
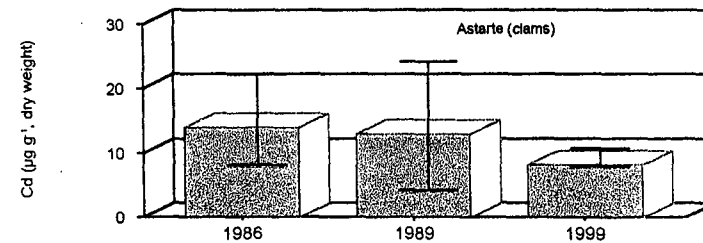
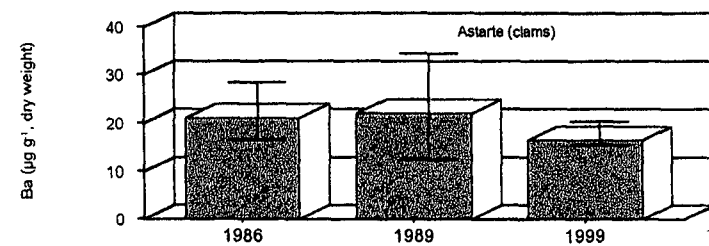


Figure 4-24. Mean Concentrations of Ba, Cd, Cu, Pb, V, and Zn in Clams (*Astarte*) Collected from Beaufort Sea Monitoring Program Stations During 1986 and 1989, and from ANIMIDA Stations During 1999

Error bars set at \pm standard deviation.

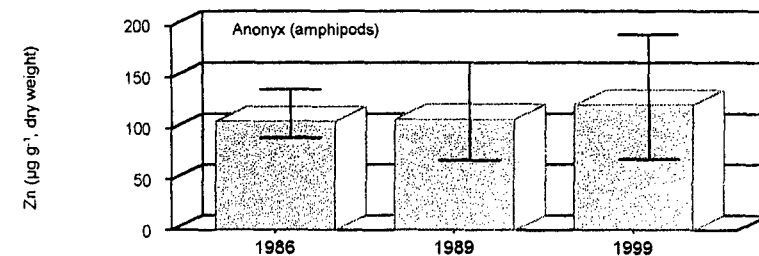
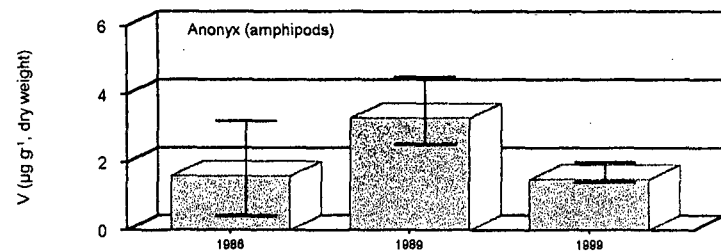
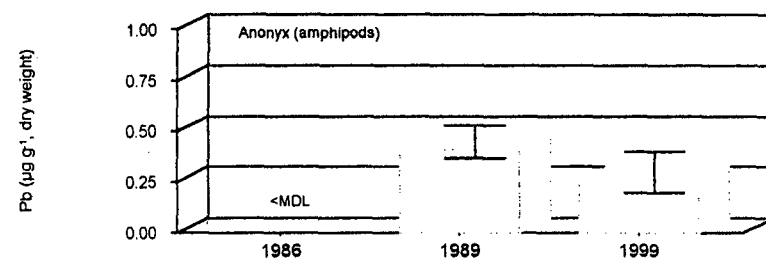
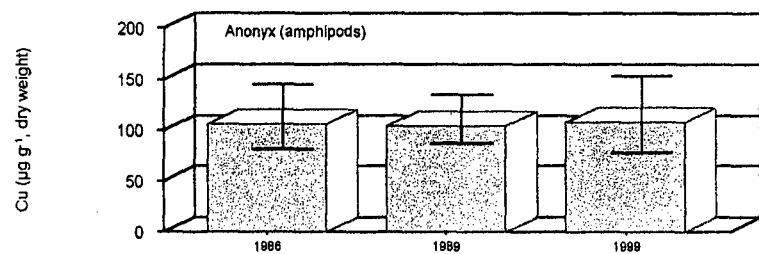
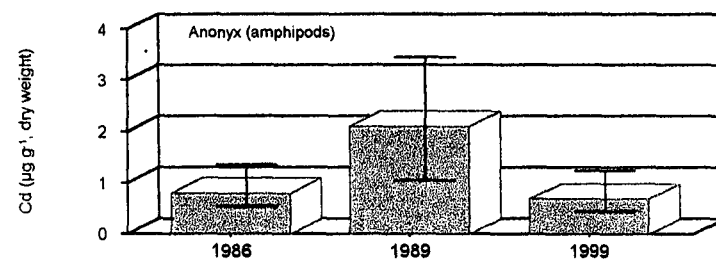
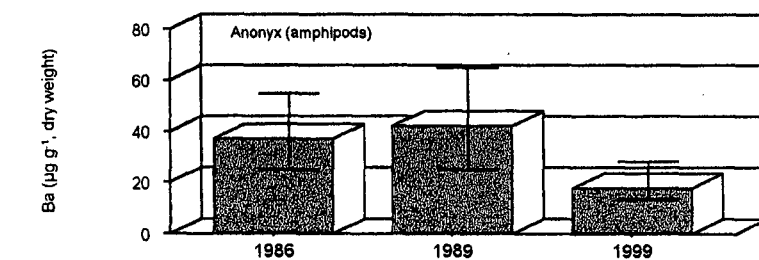


Figure 4-25. Mean Concentrations of Ba, Cd, Cu, Pb, V, and Zn in Amphipods (*Anonyx*) Collected from Beaufort Sea Monitoring Program Stations During 1986 and 1989, and from ANIMIDA Stations During 1999

Error bars set at \pm standard deviation.

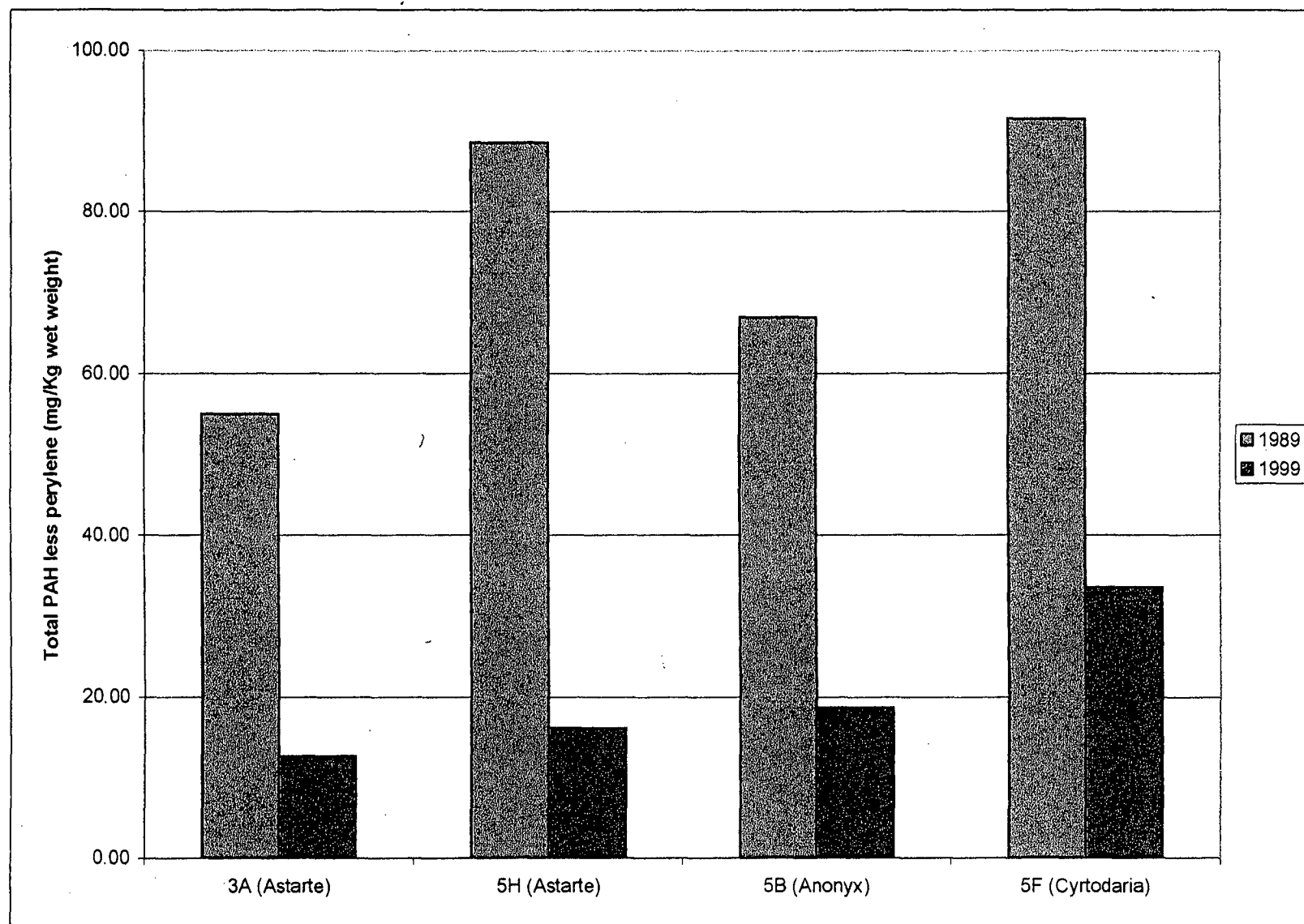


Figure 4-27. Total Polynuclear Aromatic Hydrocarbon Less Perylene Concentrations of Beaufort Sea Monitoring Program Organisms for 1989 and 1999

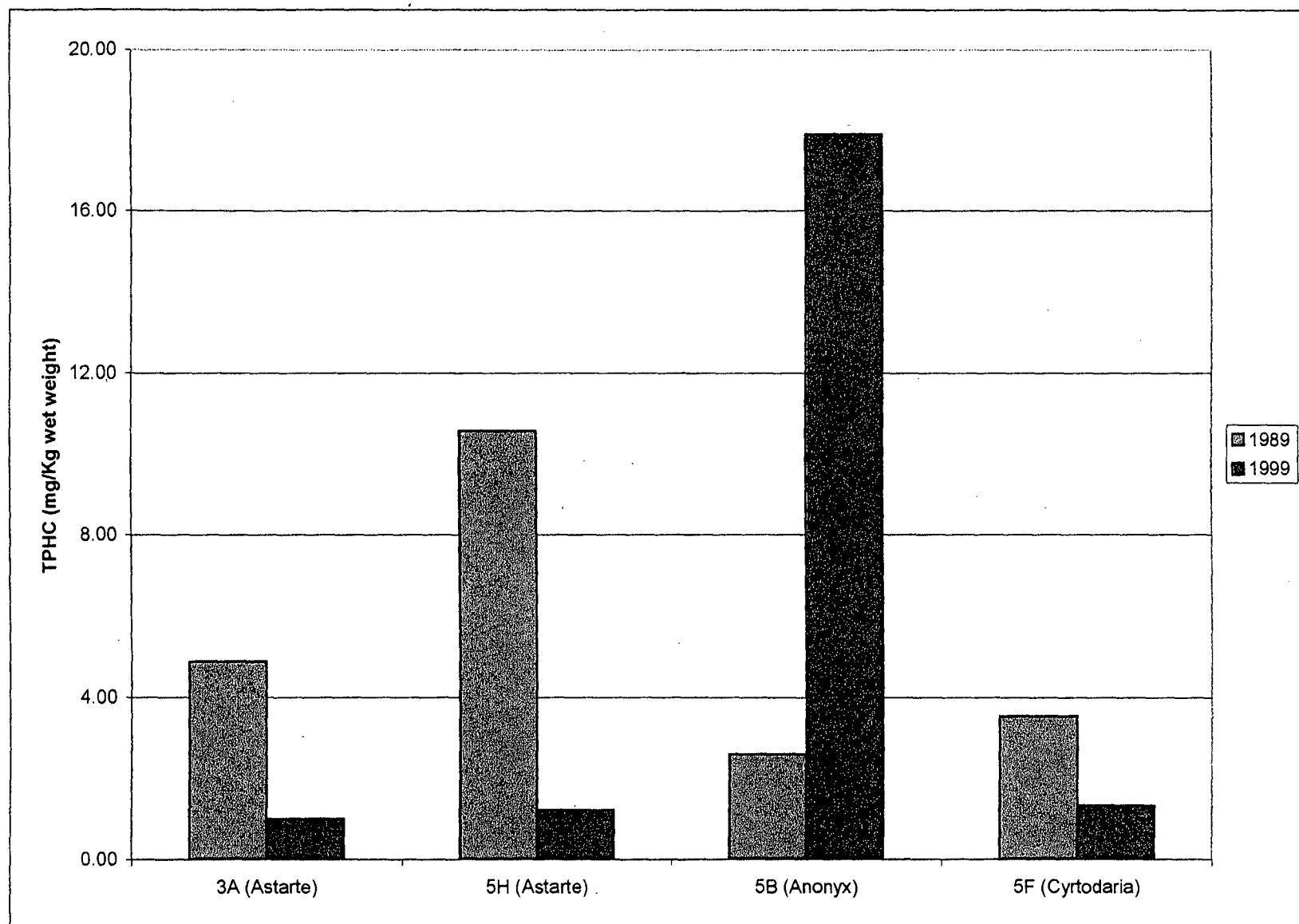


Figure 4-28. Total Petroleum Hydrocarbon Concentrations of Beaufort Sea Monitoring Program Organisms for 1989 and 1999

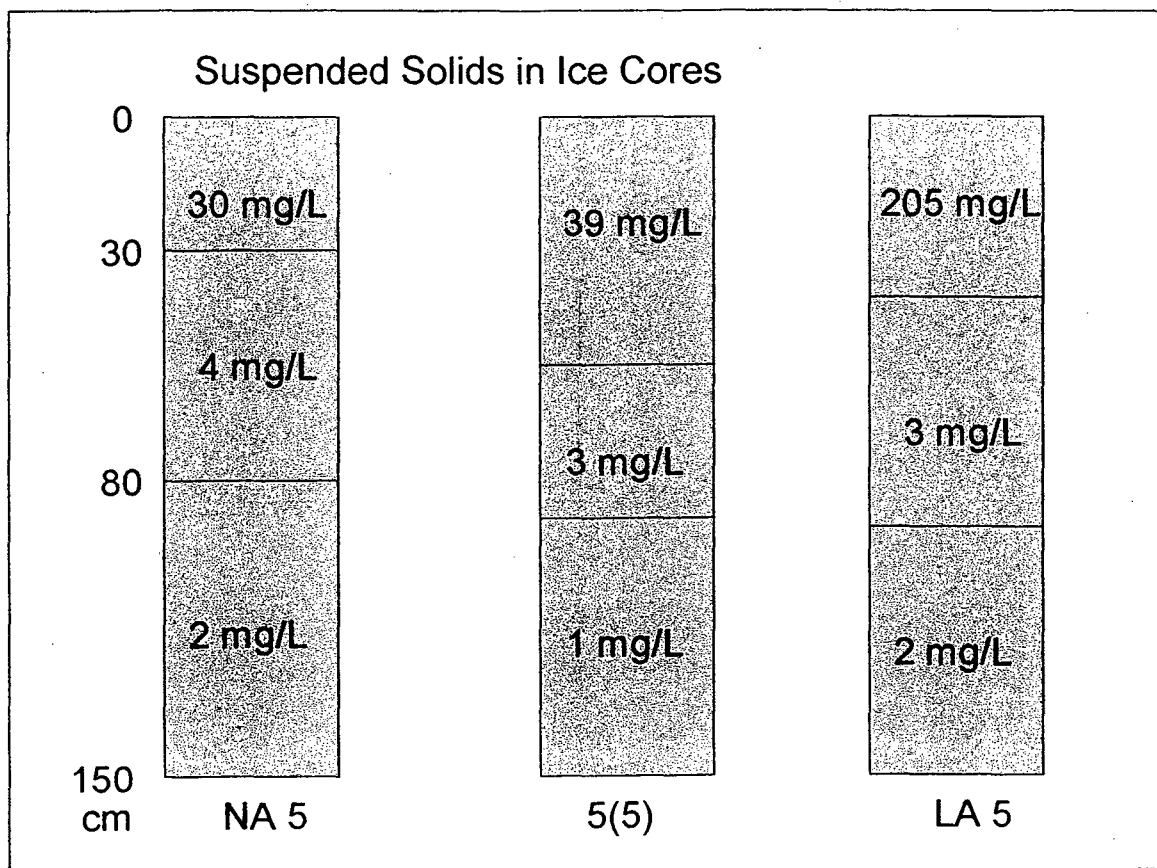


Figure 4-30. Vertical Distribution of Sediment in Ice Cores Collected During April 2000

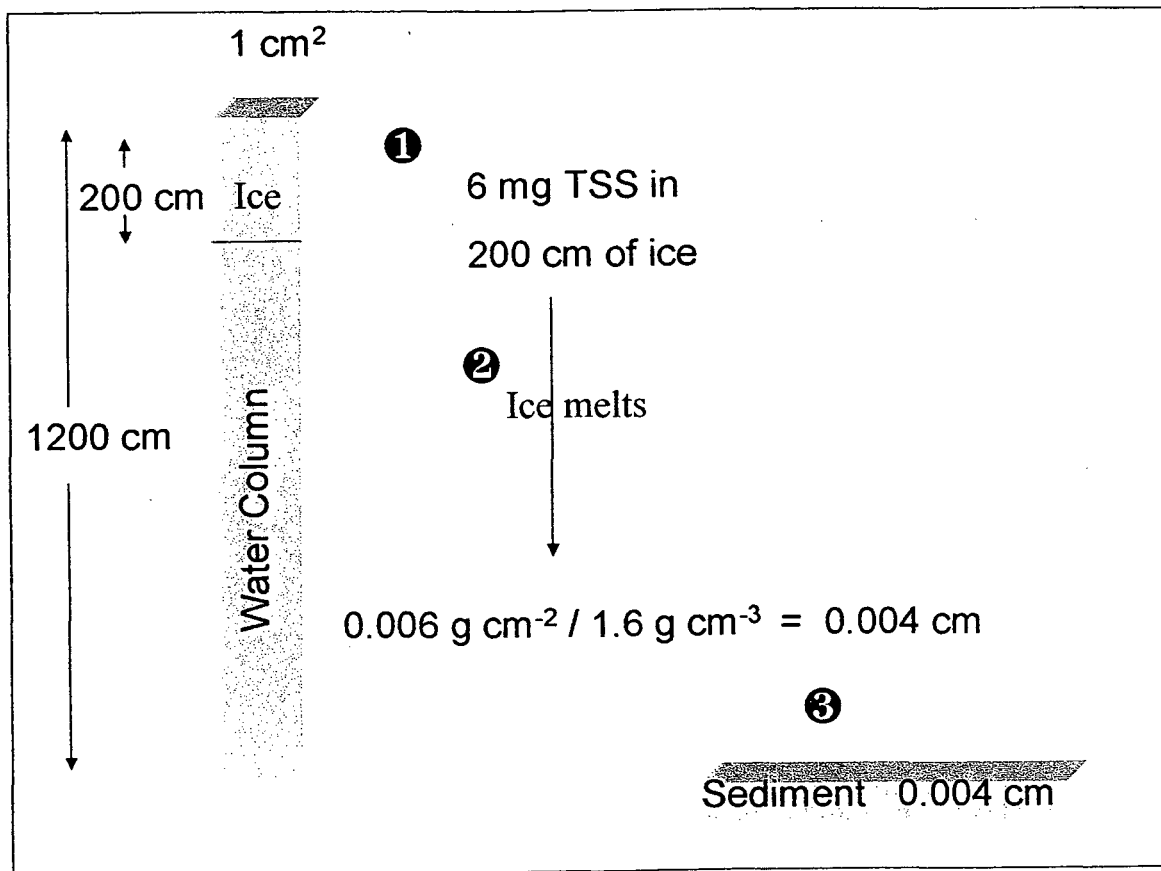


Figure 4-31. Schematic Representation of Release of Sediment from Melting Surface Ice

In the following steps:

1. Integrated amount of sediment in the ice core as determined from core data
2. Release of sediment to seafloor when ice melts
3. Calculated depth of sediment layer formed from sediment in sea ice

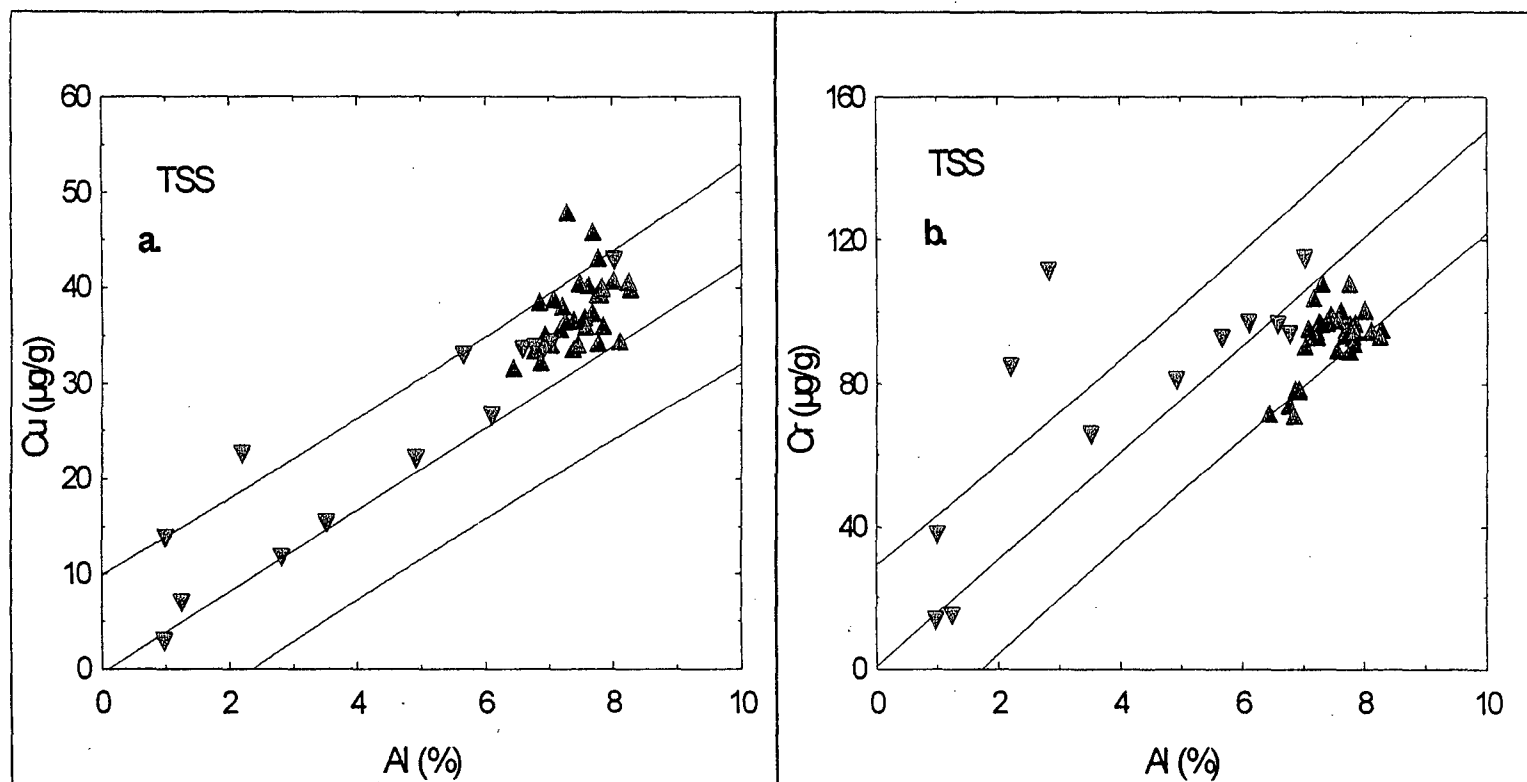


Figure 4-32. Concentrations of Al versus (a) Cu and (b) Cr for Total Suspended Solids and Source Material Samples Collected During August 1999

TSS samples collected during August 1999 (Northstar - red, Liberty - green, and BSMP - blue triangles). Source material sample collected during August 1999 (inverted orange triangles). Lines show linear regression fit to sediment data with 99% prediction intervals.

5.0 Recommendations and Phase II Plan Summary

5.1 Recommendations

Based on the results and preliminary interpretation and discussion of the samples collected from the summer 1999 and winter 2000 field programs, there are a number of recommendations for future ANIMIDA Phase II studies. The preliminary recommendations provided here focus on the sediment, suspended sediment, and biota sampling and analysis components of the ANIMIDA program. Subsequent recommendations related to the overall ANIMIDA Phase II program tasks are included in the Phase II Plan Summary.

- Collect sediment cores at selected stations to further evaluate historical trends in hydrocarbon and metal concentrations, and determine rates of sediment accumulation in the study area
- Perform replicate sampling at stations 5D, 5E, L08, and 5(10) (or adjacent sampling at new stations) to confirm contamination observed in the 1999 sediments
- Focus efforts on collection of tissue samples (clams and amphipods) to increase overall replication and power of interpretation (collect additional *Astarte* near Liberty)
- Obtain additional data on sediment transport pathways through target aerial photography and/or satellite photos
- Analyze additional source samples, including field oils from different production wells/formations, additional river sediment samples, and coal formations
- Analyze all future sediment and tissue samples for S/Ts
- Analyze several historical 1989 BSMP sediments for QC comparisons

5.2 Phase II Plan Summary

Phase II of the ANIMIDA program commenced with the 2000 summer program and will continue through FY 2004. The recommendations for the Phase II effort began to evolve at the ANIMIDA Phase I program's annual meeting in October 1999, when a draft, "strawman" plan was discussed. Subsequent discussions with the SRB and MMS led to the issuance of Requests for Proposals (RFPs) for eight different tasks. MMS added a new objective (with additional funding) for Phase II. This objective is to identify multiple and cumulative exposures to anthropogenic contaminants in the study area per Executive Order 12988 on Environmental Justice. For the Beaufort Sea coastal environment, regionally prioritized contaminants of concern are persistent organic pollutants (POPs) and trace metals. This section summarizes the statements of work for the eight tasks (the recommendations for the Phase II program). Additional refinements, stemming from actual field experience and comments received at the Annual Program Meeting held in October 2000 (and subsequent annual meetings), are

anticipated. The background and objectives of the eight proposed Phase II Task Orders are presented below.

Provide for ANIMIDA Program Coordination: Task Order 001: "The Arctic Nearshore Impact Monitoring In the Development Area (ANIMIDA) Program (Phase II) – Core Contractor Program Management, Logistics, Database, and Reporting"

The Phase II work will involve a number of tasks. Recommendations made by ADL and endorsed by MMS included work by a "core contractor" to coordinate and manage logistics and data management elements. This work will be accomplished during the period of FYs 2000 through 2004.

Background: Both offshore and onshore oil and gas development and production activities are planned for the coming years at the Northstar and Liberty sites in the nearshore Beaufort Sea. Coastal indigenous peoples are concerned about the long-term effects of these developments, as well as long-term effects of any development associated with offshore lease sales. Historical data in the region have been collected over several decades. However, the sensitivity of the region adjacent to Northstar and Liberty, and the highly variable and complex environmental conditions, make further monitoring necessary. In response to interagency reviews of related EISs and development and production plans, the ANIMIDA Phase I program was initiated as a comprehensive long-term program for monitoring potential impacts of Northstar and Liberty. ANIMIDA Phase I was started in June 1999, and will continue into FY 2001. During Phase I, chemistry and acoustic measurements were made during August 1999 and April 2000 near both the Northstar and Liberty sites.

Objectives: The ANIMIDA Phase II Core Contractor Support Task is intended to provide overall program management and logistics support for future tasks associated with Phase II of the ANIMIDA program.

The specific objectives of the core contractor will include:

1. Provide annual updates to the ANIMIDA Phase I literature review.
2. Provide logistics support and field personnel for future Phase II field programs, including coordination of field activities, communications, transportation, and providing a skipper for the MMS *Launch 1273*.
3. Hold annual Public Workshops in October with MMS, other Phase II contractors, the SRB, and other government/academic representatives. The meetings will also include provisions for public involvement (local residents, industry, environmental and other public groups, etc.). The SRB will meet the following two days. A second two-day SRB meeting will be assumed to take place in February each year, in Seattle.
4. Develop and implement communication/involvement plan for North Slope residents.

5. Develop Phase II database design and analysis tools, import forms and metadata source file and integrate with the MMS CORIS database.
6. Overall Phase II program management, including program management plan, data management plan, coordination of Phase II contractors, presentation slides, and quarterly progress reports.
7. Prepare annual Phase II reports, including annual reports, final report, technical summary, and journal article.
8. Compile individual task reports into single annual or final report, adding introduction and executive summary.
9. Provide draft annual or draft final reports to SRB and Contracting Officer's Technical Representative (COTR) two weeks prior to annual Public Workshop. Provide revised reports to SRB and COTR prior to annual February SRB meetings.

Continue Chemical Monitoring Effort: Task Order 002: "Hydrocarbon and Metal Characterization of Sediments, Bivalves, and Amphipods in the ANIMIDA Study Area"

This work will be accomplished during the period of FYs 2000 through 2004.

Background: The MMS initiated an environmental monitoring program in the Beaufort Sea in 1984 to assess the potential area-wide or cumulative effects of gas and oil exploration and development. The program was designed to detect and quantify long-term changes in the concentrations of metals and hydrocarbons in sediments and animal tissues. Its design is based on recommendations from a workshop conducted by MMS and NOAA in 1983. The initial phase of the monitoring study was a three-year program, with field sampling and analyses taking place in 1984, 1985, and 1986. Subsequent sampling was recommended for every third year, but took place only in 1989. Some data are also available from a MMS/University of Alaska Fairbanks, Coastal Marine Institute (CMI) study that sampled nearshore sediment stations in the vicinity in 1997 and from a BPXA study that sampled nine sediment stations near the proposed Northstar Development and pipeline route in February 1999.

The sensitivity of the region adjacent to Northstar and Liberty, and the highly variable and complex environmental conditions, make further monitoring necessary. Because current practice is to not discharge muds, cuttings, and formation waters during development and production, environmental concerns are shifting toward gravel-construction effects, such as may have occurred at Endicott, and to pre-potential spill baselines. During Phase I, chemistry measurements were made during the open-water season near the Northstar and Liberty sites, and at BSMP stations. A winter sampling program was also conducted under Phase I to collect data under ice-covered conditions.

Objectives: This task will characterize the sediments near ongoing and proposed offshore oil development related to potential contaminants and will serve as a continuation of the Phase I organic and inorganic chemistry monitoring program. The specific objectives of the chemistry monitoring program include:

- Perform annual or biannual field studies (FYs 2000 to 2003) for the monitoring of sediment and biota chemistry in the nearshore Beaufort Sea, focusing on potential impacts from the Northstar and Liberty developments
- Coordinate chemistry monitoring with other ANIMIDA Phase II tasks (acoustics, biology, and sediment transport), and with ANIMIDA-coordinated studies (e.g., physical oceanography)
- Perform organic and inorganic chemical analyses that are consistent with previous measurements and thus capable of determining any observed incremental impacts

In addition, it is recommended that studies (i.e., sampling, analyses, and data analyses) be undertaken to help interpret the findings, presented in this report, of temporal changes (e.g., those changes in PAH composition – Section 4) observed to have occurred between the 1989 and 1999 samplings.

**Continue Acoustic Monitoring Effort (Augment Ongoing Studies): Task Order 003:
"Baseline Acoustic Monitoring: Bowhead Whale Migration Corridor"**

This work is currently under consideration for FYs 2000 through 2003.

Background: Both offshore and onshore oil and gas development and production activities are planned for the coming years at the Northstar and Liberty sites. Coastal indigenous peoples are concerned about the long-term effects of noise and vibration on nearshore biota. Historical data in the region have been collected over several decades. However, the highly variable and complex environmental conditions make site-specific evaluation the most reliable and robust approach. During Phase I, acoustic and vibration measurements were made in August 1999 and April 2000, at locations near both the Northstar and Liberty sites. Since ANIMIDA Phase I was initially designed, BPXA has undertaken a comprehensive noise and noise-effects monitoring program in the study area.

Objectives: The primary objective of this task is to augment the BPXA design for acoustic monitoring of the bowhead migration offshore of Northstar by adding one to two seafloor recorder systems further offshore of BP recorders. Task 7 of *Technical Plan for Marine Mammal and Acoustic Monitoring during Construction of BP's Northstar Oil Development in the Alaskan Beaufort Sea, 2000*, dated August 20, 1999, presents the design for BP's efforts.

A high degree of coordination with the BP industrial team is recommended.

Monitor the Subsistence Whaling Effort: Task Order 004: "Annual Assessment of Subsistence Bowhead Whaling Near Cross Island"

This work will be accomplished during the period of FYs 2000 through 2004.

Background: The effects that offshore development may have on subsistence activities, particularly bowhead whaling at and near Cross Island, are of primary concern to the Village of Nuiqsut. Therefore, an effort should be made to monitor the subsistence whaling effort and its success.

Objective: To provide an annual narrative report showing the subsistence bowhead whaling activities, resources, and harvest on and near offshore Cross Island. The effort should focus on where whalers go and where they have strikes.

Examine the Effects of Oil Development on Suspended Particulates: Task Order 005: "Sources, Concentrations, and Dispersion Pathways for Suspended Sediment in Areas of Oil and Gas Development along the Coastal Beaufort Sea"

This work will be accomplished during the period of FYs 2000 through 2004.

Background: A primary concern regarding oil and gas development in the coastal Beaufort Sea is increased turbidity during and after construction of offshore islands and pipelines. Suspended sediment may be released from storage areas on the ice (after the ice melts), from erosion of seafloor piles of sediment (removed from pipeline trenches) and/or from the island. Inputs of suspended sediment from these sources could increase turbidity, decrease the amount of available light for growth of marine plants, and/or increase sediment accumulation rates and thus alter benthic habitats. However, the sources and dispersion pathways for suspended sediment are not well defined and the annual contribution of suspended sediment to the study area from river inputs is not well known. Various, limited data sets for TSS and turbidity are available for open-water periods, with less information available for ice-covered periods. One model for dispersion of suspended matter has been run for the Liberty area. Some TSS data from Endicott water-quality monitoring are available from BPXA for inshore of the Liberty area. (Endicott currently monitors effluent TSS, but not ambient TSS). No data on chemical signatures exist that would help identify sources of suspended sediment. The FY 1999 effort of the ANIMIDA project made a first attempt at tracing sources of suspended sediment. Studies of upcoming activities at the Northstar and Liberty sites provide valuable opportunities to validate present models of sediment dispersion and to establish the spatial and temporal extent of suspended sediment dispersion.

Objectives: The overall objectives of this task is to detect changes to the quantity and quality of suspended particulates from oil development.

The specific objectives for this task are to:

1. Determine concentrations of suspended sediment at varying distances from construction-related deposits of gravel and related material during open-water and ice-covered periods and as a function of time during and after construction
2. Help validate previous models of dispersion pathways and distances for suspended sediment in the study area.
3. Determine sources of suspended sediment in the areas of the Northstar and Liberty projects and to discriminate among various sources.
4. Contribute to an effort to determine the amount of sediment introduced to the coastal Beaufort Sea from rivers
5. Use data from the Northstar and Liberty studies to predict net and cumulative changes in suspended sediment levels from additional offshore islands and pipelines

Conduct Biological Monitoring of Sensitive Habitats (i.e., the Boulder Patch area): Task Order 006: "Monitoring the "Boulder Patch" as part of the Arctic Nearshore Impact Monitoring In the Development Area (ANIMIDA) Program (Phase II)"

This work will be accomplished during the period of FYs 2000 through 2004.

Background: The "Boulder Patch" area in Stefansson Sound, adjacent to the proposed Liberty development, is characterized by a diverse arctic kelp community in patchy areas where boulder cover greater than 10 percent is found. With the expected construction of the Liberty production island adjacent to the "Boulder Patch," there is increased potential for impacts and effects on this biological community.

Objective: The objective of this task is to conduct a program to monitor the potential effects of the Liberty island and pipeline construction on the Boulder Patch community.

Examine Partitioning of Organics and Metals: Task Order 007: "Partitioning of Potential Contaminants between Dissolved and Particulate Phases in Waters of the Coastal Beaufort Sea"

This work will be accomplished during the period of FYs 2000 through 2003.

Background: Considerable interest has been expressed in selected metal and organic contaminants in waters of the coastal Beaufort Sea. These contaminant metals and organic substances may be particulate, colloidal, or dissolved in form, with the dissolved contaminants generally being more biologically available. During resuspension of bottom sediments by storm

events, some contaminants may be released from sediment particles and added to the water column, while others may be adsorbed to particles and removed from the water column. Little or no data are available on dissolved contaminants in the coastal Beaufort Sea. No data are available to predict and model the behavior and uptake or release of contaminants from resuspended sediments. One ongoing MMS CMI study, *Kinetics and Mechanisms of Slow PAH Desorption from Lower Cook Inlet and Beaufort Sea Sediments*, is examining longer-term kinetics (1 to 180 days) for PAH.

Objectives: The specific objectives for this task are the following:

1. To determine concentrations of selected metals and organic substances in dissolved and particulate forms in waters of the coastal Beaufort Sea
2. To determine partition coefficients (particulate/dissolved) for selected metals and organic substances in waters of the coastal Beaufort Sea
3. To determine the equilibrium kinetics for release or uptake of selected metals and organic substances during sediment resuspension events

**Evaluate the Levels of Contaminants and Biochemical Indices on Marine Organisms:
Task Order 008: "Baseline Characterization of Anthropogenic Contaminants in Biota
Associated with the Alaska OCS Liberty and Northstar Oil and Gas Production Units in
the Nearshore Beaufort Sea"**

This work will be accomplished during the period of FYs 2000 through 2003.

Background: Biomarker and contaminant analyses of marine mammals, birds, and fish provide an opportunity to learn more about the effects of bioaccumulation of anthropogenic compounds in Arctic food chains. Anthropogenic contaminants of Arctic concern are POPs and metals. The POPs include polycyclic and polyhalogenated aromatic hydrocarbons and are globally distributed. However, due to their chemical characteristics and atmospheric transport, rates of deposition are much greater than rates of production in the Arctic. Some POPs are poorly metabolized, and may bioaccumulate or biomagnify in tissue. Although PAHs can be metabolized in mammal tissues, lessening their concentrations, PAH concentrations in edible tissue are still a concern, because of subsistence use and potential local or regional oil industry or spill sources.

Some aromatic compounds found in the Arctic induce enzyme P4501A in fish, birds, and marine mammals. The induction of this enzyme facilitates metabolism of aromatic compounds and the intermediate reaction products can react with cellular molecules, such as deoxyribonucleic acid (DNA), causing cellular damage. Measurement of P4501A may provide evidence of exposure to these compounds, their metabolism, and the subsequent risk to induced animals. In addition, analyses of a variety of tissues and cell types can indicate the route of uptake and exposure.

Strandings of both beluga and pilot whales in temperate climates have shown that induced cytochrome P4501A1 occurs in cetacean liver. Recently a correlation was described between hepatic CYP1A content and the content of co-planar PCBs in the blubber of beluga whales consistent with an environmental chemical induction in these animals. The extent of such induction in extrahepatic organs of cetaceans was not known until recently, when a variety of tissues from stranded pilot whales were collected, analyzed, and found to have P4501 induction. If correlations of P4501A induction were to be found with the concentrations of polyhalogenated aromatic hydrocarbons in Arctic whales, seals, birds, or fish, for example, then these compounds are the most likely proximate cause of such effects.

Regional studies of contaminants in marine mammals in the Beaufort Sea are presently being performed by the North Slope Borough (NSB) and by the Alaska Marine Mammal Tissue Archival Program (AMMTAP). The USGS Biological Resource Division (BRD) has collected and stored blood samples from polar bears for several years, as well as from common eiders, oldsquaw, and nonviable eggs from common eiders in the ANIMIDA area and adjoining shoreline, starting in 1999.

Objectives: The objective of this task is to detect changes or impacts from oil development and other contaminant sources.

Specific objectives include:

1. Determine baseline levels of anthropogenic compounds and contaminant biomarkers in representative upper-trophic biota (e.g., whales, seals, birds, and/or fish). Include both waterfowl (common eider and/or oldsquaw) and one or more important subsistence species. Include at least some analyses of PAH in subsistence food (tissue).
2. Evaluate whether the concentration of contaminants and contaminant biomarkers indicates significant risks to associated biota and/or health risks to subsistence consumers of chosen biota.
3. Coordinate the field and analytical aspects of this task a) with the biological contaminant studies presently being conducted by the NSB, AMMTAP, U.S. Fish and Wildlife Service (USFWS), and BRD and b) with community residents (Barrow and Nuiqsut) to identify species of local subsistence interest.
4. Develop a strategy for longer-term, upper-trophic contaminant monitoring.

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The Department of the Interior Mission

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.



The Minerals Management Service Mission

As a bureau of the Department of the Interior, the Minerals Management Service's (MMS) primary responsibilities are to manage the mineral resources located on the Nation's Outer Continental Shelf (OCS), collect revenue from the Federal OCS and onshore Federal and Indian lands, and distribute those revenues.

Moreover, in working to meet its responsibilities, the **Offshore Minerals Management Program** administers the OCS competitive leasing program and oversees the safe and environmentally sound exploration and production of our Nation's offshore natural gas, oil and other mineral resources. The **MMS Royalty Management Program** meets its responsibilities by ensuring the efficient, timely and accurate collection and disbursement of revenue from mineral leasing and production due to Indian tribes and allottees, States and the U.S. Treasury.

The MMS strives to fulfill its responsibilities through the general guiding principles of: (1) being responsive to the public's concerns and interests by maintaining a dialogue with all potentially affected parties and (2) carrying out its programs with an emphasis on working to enhance the quality of life for all Americans by lending MMS assistance and expertise to economic development and environmental protection.