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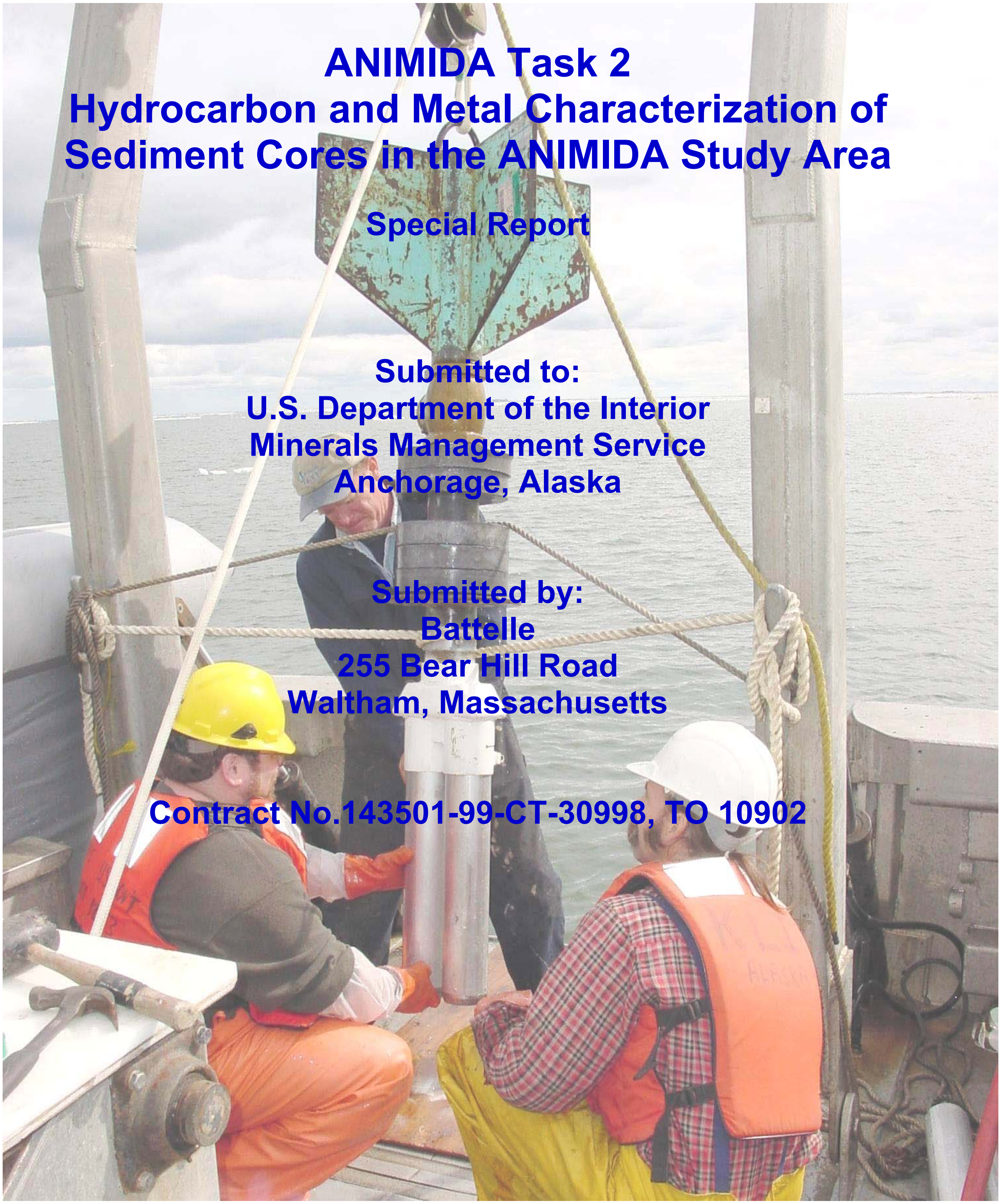

ANIMIDA Task 2
Hydrocarbon and Metal Characterization of Sediment Cores in the ANIMIDA Study Area

Special Report

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U.S. Department of the Interior
Minerals Management Service
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Hydrocarbon and Metal Characterization of Sediment Cores in the ANIMIDA Study Area

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Table of Contents

Table of Contents (continued)

List of Appendices

List of Tables

Section 2

Section 3

Section 4

List of Figures

Section 1

Section 2

Section 3

Section 4

List of Acronyms and Abbreviations

ADL	Arthur D. Little, Inc.
AMS	Applied Marine Sciences
ANIMIDA	Arctic Nearshore Impact Monitoring in the Development Area
BPXA	British Petroleum Exploration Alaska
BS	Blank Spike
BSMP	Beaufort Sea Monitoring Program
°C	Degrees Celsius
C	Carbon
CI	Confidence Interval
cm	Centimeter
COC	Chain of Custody
CORIS	Coastal and Offshore Resource Information System
CPI	Carbon Preference Index
CRM	Certified Reference Material
CV	Coefficient of Variation
CVAAS	Cold Vapor Atomic Absorption Spectrometry
%D	Percent Difference
DDW	Distilled, Deionized Water
dpm	Decompositions per Minute
DQO	Data Quality Objectives
EICP	Extracted Ion Chromatogram Profile
EIS	Environmental Impact Statement
ERL	Effects Range-Low
ERM	Effects Range-Median
FAAS	Flame Atomic Absorption Spectrometry
FID	Flame Ionization Detection
FIT	Florida Institute of Technology
FY	Fiscal Year
g	Gram
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
H_3PO_4	Phosphoric Acid
H_2SO_4	Sulfuric Acid
HCl	Hydrochloric Acid
$HClO_4$	Perchloric Acid
HDM	Harvard Design and Mapping
HF	Hydrogen Fluoride
HNO_3	Nitric Acid
ICF	ICF Consulting
ICP/MS	Inductively Coupled Plasma/Mass Spectrometry
ID	Inner Diameter
IRM	Instrument Reference Material
K-D	Kuderna-Danish
KeV	Kilo Electron Volts
Kg	Kilogram

List of Acronyms and Abbreviations (continued)

KLI	Kinnetic Laboratories, Inc.
km	Kilometer
LALK	Lower-Molecular-Weight Alkanes
m	Meter
MDL	Method Detection Limit
mg	Milligram
mL	Milliliter
mm	Millimeter
MMS	Minerals Management Service
MRL	Minimum Reporting Limit
MS	Mass Spectrometry
N	Normal
N/P	Naphthalene/Phenanthrene Ratio
NIST	National Institute of Standards and Technology
NRC	National Research Council of Canada
OCS	Outer Continental Shelf
OCSLA	Outer Continental Shelf Lands Act
ORS	Oil Reference Standard
PAH	Polynuclear Aromatic Hydrocarbon
PB	Procedural Blank
PBOC	Prudhoe Bay Operations Camp
PCB	Polychlorinated Biphenyl
PHC	Petroleum Hydrocarbons
QA	Quality Assurance
QAM	Quality Assurance Manual
QC	Quality Control
R/V	Research Vessel
RF	Response Factor
RL	Reporting Limit
RPD	Relative Percent Difference
rpm	Revolutions per Minute
RSD	Relative Standard Deviation
S	Sedimentation Rates
S/T	Steranes/Triterpanes
SD	Standard Deviation
SHC	Saturated Hydrocarbons
SIM	Selected Ion Monitoring
SOP	Standard Operating Procedure
SPMD	Semipermeable Membrane Device
SRB	Scientific Review Board
SRM	Standard Reference Material
TALK	Total n-Alkanes
TOC	Total Organic Carbon
TPHC	Total Petroleum Hydrocarbons
µg	Microgram
µL	Microliter

List of Acronyms and Abbreviations (continued)

μm	Micrometer
URSGWC	URS Greiner Woodward Clyde
USACE	U.S. Army Corps of Engineers
USAEDA	United States Army Engineering District, Alaska
USDOI	United States Department of the Interior
USEPA	United States Environmental Protection Agency
V/V	Volume to Volume
WBS	Work Breakdown Structure
ZGFAAS	Zeeman Graphite Furnace Atomic Absorption Spectrometry

Executive Summary

Overview

The ANIMIDA program was designed to address the potential environmental impacts of two oil and gas developments in the Beaufort Sea, namely the Northstar and Liberty developments. The Phase I Report (Boehm et al. 2001b) presented the initial findings on the ANIMIDA program. Phase I provided one-year of pre-development baseline data for Northstar and Liberty. Based on Phase I results, several tasks were implemented in Phase II. The tasks included Task 2: Continued Chemical Monitoring Effort: Hydrocarbon and Metal Characterization of Sediments, Bivalves, and Amphipods in the ANIMIDA Study Area.

The resulting information from Task 2 is intended to be used to:

- assess baseline environmental conditions prior to Northstar and/or Liberty oil development and production activities;
- assess the potential impacts from Northstar and/or Liberty oil development and production activities by measuring parameters that are indicators of environmental impacts; and
- provide information needed in post-leasing decisions to help minimize these impacts.

Phase II Task 2 was implemented in the summer of 2000 and the findings for this initial part of Phase II were reported in Brown et al. (2002).

Phase II began in summer 2000 and was planned to monitor the effects of construction and operation of the Northstar and Liberty developments. Northstar construction began as planned and was completed in October 2000. First production of oil began late in 2001. The Liberty development plans were halted in mid-2002 and no activity has occurred. However, there remains the possibility that development plans using directional drilling from a location adjacent to the Endicott causeway complex may proceed in the future.

The initial Phase II results (i.e., the 2000 field season results) reported by Brown et al. (2002) were the first non-baseline hydrocarbon monitoring of the Northstar development during the construction of the gravel island and pipeline and represented continued baseline monitoring at Liberty. These results indicated that the chemical inputs – organic and metal constituents normally associated with oil development – were not detected in the surface sediments and that any observed changes were well within the regional natural variability (i.e., the baseline). Because some anomalies were noted in the Northstar study area (which appeared to be changes in target chemical constituents associated with co-varying grain-size changes), recommendations for future work included a 2001 field program focusing, in part, on the collection and analysis of sediment cores. Thus, the 2001 field season's program was intended to gain further information on historical trends so as to be able to better interpret pre- and post-Northstar development data (from ANIMIDA Phase I and previous studies e.g., Beaufort Sea Monitoring Program).

Objectives – Task 2

The ANIMIDA program was designed to address a series of scientific questions concerning the potential impacts of the Northstar and Liberty developments. In turn testable hypotheses guided the design of the technical program. The key questions that drive Task 2 of ANIMIDA are:

Question 1. What are the background levels and temporal trends 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 Northstar and/or Liberty developments?

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

Task 2 addresses the first question. Tasks 2, 6, and 8 are needed collectively to address the second question.

To provide the data needed to address these questions, the specific objectives of Task 2 include:

- Perform annual or biannual field studies (fiscal years [FYs] 2000 to 2003) to monitor sediment and biota chemistry in the nearshore Beaufort Sea, focusing on the Northstar and Liberty developments

- Coordinate chemistry monitoring coupled with other ANIMIDA Phase II tasks (biology and sediment transport), and with ANIMIDA-coordinated studies (e.g., physical oceanography).

- Perform organic and inorganic chemical analyses and analysis of data to document any incremental input of contaminants.

An explicit goal is to examine temporal changes and to determine if any observed changes in concentration and/or composition are related to the Northstar development.

ANIMIDA Study Design – Task 2

To meet the objectives of the ANIMIDA program, the study design of Task 2 focuses on the detection of contaminant inputs and their temporal trends: measuring those parameters that would be leading indicators of, or related to, environmental impacts from the Northstar and Liberty oil development projects (Figure 1-1).

This approach also included the determination of the natural baseline of targeted chemical constituents, historical trends, and performing a screening-level evaluation of potential environmental risk as a result of these contaminant inputs, through comparison to known benchmarks.

The constituents of primary focus included:

- hydrocarbons and associated polycyclic aromatic hydrocarbons (PAHs); and metals as primary contaminants of concern
- sediment contamination
- bioaccumulation of contaminants
- other natural and anthropogenic sources of contaminants of concern

The study design for Phase II 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 (BSMP) (1984 to 1990)
- sample reference stations
- identification of source samples for collection (e.g., river sediments)
- addition of Phase II sampling stations along the pipeline route

In 2001, a sediment coring effort was added to the program. This report focuses solely on the collection, analyses, and results for the sediment core samples.

2001 Sediment Coring Effort

Based on recommendations from the 2000 efforts (Brown et al., 2002) a sediment coring program was implemented in the summer of 2001 to examine the historical baseline and the recent temporal trends as reflected in the geochronology of the sediments. 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 encompasses both the Liberty and Northstar prospect areas, and much of the shoreline where regional Prudhoe Bay oil production activities are occurring. One open-water survey was conducted from July 24 to August 14, 2001.

Sediment cores were collected from nearshore areas of the Beaufort Sea adjacent to Liberty prospect, Northstar Island, and reference sites to determine the geochronology of the cores and analyze them for oil industry-related contaminants – metals and organics. Stations for sediment core sampling were selected based on historical data from BSMP, ANIMIDA Phase II (2000) results from Northstar Island, and Liberty Prospect stations. Historical grain-size data were used to identify those stations that had fine-grained sediments and would be good candidates for depositional areas. Sediment cores were collected at 11 nearshore and offshore stations: 4 historic BSMP stations, 2 Northstar area stations, 3 Liberty stations, 1 Sagavanirktok River Delta (Endicott) station, and 1 Prudhoe Bay station. Of these collected cores, eight (8) were selected for age dating. Age dating was accomplished through a combination of ^{210}Pb and ^{137}Cs measurements and dating techniques.

Findings

The summer 2001 field sampling program resulted in the successful acquisition of sediment core samples suitable for age dating from eight stations. Of the eight cores, reliable and detailed results for geochronology were obtained for three stations: 1) station P01 in Prudhoe Bay, 2) station E01, just east of the Endicott development near the mouth of the Sagavanirktok River, and 3) station 6G near the eastern area of the Colville River Delta (Figure 2-1).

Geochronology and Sedimentation Rates

Results show sedimentation rates that range from ~0.04 centimeters (cm)/year (yr) to ~0.10 cm/yr, with several sites having little or no net accumulation of sediment during at least the past 50 years. At three sites, 3- to 5-cm thick layers of sediment were identified that were deposited since North Slope development began (approximately 1970). Overall results are consistent with those of Naidu et al. (2001) for the same area. The presence of fine-grained sediment at a given location can vary from year to year and the sediments along much of the shallow, coastal Beaufort Sea are quite dynamic.

In Prudhoe Bay (station P01), the vertical profile for ^{137}Cs supports the results from excess ^{210}Pb with a sedimentation rate of ~0.10 ± 0.02 cm/yr based on the 1950 appearance of ^{137}Cs at ~5 cm and the observed 1963 peak at ~3.75 cm. Samples from depths >4 cm were most likely deposited before extensive development activities began around 1970 in the area of Prudhoe Bay.

At station E01, the calculated sedimentation rate based on excess ^{210}Pb is about 0.04 ± 0.02 cm/yr. Activities of ^{137}Cs are detectable to a depth of 3.25 cm, yielding a sedimentation rate of ~0.06 ± 0.02 cm/yr, a value that is reasonably consistent with that obtained from the profile for excess ^{210}Pb considering the uncertainty in the data. These data for station E01 support the likelihood that sediments at depths >4 cm pre-date oil and gas development.

In the Colville River Delta at station 6G, the ^{137}Cs profile supports a sediment accumulation rate of ~0.06 ± 0.02 cm/yr. The record of sediment input since the 1950s is sequestered into the top 4 to 5 cm of sediment.

Organics – Saturated and Polycyclic Aromatic Hydrocarbons

Concentrations of total petroleum hydrocarbons (TPHC) in sediment core samples from the summer 2001 survey ranged from 3.2 to 17 milligrams (mg)/Kilogram (kg), with one anomalous concentration of 31 mg/Kg detected at core station 6G in the 0- to 2-cm interval. However, when normalized to the clay fraction[1], the 0- to 2-cm interval from core sample 6G falls within the range of the results for the other 6G core, indicating that the observed enrichment of hydrocarbons was due to the accumulation of fine-grained material at the surface of this core. The mean TPHC concentrations for the eight cores ranged from 4.6 to 11 mg/kg.

In general, comparisons of the core profiles for key diagnostic organic parameters for all of the cores do not show any clear trends that would indicate an increase in petroleum hydrocarbons

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[1] Clay only was used to normalized the results for core 6G due to a high percent clay result for the 0-2 cm sample. The remaining cores were normalized to the silt+clay parameter.

over time. The core profiles from the five stations where geochronology could not be established (likely representing a historical pre-development record) are generally uniform and show little variability of the hydrocarbon parameters over time. The cores for which pre- and post-oil and gas development dates can be established (P01, E01, and 6G) generally show uniform distributions of key parameters throughout the cores, with some variability in specific core intervals.

The composition of saturated hydrocarbons (SHC) through the depth of all the sediment cores was generally similar (see representative sample tri-plot in Figure ES-1), indicating a common TPHC source relationship between pre-1970 and post-1970 sediments. For example, similar patterns are noted in the GC/FID chromatograms for the pre-1970 and post-1970 sediments from cores P01 and 6G (see Figures 4-6 through 4-9).

Concentrations of Total PAH in sediment core samples from the summer 2001 survey ranged from 284 to 932 micrograms (μg)/Kg, with one anomalous concentration of 1,990 μg/Kg detected at core station 6G in the 0- to 2-cm interval. However, when normalized to the clay fraction, the 0- to 2-cm interval from core sample 6G falls within the range of results for the other 6G core sections and is no longer an outlier, further supporting the earlier observation that the high result is due to a grain-size effect. The mean Total PAH concentrations for the eight cores ranged from 383 to 657 μg/Kg. Overall, the levels of SHC and PAH measured during the sediment core survey are within the range of values reported from previous studies of the region and other Alaskan coastal areas.

A plot of the 2001 core data, along with the 1999 and 2000 surface sediment data for total PAH minus perylene versus silt plus clay, is shown in Figure ES-2. The plot shows that all the 2001 core samples fall within the 95% prediction intervals, indicating that the 2001 core sediment samples are not different in Total PAH content from the historical natural background of the region.

An analysis of PAH compositional data for the core samples through a comparison of the pyrogenic-to-petrogenic PAH ratios reveals a generally consistent abundance of petrogenic PAH relative to pyrogenic PAH across all core samples. Petrogenic PAH comprise consistently 90% of the total PAH in all samples from all cores, with a slightly higher pyrogenic abundance (13%) at station 6G, offshore the Colville River (see Figure ES-3).

Effects Range Low (ERL) and Effects Range Median (ERM) values have been developed as sediment quality guidelines for 13 individual PAH compounds and 3 classes of PAH (low- and high-molecular-weight PAH, and Total PAH). A comparison of the Total PAH from all ANIMIDA core sediments to the ERL and ERM criteria shows that none of the Total PAH concentrations determined in this study exceed the ERL. The station 6G surface interval (0- to 2-cm), which had the highest measured Total PAH at 1,990 μg/Kg, was still well below the ERL value of 4,022 μg/Kg. The mean Total PAH values from each core were generally an order of magnitude lower than the ERL. Similarly, the individual PAH concentrations did not exceed the ERL for the individual 13 PAH, which could be compared directly. In summary, based on sediment quality criteria, the concentrations of PAH found in the sediment core samples are not likely to pose immediate ecological risk to marine organisms in the area.

Metals

Collectively, the data for cores from Prudhoe Bay (station P01), near Endicott Island (station E01), and east of the Colville River Delta (station 6G) show that normalized concentrations of Ba, Be, Cr, Cu, Ni, Pb, Sb, Tl, and V are constant over time, supporting a finding of no detectable anthropogenic contributions and no impacts due to early chemical diagenesis. The continuum of uniform metal/Al values from river suspended sediment to recent bottom sediment to older bottom sediment provides strong support for the very limited impacts with respect to trace metals in sediments in the study area.

In Prudhoe Bay (station P01), concentrations of Al and Fe follow parallel trends downcore. Vertical distributions for Ba, Pb, Cr, V, and Zn, as well as Be, Cu, Ni, Sb, and Tl, follow trends similar to those observed for Al and Fe, with the coefficients of variation (CVs) for the metal/Al ratios all <8%. According to the age-dating results, pre-oil and gas development sediment is clearly present at depths >5 cm and post-development (since 1970) sediment would most likely be found in the top 5 cm of the sediment column. At the station located just east of Endicott Island (station E01), post-development sediment appears to be restricted to the top 4 cm of the sediment column. No discernible differences in metal/Al ratios (i.e., downcore variability <10%) are observed for all metals except As, Mn, Cd, and Ag, the same trend observed for the core from station P01.

At station 6G, on the Colville River Delta, post-development sediment appears to be restricted to the top 3 cm of the sediment column. Once again, no discernible differences in metal/Al ratios (i.e., downcore variability <10%) are observed for all metals except Mn, As, Cd, and Ag, the same trend observed for the cores from stations P01 and E01.

Nine (Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) of the 16 metals investigated during this study have been assigned ERL and ERM concentrations by Long et al. (1995). These guidelines are evolving as demonstrated by the extensive efforts of Field et al. (1999) to validate values for Hg, Pb, and Zn. Some difficulties still exist with ERL values for Cr, Cu, and Ni, as discussed below. Overall, the sediment quality data should be used primarily as guidelines at this time. No concentrations of any of the 9 metals in surficial sediments or the 2001 core samples exceed their respective values for the ERM . Therefore, adverse biological effects are not expected to be a frequent occurrence at any site in the study area as the result of trace metals. Furthermore, no concentrations of Ag, Cd, Hg, Pb, or Zn from this study exceed the respective values for the ERL and thus adverse biological effects from these 4 metals would be rare. Many points on the Al versus Cu and Cr plots exceed the present ERL. However, the ERL for each of these metals is less than or very close to the values for average crustal abundance and natural levels found in many types of sediment.

Summary and Recommendations

The results of the 2001 coring program indicate that depositional areas do exist within the study area, though most of the area is erosional in nature. Where net deposition is occurring the sedimentation rates are low (<0.1cm/year) in spite of massive inputs of sediment from rivers within these areas. The hydrocarbon and metals results show no evidence of anthropogenic inputs from the Northstar development and current concentrations and sources are very similar to what have occurred historically (well before development) in the study area.

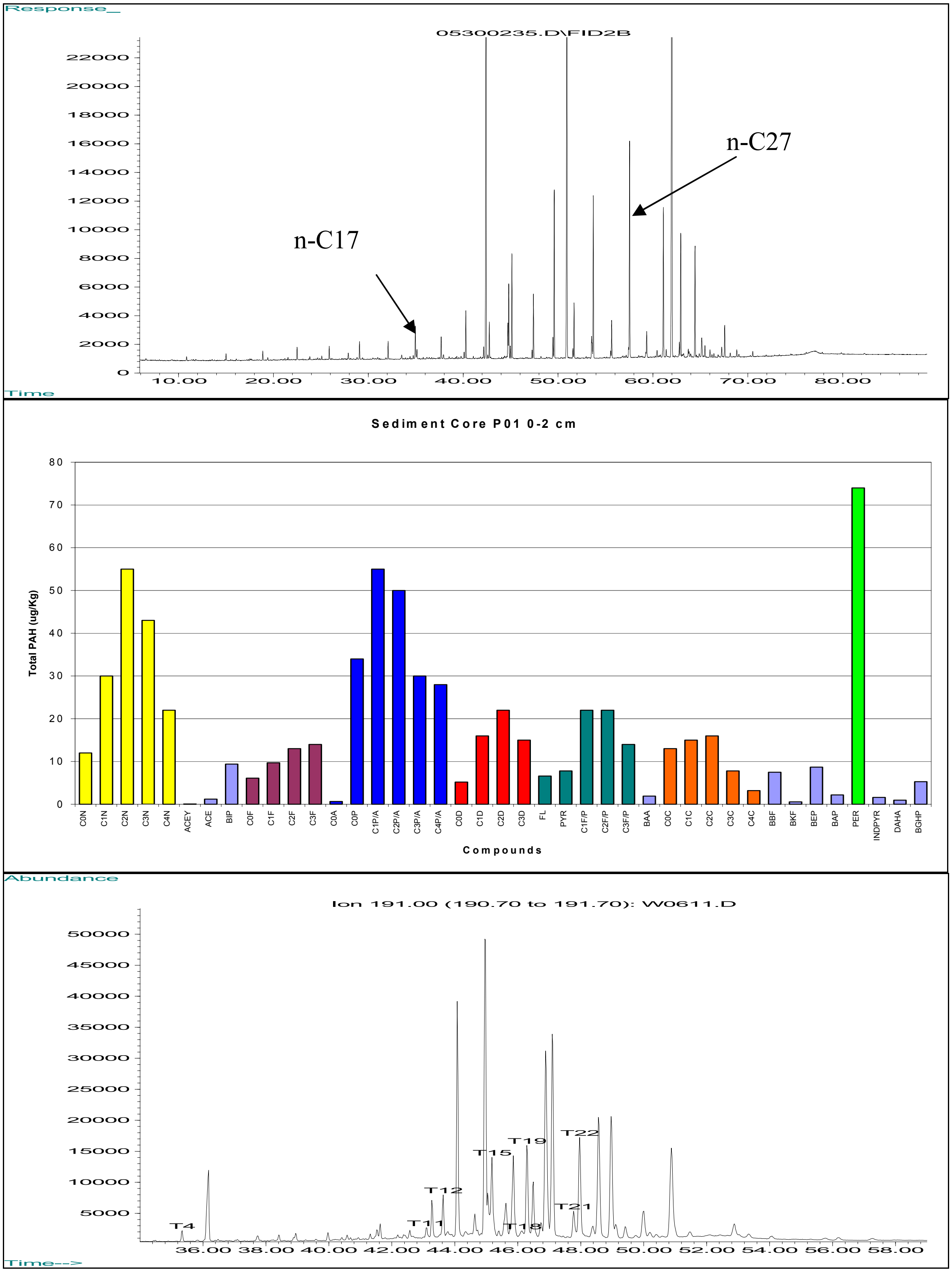


Figure ES-1. Example of Compositional "Triplot" from Sediment Core P01 Interval 0-2 cm – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

PAH compound name abbreviations are defined in Table 2-3

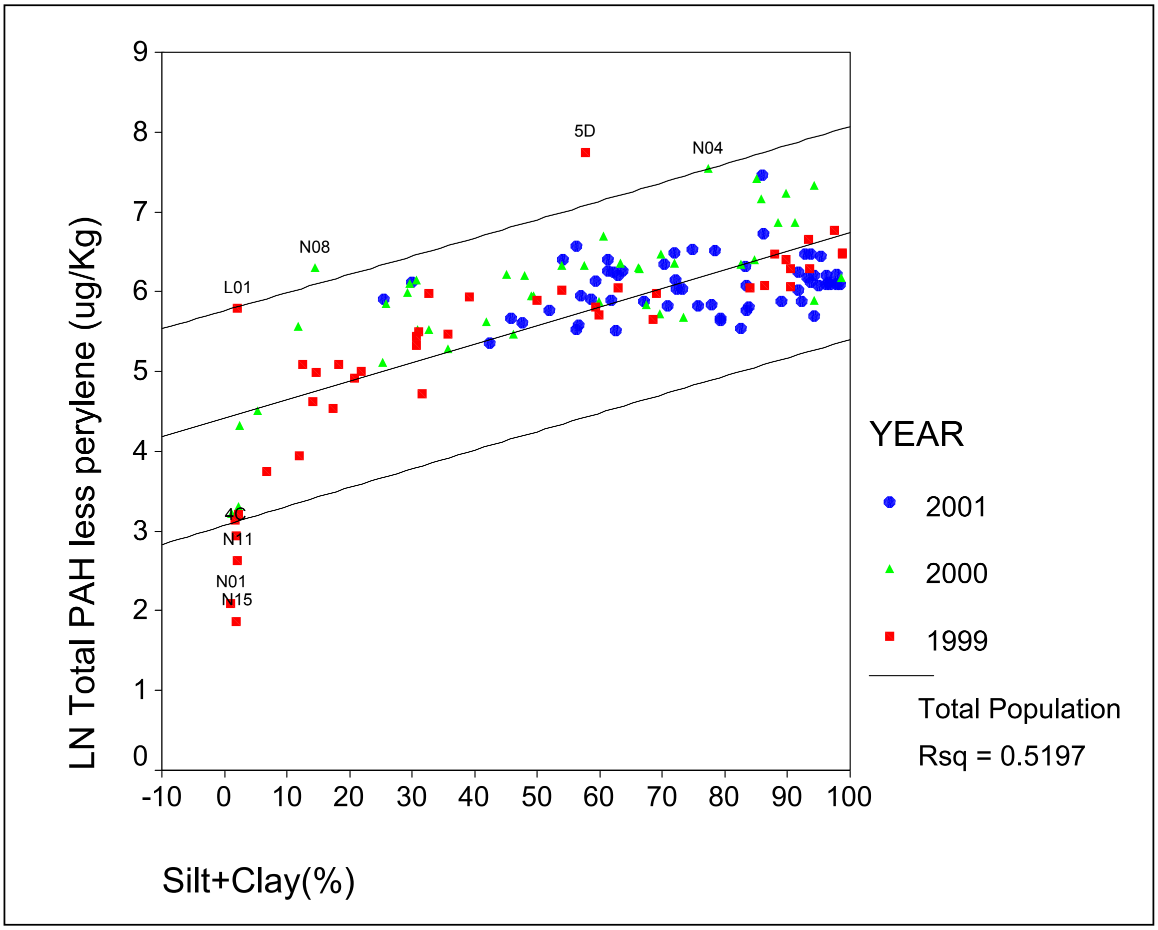


Figure ES-2. Regression of Total PAHs versus Silt+Clay in 2001 Cores Samples Compared with 1999 and 2000 Surface Sediment Samples

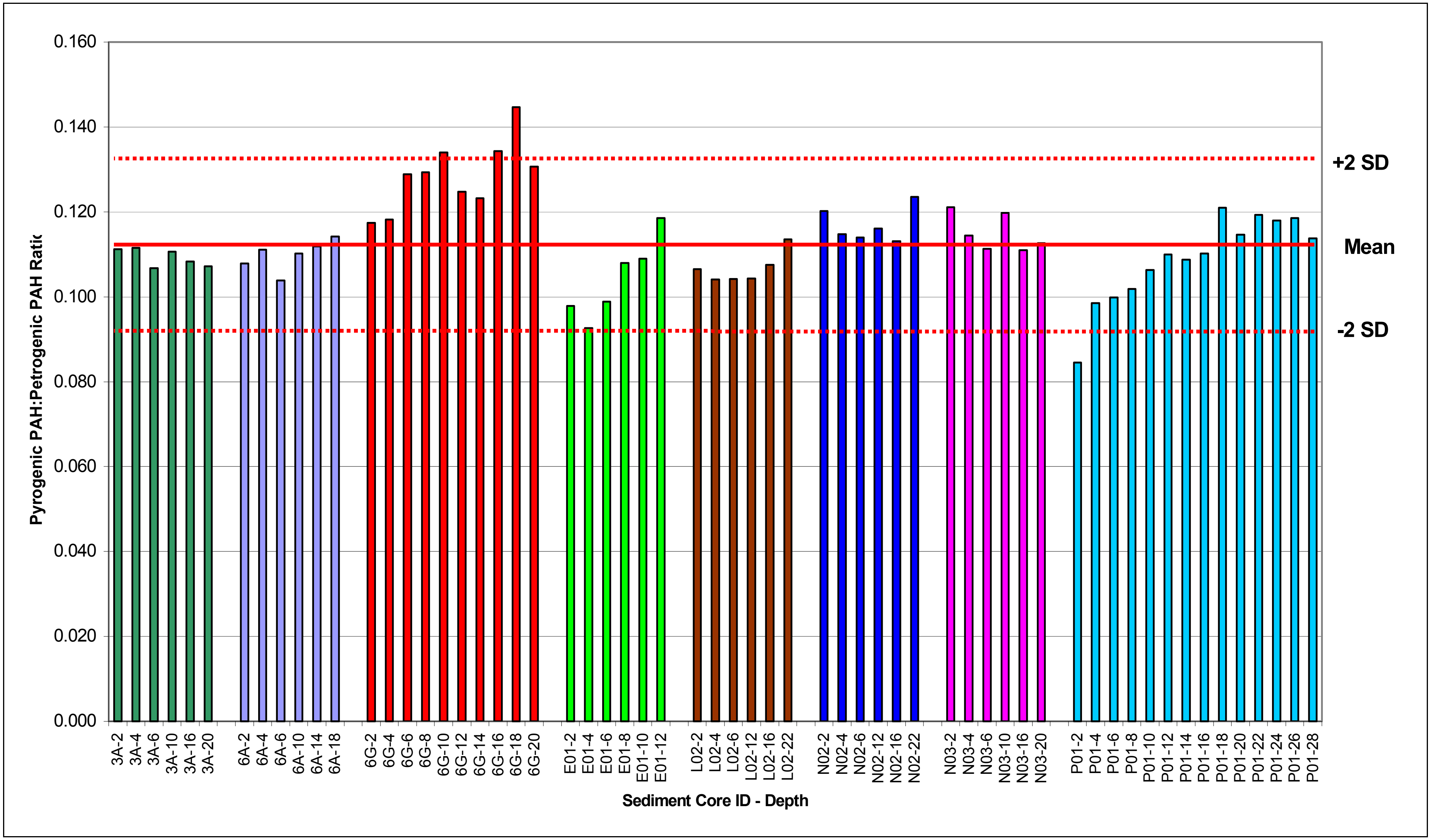


Figure ES-3. Pyrogenic/Petrogenic PAH Ratios for 2001 Sediment Cores – all Depth Intervals

Dotted lines represent upper and lower 95% confidence intervals for all samples.

1.0 Introduction

The Outer Continental Shelf Lands Act (OCSLA) Amendments of 1978 (92 Stat. 629) established a policy for the management of oil in the Outer Continental Shelf (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 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 initially proposed for both the Northstar and Liberty sites by British Petroleum Exploration Alaska, Inc. (BPXA) are currently underway at Northstar and halted until further notice at Liberty. At Northstar, the oil field was developed from a gravel island and is currently producing oil, which is transported to land-based pipelines through a sub-sea pipeline. 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, 2002).

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 both 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 Study Area

The Alaskan Beaufort Sea comprises the southern part of the Arctic Ocean; it 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 Alaskan Beaufort Sea extends north 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 (Figure 1-1) is seaward of the barrier islands and the Liberty site is landward of several barrier islands. The area of the 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 was constructed partly on the remains of Seal Island, which was built by Shell Oil Company during the 1980s (USAEDA, 1999). The Liberty site is 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.

1.2 Development History in the Study Area

Over the past three decades, numerous onshore and offshore oil exploration and development projects have commenced in both the Alaskan and Canadian Beaufort Seas. Over 20 discoveries have been made, including 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 is not 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 the developments located in the eastern Alaskan Beaufort Sea is presented in Figure 1-2.

Since 1975, 17 gravel islands have been constructed in waters less than 50 feet (15 m) 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).

1.3 Current/Proposed Oil Development

1.3.1 Northstar

The BPXA Northstar development project is located about 6 miles (~10 km) northwest of Prudhoe Bay. While the Northstar Island is in state waters, 6 to 7 wells are or will be in federal waters on the OCS. The U.S. Army Corps of Engineers (USACE) approved the Northstar 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. At this site, a sub-sea pipeline system connects the island and discovered oil to onshore processing facilities. Construction of the island was completed by October 2000 and first production began late in 2001. Recoverable reserves are estimated at 175 million barrels of oil. A schematic of the development is shown in Figure 1-3.

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 is surrounded by a linked concrete mat armor island slope protection system and the working surface of the island is 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 km^2) (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 1,170 feet). Exploration drilling had taken place at Seal Island dating back to the 1980s.

1.3.2 Liberty

In mid-2002 BPXA announced that they had halted their plans to develop the Liberty Prospect in Foggy Island Bay (Figure 1-1). Liberty Prospect is located about 6 miles east of the Endicott Project. The proposed location was adjacent to Tern Island, which was the site of exploration drilling dating back to 1982. MMS published a final EIS report for Liberty in 2002 (USDOI, 2002). However, recent information from the oil industry has indicated that there are revitalized plans to develop Liberty by directionally drilling from a gravel pad connected to the existing Endicott causeway complex. This scenario would greatly reduce the development logistics and potential environmental complexities associated with an offshore production island and pipeline as originally proposed. The final status of the Liberty Prospect development will influence the design of any future monitoring strategies for this prospect.

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.

The majority of wastes generated during construction and developmental drilling would consist of drill cuttings and spent muds. Drilling fluids would be disposed 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 a 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 end within a few days after construction stops. Trenching for the oil pipeline at Northstar may have caused resuspension of existing bottom sediments. Both island and pipeline construction may have resulted in incorporation of suspended sediment into sea ice. Research findings concerning sources, concentrations, and dispersion pathways for suspended sediment are presented in separate reports for Task 5 and Task 7 of the ANIMIDA program.

1.5 Study Objectives

The primary objectives of the overall 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 ANIMIDA program is being implemented in two phases. During Phase I, chemistry measurements were made during the open-water season near the Northstar and Liberty sites, and at Beaufort Sea Monitoring Program (BSMP) stations. A winter sampling program was also conducted under Phase I to collect data under ice-covered conditions. The 1999 open-water sampling represented pre-construction baselines at both the Northstar and Liberty locations. The winter sampling represented the first construction-monitoring period for Northstar and additional pre-construction data at Liberty. The overall objectives of Phase I were to implement a baseline/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 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. The overall objective for Phase II Task 2 is to characterize the sediments near ongoing and proposed offshore oil development related to potential contaminants and serve as a continuation of the Phase I organic and inorganic chemistry monitoring program. The specific objectives for Phase II Task Order 2 are listed below:

- Perform annual or biannual field studies (fiscal years [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

- Perform organic and inorganic chemical analyses that are consistent with previous measurements and thus capable of determining any observed incremental impacts

- Coordinate chemistry monitoring with other ANIMIDA Phase II tasks (biology and sediment transport) and with ANIMIDA-coordinated studies (e.g., physical oceanography)

The results of the post-Northstar construction Phase II Task 2 sediment and biota sampling (summer 2000) indicated that no organic and metal contaminant inputs from Northstar were detected, and that any observed changes were well within the natural variability (Brown et al., 2002). However, some hydrocarbon and sediment grain-size trends were observed near Northstar, which warranted further investigation in 2001. Based on these observations, a Phase II Task 2 sediment core sampling program was initiated in the summer of 2001 to further evaluate trends of hydrocarbons and metals in the historical record of sediment cores from the monitoring area.

1.5.1 Sediment Core Research Questions and Hypotheses

The objectives of the ANIMIDA program address a series of scientific questions concerning the potential impacts of the Northstar and Liberty developments. Each question can be turned into a testable hypothesis, which guides the design of the technical program. Two pairs of questions (Q) and candidate hypotheses (H) applicable to the Task 2 2001 sediment core sampling follow.

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

H1a. The concentrations of organic pollutants in sediments do not show any trend within the sediment core as a result of past and present oil exploration, development, and production activities.
H1b. The concentrations of metal pollutants in sediments do not show any trend within the sediment core as a result of past and present oil exploration, development, and production activities.

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

H2a. Concentrations of organic pollutants in the sediment cores do not pose an ecological risk to marine organisms as determined by sediment quality benchmarks.
H2b. Concentrations of trace-metal pollutants in the sediment cores do not pose an ecological risk to marine organisms as determined by sediment quality benchmarks.

Incremental variations in hydrocarbons, polynuclear aromatic hydrocarbons (PAHs), and metals will be difficult to measure because of the known high background levels and high variability from natural inputs – eroded shales, coals, peat, etc. These changes 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. 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 pre- and post-development monitoring efforts.

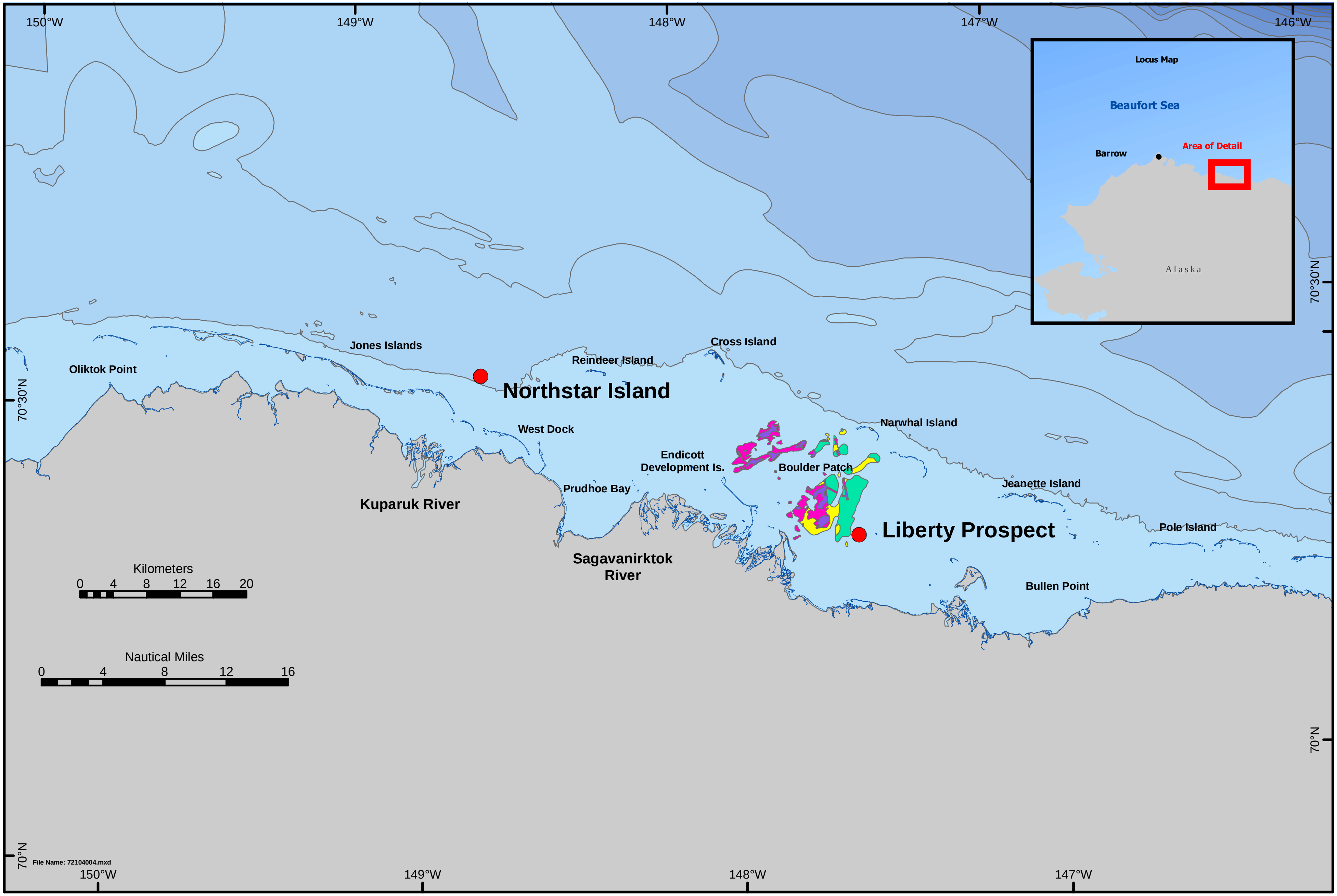


Figure 1-1. Map of the ANIMIDA Study Area

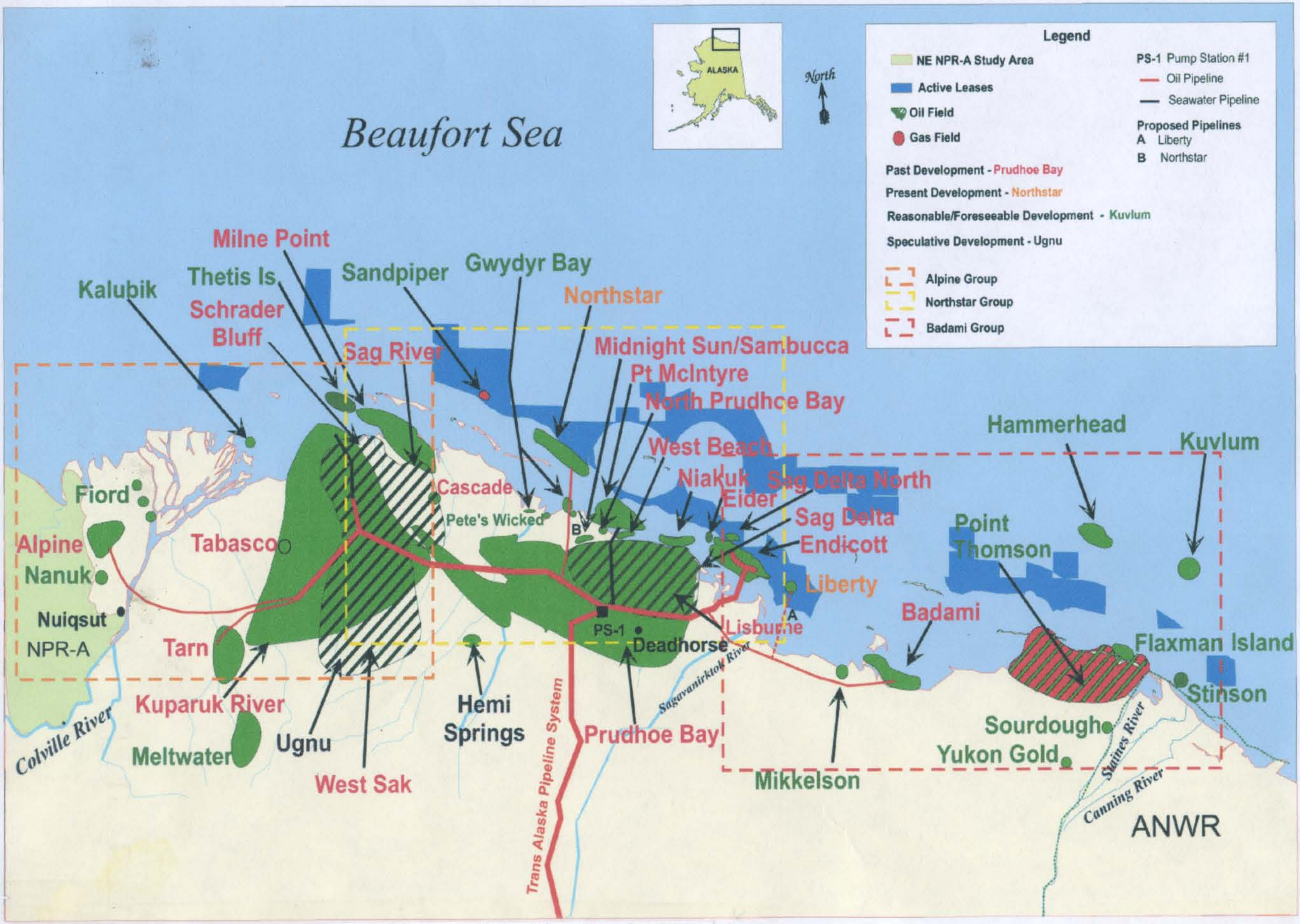


Figure 1-2. General Map of Onshore and Offshore Oil and Gas Development In the Study Areas

Source: USDOI, 2001

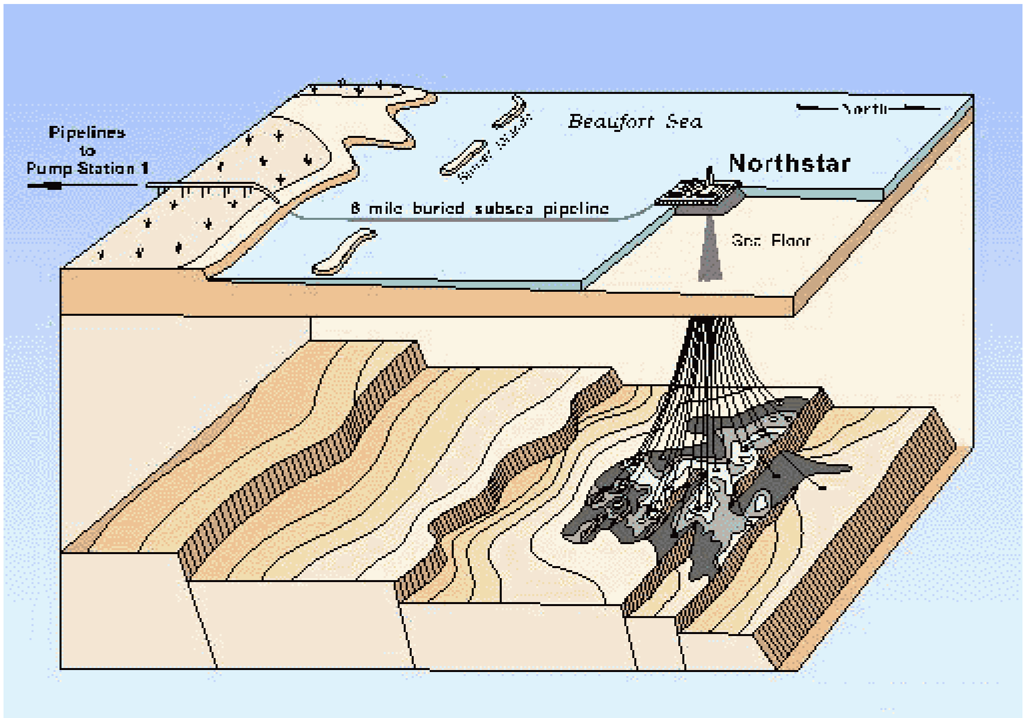


Figure 1-3: Schematic of BP's Northstar Development
(from: http://www.bp.com/alaska/index_nstar.htm)

2.0 Methods

This section describes the methods used in field sampling, field measurements, laboratory analyses, and data 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 encompasses both the Liberty and Northstar prospect areas, and much of the shoreline where regional Prudhoe Bay oil production activities are occurring. One open-water survey was conducted from July 24 to August 14, 2001 under Phase II of the ANIMIDA program. The scientific crew, on board the MMS *Research Vessel (R/V) 1273,* collected sediment cores, water samples, and biota (fish) samples for chemical analyses from the program study area. This report focuses solely on the collection, analyses, and results for the sediment core samples.

Sediment cores were collected from nearshore areas of the Beaufort Sea adjacent to Liberty prospect, Northstar Island, and reference sites to determine the geochronology of the cores and analyze them for oil industry-related contaminants (metals and organics). Stations for sediment core sampling were selected based on historical data from BSMP, Northstar Island, and Liberty prospect stations. Historical grain-size data were used to identify those stations that had fine-grained sediments and would be good candidates for depositional areas. The stations where sediment cores were collected are listed in Table 2-1 and are shown in Figure 2-1.

2.1.2 Summer 2001 Field Sampling

The summer 2001 cruise was conducted from July 24 to August 14, 2001, and coincided with a period of expected favorable ice and weather conditions in the program study area. Members of the field team arrived in Prudhoe Bay, Alaska on July 24, with additional team members joining the effort through August 1, 2001. The field sampling and logistics plan (Arthur D. Little, 2001) prepared for the summer 2001 field survey provides detailed explanations of the field methods for sample collection, equipment decontamination, and subsampling of sediment cores. Field sampling personnel from Battelle, Arthur D. Little (ADL), Florida Institute of Technology (FIT), Applied Marine Sciences (AMS), and Kinnetic Laboratories (KLI) participated in the survey. The scientific team and ship's captain (Mark Mertz - TEG Ocean Services) conducted the work on a 12- to 20-hour-a-day basis, depending on favorable operating conditions. A detailed description of the activities conducted during the survey, including a log of the daily activities, is included in the Cruise Report (ICF, 2003). A summary of the field sampling activities and methods follows in this section.

Samples

The scientific crew collected sediment core samples for chemical analyses from the program study area. Sediment cores were collected at 11 nearshore and offshore stations: 4 historic BSMP stations, 2 Northstar area stations, 3 Liberty stations, 1 Sagavanirktok River Delta (Endicott) station, and 1 Prudhoe Bay station.

A complete list of the sediment core sampling stations that were occupied and sampled in the study area is included in Table 2-1. Table 2-1 also provides the station identification, station type, latitude and longitude, depth, date and time of sampling, and the type of chemical and geophysical analyses for each sample. Figure 2-1, a map of the ANIMIDA study area, shows the locations of the summer 2001 sediment core sampling stations. Additional daily survey and sampling station information is included in the 2001 station logs contained in the Cruise Report (ICF, 2003).

Field Sampling Procedures

Standard sampling procedures were followed at each sampling station, according to the Summer 2001 Field Logistics and Sampling Plan for the MMS ANIMIDA Program (ADL, 2001). The sediment core sampling procedure included deployment of a dual-barrel gravity corer with ~300 pounds of extra lead weight by ~ 10-foot "freefall" into the bottom to collect "side-by-side" cores for geochronology and chemistry.

The most significant technical difficulty during this survey was obtaining gravity core samples of adequate length and appropriate sediment type (i.e., sediment representative of a depositional environment). Minor modifications were made to the dual-barrel core sampler in the field to maximize sediment penetration and minimize sediment core disturbance (extra weights were added and core cutters were removed). The core sample collections were limited to areas where soft, fine-grained sediment could be found. Core attempts were made at many stations where promising fine-grained surface sediment was underlain by hard clays, gravels, or sandy substrates. Core penetrations in such circumstances were often limited to 15 to 20 centimeters (cm), were prone to washouts, and core samples were subsequently not collected. However, favorable cores of 20 to 35 cm in depth were collected at 11 stations throughout the study area.

Field scientists maintained field notes throughout the survey in logbooks and in field forms (station logs). Any exceptions to the procedures described in the logistics and sampling plan were recorded in the appropriate field record(s). Photodocumentation was conducted during the survey using a 35-millimeter (mm) camera and digital still/video camera (capable of 15- to 60-second clips). Field activities were photographed and videotaped to record specific samples, sampling procedures, and unusual sediment types. All photodocumentation will be provided to MMS on compact discs.

2.2 Analytical Methods

2.2.1. Geochronology of Sediment Cores

Sediment samples used for age dating were sub-sectioned in 0.5-cm intervals. Approximately 8 to 10 grams (g) of freeze-dried sediment from each layer (0.5-cm thick) of the sediment cores were ground to a fine powder using a Spex 8000 mixer mill. The samples were then tightly packed into a 2-cm diameter, 5-cm long polycarbonate vial to a depth of 30±1 mm. A rubber stopper was used to seal the vial and was cemented into place with two-part epoxy to prevent leakage of Rn-222 and disruption of secular equilibrium between Ra-226 and Pb-210. The samples were then set aside for at least 20 days to establish secular equilibrium and the activities of the various radionuclides were then determined by counting.

For counting, the sealed vial was placed in a well-type intrinsic germanium detector (WiGe, Princeton Gamma Tech Model IGW11023). The samples were then counted for a period of 2 to 3 days or until sufficient counts of the pertinent radionuclides were obtained (>1,000 net counts for Pb-210). The peaks monitored for the purposes of this study were: Pb-210 at 46.5 kilo electron volts (KeV), Pb-214 at 295.2 KeV and 351.9 KeV, Bi-214 at 609.3 KeV, and Cs-137 at 661.6 KeV. The Ra-226 daughter isotopes Pb-214 (2 peaks) and Bi-214 were used to determine the activity of Ra-226. Detector efficiency and counting accuracy were standardized using standard reference river sediment 4350B (Cs-137) from the U.S. National Institute of Standards and Technology (NIST) and RGU-1 (Pb-210) from the International Atomic Energy Agency. The specific activity as decompositions per minute (dpm) per gram of each sediment sample was calculated from the detector efficiency, gamma intensity, geometry factor, and sample weight (Kang et al., 2000). All values are reported as the activity on the date of coring. Errors are shown based on 1-sigma counting statistics.

Sedimentation rates (S) in cm/year were calculated using the following equations with the assumptions being made that there is no sediment mixing:

Cs-137:

$$S = \frac{\text{Depth in cm at which Activity}_{\text{Cs-137}} = \text{maximum}}{[\text{Year} - (1963 \text{ and/or } 1950)] \text{ in years}}$$

Pb-210:

$$S = \frac{(-) \text{ decay constant for Pb-210 } (0.0311 \text{ year}^{-1})}{\text{Slope for plot of natural logarithm (ln) excess Pb-210 vs. sediment depth}}$$

The excess Pb-210 is calculated by subtracting the mean of $A_{(\text{Pb-214, Bi-214})}$ from $A_{\text{Pb-210.}}$

2.2.2 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 g 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 distilled-deionized water (DDW) was added to the dish, clay lumps were broken up with a gloved finger, and the wetted sample was poured into a 200-milliliter (mL) glass bottle and shaken vigorously for a few minutes. Then the sample was poured through 2 mm (gravel) and 63 micrometer (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 weighed 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. Dispersant was not needed in these samples of marine sediment since the mud fraction dispersed extremely well. After 20 seconds, 20 mL of sample was withdrawn from a depth of 20 cm using a Class A pipette. The pipette sample was drained into weighed 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 weighed 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 x beaker #3) – (50 x beaker #4)]/sum} x 100%
- % clay = [(50 x beaker #4)/sum] x 100%

2.2.1.2 Total Organic Carbon

A 0.5- to –1-g portion of the freeze-dried sediment was placed in a 20-mL Pyrex® beaker. Five mL of 10% phosphoric acid (H_3PO_4) were added 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 calcium phosphate from adding H_3PO_4. Then, approximately 200 to 400 milligrams (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 total organic carbon (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 H_3PO_4. The calibration curve was checked every 10 samples by analyzing certified reference material (CRM) MESS-2, a marine sediment issued by the National Research Council of Canada (NRC).

2.2.3 Organic Chemical Parameters

Analysis for organic contaminants was conducted by ADL/ICF's environmental chemistry laboratory. The analyses were conducted in accordance with the laboratory's standard operating procedures (SOPs) and generally followed the same procedures used in previous BSMP studies (Boehm et al., 1990).

During the course of this program, the prime contractor ADL filed for bankruptcy protection and was subsequently sold off by division. The environmental consulting and laboratory division of ADL was purchased by ICF in May 2002. The ADL SOPs were adopted, as is, with no technical changes by ICF. The ADL/ICF laboratory SOPs are archived at ICF's Lexington, MA office. To avoid confusion and remain consistent, the laboratory will be referred to throughout this report as the ADL/ICF laboratory.

The organic analyses for the sediment core 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 2-2, 2-3, and 2-4. This section describes the analytical methods that were used in performing the organic chemical analyses.

Sediment Sample Preparation

The sediment samples were prepared using a procedure based on United States Environmental Protection Agency (USEPA) Method 3550A, Ultrasonic Extraction (USEPA, 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 g (wet weight) of the homogenized sediment were weighed into a Teflon® jar and dried with sodium sulfate. Another 5-g 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, 5a-androstane and d50-tetracosane for SHC analysis, and d66-dotriacontane 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.

Extract Fractionation

The sediment 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 microliters (µL) 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 micrograms (µg) per mL. The amount of PAH and S/T internal standard added to the extract was adjusted to obtain a target concentration of 1 µg/mL.

Organic Instrumental Analysis

Instrumental analysis of the sediment samples included SHC by GC/FID, PAH by GC/MS, and S/T by GC/MS. 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 and in Tables 2-7 and 2-8.

Saturated Hydrocarbons by Gas Chromatography/Flame Ionization Detection

Analysis for SHCs was performed using a method based on USEPA Method 8015 (USEPA, 1993). Target compounds for the method are SHCs, including normal alkanes from n-C9 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-C9 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 USEPA Method 8270 (USEPA, 1993). The method modifications include analysis for an expanded list of PAHs 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

Analysis for S/Ts was performed by GC/MS in the 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.

2.2.4 Inorganic Parameters

Analysis for inorganic parameters was conducted by FIT. The analyses were conducted in accordance with FIT's SOPs. The inorganic analyses for the sediment samples were trace and major metals. Targeted analytes and associated MDLs are listed in Table 2-5. This section describes the analytical methods that were used in performing the chemical analyses.

2.2.4.1 Trace and Major Metals Analysis in Sediment

Sediment 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. Approximately 20 g of each sample were 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 g of sample were transferred into Pyrex® centrifuge tubes to determine the Hg content of the sediments (element symbols are defined in Table 2-5). 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 g of freeze-dried, homogenized sediment and CRM sediment (MESS-2) were totally digested in Teflon® beakers using concentrated, high-purity hydrogen fluoride (HF)-nitric acid (HNO_3)-perchloric acid ($HClO_4$). 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 $HClO_4$, 1 mL HNO_3, 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 HNO_3 and 3 mL HF before bringing the sample to dryness. Finally, 1 mL HNO_3 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 g of wet sediment in acid-washed, Pyrex® centrifuge tubes with 4 mL HNO_3 and 2 mL sulfuric acid (H_2SO_4). Sample tubes were heated for 1 hour in a 90°C water bath and allowed to cool. Each tube was centrifuged at 2,000 revolutions per minute (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 8 Normal (N) HNO_3 and rinsed three times with DDW. Two procedural blanks, two duplicate samples, and two CRMs were prepared with each set of 40 samples. The CRM used was MESS-2, a sediment sample issued by the NRC.

Sediment samples, CRMs, and procedural and reagent blanks were analyzed by flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS; Zeeman or Continuum background correction), cold vapor atomic absorption spectrometry (CVAAS), or inductively coupled plasma/mass spectrometry (ICP/MS). Mercury concentrations were measured by CVAAS. The method used for each element and the corresponding MDLs are presented in Table 2-5. All analytical techniques followed manufacturers' specifications, laboratory SOPs, and the details provided in Section 2.3 below. These methods are based on USEPA methods described for Series 7000 (FAAS and GFAAS), Series 7470 (CVAAS), and Series 6010A (ICP/MS) (USEPA, 1991).

2.3 Quality Assurance/Quality Control

A quality assurance (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 QA 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 Program Manager, Mr. John Brown 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 Manager was kept apprised of the program's status by the field sampling and analytical laboratory leaders.

Field

John Brown also served as the Field Team Leader for the sediment core collection survey and, as such, was responsible for completion of all field activities in accordance with the field sampling and logistics plan and communication with 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 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, Ms. Linda Cook was responsible for oversight of the organics analyses performed by the ADL/ICF's 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 the following specific responsibilities:

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

Prior to the start of laboratory analyses, the laboratory staff were provided project-specific training, including a discussion of the project background and objectives; project organization; sample preparation and instrumental analysis procedures; DQOs; 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; and,
- 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; and,
- Details of preservation used.

The types of sample containers used and the sample storage methods are provided in Table 2-6. 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 the samples to ensure that all samples were collected and returned to the custody area on board, documenting all samples in field logs, and preparing the COC form.

Sample Shipment

Following completion of the cruise, samples were packed in coolers for overnight shipment from the Prudhoe Bay Operations Camp (PBOC) in Deadhorse, Alaska using Federal Express airfreight courier. The samples were frozen prior to transportation and shipped to the appropriate analytical laboratories (Table 2-6) 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 when samples were received at the laboratory. The laboratory sample custodian received all samples. The coolers were checked for the presence of intact custody seals before they were opened. The coolers were 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 recorded 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 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 samples for trace-metal analysis were kept frozen (-20°C) until processed for analysis. Sediment samples for grain-size determination were kept refrigerated (4°C ± 2°C) until processing began.

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 Documentation

The scientists maintained field notes throughout the field surveys in logbooks 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 2-7 and 2-8.

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 (PB), one blank spike (BS), and one standard reference material (SRM; sediment SRM 1944) per batch. The BS sample was fortified with PAH matrix spike solution and SHC matrix spike solution.

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
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 for PAH samples. 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 to aid in qualitative identification of target compounds.

Procedural Blank
A PB 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 BS 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 SRM of a well-characterized sample of known concentration was processed through sample preparation and instrumental analysis with each batch of sediment samples. The results were compared to externally certified values to assess method accuracy. This program used SRM 1944 provided by NIST.

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; and
- 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/ICF 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 and CRM analysis, PB analysis, and standard checks. With each batch of up to 40 samples, 2 PBs, 2 SRMs and/or CRMs, 2 duplicate samples and 2 matrix spike samples were analyzed. Data quality objectives for these QC measurements are provided in Table 2-9.

Instrument Calibration

Electronic balances used for weighing samples and reagents were calibrated prior to each use with certified (NIST-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 3- to 5-point calibration with a linear correlation coefficient of $r \geq 0.999$ required before experimental samples could be analyzed. Analysis of complete 3- to 5-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 PBs 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 and CRM Analysis

A common method used to evaluate the accuracy of environmental data is to analyze SRMs and CRMs, samples for which consensus or "accepted" analyte concentrations exist. The following reference materials were used: Marine Sediment MESS-2 (NRC) and SRM Trace Elements in Water #1643d (NIST). Metal concentrations obtained for the reference materials were required to be within ±20 percent of accepted values for >85 percent of other certified analytes. When no certified values existed for a metal, matrix spikes were used to evaluate analytical accuracy.

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/ICF for completing the database design and data management. All final ANIMIDA data will be archived in the MMS CORIS database.

Table 2-1. Summer 2001 MMS ANIMIDA Sediment Core Stations

Station ID	Station Type	Sample Type	Latitude	Longitude	Depth (ft)	Date	Analysis/Replicates		Comments
							Sediment Cores		
							Organics/ Metals	Dating/GS/TOC	
3A	BSMP	Sed. Core	**70°18.975**	**147°05.430**	22	8/3/01	1	2	(8) organics (1) metals surface water, metals - mid/bottom
5A	BSMP	Sed. Core	70°29.710	148°46.099	37	7/27/01	*	*	(7/27) 3 attempts, all washouts
5A	BSMP	Sed. Core	**70°29.708**	**148°46.078**	38	8/9/01	*	1	(8/9) end- 70°30.721, 148°44.247, metals (surface/mid/bottom) water
5A	BSMP	Sed. Core-RE2	70°29.720	148°46.186	37		*	NA	
5A	BSMP	Sed. Core-RE3	70°29.765	148°46.416	37		*	NA	
5D	BSMP	Sed. Core	70°24.507	148°33.214	8	7/27/01	*	*	no mud available, 2 replicates washouts, moved station
6A	BSMP	Sed. Core	**70°32.217**	**149°57.732**	12	7/30/01	1	1	mud/clay
6B	BSMP	Sed. Core	**70°33.327**	**150°24.635**	23	7/30/01	1	1	mud/clay
6G	BSMP	Sed. Core	**70°31.392**	**149°54.602**	9	7/30/01	1	1	mud/clay
L02	Liberty	Sed. Core	**70°17.825**	**147°32.958**	23	8/3/01	1	1	clay
L03	Liberty	Sed. Core	**70°17.319**	**147°33.412**	23	8/6/01		1	1 core for archive - metals/geochron only
L12	Liberty	Sed. Core	**70°14.585**	**147°34.157**	19	8/4/01	*	1	metals - surface/mid(2m)/bottom(5m), 1 core for possible geochron
N02	Northstar	Sed. Core 1st	**70°30.515**	**148°41.320**	44	7/31/01	1	1	2 attempts - 1 core from each (70°30.507, 148°41.281 - 2nd attempt)
N03	Northstar	Sed. Core	**70°29.990**	**148°41.569**	44	7/28/01	1	1	sandy clay
N05	Northstar	Sed. Core	70°29.613	148°46.086	37	7/31/01	*	*	1st core washout, 2nd attempt clay plugs
N07	Northstar	Sed. Core	70°29.565	148°40.161	40	7/31/01	*	*	attempted 2 replicates; soft clay will not hold in core liner
N10	Northstar	Sed. Core, 1st	70°28.933	148°42.018	31	7/27/01	*	*	(7/28) 2 replicates, both washouts - hard clay
N10	Northstar	Sed. Core, 2nd	70°28.998	148°41.742	31	7/28/01	*	*	(7/28) 1 replicate - washout
N10	Northstar	Sed. Core, 3rd	70°28.933	148°42.018	31	7/31/01	*	*	(7/31) returned to try again; 4 reps. all washouts-abandon station
N24A	Northstar	Sed. Core, 1st	70°33.632	148°41.699	62	7/28/01	*	*	sand and washout, moved to deeper water
N24A	Northstar	Sed. Core, 2nd	70°34.254	148°41.702	61	7/28/01	*	*	washout
N24A	Northstar	Sed. Core, 3rd	70°34.928	148°40.933	64	7/28/01	*	*	washout
M01	McCovey	Sed. Core	70°30.765	148°27.374	39	7/31/01	*	*	2 replicates, both washouts
BPS	Source	Sed. sheen on shore	**70°10.605**	**146°51.450**	NA	8/12/01	1	NA	shoreline sheen sample from Bullen Point site
E01	Endicott	Sed. Core	**70°21.101**	**147°56.088**	13	8/4/01	1	1	core from east of Endicott Island
P01	Prudhoe Bay	Sed. Core	**70°18.806**	**148°23.229**	9	8/1/01	1	1	core from center of Prudhoe Bay
SAG02	Source	Sed.	NR	NR	NA	8/10/01	1		Sag River sed at PBOC Bridge
Oil	Source	Kuparuk Crude	NA	NA	NA	7/27/01	1		crude oil sample from Kuparuk Field Well

Notes:
* = On station, sampling attempted, but none collected (for cores or fish)
NA = Not applicable/not available
NR = Not Reported

Table 2-2. Saturated Hydrocarbons Target List

Compound	Reporting Code	Internal Standard/ Surrogate Reference	Compound	Reporting Code	Internal Standard/ Surrogate Reference
n-Nonane	C9	A/1	n-Hexacosane	C26	A/1
n-Decane	C10	A/1	n-Heptacosane	C27	A/1
n-Undecane	C11	A/1	n-Octacosane	C28	A/1
n-Dodecane	C12	A/1	n-Nonacosane	C29	A/1
n-Tridecane	C13	A/1	n-Triacontane	C30	A/1
Isoprenoid RRT 1380	1380	A/1	n-Hentriacontane	C31	A/1
n-Tetradecane	C14	A/1	n-Dotriacontane	C32	A/1
Isoprenoid RRT 1470	1470	A/1	n-Tritriacontane	C33	A/1
n-Pentadecane	C15	A/1	n-Tetratriacontane	C34	A/1
Isoprenoid RRT 1650	1650	A/1	n-Pentatriacontane	C35	A/1
n-Hexadecane	C16	A/1	n-Hexatriacontane	C36	A/1
n-Heptadecane	C17	A/1	n-Heptatriacontane	C37	A/1
Pristane	PRIS	A/1	n-Octatriacontane	C38	A/1
n-Octadecane	C18	A/1	n-Nonatriacontane	C39	A/1
Phytane	PHYT	A/1	n-Tetracontane	C40	A/1
n-Nonadecane	C19	A/1			
n-Eicosane	C20	A/1	Surrogate Compounds		
n-Heneicosane	C21	A/1	Tetracosane-d_{50}	D50T	A/1
n-Docosane	C22	A/1	5a-Androstane	5AA	B/1
n-Tricosane	C23	A/1			
n-Tetracosane	C24	A/1	Internal Standard		
n-Pentacosane	C25	A/1	Triacontane-d_{62}	D62T	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 2-3. 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
Acenaphthylene	ACEY	A/2	C$_4$-Chrysenes	C4C	B/3
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	Surrogate Compounds		
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	Internal Standard		
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 dibenzo(a,h)anthracene
Benzo(g,h,i)perylene is a 6-ring PAH

Table 2-4. Sterane and Triterpane Target List

Compound	Reporting Code	Internal Standard/ Surrogate Reference	Compound	Reporting Code	Internal Standard/ Surrogate Reference
C_{23} Diterpane	T4	A/1	<u>Surrogate Compounds</u>		
13b,17a-diacholestane(20S)	S4	A/1	5b(H)-cholane	5B	2
13b,17a-diacholestane(20R)	S5	A/1			
C_{29} Tricyclictriterpane	T9	A/1	<u>Internal Standards</u>		
C_{29} Tricyclictriterpane	T10	A/1	Chrysene-d_{12}	D12C	A
## 5a,14a,17a-cholestane(20R)	S17	A/1			
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 2-5. Summary of Instrumental Methods and Method Detection Limits for Metal Analysis of Sediment

	Sediments	
Metal	**Method**	**MDLs (μg metal/ g dry sediment)**
Ag – silver	ZGFAAS	0.007
Al – aluminum	FAAS	10
As – arsenic	ZGFAAS	0.2
Ba – barium	ICP-MS	1
Be – beryllium	ICP-MS	0.1
Cd – cadmium	ICP-MS	0.02
Co – cobalt	ICP-MS	0.3
Cr – chromium	FAAS	1
Cu – copper	FAAS	2
Fe – iron	FAAS	10
Hg – mercury	CVAAS	0.001
Mn – manganese	FAAS	3
Ni – nickel	ICP-MS	0.5
Pb – lead	ICP-MS	0.2
Sb – antimony	ICP-MS	0.04
Tl – thallium	ICP-MS	0.04
V – vanadium	FAAS	10
Zn – zinc	FAAS	2
Other Parameters		
Grain Size	Sieve and Pipet	---
TOC	Shimadzu Carbon System	0.06%

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 2-6. 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	ICF Consulting
Sediment	Metals, TOC	Plastic jar	Frozen -20°C	Florida Institute of Technology
Sediment	Grain Size	Plastic bag	Stored at 4°C	Florida Institute of Technology

Table 2-7. 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 (1944)	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 2-8. 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 2-9. 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 ≥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 and Certified 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

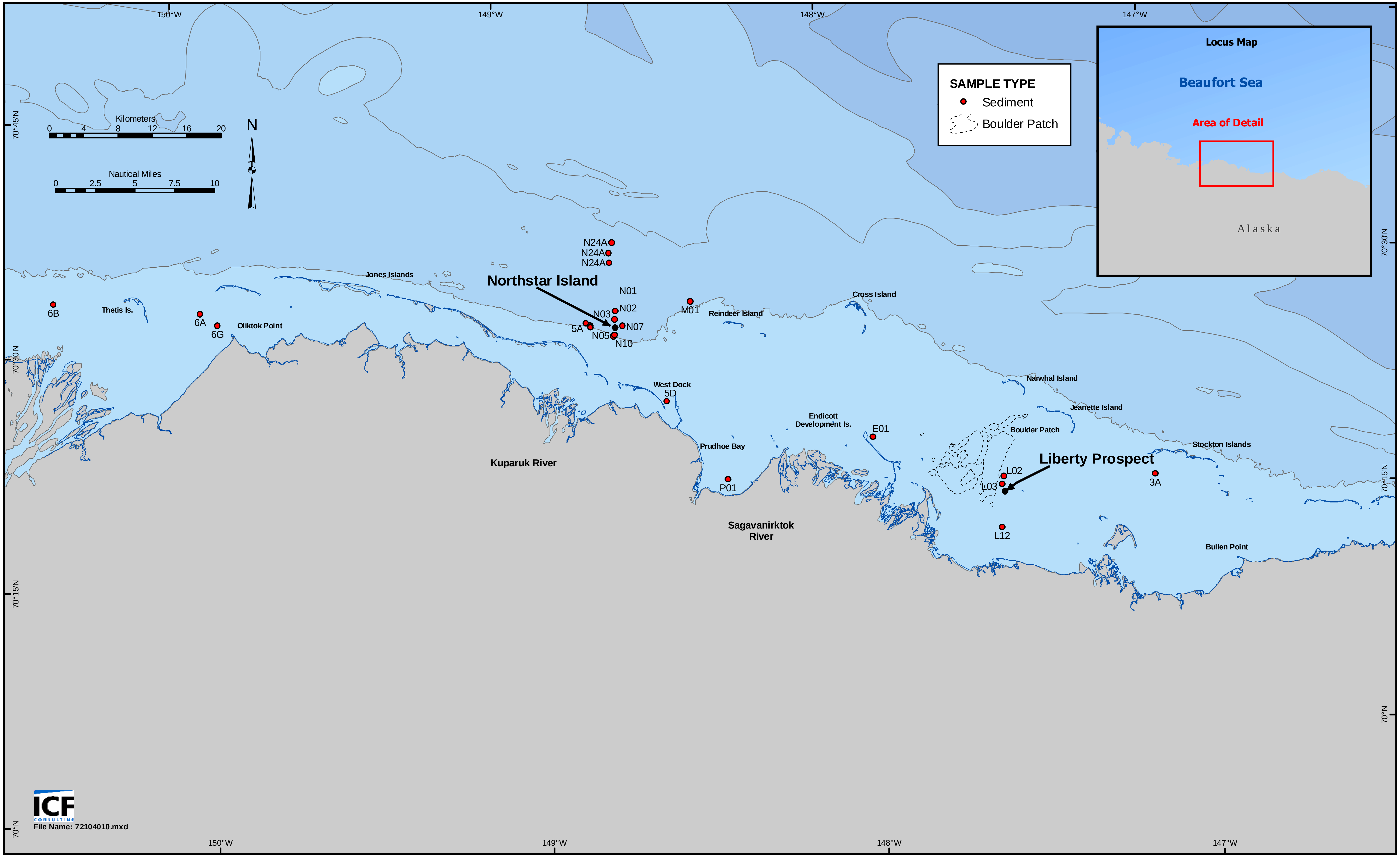


Figure 2-1 - ANIMIDA Task 2 Summer 2001
Sediment Core Survey Stations

3.0 Results

This section presents the results for the general chemistry, organic, and inorganic analyses for the sediment core samples collected from the Beaufort Sea during July and August 2001.

3.1 Sediment Cores

The results and general trends in the TOC, grain size, organic, and inorganic data from the sediment core samples collected during the summer 2001 ANIMIDA field survey are presented in this subsection.

3.1.1 Geochronology of Sediments

Collecting sediment cores suitable for age-dating in the coastal Beaufort Sea is complicated by bottom-fast ice, ice gouging, low net sediment accumulation rates, low activities of excess ^{210}Pb and ^{137}Cs, and storm-induced resuspension and transport of sediment offshore into deeper water. Even though our coring sites were chosen based on bathymetry (i.e., semi-restricted basins) or surface sediment composition (i.e., >90% silt + clay), only 8 of the 11 cores were viable for geochronology and chemistry measurements and only 3 of these yielded a reliable geochronology over the past 50 to 100 years. In many instances, extremely low levels or no detectable amounts of excess ^{210}Pb (<0.2 dpm/g) or ^{137}Cs (<0.02 dpm/g) were found, even in the top 0.5 cm of sediment. Such observations are consistent with previous reports that characterize this coastal area as a net erosional environment (Reimnitz and Wolf, 1998) and recent attempts at age-dating area sediments (Naidu et al., 2001).

Detailed results for geochronology were obtained for three sites: (1) station P01 in Prudhoe Bay, (2) station E01, just east of the Endicott development near the mouth of the Sagavanirktok River, and (3) station 6G, near the eastern area of the Colville River delta (Figure 2-1). At stations L02, 3A, N02, N03, and 6A, either no detectable excess ^{210}Pb and ^{137}Cs were found or very low levels were found only in the top 0.5 cm (Appendix A). The locations of these five sites with little or no detectable recent sediment extend across the study area and support the contention that deposition of modern sediment is patchy and thin.

In Prudhoe Bay (station P01), the maximum activity of excess ^{210}Pb in the surface layer of sediment is 0.84 dpm/g, with detectable decay to a depth of ~5 cm and a calculated sedimentation rate of 0.11 ± 0.02 cm/year (Figure 3-1). The vertical profile for ^{137}Cs supports the results from excess ^{210}Pb with a sedimentation rate of ~0.10 ± 0.02 cm/year based on the 1950 appearance of ^{137}Cs at ~5 cm and the observed 1963 peak at ~3.75 cm (Figure 3-1). Samples from depths >4 cm were most likely deposited before extensive development activities began around 1970 in the area of Prudhoe Bay. Preservation of such detail in the geochronological record over such a short depth interval for this site is surprising; however, boat traffic in the inner portion of the Prudhoe Bay is rare and water depths in the deepest portion of the bay (~3 m) are sufficient to minimize ice effects. Even if a combination of sediment deposition and winnowing at station P01 create an apparent sedimentation rate, it seems reasonable to suggest that the top 1 to 2 cm contain post-development sediment and that sediment found deeper than 4 to 5 cm is sediment deposited prior to development.

At station E01, the activity of excess ^{210}Pb is 1.1 dpm/g at 0 to 0.5 cm and 1.5 dpm/g at 0.5 to 1.0 cm (Figure 3-1). The calculated sedimentation rate based on excess ^{210}Pb is about 0.04 ± 0.02 cm/y. Activities of ^{137}Cs are detectable to a depth of 3.25 cm, yielding a sedimentation rate of ~0.06 ±0.02 cm/y, a value that is reasonably consistent with that obtained from the profile for excess ^{210}Pb, considering the uncertainty in the data. These data for station E01 support the likelihood that sediments at depths >4 cm pre-date development.

In the Colville River delta at station 6G, the maximum activity of excess ^{210}Pb is 0.76 dpm/g and the calculated sedimentation rate is 0.04 ± 0.02 cm/year (Figure 3-1). The ^{137}Cs profile supports a sediment accumulation rate of ~0.06 ± 0.02 cm/year. Once again, the record of sediment input since the 1950s is sequestered into the top 4 to 5 cm of sediment. At nearby station 6A, detectable levels of excess ^{210}Pb at 0.27 dpm/g were observed only in the top 0.5 cm of the sediment column.

3.1.2 Grain Size

The choice of locations for sediment cores was based, as much as possible, on the presence of fine-grained sediments that would indicate a depositional area and increase the chance for obtaining a useful record of input of metals and organic substances. Thus, the mean fraction of the sediment that was silt plus clay in the cores collected during 2001 was 73.6%, relative to 40.7% for surface sediments collected throughout the study area in 2000 (as shown in the inset table below and in Appendix A). The primary difference between the cores and the surface samples was in the amount of silt (61.5% average in 2001 cores versus 37.8% in the surface sediment from 2000). The most fine-grained sediment was collected at station N02 (average >80% silt plus clay). Sandy layers (>50% sand) were found in cores from stations 3A, 6A, 6G, and E01 (Appendix A). The grain-size data are used to help normalize concentrations of organic substances.

	Gravel (%)	**Sand (%)**	**Silt (%)**	**Clay (%)**
Sediment Cores (2001)				
Mean	0.5	25.8	**61.5**	12.1
Standard Deviation	2.3	18.6	17.2	6.5
Maximum	16.3	75.8	89.5	25.5
Minimum	0.0	1.6	15.5	1.3
Surface Sediments (2000)				
Mean	2.6	46.7	**37.8**	12.9
Standard Deviation	9.8	28.4	23.1	9.1
Maximum	60.3	98.8	86.8	35.5
Minimum	0.0	1.4	0.4	0.3

3.1.3 Organics

Concentrations of organics were determined for 60 samples from 8 sediment cores (P01, E01, 6A, 6G, 3A, N02, N03, and L02). Each core was sectioned into 2-cm layers. Organic parameter results for the sediment core samples are summarized in Table 3-1. The summary results include

Total 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), Total S/T (the sum of the sterane and triterpane target compounds), the percent of the fine grain-size fraction (the sum of the silt + clay grain-size fraction), and the ratio of pyrogenic PAHs to petrogenic PAHs. The results are separated into groupings by core locations. Descriptions of key diagnostic parameters, which are useful in describing the overall organics dataset are provided in Table 3-2. Vertical core profiles of 9 key parameters for each core are included in Figures 3-2 through 3-9. As discussed earlier, only 3 of the core samples (6G, E01, and P01) yielded geochronology results that allowed accurate determination of sedimentation rates, and thus estimates of deposition dates. According to the age-dating results (Figure 3-1), pre-development sediment is clearly present at depths > 4 to 5 cm and post-development (since 1970) sediment would most likely be found in the top 5 cm of the sediment column. As a conservative marker for development, a line representing 1950 is provided for the organic parameter core profiles in the 3 cores with accurate age dates (Figures 3-4, 3-5, and 3-9). The complete organics data, including concentrations for individual PAH, SHC, and S/T target compounds, are included in Appendix B.

3.1.3.1 Saturated Hydrocarbons

Concentrations of TPHC in sediment core samples from the summer 2001 survey ranged from 3.2 to 17 mg/Kilogram (Kg) with one anomalous concentration of 31 mg/Kg detected at core station 6G in the 0- to 2-cm interval. However, when normalized to the clay fraction, the 0- to 2-cm interval from core sample 6G falls within the range of results for the other 6G core intervals (see Figure 3-4), indicating that the observed enrichment of hydrocarbons was due to the accumulation of fine-grained material at the surface of this core. The mean TPHC concentrations for the 8 cores ranged from 4.6 to 11 mg/Kg (Table 3-1).

The composition of SHCs through the depth of all the sediment cores was generally similar, indicating a common TPHC source relationship between pre-1970 and post-1970 sediments. For example, similar patterns are noted in the GC/FID chromatograms for the pre-1970 and post-1970 sediments from cores P01 (Figures 4-6 and 4-7) and 6G (Figures 4-8 and 4-9).

Overall, the levels of TPHC measured during the sediment core survey are within the range of values reported from previous studies of the region and other Alaskan coastal areas (Table 3-3).

3.1.3.2 Polynuclear Aromatic Hydrocarbons

Concentrations of Total PAH in sediment core samples from the summer 2001 survey ranged from 284 to 932 μg/Kg, with one anomalous concentration of 1,990 μg/Kg detected at core station 6G in the 0- to 2-cm interval. However, when normalized to the clay fraction, the 0- to 2-cm interval from core sample 6G falls within the range of results for the other 6G core sections and is no longer an outlier (see Figure 3-4), further supporting the earlier observation that the high result is due to a grain-size effect. The mean Total PAH concentrations for the 8 cores ranged from 383 to 657 μg/Kg (Table 3-1).

As noted with the SHC composition, the composition of Total PAH in the pre-1970 and post-1970 sediments was similar, indicating a common PAH source relationship. For example, similar patterns are noted in the PAH histograms for the pre-1970 and post-1970 sediments from cores P01 (Figures 4-6 and 4-7) and 6G (Figures 4-8 and 4-9).

Overall, the levels of PAH measured during the sediment core survey are within the range of values reported from previous studies of the region and other Alaskan coastal areas (Table 3-3).

3.1.3.3 Steranes and Triterpanes

Concentrations of Total S/T in sediment core samples from the summer 2001 survey ranged from 22 to 129 μg/Kg. Similar to the PAH and SHC results, one anomalous concentration of 225 μg/Kg was detected at the 0- to 2-cm interval in core 6G. Once again, when normalized to clay, the 0- to 2-cm interval from core sample 6G falls within the range of results for the other 6G core sections. The mean Total S/T concentrations for the 8 cores ranged from 31 to 94 μg/Kg (Table 3-1).

Overall, the levels of Total S/T measured during the sediment core survey are within the range of values reported from previous studies of the region and other Alaskan coastal areas (Table 3-3).

3.1.4 Metals

Concentrations of trace metals were determined for 104 samples from six cores (P01, E01, 6A, N02, 6G, and 3A). Each core was sectioned into 0.5- to 2.0-cm layers. Some variability in concentrations of metals is observed in each core (Table 3-4), mainly due to shifts in amounts of fine-grained sediment. However, the coefficient of variation (CV) for metal/Al ratios averaged <10% in each of the 6 cores for Ni, V, Zn, Fe, Cr, Ba, Co, Tl, Be, Pb, Sb, and Cu (Table 3-5). Such uniform deposition supports long-term sedimentation of uniform composition with no observable impact from diagenesis for these metals. Diagenetic effects were observed for Mn, As, and perhaps Cd, as described in more detail in Section 4.

In Prudhoe Bay (station P01), concentrations of Al and Fe follow parallel trends downcore (Figure 3-10). Vertical distributions for Ba, Pb, Cr, V, and Zn (Figure 3-10), as well as Be, Cu, Ni, Sb and Tl (Figure 3-11), follow trends similar to those observed for Al and Fe, with the CVs for the metal/Al ratios all <8%. According to the age-dating results (Figure 3-1), pre-development sediment is clearly present at depths >5 cm and post-development (since 1970) sediment would most likely be found in the top 5 cm of the sediment column. A depth of 5 cm was chosen as a separation point between pre- and post-development because the presence of ^{137}Cs is limited to the top 5 cm. Therefore, any biological and physical mixing of sediment that may carry post-development sediment downcore is probably limited to the top 5 cm.

Where data for suspended sediment (source material) from the Sagavanirktok River are available for the metals mentioned above (Fe, Al, Pb, Cr, Zn; Figures 3-10 and 3-11), the metal concentrations or the metal/Al ratios for suspended sediment are coincident with values found in the surficial layers of the core. Such trends support long-term deposition of sediment with metal concentrations that are consistent with mixtures of river suspended matter containing varying amounts of coarser-grained, metal-poorer sands with no discernible diagenetic alteration of metal distributions. Variations in the Ag/Al ratio downcore are related to low levels of Ag and higher analytical variability at these low absolute levels of Ag. Sediment samples analyzed for Hg are from separate, larger-spaced layers than for the other metals and we do not presently have Al data for normalization; this gap is being resolved now for the final report.

Concentrations of TOC (and the TOC/Al ratio) are elevated by about 30% in the top 0.5 cm and by a factor of ~2 at about 20 cm (Figure 3-10). Coincident with elevated levels of TOC in the surface layer of sediment are increased concentrations of As/Al and Mn/Al (Figure 3-10). Furthermore, concentrations of Mn/Al are enriched above the layer at 20 cm, where concentrations of TOC are also high. These deviations from uniform vertical trends (including Cd) are related to early chemical diagenesis in the sediments and are discussed in more detail in Section 4.

At the station located just east of Endicott Island (station E01), post-development sediment appears to be restricted to the top 4 cm of the sediment column (Figure 3-1). No discernible differences in metal/Al ratios (i.e., downcore variability <10%) are observed for all metals except As, Mn, Cd, and Ag (Figures 3-12 and 3-13), the same trend observed for the core from station P01. Concentrations of As, Mn, and Cd may be influenced by early chemical diagenesis, as discussed in Section 4.

At station 6G, on the Colville River delta, post-development sediment appears to be restricted to the top 3 cm of the sediment column (Figure 3-1). Once again, no discernible differences in metal/Al ratios (i.e., downcore variability <10%) are observed for all metals except Mn, As, Cd, and Ag (Figure 3-14 and 3-15), the same trend observed for the cores from stations P01 and E01.

The cores from stations N02 (Figures 3-16 and 3-17), 6A (Figures 3-18 and 3-19), and 3A (Figures 3-20 and 3-21) have no or only trace amounts of ^{137}Cs or excess ^{210}Pb in the top 1-2 cm. Therefore, these 3 sites are of limited value for comparing metal levels in pre- versus post-development. However, the subsurface sediments from these cores help enrich the overall database for pre-development conditions. In the final report, we will use a combination of cores and surface sediments from 1989, 1999, 2000, and 2001 to more thoroughly address the contamination issue. Overall, variability in the core for the same 4 elements (As, Mn, Cd, and Ag) was observed. In addition, concentrations of Pb (stations N02 and 6A), Be (station 6A), Cu (all 3 sites) and Sb (stations N02 and 6A) were more variable (>10%). These additional deviations seem to be minor and unrelated to any diagenetic effects; they will be given further consideration during preparation of the final report.

3.2 Quality Control Results

This section provides an evaluation of the quality and usability of the environmental data based on the results for the laboratory QC samples analyzed during this program. Tables 3-6 through 3-8 summarize the organic laboratory QC results. Tables 3-9 and 3-10 summarize the inorganic 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.

3.2.1 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 ICF's SOPs and the Field Sampling and Logistics Plan (Arthur D. Little, 2001). For this program, the following laboratory QC samples and measures were used to evaluate accuracy and precision of the analytical data: surrogate recoveries, PBs, BSs, laboratory duplicates, SRMs, and oil reference standards (ORS). 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.

3.2.1.1 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 only one exception. The surrogate naphthalene-d8 recovered low (33%) in sample 01-N02-01-12-PHC-SC. The associated result for the target analyte naphthalene in this sample should be considered an estimated value.

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

3.2.1.2 Procedural Blanks

A laboratory 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. PBs are used to assess the potential contamination introduced during sample preparation and analysis. PAH, S/T, and SHC analyses were performed on each PB.

Between 13 and 23 target PAH compounds were detected at trace concentrations (less than the minimum reporting limit [MRL]) in all of the sediment PBs, with the exception of phenanthrene. Two PBs had phenanthrene detected at concentrations greater than the MRL. All associated samples had concentrations of phenanthrene greater than 10 times the blank concentration, thus no sample results were qualified due to this exceedance. Between 17 and 24 SHC target compounds ranging from n-C16 to n-C40 were detected at trace concentrations less than one-fifth the MRL in the sediment PBs. No S/T target compounds were detected in the 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 MRL.

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 could indicate a possible false-positive measurement.

3.2.1.3 Blank Spike Sample Recoveries

A BS sample was prepared with each sample preparation batch by spiking a blank sample matrix with known concentrations of a subset of the target compounds. Blank spike samples are used to assess the accuracy of the sample preparation and analysis procedures independent of sample matrix effects. PAH and SHC analyses were performed on each BS. S/T analyses were not performed on the BSs due to the availability and cost of native S/T compounds.

For the PAH analyses, the recoveries of several compounds in the BS exceeded the acceptance criteria. The recovery of benzo[b]fluoranthene (130%) in one BS and the recoveries of benzo[b]fluoranthene (140%), benzo[k]fluoranthene (126%), dibenzo(a,h)anthracene (128%), and benzo(g,h,i)perylene (126%) in one BS slightly exceeded the upper recovery criterion; all other sediment BS recoveries were within acceptance limits. These BS recovery exceedances do not adversely affect the quality or usability of the associated sample data.

For the SHC analyses, all of the BS recoveries were within the recovery acceptance limits, without exception.

3.2.1.4 Laboratory Duplicates

Laboratory duplicates were prepared with each sample preparation batch by extracting a second, separate aliquot of an arbitrarily selected environmental sample. Laboratory duplicates were evaluated to assess analytical precision related to laboratory performance and sample matrix. PAH, S/T, and SHC analyses were performed on each laboratory duplicate.

For the sediment PAH, SHC, and S/T analyses, good laboratory duplicate precision was noted, with relative percent differences (RPDs) less than 30 percent for all of the compounds detected at concentrations above the MRL and for the majority of the compounds detected at concentrations below the MRL. The laboratory duplicate precision criterion does not apply to compounds detected below the MRL (or less than 10 times the MDL) due to increased variability at these low concentrations (RPD was calculated as the absolute difference between the two measurements divided by the mean of the two measurements).

3.2.1.5 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. NIST 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 performance and calibrations were acceptable.

Sediment SRM. A sediment SRM (NIST SRM 1941a – a freeze-dried marine sediment with certified concentrations for PAHs) was prepared and analyzed for PAHs along with each sediment sample batch. 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 5 of the sediment SRMs was greater than 30 percent lower than the certified value (-53.2%, -53.9%, -60.3%, -61.4%, and -69.3%). The response for benzo[k]fluoranthene was also more than 30 percent lower than the certified value (-41.3% and –40.9%) in 2 sediment SRM analyses. These results indicate that the measurement of naphthalene and benzo[k]fluoranthene in the sediment samples may be biased low. These SRM exceedances 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.

3.2.1.6 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 comparison 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.

3.2.2 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: PBs, matrix spike samples, laboratory duplicates, and SRMs. The results for the inorganic QC samples and measures are presented in Table 3-9 and Appendix A, along with the results for the associated environmental samples. Discussion and interpretation of the results are provided in the following sections.

3.2.2.1 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 MDLs. The MDLs for this study are given in Table 2-5. The DQOs are given in Table 2-9.

3.2.2.2 Matrix Spike Sample

Matrix spike samples were analyzed with each batch of sediment 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 samples are shown in Table 2-5, and are within the 80- to 120-percent range specified in the DQOs (Table 2-9).

3.2.2.3 Laboratory Duplicates

Duplicate subsamples taken from individual sediment samples in the laboratory were analyzed in order to estimate analytical precision [RSD = (std. deviation/mean) x 100 percent]. Average analytical precision for sediment metal analyses (n = 4 pair of duplicate samples) ranged from 0.8% RSD for V to 2.8% RSD for Be and V. Average analytical precision of sediment TOC analyses averaged 2.9% RSD (n = 7).

3.2.2.4 Standard Reference Materials

Certified and Standard Reference Materials were processed and analyzed for trace metals along with the experimental samples, as described in the Methods section (Section 2.2). The results of these analyses are shown in Table 3-10. The metal concentrations determined for each CRM and SRM were all within the range of certified values or within the DQO limits of the reference values provided by the certifying agencies.

TOC analyses used the marine sediment CRM MESS-2 as a QA sample. This CRM is certified for total carbon content (inorganic plus organic), which is the reason the organic carbon value in Table 3-10 falls below the certified total carbon value. However, the TOC value determined for MESS-2 was consistently reproducible with percent RSD of ~ 1%.

Table 3-1. Table of Concentration of Selected Organic Parameters in Sediment Core Samples

Core Station/ Depth (cm)	Total PAH (μg/Kg)	TPHC (mg/Kg)	Total S/T (μg/Kg)	Silt+Clay (%)	Pyrogenic/ Petrogenic (ratio)
3A					
2	381	6.1	38	71	0.111
4	388	5.3	40	78	0.111
6	379	4.3	34	76	0.107
10	330	3.2	28	46	0.111
16	412	4.2	35	62	0.108
20	405	4.8	42	67	0.107
Mean (SD)	383 (28.8)	4.6 (1.0)	36 (5.1)	66 (11)	0.109 (0.002)
6A					
2	932	14	105	86	0.108
4	742	8.9	91	72	0.111
6	582	6.8	57	62	0.104
10	678	8.6	68	54	0.110
14	419	4.6	41	26	0.112
18	425	4.9	42	59	0.114
Mean (SD)	630 (197)	8.0 (3.5)	67 (26)	60 (20)	0.110 (0.004)
6G					
2	1990	31	225	86	0.117
4	831	11	108	56	0.118
6	619	9.6	87	61	0.129
8	548	8.6	78	59	0.129
10	586	8.9	83	63	0.134
12	668	8.6	79	70	0.125
14	616	10	88	64	0.123
16	711	13	103	61	0.134
18	800	17	129	75	0.145
20	535	9.9	87	30	0.131
Mean (SD)	657 (105)	11 (2.7)	94 (17)	60 (13)	0.130 (0.008)
E01					
2	589	12	63	92	0.098
4	365	5.6	32	83	0.093
6	330	4.4	30	48	0.099
8	284	3.4	23	42	0.108
10	401	4.6	34	79	0.109
12	347	4.5	30	63	0.119
Mean (SD)	386 (107)	5.8 (3.1)	35 (14)	68 (20)	0.104 (0.009)
L02					
2	285	4.6	23	56	0.107
4	298	5.0	24	57	0.104
6	431	6.3	29	57	0.104
12	361	6.4	25	52	0.104
16	632	11	47	83	0.107
22	756	14	60	78	0.114
Mean (SD)	460 (192)	7.9 (3.7)	35 (15)	64 (13)	0.107 (0.004)

Table 3-1. Table of Concentration of Selected Organic Parameters in Sediment Core Samples (continued)

Core Station/ Depth (cm)	Total PAH (μg/Kg)	Total PHC (mg/Kg)	Total S/T (μg/Kg)	Silt+Clay (%)	Pyrogenic/ Petrogenic (ratio)
N02					
2	535	8.8	57	72	0.120
4	476	7.7	43	72	0.115
6	502	7.6	46	83	0.114
12	475	8.3	50	73	0.116
16	331	5.2	27	79	0.113
22	742	14	73	94	0.124
Mean (SD)	510 (133)	8.6 (2.9)	50 (15)	79 (8.5)	0.117 (0.004)
N03					
2	410	6.6	36	89	0.121
4	407	6.7	35	92	0.114
6	379	5.9	29	84	0.111
10	474	11	39	92	0.120
16	337	7.2	25	94	0.111
20	289	6.5	22	83	0.113
Mean (SD)	383 (64)	7.3 (1.8)	31 (6.8)	89 (4.8)	0.115 (0.004)
P01					
2	701	17	81	95	0.085
4	549	14	69	93	0.099
6	523	9.6	53	97	0.100
8	520	11	54	97	0.102
10	588	12	68	96	0.106
12	528	10	61	95	0.110
14	548	9.4	58	98	0.109
16	536	10	69	98	0.110
18	540	9.6	71	98	0.121
20	556	14	80	94	0.115
22	800	16	98	93	0.119
24	611	12	61	98	0.118
26	613	8.8	71	94	0.119
28	537	6.5	54	96	0.114
Mean (SD)	582 (80)	11 (2.9)	68 (13)	96 (1.9)	0.109 (0.010)

Table 3-2. 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.
Lower-Molecular-Weight Alkanes (LALK)	The sum of lower-molecular-weight n-alkanes (n-C_9 to n-C_{20}) generally associated with "fresh" petroleum inputs.
Total Alkanes (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 LALK, which includes those of biogenic origin.
Phytane/Pristane (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.
Carbon Preference Index (CPI)	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 to 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)	
Naphthalenes/ Phenanthrenes (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 to 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 to C4], acenaphthene, acenaphthylene, fluorene [C0 to C3], phenanthrenes [C0 to C4], dibenzothiophenes [C0 to C3], chrysenes [C1 to C4], and fluoranthenes/pyrenes [C1 to 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 3-2. Diagnostic Ratios and Parameters of Saturated Hydrocarbons, Polynuclear Aromatic Hydrocarbons, and Steranes and Triterpanes (continued)

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.

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

	Total PAH (μg/g)	Total PHC[d] (μg/g)	Total S/T (μg/g)
Concentrations in Alaska Marine Sediments[a]	0.016 - 2.4	0.47 - 38	NA
Concentrations in Cook Inlet and Shelikof Strait Sediments[b]	0.001 – 1.080	0.9 - 69.0	0.009 – 0.087
Average (Range) Concentrations for ANIMIDA Study Area Surficial Sediments[c]	0.49 (0.007 – 2.7)	9.0 (0.21 – 50)	0.051 (0.002 – 0.176)
Average (Range) Concentrations for ANIMIDA Study Area Sediment Cores	0.54 (0.28 – 1.99)	9.0 (3.2 – 31)	0.059 (0.021 – 0.225)

[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] Brown et al., 2002.

[d] Total PHC concentrations for the ANIMIDA studies included saturated hydrocarbons only, while Total PHC concentrations for the other studies included saturated and aromatic hydrocarbons.

NA – not applicable.

Table 3-4. Summary Data for Metals, Total Organic Carbon (TOC), and Grain Size in Sediments from the Coastal Beaufort Sea

Samples		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 (%)
Surface Sediment 1999 & 2000	Mean ± Std. Dev. (n = 88)	0.11 ±0.05	3.93 ±1.63	11.1 ±4.1	394 ±146	1.2 ±0.50	0.22 ±0.12	7.3 ±3.3	56.9 ±23.4	18.9 ±10.5	2.21 ±0.87
Sediment Cores 2001	Mean ± Std. Dev. (n = 104)	0.12 ±0.05	4.48 ±0.80	9.3 ±3.2	460 ±60	1.1 ±0.2	0.26 ±0.10	9.0 ±2.0	64.4 ±9.6	21.8 ±6.5	2.30 ±0.44
All Data	Range	0.03-0.44	1.1-7.3	4.2-28.4	155-753	0.3-2.3	0.03-0.82	2.2-18.6	12.7-104	3.6-50.2	0.7-3.9

Samples		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 (%)
Surface Sediment 1999 & 2000	Mean ± Std. Dev. (n = 88)	0.041 ±0.029	317 ±144	24.3 ±10.5	9.7 ±4.9	0.50 ±0.21	0.40 ±0.18	92.6 ±40.1	70.1 ±31.7	0.86 ±0.70	46.9 ±30.4
Sediment Cores 2001	Mean ± Std. Dev. (n = 104)	0.054 ±0.011	294 ±117	31.9 ±6.3	10.3 ±2.5	0.62 ±0.12	0.47 ±0.07	99.7 ±17.4	91.5 ±22.6	1.13 ±0.54	72.8 ±18.8
All Data	Range	0.003-0.20	62-898	6.0-48.4	3.2-22.3	0.15-1.14	0.12-0.92	26.9-173	14.8-157	0.01-4.41	1.0-98.8

Table 3-5. Summary of Results for Metal/Al Ratios in Sediment Cores

Results presented in this table include the following locations: Prudhoe Bay (P01, n = 29), Endicott (E01, n = 13), Pole Island 3A (n = 10), Colville Delta (6A, n = 23; 6G, n = 14), Northstar 2 (n = 15).

Metal	(Metal/Al) (x 10^{-4}) All 104 Samples	Range for CV (%) for (Metal/Al) for All 6 Cores	Average CV (%) for (Metal/Al) from 6 Cores
Ni/Al	7.1 ± 0.9	2-6	3.5
V/Al	22.3 ± 1.2	3-6	3.6
Zn/Al	20.3 ± 2.6	2-6	4.4
Fe/Al	5100*	2-10	4.6
Cr/Al	14.6 ± 1.8	4-6	5.1
Ba/Al	105 ± 16	5-8	5.8
Co/Al	2.0 ± 0.4	3-10	6.1
Tl/Al	0.11 ± 0.01	4-11	6.4
Be/Al	0.24 ± 0.3	5-14	7.7
Pb/Al	2.3 ± 0.4	4-16	8.7
Sb/Al	0.14 ± 0.02	5-15	9.4
Cu/Al	4.8 ± 1.0	7-14	10.2
Cd/Al	0.06 ± 0.02	12-19	14.8
As/Al	2.1 ± 0.7	11-22	15.1
Mn/Al	65 ± 19	8-42	20.4
Ag/Al	0.03 ± 0.01	16-39	26.5

* Ratio for Fe/Al is 0.51.

Table 3-6. 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
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 a low d8-naphthalene recovery in sample N02-12.	Minor. The results for sample 01-N02-01—12-PHC-SC should be considered estimated values due to low surrogate recoveries.
Procedural Blank	No compound to exceed 5 times the MDL unless sample amount is >10 times blank amount	Several PAHs were detected in the sediment blanks at trace concentrations below the MRL. The associated sample concentrations were > 5 times the blank concentrations, with the exception of acenaphthylene.	Minor. The acenaphthylene 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	Several PAHs were recovered at >125% in the sediment BS.	Minor. Results for these compounds in the associated samples may be biased high.
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 (1944)	Measured values must be within 30% of 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 in 5 of 5 analyses and benzo[k]fluoranthene in 2 of 5 analyses.	Minor. The naphthalene and benzo[k]fluoranthene results in the associated sediment samples may be biased low.
Oil Reference Standard (North Slope Crude)	%D <35% for compounds above the reporting limit (RL).	All criteria were met.	None.

Table 3-7. 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
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	Many SHCs were detected in the blanks at trace concentrations less than the MDL and/or less than 1/5 the MRL.	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 MRL.
Blank Spike Sample Recoveries	35 to 125% recovery for spiked compounds	All criteria were met.	None.
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 3-8. 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
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.
Laboratory Duplicate	RPD <30% for all compounds >10 times the MDL; mean RPD <30%	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.	None.
Oil Reference Standard (North Slope Crude)	%D <35% for compounds above the RL	All criteria were met.	None.

Table 3-9. 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
Initial Calibration	Standard Curve correlation coefficient *r* ≥ 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	80 to 120% recovery for all trace metals	All criteria were met.	None.
Procedural Blanks	No more than 2 trace-metal concentrations to exceed 5 times the MDL unless analyte is not detected in associated samples	All criteria were met.	None.
Laboratory Duplicates	RSD <25% for 65% of the trace-metal concentrations	All criteria were met.	None.
Sediment and Certified Reference Materials (MESS-2 and 1643d)	Measured values must be within 20% of the certified or reference values for >85% of the SRM analyses or within 25% of the certified HG value	All criteria were met.	None.

Table 3-10. Results for Marine Sediment Certified and Standard Reference Materials and Metals Spike Recoveries

Sample ID	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 (%)
CRM MESS-2 This Study, 2001 (n = 8-10)	0.18 ±0.01	8.45 ±0.12	20.6 ±0.4	1008 ±13	2.27 ±0.05	0.24 ±0.01	13.4 ±0.4	99.3 ±1.5	38.3 ±0.4	4.23 ±0.05
CRM MESS-2 NRC Certified	0.18 ±0.02	8.57 ±0.26	20.7 ±0.8	--	2.32 ±0.12	0.24 ±0.01	13.8 ±1.4	106 ±8	39.3 ±2.0	4.35 ±0.22
SRM #1643d This Study, 2001 (n = 4)	--	--	--	511.2 ±5.4	--	--	--	--	--	--
SRM #1643d NIST Certified	--	--	--	506.5 ±8.9	--	--	--	--	--	--
Spike Recovery (%) 2001	87.6 ±10.5	102.0 ±3.3	99.6 ±5.3	97.2 ±1.9	94.9 ±3.6	93.2 ±3.3	92.6 ±2.4	101.0 ±4.4	98.0 ±4.1	98.0 ±2.2

Sample ID	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 (%)
CRM MESS-2 This Study, 2001 (n = 8-10)	0.093 ±0.005	370 ±8	48.2 ±1.2	21.4 ±0.4	1.17 ±0.02	0.94 ±0.04	247 ±1	176 ±10	2.03 ±0.03
CRM MESS-2 NRC Certified	0.092 ±0.009	365 ±12	49.3 ±1.8	21.9 ±1.2	1.09 ±0.13	(0.98)	252 ±10	172 ±16	2.14* ±0.03
SRM #1643d This Study, 2001 (n = 4)	--	--	--	--	--	--	--	--	--
SRM #1643d NIST Certified	--	--	--	--	--	--	--	--	--
Spike Recovery (%) 2001	87.7 ±9.5	100.0 ±5.2	91.9 ±4.0	92.6 ±2.0	100.4 ±1.6	95.3 ±1.5	117 ±6.0	94.6 ±0.9	N.A.

Notes:
CRM MESS-2 was issued by NRC and the SRM Trace Elements in Water #1643d was issued by NIST.
Values in parenthesis are for reference only; SRM not certified by the NRC.
N.A. = Not Available
* Total Carbon (Inorganic plus Organic)

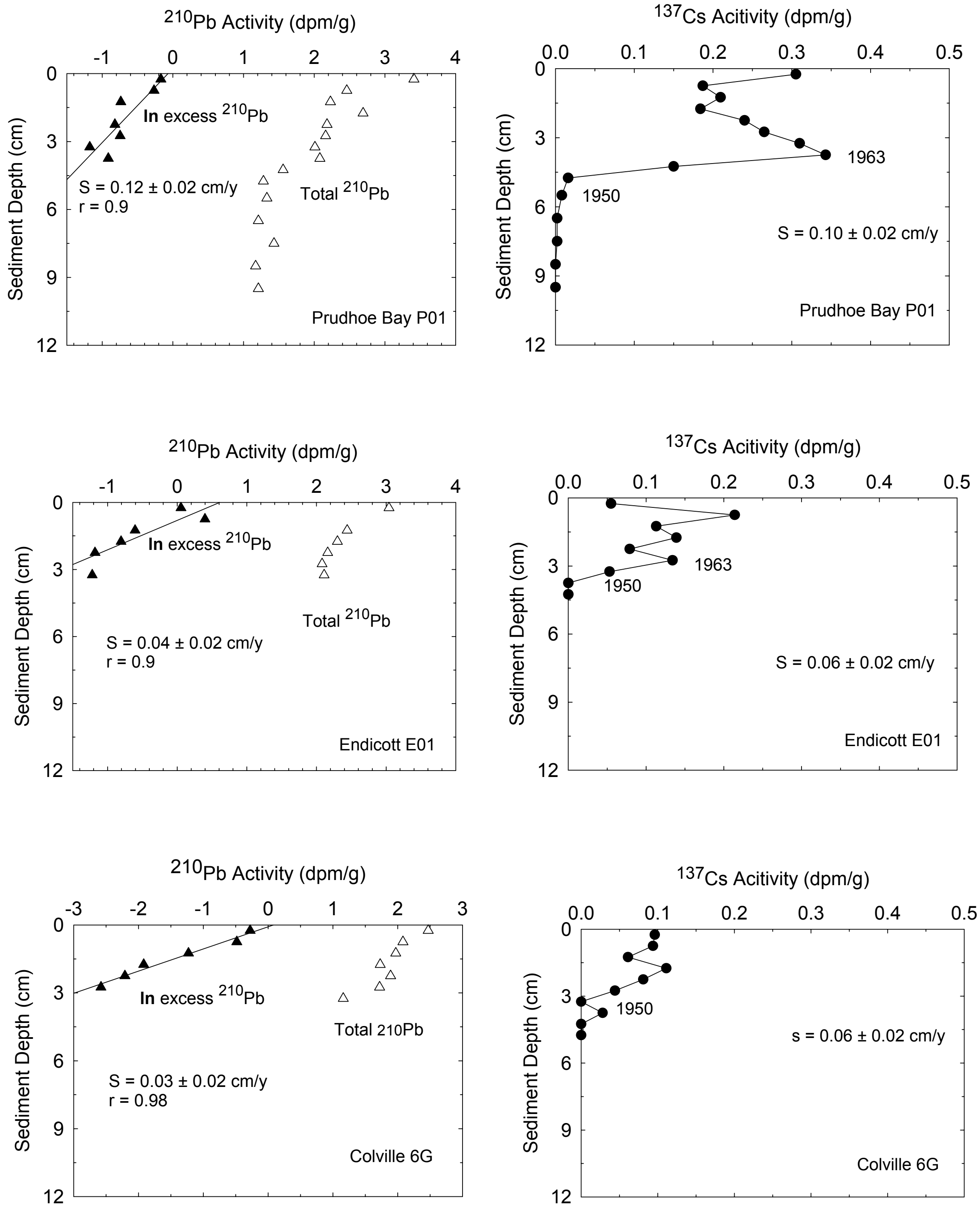


Figure 3-1. Vertical Profiles Showing Activities of Excess ^{210}Pb, Total ^{210}Pb, and ^{137}Cs for Sediment Cores from Stations P01 (Prudhoe Bay), E01 (East of Endicott Island) and 6G (Eastern Portion of Colville River Delta)

Sedimentation rates (S) and correlation coefficients (r) for linear regression line are shown for excess ^{210}Pb. Dates of 1950 and 1963 on ^{137}Cs plots identify the dates of initial input (1950) and maximum input (1963), respectively, of ^{137}Cs to the atmosphere from bomb testing.

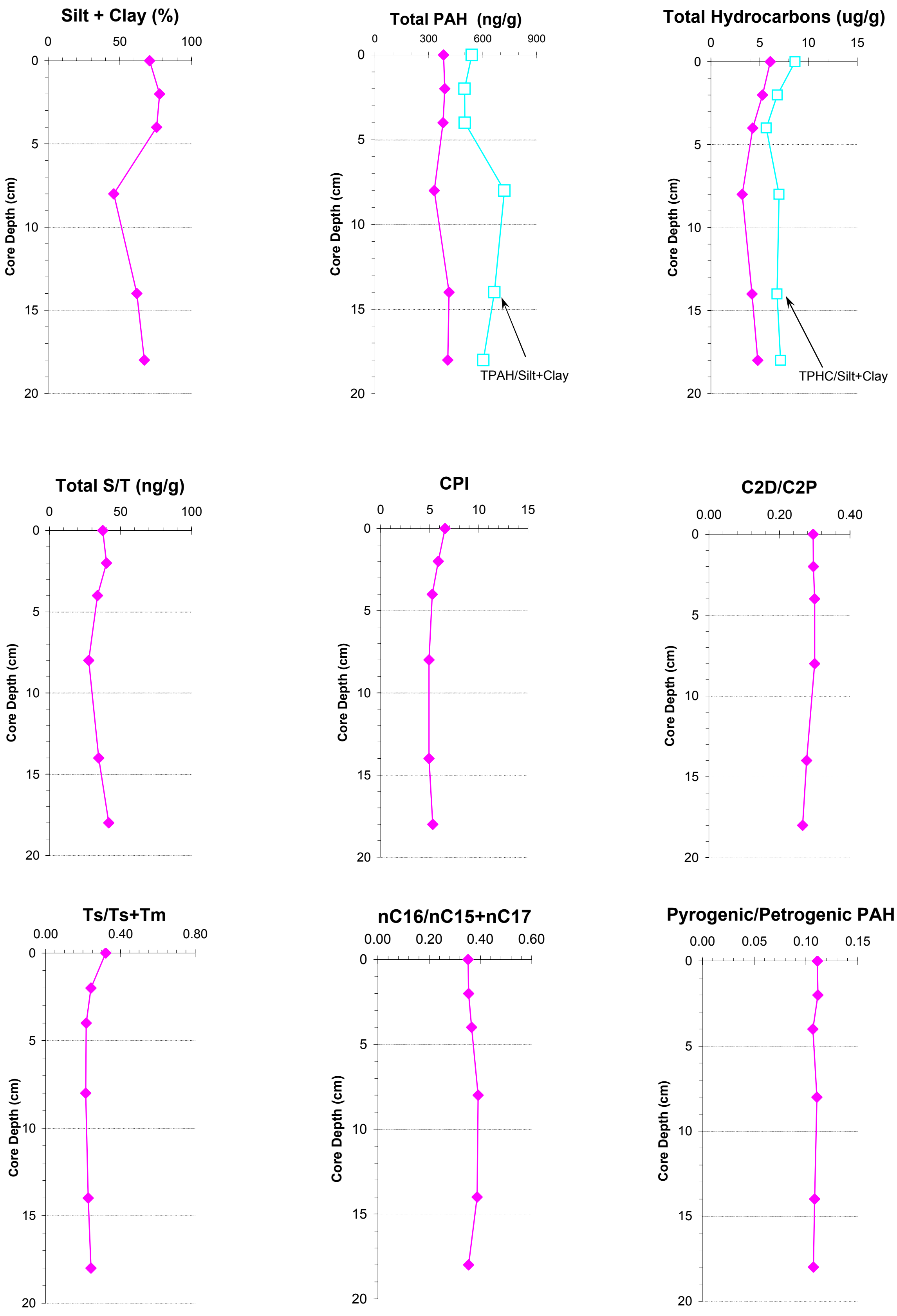


Figure 3-2. Vertical Profiles for Selected Organic Parameters in Sediment Core from Near Pole Island (Station 3A)

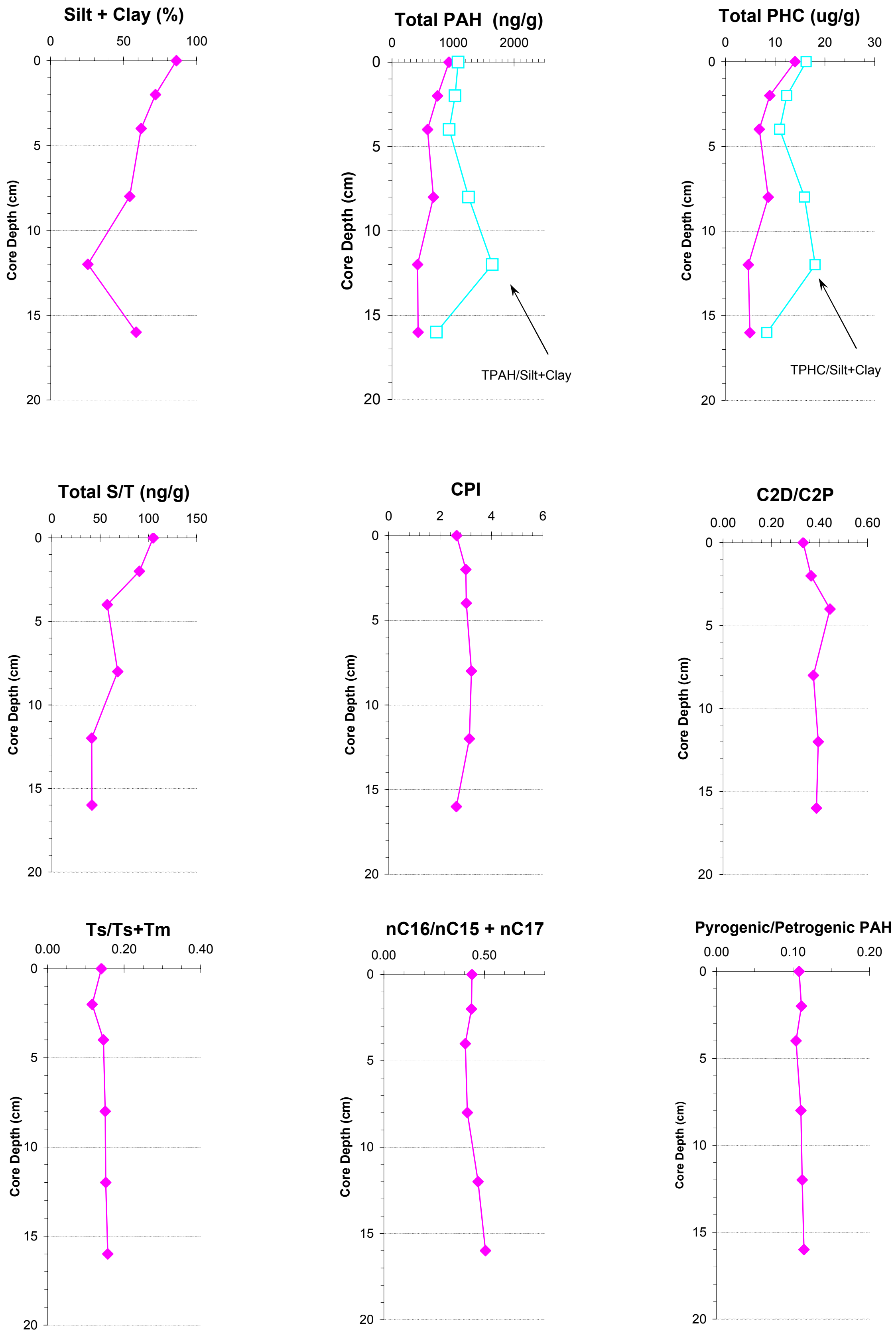


Figure 3-3. Vertical Profiles for Selected Organic Parameters in Sediment Core from near Colville River Delta (Station 6A)

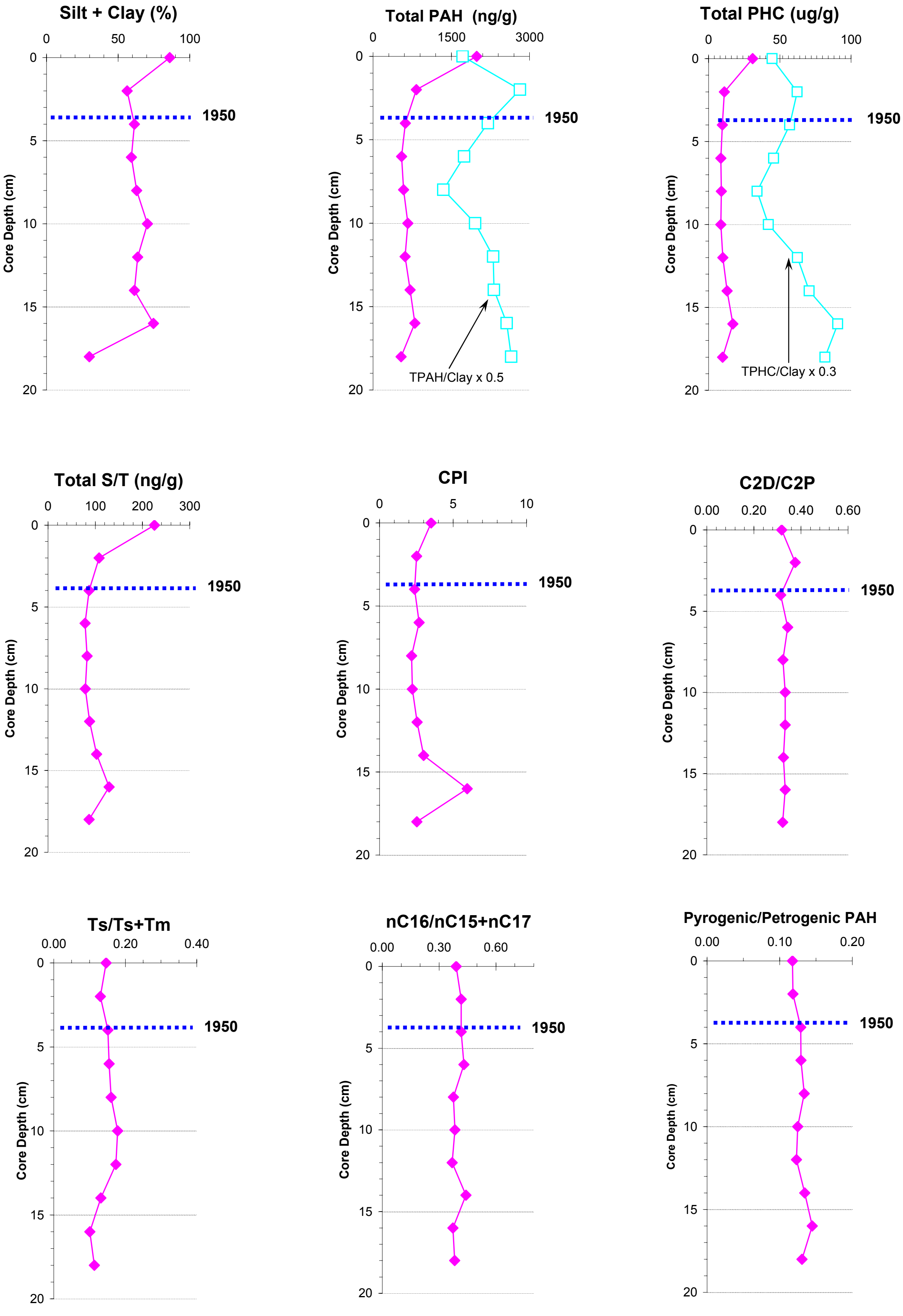


Figure 3-4. Vertical Profiles for Selected Organic Parameters in Sediment Core from Colville River Delta (Station 6G)

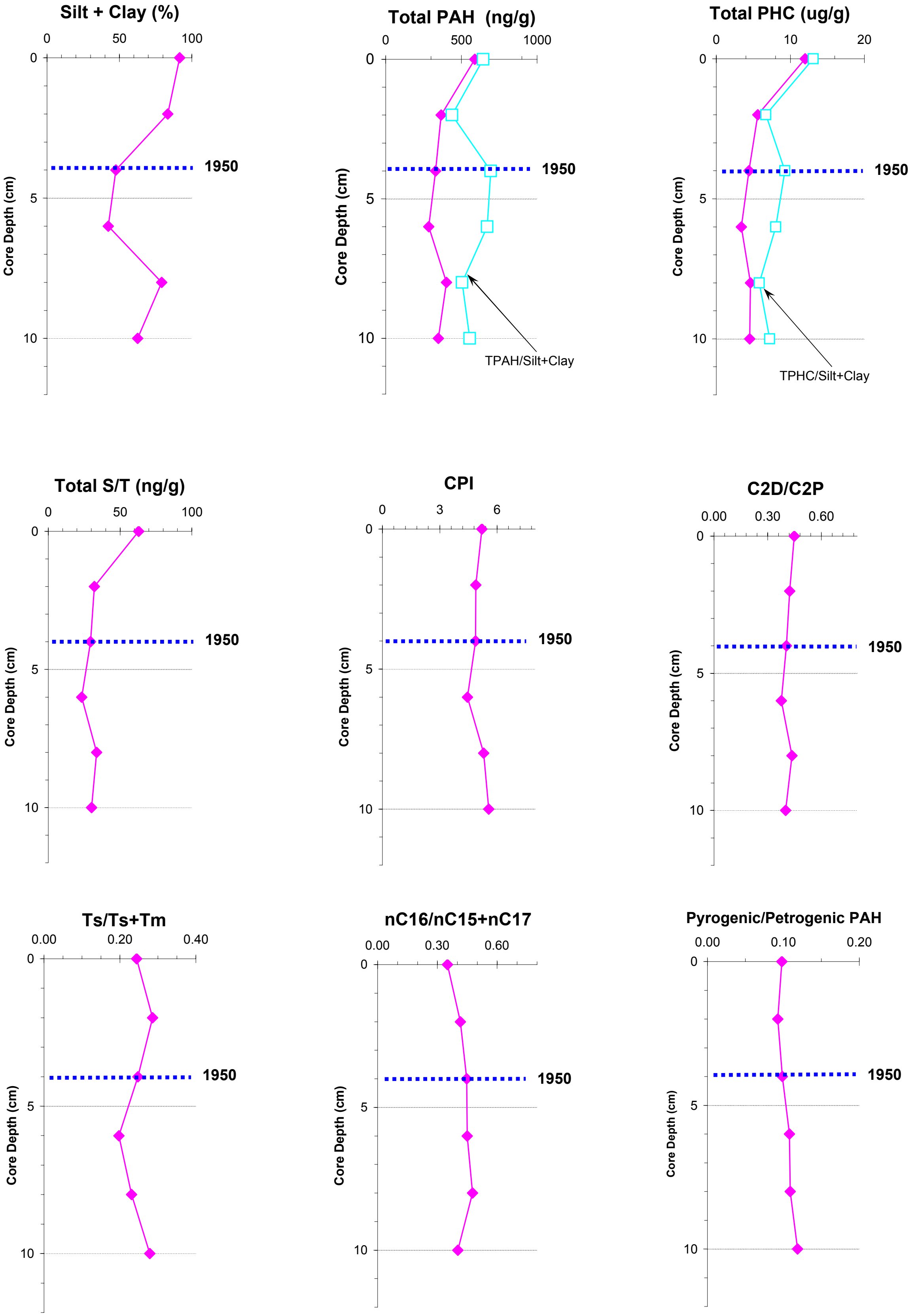


Figure 3-5. Vertical Profiles for Selected Organic Parameters in Sediment Core from near Endicott Island (Station E01)

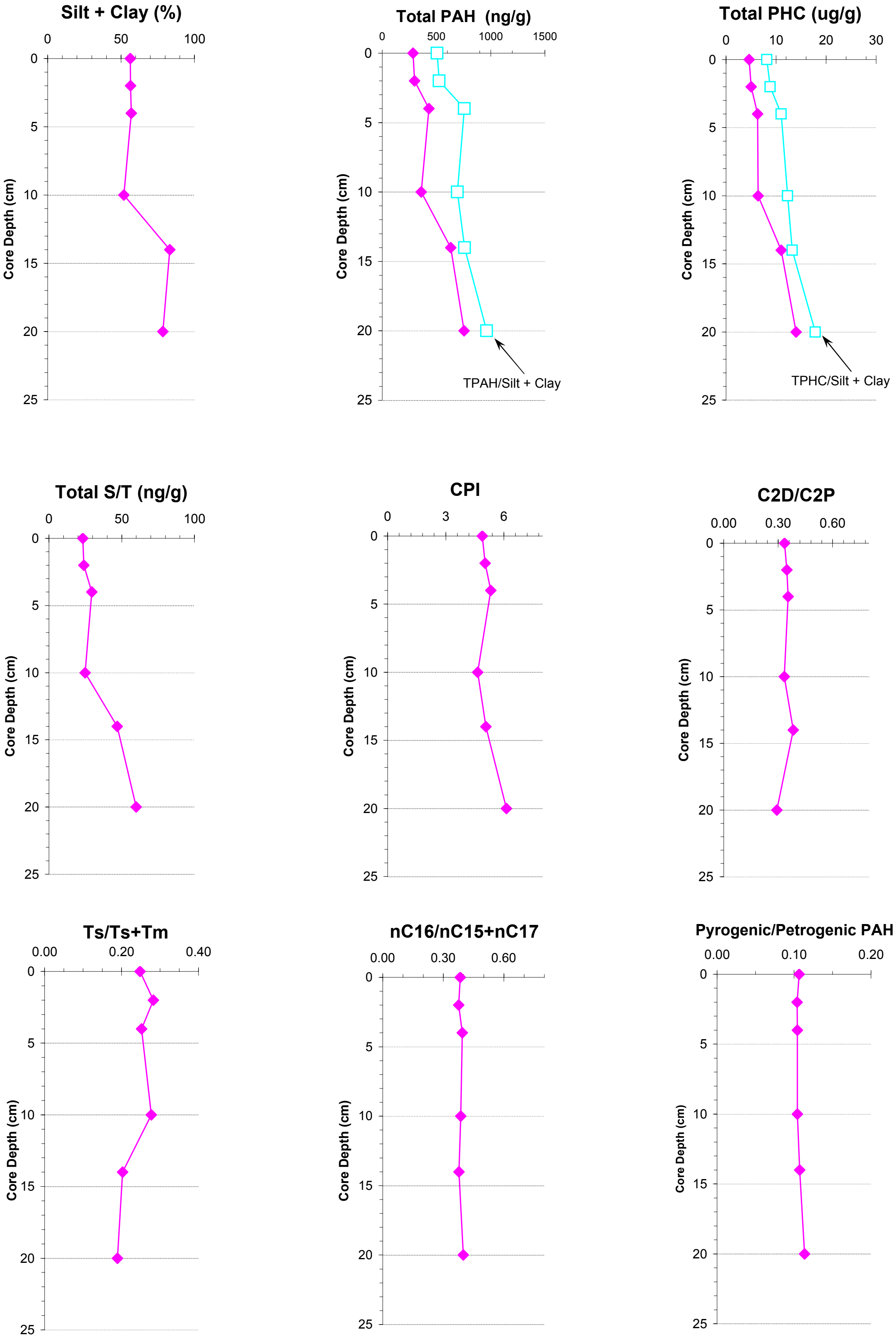


Figure 3-6. Vertical Profiles for Selected Organic Parameters in Sediment Core from Near Liberty Prospect (Station L02)

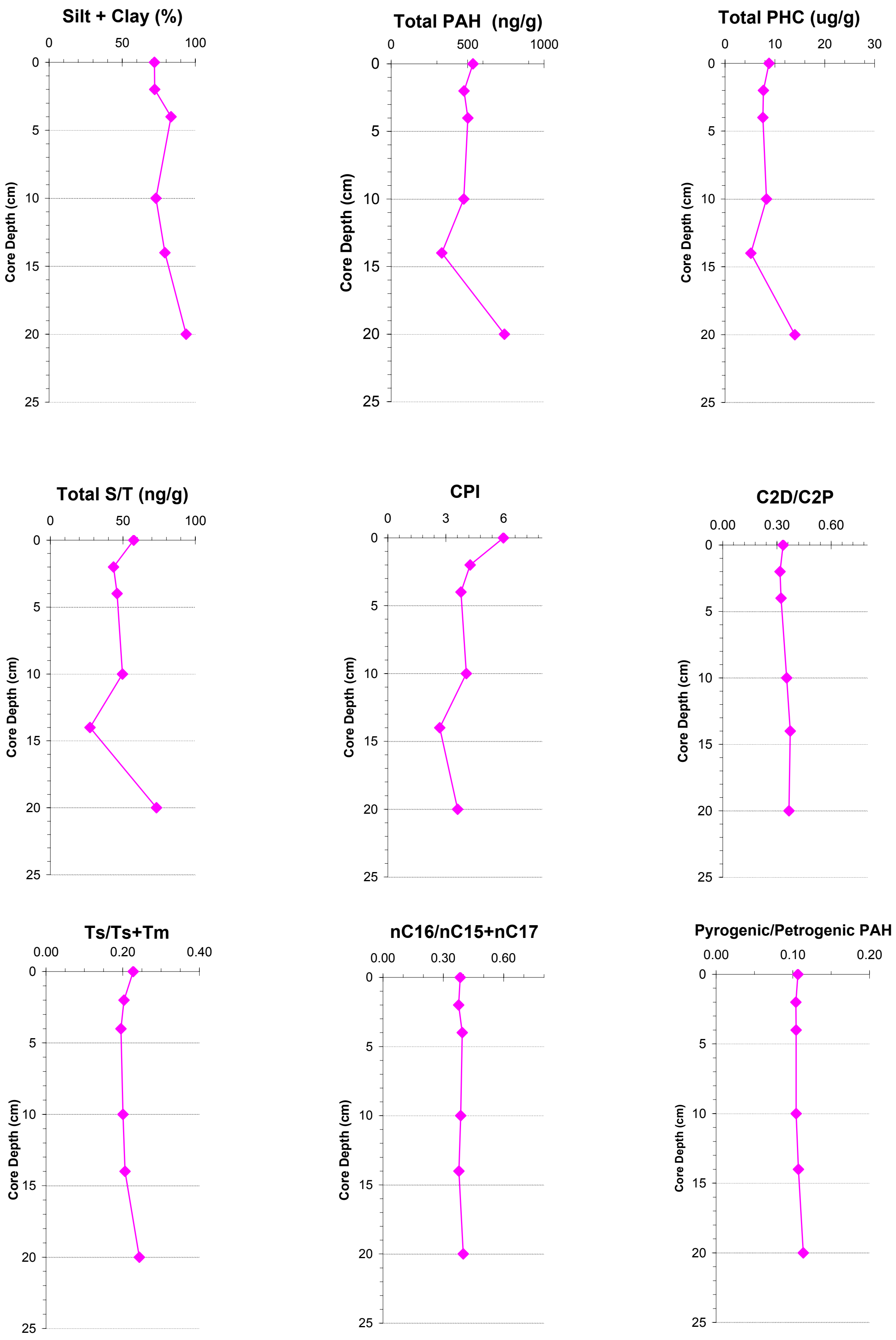


Figure 3-7. Vertical Profiles for Selected Organic Parameters in Sediment Core from Near Northstar Island (Station N02)

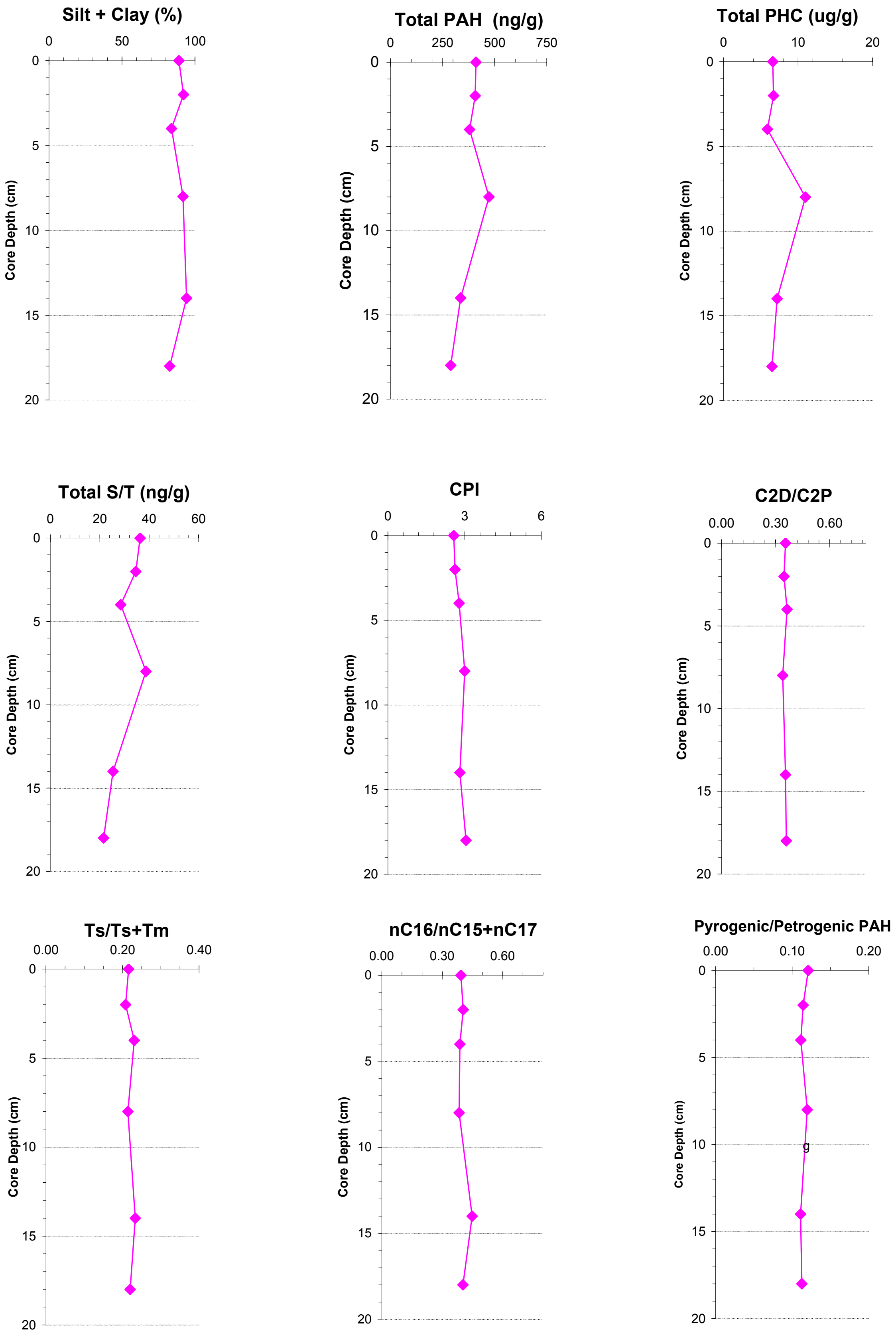


Figure 3-8. Vertical Profiles for Selected Organic Parameters in Sediment Core from Near Northstar Island (Station N03)

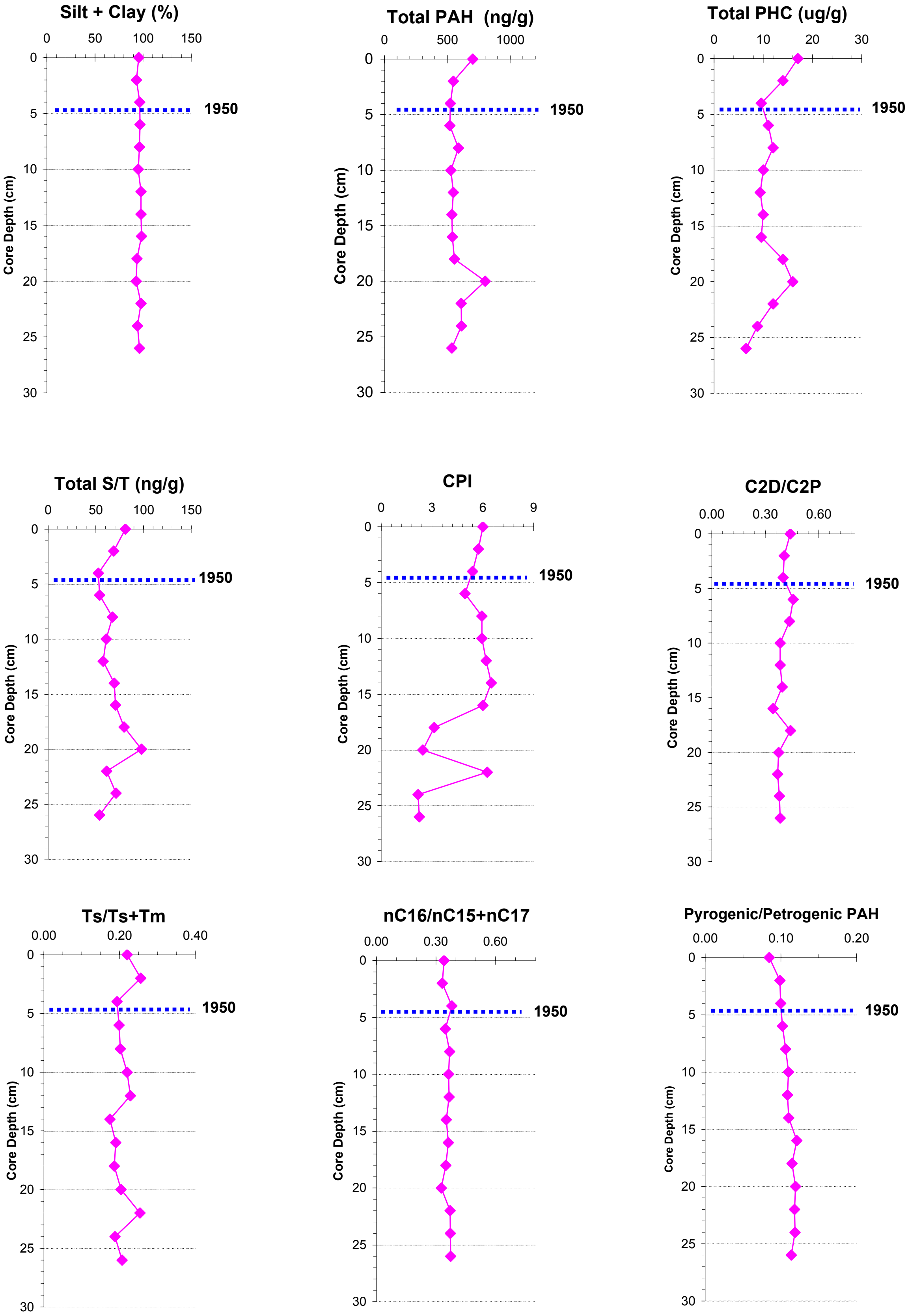


Figure 3-9. Vertical Profiles for Selected Organic Parameters in Sediment Core from Prudhoe Bay (Station P01)

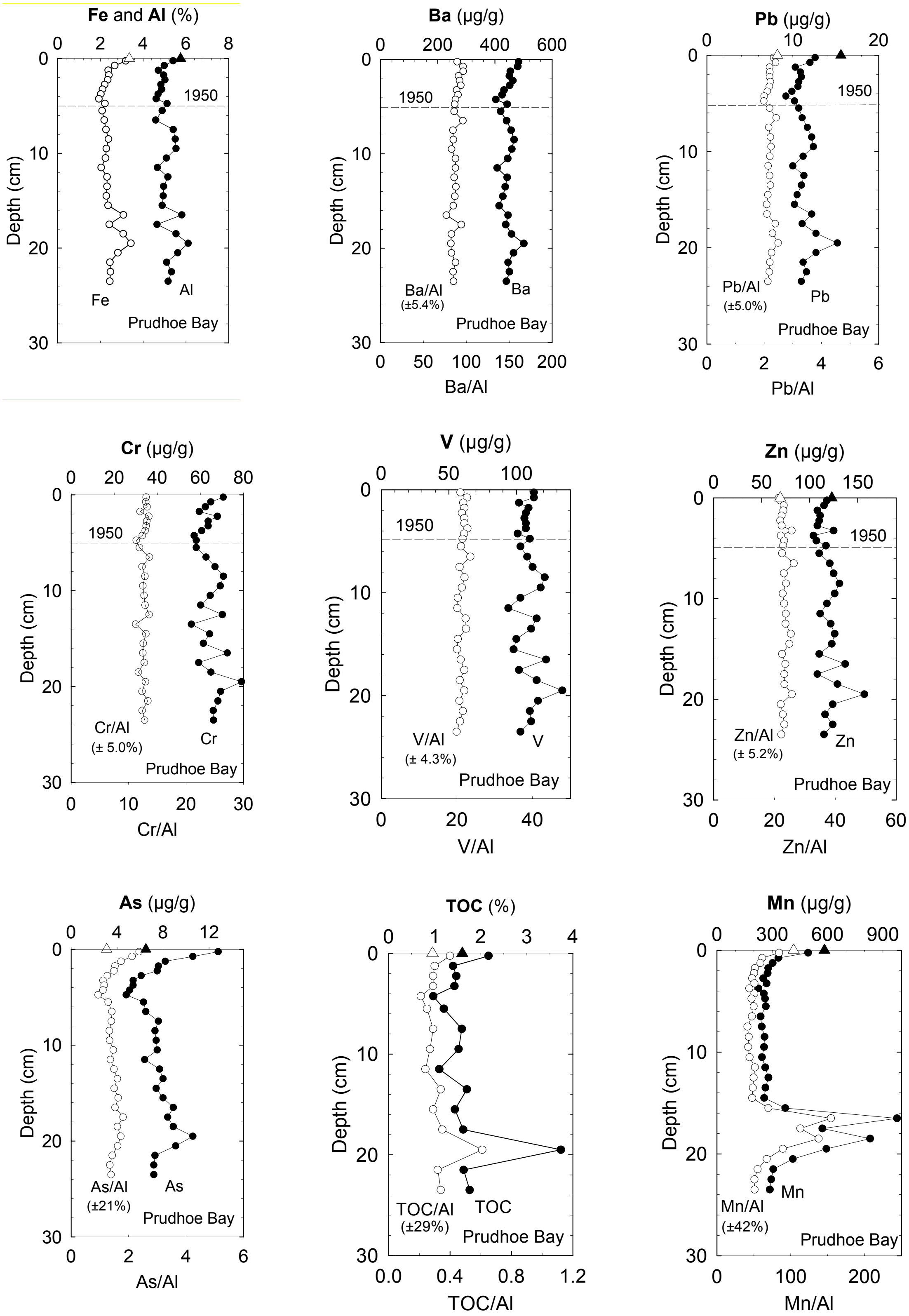


Figure 3-10. Vertical Profiles for Metals and Total Organic Carbon in Sediment Core from Prudhoe Bay (Station P01)

Triangles at top of some profiles show mean values for suspended sediment from the Sagavanirktok River. Numbers in parentheses give CV for metal/Al ratio. Graphs with no line for 1950 (As, TOC and Mn) lack geochronological significance due post-depositional diagenesis/diffusion.

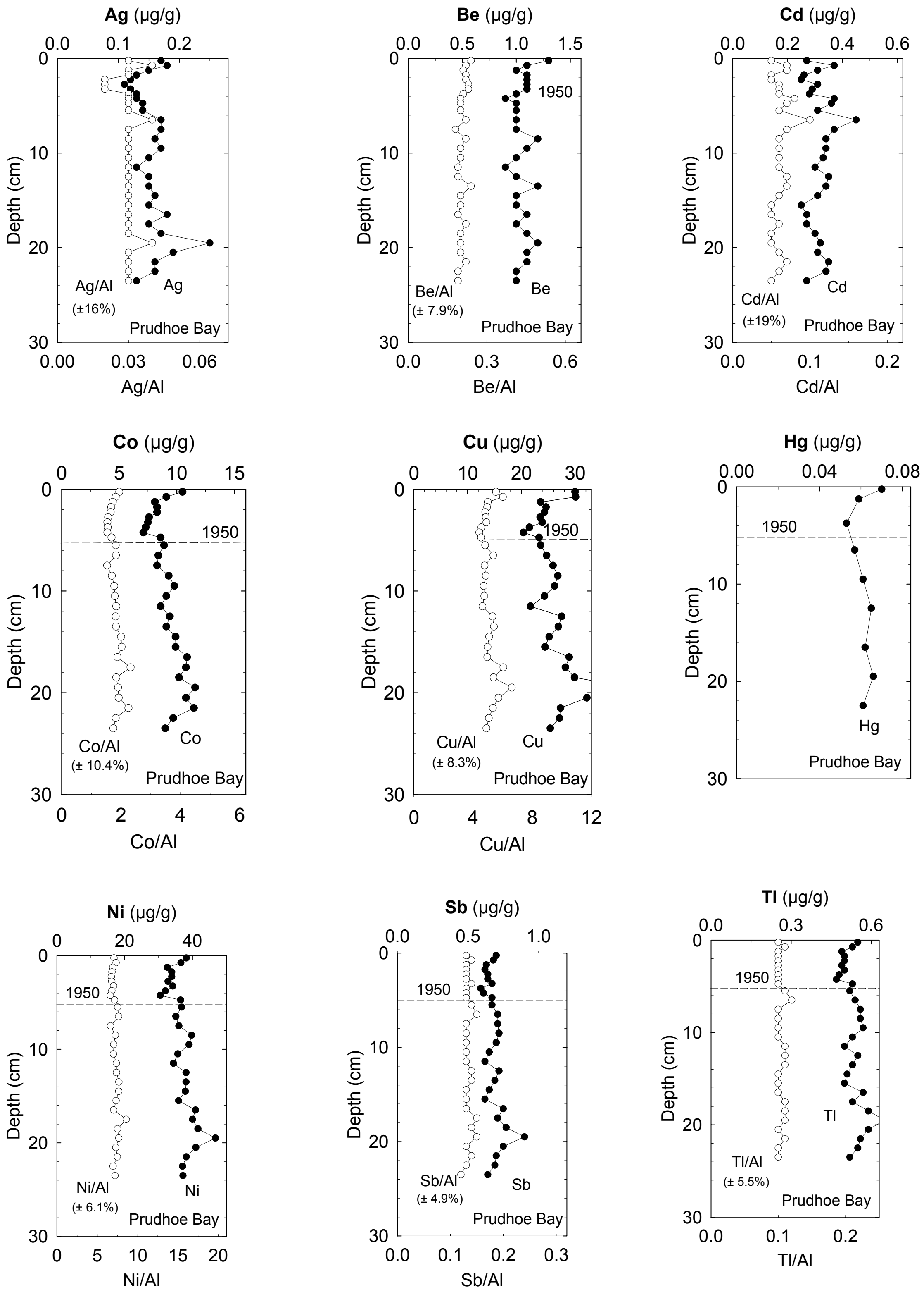


Figure 3-11. Vertical Profiles for Metals in Sediment Core from Prudhoe Bay (Station P01)

Triangles at top of some profiles show mean values for suspended sediment from the Sagavanirktok River. Numbers in parentheses give CV for metal/Al ratio. Graphs with no line for 1950 lack geochronological significance due post-depositional diagenesis/diffusion (Cd) or large variability due to low concentrations (Ag).

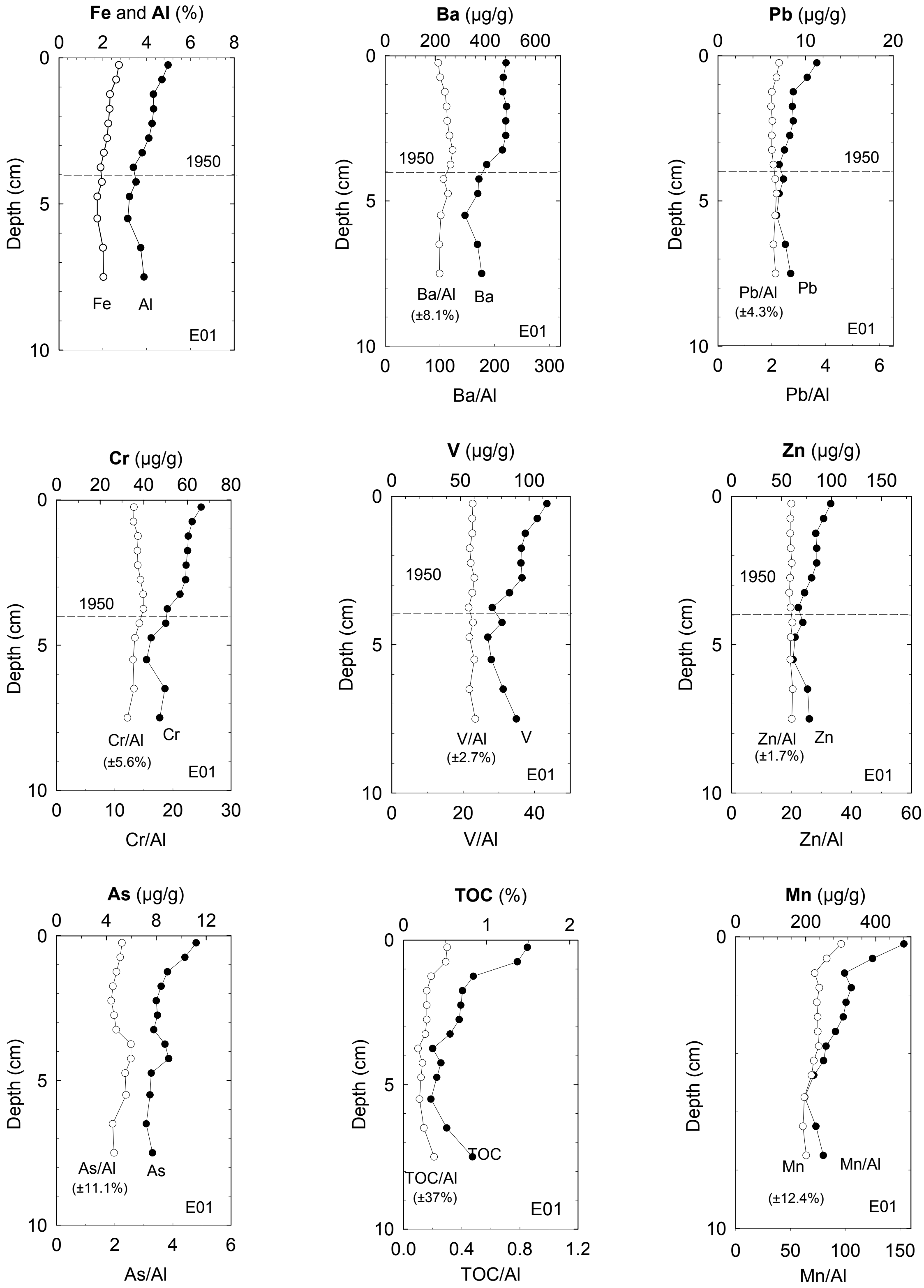


Figure 3-12. Vertical Profiles for Metals and Total Organic Carbon in Sediment Core from Near Endicott Island (Station E01)

Numbers in parentheses give CV for metal/Al ratio. Graphs with no line for 1950 (As, TOC and Mn) lack geochronological significance due post-depositional diagenesis/diffusion.

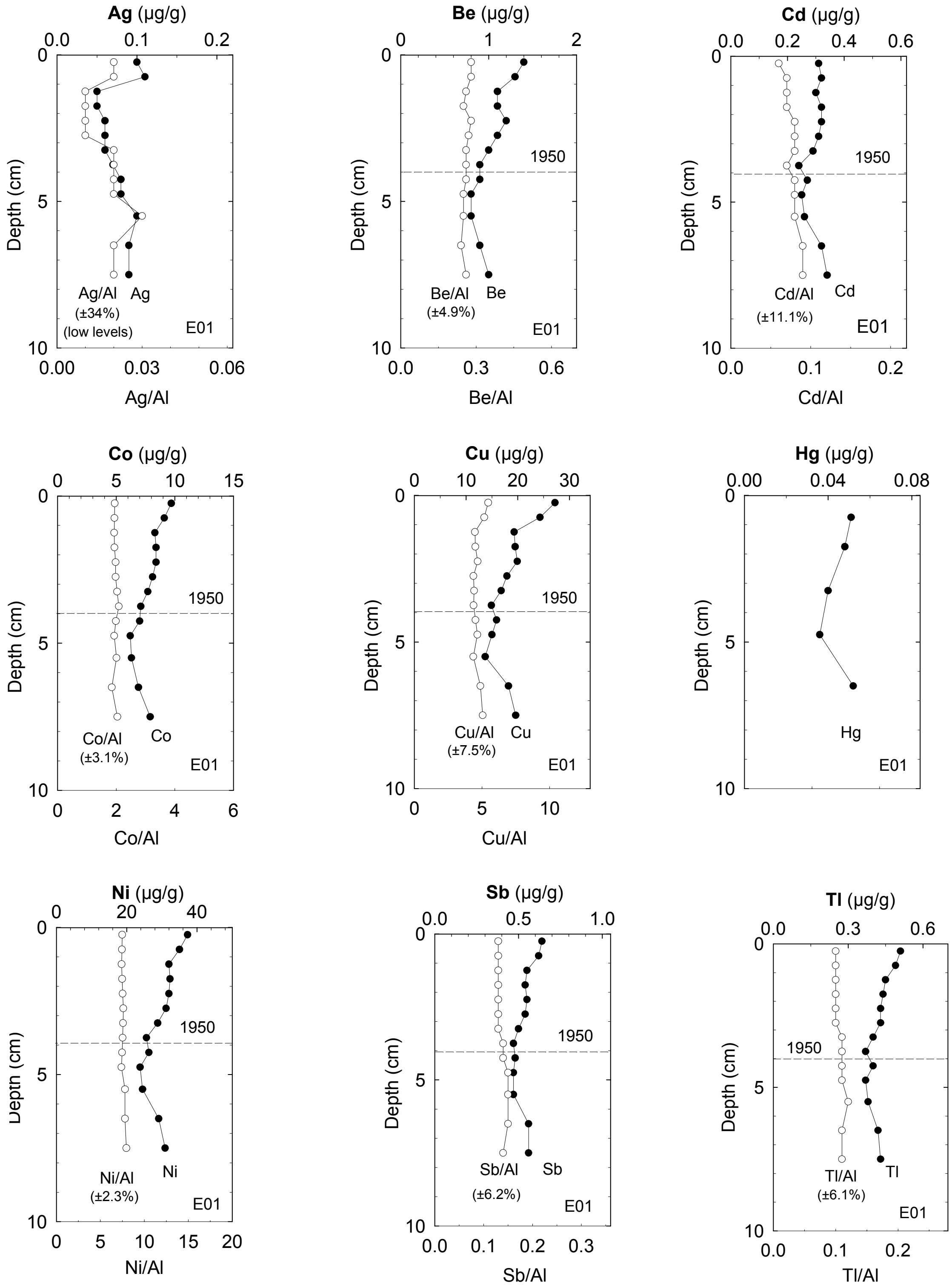


Figure 3-13. Vertical Profiles for Metals in Sediment Core from Near Endicott Island (Station E01)

Numbers in parentheses give CV for metal/Al ratio. Graphs with no line for 1950 lack geochronological significance due to large variability due to low concentrations (Ag) or inexact matches with depth for Al values (Hg).

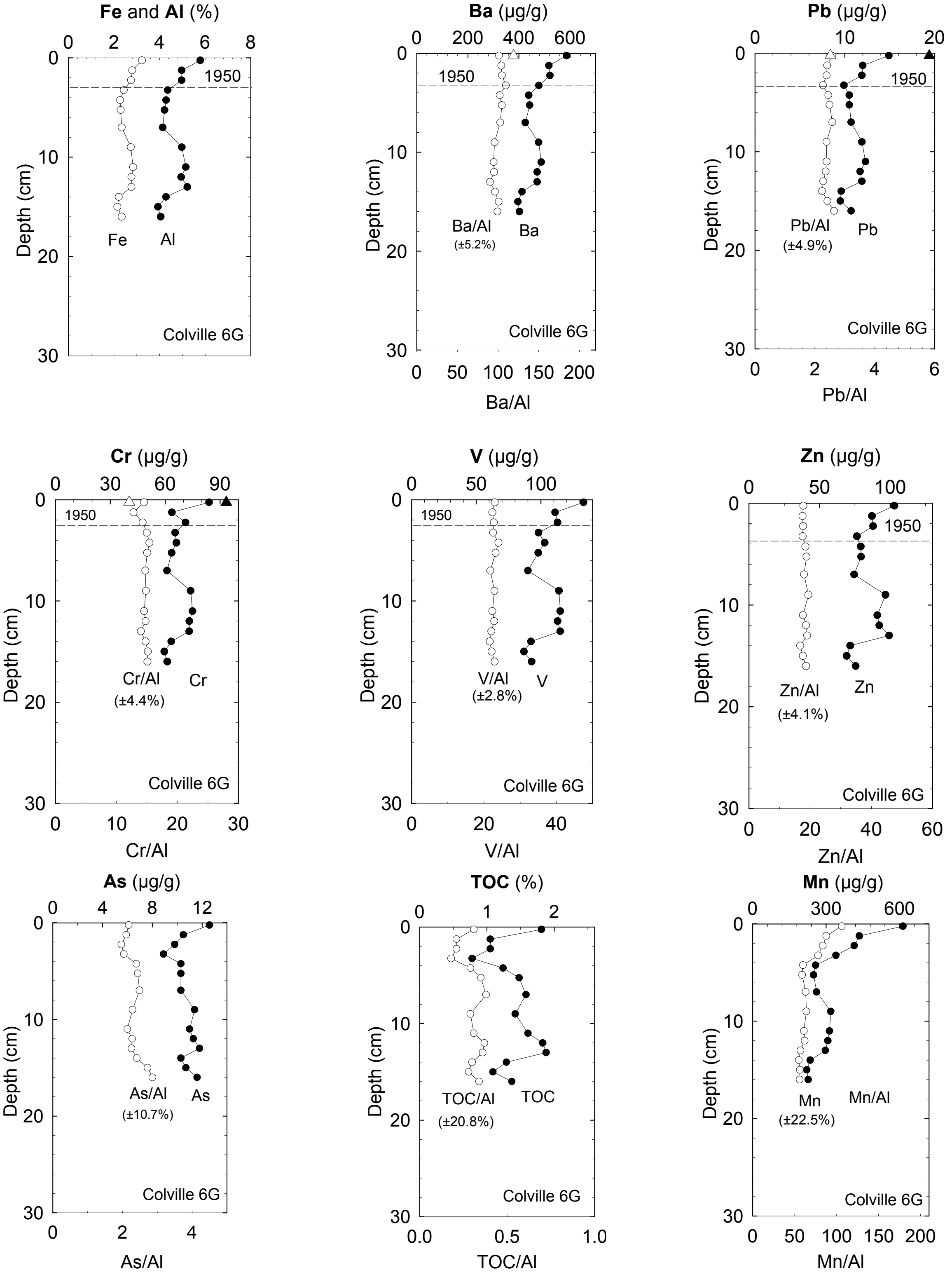


Figure 3-14. Vertical Profiles for Metals and Total Organic Carbon in Sediment Core from Colville River Delta (Station 6G)

Triangles at top of some profiles show mean values for suspended sediment from the Colville River. Numbers in parentheses give CV for metal/Al ratio. Graphs with no line for 1950 (As, TOC and Mn) lack geochronological significance due post-depositional diagenesis/diffusion.

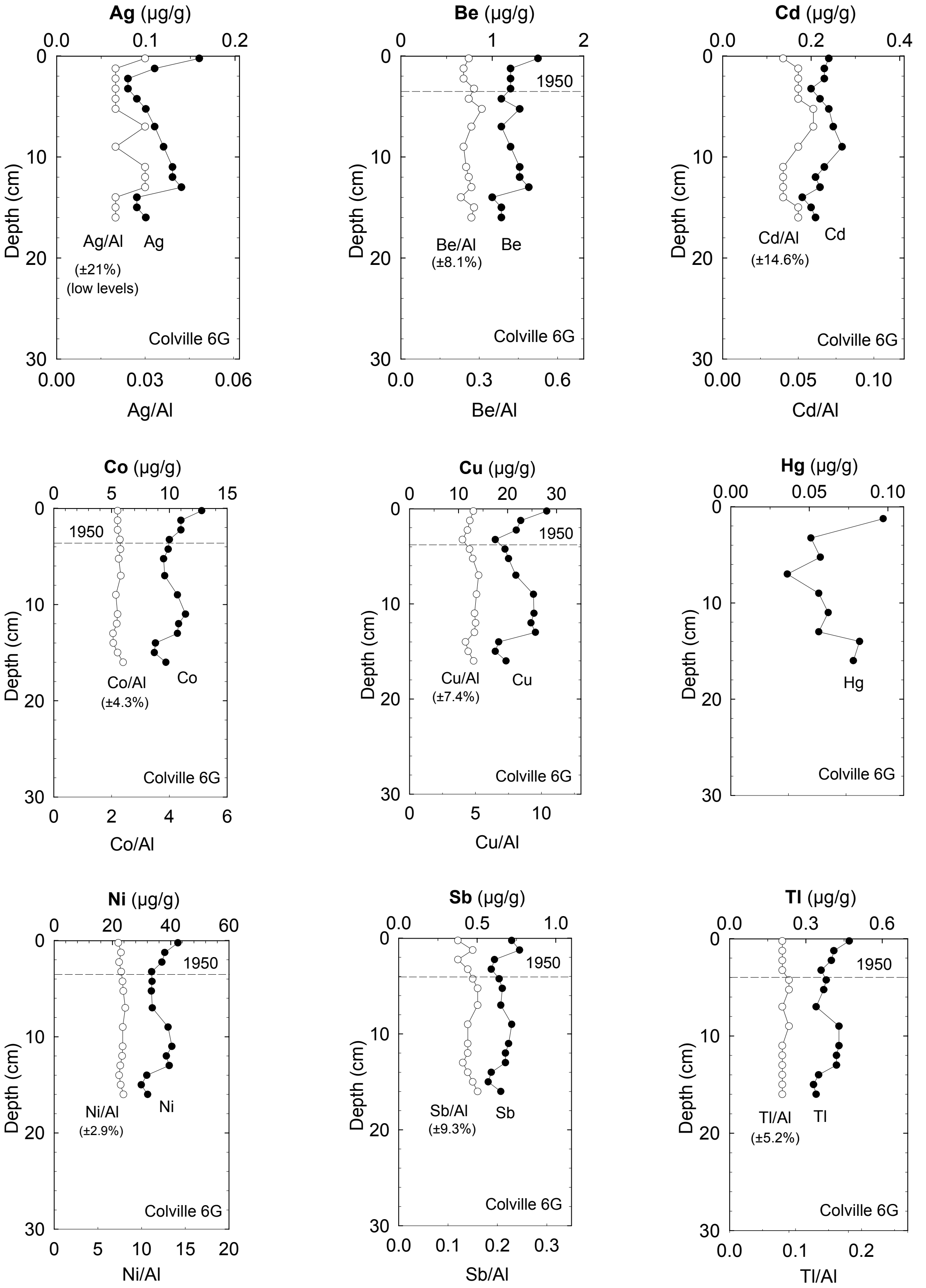


Figure 3-15. Vertical Profiles for Metals in Sediment Core from Colville River Delta (Station 6G)

Triangles at top of some profiles show mean values for suspended sediment from the Colville River. Numbers in parentheses give CV for metal/Al ratio. Graphs with no line for 1950 lack geochronological significance due large variability due to low concentrations (Ag), inexact matches with depth for Al values (Hg) or post-depositional diagenesis/diffusion (Cd).

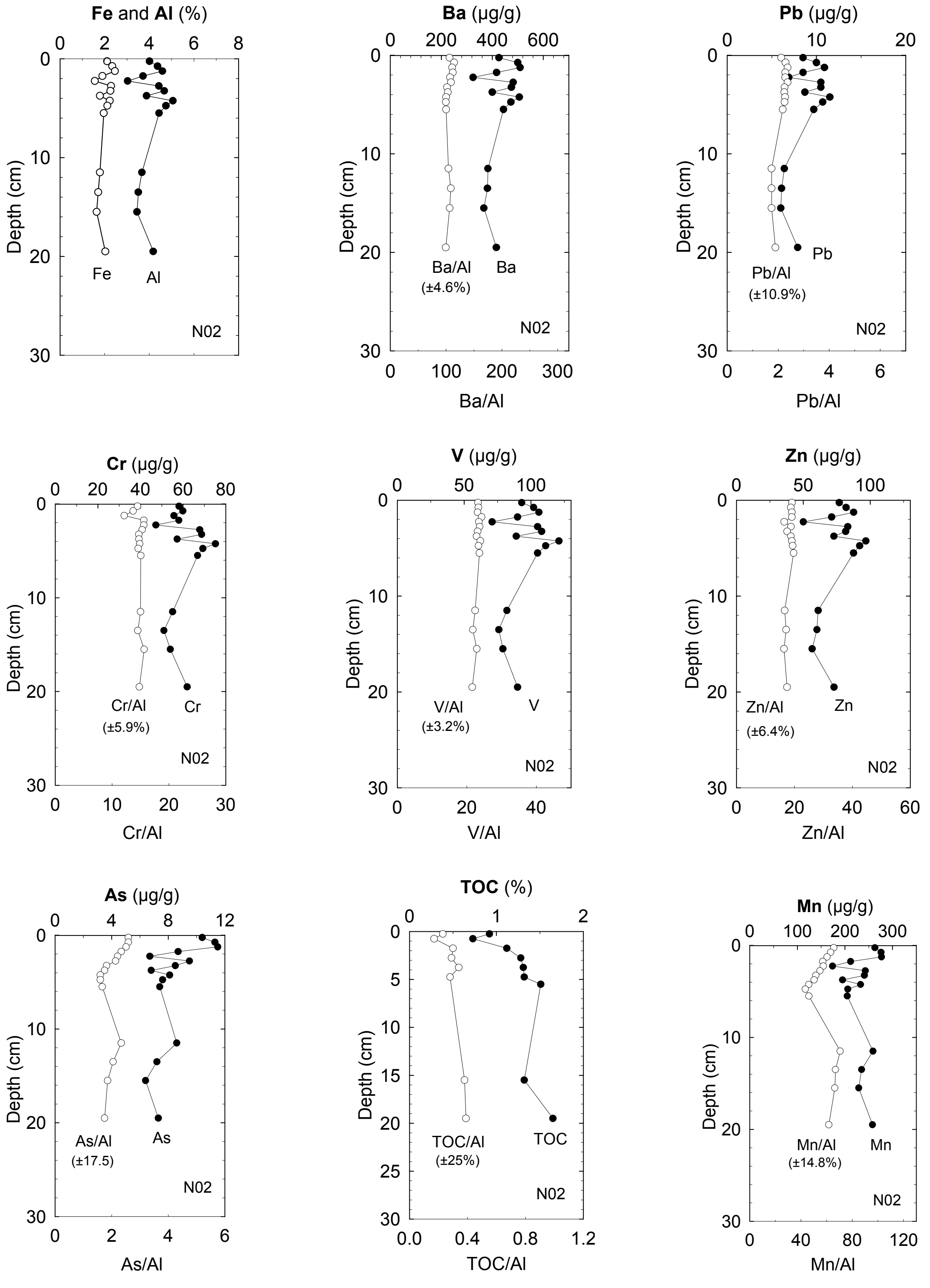


Figure 3-16. Vertical Profiles for Metals and Total Organic Carbon in Sediment Core from Near Northstar Island (Station N02)

Numbers in parentheses give CV for metal/Al ratio.

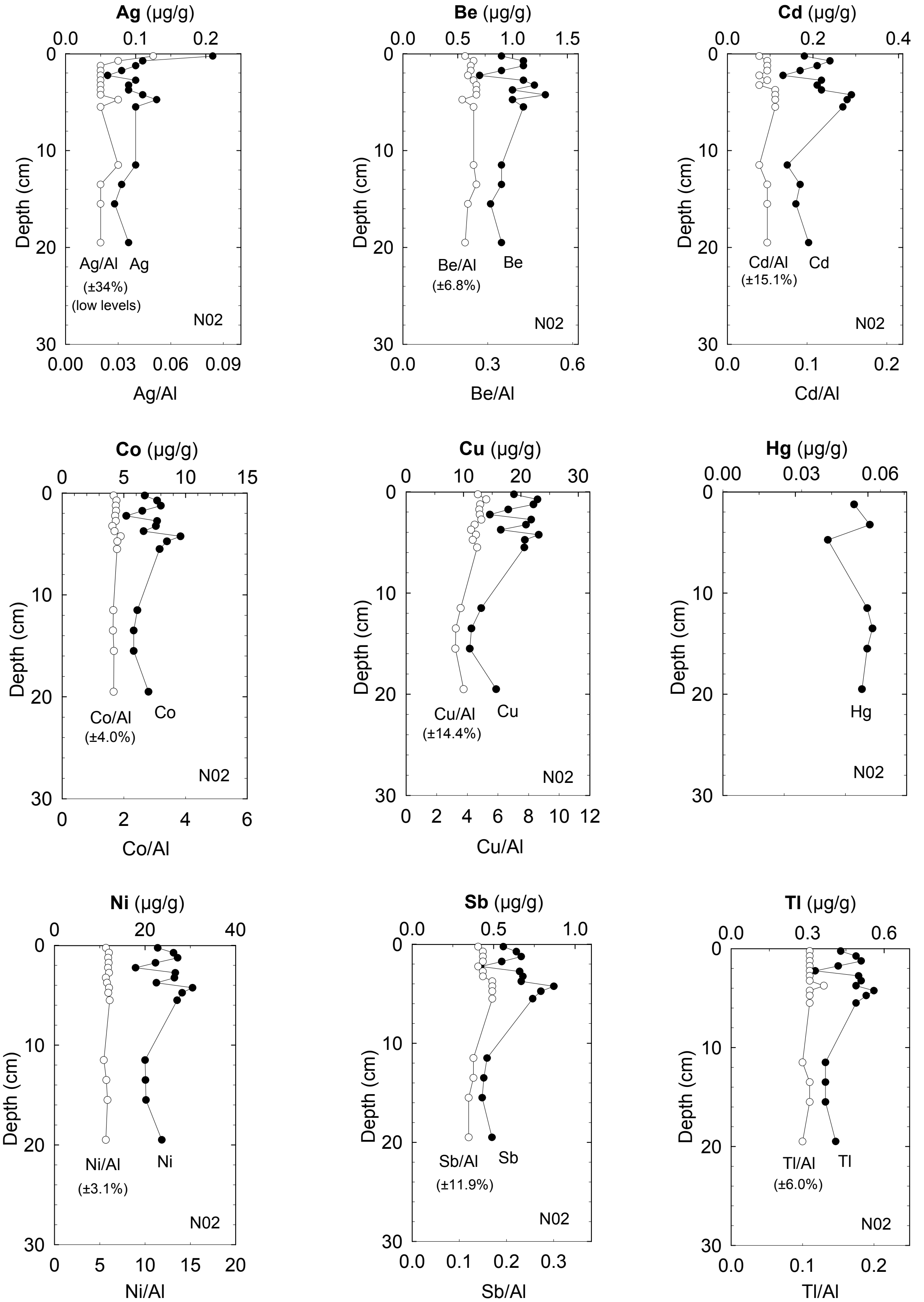


Figure 3-17. Vertical Profiles for Metals in Sediment Core from Near Northstar Island (Station N02)

Numbers in parentheses give CV for metal/Al ratio.

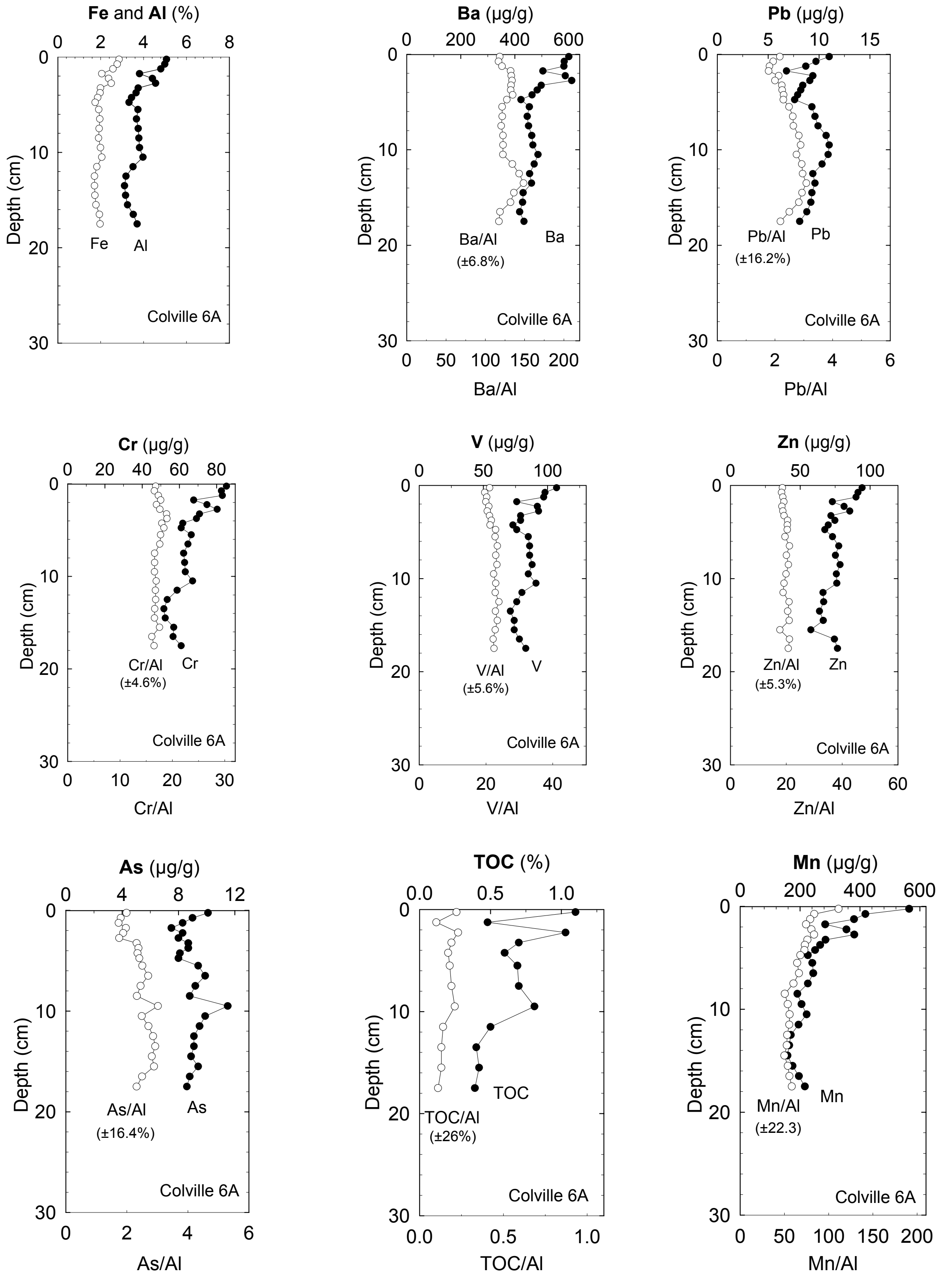


Figure 3-18. Vertical Profiles for Metals and Total Organic Carbon in Sediment Core from Near Colville River Delta (Station 6A)

Numbers in parentheses give CV for metal/Al ratio.

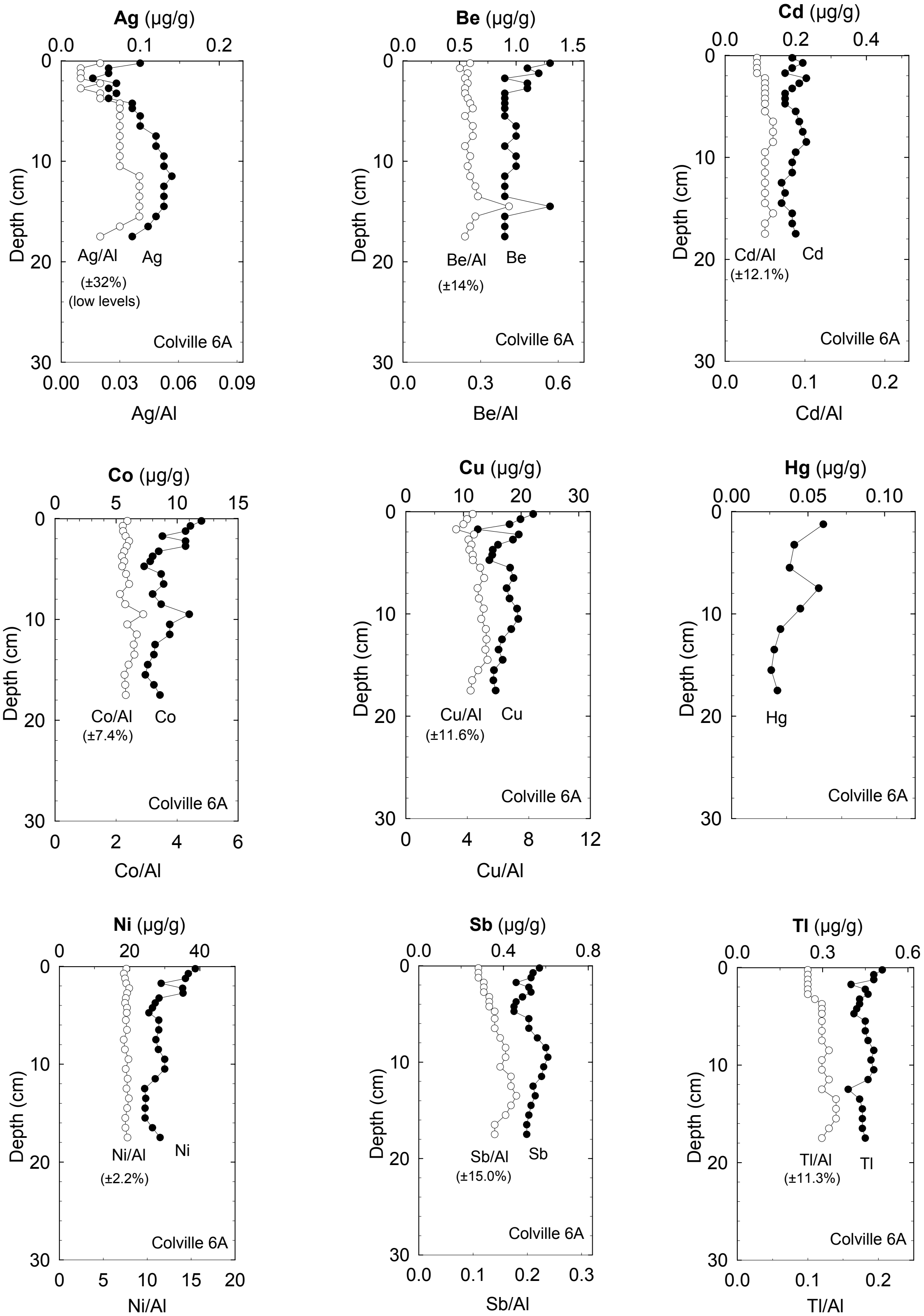


Figure 3-19. Vertical Profiles for Metals in Sediment Core from Near Colville River Delta (Station 6A)

Numbers in parentheses give CV for metal/Al ratio.

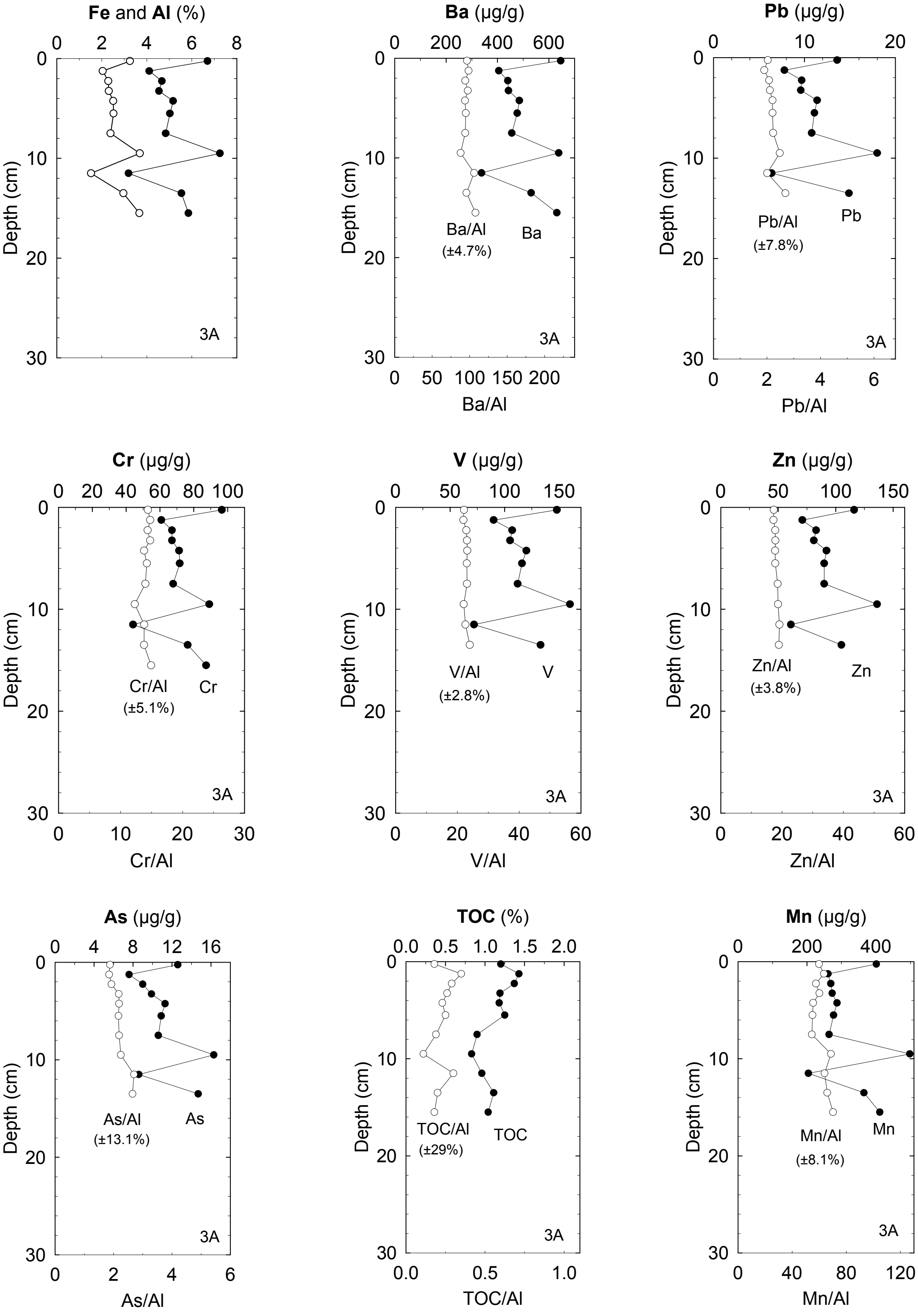


Figure 3-20. Vertical Profiles for Metals and Total Organic Carbon in Sediment Core from Near Pole Island (Station 3A)

Numbers in parentheses give CV for metal/Al ratio.

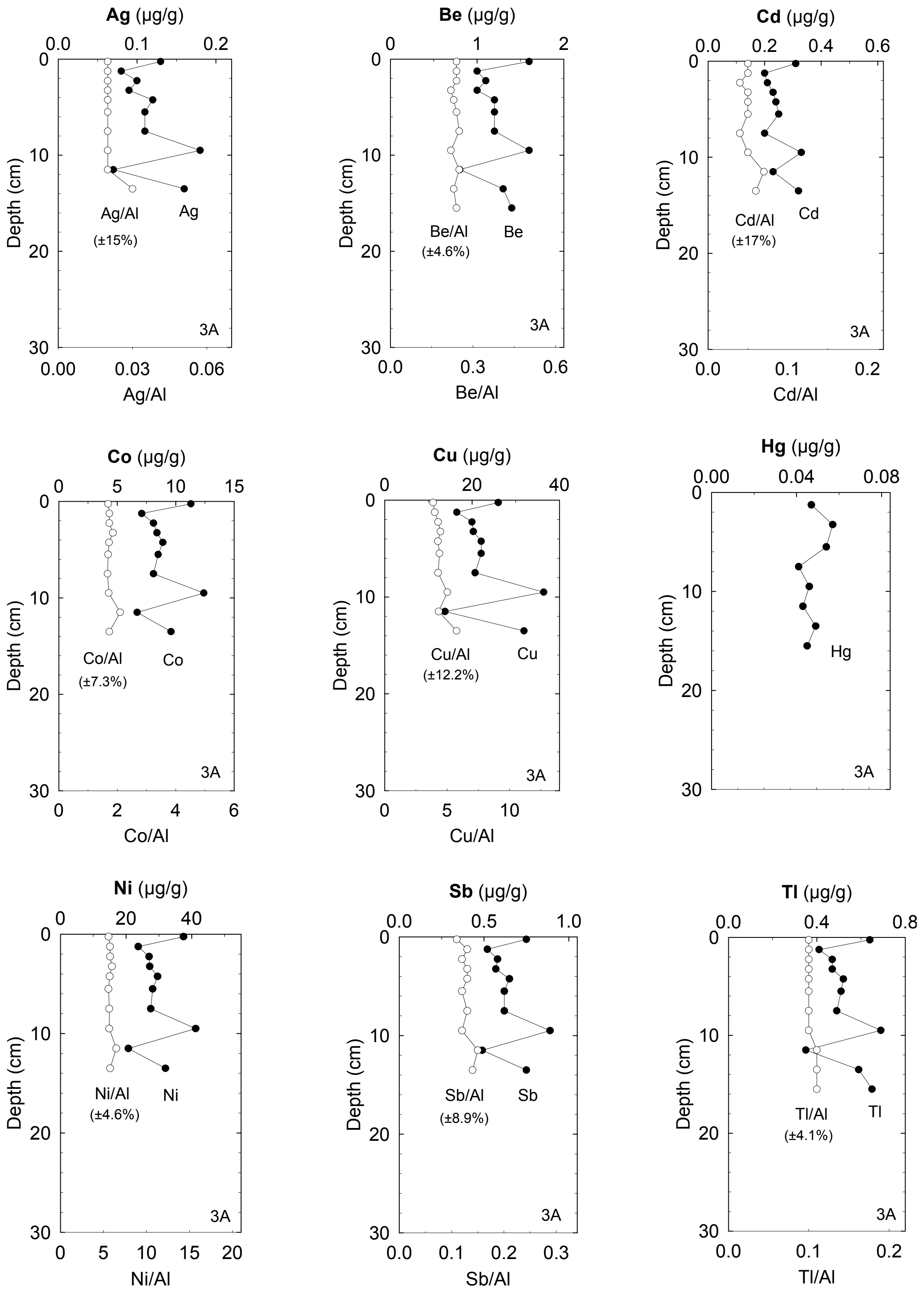


Figure 3-21. Vertical Profiles for Metals in Sediment Core from Near Pole Island (Station 3A)

Numbers in parentheses give CV for metal/Al ratio.

4.0 Discussion

The summer 2001 field sampling program successfully obtained core samples suitable for age dating from eight stations. Of the eight cores, reliable and detailed results for geochronology were obtained for three stations: 1) station P01 in Prudhoe Bay, 2) station E01, just east of the Endicott development near the mouth of the Sagavanirktok River, and 3) station 6G near the eastern area of the Colville River delta (Figure 2-1). In this section of the report the results of the sediment core analyses for these three stations, as well as the others, will be further evaluated for general trends and relationships, and comparisons of the pre- and post-development results will be discussed.

4.1 Geochronology

Previous efforts to reconstruct recent geochronology for coastal sediment from this nearshore area of the Beaufort Sea (Weiss and Naidu, 1986; Naidu et al., 2001) have encountered many of the same difficulties reported by us in Section 3. Weiss and Naidu (1986) used vertical profiles for the activity of total ^{210}Pb to calculate sedimentation rates of 0.6 to 1 cm/year at sites in Simpson Lagoon, near our stations 6A and 6G; however, the total activities for ^{210}Pb averaged <2 dpm/g with variable texture in each core. In recent work, Naidu et al. (2001) reported no excess ^{210}Pb and no detectable ^{137}Cs in a core from Simpson Lagoon. However, Naidu et al. (2001) reported excess ^{210}Pb levels of 0.9 to 1.2 dpm/g and ^{137}Cs activities of 0.2 dpm/g at a site near our station 3B. Based on inherent difficulties with area sediments, a primary goal of our geochronology effort was to collect some sediment that was deposited prior to the onset of development during the late 1960s and some sediment that was deposited post-development.

Our results show sedimentation rates that range from ~0.04 cm/year to ~0.10 cm/year, with several sites having little or no net accumulation of sediment during at least the past 50 years. At three sites, we identify 3- to 5-cm thick layers of sediment that were deposited since development began (approximately 1970). Our overall results are consistent with those of Naidu et al. (2001) for the same area. We know from our previous work that the presence of fine-grained sediment at a given location can vary from year to year and that the sediments along much of the shallow, coastal Beaufort Sea are quite dynamic.

Additional support for low sedimentation rates at stations P01 and E01 can be developed from data for river inputs of sediment. The Sagavanirktok River, the major river carrying sediment into this area, is estimated to have an annual sediment load of about 6 x 10^5 metric tons. The depositional area for this sediment in coastal Beaufort Sea is about 1000 km^2 (the approximate area bounded by the mainland to the south, the outer islands such as Cross Island to the north, and between 147.0° N and 148.5° W) to yield an estimated deposition rate of ~0.04 cm/year based on a sediment bulk density of 1.6 g/cm^3 ([0.6 x 10^{12} g dry sediment/10 x 10^{12} cm^2] x [(1.6 g wet sediment/cm$^{3)}$/(2.6 g dry sediment/cm^3)]). As previously noted, however, the coastal Beaufort Sea in this area may be net erosional at this time (Reimnitz and Wolf, 1998).

Despite difficulties in determining sedimentation rates, we now have sediment samples that we know pre-date and post-date development. We also have surface sediments from 1989, 1999, 2000, and 2002 cores that will be used in the final report to complete the analysis of any recent trends in deposition of potential contaminants.

4.1.1 Geochronology of Hydrocarbons

The hydrocarbon dataset for the core sediments from 2001 includes SHC, PAH, and S/T data from all eight core samples collected. As noted previously, three of the cores have reliable deposition rates and detailed geochronology. The remaining five cores were all analyzed for organic parameters to further expand our knowledge of the historical record of hydrocarbons in the study area. Even though we cannot accurately estimate the historical timeframe of these sediments, we do know that they primarily represent pre-development (i.e., pre-1970) sediment levels and are likely much older. These data are assessed in part by using a suite of key diagnostic parameters and ratios (Table 3-2) that are useful in describing hydrocarbon trends in the marine environmental (Boehm et al., 2001a; Brown et al., 2002). 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) geochronology of hydrocarbons (comparisons over time), and 3) comparisons to sediment quality benchmarks or "guidelines."

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 (EICPs) for representative samples from the core samples and selected source samples are presented in Figures 4-1 through 4-11. The samples selected for presentation are as follows:

- North Slope Crude Oil – composite pipeline sample (Figure 4-1)
- Colville River Sediment, Year 1999 - (Figure 4-2)
- Sediment Core P01 – 0- to 2-cm interval (Figure 4-3)
- Sediment Core P01 – 24- to 26-cm interval (Figure 4-4)
- Sediment Core 6G – 0- to 2-cm interval (Figure 4-5)
- Sediment Core 6G – 16- to 18-cm interval (Figure 4-6)
- Sediment Core 3A – 0- to 2-cm interval (Figure 4-7)
- Sediment Core E01 – 0- to 2-cm interval (Figure 4-8)
- Sediment Core L02 – 0- to 2-cm interval (Figure 4-9)
- Sediment Core N02 – 0- to 2-cm interval (Figure 4-10)
- Sediment Core 6A – 0- to 2-cm interval (Figure 4-11)

Saturated Hydrocarbons

In general, the sediments in the core samples (GC/FID chromatograms in Figures 4-3 through 4-11) exhibit a mixture of primarily terrestrial biogenic hydrocarbons and lower levels of petroleum hydrocarbons (Figure 4-1 shows a North Slope Crude Oil for 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 2.18 to 6.5 for most samples, which is characteristic of sediments influenced by terrigenous plant inputs (Wakeham and Carpenter, 1976; Boehm, 1984).

Traces of lower molecular weight alkanes (LALK; n-C9 through n-C20 alkanes), indicative of petroleum sources, are visible as more minor components relative to the plant wax alkanes in the core sediments and in the Colville River sample for comparison (Figures 4-2 through 4-11). This natural "background" petroleum alkane signature in the sediments has been well documented by previous studies in the region, including earlier ANIMIDA work (Boehm et al., 1987; Steinhauer and Boehm, 1992; Boehm et al., 1990; Boehm et al., 2001b; Brown et al., 2002).

Polynuclear Aromatic Hydrocarbons

The PAH distributions for the core sediments show that the PAHs are primarily of a combined fossil fuel origin (i.e., petroleum and coal) and lesser contributions of pyrogenic or combustion-related compounds (e.g., 4-, 5-, and 6-ring PAHs), with a somewhat variable biogenic component (perylene). The petrogenic PAHs account for >85 percent of the Total PAH less perylene throughout the core samples. Perylene was abundant in the core sediments, and often the most abundant single PAH compound in the overall PAH distribution (Figures 4-3 through 4-11). Perylene is a naturally occurring PAH formed during early diagenesis in sediments from biological source precursors (Wakeham and Farrington, 1980; Wakeham et al., 1980). Perylene has also been shown to increase with depth in sediment cores, as historical diagenesis is enhanced in deeper core sections (Wakeham and Farrington, 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 surficial sediments (Boehm et al., 1990).

The variations in PAH composition of representative core sediments from the region are shown in the PAH distribution plots in Figures 4-3 through 4-11. For comparison, the PAH distribution plot of a North Slope Crude oil is shown in Figure 4-1. The PAH distributions are generally similar in all the cores at surface and at depth, 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 4-2), which supports 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.

Triterpanes

In general, the triterpane distributions in the sediment core samples are indicative of a petroleum source (Figures 4-3 through 4-11), 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 4-1 for the North Slope Crude oil. The triterpane distributions for the sediment samples are composed of a mixture of these characteristic petroleum triterpanes, along with recent organic or biogenic markers such as diploptene (the large peak to the right of the T21 and T22 doublet - Figure 4-5) and other unnamed triterpanes (the large peaks that elute prior to T15 and in the 44- to 47-minute range – Peters and Moldowan, 1993). In addition, the relative abundance of T22 at much greater levels than T21 in most samples provides further evidence of substantial recent organic matter inputs to the sediments. Most of the sediment core samples (with the exception of the core from 6G from near the mouth of the Colville River) 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 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 (Figure 4-2), Sagavanirktok River, and Kuparuk River sediments have recent organic matter and petroleum hydrocarbon triterpane patterns with some similarities to those observed in the sediment samples. This similarity suggests that there is a strong link between the 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.

4.1.1.1 Comparisons of Hydrocarbons over Time

The key diagnostic organic parameters (Table 3-2) calculated for sediment core sections are important in examining the historical trends of hydrocarbons in the sediment record. As discussed earlier, reliable geochronology could be established for only three of the eight sediment cores. As a result, the data set was too limited to allow meaningful multivariate statistical comparisons of pre- and post-development core samples as originally planned. However, comparisons of selected key diagnostic parameters in the form of core profiles (Figures 3-2 through 3-9), in conjunction with simple statistical treatments, allow an accurate assessment of pre- and post-development hydrocarbon trends over time.

In general, comparisons of the core profiles for key diagnostic organic parameters for all of the cores do not show any clear trends that would indicate an increase in petroleum hydrocarbons over time. The core profiles from the five stations where geochronology could not be established (likely representing a historical pre-development record) are generally uniform and show little variability of the hydrocarbon parameters over time (CVs <16.2% for key source ratios, with the exception of CPI with a maximum CV of 26 %, and CVs <57 % for bulk parameters). The cores for which pre- and post-development dates can be established (P01, E01, and 6G) generally show uniform distributions of key parameters throughout the cores, with some variability in specific core sections. However, there are several apparent trends or anomalies that merit further discussion.

In the core from 6G, the surface interval (0- to 2-cm post-development) shows a significant increase in Total PAH, TPHC, and Total S/T, from the pre-development core intervals [within the 95% confidence interval (CI) from the pre-development core mean). This could suggest a link between the observed increase and the onset of oil and gas development in the region. However, when the data are normalized to the fine-grained clay fraction, the surface interval falls within the range of the other core sections (Figure 3-4) for the Total PAH, TPHC, and Total S/T parameters, indicating that the observed increase at the surface was due to a surface grain-size effect, and not a development effect. A similar trend is observed for the core from station E01, where the same three parameters show a significant increase (within the 95% CI from the pre-development core mean) at the surface interval (i.e., 0- to 2-cm post-development). Once again, when the data are normalized to silt plus clay (Figure 3-5) the surface interval falls within the range of the other core sections (with the exception of TPHC, which remains slightly higher than the upper 95% CI – 0.13 μg/g silt plus clay versus 0.11 μg/g silt plus clay), indicating surface hydrocarbon enrichment primarily due to a grain-size effect. The conclusion that the observed increase in hydrocarbons in the surface interval of these two cores is a grain-size effect is further supported by the uniform trend of other key hydrocarbon source and diagnostic parameters, which do not show any significant deviations from the core means (within the 95% CI) from pre-development core intervals.

In the P01 Prudhoe Bay core, the surface interval (0- to 2-cm post-development) shows an increase in Total PAH, TPHC, and Total S/T from the pre-development core intervals. However, this observed increase is not significantly different from the pre-development core sections (within 95% CI for the pre-development core mean – with the exception of TPHC with a value of 17μg/g versus an upper 95% CI of 16.4 μg/g), primarily due to higher variability of these parameters at depth in the core (particularly the 18- to 20-cm core interval). However, the 0- to 2-cm surface interval of one of the key diagnostic parameters (pyrogenic/petrogenic PAH) shows a small but significant (less than lower 95% CI from the pre-development core mean) post-development decrease. The observed decrease in this ratio indicates an increase in the petroleum component of the PAH assemblage. This result suggests a subtle increase in petroleum inputs at this station from composite of historical development activity sources in the Prudhoe Bay area. Although this trend cannot be confirmed by corresponding significant increases in the bulk hydrocarbon parameters, it does indicate that the parameters and techniques used are capable of detecting and beginning to identify very subtle changes in the hydrocarbon inputs to the region.

4.1.1.2 Comparisons of Hydrocarbons in Cores and Surface Sediments

In examining hydrocarbon trends in all of the cores, one useful technique (discussed earlier) involves examining the relationship between the organic parameter of interest and TOC content or alternatively, the percent silt plus clay. The natural background concentrations of organics will often vary as a function of fine-grained sediment (silt plus 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. This regression plot technique was used effectively for the 1999 and 2000 ANIMIDA surface sediment data to identify sediments enriched in hydrocarbons and data outliers (Brown et al., 2002).

A plot of all the 2001 core data and the 1999 and 2000 surface sediment data for total PAH minus perylene versus silt plus clay is shown in Figure 4-12. The Total PAH less perylene is used to reduce variability introduced to the Total PAH data by perylene, which can vary widely in abundance based on sediment type and core depth (Hyland et al., 1995; Boehm et al., 2001a). In this plot a regression and 95% prediction intervals are shown for all data, where the regression defines the natural geological/geochemical background of all the sediments. The plot shows that all the 2001 core samples fall within the 95% prediction intervals, indicating that the 2001 core sediment samples are not different in Total PAH content from the historical natural background of the region.

Another examination of the PAH data for the core samples can be summarized by a comparison of the pyrogenic-to-petrogenic PAH ratios. This ratio was discussed previously for core P01 and a comparison of this ratio for all core intervals from all stations is provided in Figure 4-13. This figure reveals a generally consistent abundance of petrogenic PAH relative to pyrogenic PAH across all core samples. There are several significant increases in this ratio for three of the pre-development core sections from core 6G, likely associated with recent organic matter (e.g., peat) inputs entrained in the sediment from this core from near the mouth of the Colville River (i.e., a known source of recent organic material). A significant decrease in the ratio (>2 x standard deviation [SD] versus all samples) is noted in the 0- to 2-cm surface interval from core P01 which, as discussed earlier, is likely an indicator of petrogenic inputs from oil and gas development activities since 1970 at this station located in central Prudhoe Bay. Overall, this ratio in the core samples indicates a generally uniform regional background of petrogenic and, to a lesser degree, pyrogenic hydrocarbons in sediments throughout the region.

Another evaluation of the sources of PAH in the core samples was performed using a dibenzothiophene-to-phenanthrene source ratio plot, which has been used in similar investigations of PAH sources in the environment and in previous ANIMIDA studies (Brown and Boehm, 1993; Page, 1998; Boehm et al., 2001a; Brown et al., 2002). An examination of the source plot for all the 2001 core sediments and additional source samples (i.e., river sediments and peat) is shown in Figure 4-14, and reveals that the source compositions of PAH in the core samples are generally similar (i.e., the data points cluster together on the plot) with some variability that can be attributed to local riverine source influences. For example, the data points for cores P01 and E01 cluster above and to the right of the main grouping of data points and intermediate to the Sagavanirktok and Kuparuk River sediments, indicating a Sagavanirktok River influence in these cores, which are adjacent to the Sagavanirktok River delta. Similarly, the data points from core 6A (near the Colville River delta) tend to cluster adjacent to the Colville River sediment data. Another source ratio plot of all the 2001 core samples, source samples, and 1999 and 2000 surface sediment samples (Figure 4-15) shows that the 2001 core data fall well within the range defined by the cluster of all of the surface sediment samples from the area. This provides further evidence that the sediment core data are representative of the regional hydrocarbon background, and do not indicate any substantial influence from post-development anthropogenic hydrocarbon inputs from the Prudhoe Bay area.

Overall, the organic analyses of the sediment cores collected during 2001 have provided an important historical perspective on hydrocarbons in the sediments from the study area. The results have shown that the concentrations and sources of hydrocarbons are generally uniformly consistent over the past 50 or more years and represent a regional background assemblage. For most organic hydrocarbon parameters, there are no significant increases (after geochemical normalization) of hydrocarbons in the sedimentary record post oil and gas development in the Prudhoe Bay area. In one case (the Prudhoe Bay core - P01) a significant difference in one key diagnostic parameter ratio suggests a slight increase in petroleum inputs at this station from development activity sources. Although this result cannot be confirmed by corresponding significant increases in other hydrocarbon parameters, is does indicate that monitoring techniques and data evaluation approaches used are very sensitive and capable of identifying subtle changes and incremental anthropogenic inputs to the system.

4.1.1.3 Sediment Quality Guidelines

Another technique of evaluating the significance of the measured sediment hydrocarbons to overall ecological risk of the region involves comparisons to sediment quality guidelines. Sediment quality guidelines have been developed to assess possible adverse biological effects from metals, polychlorinated biphenyls (PCBs), pesticides, and PAH. The commonly utilized criteria are the effects range-low (ERL) and effects range-median (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 3 classes of PAH (low- and high-molecular-weight PAH, and Total PAH). A comparison of the Total PAH from all ANIMIDA core sediments to the ERL and ERM criteria is shown in Figure 4-16. None of the Total PAH concentrations determined in this study exceed the ERL. The station 6G surface interval (0- to 2-cm), which had the highest measured Total PAH at 1,990 µg/Kg, was still well below the ERL value of 4,022 µg/Kg. The mean Total PAH values from each core were generally an order of magnitude lower than the ERL. Similarly, the individual PAH concentrations did not exceed the ERL for the individual 13 PAH, which could be compared directly. The target parameter C1-naphthalenes, which was reported in this study, is the sum of the two individual PAH compounds – 1-methylnaphthalene and 2-methylnaphthalene. The C1-naphthalenes value at station 6G (0- to 2-cm interval) of 100 µg/Kg was higher than the ERL value listed for the single 2-methylnaphthalene isomer (70 µg/Kg). However, this value would be less than the ERL using an estimate of 50 percent contribution of 2-methylnaphthalene to the C1-naphthalenes target parameter. In summary, based on sediment quality criteria, the concentrations of PAH found in the sediment core samples are not likely to pose immediate ecological risk to marine organisms in the area.

4.1.2 Geochronology of Metals - Concentrations of Metals over Time

Considerable variability is observed for concentrations of all 18 metals, TOC, and granulometry in surface and subsurface sediments from the study area, as suggested by the ranges in Table 3-4. Such a patchwork of metal concentrations can result from natural variations, anthropogenic inputs, or diagenetic impacts. We previously showed (Crecelius et al., 1991) that sediment grain size was a primary variable controlling metal concentrations in surface sediment from the study area where levels of silt plus clay range from 1 to 98.8%. To help resolve observed variability, sediment metal values from our study were initially normalized to concentrations of Al. Natural levels of Al and many trace metals vary collectively as a function of sediment grain size, organic carbon content, and mineralogy, with higher metal levels in fine-grained aluminosilicates (clays) and lower metal levels in coarse-grained quartz sand and carbonate shell fragments.

Normalization is a useful precursor to more detailed discussion of historical trends, as well as possible diagenetic effects on metal concentrations, as discussed in more detail below.

In sediment from this study, positive linear relationships are observed for Al versus percent silt plus clay (r = 0.89; Figure 4-17a), percent clay (r = 0.75), and TOC (r = 0.74). Aluminum concentrations also correlate well with levels of Fe (r = 0.94) throughout the study area using data for surface samples from 1999 and 2000 and all sediment core data from 2001 (Figure 4-17b). Aluminum and Fe are present at percent levels in the sediment, relative to concentrations in parts per million (µg/g) for trace metals and Al and Fe are not commonly introduced to marine sediment in sizeable amounts by anthropogenic processes. Therefore, any fractional changes in concentrations of Al and Fe are expected to be small relative to possible shifts in concentrations of trace metals due to anthropogenic or diagenetic influences. Concentrations of Fe can be altered during early chemical diagenesis; however, the net effect on solid-phase concentrations of Fe is generally small (e.g., <10% change in Fe/Al ratio, Trefry and Presley, 1982).

Mean concentrations of Al and Fe in suspended sediments collected during 2000 and 2001 from the Sagavanirktok and Colville Rivers that supply sediment to the study area fit the 99% prediction intervals developed for bottom sediment (Figure 4-17b). Furthermore, concentrations of Al and Fe in the river suspended sediment plot at the higher end of the continuum in Figure 4-17b are due to a greater fraction of clay-rich particles suspended in the rivers. Suspended sediment from the Kuparuk River has higher levels of Fe during part of the summer, when concentrations of suspended solids are low (<2 mg/L) (Rember and Trefry, 2003), thereby shifting the point on Figure 4-17b.

Under natural conditions, concentrations of selected trace metals in sediments will commonly follow a strong linear trend versus Al and/or Fe in a given depositional environment. For example, concentrations of V correlate well with Al (r = 0.97, Figure 4-17c) and Fe (r = 0.96) in all surface and subsurface sediment samples collected from 1999 to 2001. The broad range in V concentrations, yet good linear fit for Al (and Fe) versus V, is consistent with mixing of relatively uniform composition, metal-rich aluminosilicate phases with metal-poor quartz sand and carbonate shell. Vanadium levels in natural sediment from the Beaufort Sea are predicted to follow the trend presented in

Figure 4-17c. Crecelius et al. (1991) used V, in the absence of data for Al and Fe, to normalize concentrations of other trace metals during a previous study of metal distribution in the coastal Beaufort Sea. All V concentrations in the 2001 sediment cores fit the prediction interval shown in Figure 4-17c. This result shows that the V/Al ratio observed in very recent, surficial sediments is consistent with the long-term V/Al ratio found in sediments that were deposited more than 50 years ago, well before the onset of development in the area. In other words, no significant, recent changes in the V/Al ratio are observed.

Plots of Al versus Pb, Cu, Cr and Ni (Figure 4-18), as well as Co, Sb, and Tl (Figure 4-19), also show strong (r>0.8) linear relationships. Once again, all data for the sediment cores fit the prediction intervals. Available metal data for suspended sediment from source rivers (Pb, Cu, Cr, Zn, Ba, As; Figures 4-18 and 4-19) also show that the metal/Al ratios fit within the prediction intervals found for bottom sediment in the coastal Beaufort Sea. The linkage between river source material and bottom sediment can be used to help confirm the constancy of metal/Al ratios and to help identify possible diagenetic impacts on the historical record for these metals in sediments. As observed for Al and Fe, concentrations of metals in the river suspended matter (Figure 4-18) generally plot at the higher end of the metal/Al continuum because the river suspended sediment is finer grained and naturally richer in clays and metals.

In contrast with the metals discussed above, concentrations at one or more locations have been previously shown to be above the upper prediction interval on the metal versus Al plots for Zn, Hg, and Ba (Figures 4-18 and 4-19). An anomalous Zn value was observed in surficial sediment collected from site 5H (near the Endicott Development Island) during 1999, and anomalous points for Hg and Ba are observed near Northstar Island for surficial samples collected during 1999 and 2000 (Figures 4-18 and 4-19). None of these anomalies were observed in samples from the 2001 cores. Considerable industrial activity is common to both areas; however, the degree of metal enrichment is generally <25% greater than the value calculated for a given concentration of Al at the upper prediction interval at the few sites where such anomalies are encountered.

In addition to the anomalies from the 1999 to 2000 data for Ba described above, concentrations of Ba in samples collected during 1989 from sites 7A and 7G in western Harrison Bay also plot above the upper limit of the 99% prediction interval. Elevated Ba levels at sites 7A and 7G in Harrison Bay during 1989 are consistent with exploratory drilling and drilling residues in the area, as previously described (Snyder-Conn et al., 1990; Crecelius et al., 1991). The sensitivity of normalizing to Al is demonstrated by introducing the concept of excess Ba, calculated as total Ba minus natural Ba (with the natural Ba level determined from Figure 4-19a as the value for Ba at the upper prediction interval for a given Al concentration). The most anomalous sample point in Figure 4-19a has an excess Ba level of 400 μg/g (1,100 μg/g – 700 μg/g) that can be explained by the presence of barite at only 0.07% of the total sediment mass (where pure barite contains Ba at 588,000 μg/g). Subtle enhancement in the Ba value at site L08 (1999) may be a remnant of exploratory drilling in the area in 1982 and 1997 (URSGWC, 2001). Although these various anomalies are minor, and are identified only at low levels of Al, they do support the sensitivity of Al versus Ba graphs and serve as indicators of locations to focus future efforts. No Ba anomalies are observed in the 2001 sediment cores. Barium concentrations in predevelopment layers of sediment from the cores help define very well natural Ba levels for the area.

Concentrations of Cr are also elevated in western Harrison Bay based on the 1989 data (stations 7A, 7B, and 7G) and western Camden Bay (2E), as shown in Figure 4-18c. Snyder-Conn et al. (1990) previously noted that Cr levels were as high as 331 µg/g adjacent to a mud discharge area near Cross Island. Again, the anomalous values can be clearly identified. No positive Cr anomalies were observed in the sediment data from the 2001 cores.

Concentrations of Ag and Be are low and somewhat more variable (Table 3-4); therefore the correlations versus Al are weaker (Ag, $r = 0.57$; Be, $r = 0.69$). Background levels of As in the study area are high relative to average marine sediment. This point was previously noted throughout the Beaufort Sea by Valette-Silver et al. (1999). We find As levels in suspended sediment from local rivers to average 15 ± 5 µg/g ($n = 17$). Several points on the As/Al graph are above the upper prediction interval. These points are related to diagenetic impacts, as discussed below. Concentrations of Mn also are affected by diagenesis.

Collectively, the data for cores from Prudhoe Bay (station P01), near Endicott Island (station E01) and east of the Colville River delta (6G) show that normalized concentrations of Ba, Be, Cr, Cu, Ni, Pb, Sb, Tl, and V are constant with time, supporting no detectable anthropogenic contributions and no impacts due to early chemical diagenesis. The continuum of uniform metal/Al values from river suspended sediment to recent bottom sediment to older bottom sediment provides strong support for the very limited impacts with respect to trace metals in sediments in the study area.

Diagenetic effects discernibly alter the vertical distributions of Mn, As, and perhaps Cd in the 2001 cores from this study. Diagenetic impacts on Mn are well studied and lead to either Mn-depleted sediment (relative to incoming suspended sediment) or to Mn-rich layers at the sediment surface or sometimes preserved at some depth in the sediment column (Trefry and Presley, 1982; Gobeil et al., 1997). Such diagenetic impacts for Mn are clearly observed in the surficial centimeters of the cores from stations P01, E01, 6G, and 6A (Figures 3-10, 3-12, 3-14, and 3-18). Likewise, the peaks in concentrations of As and Cd also are most likely due to diagenetic processes (Gobeil et al., 1997; Anawar et al., 2002).

4.1.2.1 Comparison of Metals to Sediment Quality Guidelines

Various investigators have developed sediment quality guidelines to assess possible adverse biological effects from trace metals (e.g., Long et al., 1995; MacDonald et al., 1996; Field et al., 1999). The guidelines introduced by Long et al. (1995) use an Effects Range-Low (ERL) and Effects Range-Median (ERM) that are based on field, laboratory, and modeling studies conducted in North America that coupled concentrations of contaminants in sediment with adverse biological effects. The ERL is defined as the concentration of a substance that affects 10 percent of the test organisms. 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. For general use, the guidelines have been applied as follows: adverse biological effects are "rarely" observed when metal levels are <ERL, "occasionally" observed when contaminants are present at levels between the ERL and ERM, and "frequently" observed when concentrations are >ERM.

Nine (Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) of the 16 metals investigated during this study have been assigned ERL and ERM concentrations by Long et al. (1995). These guidelines are evolving, as demonstrated by the extensive efforts of Field et al. (1999) to validate values for Hg, Pb and Zn. Some difficulties still exist with ERL values for Cr, Cu, and Ni, as discussed below. Overall, the sediment quality data should be used primarily as guidelines at this time. No concentrations of any of the nine metals in surficial sediments or the 2001 core samples exceed their respective values for the ERM (Table 4-1). Therefore, adverse biological effects are not expected to be a frequent occurrence at any site in the study area as the result of trace metals. Furthermore, no concentrations of Ag, Cd, Hg, Pb, or Zn from this study exceed the respective values for the ERL (Table 4-1) and thus adverse biological effects from these four metals would be rare.

The Hg values for surficial sediment from sites N10 and N17 (2000) and from core 6G (2001) are slightly above the predicted natural level, but well below the ERL (Figure 4-18). No ERL or ERM is available for Ba and previous studies suggest that sediment Ba levels of several thousand µg/g do not induce adverse biological effects in sediment (Tagatz and Tobia, 1978).

Many points on the Al versus Cu and Cr plots exceed the present ERL (Figure 4-18). However, the ERL for each of these metals is less than or very close to the values for average crustal abundance and natural levels found in many types of sediment (Naidu et al., 1997; Valette-Silver et al., 1999; Boehm et al., 2001b). These discrepancies may occur if some of the Cu, Ni, and Cr values in the database compiled by Long et al. (1995) were obtained following an acid leach of the sediment rather than a total digestion. For example, Sinex et al. (1980) found that only 40 ± 18% of the total Cr was removed using a concentrated 9:1 HNO_3:hydrochloric acid (HCl) treatment of 12 randomly selected sediment samples. Thus, an acid-leachable Cr value equal to the ERL level of 82 µg/g is more likely comparable with a total Cr level closer to 200 µg/g, a value considerably higher than Cr values for continental crust or any samples from this study. A similar situation exists for Cu and Ni. However, for other metals such as Cd, Pb, and Zn, a higher fraction of the total metal content (50 to 90%, Trefry and Presley, 1976; Sinex et al., 1980) is solubilized with an acid leach, especially when a large fraction of the total metal concentration is derived from anthropogenic sources. Thus, the ERL and ERM values for Cr, Cu, and Ni most likely need to be revised in subsequent iterations of these sediment quality guidelines. Certainly, the method for digesting the sediment needs to be noted along with the guidelines.

Early detection of potential environmental problems near industrial sites is the goal at many locations around the earth, including the coastal waters of the western Beaufort Sea. Because many trace metals are a ubiquitous part of modern industry, metals in sediment can offer the potential for identifying subtle increases in the accumulation of potential pollutants before they lead to an adverse environmental consequence. For example, in sediment with an Al concentration of 6.0%, natural Pb levels in the coastal Beaufort Sea are predicted to be 15 ± 6 µg/g with 99% confidence. As metal levels rise to the upper limit of 21 µg/g, a caution can be signaled before sediment Pb concentrations reach the ERL of 47 µg/g. Then, additional samples can be collected near this "warm" spot before it develops into a "hot" spot. Other sensitive components of a more comprehensive assessment also may be investigated.

Overall, the sediment cores collected during 2001 have provided an important look back in time to show that present-day concentrations of metals in bottom sediments and river suspended sediments are statistically the same as found in sediments that are >50 years old and pre-date development in the study area. The core data have also identified diagenetic alterations of sediment concentrations of Mn, As, and Cd. Although such alterations are quite reasonable and common, they may provide a useful tracer of future changes in the area as they record the present-day redox state in the sediments. Subtle impacts in sediment redox state due to future climatological shifts, or changes due to regional development, may be recorded in the vertical profiles for Mn, As, Cd, and TOC.

Table 4-1. Values for the Effects Range-Low (ERL) and Effects Range-Median (ERM) from Long et al. (1995) and Results from this Study

Metal	ERL (µg/g)	ERM (µg/g)	Maximum Value this Study (µg/g)	Sites with Values >Upper Prediction Interval (UPI)	Sites with Values >UPI and >ERL
Ag	1.0	3.7	0.44	N13 (99) N14(99) N22 (00)	None
As	8.2	70	27.3	5D (99)	5D (99)
Cd	1.2	9.6	0.79	5D (99)	None
Cr	(81)*	370	126	7A, &B, 7G, 2E (all 89) N17 (00)	[7A, 7B, 7G, 2E in 89]*
Cu	(34)*	270	46.9	5D (99), N14 (00), N17 (00), N23(00)	[5D (99), N14 (00), N23(00)]*
Hg	0.150	0.710	0.200	5D (99) N10 (00) N17 (00)	5D (99)
Ni	(20.9)*	51.6	48.4	5D (99) N17 (00)	5D (99)
Pb	46.7	218	22.3	5D (99)	None
Zn	150	410	131	5H (99) N17 (00)	None

*ERL comparable with or lower than value for average continental crust and in need of reevaluation.

Figure 4-1. North Slope Crude Oil – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

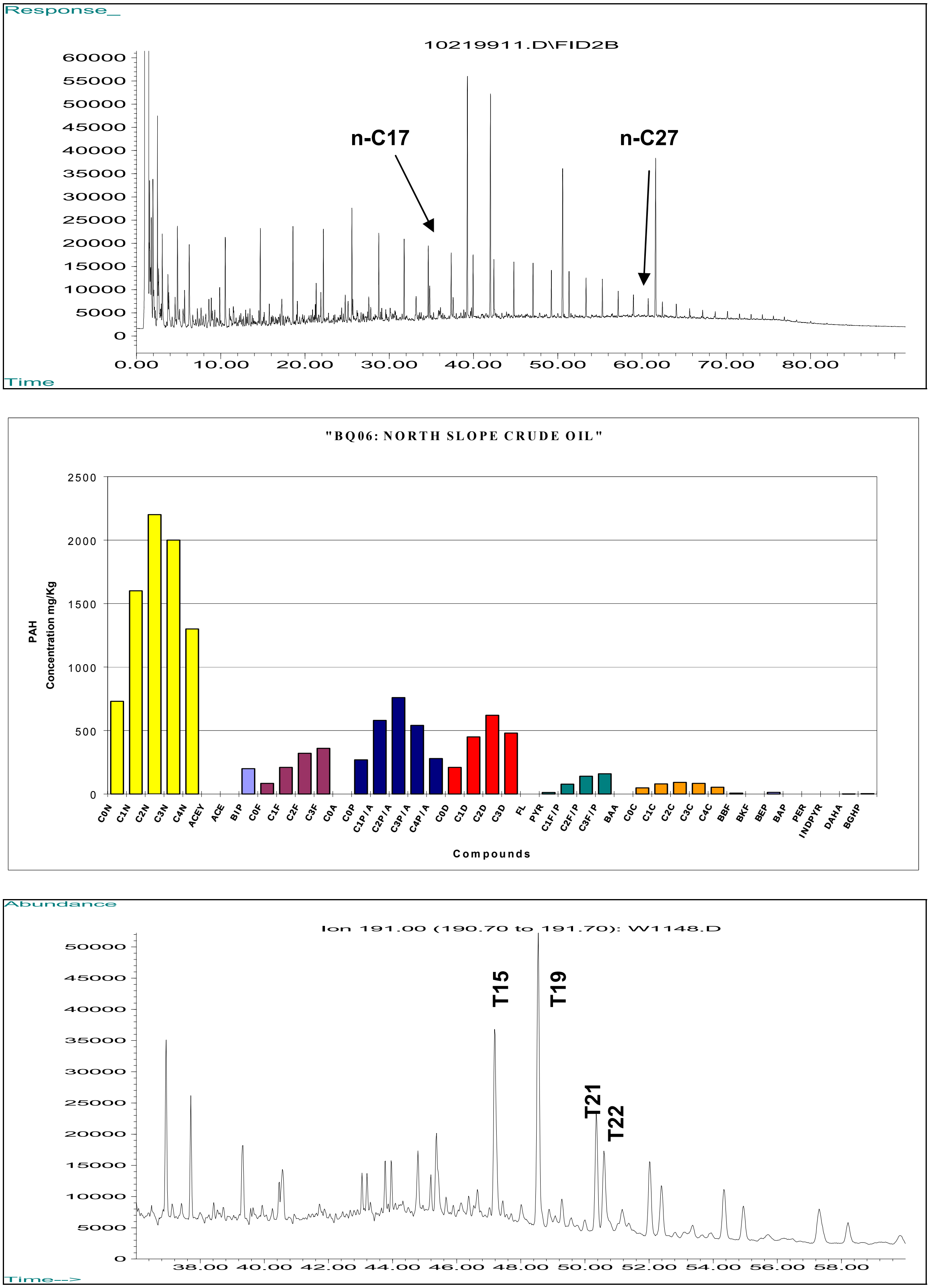


Figure 4-2. Colville River Sediment, Year 1999 – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

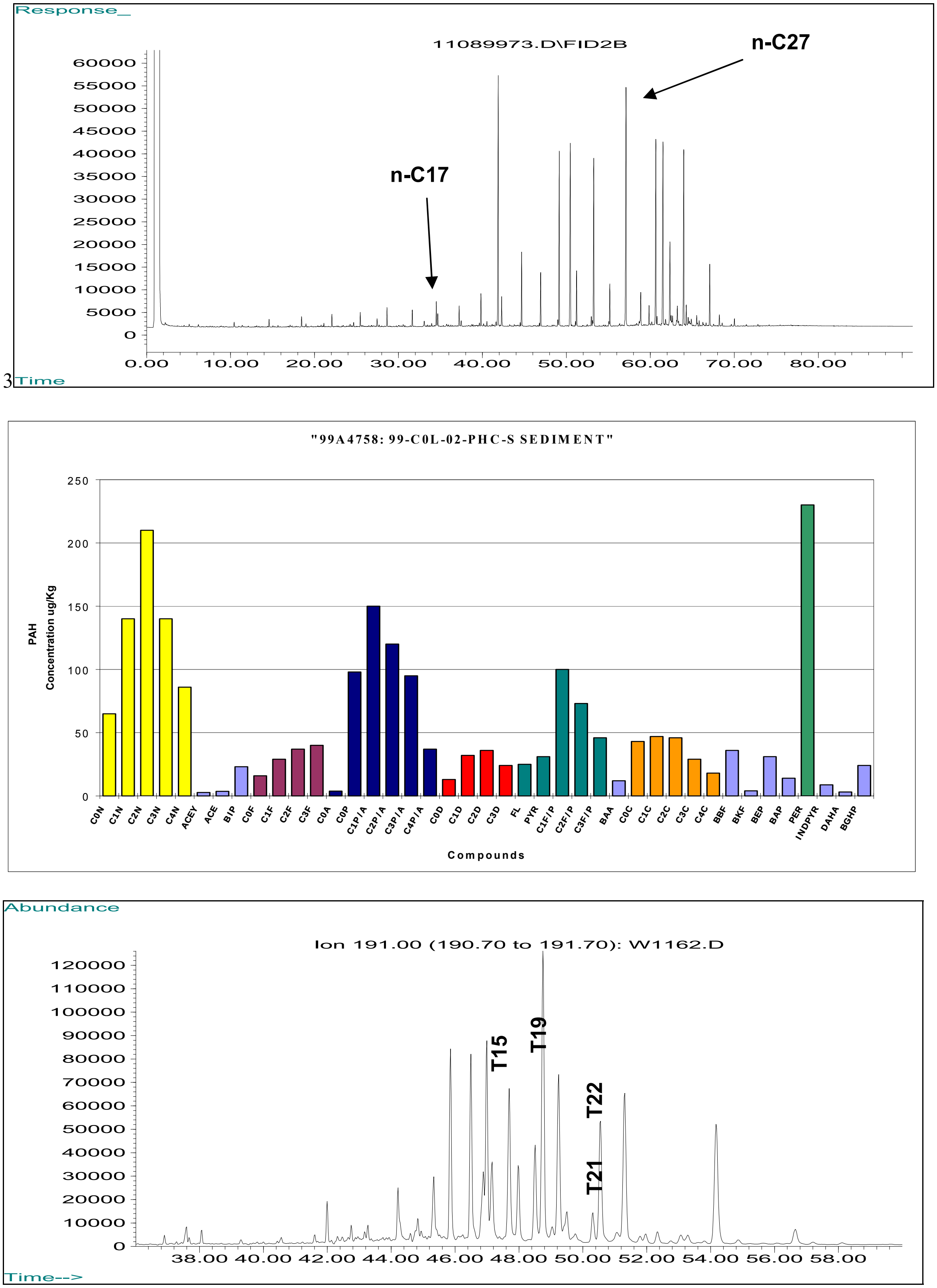


Figure 4-3. Sediment Core P01 Interval 0-2 cm – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

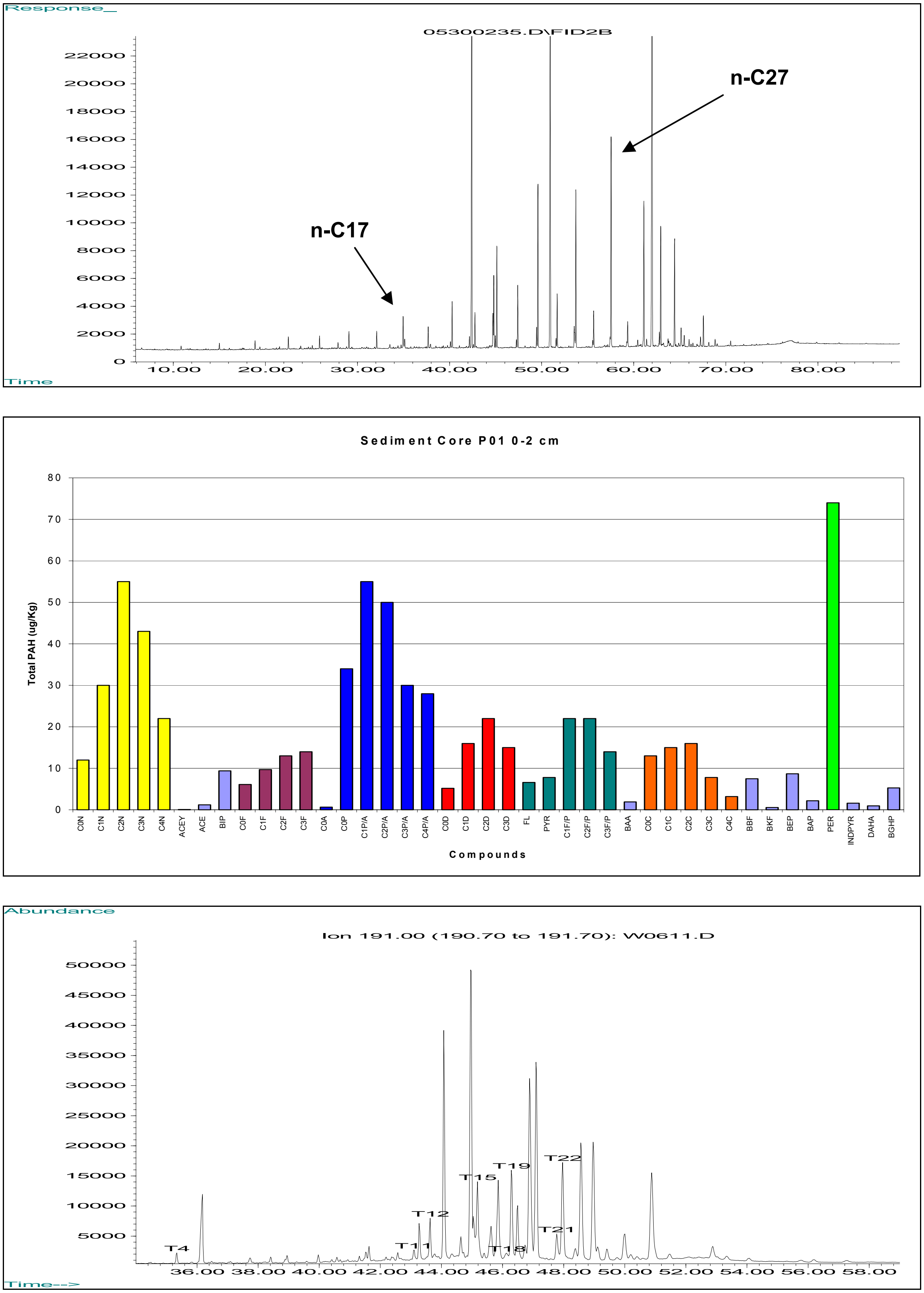
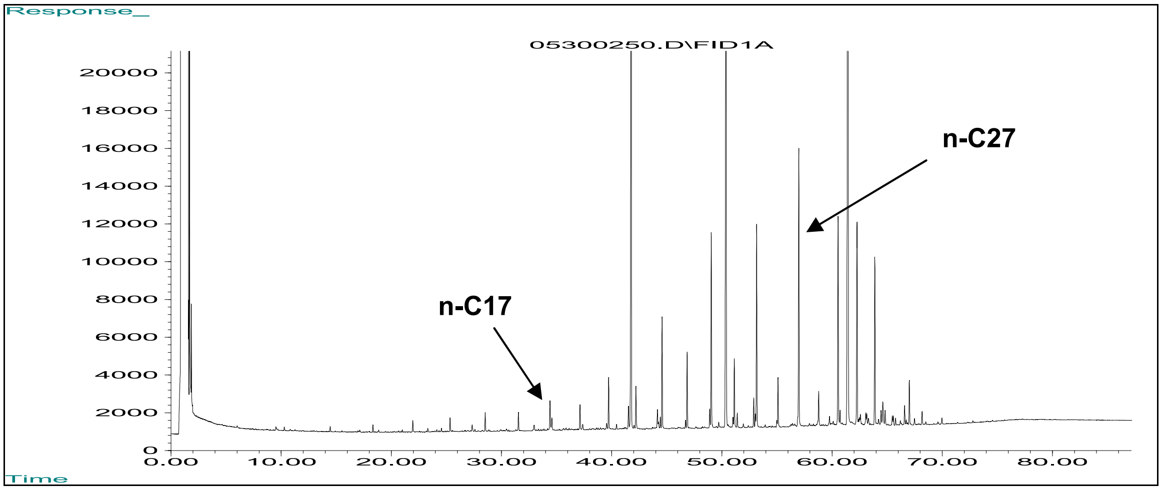
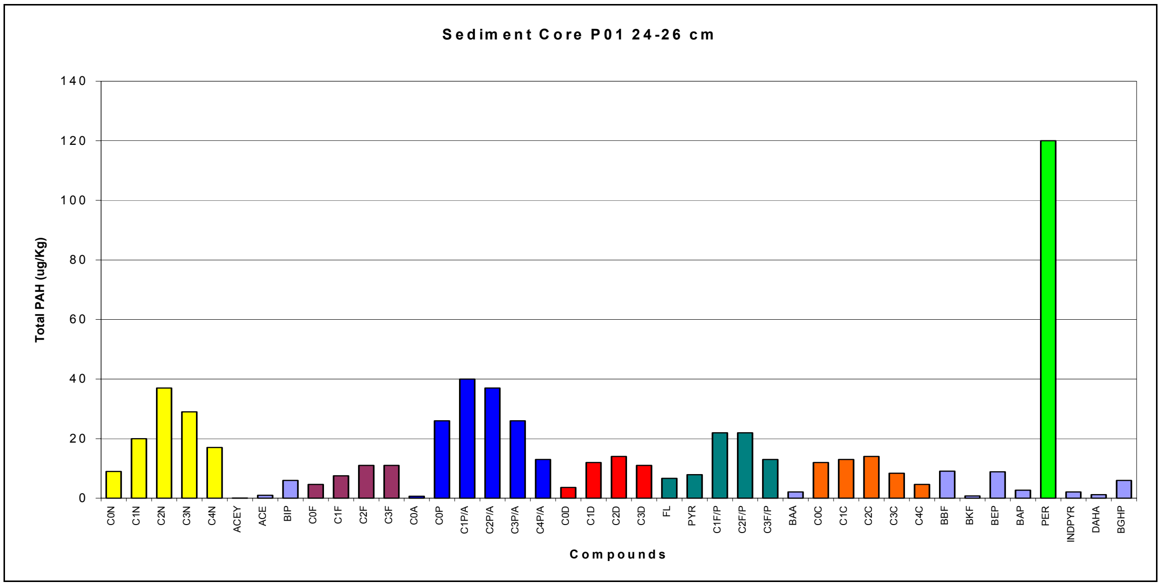


Figure 4-4. Sediment Core P01 Interval 24-26 cm – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)





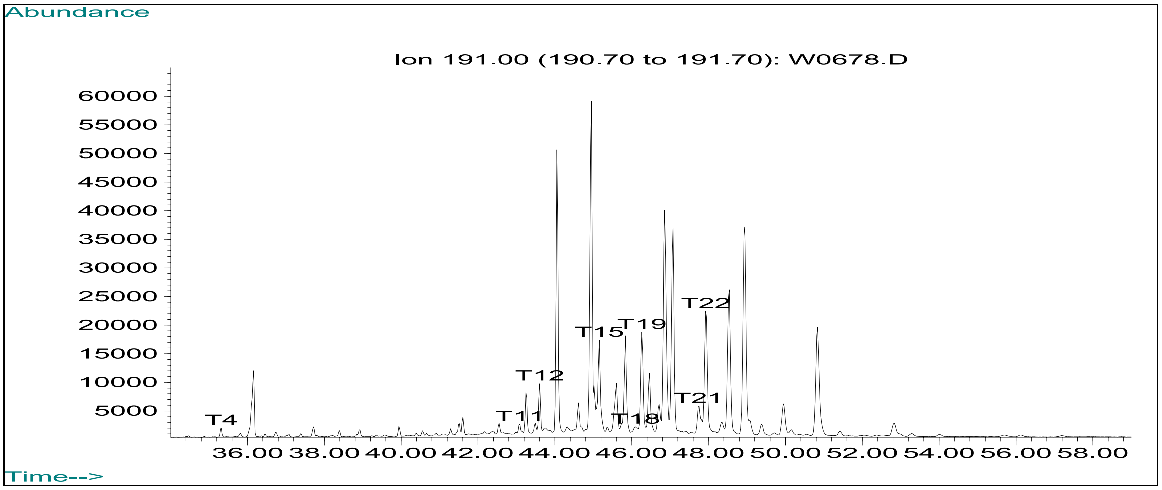


Figure 4-5. Sediment Core 6G Interval 0-2 cm – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

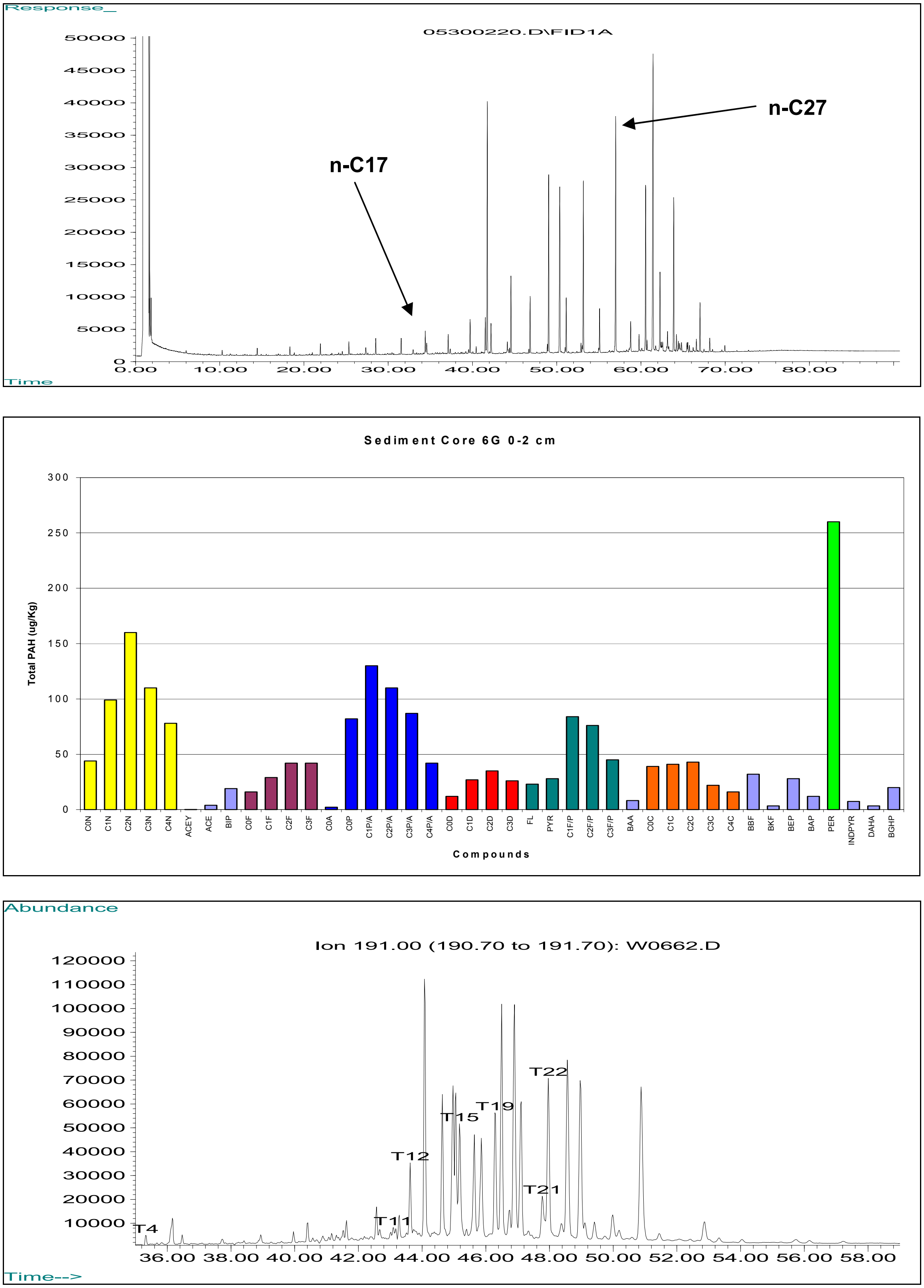


Figure 4-6. Sediment Core 6G Interval 16-18 cm – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

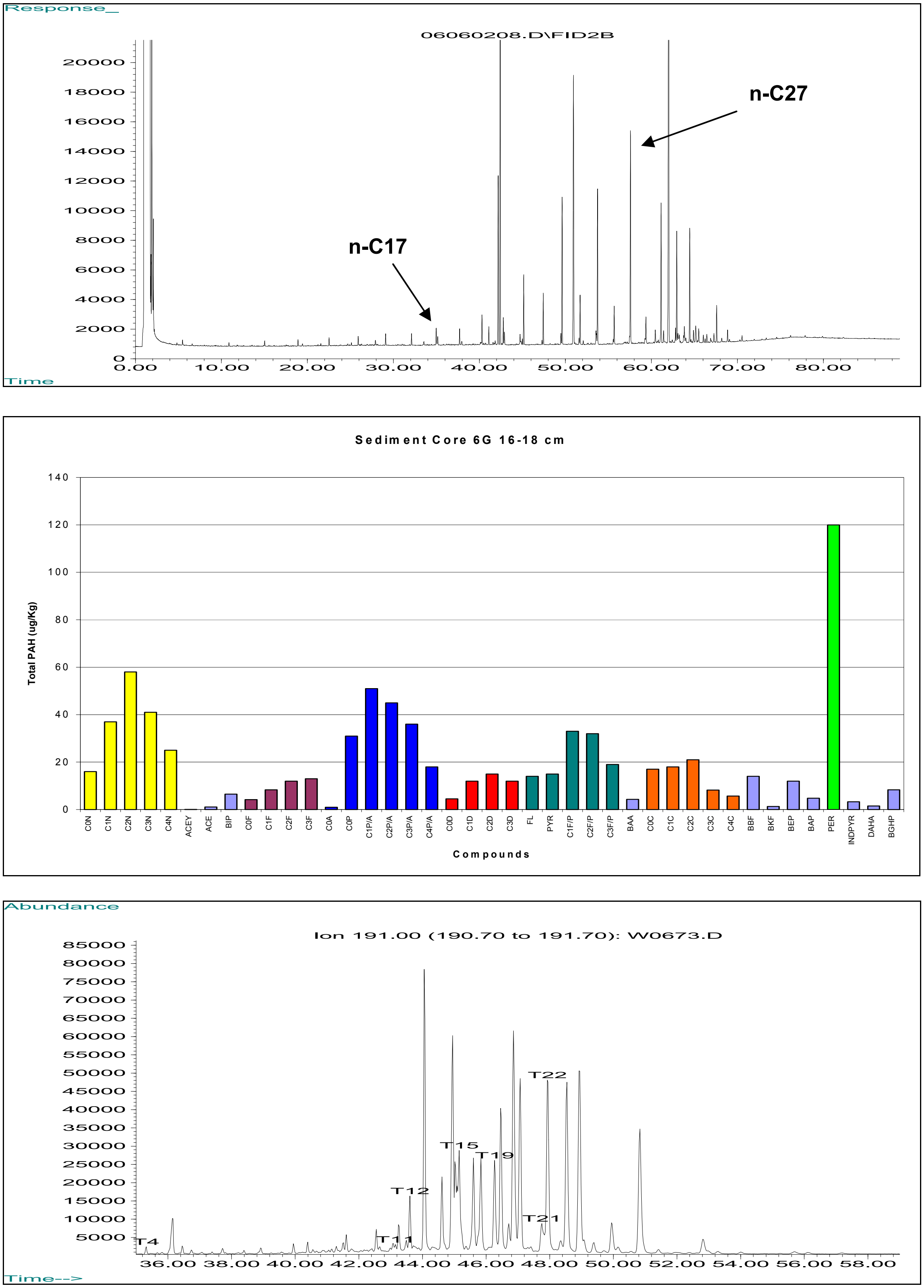


Figure 4-7. Sediment Core 3A Interval 0-2 cm – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

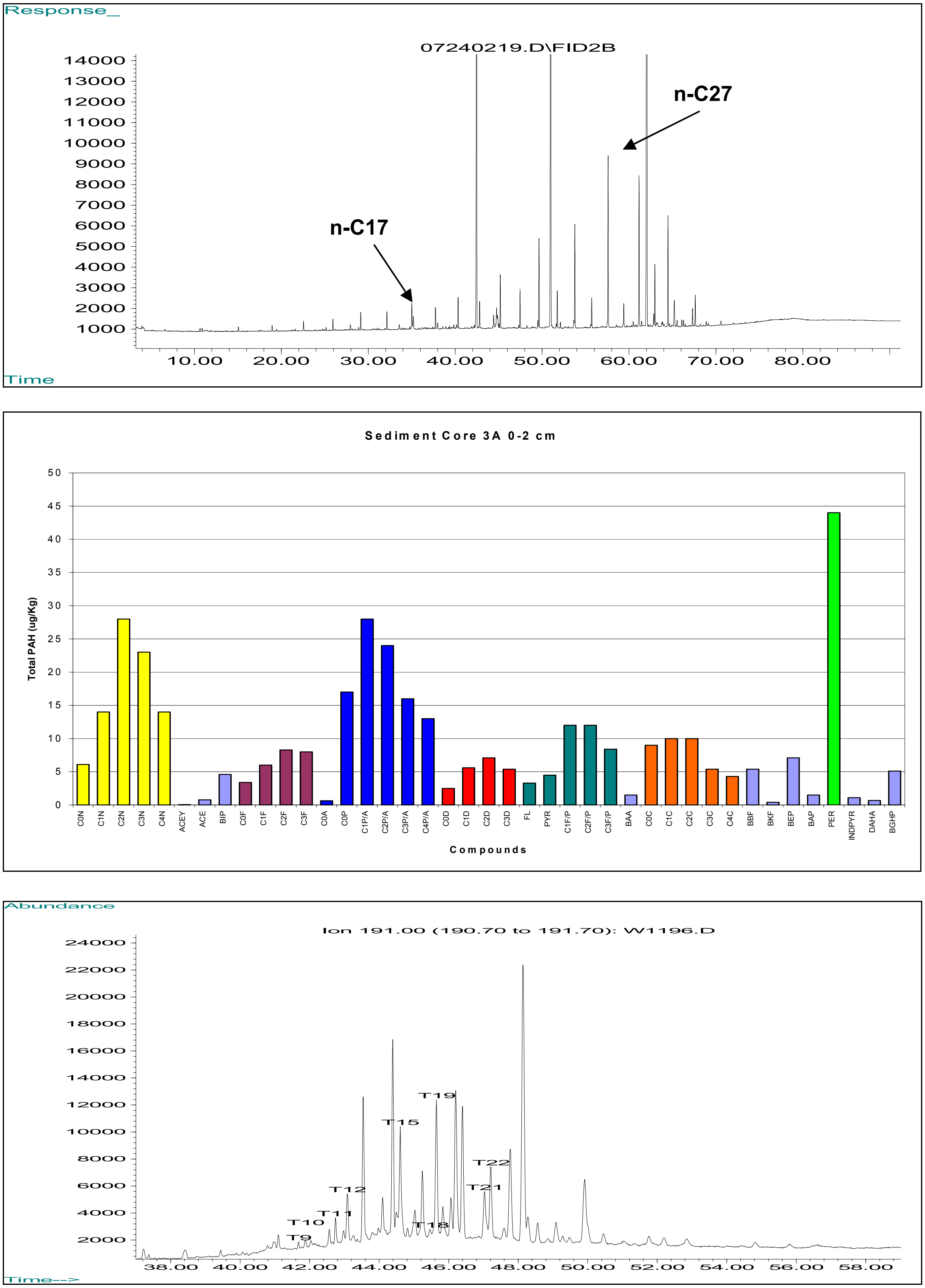


Figure 4-8. Sediment Core E01 Interval 0-2 cm – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

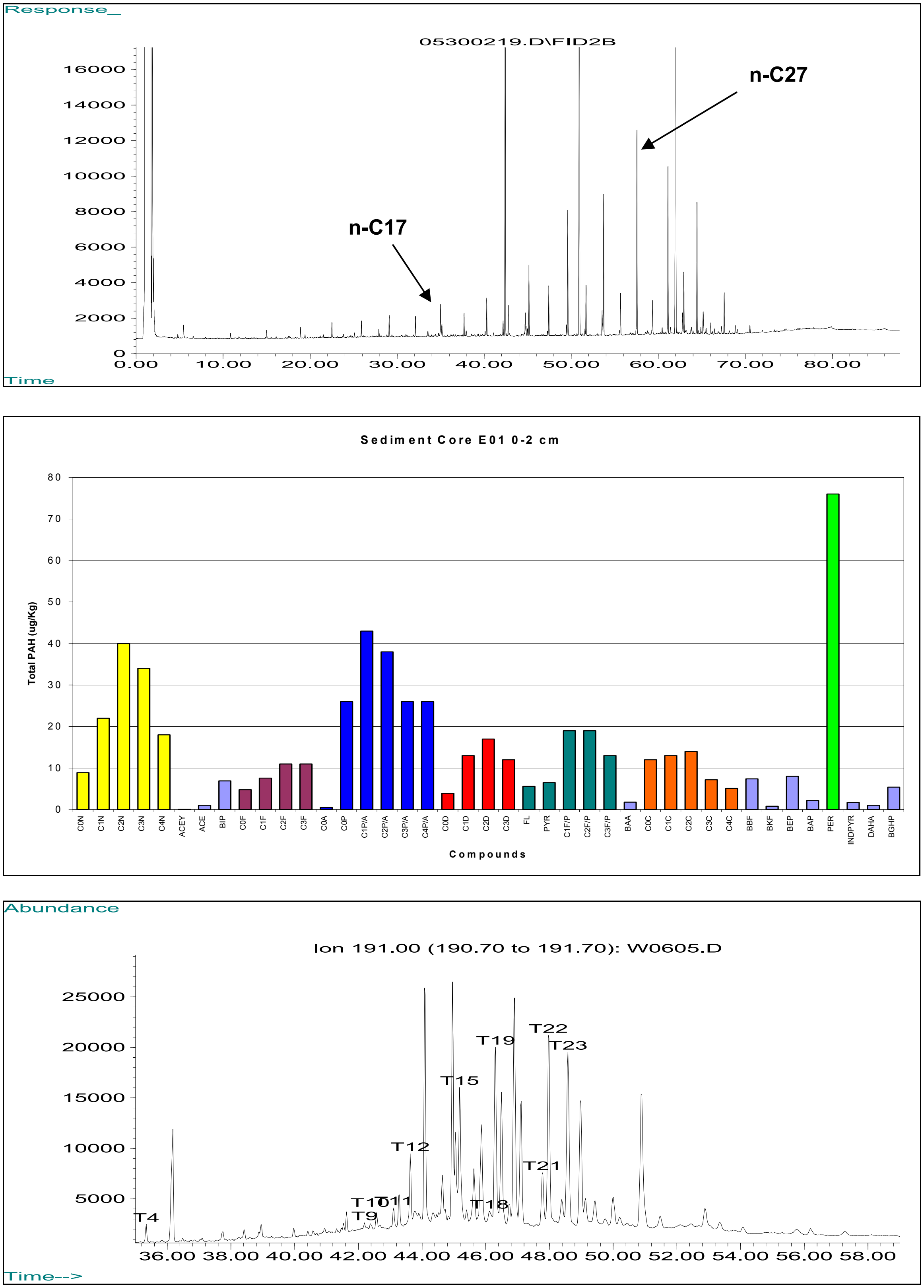


Figure 4-9. Sediment Core L02 Interval 0-2 cm – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

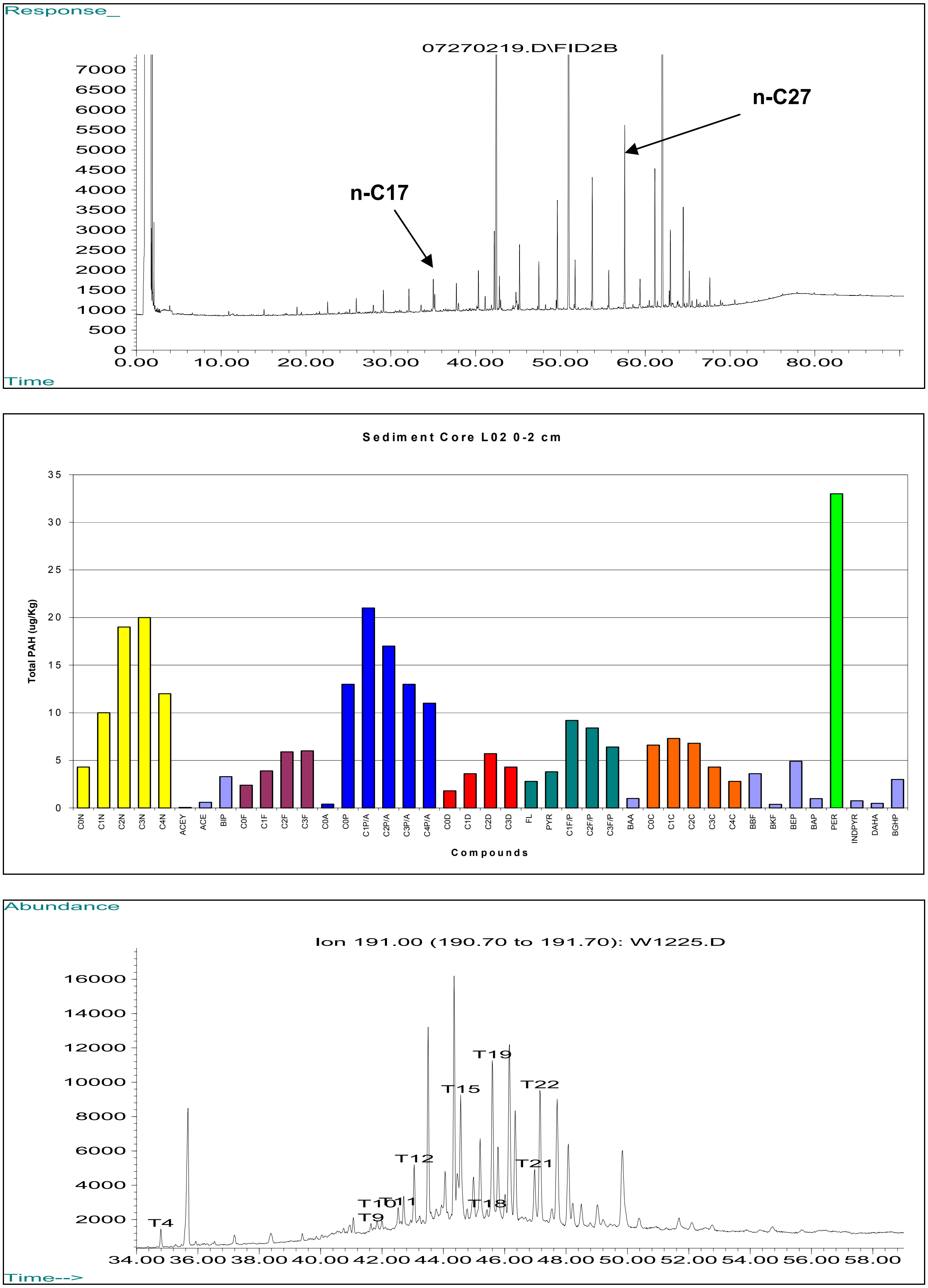
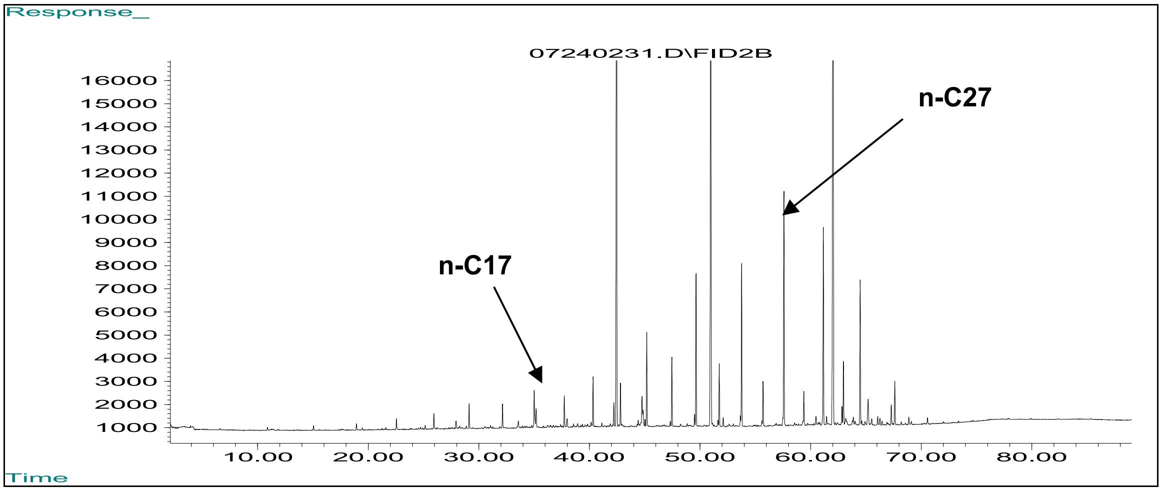
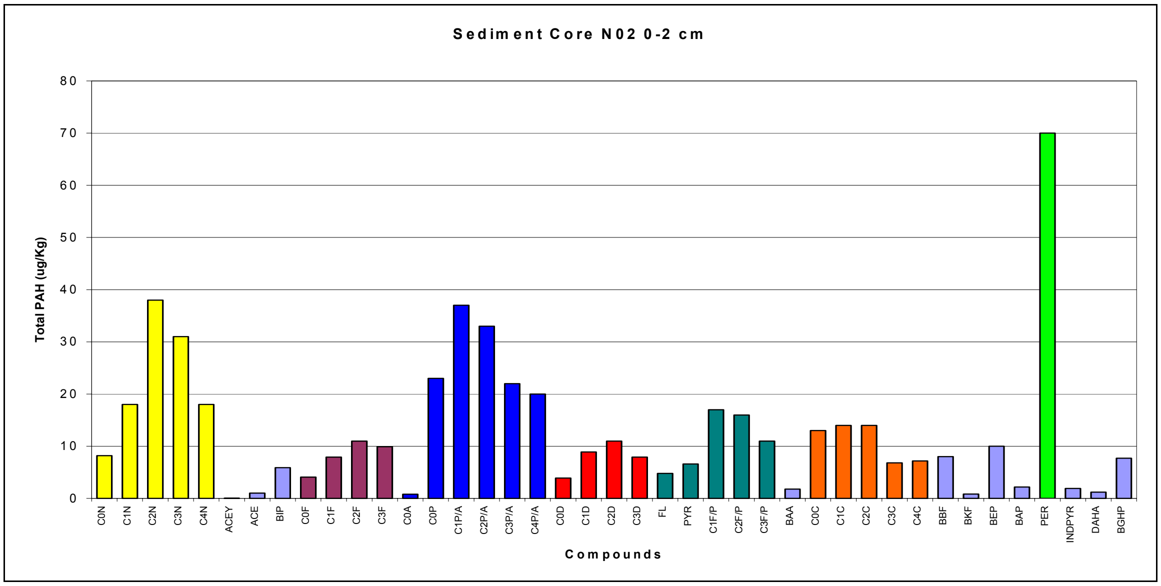


Figure 4-10. Sediment Core N02 Interval 0-2 cm – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)





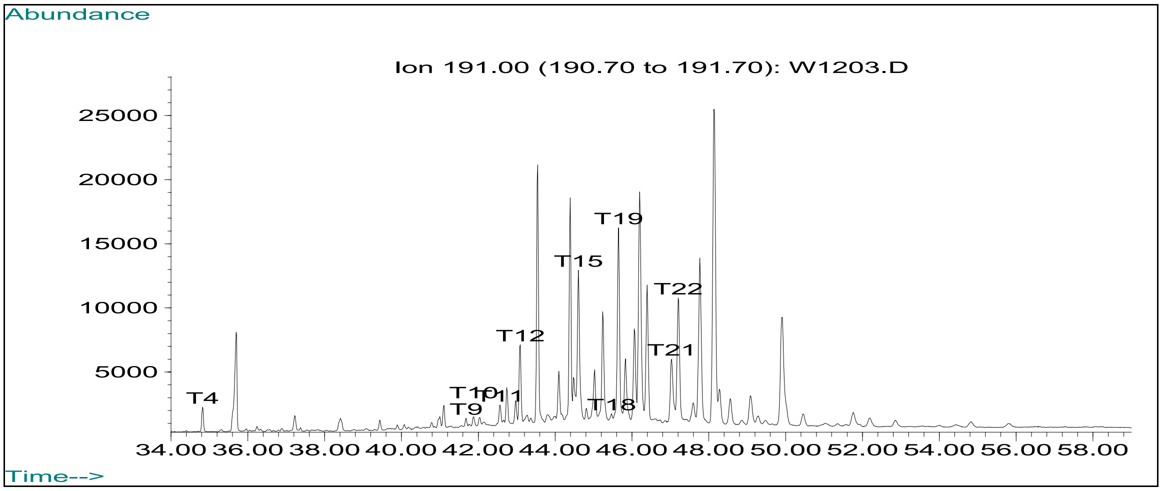
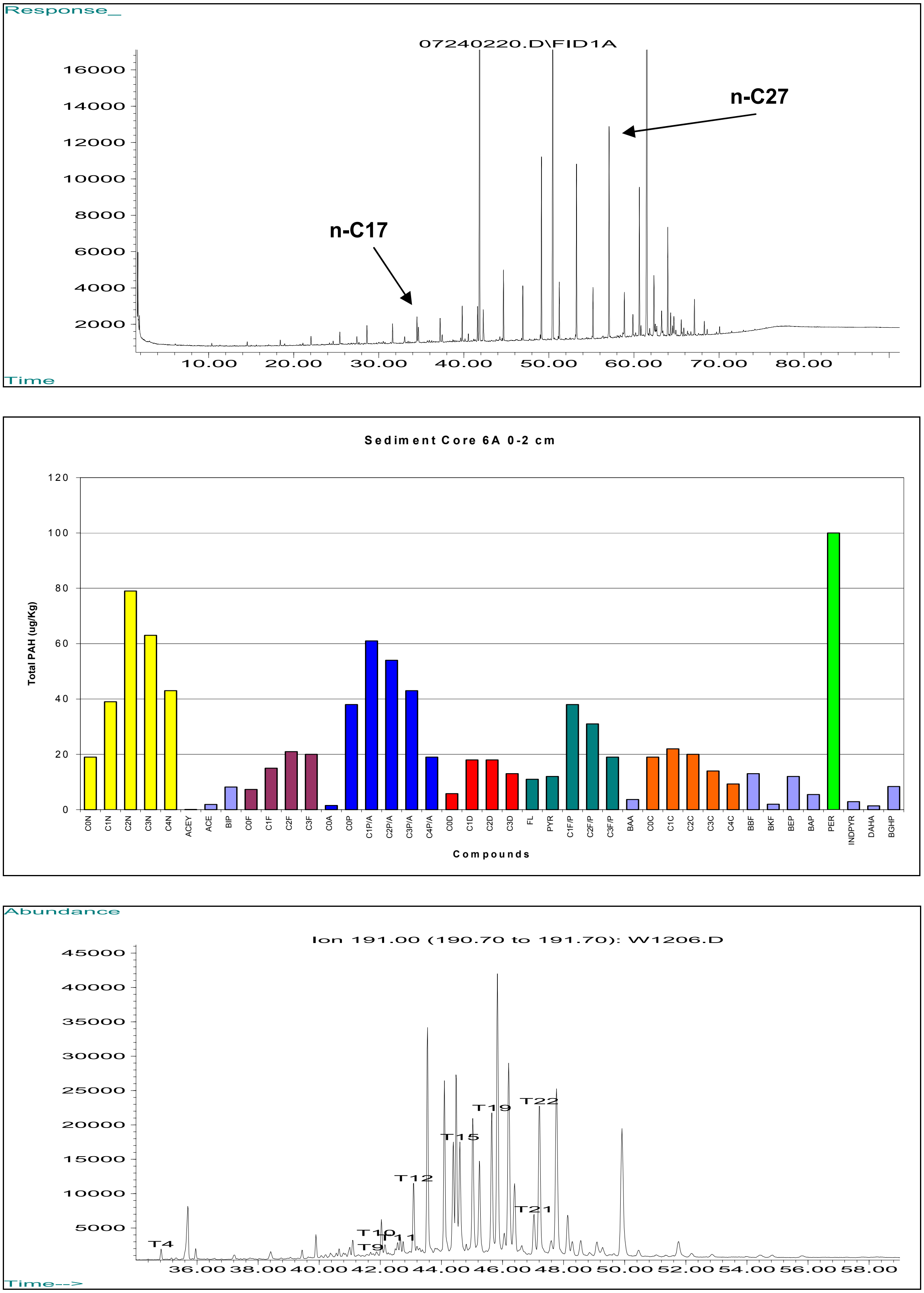


Figure 4-11. Sediment Core 6A Interval 0-2 cm – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)



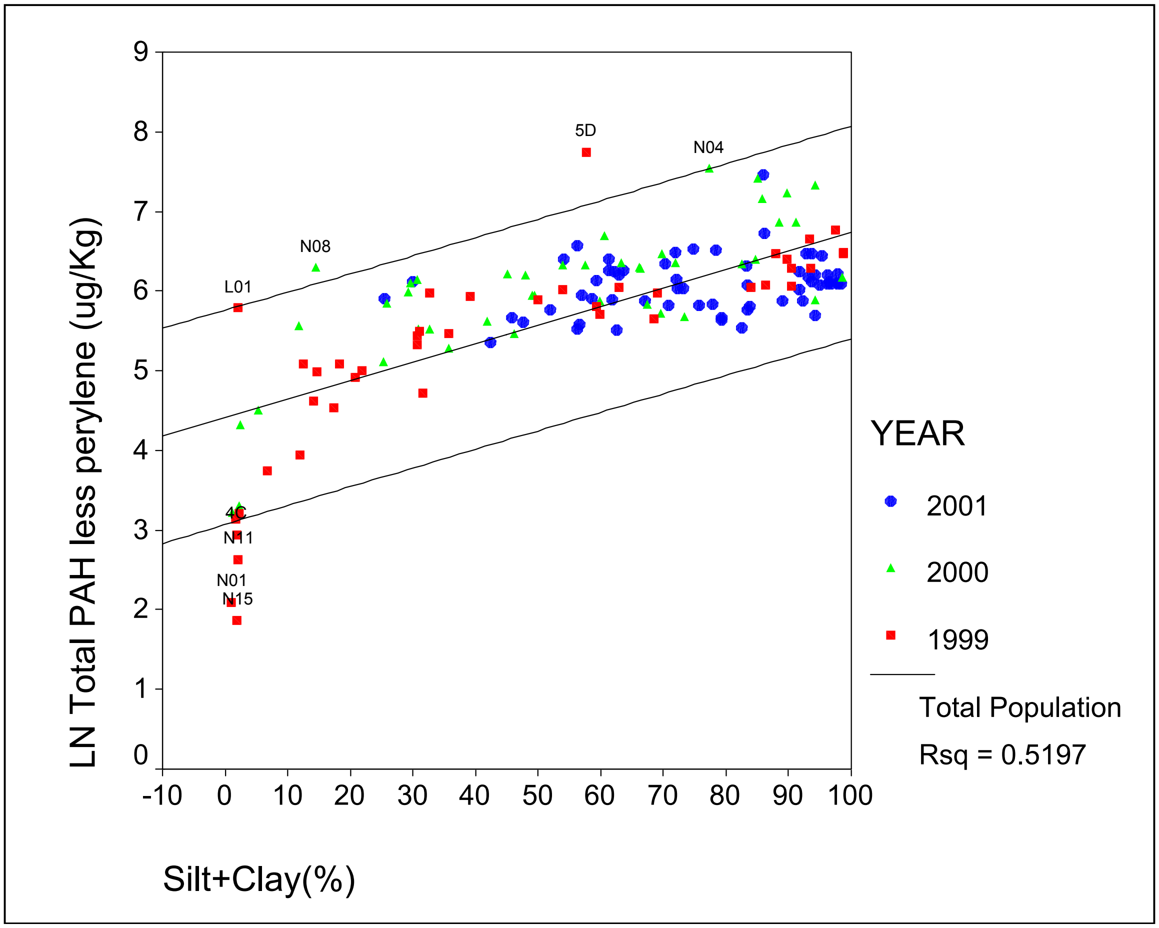


Figure 4-12. Regression Plot of Total PAH less Perylene versus Silt + Clay for 2001 Sediment Samples and 1999 and 2000 Surficial Sediment Samples

The linear regression and 95% prediction intervals are based on the total population.

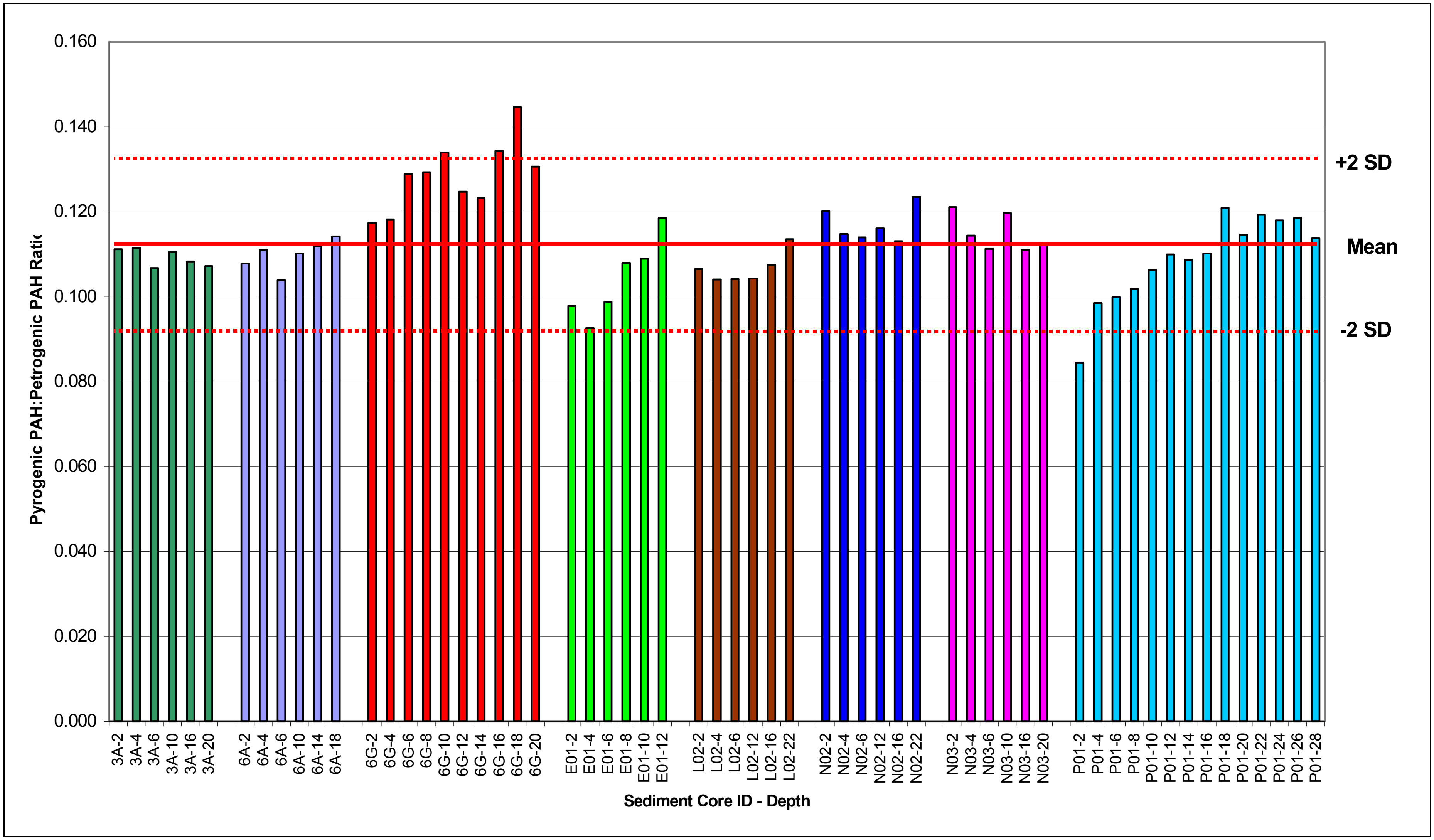


Figure 4-13. Pyrogenic/Petrogenic PAH Ratios for 2001 Sediment Cores – all Depth Intervals

Dotted lines represent upper and lower 95% confidence intervals for all samples.

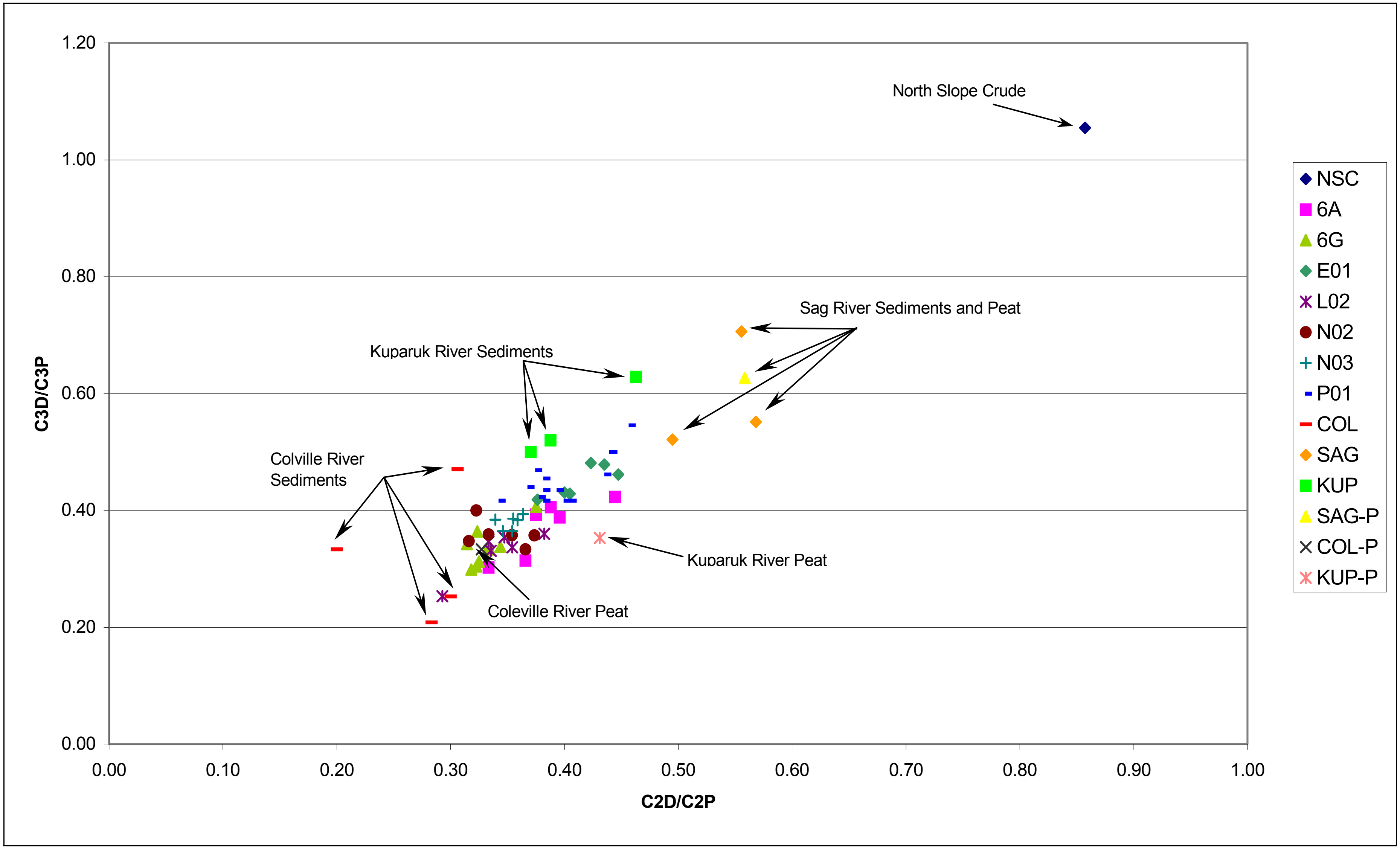


Figure 4-14. Double Source Ratio Plot of C2 D/C2P vs C3D/C3P for all Core Samples and Source Samples

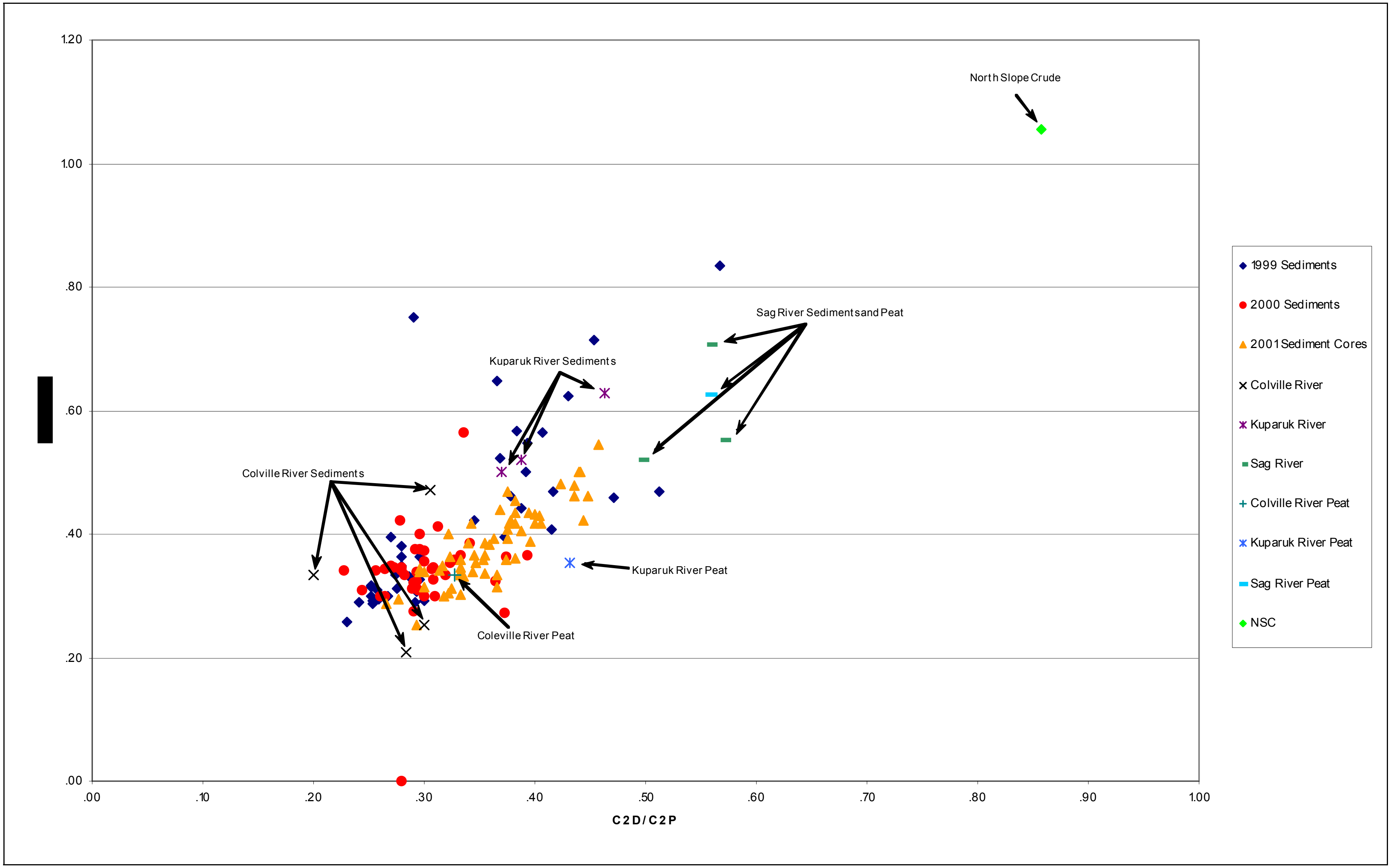


Figure 4-15. Double Source Ratio Plot of C2D/C2P vs C3D/C3P for all 2001 Core Samples, Source Samples, and 1999 and 2000 Surficial Sediment Samples

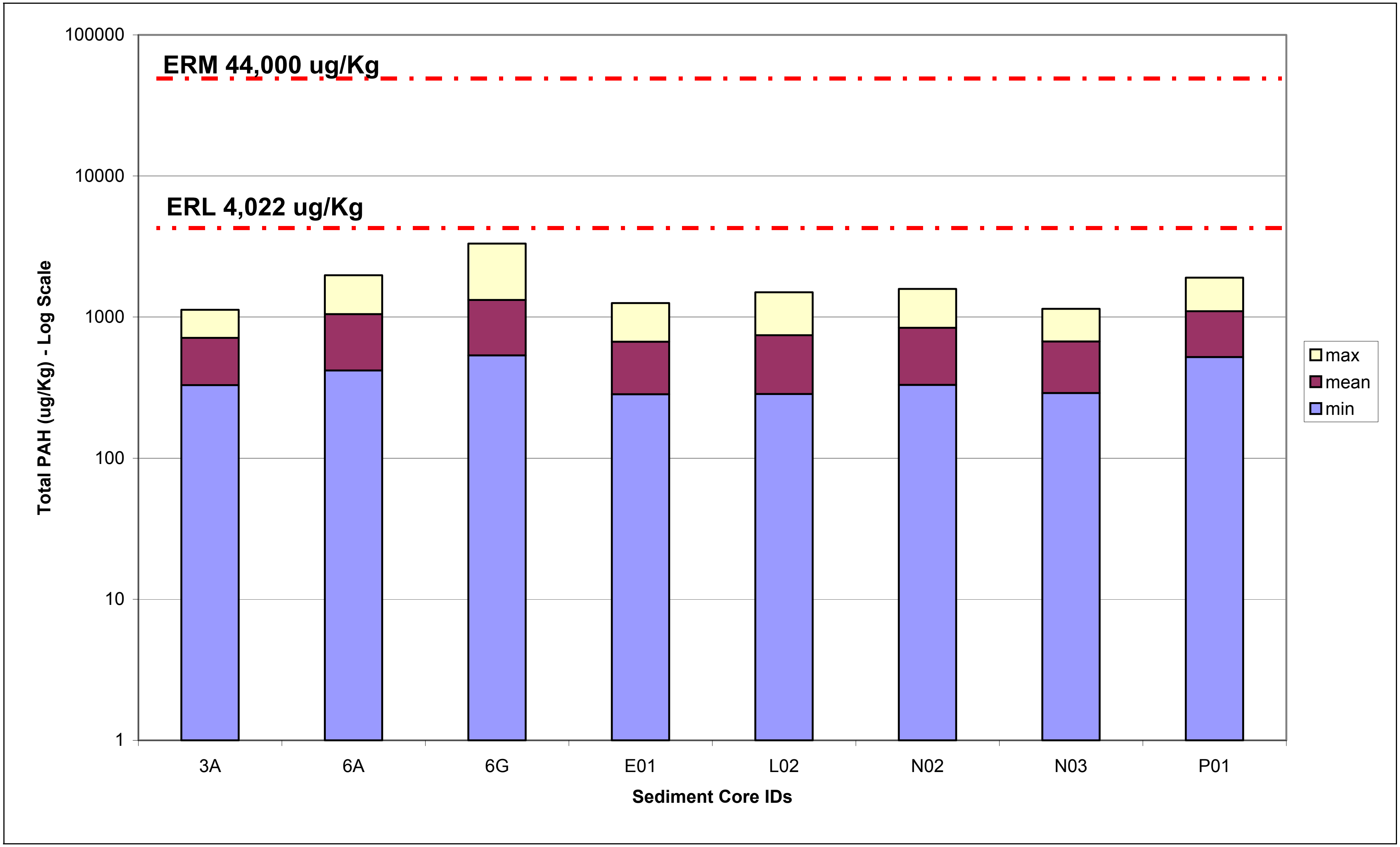


Figure 4-16. Comparison of 2001 Core Sample Total PAH Concentrations to Sediment Quality Guideline Effects Range Low (ERL) and Effects Rang Median (ERM) Values (Long et al., 1995) -- Note y-axis log scale

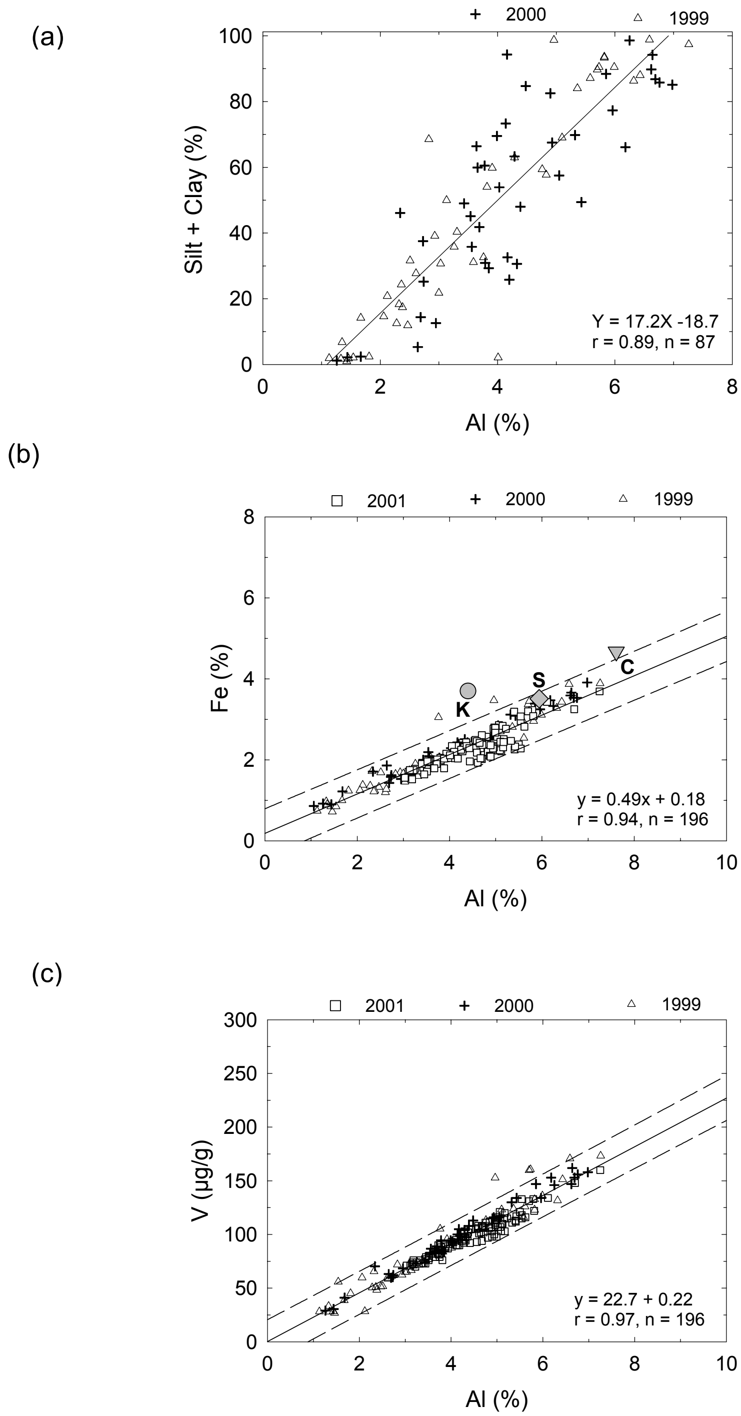


Figure 4-17. Plots of Al versus (a) Silt plus Clay, (b) Iron, and (c) Vanadium for Surficial Sediments from 1999 and 2000 and Sediment Cores from 2001

Solid line shows linear regression line, dashed lines show 99% prediction interval. Equations are from linear regressions and r is correlation coefficient and n is number of samples. Large marks with letters represent suspended sediments from the Sagavanirktok (S), Kuparuk (K) and Colville (C) rivers.

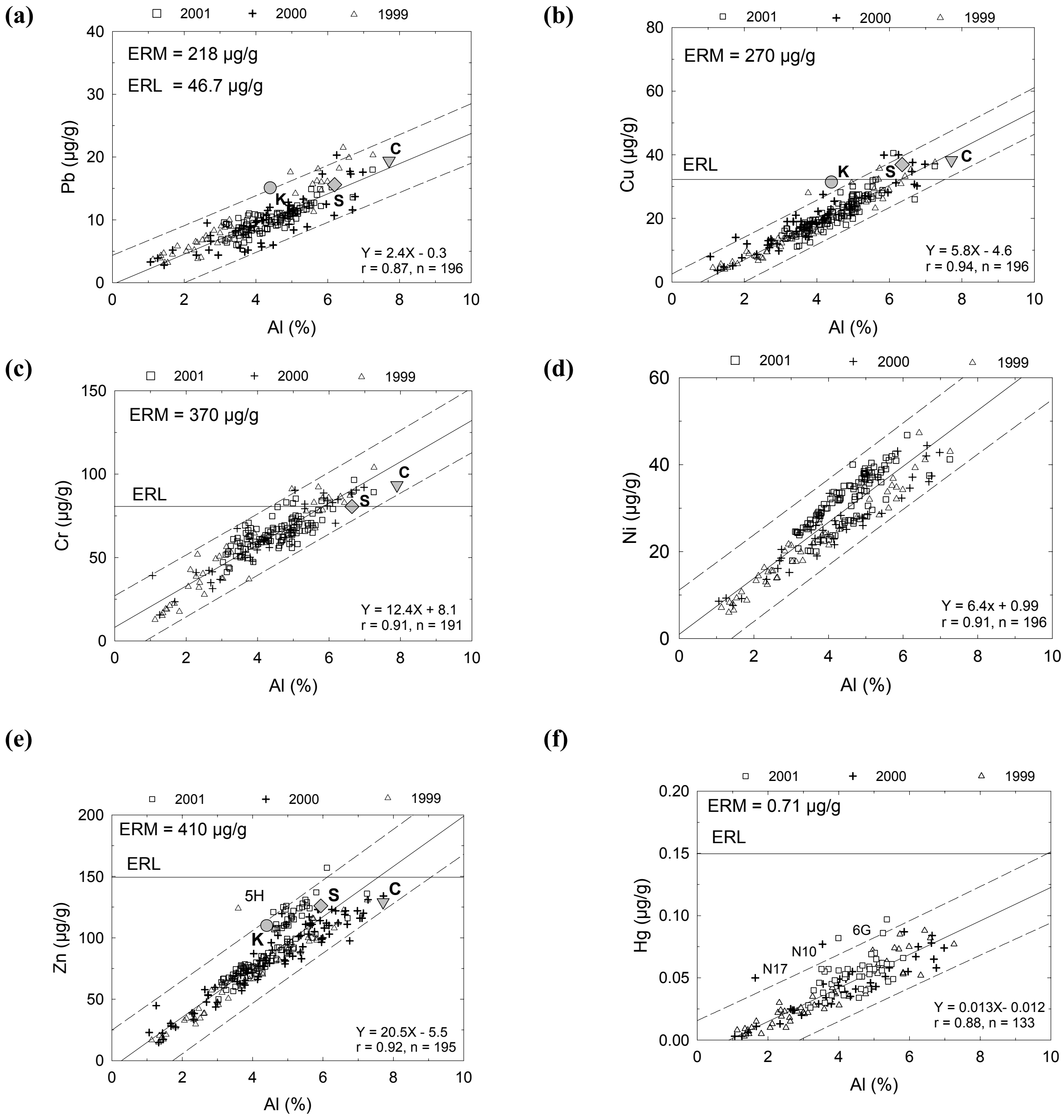


Figure 4-18. Plots of Al versus (a) Lead, (b) Copper, (c) Chromium, (d) Nickel, (e) Zinc and (f) Mercury for Surficial Sediments from 1999 and 2000 and Sediment Cores from 2001

Solid line shows linear regression line, dashed lines show 99% prediction interval. Equations are from linear regressions and r is correlation coefficient and n is number of samples. Large marks with letters represent suspended sediments from the Sagavanirktok (S), Kuparuk (K) and Colville (C) rivers. Effects Range Low (ERL) and Effects Range Median (ERM) from Long et al. (1995) also shown on some graphs.

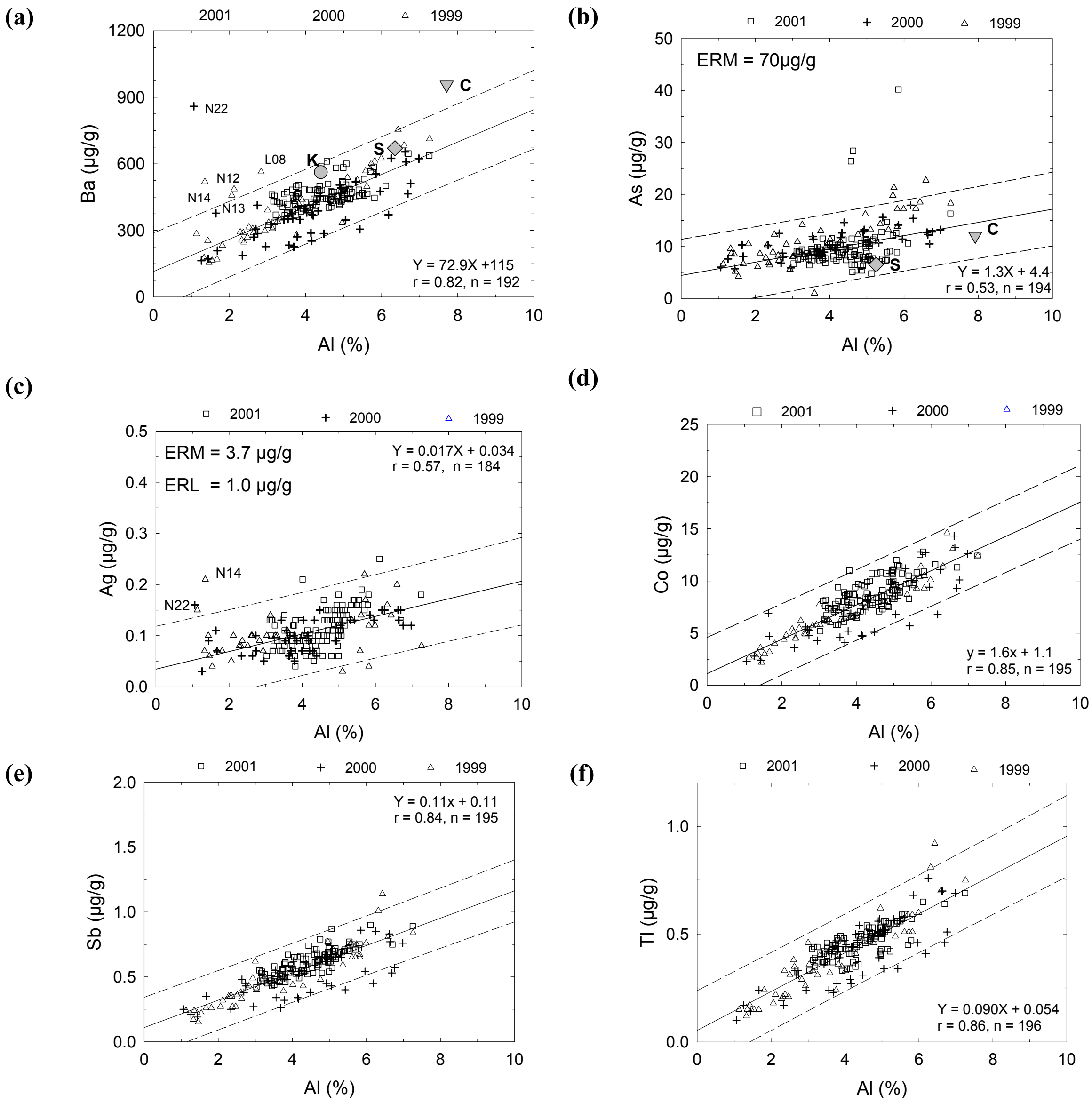


Figure 4-19. Plots of Al versus (a) Barium, (b) Arsenic, (c) Silver, (d) Cobalt, (e) Antimony and (f) Thallium for Surficial sediments from 1999 and 2000 and Sediment Cores from 2001. Solid line shows linear regression line, dashed lines show 99% prediction interval. Equations are from linear regressions and r is correlation coefficient and n is number of samples. Large marks with letters represent suspended sediments from the Sagavanirktok (S), Kuparuk (K) and Colville (C) rivers. Effects Range Low (ERL) and Effects Range Median (ERM) from Long et al. (1995) also shown on some graphs.

5.0 Recommendations

Based on the results, interpretations, and discussion of the sediment core samples collected during the 2001 field program, there are a number of recommendations for future work under ANIMIDA Phase II Task 2. The recommendations for future work should serve to increase the focus of monitoring on the potential bioavailability of contaminants in the study area. Some of these recommendations incorporate Task 2 work that has already been initiated in 2002, while others may be added to future Task 2 work.

- Perform another year of BSMP/Liberty/Northstar sediment chemistry monitoring to further evaluate the observed trend in hydrocarbons at Northstar (ANIMIDA year 4 monitoring was completed in the summer of 2002 as part of Task 2 and will be incorporated into the Task 2 Final Report)

- Perform sediment and biota chemistry monitoring adjacent to any newly proposed or modified Liberty Prospect development to establish a pre-construction baseline for future monitoring

- Focus future collection and analysis on tissue samples (bivalves, amphipods, and fish) co-sampled with sediments to increase the interpretative power of the analyses and evaluate the bioavailability of organic and inorganic contaminants

- Augment the tissue sample collections with caged bivalves and semi-permeable membrane devices (SPMDs) to further investigate the bioavailability of contaminants (SPMDs and caged mussels were successfully deployed in the summer of 2002 and results will be incorporated into the Task 2 Final Report)

- Future (post-2003) sampling should include re-sampling historic BSMP stations throughout the region (Cape Halkett to Barter Island) to re-evaluate the organic and inorganic sedimentary regime and establish additional baseline data offshore of Alaska National Wildlife Refuge and the National Petroleum Reserve - Alaska

- Collect and analyze additional river sediment samples (Canning and McKenzie Rivers) for metals and hydrocarbons to evaluate other regional sources of sediment (Canning River sediment was collected in the summer of 2002)

- Continue to analyze additional North Slope field oils (particularly Northstar production oil), and seep oils/source rock/coal samples to enhance the differentiation of hydrocarbon sources

- Future core sampling and geochronology work offshore of the study area should be considered to further identify and evaluate depositional areas where contaminants could be entrained in bottom sediments

6.0 References

Arthur D. Little, Inc. 2001. 2001 Field Sampling and Logistics Plan for the Minerals Management Service ANIMIDA Field Survey. Prepared for Minerals Management Service. July.

Anawar, H.M., K. Komaki, J. Akai, J. Takada, T. Ishizuka, T. Takahashi, T. Yoshioka, and K. Kato. 2002. Diagenetic Control on Arsenic Partitioning in Sediments of the Meghna River Delta, Bangaladesh. *Environmental Geology* 41:816-825.

Banet, Arthur C., Jr., 1995. A Comparison of Crude Oil Chemistry on America's North Slope: Chukchi Sea – McKenzie Delta, BLM – Alaska Technical Report No. 16.

Bence, A.E., K.A. Kvenvolden, and M.S. Kennicutt, II. 1996. Organic Geochemistry Applied to Environmental Assessments of Prince William Sound, Alaska, after the *Exxon Valdez* Oil Spill. *Org. Geochem.* 24:7-42. January.

Boehm, P.D. 1984. Aspects of the Saturated Hydrocarbon Geochemistry of Recent Sediments in the Georges Bank Region. *Org. Geochem.* 7:11-23.

Boehm, P.D., E. Crecelius, J.M. Neff, C.E. Tuckfield, and M. Steinhauer. 1987. Final Report on Beaufort Sea Monitoring Program: Analysis of Trace Metals and Hydrocarbons from Outer Continental Shelf (OCS) Activities. Submitted to Minerals Management Service, Alaska OCS Region, Anchorage, AK.

Boehm, P.D., L. LeBlanc, J. Trefry, P. Marajh-Whittemore, J. Brown, A. Schutzberg, and A. Kick. 1990. Monitoring Hydrocarbons and Trace Metals in Beaufort Sea Sediments and Organisms. Final Report to U.S. Department of the Interior, Minerals Management Service, Anchorage, Alaska.

Boehm, P.D. et al. 2001a. Sediment Quality in Depositional Areas of Shelikof Strait and Outermost Cook Inlet. Final Report to U.S. Department of the Interior, Minerals Management Service, Anchorage, Alaska.

Boehm, P.D. et al. 2001b. ANIMIDA Phase I: Arctic Nearshore Impact Monitoring in the Development Area - Final Report. OCS Study MMS2001-104, Anchorage, AK: Minerals Management Service, U.S. Department of Interior.

Brown, J.S. and P.D. Boehm. 1993. *The Use of Double Ratio Plots of Polynuclear Aromatic Hydrocarbon (PAH) Alkyl Homologues for Petroleum Source Identification. In* Proceedings, 1993 International Oil Spill Conference (Prevention, Preparedness, Response). American Petroleum Institute, Washington, DC. Pp. 799-804.

Brown, J. et al. 2002. ANIMIDA Task 2: Hydrocarbon and Metal Characterization of Sediments, Bivalves and Amphipods in the ANIMIDA Study Area. Interim Report to U.S. Department of the Interior, Minerals Management Service, Anchorage, Alaska.

Crecelius, E.A., J.H. Trefry, M.S. Steinhauer, and P.D. Boehm. 1991. Trace Metals in Sediments from the Inner Continental Shelf of the Western Beaufort Sea. *Environmental Geology and Water Science* 18: 71-79.

Field, L.J., D.D. MacDonald, S.B. Norton, C.G. Severn, and C.G. Ingersoll. 1999. Evaluating Sediment Chemistry and Toxicity Data using Logistic Regression Modeling. *Environmental Toxicology and Chemistry* 18(6):1311-1322.

Folk, R. L. 1974. *Petrology of Sedimentary Rocks*. Austin, Texas: Hemphill Publishing Co. pp. 182.

Gobeil, C, R.W. MacDonald, and B. Sundby. 1997. Diagenetic Separation of Cadmium and Manganese in Suboxic Continental Margin Sediments. *Geochimica et Cosmochimica Acta.* 61(21):4647-4654.

Hyland, J.L., J.S. Brown, T.C. Sauer, Jr., S. Tate, and H.J. Tsomides. 1995. *Cook Inlet Pilot Monitoring Study, Phase I of Design and Implementation of a Prototype Environmental Sampling Program for Cook Inlet, Alaska, Final Report.* Prepared for Cook Inlet Regional Citizens Advisory Council, Kenai, Alaska. March.

ICF. 2003. Cruise Report for the Summer 2001 Minerals Management Service Field Survey. Prepared for Minerals Management Service. January.

Kang, W-J., J.H. Trefry, T.A. Nelsen, and H.R. Wanless. 2000. Direct Atmospheric Inputs versus Runoff Fluxes of Mercury to the Lower Everglades and Florida Bay. *Environmental Science & Technology* 34:4058-4063.

Long, E.R., D.D. Macdonald, S.L. Smith, and F.D. Calder. 1995. Incidence of Adverse Biological Effects within Ranges of Chemical Concentrations in Marine and Estuarine Sediments. *Environ. Management* 19: 81-97.

MacDonald, D.D., R.S. Carr, F.D. Calder, and E.R. Long. 1996. Development and Evaluation of Sediment Quality Guidelines for Florida Coastal Waters. *Ecotoxicology* 5:253-278.

Naidu, A.S., A. Blanchard, J.J. Kelley, J.J. Goering, M.J. Hameed, and M. Baskaran. 1997. Heavy Metals in Chukchi Sea Sediments as Compared to Selected Circum-Arctic Shelves. *Marine Pollution Bulletin* 35(7-12):260-269.

Naidu, A.S., J.J. Goering, J.J. Kelley, and M.I. Venkatesan. 2001. Historical Changes in Trace Metals and Hydrocarbons in the Inner Shelf Sediments, Beaufort Sea: Prior and Subsequent to Petroleum-related Industrial Developments. Final Report to MMS, OCS Study, MMS2001-061, 80 pp.

Page, D.S., P.D. Boehm, G.S. Douglas, A.E. Bence, W.A. Burns, and P.J. Mankiewicz. 1998. Petroleum Sources in the Western Gulf of Alaska/Shelikof Strait Area. *Marine Pollution Bulletin* 36(12): 1004-1021.

Peters, K.E. and J.M Moldowan. 1993. *The Biomarker Guide. Interpreting Molecular Fossils in Petroleum and Ancient Sediments.* Prentice Hall. Englewood Cliffs, New Jersey.

Reimnitz, E. and S.C. Wolf. 1998. Are North Slope Surface Alluvial Fans Pre-Holocene Relics USGA Professional Paper 1605, 9 pp.

Rember, R.D. and J.H. Trefry. 2003. Increased Concentrations of Dissolved Trace Metals and Organic Carbon during the Spring Snowmelt in Rivers of the Alaskan Arctic. In review: *Geochimica et Cosmochimica Acta*.

Ridgway, L.M. and N.B. Price. 1987. Geochemical Associations and Post-depositional Mobility of Heavy Metals in Coastal Sediments: Loch Etive, Scotland. *Marine Chemistry* 21:229-248.

Salomons, W., and U. Förstner. 1984. Metals in the Hydrocycle. Berlin: Springer-Verlag.

Schropp, S.J., F.G. Lewis, H.L. Windom et al. 1990. Interpretation of Metal Concentrations in Estuarine Sediments of Florida using Aluminum as a Reference Element. *Estuaries* 13:227-235.

Sinex, W.A., A.Y. Cantillo, and G.R. Helz. 1980. Accuracy of Acid Extraction Methods forTrace Metals in Sediments. *Analytical Chemistry* 52:2342-2346.

Snyder-Conn, E., D. Densmore, C. Moitoret, and J. Stroebele. 1990. Persistence of Trace Metals in Shallow Arctic Marine Sediments Contaminated by Drilling Effluents. *Oil & Chemical Pollution* 7:225-247.

Steinhauer, M.S. and P.D. Boehm. 1992. The Composition and Distribution of Saturated and Aromatic Hydrocarbons in Nearshore Sediments, River Sediments, and Coastal Peat of the Alaskan Beaufort Sea: Implications for Detecting Anthropogenic Inputs. *Marine Environmental Research* 33: 223-253.

Sweeney, M.D., and A.S. Naidu. 1989. Heavy Metals in Sediments of the Inner Shelf of the Beaufort Sea, Northern Arctic Alaska. *Marine Pollution Bulletin* 20(3):140-143.

Tagatz, M.E., and M. Tobia. 1978. Effect of Barite ($BaSO_4$) on Development of Estuarine Communities. *Estuarine and Coastal Marine Science* 7(4):401-407.

Trefry, J.H. and S. Metz. 1984. Selective Leaching of Trace Metals from Sediments as a Function of pH. *Analytical Chemistry* 56(4):745-749.

Trefry, J.H. and B.J. Presley. 1982. Manganese Fluxes from Mississippi Delta Sediments. *Geochimica et Cosmochimica Acta* 46:1715-1726.

Trefry, J.H. and B.J. Presley. 1976. Heavy Metals in Sediment from San Antonio Bay and the Northwest Gulf of Mexico. *Environmental Geology* 1: 283-294.

URSGWC. 2001. Liberty Development 2001 Sediment Quality Study. Final Report to B.P. Exploration (Alaska), Inc.

URSGWC. 1998. In Support of the Liberty Development Project US Army Corps of Engineers Permit Application. Section 103 Marine Protection Research and Sanctuaries Act Dredged Material Disposal Site Evaluation. Prepared for BP Exploration (Alaska) Inc.

USAEDA. 1999. Final Environmental Impact Statement, Beaufort Sea Oil and Gas Development/Northstar Project. Volumes I – IV. Appendices A – K. Anchorage, Alaska.

USDOI. 1990. Alaska Outer Continental Shelf Beaufort Sea Planning Area. Oil and Gas Lease Sale 124. Environmental Impact Statement. OCS EIS/EA, MMS 90-0063. Anchorage, Alaska.

USDOI. 1996. Beaufort Sea Planning Area. Oil and Gas Lease Sale 144. Final Environmental Impact Statement. OCS EIS/EA, MMS 90-0012. Anchorage, Alaska.

USDOI. 2002. Liberty Development and Production Plan Final Environmental Impact Statement. OCS EIS/EA, MMS 2002-0019. Anchorage, Alaska.

U.S. EPA. 1991. Methods for the Determination of Metals in Environmental Samples. Office of Research & Development, U.S. EPA, Cincinnati, Ohio.

U.S. EPA. 1993. *Test Methods for Evaluating Solid Waste, SW-846, Third Edition*. Office of Solid Waste, Washington, D.C. August.

Valette-Silver, N., M.J. Hameed, D.W. Efurd, and A. Robertson. 1999. Status of the Contamination in Sediments and Biota from the Western Beaufort Sea (Alaska). *Marine Pollution Bulletin* 38 (8):702-722.

Wakeham, S.G. and R. Carpenter. 1976. Aliphatic Hydrocarbons in Sediments of Lake Washington. *Limnol. Oceanogr.* 21:711-723.

Wakeham, S.G. and J.W. Farrington. 1980. Hydrocarbons in Contemporary Aquatic Sediments. *In: Contaminants and Sediments*, Volume 1. Edited by R.A. Baker. pp. 3-27.

Wakeham, S.G., C. Schaeffiner, and W. Giger. 1980. Polycyclic Aromatic Hydrocarbons in Recent Lake Sediments-II, Compounds Derived from Biogenic Precursors During Early Diagenesis. *Geochim Cosmochim Acta* 44:415-429.

Wedepohl, K.H. 1995. The Composition of the Continental Crust. *Geochimica et Cosmochimica Acta* 59 (7): 1217-1232.

Weiss, H.V. and A.S. Naidu. 1986. ^{210}Pb Flux in an Arctic Coastal Region. *Arctic* 39(1): 59-64.