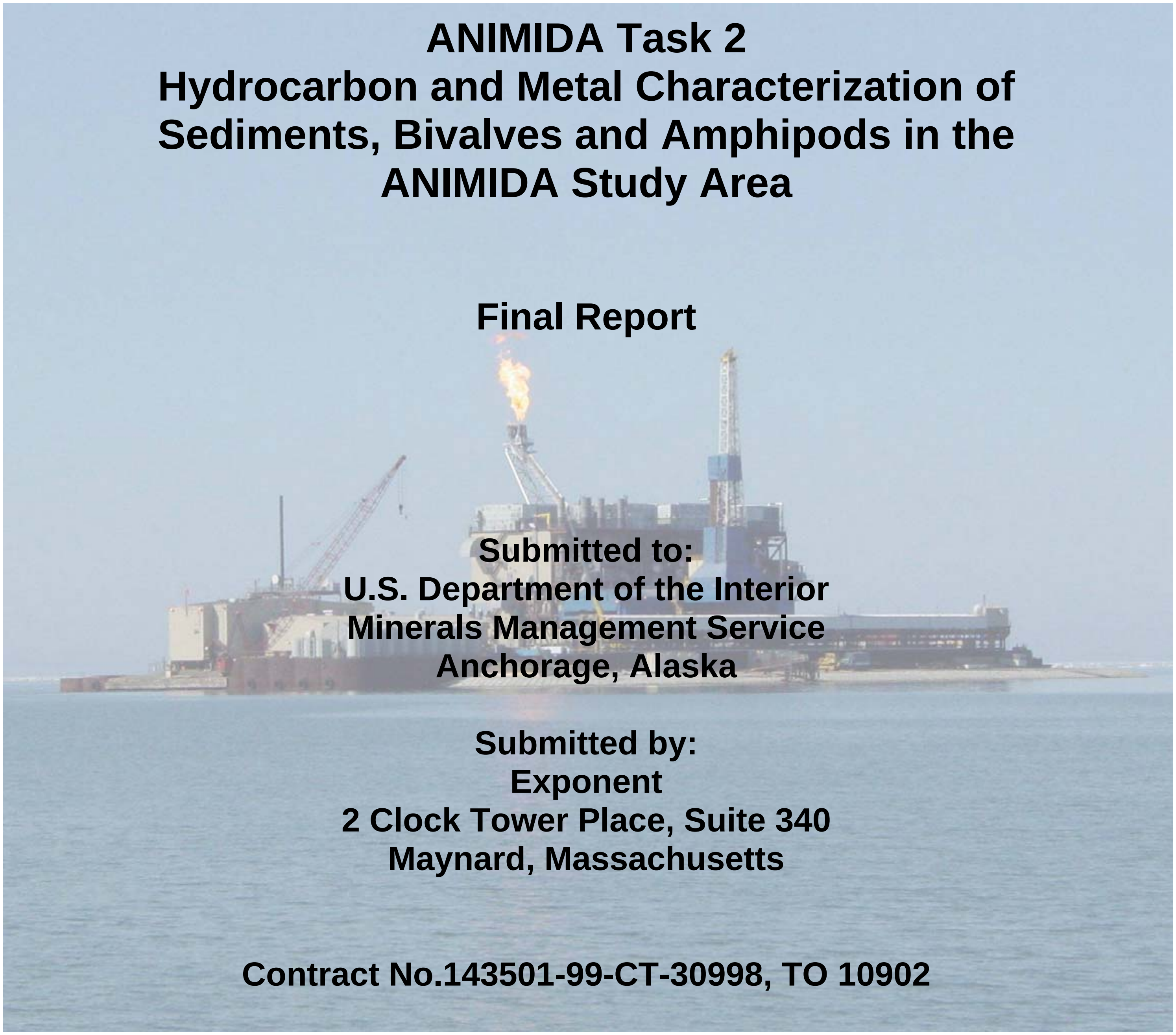
OCS Study MMS 2004-024



ANIMIDA Task 2
Hydrocarbon and Metal Characterization of Sediments, Bivalves and Amphipods in the ANIMIDA Study Area

Final Report

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U.S. Department of the Interior
Minerals Management Service
Alaska Outer Continental Shelf Region

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List of Acronyms and Abbreviations

ADF&G	State of Alaska Department of Fish and Game
ADL	Arthur D. Little, Inc.
AMS	Applied Marine Sciences
ANIMIDA	Arctic Nearshore Impact Monitoring in the Development Area
ANOVA	Analysis of Variance
BPXA	British Petroleum Exploration Alaska
BS	Blank Spike
BSMP	Beaufort Sea Monitoring Program
°C	Degrees Celsius
C	Carbon
$CaCl_2$	Calcium Chloride
CD	Compact Disc
cm	Centimeter
COC	Chain of Custody
CORIS	Coastal and Offshore Resource Information System
CPI	Carbon Preference Index
CV	Coefficient of Variation
CVAAS	Cold Vapor Atomic Absorption Spectrometry
%D	Percent Difference
DDW	Distilled, Deionized Water
dpm/g	Decompositions per Minute per Gram
DQO	Data Quality Objectives
EIS	Environmental Impact Statement
ERL	Effects Range-Low
ERM	Effects Range-Medium
FAAS	Flame Atomic Absorption Spectrometry
FID	Flame Ionization Detection
FIT	Florida Institute of Technology
FY	Fiscal Year
g	Gram
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
H	Hypothesis
H_2O	Water
H_2O_2	Hydrogen Peroxide
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

List of Acronyms and Abbreviations (continued)

K-D	Kuderna-Danish
Kg	Kilogram
KLI	Kinnetics Laboratory Inc.
km	Kilometer
L	Liter
LALK	Lower-Molecular-Weight Alkanes
LN	Log-normal
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
NBS	National Bureau of Standards
NIST	National Institute of Standards and Technology
nm	Nautical Mile
NOAA	National Oceanic and Atmospheric Administration
NRC	National Research Council of Canada
NSB	North Slope Borough
OCS	Outer Continental Shelf
OCSLA	Outer Continental Shelf Lands Act
PAH	Polynuclear Aromatic Hydrocarbon
PB	Procedural Blank
PBOC	Prudhoe Bay Operations Camp
PCB	Polychlorinated Biphenyl
ppb	Parts Per Billion
ppm	Parts Per Million
ppt	Parts Per Trillion
Q	Question
QA	Quality Assurance
QAM	Quality Assurance Manual
QC	Quality Control
%REC	Percent Recovery
RF	Response Factor
RPD	Relative Percent Difference
rpm	Revolutions Per Minute
RRF	Relative Response Factor
RSD	Relative Standard Deviation
S/T	Steranes/Triterpanes
SD	Standard Deviation
SHC	Saturated Hydrocarbons
SIM	Selected Ion Monitoring

List of Acronyms and Abbreviations (continued)

SOP	Standard Operating Procedure
SPMD	Semi-permeable membrane device
SRB	Scientific Review Board
SRM	Standard Reference Material
TALK	Total Alkanes
TOC	Total Organic Carbon
Total N	Total Naphthalenes
TPHC	Total Petroleum Hydrocarbons
μg	Microgram
μL	Microliter
μm	Micrometer
UCM	Unresolved Complex Mixture
URSGWC	URS Greiner Woodward Clyde
USACE	United States Army Corps of Engineers
USAEDA	United States Army Engineering District, Alaska
USDOI	United States Department of the Interior
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
V/V	Volume to Volume
WBS	Work Breakdown Structure
ZGFAAS	Zeeman Graphite Furnace Atomic Absorption Spectrometry

Executive Summary

OVERVIEW

The Arctic Nearshore Impact Monitoring in the Development Area (ANIMIDA) Program was designed to assess potential environmental contaminant inputs from 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 associated with the pre-Northstar construction environment. Based on Phase I results, several tasks were recommended for implementation in Phase II and accepted by Minerals Management Service (MMS). The tasks included Task 2- Continue Chemical Monitoring Effort: "Hydrocarbon and Metal Characterization of Sediments, Bivalves and Amphipods in the ANIMIDA Study Area. The resulting information from Task 2 will be used to:

- Assess environmental conditions prior to Northstar and Liberty oil development and production activities,
- Monitor temporal and spatial changes in sediment and biota chemistry associated with Northstar and Liberty oil development and production activities, and
- Provide information needed in post-leasing decisions to help minimize these changes.

Phase II – Task 2 sampling activities began during the summer of 2000 and were completed during the summer of 2003. The associated Task 2 findings for the summer field sampling programs conducted in 1999 (Phase I), 2000, 2001, and 2002 are reported and discussed in this report. For Task 2, data were acquired on surficial sediments, riverine sediments and peat, biota (clams and amphipods), semi-permeable membrane devices (SPMDs), caged mussels, and sediment cores in the ANIMIDA study area. The results and discussion associated with the sediment core program (2001 field program) are contained in a separate MMS Report (Brown, et al., 2003) and briefly addressed in this report.

Phase II was designed to monitor the spatial and temporal shifts in chemical parameters associated with the construction and operation of the Northstar and Liberty developments. Northstar construction began in late 1999, island construction was completed in early 2000, and the first Northstar oil was produced at the end of 2001. The Liberty development was delayed by British Petroleum Exploration Alaska (BPXA) and has not been restarted as of this writing. Organic and metal parameters were analyzed to investigate the hypothesis that there was a shift in these parameters associated with the island construction and oil production activities at Northstar. The summer 1999 survey data represent pre-construction activities at Liberty and Northstar, the summer 2000 and 2001 survey data represent post-construction, pre-production measurements at Northstar and additional pre-construction measurements at Liberty, and the summer 2002 survey data represent post-construction, and ongoing production measurements at Northstar and additional pre-construction measurements at Liberty. Thus, the data collected and the results reported here represent the monitoring of the Northstar development during the construction of the gravel island, pipeline, and facility; the monitoring of the Northstar development during continued oil production; and continued pre-construction monitoring at the Liberty prospect area.

OBJECTIVES

The ANIMIDA Program was designed to address a series of scientific questions concerning the potential for shifts in environmental chemistry parameters associated with the Northstar and Liberty developments. Each question can then be turned into a testable hypothesis, which guides the design of the technical program. The key questions, which drive Task 2 of ANIMIDA, are as follows:

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

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

Task 2 addresses the first question and Task 2 along with two additional ANIMIDA Tasks (Task 6 and Task 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 field studies (Fiscal Years [FYs] 1999 - 2002) to monitor sediment and/or biota chemistry in the nearshore Beaufort Sea, focusing on potential contaminant inputs from the Northstar development.
- Coordinate chemistry monitoring coupled with other ANIMIDA Phase II tasks (biology, 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.

It is an explicit goal of the ANIMIDA Program to examine temporal and spatial changes and to determine if any observed changes in concentration and/or composition are related to the Northstar development.

ANIMIDA TASK 2 STUDY DESIGN

To meet the objectives of the ANIMIDA program, the study design of Task 2 focused on measuring those parameters that would be leading indicators of, or related to environmental contaminant inputs from the Northstar and Liberty oil development projects. The elements of primary focus included:

- Hydrocarbons and associate polycyclic aromatic hydrocarbons (PAHs), and metals as primary contaminants of concern
- Sediment contamination
- Bioaccumulation of contaminants

- Other natural and anthropogenic sources of chemicals of concern

The study design for Phase II built on the Phase I design (Boehm et al. 2001b) and 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; Boehm et al. 1991)
- Location and sampling of reference stations
- Identification of source samples for collection (e.g. river sediments)
- Addition of Phase II sampling stations along the pipeline route.

FINDINGS

Sediments

As part of ANIMIDA Phase II, surficial sediment samples were collected from the ANIMIDA study area during the summers of 2000 and 2002 and sediment core samples were collected during the summer of 2001. All samples were analyzed for PAH, saturated hydrocarbons (SHC), steranes/triterpanes (S/T), metals, grain size, and total organic carbon (TOC). The sediment core samples were also analyzed for radionuclides for age-dating. This report also presents surficial sediment sample data collected in the 1980's as part of the BSMP (Boehm et al. 1991) and in 1999 as part of ANIMIDA Phase I (Boehm et al. 2001b).

Sediment Characteristics. Comparison of grain size data from 1999 with data from 2000 shows some inter-annual shifts in the texture of surficial sediment throughout the study area as well as some possible influences from Northstar Island. The largest changes in grain size distribution occurred at nearshore stations, landward of Northstar Island. During 1999, surficial sediment at stations N11-N14 was essentially all sand and gravel. In contrast, the 2000 samples were dominated by silt and clay (Figure 1). Although the exact mechanism for this shift is unknown, the 1999 samples were collected after a 6-day storm with winds >25 knots that may have eroded away finer-grained material. No such storms preceded collection of the 2000 samples that probably contained finer-grained material carried in by the Kuparuk River during the spring of 2000. At stations N06 and N10 (Figure 1), both close to Northstar Island, much finer-grained particles were collected during 1999 than 2000, possibly resulting from inputs of coarser material at these sites in association with construction of the island. Most importantly, Figure 1 depicts the marked patchiness in sediment composition and the spatial and temporal variability of sediment in the area.

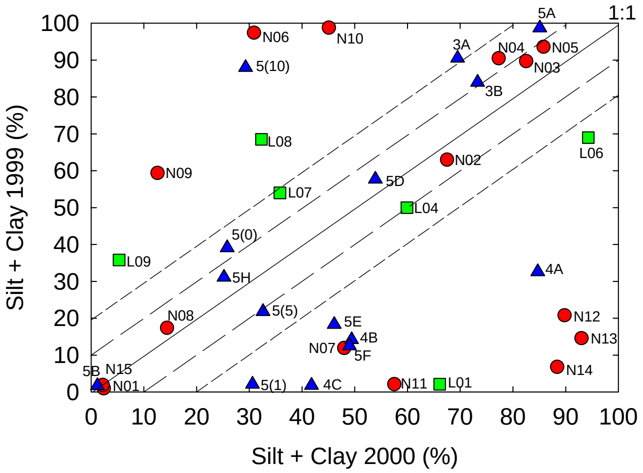


Figure 1. Values for silt + clay in surficial sediment from the coastal Beaufort Sea for 2000 versus 1999 with data from Northstar area (circles) Liberty Prospect (squares) and adjacent areas (triangles).

The largest changes in grain size distribution observed during this study occurred between 1999 and 2000. Differences in grain size distribution between the 2000 and 2002 sampling are less than observed between 1999 and 2000.

The most important finding derived from the grain size data is that sediments in many locations throughout the ANIMIDA study area are regularly shifting and that the sediment grain sizes found during one year may shift prior to sampling during a subsequent year. Thus, techniques that normalize sediment chemistry to account for differences in grain size need to be used.

Hydrocarbons. In contrast to a crude oil composition (Figure 2), the surficial sediments in the Northstar area and indeed for the whole region (e.g., Figure 3) exhibit a mixture of primarily terrestrial biogenic hydrocarbons and lower levels of petroleum hydrocarbons. This assemblage is clearly dominated by plant wax normal (i.e., straight-chain) alkanes in the n-C27 through n-C33 carbon range. This is further demonstrated by carbon preference index (CPI) values that range from two to seven for most samples, which is characteristic of sediments influenced by terrigenous plant inputs (Wakeham and Carpenter, 1976; Boehm, 1984).

The PAH distributions for most of the surficial sediments (e.g., Figure 3) show that the PAHs are primarily of a combined fossil fuel origin (i.e., petroleum and coal) with a biogenic component (perylene), and lesser contributions of pyrogenic or combustion-related compounds (e.g., 4-, 5-, and 6-ring PAHs). The petrogenic PAHs account for approximately 90 percent of the Total PAH less perylene throughout the study area (Figure 4). Perylene was abundant in surficial sediments, often the most abundant single PAH compound in the overall PAH distribution.

Concentrations of hydrocarbons in the sediments adjacent to Northstar and Liberty are generally within the observed historical range for these parameters in the overall study area. Background concentrations of Total PAHs (a sum of 2 to 6 ringed parent and alkylated PAHs) in recent Alaskan surficial sediment studies range from <10 parts per billion (ppb) to 1000 ppb. Typically PAH profiles indicate significant levels of a fossil fuel-type signature, which appears to be sourced in organics shales brought to the sediments from river runoff and coastal peat. PAH compositional results (i.e., petrogenic PAHs vs. pyrogenic PAHs) (Figure 4), illustrate no significant changes in PAH composition year over year related to Northstar construction and production activities.

The observation that the Northstar 1999 sediments may be depleted in hydrocarbons relative to the other 1999, 2000 and 2002 sediments is supported by a Total PAH less perylene versus silt + clay regression plot for all the 1999, 2000, and 2002 sediment data. In this plot (Figure 5), the regression and 95% prediction intervals are shown for all data. The plot shows a small cluster of Northstar 1999 samples which are below the 95% prediction interval, indicating that these samples are significantly lower in PAH versus silt + clay than the overall population of 1999, 2000 and 2002 samples. An analysis of the comparison of the Northstar 2000 and 2002 samples versus the BSMP and Liberty 2000 and 2002 samples resulted in no significant difference for all bulk hydrocarbon parameters and most of the diagnostic ratios. The results of this analysis are illustrated by a PAH regression plot (Figure 6) which shows complete overlap between the regression lines and 95% prediction intervals (i.e., no significant difference) for the Northstar, BSMP, and Liberty sediments for 2000 and 2002. No evidence of any inputs of Northstar-related petroleum hydrocarbons were observed in the surface sediments. Additionally, a comparison of the Total PAH from all ANIMIDA sediments from the study region in 1999, 2000, and 2002 to the Effects Range Low (ERL) and Effects Range Median (ERM) sediment quality guidelines reveals that none of the Total PAH concentrations determined in this study exceed the guidelines.

Figure 2. Northstar Oil – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

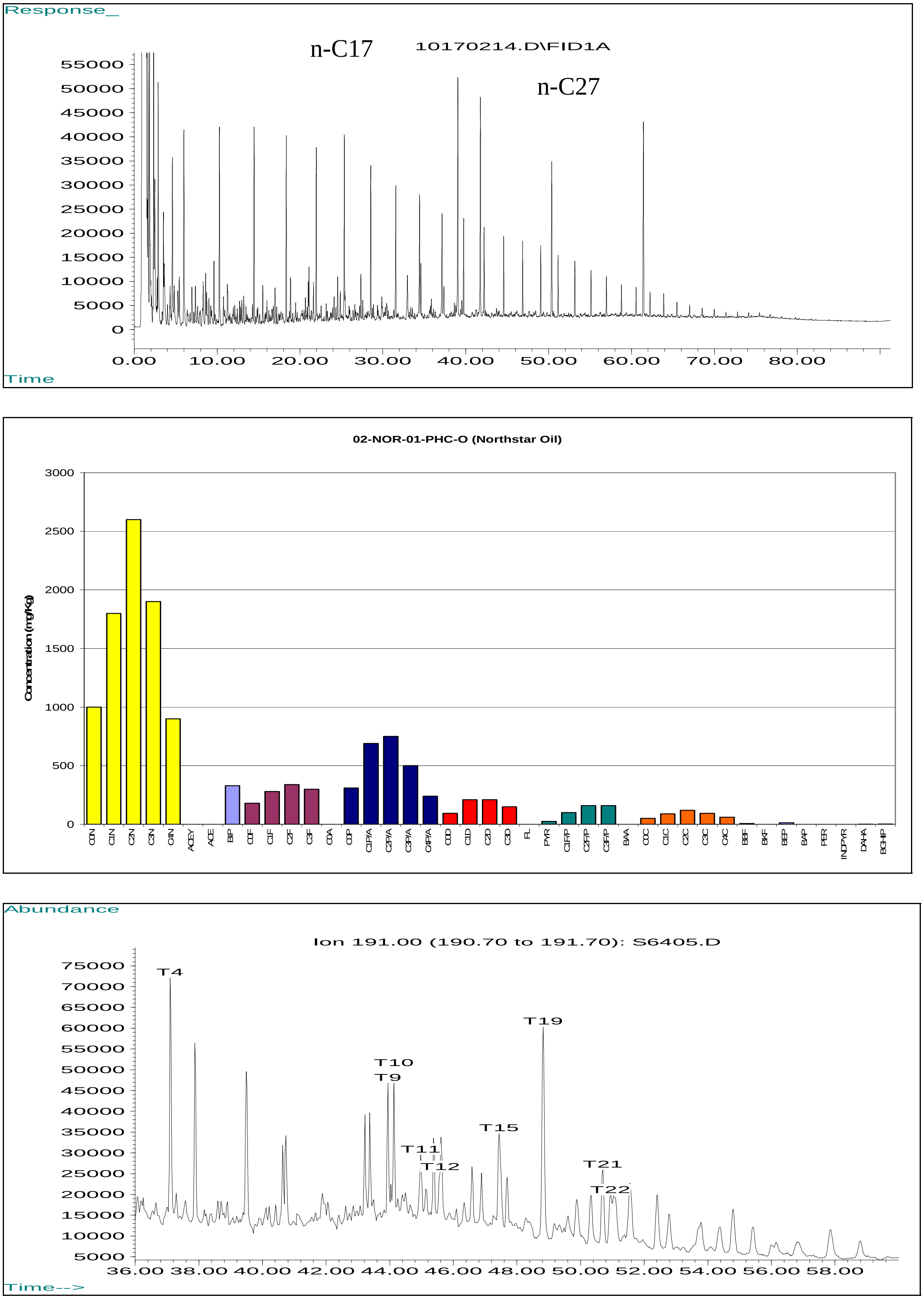
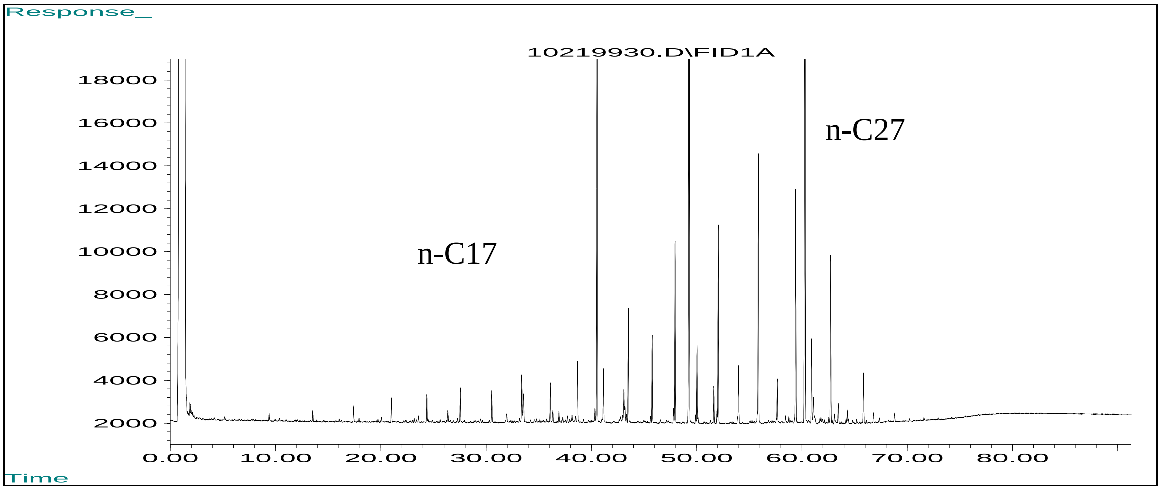
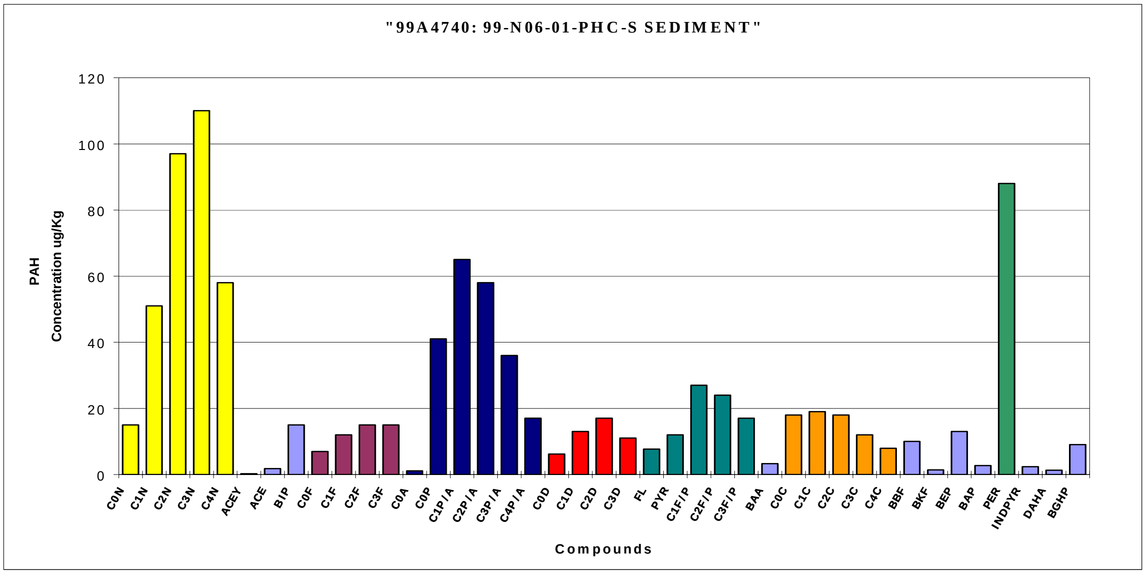
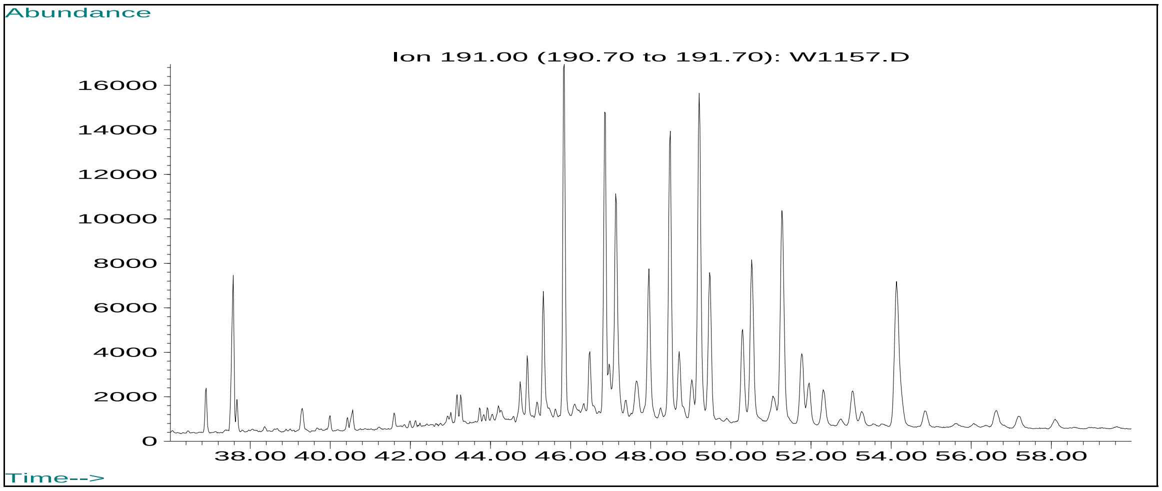


Figure 3. Northstar Station 6 Sediment, Year 1999 – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)







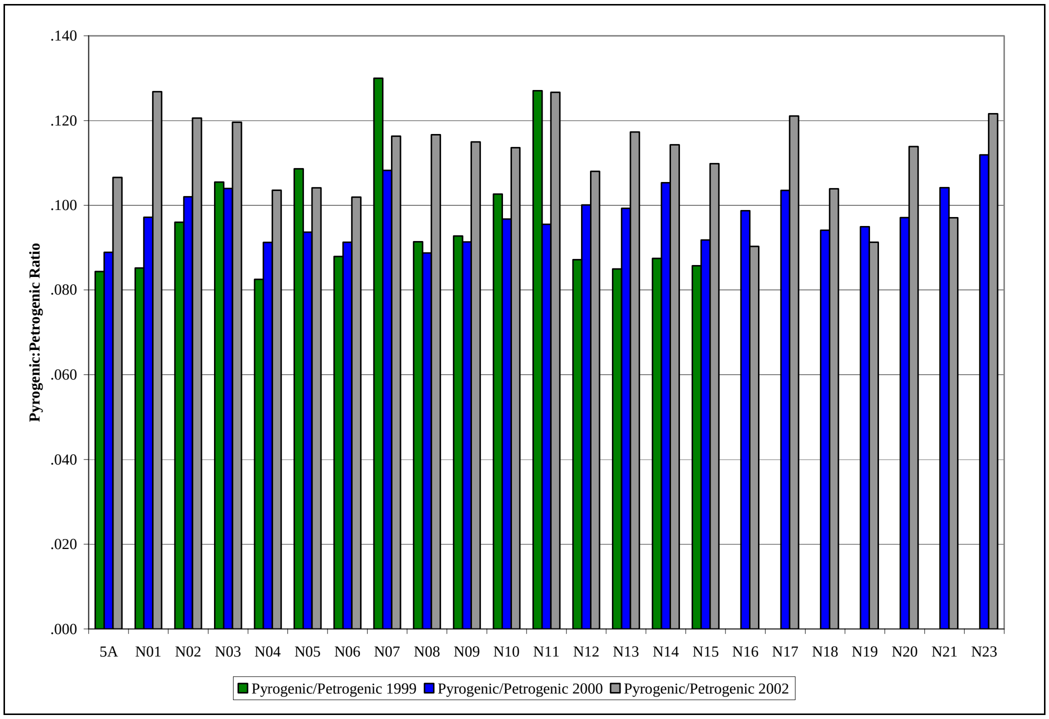


Figure 4. Pyrogenic:Petrogenic Ratios of Northstar Surficial Sediment Samples for 1999, 2000, and 2002

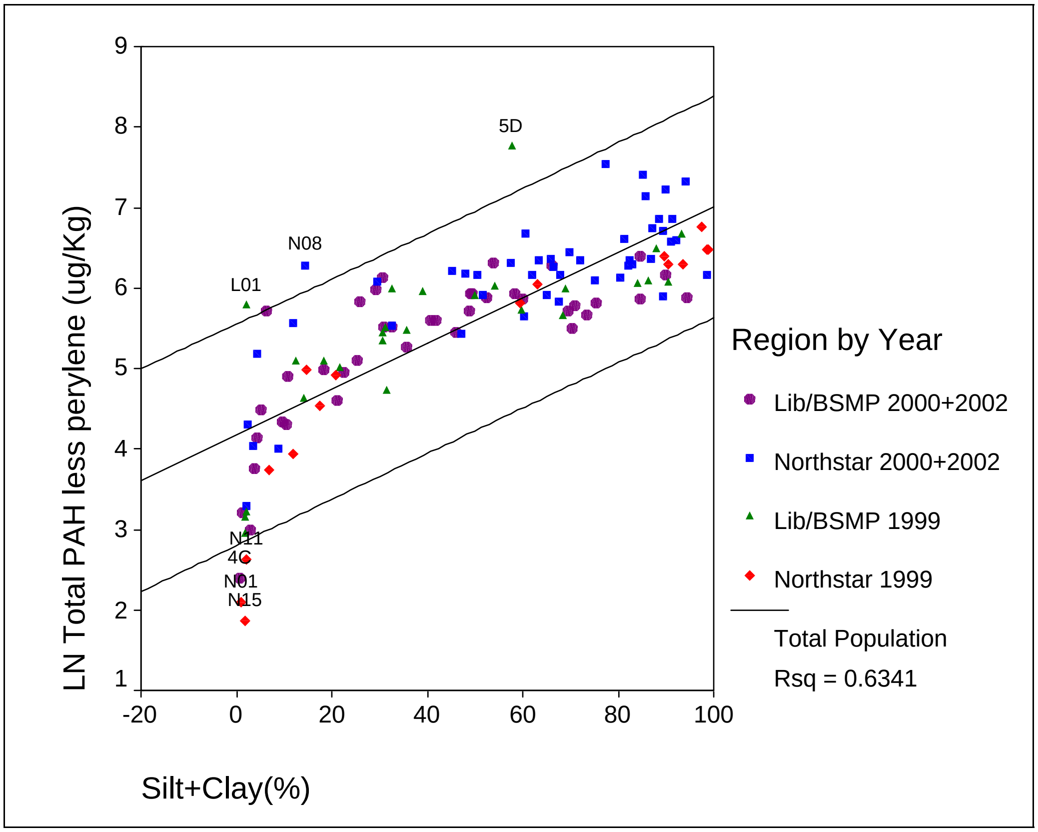


Figure 5. Regression Plot of Total PAH less Perylene versus Silt + Clay for all 1999, 2000, and 2002 Northstar, Liberty and BSMP Sediments

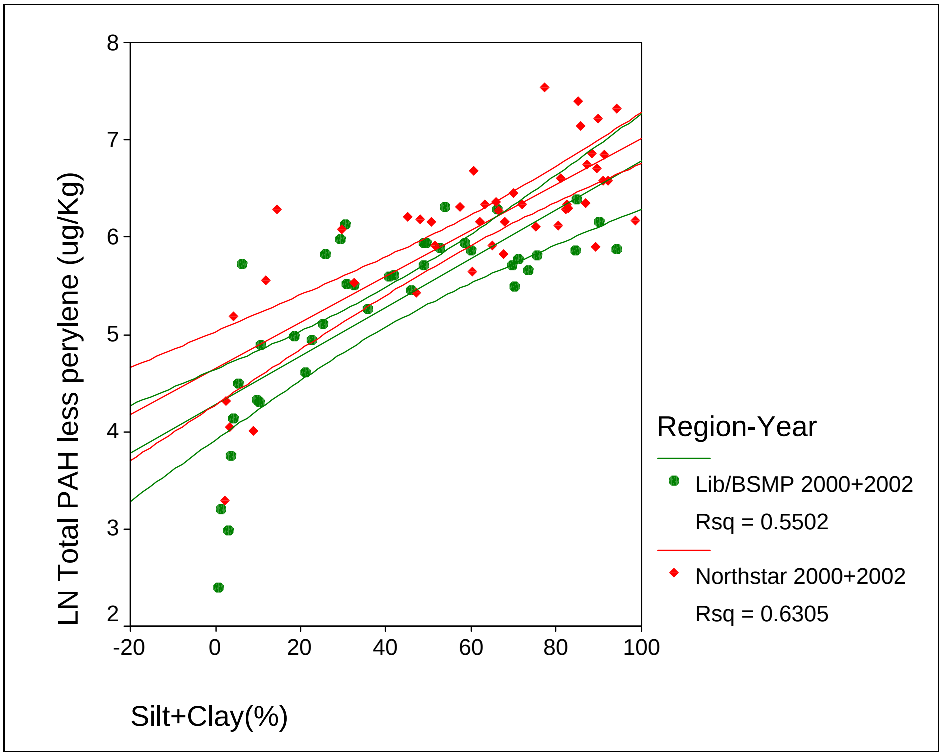


Figure 6. Regression Plot of LN Total PAH less Perylene versus Silt + Clay for all 2000 and 2002 Northstar, Liberty and BSMP Sediments. The lines, Rsq, and 95% prediction intervals are from linear regression and related statistical calculations

Trace Metals. Concentrations of metals in sediment help identify spatial and temporal trends in the distribution of potential anthropogenic chemicals. Fourteen metals (Ag, As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Tl, V and Zn - element symbols are defined in Table 2-6) were analyzed in sediment from this study because of their potential as pollutants. Four other metals (Al, Fe, Ba, and Mn) were included in the study as indicator metals because they provide insight to sediment composition (Al in clays and Fe in iron oxide coatings), the presence of drilling discharges (Ba in barite, a common additive in drilling fluids), and sediment redox conditions (Mn, a redox-sensitive metal).

A spatial patchwork in concentrations of metals in sediment was observed as a function of variability in the distribution of sediment texture as described above. However, concentrations of trace metals generally correlated well with concentrations of Al and Fe because concentrations of most metals are very low in quartz sand or carbonate shell material and much higher in fine-grained, metal-bearing aluminosilicates. Anthropogenic processes rarely affect Al and Fe concentrations because these major elements are naturally present at percent levels in most sediment relative to part per million (ppm) levels for trace metals. Thus, Al and Fe provided a valuable normalization tool for this study that incorporated the metal-controlling variables of grain size, organic carbon content and mineralogy. In the ideal case, a good linear correlation was observed between concentrations of a trace metal and Al and/or Fe. Significant, positive deviations from this linear trend helped identify metal contamination.

Concentrations of all trace metals in sediment from all study years have been plotted versus Al. Each plot has been fit with a linear regression line and a 99% prediction interval. These plots serve as templates for identifying past and future metal contamination. Each plot reveals a consistent pattern of Al versus metal for the study period. For example, the Al versus Cr plot (Figure 7a) shows that all data points fit the 99% prediction interval very well and thus no anthropogenic inputs of Cr to the study area were encountered. The graph for Al versus Ba (Figure 7b) shows a reasonably good fit for most of the data; however, several data points plot at more than 10% above the upper prediction interval. The anomalous points were from sites where minor inputs of Ba via runoff from land operations or from activity at Northstar Island or as remnants of prior exploratory drilling may have occurred, as explained in the report. A few other instances of slightly elevated levels of Hg (Figure 7c), Ag, Sb and Zn were found in a total of ~10 instances or only 0.8% of the >1200 data points for metals in sediment. Although these various anomalies are minor, and are generally identified at low levels of Al, they do support the sensitivity of Al versus Ba graphs and help identify locations where future monitoring efforts can be focused.

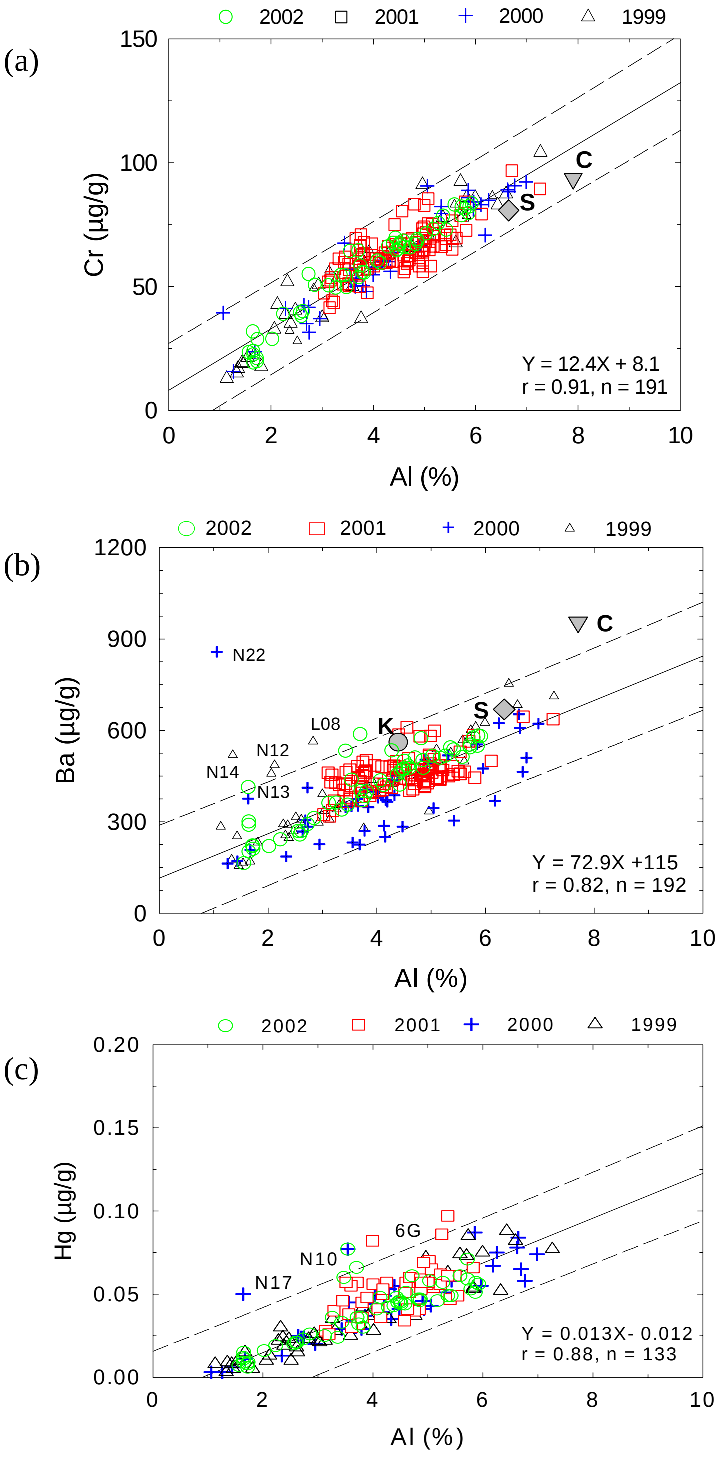


Figure 7. Concentrations of aluminum versus (a) chromium, (b) barium, and (c) mercury for sediment from the ANIMIDA study area

Equations are from linear regression calculations and r is the correlation coefficient. Dashed lines show the 99% prediction interval. Points marked with large letters are for suspended sediment from the Sagavanirktok (S), Kuparuk (K) and Colville (C) rivers. Data for sites identified on the graphs were not included in the regression calculations.

Biological Samples

As part of ANIMIDA Phase II, biota samples were collected from the ANIMIDA study area during the summers of 2000 and 2002. All samples were analyzed for PAH, SHC, S/T, and metals. This report also presents biota sample data collected in the 1980's as part of the BSMP (Boehm et al. 1991) and in 1999 as part of ANIMIDA Phase I (Boehm et al. 2001b).

Hydrocarbons. As with the pre-construction (1999) data, the amphipods (*Anonyx*) and clams (*Astarte sp.*) indicate that hydrocarbons in the sediment system are not readily bioavailable as these species exhibit little ability to bioaccumulate saturated and aromatic hydrocarbons from sediment or from the overlying water column. PAH levels are very low, showing consistent concentrations of contaminants over time in the study area.

Metals. Mean concentrations of Ba, Cu, Pb, V and Zn in clams (*Astarte sp*.) sampled during 1986, 1989, 1999, 2000, and 2002 are relatively uniform among years. Such uniformity is encouraging with respect to using body burdens for metals as long-term indicators of metal availability. This uniformity also indicates that no detectable shifts in metal levels in *Astarte* occurred between 1986 and 2000. However, the standard deviation for a given metal in an individual year is sometimes large. Such variability limits statistical discrimination of changes in metal levels.

Among the metals for which data are available for all five years, concentrations of Cu and Zn in the amphipod *Anonyx* are highest, yet, most uniform. Levels of these two essential metals are controlled by osmoregulation within the organism and anomalous body burdens for these metals may imply a physiological imbalance. However, the results based on these two metals indicate no imbalance at this time. Concentrations of Pb, a non-essential metal, are low, yet, reasonably uniform. The data for 1999, 2000 and 2002 for Ba, Cd, Cu, Pb, V, and Zn in *Anonyx* (Figure 8) as well as the other trace metals show marked similarity among years and no influence of anthropogenic input from the Northstar development. Overall, the metal data for the amphipods provide a useful baseline for monitoring shifts in concentrations over time.

SPMDs

The SPMDs from the reference site and from the Northstar site showed no significant differences in most of the key PAH parameters measured. The Total PAH concentrations in the SPMDs were low (210 – 260 ng/g). An evaluation of the PAH distribution in the SPMD samples (Figure 9) reveals composition of primarily petroleum PAH in both the Northstar and reference SPMDs, mixed with trace levels of pyrogenic PAH.

Caged Mussels

The caged mussels from the Northstar and reference deployments showed no significant differences in most of the key hydrocarbon parameters measured. The PAH concentrations in the mussels were very low (13 – 17 ng/g Total PAH), however, the concentrations were substantially higher than the pre-deployment reference levels indicating that the mussels bioaccumulated trace levels of hydrocarbons. No significant differences were observed between concentrations of metals in samples from the reference site in the coastal Beaufort Sea versus Northstar Island.

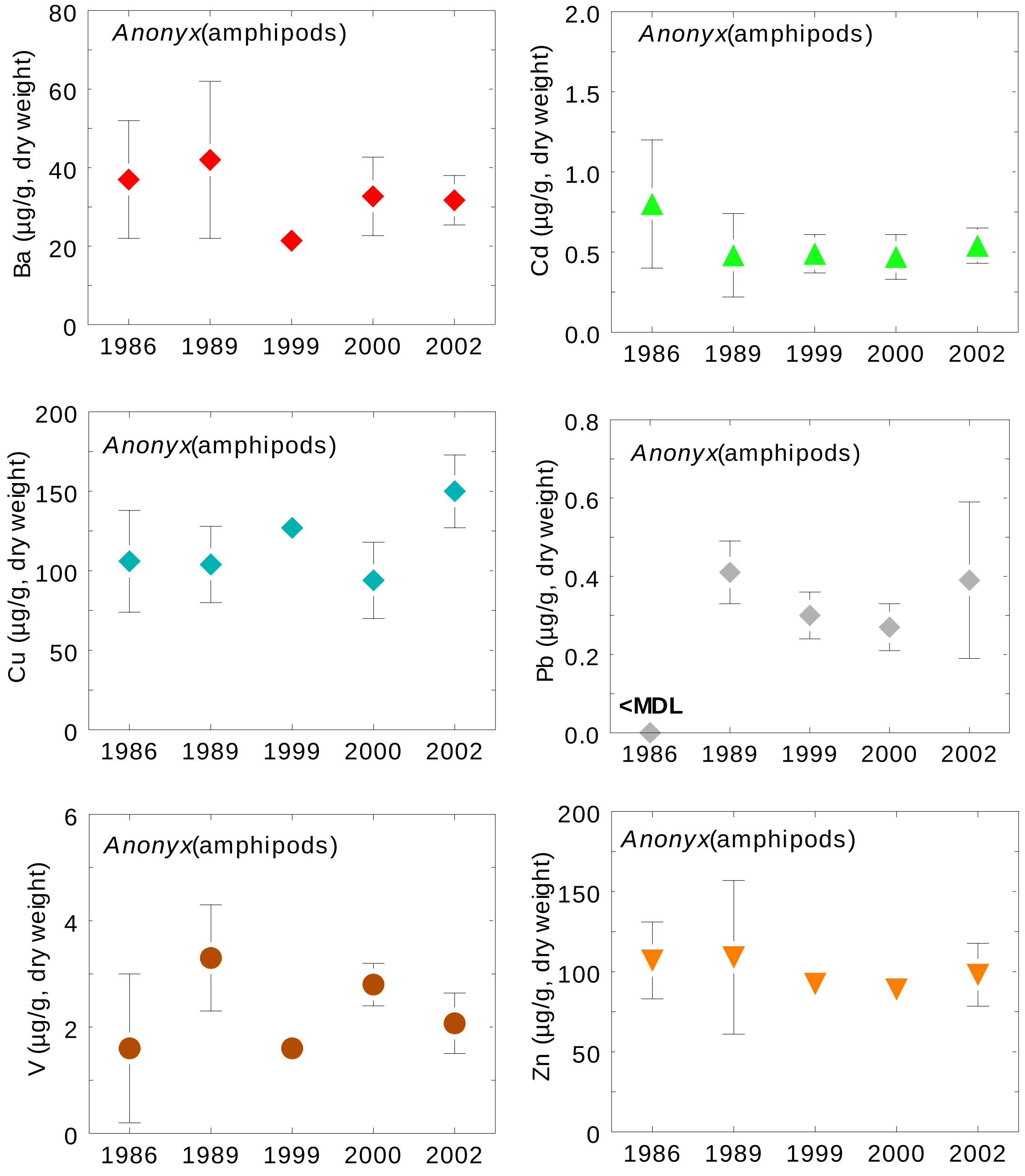
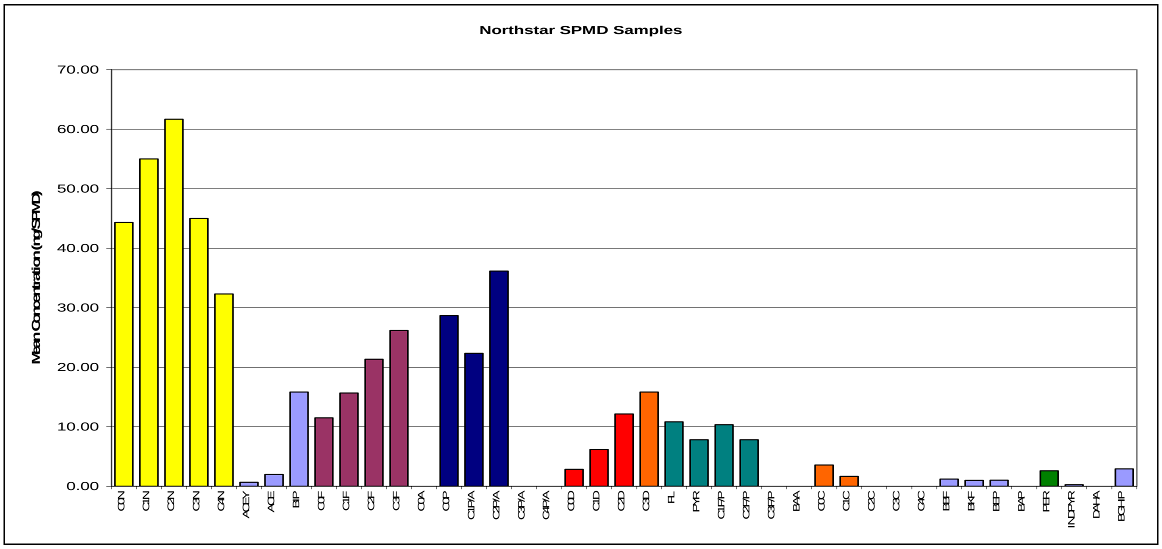


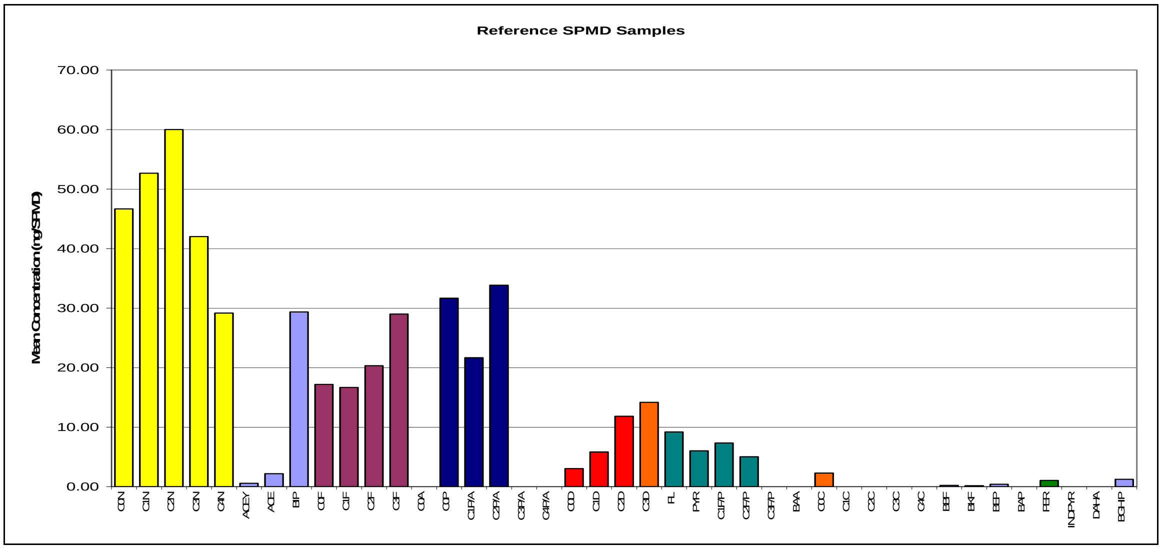
Figure 8. Mean concentrations (± standard deviation) of Ba, Cd, Cu, Pb, V and Zn in amphipods (Anonyx) collected from sites in the BSMP during 1986, 1989 and for ANIMIDA during 1999, 2000 and 2002.

Figure 9. Composition of PAHs in SPMDs from Reference Site (A) and Northstar Site (B)

(A)


Northstar SPMD Samples
Mean Concentration (ng/SPMD)
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
C0N
C1N
C2N
C3N
C4N
ACEY
ACE
BIP
C0F
C1F
C2F
C3F
C0A
C0P
C1P/A
C2P/A
C3P/A
C4P/A
C0D
C1D
C2D
C3D
FL
PYR
C1F/P
C2F/P
C3F/P
BAA
C0C
C1C
C2C
C3C
C4C
BBF
BKF
BEP
BAP
PER
INDPYR
DAHA
BGHP

(B)


Reference SPMD Samples
Mean Concentration (ng/SPMD)
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
C0N
C1N
C2N
C3N
C4N
ACEY
ACE
BIP
C0F
C1F
C2F
C3F
C0A
C0P
C1P/A
C2P/A
C3P/A
C4P/A
C0D
C1D
C2D
C3D
FL
PYR
C1F/P
C2F/P
C3F/P
BAA
C0C
C1C
C2C
C3C
C4C
BBF
BKF
BEP
BAP
PER
INDPYR
DAHA
BGHP

SUMMARY

Phase II sampling efforts began with the summer 2000 field survey and proceeded through the summer of 2002. Phase I sampling was conducted during the summer of 1999. During this period, construction of the Northstar Island and pipeline was completed in 2000 and production of oil began 2001.

Overall, the results of the ANIMIDA Phase I and II, Task 2 effort indicated that no significant contaminant inputs from Northstar development activities were detected and that any observed changes in the monitored environmental conditions were well within the natural variability of the study area. At the same time, the results, coupled to increased knowledge of the chemistry of natural sources of hydrocarbons and metals, indicated that the monitoring and data interpretation approaches as designed are very sensitive to changes and that if inputs were to occur, the measurement systems set in place would be powerful and sensitive enough to detect such inputs.

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-construction environment near Northstar and Liberty and to monitor selected parameters over time as part of a long-term program to assess potential spatial and temporal changes related to 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 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 monitoring efforts directed at the Northstar and Liberty developments. Priorities were placed on characterizing the pre-construction environment and establishing a scientific basis for post-construction and production monitoring. The monitoring elements included: performing chemical analyses on sediments and selected marine biota in the area; analyzing the amount and chemistry of the total suspended matter in area river and sea water; obtaining information on other natural and anthropogenic sources of contaminants of concern (hydrocarbons and trace metals); and assessing bioaccumulation in select 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 Northstar development island is located about 6 miles (~10 km) offshore of Point Storkersen in the Beaufort Sea in a water depth of approximately 40 feet (~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 proposed 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). Table 1-1 summarizes past oil and gas development and production activities in the Beaufort Sea dating back to 1949.

1.3 Current/Proposed Oil Development

1.3.1 Northstar

The BPXA Northstar development project is located about 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 in 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 disturbances 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 levels 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 disturbances 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 regional Beaufort Sea Monitoring Program (BSMP) stations. The 1999 open-water sampling represented pre-construction conditions at both the Northstar and Liberty locations. The overall objectives of Phase I were to implement a monitoring program focused on those measurements and parameters that could be used to determine the existence, extent, and magnitude of future environmental disturbances 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) review 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 to 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 contaminant inputs from the Northstar and Liberty developments

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

- 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 survey conducted in 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. 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. The results of the sediment core survey are presented in a separate MMS report (Brown et al., 2003).

1.5.1 Task Order 2 Research Questions and Hypotheses

The objectives of the ANIMIDA program address a series of scientific questions concerning the potential contaminant inputs from 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 Task 2 surficial sediments and biota samples follow.

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

H1a. The concentrations of organic pollutants in sediments do not show any increase as a result of the development of the Northstar and/or Liberty units.
H1b. The concentrations of metal pollutants in sediments do not show any increase as a result of the development *of the Northstar and/or Liberty units.*

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

H2a. Concentrations of organic pollutants adjacent to the Northstar and/or Liberty developments do not pose an ecological risk to marine organisms as determined by sediment quality benchmarks.
H2b. Concentrations of organic pollutants adjacent to the Northstar and/or Liberty developments do not pose an ecological risk to marine organisms as determined by changes in bioaccumulation by marine bivalves and amphipods.
H2c. Concentrations of trace-metal pollutants adjacent to the Northstar and/or Liberty developments do not pose an ecological risk to marine organisms as determined by sediment quality benchmarks.
H2d. Concentrations of trace-metal pollutants adjacent to the Northstar and/or Liberty developments do not pose an ecological risk to marine organisms as determined by changes in bioaccumulation by marine bivalves and amphipods.

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. While all of these elements are built into this program, 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.

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

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

Source: USDOI, 2002.

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

Note [1] – Satellite associated with Duck Island production unit
Note [2] – Satellite associated with Kuparuk River production unit
Note [3] – Satellite associated with Milne Point production unit
Note [4] – Satellite associated with Prudhoe Bay production unit

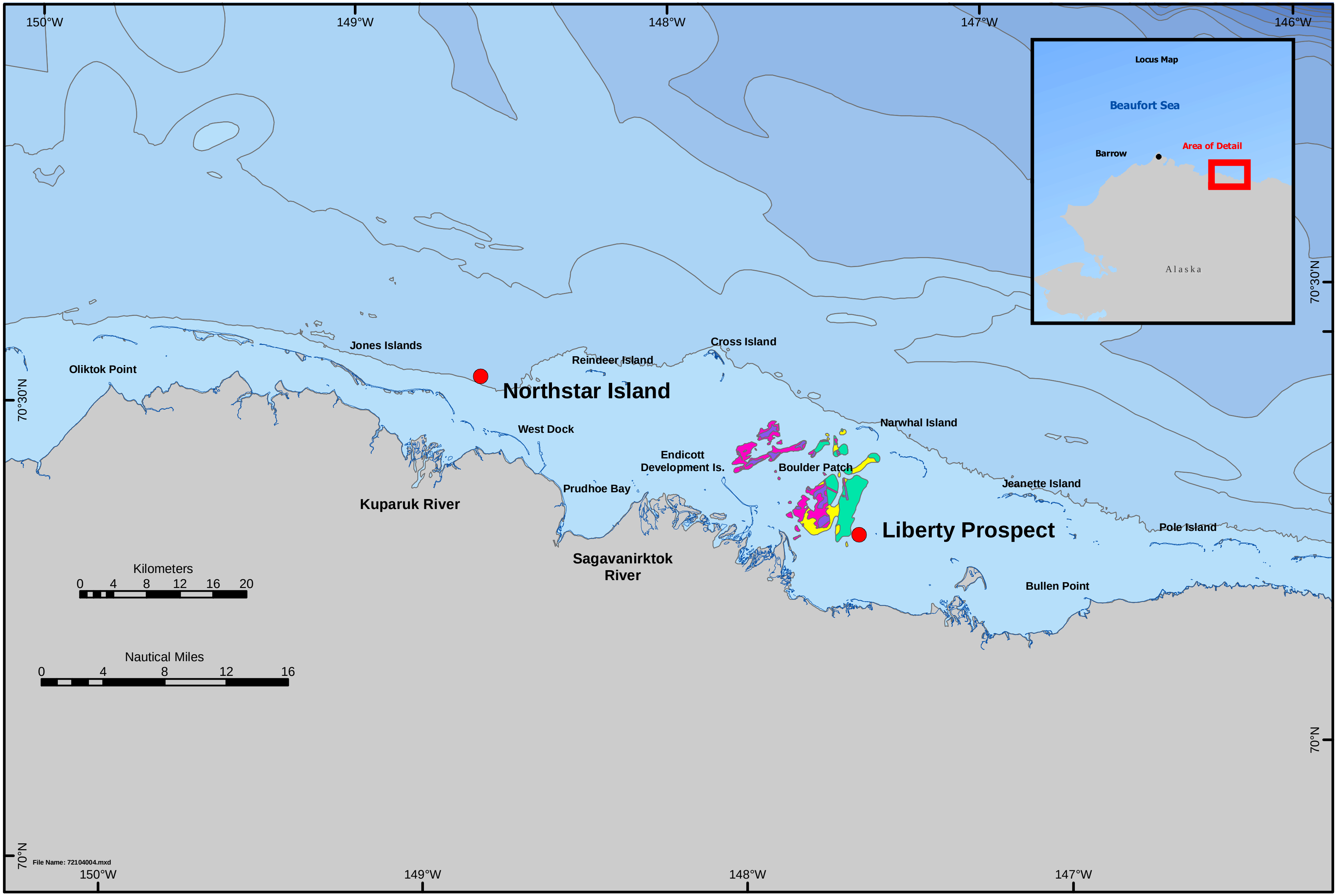


Figure 1-1. Map of the ANIMIDA Study Area

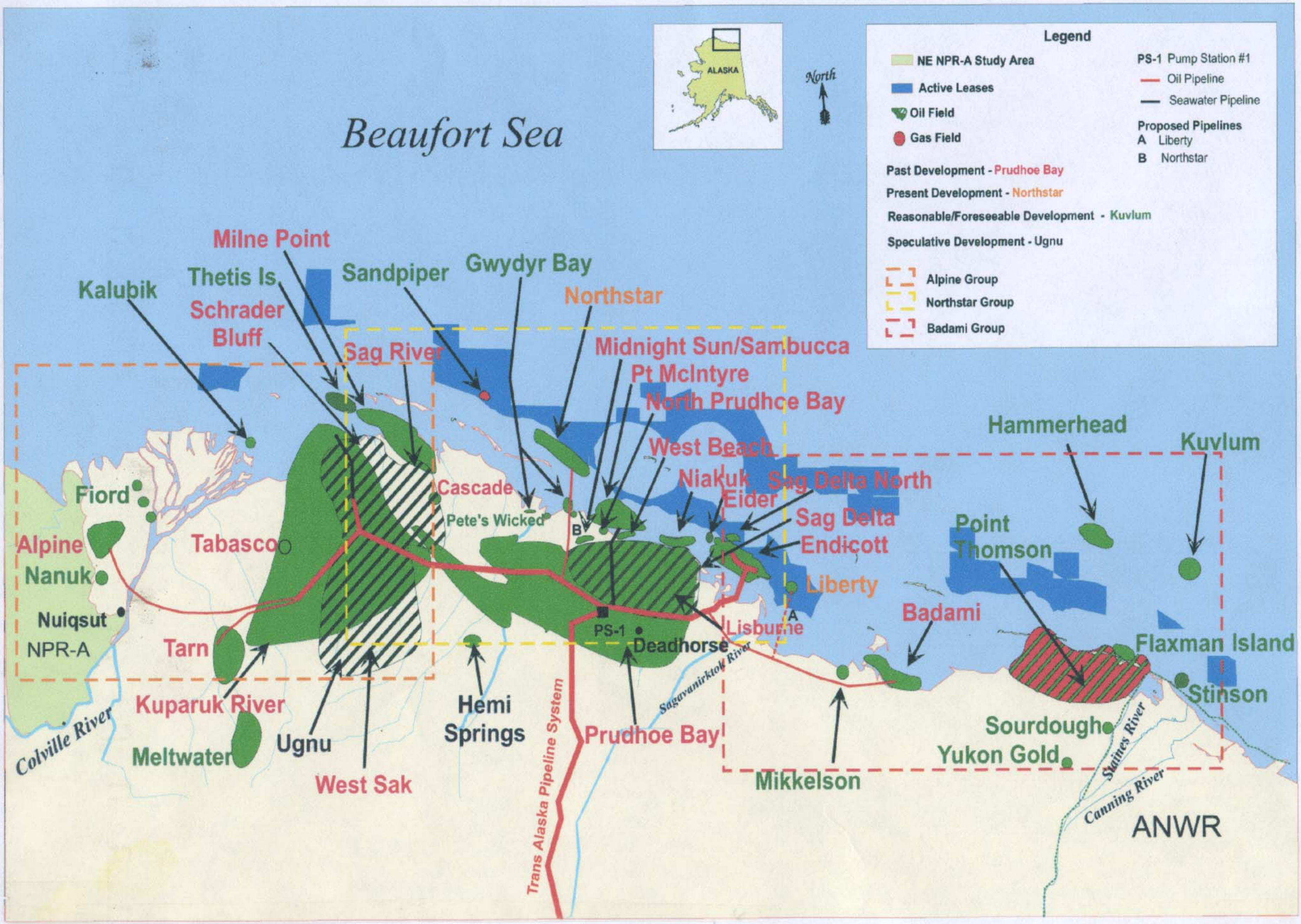


Figure 1-2. General Map of Onshore and Offshore Oil and Gas Development In the Study Areas

Source: USDOI, 2001

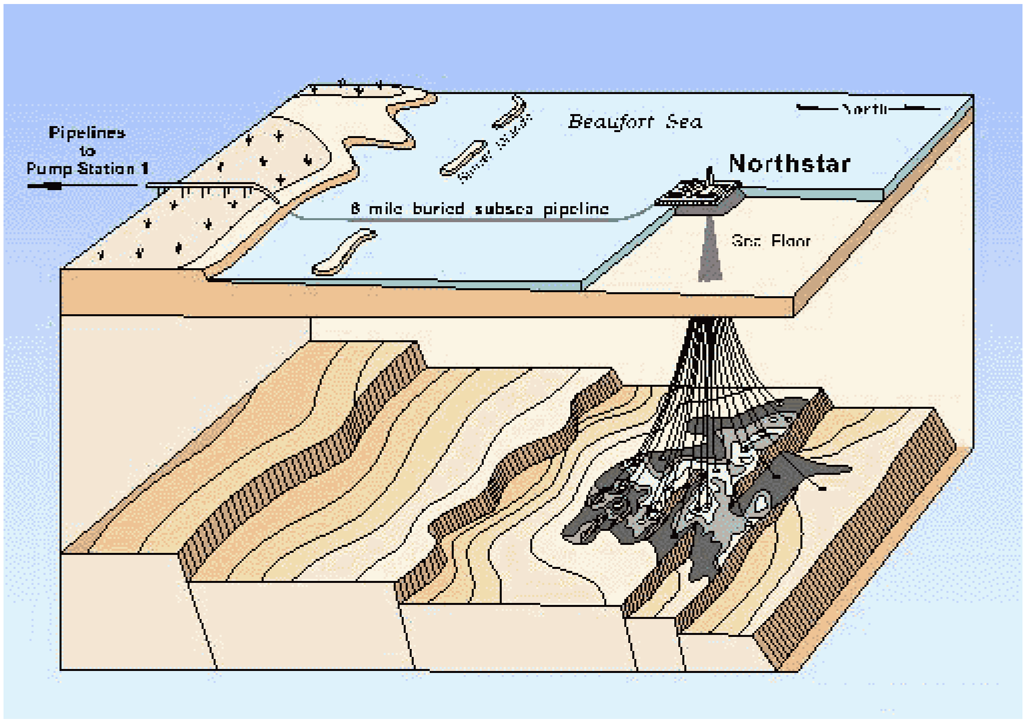


Figure 1-3: Schematic of BP's Northstar Development
(from: http://www.bp.com/alaska/index_nstar.htm)

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 encompassed both the Liberty and Northstar prospect areas, and much of the shoreline where regional Prudhoe Bay oil production activities are occurring. Two open-water surveys were conducted in August 2000 and in July-August 2002 under Task Order 2 of Phase II of the ANIMIDA program. These surveys included collection of sediment and biota samples and provided post-Northstar construction sampling which corresponds to the pre-Northstar construction samples collected in 1999 as part of the Phase I field survey described in Boehm et al., 2001b. Caged mussels and semi-permeable membrane devices (SPMDs) were also deployed and retrieved during the summer 2002 survey.

The overall design of the field program incorporated a sampling program using a combination of site-specific fixed stations around the Liberty and Northstar developments, and regional, historical BSMP stations (Figure 2-1 [Summer 2000 and 2002 Sampling Stations] and Boehm, 1987). The site-specific Liberty and Northstar stations were located in four radial transects centering on the proposed prospect sites. The radials were located at 0.5, 1, 2, and 4 km intervals and the transects were oriented approximately North – South and East – West (Figure 2-1). The radial transect orientation enables station comparison spatially away from the development islands, as well as onshore – offshore station comparison, and East – West station comparison to account for the prevailing East – West currents in the region. In addition, five pipeline route stations and four 0.5 km radial stations were added in 2000 and 2002 to enhance the sample station resolution for the Northstar pipeline and development island. This overall design allowed a combination of site-specific stations to be sampled for sediment and biota (tissue) chemistry.

The summer 2000 and 2002 field surveys included extensive sampling at the Northstar development to provide sufficient data to assess potential post-construction changes. Samples collected at the Liberty prospect and the majority of the BSMP stations serve as additional baseline samples for the overall ANIMIDA program (Figure 2-1). Several of the BSMP stations [5F, 5D, and 5(10)] are located within 11 km of the Northstar development and BSMP station 5A is within 3 km of Northstar; samples collected from these stations provide additional data to assess post-construction changes at Northstar.

The summer 2002 field survey included deployment and retrieval of paired mussel cages and SPMDs to further investigate the bioavailability of contaminants. Three caged mussel/SPMD moorings were deployed adjacent to Northstar and 3 moorings were deployed in a reference location approximately 4 km southwest of Pole Island (Figure 2-1).

2.1.2 Summer 2000 Field Sampling

The summer 2000 field sampling was conducted from August 12 to August 28, 2000. The scientific crew, aboard the MMS *Vessel 1273*, collected samples for chemical and other analyses from the program study area. The field sampling methods were conducted in accordance with Arthur D. Little, Inc. (ADL)/ICF Consulting (ICF) Standard Operating Procedures (SOPs). The field sampling and logistics plan (Arthur D. Little, 2000) prepared for the summer 2000 field survey provides detailed explanations of the field methods for sample collection, equipment decontamination, and subsampling of sediment cores. Field sampling personnel from ADL/ICF, Florida Institute of Technology (FIT), and Applied Marine Sciences (AMS) participated in the survey. The scientific team and ship's captain (Mark Mertz - TEG Ocean Services) conducted the work on an 18-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 (Arthur D. Little, 2001). A summary of the field sampling activities and methods follows in this section.

Samples

The scientific crew collected samples for chemical analyses from the program study area. The following components were successfully completed:

- Collected samples at 44 stations

15 historic BSMP stations
23 Northstar and Northstar pipeline stations
6 Liberty stations

Collected 48 surficial sediment samples (0 to 1 centimeter [cm]) for hydrocarbon and metals chemistry (triplicates at 2 stations – stations L08 and N13)

- Collected 11 bivalve/amphipod samples

Collected 5 source sediment/peat samples (4 river stations)

Delivered field samples to analytical laboratories for appropriate analyses

Several source samples were collected as part of the summer survey. The source samples collected included sediment for hydrocarbon and metals analyses, from the Sagavanirktok, Kuparuk, and Colville Rivers. Additionally, one peat sample was obtained from the bank of the Kuparuk River.

A complete list of the 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 2000 (and 2002) sampling stations. Additional daily survey and sampling station information is included in the 2000 station logs contained in the Cruise Report (Arthur D. Little, 2001).

2.1.3 Summer 2002 Field Sampling

The summer 2002 field sampling was conducted from July 27 to August 22, 2002, and coincided with a period of expected favorable ice conditions in the program study area. The scientific crew, aboard the MMS *Vessel 1273*, collected samples for chemical and other analyses from the program study area. The field sampling methods were conducted in accordance with ADL/ICF SOPs. The field sampling and logistics plan (ICF, 2002a) prepared for the summer 2002 field survey provides detailed explanations of the field methods for sample collection, equipment decontamination, and subsampling of sediment cores. Field sampling personnel from Battelle, FIT, and Kinnetics Laboratory (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, 2002b). A summary of the field sampling activities and methods follows in this section.

Samples

The scientific crew collected samples for chemical analyses from the program study area. The following components were successfully completed:

- Collected samples at 43 offshore stations

15 historic BSMP stations
- 22 Northstar and Northstar pipeline stations
6 Liberty stations

Collected 48 surficial sediment samples (0 to 1 cm) for hydrocarbon and metals chemistry (triplicates at 2 stations – stations 5D and N03)

Deployed and retrieved 6 moorings, 3 adjacent to Northstar and 3 in a reference location, each with paired mussel cages and SPMDs

- Collected 13 bivalve/amphipod samples

Collected 11 source sediment/peat samples (5 river stations)

Delivered field samples to analytical laboratories for appropriate analyses

Several source samples were collected as part of the summer survey. The source samples collected included sediment and peat for hydrocarbon and metals analyses from the Sagavanirktok, Kuparuk, Colville, and Canning Rivers.

A complete list of the sampling stations that were occupied and sampled in the study area is included in Table 2-2. Table 2-2 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 2000 and 2002 sampling stations. Additional daily survey and sampling station information is included in the 2002 station logs contained in the Cruise Report (ICF, 2002b).

2.1.4 Field Sampling Procedures

Standard sampling procedures were followed at each sampling station according to the Field Logistics and Sampling Plans for the 2000 and 2002 MMS Field Surveys (Arthur D. Little, 2000 and ICF, 2002a).

The sequence of events at each sampling station followed specific procedures, described in detail below, including:

- Identify station (latitude and longitude)
- Navigate to station position within 0.2 nautical miles (nm) radius of location
- Deploy amphipod traps (as required)
- Deploy caged mussel/SPMD mooring (as required)
- Collect sediment and bivalves using a modified Van-Veen grab sampler
- Retrieve amphipod traps (as required)
- Retrieve caged mussel/SPMD mooring (as required)
- Navigate to next station

Photodocumentation, station logs, and field notes were recorded during the field survey. The station logs for each sampling station are included in the cruise reports (Arthur D. Little, 2001 and ICF, 2002b). Copies of the cruise reports are included in Appendix D. Each station log includes a description of the sampling location, observations, number and type(s) of samples collected, and comments.

Surficial Sediment Sampling

Sediment samples were collected using a modified Van-Veen grab sampler. During the collection and handling of sediment samples from the grab sampler, extreme care was taken to avoid contact with metal and hydrocarbon sources. Samples were taken away from the sides of the grab and metal spatulas were not used for the trace metal samples. The grab sampler was protected from stack smoke, grease drips from winches and wire, and other potential airborne contamination during the sampling process.

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

Biota Sampling

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

Amphipods (*Anonyx spp.)* were collected using Nitex® mesh-lined, Kynar®-coated minnow traps, baited with sardines. The traps were generally deployed for two to six hours (depending on other sampling activities at adjacent stations) with an anchor and float equipped with a radar reflector to facilitate retrieval of the traps. The sardine bait was placed in an enclosed Nitex® mesh pouch to reduce the possibility of sardine particles becoming entrained with the amphipods. Multiple amphipods were collected at each sampling station to obtain enough mass for a single sample. The target sample volume was 100 milliliter (mL) for amphipods. However due to scarcity at some sampling stations as few as 10-12 mL of amphipods were collected and submitted as a sample. In 1999 and 2000, the scarcity of amphipods relative to previous BSMP surveys may have been related to the lack of ice in the nearshore waters of the survey area. Amphipods are known to occur in areas with ice cover, and the vast stretches of open water encountered during these surveys may have restricted the amphipods to areas of denser ice cover, offshore of the survey area. During the summer 2000 survey, only 6 amphipod samples of sufficient size for chemical analysis were collected. However, during the summer 2002 survey, there was greater ice cover in the nearshore waters along with a greater abundance of amphipods available for sample collection at seven selected sampling stations. Amphipods were removed from the traps, washed with clean seawater, and placed in a clean sieve for sorting. Any isopods and non-*Anonyx spp*. amphipods were removed with clean forceps prior to transfer of the sample into the appropriate sample container.

Bivalve samples were collected using a modified Van-Veen grab sampler (as in previous BSMP collections). Multiple grabs were collected and sieved through a 1 cm Nitex® screen to isolate target species of bivalves. Target bivalves were then carefully removed to a clean sieve, rinsed with clean seawater, and transferred into the appropriate sample containers using clean forceps or spatulas. Multiple bivalves were collected at each sampling station to obtain enough mass for a single sample. The target sample volume was 200 mL for bivalves. Generally, 20 to 40 grabs yielded a sufficient volume of bivalves for a single sample. Bivalves were determined to be in good condition if they were alive.

Source Sampling

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

The source samples collected included sediment and peat samples from the Sagavanirktok, Kuparuk, Colville, and Canning (summer 2002 only) Rivers for organic and inorganic analysis. In addition, a water sample was collected during the summer 2002 survey for suspended sediment (inorganics only) from the Canning River, and a biogenic surface residue sample from an adjacent tundra pond was also collected as a potential source sample for hydrocarbons.

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

SPMD and Caged Mussel Deployment and Retrieval

During the 2002 summer survey, SPMDs and caged mussels samples were deployed for approximately 21 days and then retrieved to examine potential bioaccumulation of organic compounds from the water column.

The most significant technical difficulty during this survey was obtaining the mussels for the mussel cage/SPMD mooring deployment. Since the deployment of mussels required the collection and transport of mussels from one part of the state to the other, a Collection Permit and a Fish Transport Permit were required by ADF&G. During the permit application process, it was determined by ADF&G that a population of mussels in Port Chatham, Alaska (Kenai Peninsula) was the only feasible source of mussels for the program. A separate collection trip to Port Chatham (via floatplane) was arranged to meet this requirement of the permit. The mussel collection was planned to coincide closely with the mooring deployments to limit stress and potential mortality of the mussels. The mussels were stored on ice and shipped by airfreight to Deadhorse within 24 hours of collection. The mussels were in very good condition upon arrival in Deadhorse, and were slowly acclimatized with Beaufort Sea water (collected from the end of West Dock) over the next 24 hours. Only two mussels died prior to deployment and their good condition both before and after deployment is indicative of the overall technical success of the mussel cage/SPMD effort.

The SPMDs and caged mussels were deployed on six moorings in the study area. Three of the moorings were deployed in a cluster approximately 1.5 km to the west of Northstar Production Island, and three of the moorings were deployed in a reference area cluster approximately 4 km southwest of Pole Island. The mussels and SPMDs were deployed in water depths of approximately 10 – 15 m with a 250-pound cement-rebar anchor, and suspended approximately 1.5 m from the bottom by a subsurface float. One SPMD cage (containing 5 individual SPMD membranes [91.4 cm long filled with 0.915 g triolein, each] prepared by the licensed distributor EST, St. Joseph, MO) was suspended approximately 1 m from the bottom anchor on each mooring. One mussel cage, containing approximately 40 mussels (M*ytilus edulus/trossulus*), was suspended at the same depth as the SPMD, but attached to mooring string so as not to interfere with the SPMD. There were no surface floats on the moorings to minimize ice entanglement, and each mooring string had an acoustic pinger and secondary anchor with a ~100 m drag line, to aid in retrieval. The SPMD and mussel cage moorings were deployed at the beginning of the survey and retrieved after a minimum of 21 days exposure. Upon retrieval, the mussel cages and SPMDs were all intact and in good condition. At Northstar, all of the 120 mussels were retrieved alive and exhibited extensive byssal thread growth. At the reference location, only 2 of the 120 mussels were found dead and the remaining mussels were alive and exhibited extensive byssal thread growth.

The mussels remaining after deployment of the moorings were taken and submitted as a pre-deployment mussel reference sample. A set of five SPMDs, exposed during each mooring deployment and retrieval, were collected and submitted as a field blank SPMD reference sample.

2.2 Analytical Methods

2.2.1 Ancillary Parameters

2.2.1.1 Grain Size

Determination of grain size followed the classic method of Folk (1974) using a combination of wet sieving and pipette techniques. Initially, 10 to 30 grams of wet sediment were placed in a wide-mouth dish using a larger mass for sandy samples and a smaller mass for muddy samples. A small amount of 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-mL glass bottle and shaken vigorously for a few minutes. Then the sample was poured through 2 millimeter (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 gram portion of the freeze-dried sediment was placed in a 10-mL Pyrex® beaker. One (1) mL of DDW and 2 mL of concentrated hydrochloric acid (HCl) 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 chlorideXwater ($CaCl_2x2H_2O$) as a result of adding HCl. Then, approximately 200 to 400 milligrams (mg) of pre-treated sediment were weighed into ceramic boats and combusted at 900 degrees Celsius (°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 HCl. The calibration curve was checked every 10 samples by analyzing standard reference material (SRM) MESS-2, a marine sediment issued by the National Research Council of Canada (NRC).

2.2.2 Organic Chemical Parameters

Analysis for organic contaminants was conducted by ADL/ICF's environmental chemistry laboratory[1]. The analyses were conducted in accordance with the laboratory's SOPs and generally followed the same procedures used in previous BSMP studies (Boehm et al., 1990). The core organic analyses for the sediment and source samples were:

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

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

2.2.2.1 Sample Preparation

Sediment Samples

The sediment samples were prepared using a procedure based on United States Environmental Protection Agency (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.

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[1] During the course of this program, the prime contractor ADL filed for bankruptcy protection and was subsequently sold off by division. ICF Consulting purchased the environmental consulting and laboratory division of ADL in May 2002. To avoid confusion and remain consistent, the laboratory will be referred to throughout this report as the ADL/ICF laboratory. The ADL/ICF laboratory performed organic analysis on sediment, SPMD, and tissue samples for the ANIMIDA program under Task Order 2. The ADL SOPs were adopted, as is, with no technical changes by ICF. In March 2003, ICF closed the environmental laboratory located in Cambridge, MA. Fortunately, all necessary sample analyses for this program were completed prior to the close of the laboratory. Copies of all SOPs and the hard-copies and electronic instrument files for the organic chemistry data are archived at the ICF Consulting office located in Lexington, MA.

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

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 5β(H)-cholane 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.

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

Biota Samples

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

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

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

The tissue sample data for the organic analyses are reported in Appendix B of this report. All tissue sample data are reported on a wet weight basis. For each sample, percent solid and percent lipid measurements are provided in Appendix B should the wet weight data need to be converted to a dry or lipid weight basis.

SPMD Samples

Prior to sample extraction, the SPMDs were thawed and “cleaned” with de-ionized water and lab wipes to remove algae growth and sediment. SPMD samples (2 of the 5 strips deployed – the remaining 3 were archived for possible re-analysis) were placed into glass or Teflon jars with 100 mL of hexane (more if needed to completely cover the SPMD strips). Each sample and blank was spiked with surrogate solution. All SPMD samples were spiked with “low-level” surrogates because target compound concentrations in the samples 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 5β(H)-cholane for S/T analysis. The extraction jars were tightly capped and the samples were placed on a shaker table and shaken for 24 hours. The solvent was decanted into an Erlenmeyer flask for each sample and the extraction was repeated with an additional 50-100 mL of hexane and another 24 hour shake. Twenty to 50 grams of sodium sulfate were added to the Erlenmeyer flasks, swirled, and let set for 30 minutes to remove water. The combined hexane extracts were decanted into K-D concentrators and concentrated.

Field Blanks

Three field blank samples consisting of distilled water rinsate of the grab sampler were collected as part of the project quality assurance (QA) program (one in 2000 and two in 2002). A “deck” blank was collected each year and consisted of an empty sample jar that had been left open on the boat deck during sampling. The deck blank was prepared by rinsing the jar three times with approximately 10 mL of methylene chloride. The methylene chloride rinsates were combined and spiked with low-level SHC, PAH, and S/T surrogates. The field blank was extracted by a liquid-liquid method with methylene chloride. Field blanks were also spiked with low-level

SHC, PAH, and S/T surrogates. The blank extracts did not require column cleanup and were prepared for instrumental analysis without further processing.

Extract Fractionation

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

The fractionation was performed using a 30-cm by 1-cm column that was wet-packed in methylene chloride with 100 percent activated silica gel/5 percent deactivated alumina/activated copper (approximately 11:1:2) 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 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 microliter (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 microgram (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.

2.2.2.2 Organic Instrumental Analysis

Instrumental analysis of the sediment, tissue, SPMD, and source 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.

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-C8 through n-C40, pristane, phytane, and selected isoprenoids (Table 2-3). Instrument analysis was performed by injection of a portion of the prepared sample extract onto a 30-m long by 0.25-mm inner-diameter (ID) fused-silica capillary column with DB-5 bonded phase. This column provides baseline resolution of n-alkanes from n-C8 to n-C40 and n-C17/pristane and n-

C18/phytane pairs (in the n-alkane nomenclature n-C8 refers to a straight chained hydrocarbon, eight carbons in length). 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 PAH (Table 2-4) 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. Total PAH concentration was calculated as the sum of all target and alkyl PAH concentrations (Table 3-5). For some data analyses, the Total PAH concentration was modified to exclude perylene (a biogenic PAH) – in such as case the parameter is identified as Total PAH less perylene.

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 (Table 2-5) was made by comparison to a reference oil analyzed with each batch.

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

2.2.3 Inorganic Parameters

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

2.2.3.1 Trace and Major Metals Analysis in Surficial Sediment

Surficial 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 grams of each sample was transferred into a pre-weighed plastic vial to determine water content. Once transferred, the wet sediment and the vial were re-weighed. In addition, about 2 to 4 grams of sample were transferred into polypropylene-copolymer centrifuge tubes to determine the Hg (element symbols are defined in Table 2-6) content of the sediments. Samples intended for water content measurement were frozen, freeze-dried, and re-weighed to determine the water content. The dried sediment samples were again homogenized using a Teflon® mixing rod.

About 0.45 grams of freeze-dried, homogenized sediment and SRM sediment (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 (element symbols are defined in Table 2-6) were digested by heating 2 to 4 grams of wet sediment in acid-washed, polypropylene-copolymer 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 rpm and the supernatant decanted into a 25-mL graduated cylinder. The sediment pellet was rinsed twice with 5 mL DDW, centrifuged, and decanted into the graduated cylinder before diluting to a final volume of 20 mL with DDW.

Labware used in the digestion process was acid-washed with hot 8N HNO_3 and rinsed three times with DDW. Two procedural blanks, two duplicate samples, and two SRMs were prepared with each set of 40 samples. SRM BCSS-1 (trace metals except Hg) and MESS-2 (Hg), sediment samples issued by the NRC, were used.

Sediment samples, SRMs, and procedural and reagent blanks were analyzed by 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 2-6. 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).

2.2.3.2 Trace and Major Metals Analysis in Organism Tissue

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

The concentrations of all metals (except Hg) were determined using 4 to 6 grams of wet-weight tissue weighed into 100-mL glass digestion flasks. These subsamples were freeze-dried, reweighed for percent water content, and then digested by the sequential addition of concentrated, high-purity HNO_3, hydrogen peroxide (H_2O_2), and HCl with gentle refluxing. Aliquots of tissue SRMs were digested along with the experimental samples. Once the tissue samples and SRMs were completely dissolved, the clear solutions were transferred to graduated cylinders, diluted to 20 mL with DDW rinses of the digestion flasks, and then stored in labeled 30-mL polyethylene screw-cap bottles for trace metal analysis.

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

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

A laboratory work plan for laboratory analysis, including laboratory procedures, analytical DQOs, QC procedures, corrective action criteria, and data entry/data management.

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

2.3.1.2 Quality Management

Program

As the 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 summer surveys and, as such, was responsible for completion of all field activities in accordance with the field sampling and logistics plans and communication with the field teams. 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; COC 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 ADL/ICF's environmental chemistry 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. COC procedures are specified in formal SOPs and are followed for all sample storage and shipment activities. COC 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 type of sample containers used and the sample storage methods are provided in Table 2-7. Pre-cleaned sample containers that had been certified as such by the vendor were used for the program.

In the field, sediment, biota, and QC samples for chemical analysis were immediately inventoried and stored in a secure area after collection. Inventory included counting 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 2-7), either frozen, packed on dry ice, or refrigerated packed with frozen blue ice via overnight service. Custody seals were used on all shipping coolers to maintain custodial security while the samples were in the possession of a third party (i.e., airfreight courier).

Receipt at ADL/ICF

QA practices were applied when samples were received at the laboratory. The laboratory sample custodian received all samples. Prior to opening the cooler, the cooler was checked for the presence of intact custody seals. The cooler was then opened and the internal temperature 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 were stored until completion of this report.

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, tissue, and source sample received by the Marine & Environmental Chemistry Laboratories at FIT was carefully inspected to ensure that it was intact and that the identification number on the sample container matched that found on the custody sheet. All sediment and source samples were kept refrigerated (4°C ± 2°C) and all tissue samples were kept frozen at about -20°C until processed for analysis.

2.3.2 Field Quality Control

2.3.2.1 Sample Handling

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

2.3.2.2 Quality Control Samples

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

Blanks

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

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

Equipment blanks were collected from rinsate of the sediment sampling equipment. The procedure for collecting an equipment blank included the following:

The equipment was decontaminated according to the SOP;

- The equipment was rinsed with high-purity, deionized water and the rinsate collected directly into two clean, prelabeled water sample containers (one container each for organics and metals);

A precleaned stainless-steel funnel was used to assist in the collection; and,
The equipment blank was stored under the same conditions as the associated field samples.

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

Field Replicates

As a QC measure, replicate samples were collected as part of the field sampling design at sample stations L08 and N13 during the summer 2000 survey and at sample stations 5D and N03 during the summer 2002 survey. At these locations, sediment samples were collected in triplicate so that the reproducibility and range of results could be evaluated.

2.3.2.3 Documentation

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

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

2.3.3 Organic Chemistry Laboratory Quality Control

2.3.3.1 Data Quality Objectives and Quality Control Samples

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

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

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

Solvent and Standard Checks

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

Instrument Calibration

Before instrumental analysis of sample extracts, a multi-level calibration was analyzed and the linearity of the analyte response factors was evaluated. A continuing calibration standard was analyzed regularly to check the stability of the instrument response. If the relative standard deviations (RSDs) for the initial calibration or the percent difference (%D) 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 procedural blank was processed and analyzed with each analytical batch in order to monitor potential contamination resulting from laboratory solvents, reagents, glassware, and processing procedures.

Blank Spike

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

Laboratory Duplicate

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

Standard Reference Materials

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

2.3.3.2 Laboratory Records

The laboratory maintained detailed records throughout the processing of the samples. All raw instrumental data were archived electronically. Completed records or copies of forms were collated into a binder for final archive storage. The final laboratory data package contains sufficient detail so that an external audit could be performed. The documentation in the final data package includes:

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

2.3.3.3 Laboratory Data Review

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

After the final laboratory data package review, it was subjected to a formal audit. The audit process is coordinated by the QA Manager and follows the procedure outlined in the ADL/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 analysis, procedural blank analysis and standard checks. With each batch of up to 40 samples, 2 procedural blanks, 2 SRMs, 2 duplicate samples and 2 matrix-spiked samples were analyzed. DQOs for these QC measurements are provided in Table 2-10.

Instrument Calibration

Electronic balances used for weighing samples and reagents were calibrated prior to each use with certified (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 three- to five-point calibration with a linear correlation coefficient of $r \geq 0.999$ required before experimental samples could be analyzed. Analysis of complete three- to five-point calibrations and/or single standard checks alternated every 5 to 10 samples until all of the analyses were complete. The RSD between complete calibration and standard check was required to be <15 percent or recalibration and reanalysis of the affected samples was performed.

Matrix Spike Analysis

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

Duplicate Sample Analysis

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

Procedural Blank Analysis

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

SRM Analysis

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

2.4 Statistical Methods

Organic and metal parameters were analyzed to investigate the hypothesis that there was a shift in these parameters associated with the island construction and oil production activities at Northstar. The datasets used in these analyses included the summer 1999, summer 2000, and summer 2002 sediment sampling surveys. The summer 1999 sampling represented pre-construction and development activities at Liberty and Northstar, the summer 2000 sampling represented post-construction, pre-production measurements at Northstar and additional pre-construction baseline measurements at Liberty, and the summer 2002 sampling represented post-construction, and ongoing production measurements at Northstar and additional pre-construction baseline measurements at Liberty.

For the statistical analyses, a standard Analysis of Variance (ANOVA) model was constructed. In this model, variation in the dependent variable was assumed to be dependent on four fixed effects; these were region, phase, station, and an interaction of region by phase. The sediment stations were divided into two general regions: the Northstar region and a region that combined the Liberty stations with the BSMP stations (BSMP station 5A is located within 3 km of the Northstar Island and thus was included as a Northstar region station for the statistical analyses). The field surveys were divided into two phases: pre-Northstar construction including the summer 1999 field survey and post-Northstar construction including the summer 2000 and 2002 field surveys. Several Liberty stations were only sampled during the summer 1999 survey and additional Northstar stations were added for the summer 2000 and 2002 surveys. For the reported ANOVA models, only those stations sampled all three years were included in the analyses. The results for BSMP station 5D from the summer 1999 survey were severe outliers and thus were excluded from the statistical analyses. Results from station 5D from the summer 2000 and 2002 surveys were not outliers but were excluded from the statistical analysis since only matched stations (stations sampled all three years) were included in the statistical analyses. The S/T key parameters were not included in the statistical analyses due to limited sample analyses performed in 1999 for these parameters.

The organic concentration variables were log-transformed prior to analysis to normalize the distribution. All organic concentration variables were adjusted for sediment type by using percent silt+clay as the covariate. Additional models were developed with log-transformed perylene as the covariate. Perylene is not an expected contaminant from the construction or production activities at Northstar and is not present in Northstar or North Slope Crude oil, but is associated with biogenic sources of hydrocarbon in the Beaufort Sea. Additional sub-models were also developed to evaluate the differences between the Northstar and BSMP/Liberty regions post-construction and to evaluate the differences between the BSMP/Liberty region pre- and post-construction. The metal variables were adjusted for sediment type by using aluminum as the covariate. The false discovery rates were controlled according to the Hochberg procedure (Benjamini and Hochberg, 1995).

Analyses were also performed to determine if there was a gradient effect away from Northstar Island. The analyses were performed using only the matched Northstar stations and included the variables Radial (distance from island in km) and construction (pre- or post-) with silt+clay or log-normal transformed (LN) perylene as the covariate for organics and aluminum as the covariate for metals. The effect of Radial was not significant in these models. An additional variable was also generated that grouped stations into three radial categories (1-2 km, 3-4 km, and 5+ km) to increase the number of samples per category. Still, the effect of Radial was not significant. Thus, Radial was removed from the final reported models. The effect of the pipeline construction at Northstar was similarly tested and found to be not significant, thus, this effect was removed from the final models.

ANOVA models were also developed using the complete sediment dataset to determine if the results obtained using only the matched samples were biased. Similar parameter estimates and *p*-values were noted when the complete dataset was used as compared to the matched dataset. Thus, only the results of the matched dataset analyses have been included in this report.

Statistical analyses were carried out using the statistical program SPSS® 8.0.

2.5 Database Management

As part of the ANIMIDA program, MMS required that the ANIMIDA data be incorporated into the MMS Coastal and Offshore Resource Information System (CORIS) database. This necessitated 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 implementing and completing the database design and program data management. All final ANIMIDA data will be archived in the MMS CORIS database and are also provided digitally on the Appendices compact disc (CD) accompanying this report for non-CORIS users.

Table 2-1: 2000 MMS Animida Stations Sampled

Station ID	Station Type	Sample Type	Latitude	Longitude	Water Depth (ft)	Date	Time	Analysis/Replicates											
								Organics	Metals	GS/TOC	13C & Methyl Hg	Tissue	Suspended Sediment	ODB	Doppler Current	CTD	QC	Comments
3A	BSMP	Sed.-Grab/Tissue	70°16.988	147°05.470	22	8/20/2000	1615-1715	1	1	1	1	1	3	1	1	1	NA	(Astarte)
3B	BSMP	Sed. Grab	70°17.917	147°02.549	15	8/20/2000	1735-1745	1	1	1	1	NA	NA	1	NA	NA	NA	
4A	BSMP	Sed.-Grab/Tissue	70°18.460	147°40.289	16	8/21/2000	1010-1030	1	1	1	1	10	NA	1	NA	NA	NA	(Annoyx,Fish)
4B	BSMP	Sed. Grab	70°21.034	147°40.007	23	8/21/2000	1705-1750	1	1	1	1	NA	3	1	1	1	NA	
4C	BSMP	Sed. Grab	70°26.144	147°42.957	30	8/21/2000	1840-1850	1	1	1	1	NA	NA	1	NA	NA	NA	
5(0)	BSMP	Sed.-Grab/Tissue	70°22.210	147°47.744	18	8/22/2000	0915-1230	1	1	1	1	1	1	1	1	1	NA	(Annonyx)
5(1)	BSMP	Sed. Grab	70°25.024	148°03.569	21	8/22/2000	1255-1256	1	1	1	1	NA	NA	1	NA	NA	NA	
5(10)	BSMP	Sed. Grab	70°27.323	148°29.980	26	8/22/2000	1420-1430	1	1	1	1	1	NA	1	NA	NA	NA	attempted biota sampling
5(5)	BSMP	Sed. Grab	70°26.106	147°18.127	23	8/22/2000	1340-1347	1	1	1	1	NA	NA	1	NA	NA	NA	
5A	BSMP	Sed. Grab	70°29.704	148°46.103	39	8/18/2000	1713-1722	1	1	1	1	NA	NA	1	NA	NA	NA	
5B	BSMP	Sed. Grab	70°34.890	148°55.040	47	8/17/2000	1120-1140	1	1	1	1	1	NA	1	NA	NA	NA	"water spiking range finder"
5D	BSMP	Sed. Grab	70°24.488	148°33.605	7	8/22/2000	1459-1505	1	1	1	1	NA	NA	1	NA	NA	NA	
5E	BSMP	Sed. Grab	70°38.392	149°16.577	63	8/17/2000	1250-1305	1	1	1	1	NA	NA	1	NA	NA	NA	
5F	BSMP	Sed.-Grab/Tissue	70°26.486	148°49.550	6	8/19/1900	1330-1430	1	1	1	1	1	NA	1	NA	NA	NA	(Cyrtodaria)
5H	BSMP	Sed.-Grab/Tissue	70°22.210	147°47.744	23	8/22/2000	1020-1110	1	1	1	1	1	NA	1	NA	NA	NA	(Astarte)
L01	Liberty	Sed. Grab	70°18.930	147°27.130	23	8/21/2000	1505-1512	1	1	1	1	NA	NA	1	NA	NA	NA	
L04	Liberty	Sed. Grab	70°17.032	147°39.897	17	8/20/2000	1400-1415	1	1	1	1	1	NA	1	NA	NA	NA	attempted biota sampling
L06	Liberty	Sed. Grab	70°16.881	147°33.978	23	8/21/2000	1055-1105	1	1	1	1	NA	NA	1	NA	NA	NA	
L07	Liberty	Sed. Grab	70°16.789	147°31.966	22	8/21/2000	1120-1130	1	1	1	1	NA	NA	1	NA	NA	NA	
L08	Liberty	Sed.-Grab/Tissue	70°16.701	147°30.298	21	8/21/2000	1140-1325	3	3	3	3	1	5	3	1	1	NA	(Astarte)
L09	Liberty	Sed.-Grab/Tissue	70°16.568	147°27.130	22	8/21/2000	1350-1420	1	1	1	1	1	NA	1	NA	NA	NA	(Astarte)
N01	Northstar	Sed. Grab	70°31.644	148°41.411	43	8/17/2000	1600-1615	1	1	1	1	NA	NA	1	NA	NA	1	
N02	Northstar	Sed. Grab	70°30.525	148°41.411	46	8/17/2000	1540-1550	1	1	1	1	NA	NA	1	NA	NA	NA	
N03	Northstar	Sed.-Grab/Tissue	70°30.005	148°41.575	43	8/17/2000	1520-1530	1	1	1	1	1	NA	1	NA	NA	NA	(Annonyx)
N04	Northstar	Sed. Grab	70°29.674	148°48.148	34	8/18/2000	1740-1750	2	2	2	2	NA	NA	2	NA	NA	NA	
N05	Northstar	Sed. Grab	70°29.662	148°44.699	41	8/18/2000	1605-1615	1	1	1	1	NA	3	1	1	1	NA	attempted biota sampling
N06	Northstar	Sed. Grab	70°29.537	148°43.194	37	8/17/2000	1837-1846	1	1	1	1	NA	NA	1	NA	NA	NA	
N07	Northstar	Sed. Grab	70°29.544	148°40.140	40	8/17/2000	1740-1750	1	1	1	1	NA	NA	1	NA	NA	NA	
N08	Northstar	Sed. Grab	70°29.407	148°38.429	38	8/18/2000	1305-1345	1	1	1	1	NA	3	1	1	1	NA	
N09	Northstar	Sed. Grab	70°29.323	148°35.214	35	8/18/2000	1900-1910	1	1	1	1	NA	NA	1	NA	NA	NA	
N10	Northstar	Sed. Grab	70°28.997	148°41.742	37	8/17/2000	1810-1817	1	1	1	1	NA	NA	1	NA	NA	NA	
N11	Northstar	Sed. Grab	70°28.424	148°41.904	30	8/18/2000	1430-1535	1	1	1	1	NA	NA	1	NA	NA	NA	attempted biota sampling
N12	Northstar	Sed.-Grab/Tissue	70°27.321	148°42.078	21	8/19/2000	1010-1020	1	1	1	1	1	NA	1	NA	NA	NA	(Annonyx)
N13	Northstar	Sed.-Grab/Tissue	70°27.004	148°43.552	15	8/19/2000	1030-1150	3	3	3	3	1	5	3	1	1	NA	(Annonyx)
N14	Northstar	Sed. Grab	70°25.978	148°40.459	12	8/19/2000	1540-1615	1	1	1	1	NA	2	1	1	1	NA	
N15	Northstar	Sed. Grab	70°26.710	148°44.570	8	8/19/2000	1205-1230	1	1	1	1	NA	2	1	1	1	NA	
N16	Northstar	Sed. Grab	70°29.910	148°42.558	41	8/17/2000	1850-1901	1	1	1	1	NA	NA	1	NA	NA	NA	
N17	Northstar	Sed. Grab	70°29.829	148°40.379	42	8/17/2000	1648-1735	1	1	1	1	NA	NA	1	NA	NA	NA	
N18	Northstar	Sed.-Grab/Tissue	70°29.082	148°42.151	37	8/17/2000	1825-1832	1	1	1	1	NA	NA	1	NA	NA	NA	(Annonyx)
N19	Northstar	Sed. Grab	70°29.097	148°40.554	37	8/17/2000	1755-1805	1	1	1	1	NA	NA	1	NA	NA	NA	attempted biota sampling
N20	Northstar	Sed. Grab	70°27.951	148°41.687	25	8/18/2000	1517-1525	2	2	2	2	NA	NA	2	NA	NA	NA	
N21	Northstar	Sed. Grab	70°26.819	148°40.587	18	8/19/2000	1654-1730	1	1	1	1	NA	3	1	1	1	NA	
N22	Northstar	Sed. Grab	70°29.340	148°41.868	28	8/23/2000	1425-1435	1	1	1	NS	NA	NA	1	NA	NA	NA	gravel from pipline "cover"
N23	Northstar	Sed. Grab	70°29.340	148°41.868	36	8/23/2000	1435-1445	1	1	1	1	NA	NA	1	NA	NA	NA	15 feet off pipeline
SAG-01	Source	Sed. Grab	70°01.680	148°33.770	NA	8/25/2000	0800-0810	1	1	NS	NS	NA	1	1	NA	NA	NA	Sagavanirktok River @ ~0.5 mi. S of Mile 401
KUP-02	Source	Peat	70°17.700	148°53.370	NA	8/24/2000	1255-1305	1	1	NS	NS	NA	1	1	NA	NA	NA	Kuparuk River ~2 mi. S. of bridge crossing
KUP-01	Source	Sed.	70°17.700	148°59.370	NA	8/24/2000	1255-1305	1	1	NS	NS	NA	1	1	NA	NA	NA	Kuparuk River at bridge crossing
COL-01	Source	Sed.	70°15.960	150°49.290	NA	8/24/2000	1100-1110	1	1	NS	NS	NA	1	1	NA	NA	NA	Colville River N. of Nuiqsut
COL-02	Source	Sed.	70°11.360	150°52.120	NA	8/24/2000	1130-1140	1	1	NS	NS	NA	1	1	NA	NA	NA	Colville River S. of Nuiqsut (sed. and peat)
L00	Liberty	Tissue	~70°23.424	~147°46.907	~22	8/27/2000	1430-1500	1	NS	NS	NS	3	NA	NS	NA	NA	NA	Otter trawl
B00	BSMP	Tissue	~70°26.144	~148°03.569	~20	8/26/2000	1730-1800	1	NS	NS	NS	3	NA	NS	NA	NA	NA	Otter trawl
N00	Northstar	Tissue/Sed.	~70°36.674	~148°30.212	~35	8/26/2000	13110-1340	1	NS	NS	NS	3	NA	NS	NA	NA	NA	Otter trawl - sed. from net

Notes:

NA = Not applicable

NS = Not sampled

Trawl sample locations are approximate

Table 2-2: 2002 MMS Animida Stations

Station ID	Station Type	Sample Type	Latitude	Longitude	Depth (ft)	Date	Time	Analysis/Samples					
								Sediment				Suspended Sed/ Current/CTD	
								Organics	Metals	GS/TOC	Tissue		Comments
3A	BSMP	Sed.-Grab/Tissue	70°16.933	147°05.489	20	07/29/02	1915	1	1	1	1	NA	(Astarte)
3B	BSMP	Sed. Grab	70°17.918	147°02.508	13	07/29/02	1830	1	1	1	NA	NA	
4A	BSMP	Sed.-Grab/Tissue	70°18.444	147°40.229	15	7/31 & 8/20/02	1000	1	1	1	2	3	(Anonyx collected on 7/31 and 8/20)
4B	BSMP	Sed. Grab	70°21.021	147°40.012	21	07/31/02	1335	1	1	1	NA	3	
4C	BSMP	Sed. Grab	70°26.085	147°42.961	27	07/31/02	1518	1	1	1	NA	3	
5(0)	BSMP	Sed.-Grab/Tissue	70°22.735	148°00.363	18	08/01/02	0915	1	1	1	1	NA	(Anonyx)
5(1)	BSMP	Sed. Grab	70°25.027	148°03.510	19.5	08/01/02	1234	1	1	1	NA	3	
5(10)	BSMP	Sed. Grab	70°27.312	148°30.026	25.5	08/01/02	1512	1	1	1	NA	NA	
5(5)	BSMP	Sed. Grab	70°26.095	147°18.125	22	08/01/02	1645	1	1	1	NA	3	
5A	BSMP	Sed. Grab	70°29.680	148°46.053	37.5	08/03/02	1532	1	1	1	NA	NA	
5B	BSMP	Sed. Grab	70°34.884	148°55.005	44	08/03/02	1333	1	1	1	NA	3	
5D	BSMP	Sed. Grab	70°24.489	148°33.598	8	08/07/02	1500	3	3	3	NA	NA	
5E	BSMP	Sed. Grab	70°38.347	149°16.376	61	08/04/02	1307	1	1	1	NA	3	
5F	BSMP	Sed.-Grab/Tissue	70°26.497	148°49.555	7.2	08/07/02	1153	1	1	1	1	NA	(Cyrtodaria)
5H	BSMP	Sed.-Grab/Tissue	70°22.221	147°47.792	23	08/01/02	1017	1	1	1	1	NA	(Astarte)
L01	Liberty	Sed. Grab	70°18.933	147°27.082	20	07/31/02	1230	1	1	1	NA	NA	
L04	Liberty	Sed. Grab	70°17.068	147°40.040	17	07/30/02	1718	1	1	1	NA	NA	
L06	Liberty	Sed. Grab	70°16.923	147°34.064	22	07/30/02	1303	1	1	1	NA	NA	(Attempted Anonyx collection)
L07	Liberty	Sed. Grab	70°16.784	147°31.990	21	07/30/02	1335	1	1	1	NA	NA	
L08	Liberty	Sed.-Grab/Tissue	70°16.700	147°30.223	20	07/30/02	1351	2	2	2	2	NA	(Astarte) Grab rep 02 for analysis, hold rep 01
L09	Liberty	Sed.-Grab/Tissue	70°16.586	147°27.152	21	07/30/02	1552	1	1	1	1	NA	(Astarte)
N01	Northstar	Sed. Grab	70°31.657	148°41.443	41	08/03/02	1101	1	1	1	NA	3	
N02	Northstar	Sed. Grab	70°30.512	148°41.376	44	08/03/02	1218	1	1	1	NA	NA	
N03	Northstar	Sed.-Grab/Tissue	70°30.005	148°41.477	43	8/5 & 8/10/2002	1122	3	3	3	1	NA	(Anonyx collected on 8/10)
N04	Northstar	Sed. Grab	70°29.676	148°48.092	33	8/3 & 8/11/2002	1516	1	1	1	1	NA	(Anonyx collected on 8/11)
N05	Northstar	Sed. Grab	70°29.631	148°44.704	38.5	08/03/02	1548	1	1	1	NA	NA	
N06	Northstar	Sed. Grab	70°29.526	148°43.230	38.5	08/02/02	1558	1	1	1	NA	NA	
N07	Northstar	Sed. Grab	70°29.573	148°40.084	40	08/05/02	1319	1	1	1	NA	NA	
N08	Northstar	Sed. Grab	70°29.424	148°38.322	39	08/05/02	1335	1	1	1	NA	NA	
N09	Northstar	Sed. Grab	70°29.343	148°35.180	35	08/05/02	1352	1	1	1	NA	NA	
N10	Northstar	Sed. Grab	70°28.997	148°41.780	34	08/02/02	1130	1	1	1	NA	3	
N11	Northstar	Sed. Grab	70°28.421	148°41.912	26	08/02/02	1508	1	1	1	NA	NA	
N12	Northstar	Sed.-Grab/Tissue	70°27.319	148°42.037	18.5	8/2 & 8/3/2002	1300	1	1	1	1	3	(Anonyx collected on 8/3)
N13	Northstar	Sed.-Grab/Tissue	70°26.982	148°43.594	14	08/04/02	1015	3	3	3	1	NA	(Anonyx)
N14	Northstar	Sed. Grab	70°26.006	148°40.429	12	08/07/02	1405	1	1	1	NA	NA	
N15	Northstar	Sed. Grab	70°26.707	148°44.618	8	08/07/02	1105	1	1	1	NA	NA	
N16	Northstar	Sed. Grab	70°29.902	148°42.395	42.5	08/05/02	1055	1	1	1	NA	NA	
N17	Northstar	Sed. Grab	70°29.833	148°40.345	42.5	08/05/02	1245	1	1	1	NA	NA	
N18	Northstar	Sed.-Grab/Tissue	70°29.080	148°42.228	34	08/02/02	1613	1	1	1	1	NA	(Anonyx)
N19	Northstar	Sed. Grab	70°29.088	148°40.557	36	08/02/02	1531	1	1	1	NA	NA	
N20	Northstar	Sed. Grab	70°27.957	148°41.687	25	08/02/02	1455	1	1	1	NA	NA	
N21	Northstar	Sed. Grab	70°26.806	148°41.738	21	08/02/02	1419	1	1	1	NA	3	
N22	Northstar	Sed. Grab	70°29.340	148°41.868	28	NA	NA	NA	NA	NA	NA	NA	Not Sampled
N23	Northstar	Sed. Grab	70°29.330	148°41.864	37	08/05/02	1426	1	1	1	NA	1	~150 feet South of Northstar
3M1	Reference	Mussel/SPMD	70°16.982	147°08.880	25	7/29 - 8/20/2002	1620	NA	NA	NA	6	NA	1 Mussel Cage (n=40) and 5 SPMDs
3M2	Reference	Mussel/SPMD	70°16.835	147°09.409	25	7/29 - 8/20/2002	1648	NA	NA	NA	6	NA	1 Mussel Cage (n=40) and 5 SPMDs
3M3	Reference	Mussel/SPMD	70°16.922	147°09.398	25	7/29 - 8/20/2002	1715	NA	NA	NA	6	NA	1 Mussel Cage (n=40) and 5 SPMDs
NM1	Northstar	Mussel/SPMD	70°29.597	148°44.199	38	7/28 - 8/18/2002	2045	NA	NA	NA	6	NA	1 Mussel Cage (n=40) and 5 SPMDs
NM2	Northstar	Mussel/SPMD	70°29.687	148°44.868	38	7/28 - 8/18/2002	2112	NA	NA	NA	6	NA	1 Mussel Cage (n=40) and 5 SPMDs
NM3	Northstar	Mussel/SPMD	70°29.618	148°44.315	39	7/28 - 8/18/2002	2200	NA	NA	NA	6	NA	1 Mussel Cage (n=40) and 5 SPMDs
SAG-01	Source	Sed/Peat	70°01.680	148°33.770	NA	08/14/02	1130	2	NA	1	NA	NA	Sagavanirktok River @ ~0.5 mi. S of Mile 401
KUP-01	Source	Sed/Peat	70°17.700	148°53.370	NA	08/06/02	1010	2	1	NA	NA	NA	Kuparuk River S. of E bridge crossing
KUP-03	Source	Sed.	70°22.910	148°51.550	NA	08/07/02	0815	2	2	NA	NA	NA	Kuparuk River "Borrow Pit" sediment
COL-01	Source	Sed/Peat	70°15.960	150°49.290	NA	08/13/02	1030	2	NA	NA	NA	NA	1 sediment and 1 peat sample
CAN-01	Source	Sed.	70°07.199	145°53.099	NA	08/09/02	1415	1	1	1	NA	1	Canning River sediment and water
CAN-02	Source	Peat	70°07.199	145°53.099	NA	08/09/02	1415	1	NA	NA	NA	NA	Canning River Peat
CAN-03	Source	Sed/Sheen	70°07.199	145°53.099	NA	08/09/02	1415	1	NA	NA	NA	NA	Canning River pond sheen

Notes:

NA = Not applicable

Table 2-3. Saturated Hydrocarbons Target List

Compound	Reporting Code	Internal Standard/ Surrogate Reference	Compound	Reporting Code	Internal Standard/ Surrogate Reference
n-Octane (optional)	C8	A/1	n-Hexacosane	C26	A/1
n-Nonane	C9	A/1	n-Heptacosane	C27	A/1
n-Decane	C10	A/1	n-Octacosane	C28	A/1
n-Undecane	C11	A/1	n-Nonacosane	C29	A/1
n-Dodecane	C12	A/1	n-Triacontane	C30	A/1
n-Tridecane	C13	A/1	n-Hentriacontane	C31	A/1
Isoprenoid RRT 1380	1380	A/1	n-Dotriacontane	C32	A/1
n-Tetradecane	C14	A/1	n-Tritriacontane	C33	A/1
Isoprenoid RRT 1470	1470	A/1	n-Tetratriacontane	C34	A/1
n-Pentadecane	C15	A/1	n-Pentatriacontane	C35	A/1
Isoprenoid RRT 1650	1650	A/1	n-Hexatriacontane	C36	A/1
n-Hexadecane	C16	A/1	n-Heptatriacontane	C37	A/1
n-Heptadecane	C17	A/1	n-Octatriacontane	C38	A/1
Pristane	PRIS	A/1	n-Nonatriacontane	C39	A/1
n-Octadecane	C18	A/1	n-Tetracontane	C40	A/1
Phytane	PHYT	A/1			
n-Nonadecane	C19	A/1	Surrogate Compounds		
n-Eicosane	C20	A/1	Tetracosane-d_{50}	D50T	A/1
n-Heneicosane	C21	A/1	5a-Androstane	5AA	B/1
n-Docosane	C22	A/1			
n-Tricosane	C23	A/1	Internal Standard		
n-Tetracosane	C24	A/1	Triacontane-d_{62}	D62T	1
n-Pentacosane	C25	A/1			

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

Also used in reporting:
TOTRES: Total of resolved compounds in sample extract
TPHC: Total of resolved and unresolved compounds in sample extract

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

Compound	Reporting Code	Internal Standard/ Surrogate Reference	Compound	Reporting Code	Internal Standard/ Surrogate Reference
Naphthalene	C0N	A/1	Benzo[a]anthracene	BAA	B/3
C1-Naphthalenes	C1N	A/2			
C$_2$-Naphthalenes	C2N	A/2	Chrysene	C0C	B/3
C$_3$-Naphthalenes	C3N	A/2	C$_1$-Chrysenes	C1C	B/3
C$_4$-Naphthalenes	C4N	A/2	C$_2$-Chrysenes	C2C	B/3
			C$_3$-Chrysenes	C3C	B/3
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: napthalenes, acenaphthylene, acenaphthene, biphenyl, and fluorenes
3-ring PAHs include: anthracenes, phenanthrenes, and dibenzothiophenes
4-ring PAHs include: fluoranthenes, pyrenes, benzo(a)anthracene, chrysenes, benzo(b)fluoranthene, and benzo(k)fluoranthene
5-ring PAHs include: benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(1,2,3-cd)pyrene, and dibenz(a,h)anthracene
Benzo(g,h,i)perylene is a 6-ring PAH

Table 2-5: Sterane and Triterpane Target List

Compound	Reporting Code	Internal Standard/ Surrogate Reference	Compound	Reporting Code	Internal Standard/ Surrogate Reference
C_{23} Diterpane	T4	A/1	Surrogate Compounds		
13β,17α-diacholestane(20S)	S4	A/1	5β(H)-cholane	5B	2
13β,17α-diacholestane(20R)	S5	A/1			
C_{29} Tricyclictriterpane	T9	A/1	Internal Standards		
C_{29} Tricyclictriterpane	T10	A/1	Chrysene-d_{12}	D12C	A
## 5α,14α,17α-cholestane(20R)	S17	A/1			
18α(H)-22,29,30-trisnorhopane(TS)	T11	A/1			
17α(H)-22,29,30-trisnorhopane(TM)	T12	A/1			
5α,14α,17α,24-methylcholestane(20R)	S24	A/1			
5α,14α,17α,24-ethylcholestane(20S)	S25	A/1			
5α,14α,17α,24-ethylcholestane(20R)	S28	A/1			
17α(H),21β(H)-30-norhopane	T15	A/1			
18α(H)-oleanane	T18	A/1			
17α(H),21β(H)-hopane	T19	A/1			
22S-17α(H),21β(H)-30-homohopane	T21	A/1			
22R-17α(H),21β(H)-30-homohopane	T22	A/1			
## 17β(H),21β(H)-hopane	T23	A/1			

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

Compound used in calibration, but not reported

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

	Sediments		Organisms	
Metal	**Method**	**MDLs (µg metal/g dry sediment)**	**Method**	**MDLs (µg metal/g tissue dry weight)**
Ag – silver	ZGFAAS	0.01	ZGFAAS	0.004
Al – aluminum	FAAS	10	FAAS	2.3
As – arsenic	ZGFAAS	0.2	ZGFAAS	0.03
Ba – barium	ICP-MS	1	ICP-MS	0.01
Be – beryllium	ICP-MS	0.1	ZGFAAS	0.002
Cd – cadmium	ICP-MS	0.02	GFAAS	0.001
Co – cobalt	ICP-MS	0.3	GFAAS	0.01
Cr – chromium	FAAS	1	GFAAS	0.01
Cu – copper	FAAS	2	FAAS	0.7
Fe – iron	FAAS	10	FAAS	2.5
Hg – mercury	CVAAS	0.001	CVAAS	0.001
Mn – manganese	FAAS	3	FAAS	1.1
Ni – nickel	ICP-MS	0.5	GFAAS	0.01
Pb – lead	ICP-MS	0.2	ICP-MS	0.003
Sb – antimony	ICP-MS	0.04	ICP-MS	0.001
Tl – thallium	ICP-MS	0.04	ICP-MS	0.001
V – vanadium	FAAS	10	GFAAS	0.01
Zn – zinc	FAAS	2	FAAS	0.4
Other Parameters				
Grain Size	Sieve and Pipet	---		
TOC	Shimadzu Carbon System	0.1%		

Notes:
CVAAS = Cold Vapor Atomic Absorption Spectrometry
FAAS = Flame Atomic Absorption Spectrometry
GFAAS = Graphite Furnace Atomic Absorption Spectrometry
ICP/MS = Inductively Coupled Plasma/Mass Spectrometry
MDL = Method Detection Limit
ZGFAAS = Zeeman Graphite Furnace Atomic Absorption Spectrometry

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

Sample Type	Analysis	Precleaned Container	Storage/ Preservative	Analytical Laboratory
Sediment	SHC, PAH, S/T	250 mL glass	Frozen -20°C	ADL/ICF Laboratory
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
Biota (Clams and Amphipods)	SHC, PAH, S/T, metals	250 mL glass	Frozen -20°C	ADL/ICF Laboratory (homogenate was sent to FIT for metals)
Mussels	SHC, PAH, S/T	250 mL glass or pre-cleaned foil	Frozen -20°C	ADL/ICF Laboratory
SPMDs	SHC, PAH, S/T	Teflon bag or pre-cleaned cans	Frozen -20°C	ADL/ICF Laboratory
Source Samples – Sediment, Gravel, Peat	SHC, PAH, S/T	250 mL glass	Frozen -20°C	ADL/ICF Laboratory
Source Samples – Sediment, Gravel, Peat	Metals	Plastic jar	Frozen -20°C	Florida Institute of Technology
Source Samples – Sediment, Gravel, Peat	Grain Size	Plastic bag	Stored at 4°C	Florida Institute of Technology
Equipment Blank/ Field Blank	SHC, PAH, S/T	250 mL glass	Frozen -20°C	ADL/ICF Laboratory
Equipment Blank/ Field Blank	Metals	Plastic jar	Frozen -20°C	Florida Institute of Technology

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

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

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

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

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

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

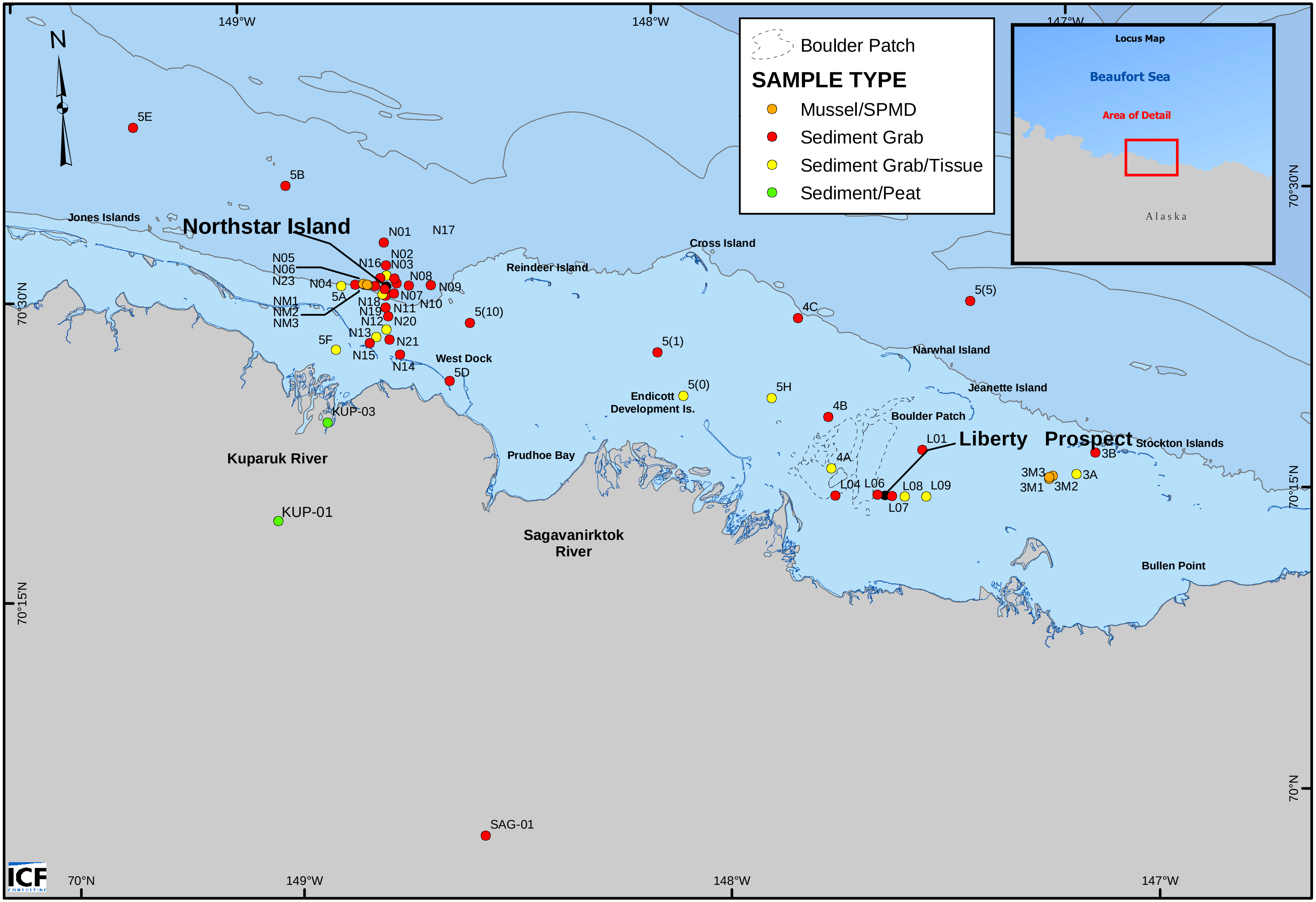


Figure 2-1 Summer 2000 and 2002 Sampling Stations

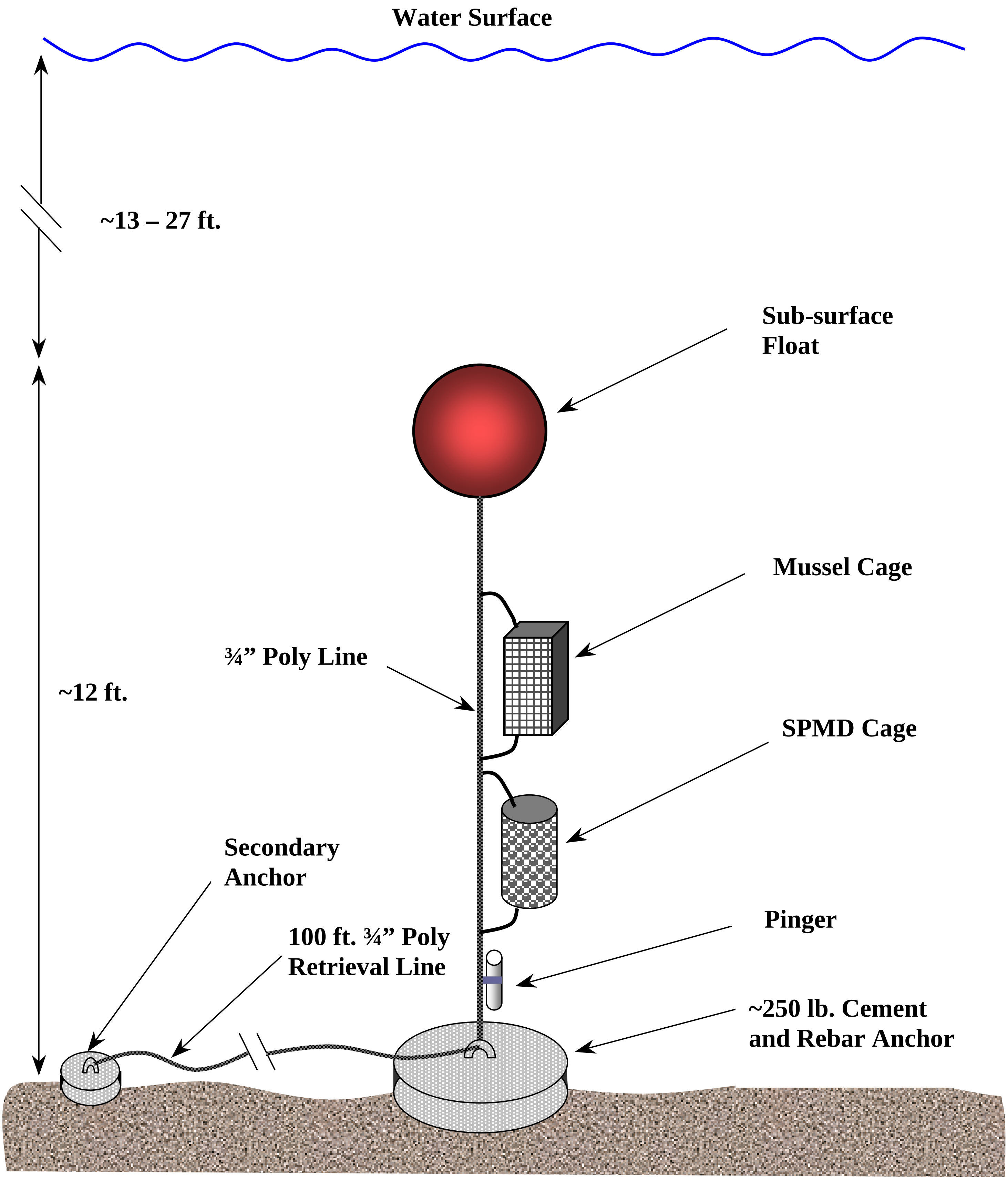


Figure 2-2. Schematic of the Mussel Cage and SPMD Mooring String

3.0 Results

This section presents the results for the general chemistry, organic, and inorganic analyses for the surficial sediment and tissue samples collected from the ANIMIDA study area during the summers of 2000 and 2002 and the results for the organic analyses for the SPMD samples and the organic and inorganic analyses for the caged mussel samples collected during the summer of 2002. The results of the sediment core survey performed during the summer of 2001 and the ANIMIDA Phase I survey performed in 1999 are presented in separate reports (Brown et al. 2003 and Boehm et al. 2001b, respectively).

3.1 Surficial Sediments (0-1 cm)

The results and general trends in the TOC, grain size, organic, and inorganic data from the surficial sediment samples collected during the summer 2000 and 2002 ANIMIDA field surveys are presented in this subsection. Results from the organic analyses of the river source samples are also discussed.

3.1.1 General Chemical and Physical Measurements

Total Organic Carbon (TOC) and Grain Size

Surficial sediments from each site during 2000 and 2002 were analyzed for TOC and grain size (percent gravel, sand, silt and clay). The TOC values for surficial sediments ranged from <0.01% in the sandy sediment at site N01 (2000) to 4.4% in a mud-rich sample from site N14 (also during 2000) (Table 3-1 and Appendix A). The mean value for TOC of 1.0 ± 0.79% for 2000 is not significantly higher than the mean of 0.74 ± 0.37% for 2002, or 1.13 ± 0.54% for 2001, because the standard deviations are large (Table 3-1). Considerable patchiness is found for TOC values across the study area, partly in response to similar patchiness in the occurrence of fine-grained sediment. Overall, the TOC concentrations are typical of values reported for Arctic shelf sediments. For example, Carsola (1954) reported a range of TOC values from 0.2-1.2 % for Beaufort Sea sediments.

The grain size results show similar variability to that described above for TOC. Gravel content (>2 mm diameter particles) during the 2000 sampling period ranged from 0% at 26 locations to 60.3% at station N22, located above the pipeline just south of Northstar Island. In 2002, gravel content was 0% at 27 stations with a maximum level of 10.5% at station N12, also near the pipeline. Likewise, the clay content (<0.002 mm) varies from about 1% at several locations during 2000 and 2002 to ~35% at station N03 and 4A in 2000 and 58% at station 4A in 2002. Sediment resuspension, along with across and along shelf transport, are dynamic components of the inner shelf of the Beaufort Sea that certainly contribute to observed variations in grain size distribution in the top 1 cm of sediment.

Based on the 2000 and 2002 grain size data, a few general trends are observed. In the area of Northstar Island during 2000, gravel was found at levels >3% only in the sample collected from the pile of backfilled material above the pipeline (station N22 with 60.3% gravel) (Figure 3-1). Just a few meters to the west of the pipeline hump at station N23, the sediment was mostly silt with no gravel or sand (Figure 3-1). Sediment to the east of Northstar Island at stations N07, N08 and N09 was rich in sand, as was observed at stations N01 and N15, at 4-6 km north and south of the island, respectively. An area containing more silt and clay follows along a southeast to northwest line to the south and west of Northstar Island. Some of this fine-grained sediment may have been carried in with spring runoff and not yet disturbed or moved offshore by storm activity. During 2002, much less sand was found at stations N06, N07, N08 and N09 than during 2000 (Figure 3-2); most likely because fine-grained sediment introduced to that area during river runoff had not yet moved farther offshore. Overall, the differences in grain size distribution between 2000 and 2002 were less than observed between 1999 and 2000 as discussed in Section 4.

The grain size trends for 2000 near the Liberty Prospect are more complex (Figure 3-3) than observed near Northstar Island. Small amounts of gravel were collected only at stations L09, L01 and 4C. The highest amounts of sand were recovered along a continuum from stations L07, L08 and L09, to the east of center point, as well as at stations 4B and 4C. A patch of mostly silt and clay was found adjacent to the west and south of the proposed site for the Liberty Prospect, at stations L12, L06 and 4A (Figure 3-3). During 2002, the sand content at stations 4C, 4B, L01, L08 and L09 (Figure 3-4) was markedly greater than observed during 2000 (Figure 3-3). In contrast with the Northstar area, less fine-grained material was present in the area of Liberty Prospect during 2002 than during 2000. Bottom sediment movement and deposition throughout the ANIMIDA region is quite dynamic as discussed in more detail in Section 4.

3.1.2 Organics

Organic parameter results for the surficial sediment samples are summarized in Tables 3-2 through 3-4. The summary results include total PAH (includes the sum of all target parent and alkyl PAHs), total petroleum hydrocarbons (TPHC; includes the sum of the resolved and unresolved saturated hydrocarbons n-C9 through n-C40), and total S/T (includes the sum of the sterane and triterpane target compounds). The data for each of these summary parameters are presented on a dry-weight sediment basis and results for field replicates are presented as the mean value with the standard deviation in parentheses. The results are separated into three regional groupings: BSMP stations (Table 3-2), Northstar stations (Table 3-3), and Liberty stations (Table 3-4). In addition, river and peat source sample summary data are included in Table 3-2. Within this report and with the associated data analyses, BSMP station 5A was designated as a Northstar station based on it's location within 4 km from the Northstar island. Descriptions of key diagnostic parameters, which are useful in describing the overall organics dataset and will be used for comparisons to historical data and future ANIMIDA program data, are provided in Table 3-5. The complete organics data, including concentrations for individual PAH, SHC, and S/T target compounds, are included in Appendix B.

3.1.2.1 Saturated Hydrocarbons

Concentrations of TPHC in surficial sediments from the offshore summer 2002 survey ranged from 0.44 to 22 mg/kilogram (Kg); the summer 2000 survey ranged from 1.00 to 27 mg/Kg; and the summer 1999 survey results ranged from 0.21 to 17 mg/Kg with one outlier at 50 mg/Kg. The highest TPHC concentration in the summer 1999 survey was 50 mg/Kg detected at station 5D. The summer 2000 and 2002 TPHC concentrations at this station dropped to 17 and 6.2 mg/Kg, respectively, within the expected TPHC concentration range. The mean TPHC concentrations for the three regions (Northstar, Liberty, and BSMP) were 10, 6.0, and 4.4 mg/Kg (Tables 3-2 through 3-4), respectively, in the summer 2002 survey and 14, 8.6, and 7.5 mg/Kg in the summer 2000 survey as compared to the 1999 mean TPHC concentrations of 5.3, 7.1, and 7.9

mg/Kg, respectively. The river sediment and peat sample TPHC concentrations ranged from 9.1 to 72 mg/Kg in summer 2002 and 0.55 to 25 mg/Kg in summer 2000 (Table 3-2). A biogenic surface residue sample collected from the Canning River had a TPHC concentration of 2,900 mg/Kg.

An increase in the mean regional concentration of TPHC at Northstar is observed between the summer 1999 pre-construction measurements and the combined summer 2000 and 2002 post-construction measurements. This increase remained statistically significant when the silt+clay variable was used as a covariate in the regression equation. However, when the concentration of TPHC was normalized to perylene (a PAH compound associated with biogenic but not anthropogenic hydrocarbon sources) in the full statistical model, no significant Northstar, construction, or interaction effects were noted (Tables 3-10 and 3-11).

The composition of SHCs in the river sediment and peat samples was similar to the surficial sediments, indicating a common TPHC source relationship between the river sediments and the nearshore surficial sediments. For example, similar patterns are noted in the GC/FID chromatograms for the Colville River (Figure 4-6), Northstar station 6 (Figure 4-7), Liberty station 6 (Figure 4-8), and BSMP station 3A (Figure 4-9). Also, the composition of the SHCs in surficial sediments in 2000 and 2002 was similar to the 1999 sediment samples, indicating that no new source of SHCs impacted these sediment samples. For example, similar patterns are noted in the GC/FID chromatograms for station N06 in 1999, 2000, and 2002 (Figures 4-7, 4-12, and 4-14).

3.1.2.2 Polynuclear Aromatic Hydrocarbons

Concentrations of Total PAH in surficial sediments from the offshore summer 2002 survey ranged from 12 to 940 μg/Kg; the summer 2000 survey ranged from 29 to 2,000 μg/Kg; and the summer 1999 survey results ranged from 6.8 to 960 μg/Kg with one outlier at 2,700 μg/Kg. The highest Total PAH concentration in the summer 1999 survey was 2,700 μg/Kg detected at station 5D. The summer 2002 and 2000 Total PAH concentration at this station dropped to 270 and 630 μg/Kg, respectively, within the expected Total PAH concentration range. The mean Total PAH concentrations for the three regions (Northstar, Liberty, and BSMP) were 520, 290, and 200 μg/Kg (Tables 3-2 through 3-4), respectively, in the summer 2002 survey and 750, 330, and 370 μg/Kg in the summer 2000 survey as compared to the 1999 mean Total PAH concentrations of 350, 380, and 440 μg/Kg, respectively. The river sediment and peat sample Total PAH concentrations ranged from 89 to 690 μg/Kg in summer 2002 and 8.6 to 2000 μg/Kg in summer 2000 (Table 3-2).

An increase in the mean regional concentration of Total PAH at Northstar was noted between the 1999 pre-construction measurements and the combined 2000 and 2002 post-construction measurements. This increase remained statistically significant when the silt+clay variable was used as a covariate in the regression equation. When the concentration of Total PAH less perylene was normalized to perylene in the full statistical model, no significant Northstar or Northstar*construction interaction effects were noted (Tables 3-10 and 3-11).

As noted with the SHC composition, the composition of Total PAH in the river sediment and peat samples was similar to the surficial sediments, indicating a common PAH source relationship between the river sediments and the nearshore surficial sediments. Also, the composition of the Total PAH in surficial sediments collected from Northstar in 2000 and 2002 was similar to the 1999 Northstar sediment samples, indicating that no new source of PAH impacted these sediment samples. For example, similar patterns are noted in the PAH distribution histograms for station N06 in 1999, 2000, and 2002 (Figures 4-7, 4-12, and 4-14).

Overall, the levels of PAH measured during the summer 2000 and 2002 surveys are within the range of values reported from previous studies of the region and other Alaskan coastal areas (Table 3-6).

3.1.2.3 Steranes and Triterpanes

Concentrations of Total S/T in surficial sediments from the offshore summer 2002 survey ranged from 1.5 to 110 μg/Kg; the summer 2000 survey ranged from 2.9 to 180 μg/Kg; and the summer 1999 survey results, on a small sub-set of the stations, ranged from 1.2 to 82 μg/Kg with one outlier at 490 μg/Kg. The highest Total S/T concentration in the summer 1999 survey was 490 μg/Kg detected at station 5D. The summer 2002 and 2000 Total S/T concentrations at this station dropped to 38 and 100 μg/Kg, respectively. The mean Total S/T concentrations for the three regions (Northstar, Liberty, and BSMP) were 55, 29, and 20 μg/Kg (Tables 3-2 through 3-4), respectively, in the summer 2002 survey and 78, 39, and 35 μg/Kg in the summer 2000 survey. Regional means are not available for the summer 1999 survey because only a select subset of the samples was analyzed for S/Ts. The river sediment and peat sample Total S/T concentrations ranged from 18 to 390 μg/Kg in summer 2002 and 2.2 to 280 μg/Kg in summer 2000 (Table 3-2).

3.1.3 Metals

All surficial sediments, (top 1 cm) collected during 2000 and 2002 were analyzed for total concentrations of Ag, Al, As, Ba, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Sn, Tl, V and Zn (Table 3-1 and Appendix C). Concentrations of metals show a similar degree of patchiness throughout the study area as shown for TOC and grain size (Tables 3-1, 3-7, 3-8, and 3-9). However, metal concentrations do vary in response to variations in grain size and TOC as will be discussed below. The highest concentrations of all metals except Ag and Ba were found in Al-rich (>5.8% Al) sediments from the area of Northstar Island (Table 3-8). However, these maximum concentrations are within natural limits for the area based on metal/Al ratios and as discussed in Section 4. Maximum concentrations of Ag and Ba were found for a gravel-rich (60% gravel) sample from station N22 (2000). The higher levels of metals reported for station 5D during 1999 were not observed during 2000, most likely due to being covered by new sediment or winnowed away by bottom currents.

In the area of the Northstar Island, sediment was collected from 15 stations in 1999, 23 stations in 2000, and 21 stations in 2002. These additional stations (N16-N23) were sited close to the island as well as along the pipeline. The lowest metal concentrations in the Northstar area were found in the sandy sediment at sites N01, N15, N17 and N22 (2000, Table 3-8) and N01, N15, and N20 (2002, Table 3-8). In accordance with the grain size distribution, the highest levels of metals occurred where silty sediment and >6% Al were present (stations N04, N05, N12, N13, N21 and N23 during 2000 and no stations during 2002; Table 3-8). Concentrations of Fe, Zn, Cu, Cr and Ni were slightly elevated in the gravel-rich, Al-poor sediment from the top of the pipeline. In the immediate area of Liberty Prospect, no clear trends in grain size or metal distribution were observed. Highest metal levels were found at sites L01 (2000) and the lowest metal values were observed at site L07 (2000), L08 and L09 (2000 and 2002; Table 3-9).

The patchwork of metal concentrations throughout the study area can be unified by normalizing metal values to either Al or Fe and thereby removing variations in metal concentrations that result from differences in grain size, TOC and/or mineralogy. The metal/Al ratios are discussed extensively in Section 4. Figure 3-5 shows a strong, positive relationship between Al and grain size. The finer-grained material is richer in Al-bearing clays whereas the coarser grained sediment contains Al-poor quartz sands and carbonate shell fragments.

Iron concentrations correlated extremely well ($r = 0.94$) with Al levels (Figure 3-6). Thus, either element can be used to normalize the other metal concentrations. By way of introduction, just one example of a metal/Al plot is given for V in Figure 3-6 to show the effectiveness of the normalization process. Additional examples for other metals, such as Ba, Pb, and Cu, are presented in Section 4. Even though individual metal concentrations are extremely variable from site to site, these differences can be explained by variations in grain size, TOC and/or mineralogy when normalized to Al. Concentrations of V and other metals follow Al in that higher levels are found in aluminosilicate clays and lower levels are found in quartz and carbonate sands. Thus, plots such as shown in Figure 3-6 show the natural trend (i.e., V/Al ratio) for area sediments. Positive deviations from a prediction interval constructed around the regression line can often be related to anthropogenic inputs of that metal. This concept is developed in detail in Section 4.

3.1.4 Statistical Results

Using the statistical model described in Section 2, the null hypotheses “The concentrations of organic pollutants in sediments do not show any increase as a result of the development of the Northstar unit” and “The concentrations of metal pollutants in sediments do not show any increase as a result of the development of the Northstar unit” were tested. The results of the statistical analyses are presented in the Tables 3-10 to 3-12.

In Tables 3-10 to 3-12, the first column gives the parameter analyzed as the dependant variable in the model. The second, third, and fourth columns give the R-squared, *p*-value, and intercept for the entire model. The R-squared is the proportion of variance explained by the ANOVA model. In most cases the R-squared is above 70%, indicating that the model adequately explained most of the sources of variation in the sampling, measurement, and analysis of these sediments. The fifth and sixth columns give the parameter estimate and *p*-value for the sediment covariate (silt+clay, LN perylene, or aluminum). The next 6 columns describe the model estimates for the three fixed effects in the same way. The first binary effect is the mean effect associated with the Northstar stations in all years 1999, 2000, and 2002. A positive (or negative) effect along with a significant *p*-value ($p\text{-value} \leq 0.05$) indicates an increase (or decrease) in the parameter associated with Northstar. The second binary effect is the increase or decrease associated with construction (years 2000 and 2002) at all stations. The third effect is the additional increase or decrease associated with Northstar stations and construction, the

Northstar*Construction effect. The last column gives the *p*-value associated with the two-sided test of the null hypothesis of no Northstar*Construction effect. *P*-value here is defined as the probability - assuming no Northstar*Construction effect - of obtaining an estimated effect as large or larger than the observed effect. The false discovery rate for this test was controlled by using the Hochberg procedure (Benjamini and Hochberg, 1995).

In general, the results show that there is an apparent increase in PAH and petroleum hydrocarbon concentrations associated with Northstar*Construction effect (2000+2002) even after adjusting for grain size. However, when the data are adjusted for LN perylene (a PAH parameter associated only with the natural sources of PAH in the region) there is no significant increase in organic concentrations associated with Northstar*Construction effect.

3.2 Tissues

Bivalve and amphipod samples were collected at selected ANIMIDA stations as part of the summer 1999, 2000, and 2002 sampling surveys. During the 1999 and 2000 sampling events, amphipods were scarce likely due to a lack of nearshore ice thus, limiting the number of amphipod samples collected. A total of five bivalve and four amphipod samples were collected in 1999, five bivalve and six amphipod samples were collected in 2000, and five bivalve and eight amphipod samples were collected in 2002. The same five bivalve stations were sampled all three years (i.e., 3A, 5H, L08, L09, and 5F). The amphipod stations varied somewhat from year to year due to amphipod scarcity. As a result of the small number of biota samples collected and the variability of year-to-year amphipod stations sampled, the biota data cannot be used to detect changes at Northstar Island due to construction activities. Nevertheless, the biota data can be used as a region-wide monitoring indicator.

3.2.1 Organics

SHC, PAH, and S/T measurements were made in pooled samples of amphipods (*Anonyx sp.*), and clams (*Astarte* and *Cyrtodaria*) at stations where sufficient organisms could be collected. The concentrations of Total PAH, TPHC, and Total S/T are presented in Table 3-13 and Appendix B (wet-weight basis). In general, the concentrations of all organic target compounds in the tissue of all species were quite low. Total PAH concentrations range from 7.4 to 39 µg/Kg in summer 2000 and 9.6 to 25 µg/Kg in summer 2002; TPHC values range up to 26 mg/Kg in summer 2000 and from 2.5 to 52 mg/Kg in summer 2002; and the Total S/T concentrations ranged from 2.0 to 8.1 µg/Kg in summer 2000 and 1.0 to 3.2 in summer 2002. For stations sampled in 1999, 2000, and 2002 for tissue samples, only small differences in concentrations were observed between years (Figure 4-36).

3.2.2 Metals

Concentrations of Ag, Al, As, Ba, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Sn, Tl, V and Zn were determined for samples of amphipods (*Anonyx sp.*) and clams (*Astarte*) at sites where they could be found. Concentrations of selected metals are presented on a dry weight basis for pooled samples in Tables 3-14 and 3-15. Data for water content are included with the complete data set in Appendix C so that metal concentrations also can be calculated on a wet weight basis.

Four of the six pooled samples of amphipods (*Anonyx sp. small*) were collected from the Northstar area, one was collected from station 5(0) near Endicott Island and one from station 4A near the Boulder Patch (see Table 3-14). Metal concentrations in the amphipods were reasonably uniform for each metal with values for the coefficient of variance (CV; [standard deviation/mean] x 100%) ≤10% for Ag, As, Be and Zn, ≤25% for As, Co, Cu, Hg, Mn, Ni, Pb, Sb, Tl and V, and ≤40% for Al, Ba, Cd, Cr and Fe (Tables 3-14 to 3-15 and Appendix C). No distinct trends were observed among maximum and minimum concentrations of metals as a function of location. Furthermore, mean concentrations of metals at the four stations from the Northstar area were not significantly different from those for stations 5(0) and 4A.

Four-pooled samples of clams (*Astarte*) were collected from sites east of the Endicott development. Metal concentrations were relatively similar among samples (Tables 3-14 to 3-15 and Appendix C) with values for the CV that were <10% for As, Cd and Zn, <25% for Ag, Cr, Cu, Fe, Pb and Sb, and less than about 40% for the remaining metals (Al, Ba, Be, Co, Hg, Mn, Ni, Tl and V). Much of the observed variance among metals was related to some lower concentrations in the pooled sample from station 3A.

3.3 Caged Mussel and SPMD Results

Transplanted caged mussels and SPMDs were added to the summer 2002 survey to augment the tissue sample collection and further investigate the bioavailability of contaminants. For this study, 6 moorings were deployed and retrieved, 3 adjacent to Northstar and 3 in a reference location, each with paired mussel cages and SPMDs. The SPMDs were analyzed for PAHs, TPHC, and S/Ts and the caged mussels were analyzed for PAHs, TPHC, S/Ts and metals. In addition to the Northstar and Reference site mussel samples, a subsample of the transplanted mussels was taken as a sample prior to deployment. The pre-deployment mussel sample was analyzed to evaluate the baseline level of organic contamination in the mussels and for comparison to the exposed Northstar and Reference site mussel samples. Each mussel sample consisted of approximately 40 individual mussels composited into one sample. Subsamples of the composite samples were then prepared for the organic and metal analyses.

The SPMD and Mussel deployments were made for approximately 21 days due to the logistical constraints of the field program. Although shorter than an optimal exposure period of ~30 days, it is expected that the SPMDs were near equilibrium for some of the lower molecular weight 2- and 3-ringed PAH which partition into the SPMD more readily. However, some of the higher molecular weight 4- and 5- ringed PAH partition more slowly, requiring more than 60 days to reach equilibrium (Booij et al., 1998), resulting in the potential enrichment of the lower molecular weight PAH in the SPMDs.

3.3.1 Caged Mussels

3.3.1.1 Organics

The concentrations of Total Napthalenes (Total N; sum of naphthalene and the alkylated naphthalenes), Total PAH, TPHC, and Total S/T are presented in Table 3-16 and Appendix B. The results for the caged mussels are presented on a wet-weight basis and the results for the

SPMDs are presented as concentration per SPMD membrane (two SPMD membranes were extracted and analyzed from each device). It should be noted that the mussels were in good condition when retrieved and exhibited extensive byssal thread growth, indicating that they were healthy and growing. Shell condition index measurements were not made as part of the mussel deployments. However, lipid measurements were made and the mean lipid levels of the Northstar and Reference post deployment mussels were higher than the pre-deployment mussels (although only significantly higher for the Reference mussels), further indicating they were healthy and actively feeding.

The mean Total PAH concentration of the Northstar samples (16 µg/Kg, standard deviation [SD] 1.2) and the Reference samples (mean 13 µg/Kg, SD 1.2) were similar and were not significantly different. The Total PAH concentration of the pre-deployment mussel sample was 7.8 µg/Kg. Overall, these levels of Total PAH very low and are consistent with uncontaminated areas in Alaska (Boehm et al., 2004) and are substantially lower than the reference mussels from a clean area of the Northeast U.S. that were used for a NOAA Mussel Watch study (Peven et al., 1996). The distribution of the PAHs in the Northstar, Reference, and pre-deployment samples were similar with subtle differences likely due to analytical variability when measuring trace concentrations at and below the minimum reporting limit (MRL; Figure 4-44). The similar PAH distributions and concentrations in the Northstar and Reference mussel samples indicate that the samples were exposed to similar sources and concentrations of petroleum hydrocarbons while deployed.

The mean TPHC concentrations of the Northstar samples (2.7 mg/Kg, SD 0.35) and the Reference samples (mean 2.7 mg/Kg, SD 0.15) were the same. The TPHC concentration of the pre-deployment mussel sample was 3.8 mg/Kg. The distribution of the n-alkanes in the Northstar, Reference, and pre-deployment samples were alike indicating a similar source of hydrocarbons in these samples. The higher TPHC concentration in the pre-deployment mussel sample along with the similar alkane distributions indicates that the alkanes detected in the Northstar and Reference samples were likely present in the mussels before deployment and were not a result of hydrocarbon uptake during deployment in the Beaufort Sea. These results also show that the deployed samples were not exposed to sufficient concentrations of TPHC during deployment to raise the sample concentrations above the baseline or to alter the alkane distribution.

The mean Total S/T concentrations of the Northstar samples (1.5 µg/Kg, SD 0.19) and the reference samples (mean 1.5 µg/Kg, SD 0.19) were the same and represent trace concentration (minimum reporting limit 1.2 µg/Kg). The Total S/T concentration of the pre-deployment mussel sample was 1.0 µg/Kg. Due to the trace levels of S/T detected, a definitive source comparison could not be performed between the Northstar, Reference, and pre-deployment mussel samples.

3.3.1.2 Metals

Data for metals in mussels from the predeployment site, the reference site in the coastal Beaufort Sea and the site near Northstar Island are presented in Table 3-17. One of three composite mussel samples for the reference site and for the Northstar site was not analyzed because of a labeling error. Concentrations of Fe for all three locations are similar enough to assume that any sediment incorporation that may be in the mussel sample is similar from site to site (Table 3-17). Variable contributions of sediment into the mussel can be important for metals that are enriched naturally in sediments relative to mussels (e.g., Fe, Ba, Be, Cr).

No significant differences were observed between concentrations of metals in samples from the reference site in the coastal Beaufort Sea versus Northstar Island (Table 3-17). In fact, the mean values agreed within 5% for most metals. Some shifts in concentrations were observed between the predeployment site and the Beaufort Sea sites. For example, Ba in the mussels from the pre-deployment site was 6.5 µg/gram (g) relative to 18 µg/g in the Beaufort Sea. This difference is probably related to differences in ambient level of dissolved Ba in the two systems and supports the contention that the organisms were actively filtering water. Similar shifts were observed for Be and Tl (Table 3-17).

3.3.2 SPMDs

The concentrations of Total N and Total PAH, are presented in Table 3-16 and Appendix B. The results for the SPMDs are presented as concentration per SPMD membrane (two SPMD membranes were extracted and analyzed from each device). In addition to the Northstar and Reference site SPMD samples, one set of SPMDs was collected as a field blank sample prior to the deployment. The field blank SPMD was opened during the deployment and retrieval of each mooring to monitor potential ambient contamination in the field. The field blank SPMD sample was also used to assess baseline level of organic contamination in the SPMDs and for comparison to the exposed Northstar and Reference site SPMD samples.

The mean Total PAH concentrations of the Northstar samples (510 ng/SPMD, SD 34) and the Reference samples (500 ng/SPMD, SD 37) were similar and were not significantly different. Overall, these PAH concentrations should be considered low and are comparable to results for relatively uncontaminated waters in Alaska (Boehm et al., 2005) and are only somewhat higher than the blanks levels of 300 – 400 ng reported by Shigenaka and Henry (1995). The Total PAH concentration of the SPMD field blank sample was 130 ng/(SPMD per exposure) of which 120 ng/(SPMD per exposure) was contributed by naphthalene and the alkylated naphthalenes (Total N). The concentrations in the SPMD field blank were adjusted by the number of field exposures; the field blank was opened and exposed at each of the six moorings. The Total N concentration in the Northstar and Reference samples averaged 240 and 230 ng/SPMD, respectively. The distributions of the PAHs in the Northstar and Reference samples were similar with subtle differences likely due to analytical variability when measuring trace concentrations at and below the MRL (Figure 4-43). The similar PAH distribution and concentrations in the Northstar and Reference SPMD samples indicate that the samples were exposed to similar sources and concentrations of petroleum hydrocarbons while deployed.

The SHC and Total S/T analyses performed on the SPMDs resulted in substantial matrix interference from the triolein material within the SPMD membrane, which masked any potential environmental accumulation in these samples. The associated data were not usable and are not included in this report. This contamination issue will need to be resolved prior to performing future SPMD monitoring in the ANIMIDA study area; otherwise, the SHC and/or Total S/T measurements should not be performed.

3.4 Quality Control Results

This section provides an evaluation of the quality and usability of the environmental data based on the results for the field and laboratory QC samples collected and analyzed during this program. Tables 3-18 through 3-20 summarize the organic field and laboratory QC results. Tables 3-21 through 3-27 summarize the inorganic field and laboratory QC results.

In general, no serious data quality issues were noted that would adversely affect the quality or use of the organic or inorganic data.

3.4.1 Field Quality Control

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

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

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

3.4.1.1 Equipment Blanks

Three equipment blanks were collected and submitted for analysis during the sediment sampling events – one from the summer 2000 sampling survey and two from the summer 2002 survey. These samples were collected by rinsing the grab sampling equipment immediately after decontamination of the equipment. PAH, S/T, SHC, and metals analyses were performed on these equipment blanks. The equipment blank results were evaluated to assess the potential for cross-contamination of samples due to inadequate sampling equipment decontamination.

Several PAH compounds including naphthalene, alkylated naphthalenes, biphenyl, fluorene, phenanthrene, C1-phenanthrene/anthracenes, dibenzothiophene, alkylated dibenzothiophenes, fluoranthene, pyrene, indeno(1,2,3-cd)pyrene, and/or benzo(g,h,i)perylene were detected at trace-level concentrations in the equipment blanks. These compounds were detected at concentrations well below the MRL; the total PAH concentrations in these blanks ranged from 0.114 to 0.260 μg/liter (L). Two S/T compounds, T15-norhopane and T19-hopane, were detected at low concentrations below the MRL in the equipment blank collected during the summer 2000 survey. Trace concentrations of several straight-chain alkanes (*i.e.*, n-C21 through n-C38) were detected in the equipment blanks. These compounds were detected at concentrations less than the MRL in two of the field blanks. One field blank collected in 2002 contained alkanes n-C25 through n-C29 at concentrations slightly above the MRL and several additional alkanes at trace concentrations below the MRL. The source of this contamination is believed to be the laboratory related, however, due to limited sample volume reanalysis could not be performed to confirm. The total TPH concentrations in these equipment blanks ranged from 220 to 450 µg/L. Concentrations of all metal analytes in the equipment blanks were less than 5 times the MDL.

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

3.4.1.2 Field Blanks

One field (deck) blank sample was collected during each summer survey with the collection of sediment samples. PAH, S/T, SHC, and metals analyses were performed on these field blanks. The field blank results were evaluated to assess the potential for atmospheric or other contamination that the field samples may have been subject to during sample collection.

Several PAH compounds were detected at trace-level concentrations in the field blanks and most of these compounds were also detected in the associated procedural blanks. All compounds were detected at levels well below the MRL; the total PAH concentration in these blanks was 0.034 µg/L (2000) and 0.035 µg/L (2002). Trace-level concentrations of several straight-chain alkanes (*i.e.*, n-C22 through n-C40) were detected in the equipment blanks. These compounds were detected at concentrations less than the MRL with one exception - n-C28 was greater than MRL in 2002 field blank; the total TPH concentrations in these blanks were 110 µg/L (2000) and 26 µg/L (2002). No S/T compounds were detected in the field blanks. The concentrations of all metal analytes were less than 5 times the MDL in the field blanks.

These results indicate that the sediment samples were not subject to atmospheric or other contamination during sample collection that would adversely affect the quality or use of the sample data.

3.4.1.3 Field Replicates

Four sets of field replicate samples were generated during the collection of the sediment samples in the form of triplicate samples collected at sampling stations N13 and L08 during the summer survey and at sampling stations 5D and N03 during the summer 2002 survey. The field replicate results were evaluated to assess analytical precision relative to sample collection procedures and sample matrix.

For the triplicate samples collected at sampling station N13, the precision criterion of less than 50 percent RSD for sediments was met for all PAH, SHC, and S/T results detected at concentrations greater than 5 times the reporting limit with only one exception. The precision criterion was exceeded for C4-phenanthrene/anthracene (51%). Overall, the field replicate precision at sampling station N13 was considered to be acceptable.

For the triplicate samples collected at sampling station L08, the precision criterion of less than 50 percent RSD for sediments was met for all PAH, SHC, and S/T results detected at concentrations greater than 5 times the reporting limit with only two exceptions. The precision criterion was exceeded for S28 – ethylcholestane (52%) and n-triacontane (61%). Overall, the field replicate precision at sampling station L08 was considered to be acceptable.

For the triplicate samples collected at sampling stations 5D and N03 in 2002, the precision criterion of less than 50 percent RSD for sediments was met for all PAH, SHC, and S/T results detected at concentrations greater than 5 times the reporting limit without exception.

3.4.2 Organics Quality Control

Laboratory QC samples were analyzed to assess precision and accuracy of the sample preparation and analytical procedures. The number and type of laboratory QC samples was based on the total number of field samples and as specified in ADL/ICF SOPs and the Field Sampling and Logistics Plans (Arthur D. Little 2000 and ICF 2002a). For this program, the following laboratory QC samples and measures were used to evaluate accuracy and precision of the analytical data: surrogate recoveries, procedural blanks, blank spike samples, laboratory duplicates, standard reference materials, and oil reference standards. The results for the organic QC samples and measures are presented in Appendix B, along with the results for the associated environmental samples. Discussion and interpretation of the results are provided in the following sections.

In addition to the program-specific QC, ADL/ICF participated in the National Oceanic & Atmospheric Administration/National Institute of Standards & Technology (NOAA/NIST) intercalibration exercises for organics in 1998, 1999, 2000, and 2001. Triplicate analyses of marine sediment and mussel tissue were analyzed for organics, including PAHs, as part of these exercises. The results of the ADL/ICF analyses were within the top 10 percent of the more than 30 laboratories participating in the exercises.

The Marine & Environmental Chemistry Laboratories at FIT participated in the most recent NOAA/NIST Intercomparison for Trace Metals that was organized by the NRC. FIT ranked at the top of 41 laboratories in the exercise. Each laboratory was given two sediment samples and two fish tissue samples to analyze for 15 trace metals including mercury, lead, copper, cadmium, tin, thallium, beryllium and others. Concentrations of some elements were required to be within 5% of established concentrations, while others were to be determined within 10-20%. Thirteen of the 41 laboratories, including FIT, were given a Superior rating for the analysis of both sediment and tissue samples. FIT was the only laboratory to correctly determined 60 different concentrations of trace metals in the sediment and tissue samples with no incorrect values.

3.4.2.1 Surrogate Results

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

For the PAH analyses, all of the environmental and QC sample surrogate recoveries were within the recovery acceptance limits, with a couple of exceptions. One of the six blank spikes associated with the sediment samples had low recoveries for all four surrogates. The method blank and all field samples associated with this blank spike had acceptable surrogate recoveries and the associated sediment SRM had acceptable target compound recoveries. Thus, these low surrogate recoveries in the blank spike do not adversely affect the quality or usability of the associated environmental sample data.

The method blank and blank spike associated with the year 2000 tissue samples had low recoveries for two surrogates ranging from 12 to 30% and the method blank associated with the year 2002 tissue samples had low recoveries for three of the four surrogates ranging from 20 to 44%. Tissue sample 00-4A-01-PHC-T-AN had low recoveries for all four surrogates, ranging from 28 to 42%. Tissue sample 02-N03-01-PHC-T-AN had a low recovery of 43% for one of the four surrogate. The tissue SRMs and remaining field samples associated with these tissue batches met all surrogate recovery criteria, thus, the low surrogate recoveries in the method blanks and blank spike do not adversely affect the quality or usability of the associated environmental sample data. The results for tissue samples 00-4A-011-PHC-T-AN and 02-N03-01-PHC-T-AN are considered to be estimated values.

For the SHC analyses, all of the environmental and QC sample surrogate recoveries were within the recovery acceptance limits, with one exception. A blank spike associated with the year 2000 sediment samples had very low recoveries for both surrogates (3%). The method blank and associated field samples had acceptable surrogate recoveries indicating that the poor extraction efficiency in the blank spike was an isolated occurrence, thus, the low surrogate recoveries in the blank spike do not adversely affect the quality or usability of the associated environmental sample data.

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

3.4.2.2 Procedural Blanks

A laboratory procedural blank (PB) was prepared with each sample preparation batch by extracting a blank sample matrix (sodium sulfate) as if it were one of the environmental samples. Procedural blanks are used to assess the potential of contamination introduced during sample preparation and analysis. PAH, S/T, and SHC analyses were performed on each PB.

Between 2 and 18 PAH target compounds were detected at trace concentrations less than the MRL in all of the tissue, water, sediment, and SPMD PBs, with the exception of the napthalenes, biphenyl, and phenanthrene. A few naphthalene, alkylated naphthalenes, biphenyl, and phenanthrene results were detected at concentrations greater than the MRL. Naphthalene was identified in all the blanks and is a common contaminant associated with the solvents used during sample preparation. Several SHC target compounds ranging from n-C16 to n-C38 were detected at trace concentrations less than the MRL in all of the tissue, water, sediment and SPMD PBs with two exceptions. Alkanes n-C26 through n-C29 were detected at concentrations greater than the MRL in two year-2002 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 may be false positives.

3.4.2.3 Blank Spike Sample Recoveries

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

For the PAHs analyses, the recoveries of several compounds in a tissue BS, a SPMD BS, and in three sediment BSs exceeded the acceptance criteria. The QC sample results were adjusted based on surrogate recoveries and these high recoveries are the result of lower surrogate recoveries in these BS analyses. These BS recovery exceedances do not adversely affect the quality or usability of the associated sample data.

For the SHC analyses, the recovery of n-C25 and n-C30 in one sediment BS exceeded the acceptance criteria, the recovery of n-C10 was low in two sediment BSs, and the recoveries of n-C10 and n-C15 were low in one tissue BS. Overall, this data quality issue does not adversely affect the quality or usability of the associated sample data since these individual alkanes contribute only a small amount to the TPHC concentration.

3.4.2.4 Laboratory Duplicates

Laboratory duplicates were prepared with several sample preparation batches by extracting a second separate aliquot of an environmental sample. Laboratory duplicates were evaluated to assess analytical precision related to laboratory performance and sample matrix. For this project, one laboratory duplicate was prepared and analyzed with each tissue and sediment sample batch. No laboratory duplicates were performed on the aqueous field QC samples or on the SPMD samples due to limited sample amount. PAH, S/T and SHC analyses were performed on each laboratory duplicate.

For the sediment and tissue 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 mean RPDs for each laboratory duplicate pair was less than 30 percent. 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 low concentrations. (RPD was calculated as the absolute difference between the two measurements divided by the mean of the two measurements).

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

3.4.2.5 Standard Reference Materials

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

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

Sediment SRM. SRM 1941a (a freeze-dried marine sediment with certified concentrations for PAHs) was prepared and analyzed for PAHs along with each of the sediment sample batches. The %Ds of the measured values versus the certified values for the PAH compounds were within the acceptance criteria of 30 percent on average per SRM and 35 percent for the individual compounds, with a few exceptions. The response for naphthalene in all SRMs was more than 30 percent lower than the certified value, indicating that the measurement of naphthalene in the sediment samples may be biased low. Acenaphthene and biphenyl were recovered low in one SRM and benzo[k]fluoranthene was recovered low in one SRM. Chrysene and indeno(1,2,3-cd)pyrene recovered high in one SRM. 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.

Tissue SRM. One SRM (NIST SRM 1974a - certified for PAHs) was prepared and analyzed for PAHs along with the year 2000 tissue samples. All of the compound concentrations were within 35 percent of the certified values, with three exceptions: naphthalene (376%D), anthracene (234%D), and benzo[b]fluoranthene (36.2%D). The high recovery of naphthalene and anthracene are consistent with the results obtained for this compound in multiple (more than 20 samples) analyses of SRM 1974a over the last four years by ADL/ICF. This QC issue does not impact the quality or usability of the associated sample data since acceptable recoveries for naphthalene and anthracene were noted in the instrument SRM analyses, and since it appears that the certified values for naphthalene and anthracene in NIST SRM 1974a are incorrect. The benzo[b]fluoranthene results in the tissue samples may be biased high as indicated by the high recovery in the tissue SRM. This SRM exceedance has a minor impact on the quality and usability of the associated sample data since the exceedance was not extreme and did not result in any data being considered unusable.

One SRM (NIST SRM 2978 – certified for PAHs) was prepared and analyzed for PAHs along with the year 2002 tissue samples. The response for 11 of the 19 certified values recovered high, with %Ds ranging up to 700%. The poor performance on this SRM analysis appears to be an anomaly as the associated PB does not show evidence of contamination, the associated BS compound recoveries were acceptable (the BS compounds include many of the SRM certified compounds), the associated IRM recoveries were acceptable, the associated control oil recoveries were acceptable, and the surrogate recoveries in the associated samples were acceptable. The SRM exceedances have a minor impact on the quality and usability of the associated sample data since the poor performance appears to be an anomaly and limited to the SRM analysis.

3.4.2.6 Control Oil Analyses

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

3.4.3 Metals Laboratory Quality Control

Laboratory QC samples were analyzed to assess precision and accuracy of the sample preparation and analytical procedures. For this program, the following laboratory QC samples and measures were used to evaluate accuracy and precision of the analytical data: PBs, matrix spike samples, laboratory duplicates, and SRM. A summary of the QC results is given in Table 3-21. The individual results for the inorganic QC samples and measures for different matrices for 2000 and 2002 are presented in Tables 3-22 through 3-27 and Appendices A and C, along with the results for the associated environmental samples. Discussion and interpretation of the results are provided in the following sections.

3.4.3.1 Procedural Blanks

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

3.4.3.2 Matrix Spike Sample

Matrix spike samples were analyzed with each batch of sediment, organism, and suspended solids samples using the method of standard additions. Results from these analyses provide information on the extent of any signal suppression or enhancement due to the matrix. Spike results for the sediment, and organism samples are shown in Tables 3-22 through 3-27, and are within the 70 to 130 percent range specified in the DQOs.

3.4.3.3 Laboratory Duplicates

Duplicate subsamples taken from individual sediment and water samples in the laboratory were analyzed to estimate analytical precision. Analytical precision for sediment metal analyses (n = 3 pairs of duplicate samples) ranged from 0.8 percent RSD for Al to 11 percent RSD for low levels of Ag. For organism tissue samples (n = 1 pair), precision of duplicate sample analysis ranged from 0 percent RSD for Be, Cr, Sb and Tl to 8 percent RSD for Pb.

3.4.3.4 Standard Reference Materials

SRMs were processed and analyzed for trace metals along with the experimental samples as described in the Methods section (Section 2). The results of these analyses are shown in Tables 3-22 and 3-25 (sediment analysis) and 3-23 and 3-26 (organism analysis), and 3-24 and 3-27 (suspended sediment and dissolved). The metal concentrations determined for each SRM, were all within the range of certified values or within the DQO limits of the reference values provided by the certifying agencies.

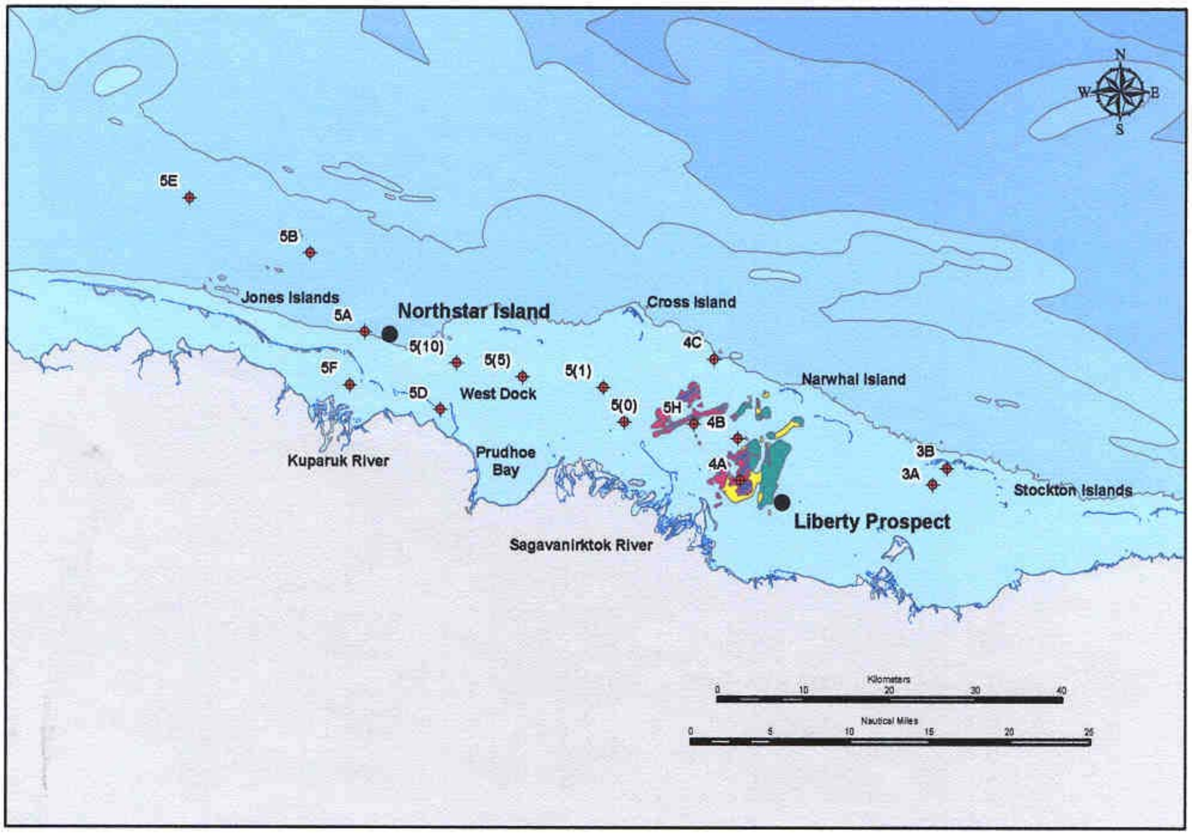
For TOC analyses, the marine sediment SRM MESS-2 was used as a QA sample. This SRM is certified for total carbon content (inorganic plus organic); therefore, the TOC values in Table 3-11 are slightly below the certified total carbon value. Nevertheless, the TOC values determined for MESS-2 were consistently reproducible with percent RSD of ~ 1 percent.

Table 3-1. Summary Data by Metals, Total Organic Carbon (TOC), and Grain Size in Sediment 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 2000	Mean ± Std. Dev. (n = 42)	0.10 ±0.04	4.13 ±1.55	10.5 ±2.7	387 ±146	1.1 ±0.5	0.22 ±0.09	7.2 ±3.0	61.6 ±19.5	20.8 ±9.3	2.36 ±0.78
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
Surface Sediment 2002	Mean ± Std. Dev. (n = 44)	0.08 ±0.05	3.74 ±1.37	9.3 ±2.6	408 ±121	0.9 ±0.3	0.16 ±0.06	8.3 ±2.8	55.0 ±19.2	15.4 ±6.8	2.12 ±0.71
All data	Range	0.01-0.44	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 2000	Mean ± Std. Dev. (n = 42)	0.043 ±0.021	364 ±137	25.9 ±9.3	9.4 ±4.3	0.49 ±0.17	0.40 ±0.16	99.7 ±35.3	75.6 ±25.9	1.03 ±0.79	52.5 ±31.9
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
Surface Sediment 2002	Mean ± Std. Dev. (n = 44)	0.036 ±0.017	353 ±151	24.8 ±9.7	9.3 ±3.0	0.43 ±0.12	0.41 ±0.13	90.4 ±34.0	66.4 ±24.0	0.74 ±0.37	50.2 ±35.0
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 3-2. Map Showing Beaufort Sea Monitoring Program Sampling Stations and Table of Concentrations for Selected Organic Parameters and Grain Size in Sediment Samples



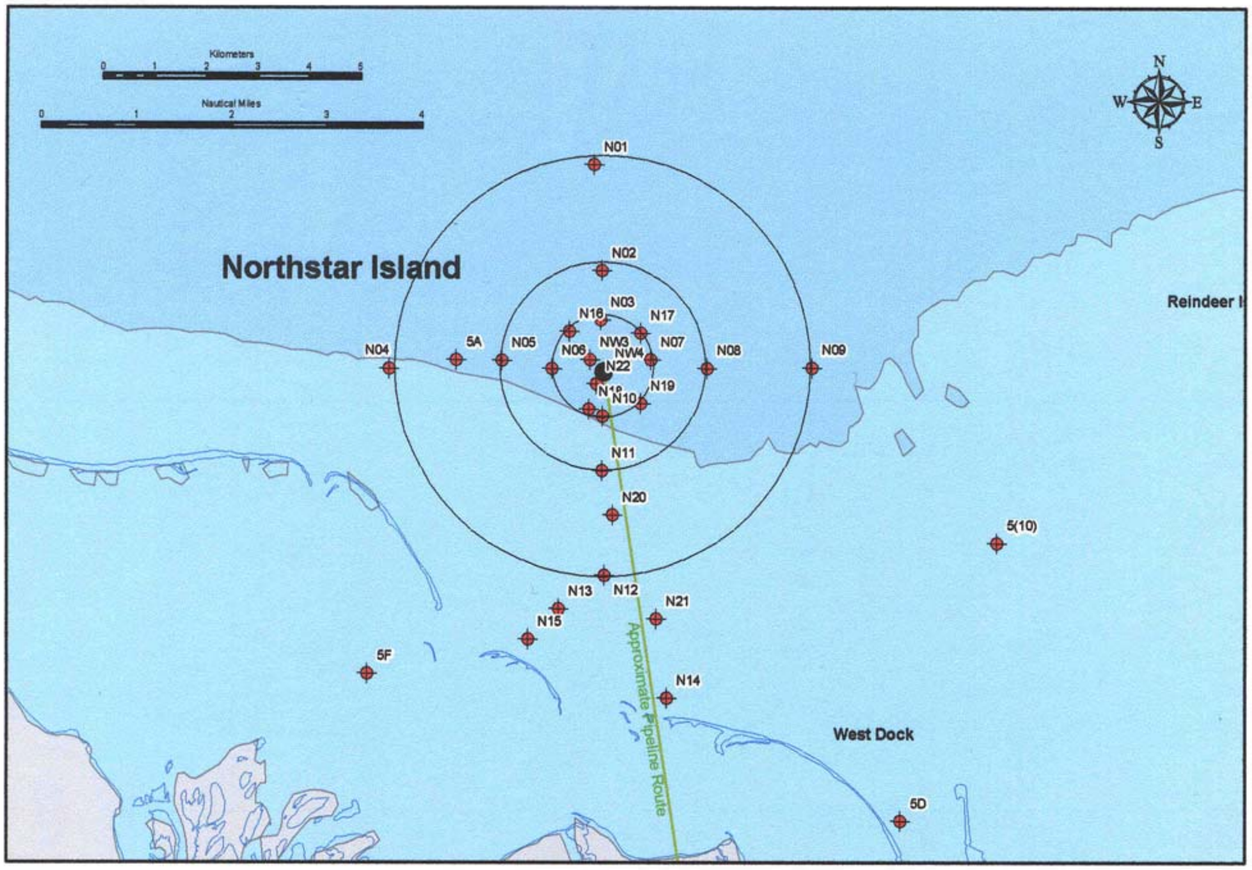
Station	Total PAH (μg/Kg)	Total PHC (mg/Kg)	Total S/T (μg/Kg)	TOC(%)	Silt+Clay(%)
BSMP - 2000					
3A	340	7.4	36	0.29	70
3B	320	6.4	28	0.58	73
4A	630	8.1	32	0.59	85
4B	420	16	55	1.2	49
4C	300	6.1	23	0.50	42
5(0)	380	6.5	25	0.96	26
5(1)	510	6.5	36	0.96	31
5(5)	440	5.6	31	1.1	29
5(10)	270	4.7	23	0.91	33
5B	26	5.9	7.8	0.06	1.2
5D	630	17	100	2.0	54
5E	260	3.5	22	<0.1	46
5F	420	7.8	48	0.51	49
5H	180	4.1	29	0.40	25
Mean (SD)	370 (160)	7.5 (4.0)	36 (23)	0.71 (0.51)	44 (22)
River Sources					
Colville (1)	140	4.3	27	0.42	2.4
Colville (2)	2000	25	280	1.8	39
Kuparuk	8.6	0.55	2.2	7.4	NA
Kuparuk Peat	100	18	51	2.4	NA
Sagavanirktok	250	6.5	30	2.8	NA

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

Station	Total PAH (μg/Kg)	Total PHC (mg/Kg)	Total S/T (μg/Kg)	TOC(%)	Silt+Clay(%)
BSMP - 2002					
3A	370	7.1	35	0.86	75
3B	390	8.0	37	0.74	84
4A	500	7.8	28	90	7.8
4B	83	1.8	7.6	0.77	10
4C	12	0.44	1.5	0.30	0.78
5(0)	170	4.0	15	0.62	18
5(1)	22	0.50	2.6	0.14	3.0
5(5)	300	5.3	30	0.58	41
5(10)	110	2.1	11	0.58	21
5B	68	3.5	6.4	0.41	4.3
5D[1]	270 (33)	6.2 (1.1)	38 (6.6)	0.96 (0.13)	70 (2.3)
5E	46	3.8	5.1	0.08	3.7
5F	370	8.3	49	1.26	71
5H	160	3.5	16	0.91	22
Mean (SD)	200 (160)	4.4 (2.7)	20 (16)	0.62 (0.33)	37 (34)
River Sources - 2002					
Canning (1)	490	9.1	23		
Canning (2)	190	19	18		
Canning Sheen	220	2900	ND		
Colville	690	11	73		
Colville Peat	360	50	110		
Kuparuk (1)	89	17	89		
Kuparuk (2)	160	22	140		
Kuparuk Peat (1)	140	71	92		
Kuparuk Peat (2)	450	72	390		
Sagavanirktok	670	18	65		
Sagavanirktok Peat	160	41	38		

Note[1] – Field Triplicates were collected at this station. The average value of the triplicates is reported with the standard deviation in parentheses.

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



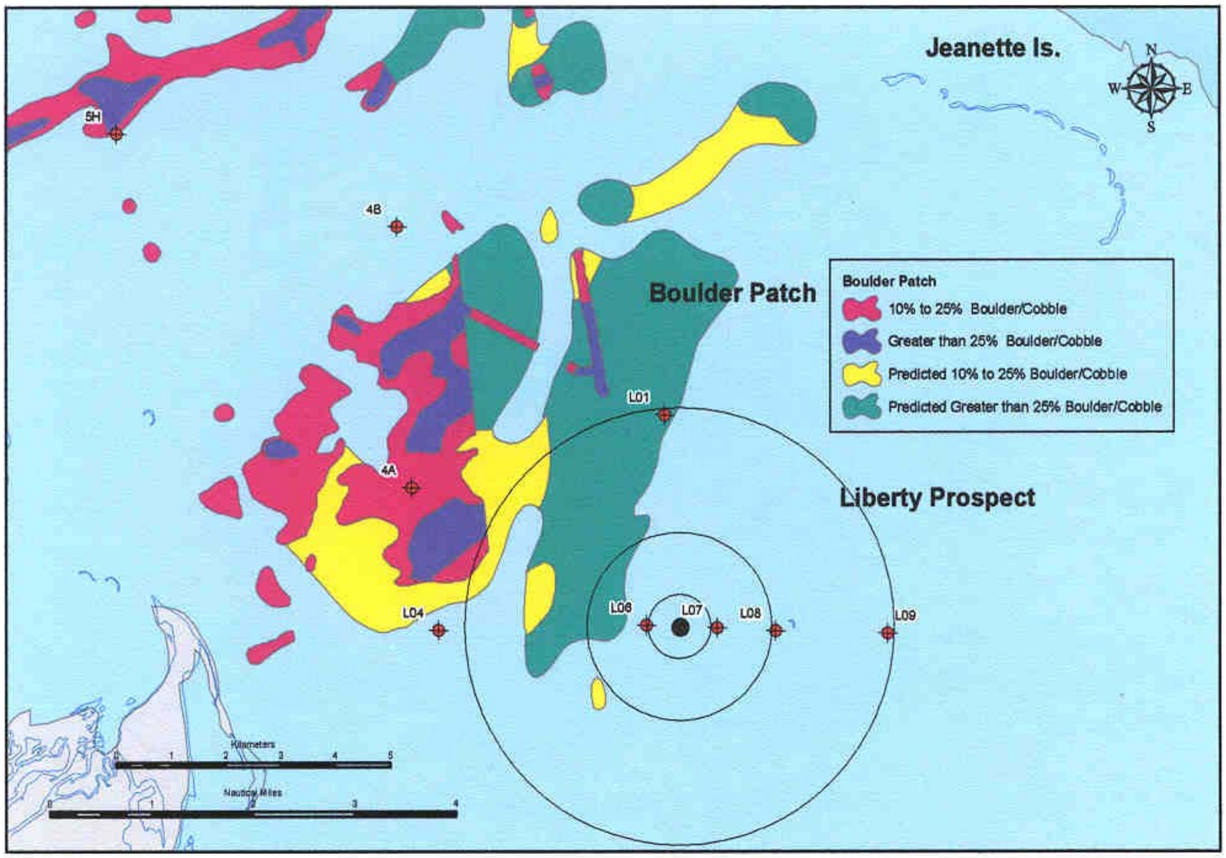
Station	Total PAH (μg/Kg)	Total PHC (mg/Kg)	Total S/T (μg/Kg)	TOC(%)	Silt+Clay(%)
Northstar – 2000					
5A	1800	22	140	1.7	85
N01	80	1.5	6.8	<0.1	2.4
N02	370	6.3	36	1.4	68
N03	620	12	59	0.74	83
N04	2000	23	150	1.7	77
N05	1400	16	97	1.6	86
N06	480	7.1	38	0.64	30
N07	540	11	62	1.2	48
N08	580	14	48	0.34	14
N09	280	4.1	20	0.78	12
N10	580	26	84	1.4	45
N11	650	20	82	1.4	58
N12	1500	24	150	1.6	90
N13[1]	1100 (140)	17 (3.1)	99 (15)	1.9 (0.3)	91 (3.9)
N14	1100	24	150	4.4	88
N15	29	1.0	2.9	<0.1	2.2
N16	600	10	63	0.86	66
N17	630	11	59	0.97	72
N18	870	12	77	0.50	61
N19	620	10	54	0.83	63
N20	720	17	79	1.7	70
N21	170	27	180	2.3	94
N23	540	10	68	1.8	99
Mean (SD)	810 (530)	14 (7.7)	78 (47)	1.3 (0.92)	61 (30)

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

Station	Total PAH (μg/Kg)	Total PHC (mg/Kg)	Total S/T (μg/Kg)	TOC(%)	Silt+Clay(%)
Northstar – 2002					
5A	810	14	77	0.97	92
N01	62	1.7	6.4	0.30	3.45
N02	420	8.2	49	0.83	65
N03[1]	600 (77)	11 (1.4)	63 (9.5)	0.90 (0.09)	82 (6.3)
N04	640	9.3	63	0.58	66
N05	940	14	90	0.90	87
N06	510	8.1	50	0.73	62
N07	280	6.2	26	1.0	33
N08	500	10	54	0.84	75
N09	310	6.0	32	0.78	60
N10	530	11	55	0.84	68
N11	340	6.6	32	0.45	47
N12	510	13	51	1.0	80
N13	830	22	110	1.8	91
N14	850	22	100	1.4	81
N15	200	3.7	22	0.19	4.3
N16	900	13	88	0.89	89
N17	620	11	70	0.85	83
N18	410	7.6	51	0.98	51
N19	510	10	52	1.2	50
N20	61	3.2	5.7	0.09	8.8
N21	650	14	64	1.0	87
N23	420	9.6	51	0.91	89
Mean (SD)	520 (250)	10 (5.1)	55 (28)	0.85 (0.37)	63 (28)

Note[1] – Field Triplicates were collected at this station. The average value of the triplicates is reported with the standard deviation in parentheses.

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



Station	Total PAH (μg/Kg)	Total PHC (mg/Kg)	Total S/T (μg/Kg)	TOC(%)	Silt+Clay(%)
Liberty - 2000					
L01	610	12	62	1.0	66
L04	400	7.7	51	0.47	60
L06	400	11	51	0.90	94
L07	220	6.9	20	1.5	36
L08[1]	280 (70)	12 (1.7)	41 (10)	0.24 (0.06)	31 (7.4)
L09	99	1.9	11	0.49	5.3
Mean (SD)	340 (180)	8.6 (3.9)	39 (20)	0.76 (0.45)	49 (31)
Liberty - 2002					
L01	150	2.9	15	0.59	11
L04	400	7.1	34	0.71	53
L06	420	6.5	32	1.2	58
L07	340	5.9	28	0.88	49
L08	340	10	52	0.67	6.4
L09	84	3.4	11	0.18	9.7
Mean (SD)	290 (140)	6.0 (2.6)	29 (15)	0.70 (0.33)	31 (24)

Note[1] – Field Triplicates were collected at this station. The average value of the triplicates is reported with the standard deviation in parentheses.

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

Parameter	Relevance in Environmental Samples
Saturated Hydrocarbons (SHC)	
Isoprenoids	The sum of selected branched isoprenoid alkanes including: phytane, pristane, farnesane [1470], and unidentified isoprenoids at relative retention indices 1380 and 1650. Isoprenoids are abundant in petroleum and are resistant to degradation relative to the corresponding n-alkanes.
LALK	The sum of lower-molecular-weight n-alkanes (n-C_9 to n-C_{20}) generally associated with “fresh” petroleum inputs.
TALK	The sum of total alkanes, which includes those of biogenic and petrogenic origin (n-C_9 to n-C_{40}).
LALK/TALK	Diagnostic alkane compositional ratio used to determine the relative abundance of lower-molecular-weight alkanes, which includes those of biogenic origin.
PHY/PRIS	Source of phytane (PHY) is mainly petroleum, whereas pristane (PRIS) is derived from both biological matter and oil. In “clean” environmental samples, this ratio is very low and increases as oil is added.
n-C_{16}/(n-C_{15} +n-C_{17})	The ratio of n-alkane hexadecane (n-C_{16}) over pentadecane (n-C_{15}) and heptadecane (n-C_{17}). At “background” levels of total hydrocarbons n-C_{15} and n-C_{17} can be used as indicators of plankton (algal) hydrocarbon inputs. As plankton productivity increases, the ratio decreases.
CPI	Carbon Preference Index. Describes the relative amounts of odd- and even-chain alkanes within a specific alkane boiling range [CPI = (n-C_{27}+ n-C_{29}+ n-C_{31})/(n-C_{26}+ n-C_{28}+ n-C_{30})]. CPI of 2 - 4 indicates terrestrial plants; as oil additions increase, the CPI is lowered to near 1.0.
TPHC	Total Saturated Hydrocarbons. The sum of the resolved plus unresolved saturated hydrocarbons.
Polynuclear Aromatic Hydrocarbons (PAH)	
N/P	The naphthalenes (N) to phenanthrenes/anthracenes (P) ratio is diagnostic for inputs of fresh petroleum, and as a weathering indicator. Naphthalenes are characteristic of fresh crude oil; the ratio decreases with increased weathering. (N= Naphthalene series [C0N + C1N + C2N + C3N + C4N]; P= Phenanthrene/Anthracene Series [C0P/A + C1P/A + C2P/A + C3P/A + C4P/A]).
C2D/C2P	Ratio of C2 alkyl dibenzothiophenes (D) and C2 alkyl phenanthrenes (P) is a useful diagnostic source ratio for petroleum.
C3D/C3P	Ratio of C3 alkyl dibenzothiophenes (D) and C3 alkyl phenanthrenes (P) is a useful diagnostic source ratio for petroleum.
Perylene	A biogenic PAH formed during the early diagenesis in marine and lacustrine sediments; may be associated with terrestrial plant source precursors.
Total PAH	The sum of all PAH target analytes; includes 2- through 6-ring parent PAH and C1 - C4 alkyl-substituted PAH.
Total PAH less perylene	The sum of all PAH target analytes with the exception of perylene.
Pyrogenic PAH	The sum of combustion PAH compounds (4-, 5-, and 6-ring PAH: fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene, and indeno[1,2,3-c,d]pyrene.
Petrogenic PAH	The sum of petrogenic PAH compounds (2-, 3-, and 4-ring PAH: naphthalenes [C0 - C4], acenaphthene, acenaphthylene, fluorene [C0 - C3], phenanthrenes [C0 - C4], dibenzothiophenes [C0 - C3], chrysenes [C1 - C4], and fluoranthenes/pyrenes [C1 - C3]).
Pyrogenic/Petrogenic	The ratio of pyrogenic PAH compounds to petrogenic PAH compounds is useful for determining the relative contribution of pyrogenic and petrogenic hydrocarbons and in differentiating hydrocarbon sources.

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

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

CPI – Carbon Preference Index
LALK – Low-molecular-weight n-alkanes
LALK/TALK – LALK:TALK ratio
PHY/PRIS – Phytane:pristane ratio
TALK – Total n-alkanes

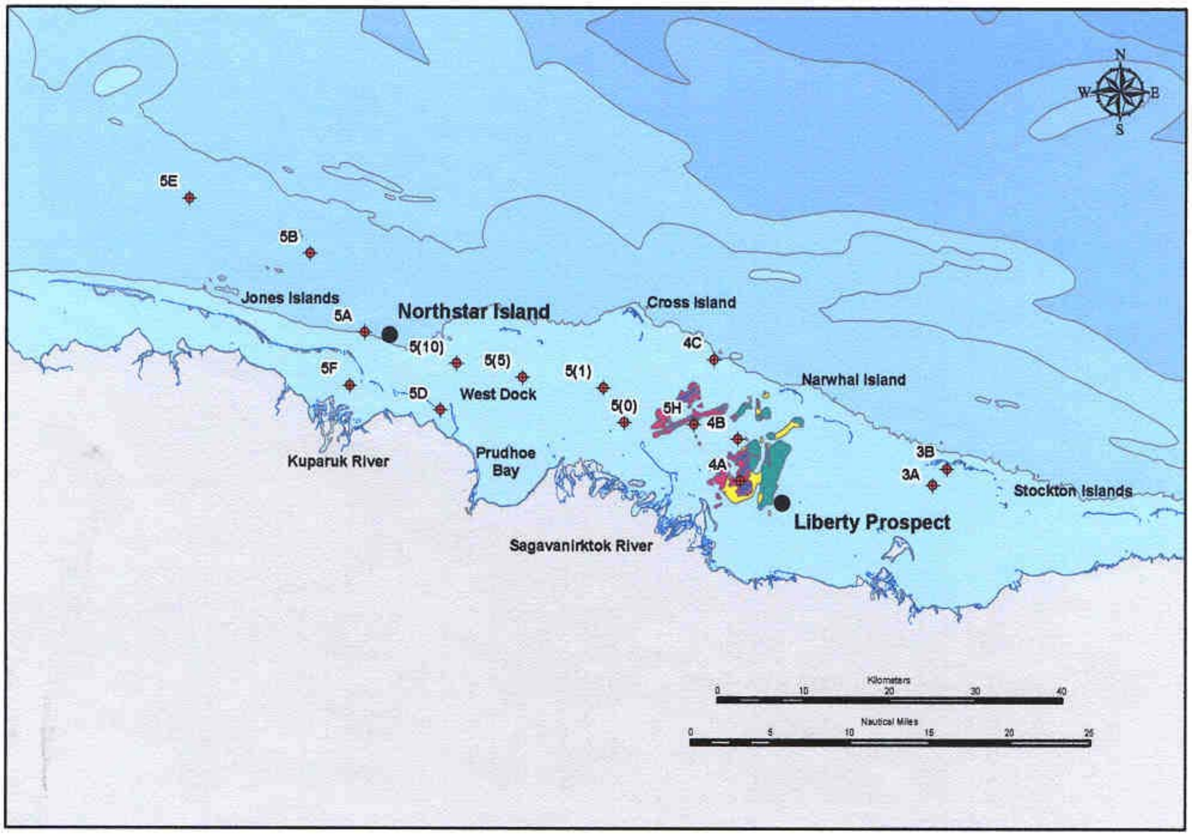
Table 3-6. Average Total Organic Concentrations in Surficial Sediments from ANIMIDA Study Area, Alaska Marine Sediments, and Cook Inlet and Shelikof Strait Sediments

	Total PAH (μg/g)	**Total PHC[f] (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 Sediment Cores[c]	0.54 (0.28 – 1.99)	9.0 (3.2 – 31)	0.059 (0.021 – 0.225)
Average (Range) Concentrations for Phase I ANIMIDA Study Area Surficial Sediments[d]	0.39 (0.007 – 2.7)	6.6 (0.21 – 50)	0.025 (0.001 – 0.082)
Average (Range) Concentrations for Phase II ANIMIDA Study Area Surficial Sediments[e]	0.49 (0.012 – 2.0)	9.5 (0.44 – 27)	0.049 (0.002 – 0.176)

[a] Prince William Sound subtidal and Beaufort Sea (Bence et al., 1996; Boehm et al., 1991).
[b] ENRI - UAA, 1995, Hyland, et al.,1995; KLI, 1996; KLI, 1997; Boehm et al., 2001a.
[c] Brown et al., 2003.
[d] Boehm et al. 2001b and this study.
[e] Results from this study.
[f] 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 3-7. Map of Beaufort Sea Monitoring Program Sampling Stations and Table of Concentrations of Selected Metals in Sediment Samples



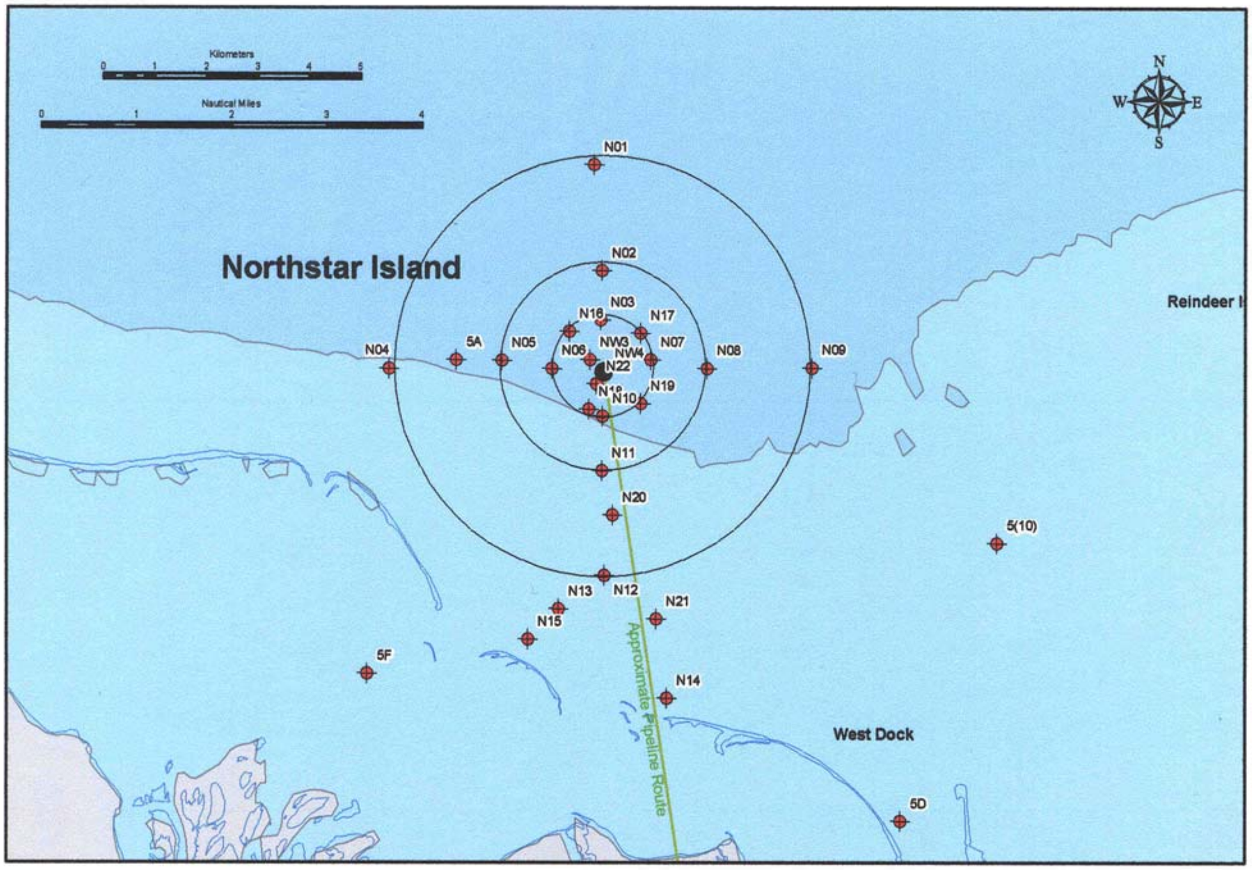
Station	Al (%)	Ba (µg/g)	Hg (µg/g)	Pb (µg/g)	Cd (µg/g)
BSMP - 2000					
3A	3.99	400	0.044	9.6	0.26
3B	4.14	288	0.038	6.3	0.17
4A	4.48	285	0.041	6.0	0.18
4B	5.43	305	0.058	8.9	0.17
4C	3.69	226	0.030	4.9	0.12
5H	2.74	285	0.024	6.6	0.21
5(0)	4.20	367	0.049	9.9	0.24
5(1)	4.33	388	0.035	11.5	0.17
5(5)	4.17	372	0.039	9.9	0.22
5(10)	3.85	349	0.037	8.9	0.21
5A	6.98	623	0.074	17.6	0.28
5B	1.26	164	0.003	3.9	0.03
5D	4.03	380	0.049	9.8	0.33
5E	2.34	187	0.013	4.4	0.06
5F	3.43	349	0.029	8.2	0.18

Table 3-7 (continued). Map of Beaufort Sea Monitoring Program Sampling Stations and Table of Concentrations of Selected Metals in Sediment Samples

Station	Al (%)	Ba (µg/g)	Hg (µg/g)	Pb (µg/g)	Cd (µg/g)
BSMP - 2002					
3A	4.71	512	0.061	12.9	0.17
3B	5.03	518	0.058	14.1	0.23
4A	4.28	535	0.042	11.6	0.31
4B	2.02	221	0.016	5.4	0.17
4C	1.56	165	0.007	4.1	0.05
5H	2.85	313	0.026	8.4	0.14
5(0)	3.12	363	0.025	6.1	0.21
5(1)	1.72	223	0.006	5.3	0.07
5(5)	3.47	357	0.060	8.6	0.13
5(10)	2.62	271	0.021	7.3	0.12
5A	5.42	538	0.049	11.0	0.19
5B	1.72	221	0.008	5.9	0.05
5D[1]	3.64 (0.25)	371 (30)	0.029 (0.004)	6.9 (1.1)	0.20 (0.03)
5E	1.65	203	0.009	5.1	0.06
5F	4.38	455	0.043	8.6	0.18

Note[1] – Field Triplicates were collected at this station. The average value of the triplicates is reported with the standard deviation in parentheses.

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



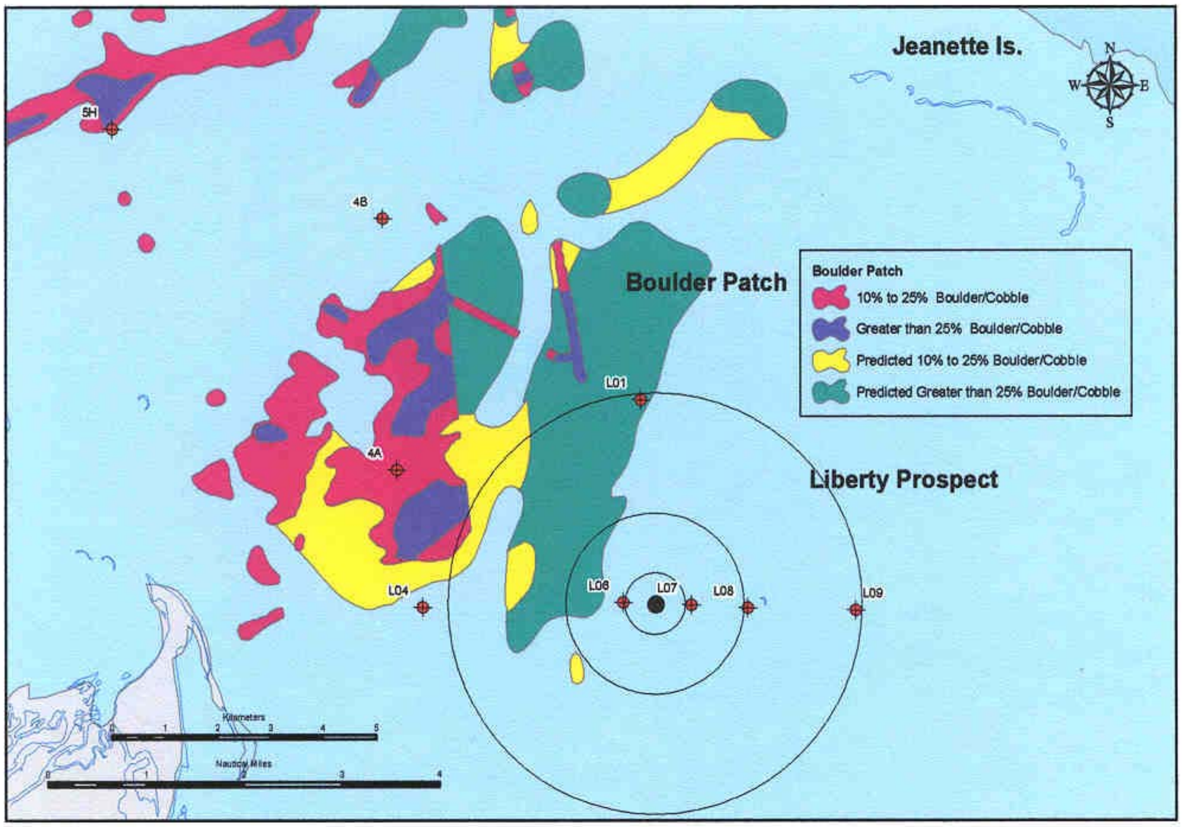
Station	Al (%)	Ba (µg/g)	Hg (µg/g)	Pb (µg/g)	Cd (µg/g)
Northstar - 2000					
N01	1.67	209	0.011	5.2	0.06
N02	4.93	491	0.041	12.3	0.23
N03	4.90	505	0.046	12.8	0.28
N04	5.96	476	0.055	12.5	0.26
N05	6.76	511	0.058	13.7	0.25
N06	3.79	406	0.029	8.0	0.25
N08	2.69	306	0.024	5.2	0.20
N09	2.95	227	0.020	4.4	0.15
N10	3.54	352	0.077	8.7	0.27
N11	5.05	346	0.043	8.4	0.22
N12	6.62	654	0.078	17.7	0.35
N13	6.69	465	0.065	11.6	0.25
N14	5.85	555	0.087	17.3	0.45
N15	1.44	172	0.006	2.8	0.06
N16	3.64	376	0.034	7.6	0.22
N17	1.64	377	0.050	9.3	0.2
N18	3.78	271	0.033	5.2	0.16
N19	4.29	437	0.053	10.7	0.24
N20	5.32	519	0.051	13.3	0.33
N21	6.64	609	0.084	17.3	0.37
N22	1.06	859	0.003	3.3	0.07
N23	6.25	625	0.075	20.3	0.43

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

Station	Al (%)	Ba (µg/g)	Hg (µg/g)	Pb (µg/g)	Cd (µg/g)
Northstar - 2002					
N01	1.73	212	0.009	6.5	0.05
N02	4.51	501	0.044	13.8	0.13
N03[1]	5.42 (0.28)	537 (23)	0.055 (0.014)	14.2 (2.8)	0.17 (0.02)
N04	4.13	422	0.048	10.3	0.14
N05	5.78	578	0.053	12.3	0.18
N06	4.85	503	0.046	12.8	0.12
N08	4.45	469	0.045	9.3	0.17
N09	3.71	402	0.036	7.3	0.16
N10	4.49	473	0.046	9.5	0.19
N11	2.73	293	0.023	8.9	0.11
N12	4.86	478	0.047	10.1	0.21
N13	5.58	514	0.061	15.3	0.22
N14	5.72	545	0.059	11.6	0.21
N15	1.65	302	0.015	6.1	0.11
N16	5.86	550	0.051	14.3	0.20
N17	5.27	518	0.057	13.8	0.21
N18	4.50	476	0.045	9.1	0.19
N19	4.60	478	0.051	9.7	0.18
N20	1.65	291	0.011	5.1	0.07
N21	4.43	423	0.048	11.3	0.21
N23	4.82	575	0.047	10.4	0.27

Note[1] – Field Triplicates were collected at this station. The average value of the triplicates is reported with the standard deviation in parentheses.

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



Station	Al (%)	Ba (µg/g)	Hg (µg/g)	Pb (µg/g)	Cd (µg/g)
Liberty – 2000					
L01	6.18	370	0.067	10.7	0.18
L04	3.66	353	0.030	9.0	0.26
L06	4.16	252	0.039	5.7	0.19
L07	3.56	233	0.045	5.5	0.19
L08[1]	2.53 (0.23)	343 (80)	0.025 (0.008)	6.4 (1.8)	0.15 (0.04)
L09	2.64	269	0.025	9.5	0.13
Liberty – 2002					
L01	2.59	259	0.021	7.2	0.10
L04	3.78	385	0.036	11.6	0.16
L06	4.58	486	0.044	9.3	0.19
L07	4.07	437	0.041	8.0	0.19
L08[2]	1.64, 3.43	415, 534	0.012, 0.033	7.2, 7.4	0.08, 0.17
L09	2.23	243	0.019	9.5	0.10

Note[1] – Field Triplicates were collected at this station. The average value of the triplicates is reported with the standard deviation in parentheses.
Note[2] – Field Duplicates were collected at this station. Both values are reported.

Table 3-10. Statistical Model Result Summary with Silt + Clay Covariate

Performed on matching data sets with 35 stations each year (includes N1-N15, six Liberty stations, and all BSMP stations except 5D). Model includes station as an additional factor and silt+clay as the covariate for the concentration variables.

Key Parameter (dependant variable)	**R^2 for model**	**p-value for model**	**Intercept**	**Silt+Clay Covariate**		**Northstar Effect[1]**		**Construction Effect**		**Northstar*Construction Effect**	
				effect	**p-value**	**Effect**	**p-value**	**effect**	**p-value**	**effect**	**p-value**
LN Total PAH (µg/Kg)	0.832	0.000	4.512	**0.022**	**0.000**	**-0.580**	**0.011**	-0.019	0.911	**0.937**	**0.000**
LN Total PAH less perylene (µg/Kg)	0.830	0.000	4.415	**0.022**	**0.000**	**-0.586**	**0.010**	-0.032	0.849	**0.936**	**0.000**
LN Perylene (µg/Kg)	0.858	0.000	2.232	**0.022**	**0.000**	-0.382	0.068	0.110	0.449	**0.751**	**0.001**
LN Petrogenic PAH (µg/Kg)	0.830	0.000	4.297	**0.021**	**0.000**	**-0.566**	**0.012**	-0.045	0.787	**0.921**	**0.000**
LN Pyrogenic PAH (µg/Kg)	0.857	0.000	2.135	**0.020**	**0.000**	**-0.438**	**0.014**	0.061	0.650	**0.767**	**0.000**
LN TPHC (mg/Kg)	0.813	0.000	1.018	**0.017**	**0.000**	**-0.362**	**0.019**	0.174	0.147	**0.580**	**0.002**
LN LALK (mg/Kg)	0.891	0.000	-1.779	**0.019**	**0.000**	**-0.325**	**0.017**	0.045	0.630	**0.519**	**0.000**
LN TALK (mg/Kg)	0.834	0.000	-0.440	**0.022**	**0.000**	**-0.529**	**0.005**	0.074	0.614	**0.854**	**0.000**
LN Isoprenoids (mg/Kg)	0.909	0.000	-2.549	**0.013**	**0.000**	**-0.202**	**0.024**	-0.060	0.286	**0.371**	**0.000**
LN TOC (%)	0.697	0.000	-1.410	**0.014**	**0.001**	-0.191	0.522	0.248	0.256	0.212	0.521
N/P	0.571	0.001	0.937			0.124	0.083	**-0.126**	**0.016**	0.016	0.837
Pyrogenic PAH/ Petrogenic PAH	0.495	0.014	0.104			0.0002	0.965	**0.012**	**0.002**	-0.003	0.582
C2D/C2P	0.464	0.041	0.293			0.023	0.235	-0.017	0.253	-0.010	0.626
C3D/C3P	0.488	0.018	0.353			**0.109**	**0.002**	-0.013	0.643	**-0.119**	**0.004**
LALK/TALK	0.551	0.001	0.204			-0.016	0.408	0.000	0.992	-0.001	0.819
C16/(C15+C17)	0.373	0.373	0.306			-0.007	0.951	0.121	0.189	-0.103	0.463
Pristane/Phytane	0.547	0.005	2.259			**0.289**	**0.002**	-0.029	0.661	-0.253	0.014 [2]
CPI	0.534	0.003	4.765			0.263	0.513	**-1.144**	**0.000**	0.455	0.316

Note[1] – Northstar effects and *p*-values are reported from an ANOVA model that excluded the station effect due to the nesting of stations within regions.

Note[2] – This result was considered to be not significant when controlling the false discovery rate (Benjamini and Hochberg, 1995).

Table 3-11. Statistical Model Result Summary with Perylene Covariate

Performed on matching data sets with 35 stations each year (includes N1-N15, six Liberty stations, and all BSMP stations except 5D). Model includes station as an additional factor and LN Perylene as the covariate for the concentration variables.

Key Parameter (dependant variable)				**LN Perylene Covariate**		**Northstar Effect[1]**		**Construction Effect**		**Northstar*Construction Effect**	
	R^2 for model	**p-value for model**	**constant**	**effect**	**p-value**	**effect**	**p-value**	**effect**	**p-value**	**effect**	**p-value**
LN Total PAH less perylene (µg/Kg)	0.983	0.000	2.068	**1.042**	**0.000**	-0.182	0.066	**-0.149**	**0.007**	0.141	0.100
LN Petrogenic PAH (µg/Kg)	0.983	0.000	1.979	**1.029**	**0.000**	-0.167	0.086	**-0.160**	**0.003**	0.136	0.107
LN Pyrogenic PAH (µg/Kg)	0.986	0.000	0.131	**0.902**	**0.000**	-0.082	0.315	-0.038	0.362	0.095	0.150
LN TPHC (mg/Kg)	0.902	0.000	-0.478	**0.686**	**0.000**	-0.110	0.353	0.101	0.243	0.085	0.532
LN LALK (mg/Kg)	0.957	0.000	-3.287	**0.700**	**0.000**	-0.031	0.729	-0.027	0.645	0.025	0.793
LN TALK (mg/Kg)	0.954	0.000	-2.504	**0.937**	**0.000**	-0.179	0.073	-0.027	0.722	0.166	0.176
LN Isoprenoids (mg/Kg)	0.938	0.000	-3.489	**0.444**	**0.000**	-0.011	0.882	**-0.105**	**0.027**	0.067	0.364
LN TOC (%)	0.739	0.000	-2.721	**0.593**	**0.000**	0.118	0.636	0.183	0.366	-0.222	0.496

Note[1] – Northstar effects and *p*-values are reported from an ANOVA model that excluded the station effect due to the nesting of stations within regions.

Table 3-12. Statistical Model Result Summary with Aluminum Covariate

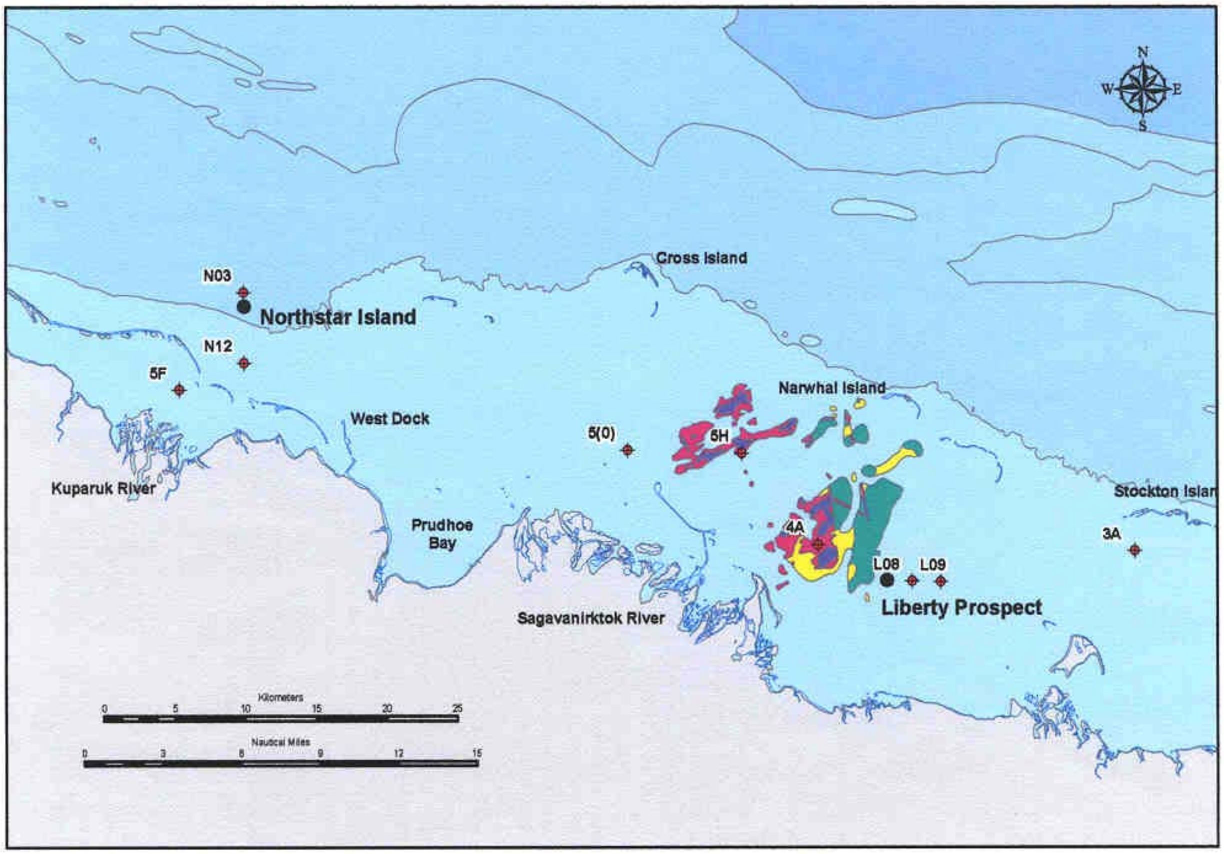
Performed on matching data sets with 35 stations each year (includes N1-N15, six Liberty stations, and all BSMP stations except 5D). Model includes station as an additional factor and Aluminum as the covariate.

Analyte (dependant variable)				Aluminum (%) Covariate		Northstar Effect[1]		Construction Effect		Northstar*Construction Effect	
	R^2 for model	p-value for model	Intercept	effect	p-value	Effect	p-value	effect	p-value	effect	p-value
Ag (µg/g)	0.586	0.000	0.040	**0.015**	**0.000**	0.006	0.654	-0.005	0.621	-0.012	0.406
As (µg/g)	0.870	0.000	7.58	**2.20**	**0.000**	0.598	0.406	-2.27	0.112	**-1.84**	**0.008**
Ba (µg/g)	0.839	0.000	150	**60.7**	**0.000**	46.7	0.081	**-45.3**	**0.024**	-4.09	0.890
Be (µg/g)	0.755	0.000	0.590	**0.225**	**0.000**	0.180	0.089	-0.092	0.722	-0.022	0.857
Cd (µg/g)	0.771	0.000	0.007	**-0.048**	**0.000**	-0.004	0.842	-0.010	0.520	-0.006	0.792
Co (µg/g)	0.812	0.000	2.553	**1.42**	**0.000**	-0.085	0.880	-1.89	0.209	1.72	0.019 [2]
Cr (µg/g)	0.945	0.000	9.14	**13.2**	**0.000**	1.44	0.560	0.584	0.749	-0.986	0.718
Cu (µg/g)	0.953	0.000	-5.46	**6.04**	**0.000**	0.761	0.391	-0.359	0.608	-1.907	0.071
Fe (%)	0.969	0.000	0.388	**0.527**	**0.000**	0.026	0.677	0.004	0.940	-0.038	0.614
Hg (µg/g)	0.910	0.000	-0.008	**-0.013**	**0.000**	0.001	0.638	-0.001	0.821	-0.002	0.544
Mn (µg/g)	0.905	0.000	-17.2	**80.2**	**0.000**	-3.25	0.884	-33.9	0.509	49.0	0.049 [2]
Ni (µg/g)	0.956	0.000	-0.910	**6.10**	**0.000**	0.117	0.911	0.499	0.501	0.353	0.750
Pb (µg/g)	0.863	0.000	3.60	**2.49**	**0.000**	0.547	0.429	-1.02	0.067	-0.430	0.601
Sb (µg/g)	0.847	0.000	0.239	**0.098**	**0.000**	-0.039	0.213	**-0.074**	**0.003**	0.044	0.220
Tl (µg/g)	0.873	0.000	0.056	**0.090**	**0.000**	0.008	0.738	0.001	0.957	0.012	0.699
V (µg/g)	0.973	0.000	-4.359	**24.4**	**0.000**	5.19	0.057	2.23	0.319	-7.04	0.038 [2]
Zn (µg/g)	0.944	0.000	6.80	**18.5**	**0.000**	-1.00	0.752	0.463	0.849	-3.18	0.383

Note[1] – Northstar effects and p-values are reported from an ANOVA model that excluded the station effect due to the nesting of stations within regions.

Note[2] – This result was considered to be not significant when controlling the false discovery rate (Benjamini and Hochberg, 1995).

Table 3-13. Map of Sampling Stations for Organisms and Table of Concentrations for Selected Organic Parameters



Station	Species	Total PAH (µg/Kg wet weight)	Total PHC (mg/Kg wet weight)	Total S/T (µg/Kg wet weight)
Summer - 2000				
N03	*Anonyx*	23	12	8.1
N12	*Anonyx*	16	26	3.2
N13	*Anonyx*	14	14	4.1
N18	*Anonyx*	12	15	2.8
L08	*Astarte*	13	ND	2.7
L09	*Astarte*	16	ND	2.5
3A	*Astarte*	7.4	1.6	2.0
4A	*Anonyx*	18	ND	2.4
5(0)	*Anonyx*	20	ND	2.0
5F	*Cyrtodaria*	39	4.4	3.6
5H	*Astarte*	15	ND	4.0

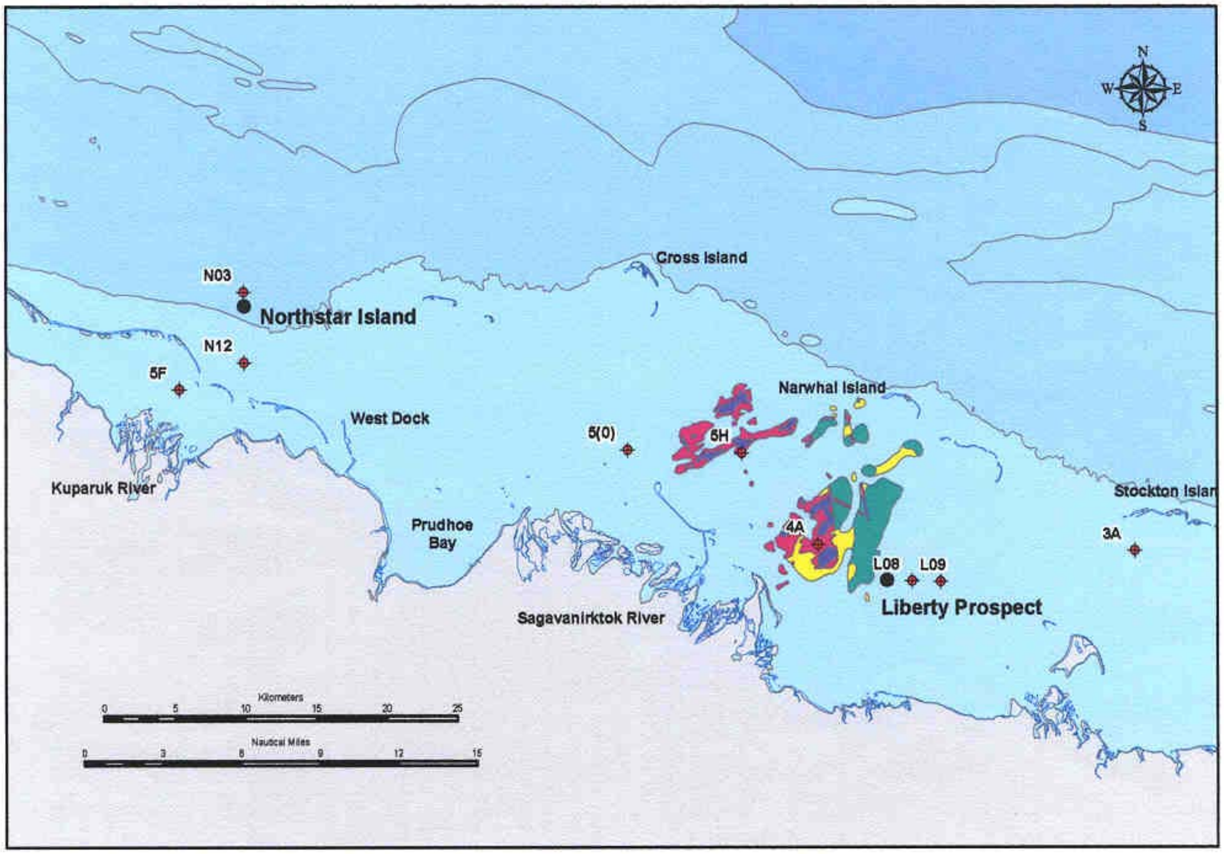
Anonyx (an amphipod), *Astarte* (a clam), *Cyrtodaria* (a clam).
ND – Not detected.

Table 3-13 (continued). Map of Sampling Stations for Organisms and Table of Concentrations for Selected Organic Parameters

Station	Species	Total PAH (μg/Kg wet weight)	Total PHC (mg/Kg wet weight)	Total S/T (μg/Kg wet weight)
Summer - 2002				
N03	*Anonyx*	13	22	3.2
N04	*Anonyx*	14	18	2.2
N12	*Anonyx*	11	4.9	1.5
N13	*Anonyx*	35	9.3	2.4
N18	*Anonyx*	14	17	1.6
4A -1	*Anonyx*	31	52	2.3
4A -2	*Anonyx*	18	20	2.1
5(0)	*Anonyx*	17	38	2.0
L08	*Astarte*	10	2.5	1.2
L09	*Astarte*	9.6	2.6	1.0
3A	*Astarte*	12	2.7	1.1
5H	*Astarte*	14	3.1	2.0
5F	*Cyrtodaria*	35	3.2	3.1

Anonyx (an amphipod), *Astarte* (a clam), *Cyrtodaria* (a clam).
ND – Not detected.

Table 3-14. Map of Sampling Stations for Organisms and Table of Concentrations for Selected Metals (Cd, Cu, Hg, and Pb)



Station	Organism	Cd (µg/g)	Cu (µg/g)	Hg (µg/g)	Pb (µg/g)
Summer - 2000					
N03	*Anonyx*, small	0.52	111	0.036	0.40
N12	*Anonyx*, small	0.41	104	0.024	0.27
N13	*Anonyx*, small	0.29	103	0.038	0.23
N18	*Anonyx*, small	0.31	41	0.022	0.22
4A	*Anonyx*, small	0.59	93	0.034	0.24
5(0)	*Anonyx*, small	0.60	102	0.024	0.26
L08	*Astarte*	10.2	12.1	0.032	0.66
L09	*Astarte*	10.8	11.6	0.032	0.69
3A	*Astarte*	10.2	7.2	0.025	0.40
5H	*Astarte*	10.3	11.2	0.048	0.64
5F	*Cyrtodaria*	1.3	12.3	0.014	0.48

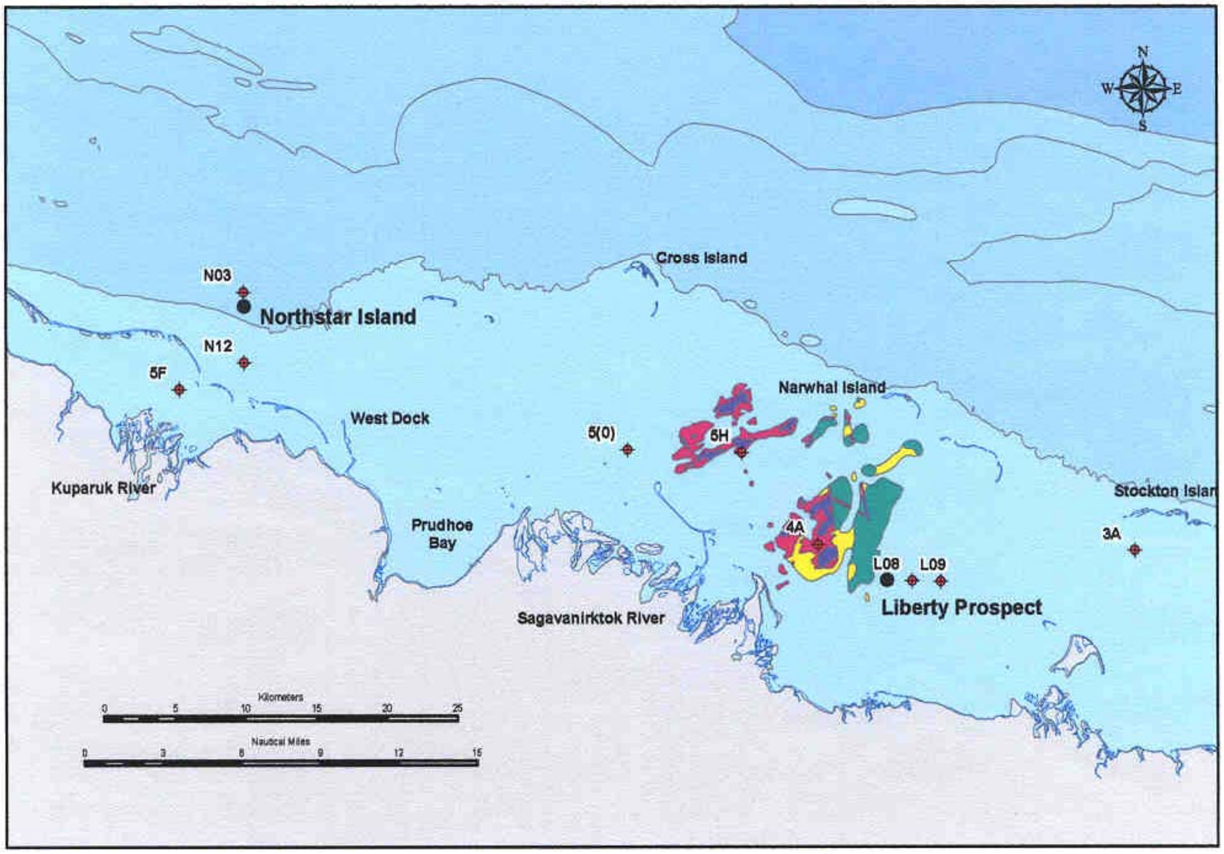
Anonyx (an amphipod), *Astarte* (a clam), *Cyrtodaria* (a clam).

Table 3-14 (continued). Map of Sampling Stations for Organisms and Table of Concentrations for Selected Metals (Cd, Cu, Hg, and Pb)

Station	Organism	Cd (µg/g)	Cu (µg/g)	Hg (µg/g)	Pb (µg/g)
Summer - 2002					
N03	*Anonyx*, small	0.47	175	0.063	0.69
N04	*Anonyx*, small	0.47	172	0.041	0.28
N12	*Anonyx*, small	0.51	148	0.060	0.25
N13	*Anonyx*, small	0.42	129	0.069	0.39
N18	*Anonyx*, small	0.51	182	0.056	0.23
4A -1	*Anonyx*, small	0.77	132	0.071	0.70
4A -2	*Anonyx*, small	0.55	127	0.067	0.40
5(0)	*Anonyx*, small	0.58	134	0.058	0.18
L08	*Astarte*	9.6	-	0.127	-
L09	*Astarte*	10.6	18.3	0.069	0.76
3A	*Astarte*	11.6	10.8	0.074	0.58
5H	*Astarte*	13.1	16.1	0.060	0.77
5F	*Cyrtodaria*	0.17	13.9	0.019	-

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

Table 3-15. Map of Sampling Stations for Organisms and Table of Concentrations for Selected Metals (As, Ba, V, and Zn)



Station	Organism	As (µg/g)	Ba (µg/g)	V (µg/g)	Zn (µg/g)
Summer - 2000					
N03	*Anonyx*, small	7.4	25	3.4	92
N12	*Anonyx*, small	6.7	30	3.1	88
N13	*Anonyx*, small	6.2	48	2.9	81
N18	*Anonyx*, small	7.0	21	2.7	88
4A	*Anonyx*, small	6.6	25	2.4	94
5(0)	*Anonyx*, small	7.0	40	2.5	91
L08	*Astarte*	10.8	18	4.1	76
L09	*Astarte*	12.1	15	3.4	68
3A	*Astarte*	11.5	11	1.9	62
5H	*Astarte*	10.7	25	5.1	74
5F	*Cyrtodaria*	7.5	12	2.7	67

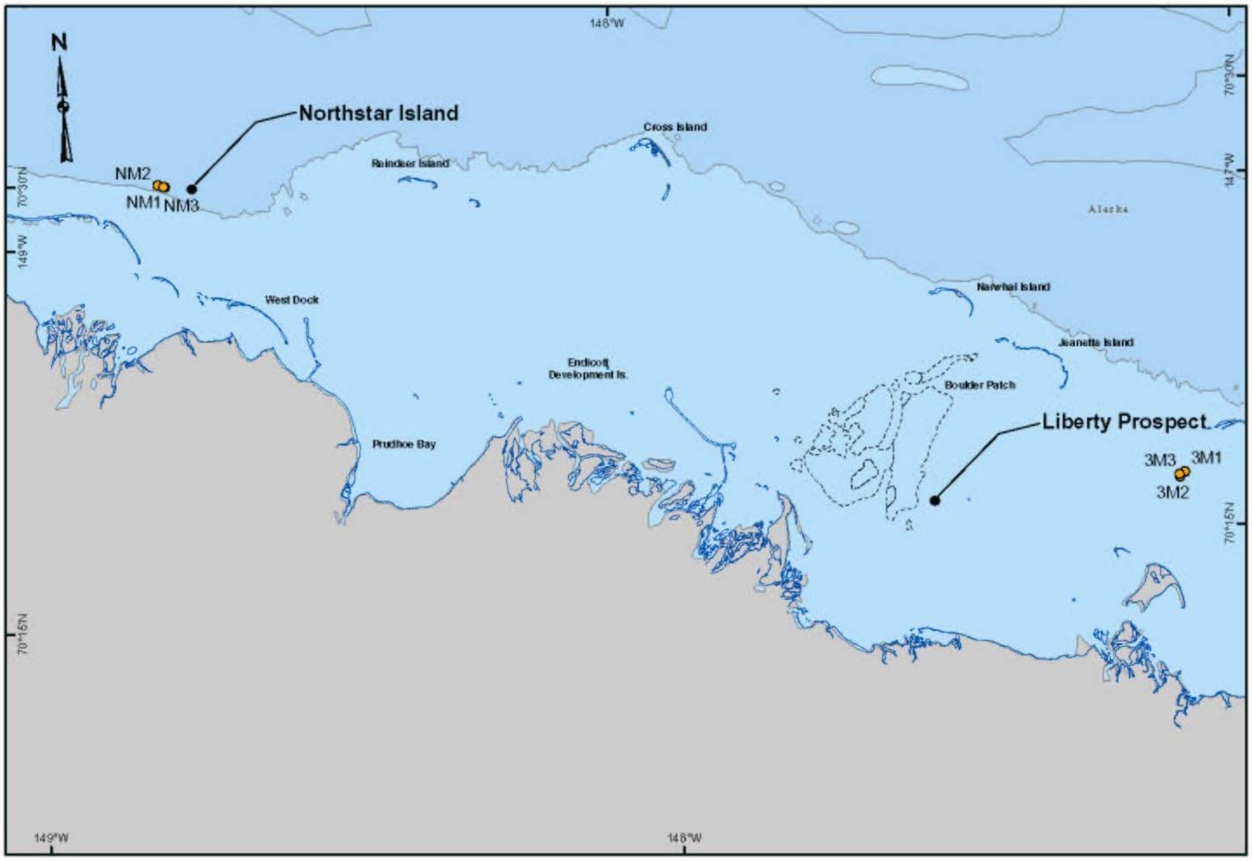
Anonyx (an amphipod), Astarte (a clam), Cyrtodaria (a clam).

Table 3-15. Map of Sampling Stations for Organisms and Table of Concentrations for Selected Metals (As, Ba, V, and Zn)

Station	Organism	As (µg/g)	Ba (µg/g)	V (µg/g)	Zn (µg/g)
Summer - 2002					
N03	*Anonyx*, small	8.5	29	2.1	114
N04	*Anonyx*, small	7.5	31	1.9	108
N12	*Anonyx*, small	4.6	25	1.3	102
N13	*Anonyx*, small	4.0	45	2.2	86
N18	*Anonyx*, small	6.4	25	1.6	104
4A -1	*Anonyx*, small	5.8	29	2.8	113
4A -2	*Anonyx*, small	5.1	36	2.9	103
5(0)	*Anonyx*, small	5.0	33	1.7	54
L08	*Astarte*	9.0	14	3.1	103
L09	*Astarte*	8.2	7	2.5	83
3A	*Astarte*	11.5	11	3.6	78
5H	*Astarte*	8.2	26	5.6	89
5F	*Cyrtodaria*	6.2	58	8.6	27

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

Table 3-16. Map of Sampling Stations for SPMDs and Caged Mussels and Table of Concentrations for Selected Organic Parameters



Station	Matrix	Total N (µg/Kg)	Total PAH (µg/Kg)	Pyrogenic PAH (µg/Kg)	Petrogenic PAH (µg/Kg)	Total ST (µg/Kg)	Total PHC (mg/Kg)
Reference							
3M1	Mussel	3.9	13	0.78	11	1.4	2.5
3M2	Mussel	5.0	14	0.76	12	1.3	2.7
3M3	Mussel	3.6	12	0.68	9.4	1.7	2.8
Mean (SD)		4.2 (0.75)	13 (1.3)	0.74 (0.05)	11 (1.3)	1.5 (0.19)	2.7 (0.15)
Northstar							
NM1	Mussel	6.8	17	0.95	13	1.5	2.9
NM2	Mussel	5.4	17	1.2	14	1.7	2.9
NM3	Mussel	5.3	15	1.2	12	1.3	2.3
Mean (SD)		5.8 (0.85)	16 (1.2)	1.1 (0.15)	13 (0.96)	1.5 (0.19)	2.7 (0.35)
Predeployment Mussels							
PM1	Mussel	2.7	7.8	0.39	6.7	1.0	3.8

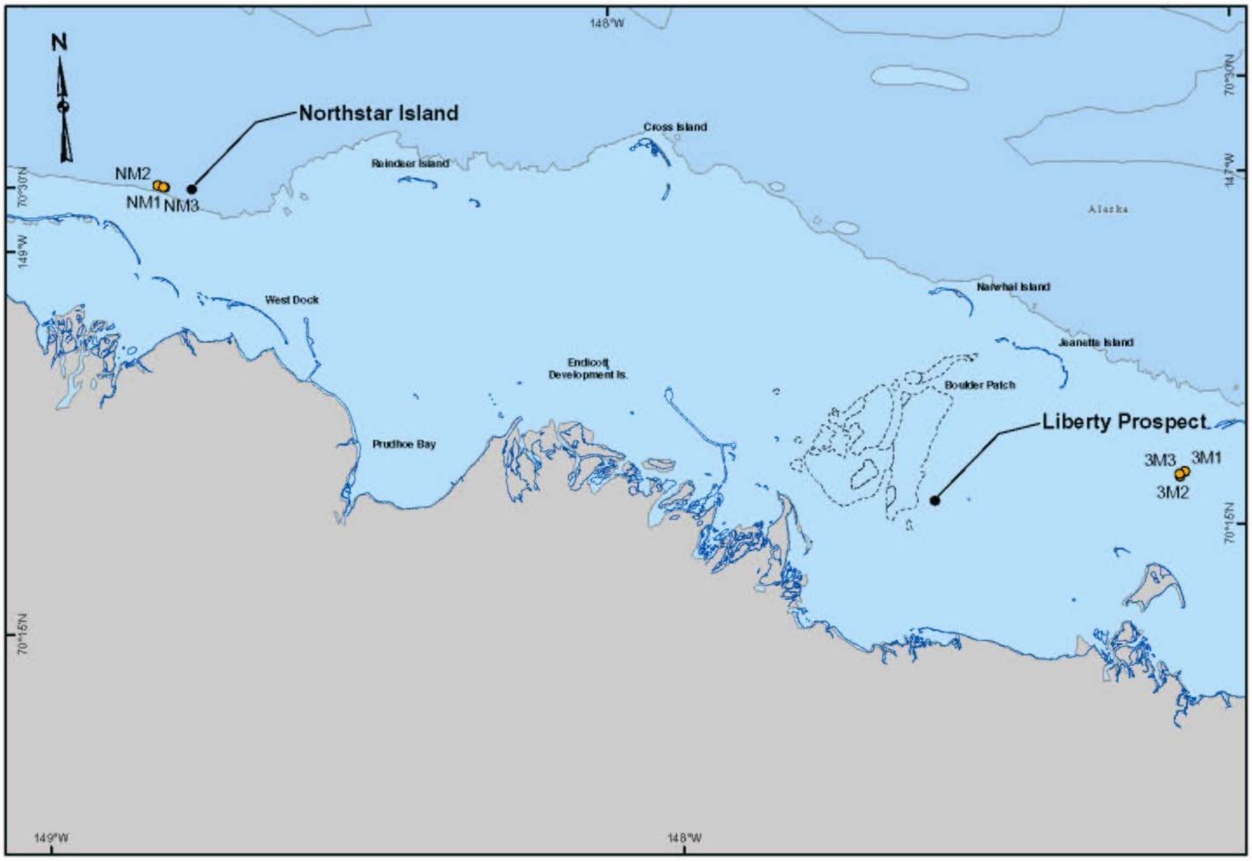
Table 3-16 (continued). Map of Sampling Stations for SPMDs and Caged Mussels and Table of Concentrations for Selected Organic Parameters

Station	Matrix	Total N (ng/SPMD)	Total PAH (ng/SPMD)	Pyrogenic PAH (ng/SPMD)	Petrogenic PAH (ng/SPMD)
Reference					
3M1	SPMD	210	470	18	430
3M2	SPMD	260	540	19	470
3M3	SPMD	220	490	20	450
Mean (SD)		230 (22)	500 (37)	19 (1.0)	450 (20)
Northstar					
NM1	SPMD	250	500	29	460
NM2	SPMD	240	540	25	480
NM3	SPMD	220	470	28	440
Mean (SD)		240 (18)	510 (34)	28 (2.0)	460 (21)
Field Blank					
FB[1]	SPMD	120	130	1.2	130

Note[1] - The concentrations in the SPMD field blank are adjusted by the number of field exposures; the field blank was opened and exposed at each of the six moorings.

ND – Not detected
C0N – Naphthalene
C1N – C1-Naphthalenes
C2N – C2-Naphthalenes
C3N – C4-Naphthalenes

Table 3-17. Map of Sampling Stations for Caged Mussels and Table of Concentrations for Selected Metals on a Dry-weight Basis



Station	Matrix	Fe (µg/g)	Ag (µg/g)	As (µg/g)	Ba (µg/g)	Be (µg/g)	Cd (µg/g)
Reference (n = 2)							
Mean (SD)	Mussel	1300 (80)	0.080 (0.008)	6.9 (0.6)	18 (3)	0.042 (0.005)	3.9 (0.4)
Northstar (n = 2)							
Mean (SD)	Mussel	1370 (130)	0.080 (0.011)	6.7 (0.1)	17 (2)	0.040 (0.003)	3.9 (0.3)
Predeployment Mussels (n = 1)							
	Mussel	1170	0.098	7.0	6.5	0.017	4.3

Station	Matrix	Cu (µg/g)	Hg (µg/g)	Pb (µg/g)	Tl (µg/g)	V (µg/g)	Zn (µg/g)
Reference (n = 2)							
Mean (SD)	Mussel	9.9 (1.4)	0.11 (0.01)	0.75 (0.10)	0.021 (0.004)	4.15 (0.01)	114 (4)
Northstar (n = 2							
Mean (SD)	Mussel	9.1 (0.1)	0.09 (0.01)	0.71 (0.05)	0.019 (0.001)	4.00 (0.50)	106 (2)
Predeployment Mussels (n = 1)							
	Mussel	8.2	0.08	0.54	0.009	4.0	121

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

QC Sample or Measurement Type	Acceptance Criteria	Quality Control Result Summary	Impact to Data Quality and Usability
Equipment Blank	No compound to exceed 5 times the MDL	All criteria were met	None
Field Blank	No compound to exceed 5 times the MDL	All criteria were met	None
SPMD Blank	Assess blank data along with sample data to determine usability	Concentrations of PAH compounds detected on the blank SPMD were greater than the sample concentrations for C0N, C1N, and C2N and of similar concentrations for the remaining PAHs	Due to background concentrations on the SPMDs greater than or equal to the sample concentrations, the usability of the sample SPMD data to assess bioavailability of organics is limited.
Field Replicate	RSD < 50% for all compounds >5 times the RL	All criteria were met	None
Initial Calibration	%RSD <25% for all compounds (up to 10% of compounds can be >25%, but <35%)	All criteria were met	None
Continuing Calibration	%D <25% for all compounds (up to 10% of compounds can be >25%, but <35%)	All criteria were met	None
Surrogate Recoveries	45 to 125% recovery (35 – 125% for d8-naphthalene)	All criteria were met for the water and SPMD samples. All criteria were met, with the exception of low recoveries in two procedural blanks, a blank spike, and two field sample for the tissue samples. All criteria were met, with the exception of low recoveries in a blank spike for the sediment samples.	Minor. The results for tissue samples 00-4A-01-PHC-T-AN and 02-N03-01-PHC-T-AN should be considered estimated values due to low surrogate recoveries. No further impact was noted since surrogate recoveries were acceptable in the remaining quality control samples and associated field samples.
Procedural Blank	No compound to exceed 5 times the MDL unless sample amount is >10 times blank amount	All criteria were met with two exceptions, 1) the napthalene concentration in a tissue blank exceeded 5 times the MDL and 2) the naphthalene and biphenyl concentrations in a SPMD blank exceeded 5 times the MDL. A few additional PAHs were detected in the sediment, tissue, and SPMD blanks at trace concentrations, but were less than 5 times the MDL	Minor. Results within 5 times the blank result were qualified “B” and may be biased high or false positives.

Table 3-18 (continued). 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
Blank Spike Sample Recoveries	35 to 125% recovery for spiked compounds	Several PAHs were recovered at >125% in a tissue BS, in the SPMD BS, and in three sediment BS.	Minor. Results for these compounds in the associated samples may be bias high.
Laboratory Duplicate	RPD <30% for all compounds >10 times the MDL; mean RPD <30%	All criteria were.	None
Instrument SRM (1491)	Measured values must be within 15% of true value for all certified compounds	All criteria were met	None
Sediment SRM (1941a)	Measured values must be within 30% of the true value on average for all compounds, not to exceed 35% of true value for more than 30% of the compounds	All criteria were met for the sediment SRMs, with the exception of low responses for naphthalene and benzo[k]fluoranthene in the 2000 sample set and low responses for naphthalene, acenaphthene, and biphenyl and high responses for chrysene and indeno(1,2,3-cd)pyrene in the 2002 sample set.	Minor. The naphthalene and benzo[k]fluoranthene results in the sediment samples collected in 2000 may be biased low. The naphthalene, acenaphthene, and biphenyl results may be biased low and the chrysene and indeno-(1,2,3-cd)pyrene results may be biased high in the samples collected in 2002.
Tissue SRM (1974a) for samples collected in 2000	Measured values must be within 30% of the true value on average for all compounds, not to exceed 35% of true value for more than 30% of the compounds	All criteria were met for the tissue SRM, with the exception of a high response for naphthalene, anthracene, and benzo[b]fluoranthene.	Minor. The certified value for naphthalene and anthracene in SRM 1974a appears to be incorrect based on consistently high anthracene results in repeated analyses over the past four years. Benzo[b]fluoranthene results may be bias high in samples collected in 2000.
Tissue SRM (2978) for samples collected in 2002	Measured values must be within 30% of the true value on average for all compounds, not to exceed 35% of true value for more than 30% of the compounds	11 of the 19 certified and reference PAH compounds were recovered high.	Minor. The other quality control indicators associated with these samples were acceptable. The associated results may be bias high for tissue samples collected in 2002.
Oil Reference Standard (North Slope Crude)	%D <35% for compounds above the RL	All criteria were met.	None

Table 3-19. Organic Quality Control Result Summary – Saturated Hydrocarbon Analyses

QC Sample or Measurement Type	Acceptance Criteria	Quality Control Result Summary	Impact to Data Quality and Usability
Equipment Blank	No compound to exceed 5 times the MDL	All criteria were met with the exception of n-C25 through n-C29 in one of the 2002 equipment blanks; these compounds were detected at concentrations greater than 5 times the MDL.	Minor. Results within 5 times the associated blank result may be biased high or may be false positives.
Field Blank	No compound to exceed 5 times the MDL	All criteria were met with the exception of n-C38 in the 2002 field blank which was detected at a concentration greater than 5 times the MDL.	Minor. Results within 5 times the associated blank result may be biased high or may be false positives.
SPMD Blank	Assess blank data along with sample data to determine usability	Concentrations of SHC compounds detected on the blank SPMD were similar to the sample concentrations.	Due to background concentrations on the SPMDs greater than or equal to the sample concentrations, the sample SPMD data are not usable to assess bioavailability of organics.
Field Replicate	RSD < 50% for all compounds >5 times the RL	All criteria were met.	None
Initial Calibration	%RSD <25% for all compounds (up to 10% of compounds can be >25%, but <35%)	All criteria were met.	None
Continuing Calibration	%D <25% for all compounds (up to 10% of compounds can be >25%, but <35%)	All criteria were met.	None
Surrogate Recoveries	45 to 125% recovery	All criteria were met, with the exception of low surrogate recoveries in one of the sediment blank spike samples.	None. Surrogate recoveries were acceptable in the remaining quality control samples and associated field samples.
Procedural Blank	No compound to exceed 5 times the MDL unless sample amount is >10 times blank amount	All criteria were met with the exception of n-C26 through n-C29 in two sediment procedural blanks; these compounds were detected at concentrations greater than 5 times the MDL. Several SHCs were detected at trace concentrations less than the MRL in all procedural blanks.	Minor. Results within 5 times the associated blank result were qualified with a “B” and may be biased high or may be false positives.
Blank Spike Sample Recoveries	35 to 125% recovery for spiked compounds	Decane was recovered at less than 35% in two sediment BSs. Pentacosane and triacontane were recovered at greater than 125% in one BS. Decane and pentadecane were recovered at less than 35% in one tissue BS.	Minor. The decane and pentadecane results in the associated samples may be biased low and the pentacosane and triacontane results may be biased high.
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 3-20. Organic Quality Control Result Summary – Sterane and Triterpane Analyses

QC Sample or Measurement Type	Acceptance Criteria	Quality Control Result Summary	Impact to Data Quality and Usability
Equipment Blank	No compound to exceed 5 times the MDL	All criteria were met.	None
Field Blank	No compound to exceed 5 times the MDL	All criteria were met.	None
SPMD Blank	Assess blank data along with sample data to determine usability	Concentrations of SHC compounds detected on the blank SPMD were similar to the sample concentrations.	Due to background concentrations on the SPMDs greater than or equal to the sample concentrations, the sample SPMD data are not usable to assess bioavailability of organics.
Field Replicate	RSD < 50% for all compounds >5 times the RL	All criteria were met with one exception. The results for S28-ethylcholestane and n-triacontane exceeded the precision criterion in one field replicate set collected in 2000.	Minor. The positive results for S28-ethylcholestane and n-triacontane are considered estimated values in the affected samples.
Initial Calibration	%RSD <25% for all compounds	All criteria were met.	None
Continuing Calibration	%D <25% for all compounds	All criteria were met.	None
Surrogate Standards	45 to 125% recovery	All criteria were met.	None
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 3-21. Inorganic Quality Control Result Summary – Trace-Metal Analyses

QC Sample or Measurement Type	Acceptance Criteria	Quality Control Result Summary	Impact to Data Quality and Usability
Equipment Blanks	No trace-metal concentration to exceed 5 times the MDL	All criteria were met.	None
Field Blanks	No trace-metal concentration to exceed 5 times the MDL	All criteria were met.	None
Field Replicates	RSD <50% for all trace metal concentrations >5 times the MDL	All criteria were met.	None
Initial Calibration	Standard Curve correlation coefficient $r \geq 0.999$ for a 3 to 5 point curve for all trace metals	All criteria were met.	None
Continuing Calibration	%D <15% for all trace metals or repeat Initial Calibration and sample analyses	All criteria were met.	None
Matrix Spike Recoveries	70 to 130% recovery for all trace metals	All criteria were met.	None
Procedural Blanks	No trace metal concentration to exceed 5 times the MDL unless the sample amount is >10 times the blank concentration	All criteria were met.	None
Laboratory Duplicates	RSD <25% for all trace metal concentrations >10 times the MDL; mean RSD <25%	All criteria were met.	None
Sediment SRMs (MESS-2, 2704, 1643d)	Measured values must be within 20% of the certified or reference values for >85% of the SRM analyses.	All criteria were met.	None
Tissue SRMs (DORM-2, 2976, 1643d)	Measured values must be within 20% of the certified or reference values for >85% of the SRM analyses.	All criteria were met.	None
Dissolved SRMs (CASS-3)	Measured values must be within 20% of the certified or reference values for >85% of the SRM analyses.	All criteria were met.	None

Table 3-22. SRM Results for Sediment Metal Analyses: MESS-2 and 1643d

Standard Reference Material	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 (%)
SRM MESS-2 This Study, 2000 (n = 5/ 7)	0.17 ±0.01	8.59 ±0.07	21.2 ±0.5	1004 ±49	2.40 ±0.02	0.25 ±0.01	13.9 ±0.5	105 ±2	37.9 ±0.5	4.20 ±0.04
SRM 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, 2000 (n = 2)	--	--	--	509.2 µg/L ±4.2	--	--	--	--	--	--
SRM 1643d NIST Certified	--	--	--	506.5 µg/L ±8.9	--	--	--	--	--	--
Spike Recovery (%) 2000 (Sediment)	95.5 ±5.5	104.9 ±4.4	97.4 ±6.6	98.2 ±4.8	99.0 ±5.8	98.9 ±2.7	101.9 ±5.3	108.4 ±11.1	102.0 ±5.9	97.2 ±3.2

Standard Reference Material	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 (%)
SRM MESS-2 This Study, 2000 (n = 5/7)	0.091 ±0.004	355 ±4	46.7 ±1.9	22.1 ±0.4	1.19 ±0.06	1.01 ±0.03	252 ±5	160 ±4	1.95 ±0.04
SRM MESS-2 NRC Certified	0.092 ±0.009	365 ±21	49.3 ±1.8	21.9 ±1.2	1.09 ±0.13	(0.98)	93.4 ±4.9	119 ±12	2.14* ±0.03
Spike Recovery (%) 2000 (Sediment)	84.4 ±6.2	99.3 ±8.5	93.7 ±1.0	97.2 ±4.5	99.4 ±5.1	102.5 ±3.6	114.7 ±5.8	97.4 ±1.5	NA

Notes: Values in parenthesis are for reference only; SRM not certified by the NRC.
Mean results ± standard deviation are presented. *MESS-2 certified TOC value is for total carbon (organic plus inorganic).
SRM MESS-2 - Marine sediment issued by NRC; SRM 1643d – Trace Elements in Water issued by NIST.

Table 3-23. SRM Results for Tissue Metal Analyses: 2976, DORM-2 and 1643d

Standard Reference Material	Ag (µg/g)	Al (µg/g)	As (µg/g)	Ba (µg/g)	Be (µg/g)	Cd (µg/g)	Co (µg/g)	Cr (µg/g)	Cu (µg/g)
SRM 2976 This Study, 2000 (n = 1)	0.014	148	13.4	0.63	0.006	0.91	0.63	0.53	3.84
SRM 2976 NIST Certified	(0.011) (±0.005)	(134) (±34)	13.3 ±1.8	--	--	0.82 ±0.16	(0.61) (±0.02)	(0.50) (±0.16)	4.02 ±0.33
SRM DORM-2 This Study, 2000 (n = 1)	0.043	12.5	17.4	2.83	0.006	0.048	0.185	37.5	2.26
SRM DORM-2 NRC Certified	0.041 ±0.013	10.9 ±1.7	18.0 ±1.1	--	--	0.043 ±0.008	0.182 ±0.031	34.7 ±5.5	2.34 ±0.16
SRM 1643d This Study, 2000 (n = 1)	--	--	--	514.9 µg/L	12.72 µg/L	--	--	--	--
SRM 1643d NIST Certified	--	--	--	506.5 µg/L ±8.9	12.53 µg/L ±0.28	--	--	--	--
Spike Recovery (%) 2000 (Tissue)	106.7 ±2.7	96.9 ±3.7	98.7 ±0.5	98.3 ±1.5	102.7 ±8.0	99.1 ±2.3	128.1 ±2.3	93.3 ±0.7	102.5 ±2.6

Notes: Values in parenthesis are for reference only; SRM not certified by the NIST or NRC. Mean results ± standard deviation are presented.
SRM 2976 – Mussel tissue issued by NIST; SRM DORM-2 – Dogfish Muscle issued by NRC; SRM 1643d – Trace Elements in Water issued by NIST.

Table 3-23 (continued). SRM Results for Tissue Metal Analyses: 2976, DORM-2 and 1643d

Standard Reference Material	Fe (µg/g)	Hg (µg/g)	Mn (µg/g)	Ni (µg/g)	Pb (µg/g)	Sb (µg/g)	Tl (µg/g)	V (µg/g)	Zn (µg/g)
SRM 2976 This Study, 2000 (n = 1/2)	174	0.061 ±0.004	34.6	0.87	1.05	0.009	0.002	0.75	145
SRM 2976 NIST Certified	171.0 ±4.9	0.061 ±0.0036	(33) (±2)	(0.93) (±0.12)	1.19 ±0.18	--	(0.001)	--	137 ±13
SRM DORM-2 This Study, 2000 (n = 1)	147	--	3.48	17.6	0.070	0.023	0.005	0.18	24.4
SRM DORM-2 NRC Certified	142 ±10	4.64 ±0.26	3.66 ±0.34	19.4 ±3.1	0.065 ±0.007	--	(0.004)	--	25.6 ±2.3
SRM 1643d This Study, 2000 (n = 1)	--	--	--	--	--	53.5 µg/L	7.34 µg/L	36.4 µg/L	--
SRM 1643d NIST Certified	--	--	--	--	--	54.1 µg/L ±1.1	7.28 µg/L ±0.25	35.1 µg/L ±1.4	--
Spike Recovery (%) 2000 (Tissue)	106.7 ±2.7	106.7 ±2.7	106.7 ±2.7	106.7 ±2.7	106.7 ±2.7	106.7 ±2.7	106.7 ±2.7	106.7 ±2.7	106.7 ±2.7

Notes: Values in parenthesis are for reference only; SRM not certified by the NIST or NRC. Mean results ± standard deviation are presented.
SRM 2976 – Mussel tissue issued by NIST; SRM DORM-2 – Dogfish Muscle issued by NRC; SRM 1643d – Trace Elements in Water issued by NIST.

Table 3-24. SRM Results for Particulate and Dissolved Metal Analyses: 2704, MESS-2, CASS-3 and SLRS-3

Standard Reference Material	Al (%)	As (µg/g)	Ba (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Hg (µg/g)	Pb (µg/g)	Zn (µg/g)	TOC (%)
SRM 2704 This Study, 2000 (n = 8)	6.17 ±0.11	23.6 ±0.4	424 ±4	3.42 ±0.11	133 ±2	98.3 ±2.6	4.15 ±0.05	--	159 ±6	437 ±6	--
SRM 2704 NIST Certified	6.11 ±0.16	23.4 ±0.8	414 ±12	3.45 ±0.22	135 ±5	98.6 ±5.0	3.45 ±0.22	--	161 ±17	438 ±12	--
SRM MESS-2 This Study, 2000 (n = 8)	--	--	--	--	--	--	--	--	--	--	--
SRM MESS-2 NRC Certified	--	--	--	--	--	--	--	--	--	--	2.14* ±0.03
SRM CASS-3 This Study, 2000 (n = 1)	--	1.15 µg/L	--	0.027 µg/L	0.095 µg/L	0.551 µg/L	--	--	0.014 µg/L	1.03 µg/L	--
SRM CASS-3 NRC Certified	--	1.09 µg/L ±0.07	--	0.030 µg/L ±0.005	0.092 µg/L ±0.006	0.517 µg/L ±0.062	--	--	0.012 µg/L ±0.004	1.24 µg/L ±0.25	--
SRM SLRS-1 This Study, 2000 (n = 1)	--	--	13.5 µg/L	--	--	--	--	--	--	--	--
SRM SLRS-3 NRC Certified	--	--	13.4 ±0.6	--	--	--	--	--	--	--	--
Spike Recovery (%) 2000 (Particulate)	99.8 ±3.2	94.4 ±5.4	99.2 ±3.0	96.4 ±2.8	97.9 ±4.2	101.7 ±2.2	97.3 ±2.9	--	101.9 ±6.1	99.3 ±2.7	NA
Spike Recovery (%) 2000 (Dissolved)	--	94.1 ±5.2	MOA**	107.6 ±2.1	98.4 ±9.1	98.7 ±7.5	--	MOA**	98.2 ±2.6	98.0 ±4.2	--

Notes: Values in parenthesis are for reference only; SRM not certified by the NIST or NRC. Mean results ± standard deviation are presented.
*MESS-2 certified TOC value is for total carbon (organic plus inorganic). ** MOA – Method of Standard Additions analysis.
SRM 2704 – Buffalo River Sediment issued by NIST; SRM MESS-2 – Marine Sediment issued by NRC; SRM CASS-3 – Nearshore Seawater issued by NRC; SRM SLRS-3 – Riverine Water issued by NRC.

Table 3-25. SRM Results for Sediment Metal Analyses: MESS-2 and 1643d

Standard Reference Material	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 (%)
SRM MESS-2 This Study, 2002 (n = 4)	0.18 ±0.01	8.59 ±0.08	21.3 ±0.1	1017 ±32	2.25 ±0.06	0.24 ±0.01	14.1 ±0.3	106 ±2	37.9 ±0.3	4.23 ±0.04
SRM 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, 2002 (n = 2)	--	--	--	508 µg/L ±1	--	--	--	--	--	--
SRM 1643d NIST Certified	--	--	--	506.5 µg/L ±8.9	--	--	--	--	--	--
Spike Recovery (%) 2002(Sediment)	92.9 ±2.5	102.0 ±2.8	98.6 ±5.7	102.9 ±4.7	93.5 ±1.8	93.3 ±1.4	98.5 ±5.3	98.5 ±4.9	98.3 ±2.9	95.1 ±4.7

Standard Reference Material	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 (%)
SRM MESS-2 This Study, 2002 (n = 4)	0.091 ±0.004	362 ±8	48.5 ±0.7	21.9 ±1.1	1.10 ±0.02	1.00 ±0.04	253 ±4	168 ±3	2.07 ±0.01
SRM MESS-2 NRC Certified	0.092 ±0.009	365 ±21	49.3 ±1.8	21.9 ±1.2	1.09 ±0.13	(0.98)	93.4 ±4.9	119 ±12	2.14* ±0.03
Spike Recovery (%) 2002 (Sediment)	93.2 ±5.8	100.3 ±1.6	96.5 ±0.4	96.9 ±3.2	96.5 ±3.1	96.9 ±4.9	116.5 ±2.5	97.8 ±3.7	NA

Notes: Values in parenthesis are for reference only; SRM not certified by the NRC.
Mean results ± standard deviation are presented. *MESS-2 certified TOC value is for total carbon (organic plus inorganic).
SRM MESS-2 - Marine sediment issued by NRC; SRM 1643d – Trace Elements in Water issued by NIST.

Table 3-26. SRM Results for Tissue Metal Analyses: 2976, DORM-2 and 1643d

Standard Reference Material	Ag (µg/g)	Al (µg/g)	As (µg/g)	Ba (µg/g)	Be (µg/g)	Cd (µg/g)	Co (µg/g)	Cr (µg/g)	Cu (µg/g)
SRM 2976 **This Study, 2002 (n = 1)**	0.009	158	12.6	0.71	0.005	0.77	0.61	0.57	4.0
SRM 2976 **NIST Certified**	(0.011) (±0.005)	(134) (±34)	13.3 ±1.8	--	--	0.82 ±0.16	(0.61) (±0.02)	(0.50) (±0.16)	4.02 ±0.33
SRM DORM-2 **This Study, 2002 (n = 1)**	0.039	10.6	17.9	2.5	0.006	0.049	0.172	32.2	2.3
SRM DORM-2 **NRC Certified**	0.041 ±0.013	10.9 ±1.7	18.0 ±1.1	--	--	0.043 ±0.008	0.182 ±0.031	34.7 ±5.5	2.34 ±0.16
SRM 1643d **This Study, 2002 (n = 1)**	--	--	--	506.3 µg/L	12.66 µg/L	--	--	--	--
SRM 1643d **NIST Certified**	--	--	--	506.5 µg/L ±8.9	12.53 µg/L ±0.28	--	--	--	--
Spike Recovery (%) **2002 (Tissue) (n = 2)**	100.3 ±1.2	96.9 ±0.3	96.0 ±4.1	98.1 ±3.2	106.9 ±3.2	97.9 ±0.8	104.7 ±0.3	95.7 ±1.3	101.9 ±3.5

Notes: Values in parenthesis are for reference only; SRM not certified by the NIST or NRC. Mean results ± standard deviation are presented.
SRM 2976 – Mussel tissue issued by NIST; SRM DORM-2 – Dogfish Muscle issued by NRC; SRM 1643d – Trace Elements in Water issued by NIST.

Table 3-26 (continued). SRM Results for Tissue Metal Analyses: 2976, DORM-2 and 1643d

Standard Reference Material	Fe (µg/g)	Hg (µg/g)	Mn (µg/g)	Ni (µg/g)	Pb (µg/g)	Sb (µg/g)	Tl (µg/g)	V (µg/g)	Zn (µg/g)
SRM 2976 **This Study, 2002 (n = 1)**	175	0.059	33.4	0.87	1.13	0.014	0.002	0.88	145
SRM 2976 **NIST Certified**	171.0 ±4.9	0.061 ±0.0036	(33) (±2)	(0.93) (±0.12)	1.19 ±0.18	--	(0.001)	--	137 ±13
SRM DORM-2 **This Study, 2002 (n = 1)**	149	--	3.4	17.5	0.069	0.027	0.004	0.19	24.3
SRM DORM-2 **NRC Certified**	142 ±10	4.64 ±0.26	3.66 ±0.34	19.4 ±3.1	0.065 ±0.007	--	(0.004)	--	25.6 ±2.3
SRM 1643d **This Study, 2002 (n = 1)**	--	--	--	--	--	54.5 µg/L	7.07 µg/L	35.8 µg/L	--
SRM 1643d **NIST Certified**	--	--	--	--	--	54.1 µg/L ±1.1	7.28 µg/L ±0.25	35.1 µg/L ±1.4	--
Spike Recovery (%) **2002 (Tissue) (n = 2)**	95.7 ±3.4	70.2 ±4.5	103.3 ±5.8	95.1 ±1.3	98.8 ±8.2	91.7 ±0.0	104.7 ±2.7	91.7 ±1.2	99.1 ±3.0

Notes: Values in parenthesis are for reference only; SRM not certified by the NIST or NRC. Mean results ± standard deviation are presented.
SRM 2976 – Mussel tissue issued by NIST; SRM DORM-2 – Dogfish Muscle issued by NRC; SRM 1643d – Trace Elements in Water issued by NIST-Final concentrations for Hg are corrected for spike recovery.

Table 3-27. SRM Results for Particulate and Dissolved Metal Analyses: 2704, MESS-2, CASS-3 and SLRS-3

Standard Reference Material	Al (%)	As (µg/g)	Ba (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Hg (µg/g)	Pb (µg/g)	Zn (µg/g)
SRM 2704 This Study, 2002 (n = 6)	6.18 ±0.03	23.0 ±0.3	417 ±8	3.41 ±0.08	135 ±3	97.2 ±3.0	4.10 ±0.02	--	159 ±5	434 ±4
SRM 2704 NIST Certified	6.11 ±0.16	23.4 ±0.8	414 ±12	3.45 ±0.22	135 ±5	98.6 ±5.0	3.45 ±0.22	--	161 ±17	438 ±12
SRM CASS-3 This Study, 2002 (n = 3)	--	1.05 µg/L ±0.03	--	0.027 µg/L ±0.001	0.097 µg/L ±0.001	0.534 µg/L ±0.011	--	--	0.012 µg/L ±0.001	1.17 µg/L ±0.04
SRM CASS-3 NRC Certified	--	1.09 µg/L ±0.07	--	0.030 µg/L ±0.005	0.092 µg/L ±0.006	0.517 µg/L ±0.062	--	--	0.012 µg/L ±0.004	1.24 µg/L ±0.25
SRM SLRS-1 This Study, 2002 (n = 2)	--	--	13.6 µg/L 13.7 µg/L	--	--	--	--	--	--	--
SRM SLRS-3 NRC Certified	--	--	13.4 ±0.6	--	--	--	--	--	--	--
Spike Recovery (%) 2002 (Particulate) (n= 4)	97.5 ±4.1	103.2 ±2.8	100.2 ±1.8	99.7 ±0.6	100.0 ±5.5	95.2 ±1.7	97.6 ±3.2	--	98.0 ±1.7	95.6 ±2.9
Spike Recovery (%) 2002 (Dissolved) (n = 3)	--	95.5 ±4.0	MOA**	101.1 ±5.3	95.5 ±1.0	100.7 ±4.0	--	MOA**	95.7 ±1.8	93.9 ±2.5

Notes: Values in parenthesis are for reference only; SRM not certified by the NIST or NRC. Mean results ± standard deviation are presented.
*MESS-2 certified TOC value is for total carbon (organic plus inorganic). ** MOA – Method of Standard Additions analysis.
SRM 2704 – Buffalo River Sediment issued by NIST; SRM MESS-2 – Marine Sediment issued by NRC; SRM CASS-3 – Nearshore Seawater issued by NRC; SRM SLRS-3 – Riverine Water issued by NRC.

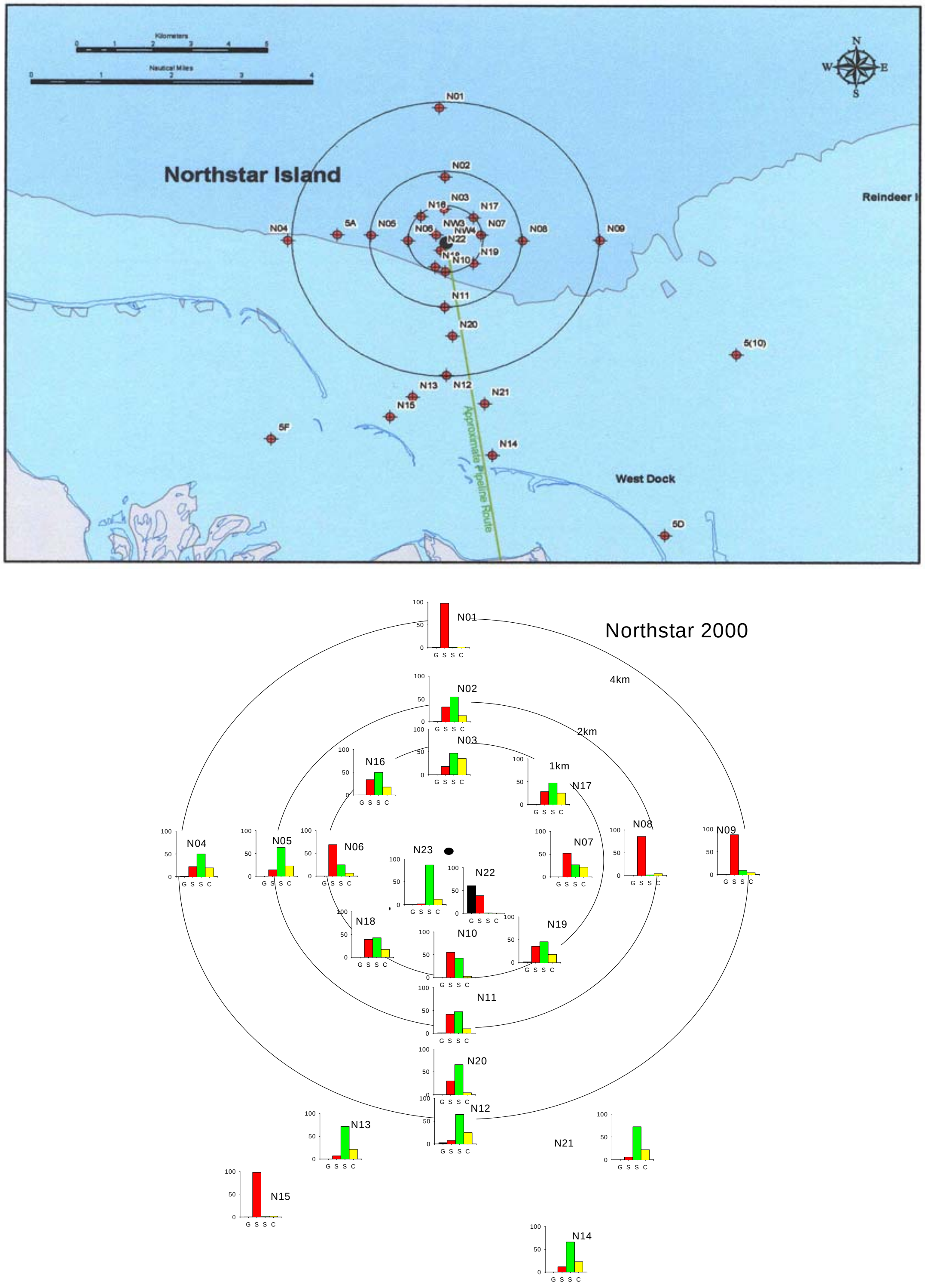


Figure 3-1. Map of Northstar 2000 Sampling Stations with Grain-Size Histograms

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

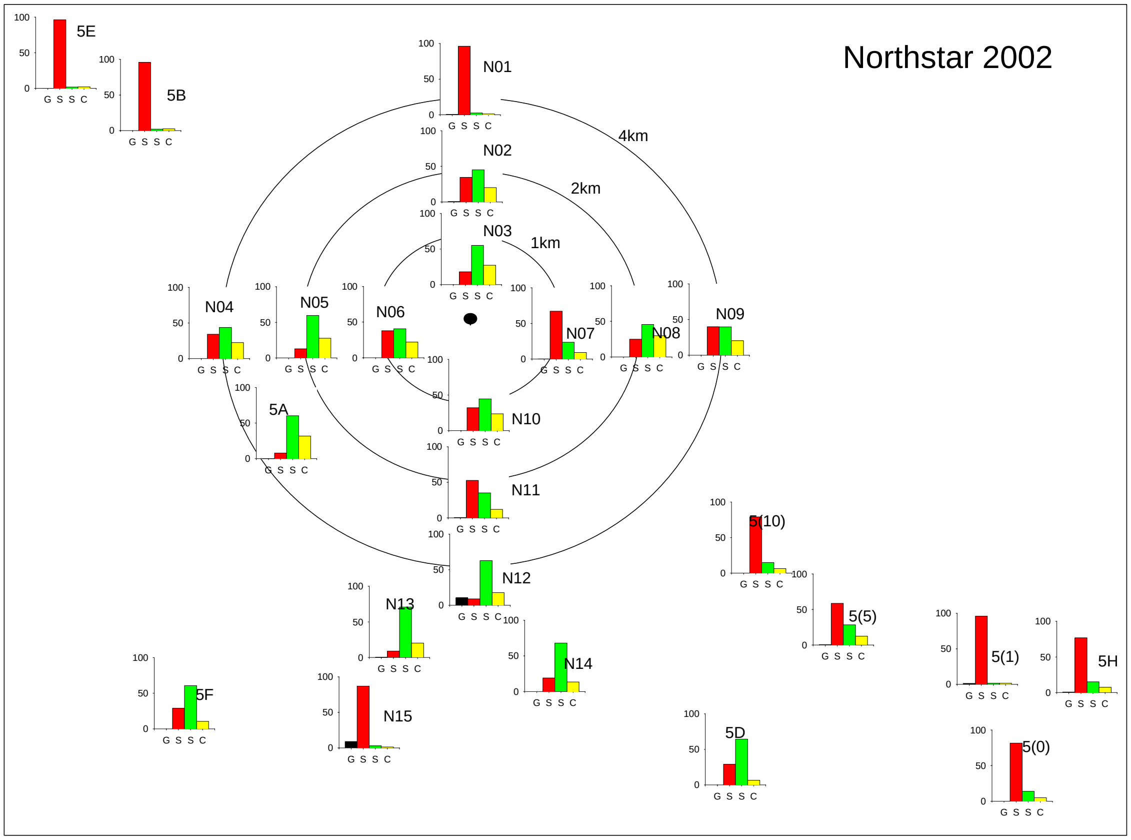


Figure 3-2. Grain-Size Histograms for Northstar 2002 Sampling Stations

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

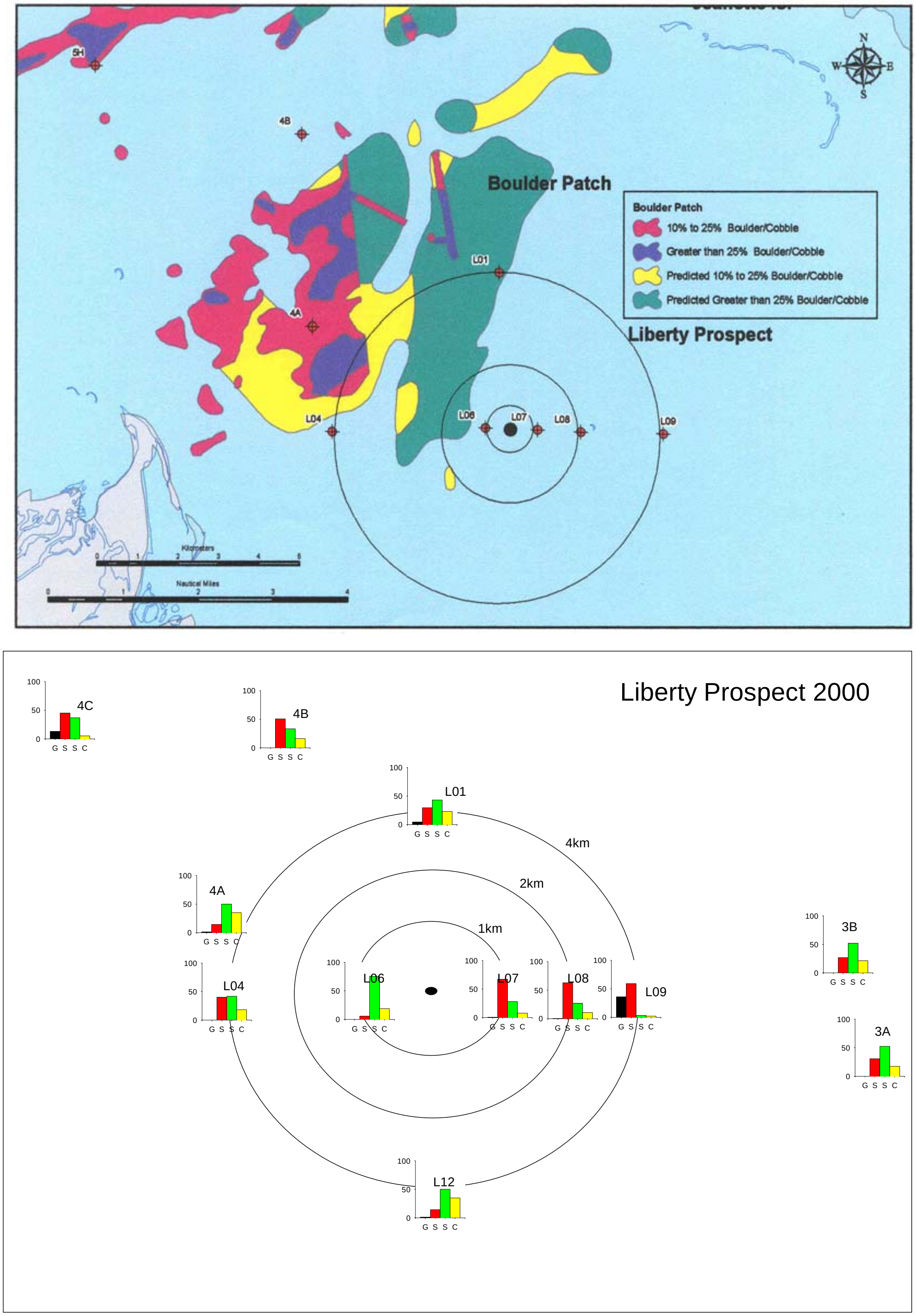


Figure 3-3. Map of Liberty 2000 Sampling Stations and Grain-Size Histograms

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

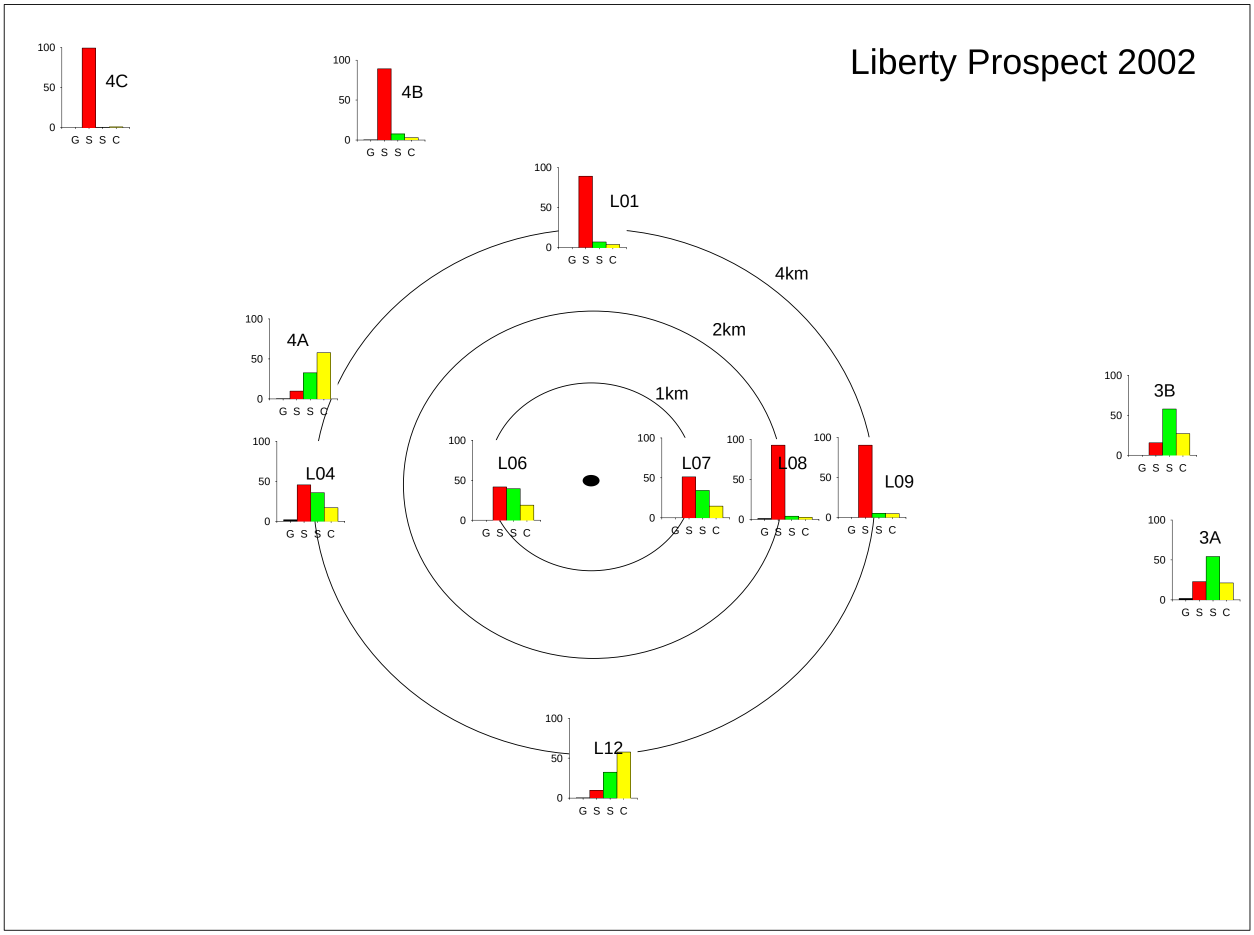


Figure 3-4. Grain-Size Histograms for Liberty Prospect 2002 Sampling Stations

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

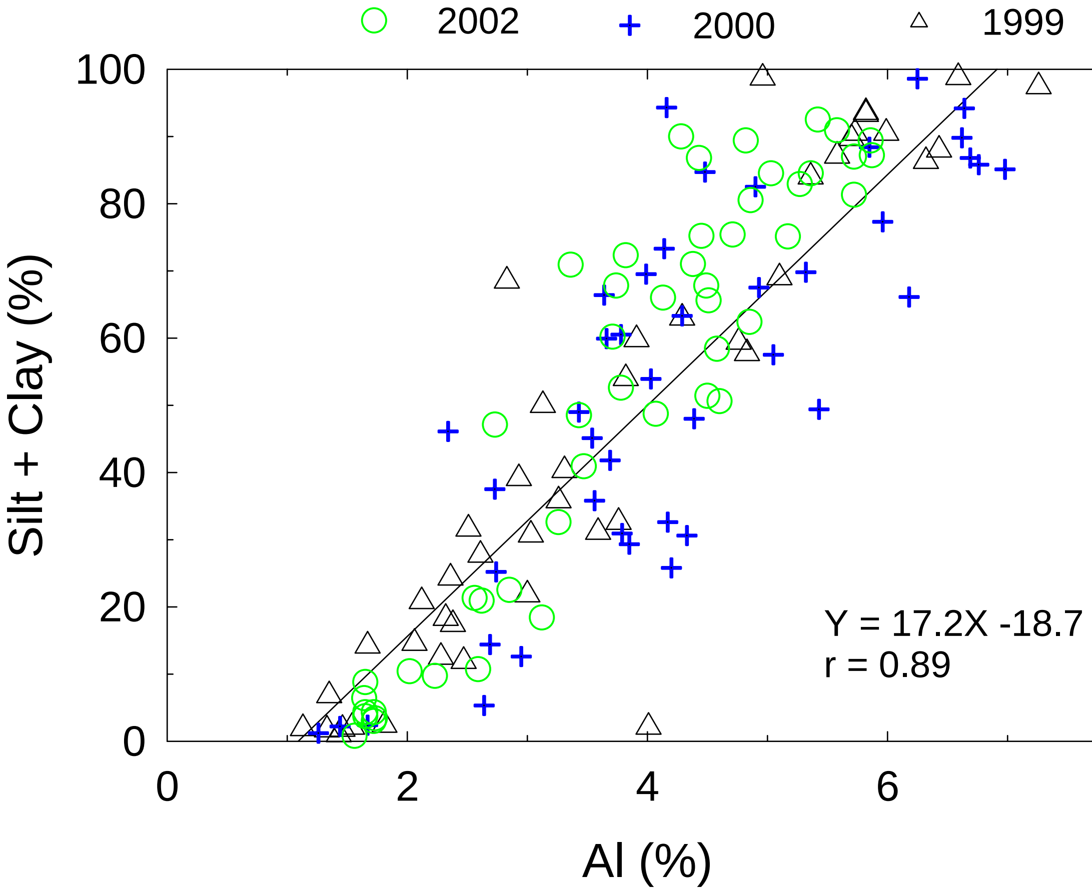


Figure 3-5. Concentrations of Al versus (a) Silt + Clay and (b) Clay for Surficial Sediment Samples from Beaufort Sea Monitoring Program, Northstar, and Liberty Stations

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

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

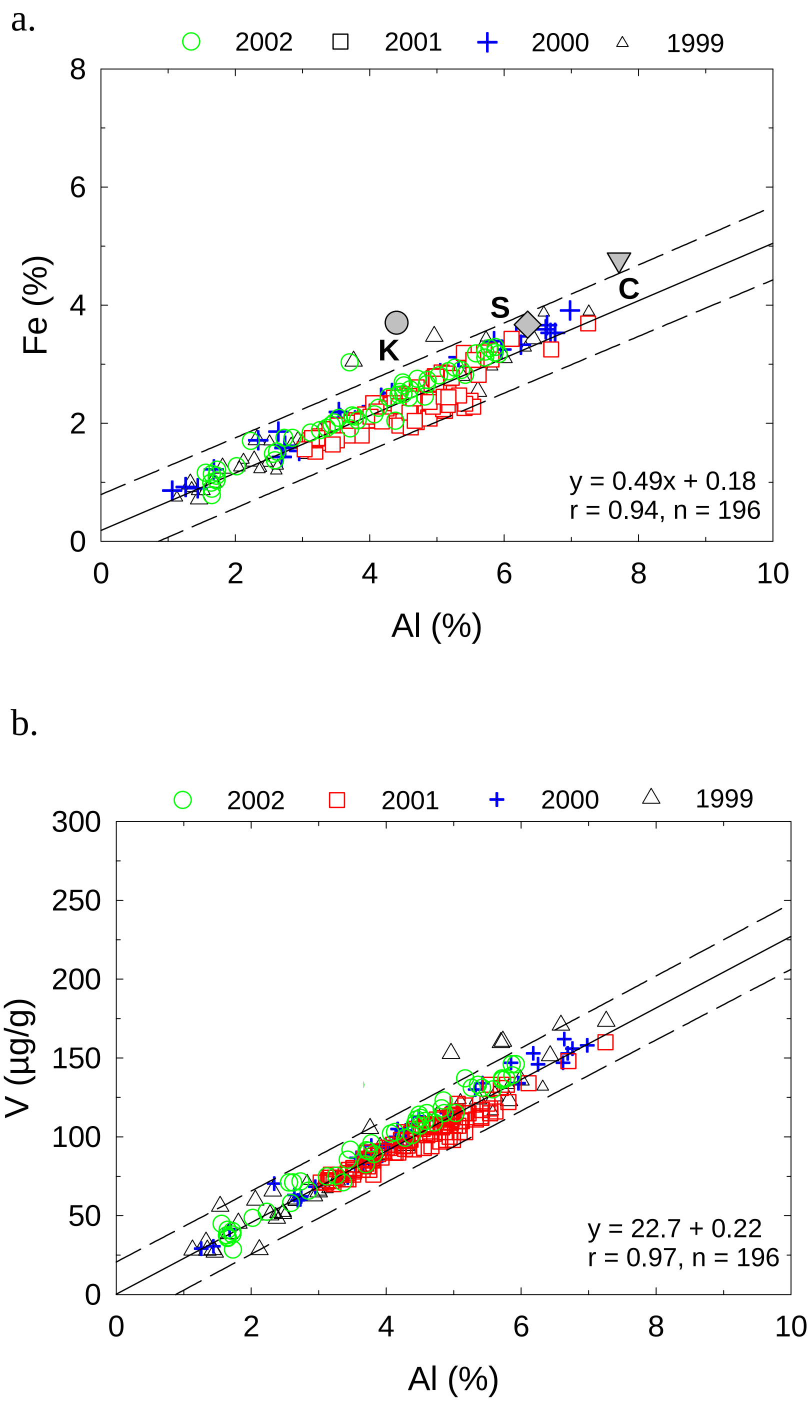


Figure 3-6. Concentrations of Al versus (a) Fe and (b) V for Surficial Sediment Samples from the 1999, 2000, 2001 and 2002 Sampling Surveys

The lines, equations, correlation coefficients (r) and 99% prediction intervals are from linear regression and related statistical calculations.
Points marked with large letters are for suspended sediment from the Sagavanirktok (S), Kuparuk (K) and Colville (C) rivers.

4.0 Discussion

The summer field sampling programs conducted in 1999, 2000, 2001, and 2002 successfully obtained data on a number of indicator measurements related to potential contaminant inputs from the Northstar development. Against a significant background “signal”, temporal changes and spatial trends in these measures were assessed. Hydrocarbon and/or metal, and supporting parameters were measured in samples of surficial sediments, riverine sediments and peat, biota (clams and amphipods), SPMDs, caged mussels, and sediment cores collected in the ANIMIDA study area. The summer 1999 data represent the pre-construction environment for the Northstar and Liberty prospects for the ANIMIDA Phase I program, and will be used for comparisons to measurements collected during the summer 2000 and 2002 sampling surveys (post-construction and production measurements at Northstar). The results and discussion associated with the sediment core program (2001 field program) are contained in a separate MMS Report (Brown, et al., 2003). In this section of the report, the results of the sediments and biota will be further evaluated for general trends and relationships, and statistical comparisons of the pre- and post-construction results will be evaluated for the purpose of hypothesis testing.

4.1 Surficial Sediments (0-1 cm)

4.1.1 Grain Size

Inter-annual shifts in the texture of surficial sediment have been observed throughout the ANIMIDA study area. The largest changes in grain size distribution observed during this study occurred between 1999 and 2000. During 1999, surficial sediment at stations N11, N12, N13 and N14 were essentially all sand and gravel (Figure 4-1). In contrast, the 2000 samples were dominated by silt and clay (Figure 4-1). Although the exact mechanism for this shift is not known, the 1999 samples were collected after a 6-day storm with winds in excess of 25 knots that may have eroded away finer-grained material. No such storms preceded collection of the 2000 samples that probably contained finer-grained material carried in by the Kuparuk River during the spring breakup of 2000. At stations N06 and N10, both close to Northstar Island, the opposite condition was observed with much finer-grained particles in the surface layer of sediment during 1999 than 2000 (Figure 4-1). This shift may have resulted from inputs of coarser material at these stations in association with construction of the island. Grain size distribution at the other Northstar stations was similar for 1999 and 2000 (Figure 4-1).

Differences in grain size distribution between the 2000 and 2002 sampling are less than observed between 1999 and 2000. During 2002, much less sand was found at stations N06, N07, N08 and N09 than during 2000 (Figure 4-2); most likely because fine-grained sediment introduced to that area during river runoff had not yet moved farther offshore. In contrast, sand has dominated at stations N01, 5B and N15 throughout the study.

Shifts in grain size in the Liberty area were noted at station L01 where finer-grained sediment was collected during the 2000 period than during 1999 and at stations L08 and L09 where the opposite trend was found (Figure 4-3). Most of the other significant shifts in grain size throughout the ANIMIDA study area are to finer-grained sediment in the 2000 samples versus the 1999 samples. These other changes also may be related to the effects of the storm activity that preceded the 1999 sampling period in tandem with the complex movement of sediment throughout the area. During 2002, the sand content at stations 4C, 4B, L01, L08 and L09 (Figure 3-4, Section 3) was markedly greater than observed during 2000 (Figure 4-3). In contrast with the Northstar area, less fine-grained material was present in the area of Liberty Prospect during 2002 than during 2000.

The most important finding from the grain size data is that sediments in many locations throughout the ANIMIDA study area are regularly shifting and that the sediment grain sizes found during one year may shift prior to sampling during a subsequent year. Thus, techniques that normalize sediment chemistry to account for differences in grain size need to be used. Furthermore, care must be taken in future sampling activities to insure that the sediment collected during any given year is recent and not relict material.

4.1.2 Organics (Hydrocarbons)

The hydrocarbon dataset for surficial sediments for 1999, 2000, and 2002 is complete and includes SHC, PAH, and S/T data. For the 1999 dataset only a subset of samples were analyzed for S/T. These data were assessed in part by using a suite of key diagnostic parameters and ratios (Table 3-5), which are useful in describing hydrocarbon trends in the marine environment (Boehm et al. 2001a). Some of the general trends observed in these data for several areas of interest are evaluated in this section. These areas include: 1) sources of hydrocarbons, 2) spatial variability, or comparisons between stations, 3) temporal variability, or comparisons between years (before and after Northstar construction including results of statistical evaluations), and 4) 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 for representative samples throughout the study area were selected and are presented in Figures 4-4 through 4-15. The samples selected for presentation are as follows:

- North Slope Crude Oil – composite pipeline sample (Figure 4-4)
- Northstar Oil – 2002 (Figure 4-5)
- Colville River sediment - 1999 (Figure 4-6)
- Station N06 – Northstar sediment - 1999 (Figure 4-7)
- Station L06 – Liberty sediment - 1999 (Figure 4-8)
- Station 3A – BSMP sediment station near Stockton Islands - 1999 (Figure 4-9)
- Station L08 – Liberty sediment - 1999 (Figure 4-10)
- Station 5D – BSMP sediment station near Stump Island/West Dock - 1999 (Figure 4-11)
- Station N06 – Northstar sediment - 2000 (Figure 4-12)
- Station L08 – Liberty sediment - 2000 (Figure 4-13)
- Station N06 – Northstar sediment – 2002 (Figure 4-14)
- Canning River sediment – 2002 (Figure 4-15)

The Northstar Oil sample was collected on May 6, 2002 from the separator oil line for Well NS-08. The North Slope Crude Oil sample was a Valdez Terminal composite crude oil collected in March 1989.

4.1.2.1 Hydrocarbon Sources

Saturated Hydrocarbons

In general, the surficial sediments (GC/FID chromatograms in Figures 4-7 through 4-14) exhibit a mixture of primarily terrestrial biogenic hydrocarbons and lower levels of petroleum hydrocarbons (Figure 4-4 shows a North Slope Crude Oil reference). This assemblage is clearly dominated by plant wax normal (i.e., straight-chain) alkanes in the n-C27 through n-C33 carbon range. This is further demonstrated by carbon preference index (CPI) values that range from two to seven for most samples, which is characteristic of sediments influenced by terrigenous plant inputs (Wakeham and Carpenter, 1976; Boehm, 1984). Eleven samples, out of a total of 128 sediment samples, have CPI ratios of less than two (4C [2002], 5(1) [2002], 5B [1999 and 2000], 5E [1999 and 2002], L06 [2000], N01 [1999 and 2002], and N15 [1999 and 2000]). With the exception of 5E [1999], the lower CPI ratios at these stations are due to low SHC concentrations (i.e., trace levels), combined with corresponding low TOC and high sand content, factors which all contribute to CPI ratio uncertainty and potential inaccuracy. However, the CPI ratio of 1.25 at station 5E [1999], with a corresponding TPHC concentration of 11 mg/Kg, is characteristic of a petroleum component present in this sample. However, in 2000 the CPI ratio at station 5E is 2.6 with a corresponding decrease in SHC concentration to 3.5 mg/Kg and in 2002 the CPI ratio at this station was 1.5 with a SHC concentration of 3.8 mg/Kg, indicating a highly variable sediment substrate at this station.

Traces of lower-molecular-weight alkanes (LALK – n-C9 through n-C20 alkanes), indicative of a petroleum source, are visible as more minor components relative to the plant wax alkanes in the sediment and river samples (Figures 4-6 through 4-9, 4-14 and 4-15). This clearly visible petroleum alkane signature in the sediments has been well documented by previous studies in the region (Boehm, et al., 1987; Steinhauer and Boehm, 1992; and Boehm et al., 1990). The clear exception to this trend is station L08 in 1999 (Figure 4-10), which has a GC/FID chromatogram with a distinct unresolved complex mixture (UCM) or "hump" in the n-C10 through n-C24 carbon range. The GC/FID pattern observed in this sample is characteristic of a diesel fuel hydrocarbon source. The diesel fuel pattern is slightly weathered, indicating a recent source of diesel fuel contamination at this station. Triplicate field replicates collected from L08 in 2000 revealed a similar diesel fuel pattern in one of the three of the field replicates (Figure 4-13) and a less pronounced diesel signature in the other two replicates. The diesel fuel pattern was not present in the single sample collected at L08 in 2002. The absence of a similar diesel fuel signature in adjacent samples and the 2002 sample suggests a very limited or patchy area of sediment contamination. These results warrant continued evaluation and monitoring in future field surveys.

Polynuclear Aromatic Hydrocarbons

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

The variations in PAH composition of representative surficial sediments from the region in 1999, 2000, and 2002 are shown in the PAH distribution plots in Figures 4-6 through 4-15. For comparison, the PAH distribution plot of a North Slope Crude oil and Northstar production oil are shown in Figures 4-4 and 4-5. The PAH distributions are generally similar throughout all the regions of the study area and are characterized by the presence of a full suite of relatively "unweathered" petroleum PAHs (i.e., naphthalenes ≥ 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 (Figures 4-6 and 4-15), which suggests the relationship of the rivers as a source of the hydrocarbons in the nearshore sediments, as noted previously for the SHCs.

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

The PAH distribution in station L08 sediment from 1999 and 2000 (Figures 4-10 and 4-13, respectively) shows a clear increase in the abundance of 2- and 3-ring petroleum PAHs, particularly the naphthalenes, relative to the other sediment samples. This further supports the GC/FID evidence of diesel fuel contamination at this station. A slight increase in the abundance of the 2- and 3-ring petroleum PAHs was also observed in the 2002 sample from L08, however, it was not as evident as in the previous years. Two samples that were identified as potentially being enriched in petroleum hydrocarbons based on SHC results in 1999 (5D and 5E) do not show evidence of a corresponding enrichment in PAH or change in PAH distribution in subsequent years. In 2000, the PAH concentration at 5E was comparable to the levels in 1999 (260 ug/Kg), but the concentration in 2002 was substantially lower at 46 ug/Kg, due to a corresponding decrease in fine-grained sediment. At 5D, the PAH concentrations were substantially lower in 2000 and 2002 with no apparent change in overall PAH distribution. These results indicate a highly variable sediment substrate at stations 5D and 5E. Additionally, the source of hydrocarbon enrichment observed at 5D in 1999 may be depleted in PAH versus SHC, relative to the regional petroleum hydrocarbon background already present in the sediments (e.g., coal).

Triterpanes

In general, the triterpane distributions in the sediment samples are indicative of a petroleum pattern (Figures 4-6 through 4-15), with varying abundances of a suite of recent organic material triterpane markers. For example, a characteristic petroleum triterpane pattern dominated by norhopane (T15) and C30-hopane (T19) is shown in Figure 4-4 for the North Slope Crude oil. The triterpane distributions for most sediment samples comprise a mixture of these characteristic petroleum triterpanes, along with recent organic or biogenic markers such as diploptene (the large peaks on left of the T21 and T22 doublet – Figure 4-12) and other unnamed triterpanes (the large peaks which elute prior to T15 and in the 45- to 47-minute range – Peters and Moldowan, 1993). In addition, the relative abundance of T22 at much greater levels than T21 in some samples provides further evidence of substantial recent organic matter inputs to the surficial sediments. In general, the 2000 and 2002 sediment samples appear to show a greater abundance of these recent organic material or biogenic biomarkers, suggesting a greater terrestrial influence (e.g., river runoff) to the sediments in 2000 and 2002. Many of the sediment samples contain trace levels of oleanane (T18), indicating the presence of a non-North Slope Crude, post-Cretaceous/Tertiary petroleum source; i.e., T18 is absent in bulk North Slope Crude oil (Bence et al., 1996 and Figure 4-4) and Northstar Oil (Figure 4-5). 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 sediments and peat (Figure 4-10) have the same mixture of recent organic matter and petroleum hydrocarbon patterns as observed in many of the sediment samples (for example, station N06 - Figures 4-7 and 4-12). This similarity suggests that there is a strong link between Colville River hydrocarbon sources – mostly erosional inputs of coal shale, peat, etc. (i.e., natural background) and the sediments. However, given the documented current transport regime of East to West in the study area, it is likely that rivers to the East, as well as the Colville River also influence the surficial sediments. For example, the triterpane distribution of the Canning River sediment collected from the East of the region in 2002 (Figure 4-15) is dominated by a suite of recent organic markers with a different distribution (specifically the unknown peak at ~52 minutes) which are found in greater abundance from some samples in the eastern study area.

The Kuparuk and Sagavanirktok River sediments contain many of the same recent organic matter triterpane markers, but generally have different distributions than the Colville River sediments. In particular, the ratio of T21/T22, where T22 is an order of magnitude higher than T21, is characteristic of an immature or recent hydrocarbon source, possibly indicative of coal. This predominant T22 pattern is also found in several of the surficial sediment samples - 5(5) [1999 and 2000], and 5(0) [2000] near the Sagavanirktok River delta, and N14 [1999 and 2002], N20 and N21 [2002], 5D [1999, 2000 and 2002], and 5F [2000 and 2002] near the mouth of the Kuparuk River – indicating the influence of these rivers to the deposition of surficial sediments at these stations. The presence of the predominant T22 pattern at station 5D (Figure 4-11) is of particular interest, since the high SHC and PAH concentrations indicate fossil fuel hydrocarbon enrichment at this station. The observed T22 pattern indicates that coal particles, possibly from the Kuparuk River, may be one of the sources of the hydrocarbon enrichment.

Several surficial sediment samples have distinctly different triterpane distributions. Stations 5E [1999, 2000 and 2002], 5B [2000 and 2002], and L08 [1999 and 2000] (Figure 4-10) have triterpane distributions more characteristic of a petroleum source, i.e., a predominance of hopanes (T15 and T19). In the case of L08, this is not surprising since other organic data clearly indicate diesel fuel contamination. However, the abundance of petroleum triterpanes also indicates a petroleum product “heavier” than diesel, as triterpanes are typically removed from diesel-range fuels during the distillation process. This result indicates that the observed petroleum contamination at L08 is a complex mixture of hydrocarbons including diesel and heavier hydrocarbons such as No. 6 fuel oil or crude oil. This could be the result of drilling mud/cutting residues from historical adjacent exploratory drilling (i.e., Tern Island), as the standard practice at the time allowed disposal of used drill muds on the ice during winter drilling. This is further supported by the elevated barium levels (when normalized to Al) observed in the sediment from L08 (1999 only). The petroleum triterpanes in the surficial sediment at 5B are at trace levels (7.8 ug/Kg Total S/T), whereas the triterpane distribution at 5E further confirms the presence of low levels of a heavy petroleum hydrocarbon source shown by the SHC and PAH results, but the specific origins of these “contaminants” are not known.

4.1.2.2 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 three classes of PAH (low- and high-molecular-weight PAH, and Total PAH). A comparison of the Total PAH from all ANIMIDA sediments from the study region in 1999, 2000 and 2002 to the ERL and ERM criteria is shown in Figure 4-24. None of the Total PAH concentrations determined in this study exceed the ERL. Station 5D in 1999, which had the highest measured Total PAH at 2,700 μg/Kg, was still well below the ERL value of 4,022 μg/Kg. The mean Total PAH values from each study region were generally an order of magnitude lower than the ERL. Similarly, the individual PAH concentrations did not exceed the ERL for the individual 13 PAH, which could be compared directly. The C1-naphthalenes parameter in this study is reported as the sum of the two individual naphthalene isomers – 1-methylnaphthalene and 2-methylnaphthalene. The C1-naphthalenes values at station 5D in 1999 and 5A in 2000 (130 μg/Kg and 100 μg/Kg, respectively) were higher than the ERL value listed for the single 2-methylnaphthalene isomer (70 μg/Kg). However, the values at both stations would be less than the ERL using an estimate of 50 percent contribution of 2-methylnaphthalene to the C1-naphthalenes parameter. In summary, based on sediment quality criteria, the concentrations of PAH found in the study area sediments are not likely to pose immediate ecological risk to marine organisms in the area

4.1.2.3 Temporal and Spatial Trends

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

This regression plot technique was used effectively for the 1999 data to identify sediments enriched in hydrocarbons and data outliers (Boehm, et al., 2001b). For 1999 data, good linear correlation was established between concentrations of Total PAH less perylene and TPHC with silt + clay ($R^2 = 0.83$ and 0.69 respectively – station 5D was determined to be a statistical outlier and was not included in the regression calculation). The value Total PAH less perylene was used to reduce variability introduced to the Total PAH data by perylene, which can vary widely in abundance based on sediment type. Total PAH less perylene has been used in other studies in evaluating sediment PAH in Cook Inlet and Alaska (Hyland, et al., 1995; Boehm et al., 2001a).

These regressions defined the natural geological/geochemical background. In both PAH and TPHC plots the data point for station 5D was well outside the calculated 99 percent prediction interval of the regression line indicating that 5D sediment was enriched in Total PAH relative to the expected background for the region. As noted previously, station 5D sediments were identified as being contaminated with hydrocarbons, although the source of this contamination is still unclear (i.e., coal versus petroleum sources). In the TPHC plot samples L08 and 5E were found to fall slightly above the upper 99 percent prediction interval. Based on the analytical data, these two samples were also previously identified as being enriched in petroleum hydrocarbons. Diesel contamination with possible crude oil was identified in L08 and a heavy hydrocarbon product depleted in PAH was identified as a possible source in 5E.

Overall, these regression techniques provided a sensitive baseline process to measure temporal trends of anthropogenic inputs into the system from Northstar, given radial sampling design around the prospect and regional BSMP station coverage. As noted earlier, statistical analyses of the 1999, 2000 and 2002 data were performed to determine if there were significant differences in the measured key diagnostic organic parameters due to the development of Northstar. The results of the statistical analyses indicated that the key bulk hydrocarbon parameters (i.e., Total PAH, TPHC, pyrogenic PAH, etc.) increased significantly at Northstar in 2000 and 2002, and several diagnostic parameters were significantly different (Section 3.1.4). The results of the statistical analyses are probably best summarized in a Total PAH minus perylene versus silt + clay regression plot for 1999, 2000 and 2002 Northstar stations (Figure 4-16). In this plot the regression lines and 95% prediction intervals do not overlap, indicating a significant increase in PAH at Northstar in 2000 and 2002 after adjusting for fines (silt + clay). A simple plot of the Total PAH normalized to fines clearly shows this trend of increasing PAH concentrations at the Northstar stations in 2000 with lower levels in 2002, but still generally higher than 1999 (Figure 4-17). Station N15 in 2002 appears as an outlier on this plot due to a very low %fines result (4.3%) and a total PAH concentration of 200 µg/Kg.

However, a closer examination of the PAH data show that although Northstar concentrations increased post-construction (2000 and 2002 combined), the distribution and composition of the PAH remained relatively unchanged. The composition of the sediment hydrocarbons at Northstar is best summarized by a comparison of the pyrogenic to petrogenic PAH ratios in 1999, 2000 and 2002. A comparison for this ratio for all paired Northstar stations (Figure 4-18) reveals no significant difference between years 1999 and 2000 indicating that there were no incremental additions of anthropogenic hydrocarbons to the Northstar area as a result of construction activities in 2000.

The pyrogenic to petrogenic PAH ratios for Northstar stations in 2002 show a slight but significant increase in year 2002 (Figure 4-18). A subsequent ANOVA revealed that pyrogenic to petrogenic ratios for Northstar 2002 and Liberty/BSMP 2002 were not significantly different from each other, but were significantly greater when compared to the 1999 and 2000 regional data sets. This result suggests a slight overall regional shift in the pyrogenic to petrogenic distribution in the surface sediments. A comparison to the pyrogenic to petrogenic PAH ratios in the 2001 core data show that 2002 results are within the historical range described by the sediment core data. The ANOVA model results presented in Table 3-11 show a significant decrease in petrogenic PAH region-wide for years 2000 and 2002, as compared to year 1999. Together these results indicate that the observed shift to a greater relative proportion of pyrogenic hydrocarbons in 2002 may be the result of decreased concentrations in petrogenic PAHs and can likely be attributed to annual variability. Thus, while concentrations of PAH appear to have increased at Northstar in 2000 and 2002, the source of the increase appears to be the same as found in sediments throughout the region and not from Northstar related hydrocarbon contamination (i.e., anthropogenic inputs).

Another evaluation of the sources of the PAH was performed using a dibenzothiophene to phenanthrene source ratio plot, which has been used in similar investigations of PAH sources in the environment (Brown and Boehm 1993; Page et. al 1998; Boehm et. al 2001a). An examination of the source plot for all 1999, 2000 and 2002 sediments and source samples (Figure 4-19) reveals that the source composition of PAH in the Northstar 2000 and 2002 sediments is in the same range as the 1999, 2000 and 2002 BSMP and Liberty stations which are representative of the regional hydrocarbon background. In the source ratio plot several of the Northstar 1999 sediments have ratios substantially higher than the "regional background" which is likely due to two factors: 1) the very low concentrations found at some of the 1999 Northstar stations which introduces variability into the ratio and generally results in a ratio increase, and 2) the localized influence of the Kuparuk river which has a ratio higher than the "regional background."

The Northstar production oil, which was first analyzed in 2002, was found to be relatively low in sulfur compounds and had a resulting dibenzothiophene to phenanthrene source ratio similar to the "regional background" (Figure 4-19). The other North Slope field crude oils have dibenzothiophene to phenanthrene source ratios that are substantially higher and are easily distinguished from the background hydrocarbons. This finding limits the use of this evaluation technique since the potential contribution of Northstar crude oil could not be determined in the case of an accidental release or incremental chronic inputs. However, another source ratio plot of the 20S to 20R epimers of steranes and triterpanes (5α,14α,17α-24-methylcholestane [S25/S28] versus 17α,21β(H)-30-homohopane [T21/T22]) shown in Figure 4-20, clearly differentiates all of the North Slope field crude oils and the Northstar production oil from the regional background signature in the surface sediments and river source samples. This ratio, which is a relative measure of the petroleum hydrocarbon maturity, relies on the relative immaturity of the biomarker compounds it the sediments versus the crude oils and provides a promising tool to evaluate potential additions of anthropogenic hydrocarbons to the region in the future.

The earlier observation that the Northstar 1999 sediments may be depleted in hydrocarbons relative to the other 1999, 2000 and 2002 sediments is further supported by a Total PAH less perylene versus silt + clay regression plot for all the 1999, 2000, and 2002 sediment data. In this plot (Figure 4-21) the regression and 95% prediction intervals are shown for all data. The plot shows a small cluster Northstar 1999 samples which are below the 95% prediction interval, indicating that these samples are significantly lower in PAH versus silt + clay than the overall population of 1999, 2000 and 2002 samples. This result corroborates the observed trend of lower hydrocarbon levels in Northstar 1999 samples. In addition, as part of the statistical analyses, a regression model comparing Northstar 1999 samples to 1999 BSMP and Liberty samples for all key parameters (Section 3.1.4), revealed that Northstar 1999 sediments were significantly lower in all bulk hydrocarbon parameters (e.g., Total PAH, TPHC, Petrogenic PAH, etc.) than 1999 BSMP and Liberty sediments. A further regression comparison of the Northstar 2000 and 2002 samples versus the BSMP and Liberty 2000 and 2002 samples resulted in no significant difference for all bulk hydrocarbon parameters and most of the diagnostic ratios. The results of this analysis are illustrated by a PAH regression plot (Figure 4-22) which shows complete overlap between the regression lines and 95% prediction intervals (i.e., no significant difference) for the Northstar, BSMP, and Liberty sediments for 2000 and 2002.

As noted previously the initial statistical comparisons revealed that Northstar 1999 sediments were significantly lower in all bulk hydrocarbon parameters (e.g., Total PAH, TPHC, Petrogenic PAH, etc.) than 1999 BSMP and Liberty sediments (Table 3-10) which resulted in a positive Northstar and Northstar/Construction effects (i.e., a significant increase in these parameters associated with Northstar). However, a subsequent statistical model with perylene as a covariate resulted in no significant increases in any of the key diagnostic hydrocarbon parameters due to Northstar or Northstar/Construction effects. The use of perylene as a covariate of a parameter to normalize sediment data is particularly effective due to the absence or only trace levels of perylene in the anthropogenic sources of hydrocarbons to the region (petroleum and pyrogenic hydrocarbons), and the relative enrichment of perylene in the regional background (river and sediment sources). This relationship is clearly shown in a cross-plot of perylene versus PAH (Figure 4-23, $R^2 = 0.94$) with 95 % prediction intervals to identify outliers. As was noted in the statistical analyses using perylene as a covariate, this plot shows no significant increase in PAH due to Northstar or Northstar/Construction effects, and only three stations fall outside the prediction intervals (4A, L08, and N11). Sediments from station N11 appear to be slightly enriched in perylene, possibly due to the proximity to the Kuparuk River that contains sediments rich in perylene. Station 4A sediments appear to be somewhat depleted in perylene relative to PAH, but show no signs of petroleum contamination. Petroleum hydrocarbon contamination was previously identified in Station L08 using other interpretative techniques. The relationship of perylene to other hydrocarbons in surface sediments clearly warrants further investigation, however, these results indicate that normalization of PAH and other hydrocarbon parameters to perylene is another valuable tool capable of identifying anthropogenic hydrocarbons inputs into the surface sediments of this dynamic coastal region.

Based on the results of the data evaluations there are several possible explanations or theories for the observed absolute increase in sediment hydrocarbon concentrations in the Northstar area in 2000 (and to a lesser degree in 2002) with no corresponding change in source or composition: 1) the increase could be related to deposition of very fine-grained material associated with the gravel used to construct Northstar Island and disturbances from the pipeline construction; 2) the ice roads made during the Northstar construction may have diverted suspended sediments from the Kuparuk river flow during break-up, and enriched the deposition of fine-grained hydrocarbon bearing sediments in the Northstar area; and 3) that the Northstar sediments in 1999 were depleted in fine-grained sediment and hydrocarbons during the 1999 sampling period.

The first two hypotheses would require that the source fine-grained material deposited in the Northstar area after 1999 (e.g., Northstar construction gravel and/or Kuparuk river sediment) was enriched in PAH and other hydrocarbons relative to the fine-grained material in the existing surface sediment. Analyses of the Kuparuk river sediments reveal that the river sediment is not enriched in hydrocarbons relative to the Northstar area sediments, and is thus unlikely to account for the observed increase. It is possible that the very fine-grained fraction of Northstar construction gravel could be enriched in hydrocarbons due to burial and compaction of the historic Kuparuk river sediments, which were the source of the gravel (the construction gravel was mined from the Kuparuk river delta). Subsequent analysis of “source material” from the Kuparuk river gravel mine (borrow pit) revealed results similar to the previously analyzed Kuparuk River sediments.

However, the most likely explanation of the three is that the Northstar sediments were depleted in hydrocarbons in 1999. The organic analyses and resulting statistical comparisons of the 1999, 2000 and 2002 Northstar, BSMP and Liberty data, support this explanation. In addition, during the 1999 sampling survey, nearly all the Northstar stations were sampled within 24 hours after a five-day gale (peak winds in excess of 25 knots). This storm was observed to resuspend substantial amounts of surface sediments into the water column (Boehm et al., 2001b) and would account for the observed depletion of hydrocarbons in the 1999 Northstar sediments and corresponding lower abundance of fine-grained sediment. Regardless of the mechanism for the observed increase in hydrocarbon concentrations at Northstar, it is critical to recognize that the hydrocarbon assemblage identified at Northstar in 1999, 2000 and 2002 represents the natural background (both in composition and concentrations) and are not indicative of anthropogenic inputs. However, equally important is the recognition that the monitoring techniques and data evaluation approaches used in this study are very sensitive and capable of identifying incremental anthropogenic inputs to the system.

In summary, the hydrocarbon measures do not reveal any detectable contaminant input that can be attributed to the Northstar operations, when viewed against the pre-construction levels in the sediments and the pre-construction hydrocarbon composition.

4.1.3 Metals

Data for concentrations of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Tl, V and Zn in sediment from the ANIMIDA study are now available for surficial sediments collected during 1999, 2000 and 2002. Metal data also are available for sediment cores collected during 2001. The patchwork of metal concentrations described in the Results section can be normalized reasonably well by plotting metal values versus concentrations of the major elements Al or Fe. Concentrations of trace metals generally correlate well with concentrations of Al and Fe because concentrations of most metals are very low in quartz sand or carbonate shell material and much higher in fine-grained aluminosilicates. Aluminum and Fe are rarely introduced by anthropogenic processes and are present at percent levels in most sediment relative to part-per-million (ppm) levels for trace metals. Thus, Al and Fe often provide valuable normalization tools that can incorporate the metal controlling variables of grain size, organic carbon content and mineralogy. In the ideal case (e.g., Figure 3-6, Section 3), a good linear correlation was observed between concentrations of a trace metal and Al and/or Fe. Significant, positive deviations from this linear trend, as explained in more detail below, usually identify metal contamination. Plots of trace metal concentrations versus Fe or Al have been used in various forms for many years to identify sediment metal contamination (e.g., Trefry and Presley, 1976; Schropp et al., 1990). The 1999, 2000, and 2001 data from the Beaufort Sea are used here to produce a series of templates that can be used to identify possible metal contamination now and in the future. These templates are further tested with the 2002 data.

Concentrations of V correlate well with Al ($r = 0.97$, Figure 3-6, Section 3) and Fe ($r = 0.96$) in all sediment samples collected during 1999, 2000, 2001 and 2002. The good linear fit for Al (and Fe) versus V is consistent with the mixing of relatively uniform composition, metal-rich aluminosilicate phases with metal-poor sand and shell. Thus, either Al or Fe can be used to normalize trace metal concentrations in this study. Occasionally, in areas where the Fe/Al relationship is not as well defined, some trace metals are better correlated with Fe, most likely due to the presence of an iron oxide phase that is somewhat independent of Al and enriched with selected metals. We have chosen Al for normalization in this study because it is the major element least affected by chemical weathering and diagenesis and because it works well for these sediments.

A 99% prediction interval was calculated and plotted around the regression line for Al versus V to establish a template for future assessments. Three points from 1999-2001 on that graph plot slightly above the upper prediction interval in Figure 3-6; however, they exceed that limit by <10% and are consistent with the statistical boundaries of a 99% prediction interval. Any future, positive deviations in V concentrations above the upper prediction interval most likely will be related to anthropogenic inputs of V. Thus, V levels in natural sediment from the Beaufort Sea are predicted to follow the trend presented in Figure 3-6. Concentrations of V in some sediment samples from the coastal Beaufort Sea are higher than reported in grand averages for continental crust or marine sediment (Figure 3-6). However, background levels of V in sediment from Shelikof Strait, Alaska, with comparable Al concentrations, are about 140-150 µg/g (Boehm et al., 2001a) and similar to values from the Beaufort Sea.

Graphs for Al versus Cu, Cr, Ni and Pb (Figures 4-25 and 4-26) also show strong ($r>0.87$) linear relationships with no points from 1999-2001 that plot at >10% above the upper prediction interval. Correlation coefficients for Al versus Co (0.85), Sb (0.84) and Tl (0.86) also are strong with no data points that plot at >10% above the upper prediction interval. Collectively, the results support the conclusion that no statistically discernible anthropogenic inputs of these seven metals can be identified. Available metal data for suspended sediments from source rivers (Fe, Al in Figure 3-6 and Cr, Cu and Pb; Figures 4-25 and 4-26) show that the metal/Al ratios for river particles fit within, or very close to, the prediction intervals found for bottom sediments in the coastal Beaufort Sea. These similarities in metal/Al ratios for river source material and bottom sediment, when linked to data for sediment cores discussed below, are used to evaluate whether diagenetic impacts distort the historical record for these metals in area sediments. Concentrations of metals in the river suspended matter plotted at the higher end of the metal/Al continuum (e.g., Figures 4-25 and 4-26) due to a greater fraction of clay-rich particles suspended in the rivers.

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. Crecelius et al. (1991) noted elevated levels of Cr in Western Harrison Bay (BSMP stations 7A, 7B and 7G) and western Camden Bay (BSMP station 2E). Such levels have not been observed during the ANIMIDA program.

In contrast with the metals discussed above, concentrations at one or more locations were >10% above the upper prediction interval on the metal versus Al plots for Zn, Hg and Ba (Figure 4-27 and 4-28). An anomalous Zn value was observed for site 5H (near Endicott Island), and anomalous values for Hg and Ba were found for sediments collected near Northstar Island (Figure 4-27 and 4-28). Considerable industrial activity is common to both areas; however, the degree of metal enrichment averaged <25% more than the value at the upper prediction limit for a given concentration of Al.

Barium has been used historically as a sensitive indicator for the presence of petroleum drilling mud in sediment because barite is such a common and distinctive additive (e.g., Chow et al., 1978). The graph for Al versus Ba (Figure 4-27) shows a reasonably good fit for most of the data; however, five points were omitted from the baseline regression calculation as discussed below. The Ba concentration from station N22, close to Northstar Island on the south side had an elevated Ba level during 2000. Data from stations N12, N13, N14 and L08 also plot slightly above the upper 99% prediction interval drawn on Figure 4-27.

Minor anomalies in Ba levels at stations N12, N13 and N14 (all during 1999) may be related to runoff from adjacent land operations via the Kuparuk River, based on data for suspended sediment in the river (Figure 4-27). The anomaly at station N22 in 2000 may be related to activity at Northstar Island. Subtle enhancement in the Ba value at station 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 where future monitoring efforts can be focused.

Concentrations of an additional eight metals (Ag, As, Be, Cd, Co, Mn, Sb and Tl) were determined for samples collected during 1999-2002. Concentrations of Ag are low and somewhat variable with most values <0.1 µg/g and in close agreement with the value of 0.07 µg/g reported by Wedepohl (1995) for average continental crust. 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). Concentrations of Be, Cd, Co, Sb and Tl also correlate relatively well with Al as shown by the example for Cd (Figure 4-28).

Even in the surface samples, variability in metal levels can occur at a given site when replicate samples are collected on the same day or during another year. This observation is consistent with the overall patchiness, both horizontally and vertically, in the composition of sediment from the study area. For example, concentrations of Pb in three replicate grab samples from station 5(1) in 1999 have a coefficient of variance [(standard deviation/mean) x 100%] of 1% relative to 17% for sediment from station L11 in 1999 (Figure 4-29). Furthermore, sediment collected at station 5(1) in 2000 is finer grained and has higher levels of both Pb and Al relative to the sample collected in 1999 (Figure 4-29). Also, a dramatic difference was observed in metal levels at station 5D between 1999 and 2000 (Figure 4-29). These patterns and observations are consistent with the dynamics of these shallow-water sediments. Fortunately, the Al versus plots normalize and therefore explain most of this variability.

4.1.3.1 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 ERL and 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.

Nine metals (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. No concentrations of any of the nine metals exceeded their respective values for the ERM (Table 4-1). Furthermore, no concentrations of Ag, Cd, Pb or Zn from this study exceeded the respective values for the ERL (Table 4-1) and thus adverse biological effects from these four metals would be rarely expected based on Long et al. (1995). One data point each for As and Hg, both from station 5D during 1999, exceeds the ERL. No anomalous metal values were found for sediment from station 5D during 2000 and 2002.

Concentrations of Cr in quite a few sediment samples (Figure 4-25) and continental crust (126 µg/g, Wedepohl, 1995) exceed the value for the ERL of 82 µg/g. Such observations are commonly made for Cr, most likely because the database compiled by Long et al. (1995) used Cr concentrations from an acid leach of the sediment rather than a total digestion. Only a small fraction (<25%) of the total Cr is removed by a strong acid leach (Trefry and Presley, 1976; Sinex *et al.,* 1980). Thus, a leachable Cr value equal to the ERL level of 82 µg/g is more likely comparable with a total Cr level of >200 µg/g, a value considerably higher than Cr values for continental crust or any samples from this study. The ERL and ERM values for Cr may need to be revised in later iterations of the sediment quality criteria. No data points exceed the established ERM for Cr.

Similar to results for Cr, several points on the Al versus Cu plot (Figure 4-25) also exceed the present ERL; however, the ERL of 34 µg/g is very close to the average crustal abundance of 25 µg/g and below natural levels for many sediments. Similar to results for Cr and Cu, many points on the Al versus Ni plot (Figure 4-26) exceed the present ERL; however, the ERL of 20.9 µg/g is less than the average crustal abundance of 56 µg/g and below natural levels for many sediments (Figure 4-26).

Overall, the sediment quality data should be used primarily as guidelines at this time. Therefore, adverse biological effects are not expected to be a frequent occurrence at any site in the ANIMIDA study area as the result of trace metals.

Early detection of potential environmental problems near industrial sites is a 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 about the upper limit of 21 µg/g, a caution can be signaled before sediment Pb concentrations reach one of the lowest effects level (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.

4.1.3.2 Temporal distribution of sediment metals

The historical record of metal levels in sediments from the coastal Beaufort Sea was developed as a separate part of the ANIMIDA project in a report from 2003 (Brown et al., 2003) from age-dated cores. A brief overview of that work is presented here because of relevance to the surface sediment component of the ANIMIDA program. The portion presented in this report is an excerpt from a recent paper by Trefry et al. (2003; included in Appendix E). The reader is referred to the previous report for sampling and laboratory methods.

Collection of sediment cores suitable for age-dating in the study area 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 sediments offshore into deeper water. Even when coring sites were chosen based on bathymetry (i.e., semi-restricted basins) or surface sediment composition (i.e., >90% silt plus clay), only one in four cores was viable for establishing a geochronology over the past 50 to 100 years. In many instances, extremely low levels or no detectable amounts of excess ^{210}Pb (<0.2 decompositions per minute per gram [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).

Past efforts to reconstruct recent geochronology for coastal sediments from this nearshore area of the Beaufort Sea (Weiss and Naidu 1986; Naidu et. al 2001) have encountered many of the same difficulties reported here. 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 BSMP stations 6A and 6G; however, the activities for total ^{210}Pb averaged <2 dpm/g with variable texture in each core. In recent work, Naidu and others (2001) reported no excess ^{210}Pb and no detectable ^{137}Cs in a core from Simpson Lagoon whereas they found levels of excess ^{210}Pb levels at 0.9 to 1.2 dpm/g and ^{137}Cs activities of 0.2 dpm/g at a site near BSMP station 3B. Based on inherent difficulties with area sediments, a primary goal of the geochronology effort for the present study was to collect some representative sediment that was deposited prior to the onset of development during the late 1960s and early 1970s and some sediment that was deposited post-development.

Detailed results for geochronology were obtained for three sites: (1) station P1 in Prudhoe Bay, (2) station E1, just east of Endicott Island near the mouth of the Sagavanirktok River, and (3) station 6G in the eastern section of the Colville River delta. At stations L2, 3A, N2 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. The locations of these sites with little or no detectable recent sediments extend across the study area and support the contention that deposition of present-day sediment is patchy and thin.

In Prudhoe Bay (station P1), the maximum activity of excess ^{210}Pb in the surface layer of sediment was 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 4-30). The vertical profile for ^{137}Cs supports the results from excess ^{210}Pb with a sedimentation rate of 0.10 cm/year based on the 1950 appearance of ^{137}Cs at ~5 cm and the observed 1963 peak at ~3.75 cm (Figure 4-30). Samples from depths >4 cm were most likely deposited before development began during the 1960s 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 secluded bay (~3 m) are sufficient to minimize the effects of bottom-fast ice and ice gouging. Even if a combination of sediment deposition and winnowing at station P1 created an apparent sedimentation rate, it seems reasonable to suggest that the top 1 to 2 cm contain post-development sediments and that sediments found deeper than 4 to 5 cm were deposited prior to development.

At station E1, the activity of excess ^{210}Pb was 1.1 dpm/g at 0 to 0.5 cm and 1.5 dpm/g at 0.5 to 1.0 cm (Figure 4-30). The calculated sedimentation rate based on excess ^{210}Pb is about 0.04 ± 0.02 cm/y. Activities of ^{137}Cs were detectable to a depth of 3.25 cm, yielding a sedimentation rate of ~0.06 cm/y (Figure 4-30d), 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 E1 support the likelihood that sediments at depths >4 cm pre-date development.

Additional support for low sedimentation rates at stations P1 and E1 can be developed from data for river inputs of sediment. The Sagavanirktok River, the major river carrying sediments into this area, is estimated to have an annual sediment load of about 0.3 x 10^6 metric tons (Rember and Trefry 2003). The depositional area for this sediments in the coastal Beaufort Sea is at least 1000 km^2 to yield an estimated deposition rate of ~0.02 cm/y based on a sediment bulk density of 1.6 g/cm^3 ([0.3 x 10^{12} g dry sediment/1000 x 10^{10} cm^2] x [(1.6 g wet sediment/cm^3)/(2.6 g dry sediment/cm^3)]). As previously noted, the coastal Beaufort Sea in this area may be net erosional at this time (Reimnitz and Wolf, 1998).

In the Colville River delta at station 6G, the maximum activity of excess ^{210}Pb was 0.76 dpm/g to yield a calculated sedimentation rate of 0.04 ± 0.02 cm/year (Figure 4-30). The ^{137}Cs profile supports a sediment accumulation rate of ~0.06 cm/year (Figure 4-30f). Once again, the record of sediment input since the 1950s is sequestered in 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. This latter result is consistent with that of Naidu and others (2001) for the same area.

Concentrations of trace metals were determined for 104 samples from six cores (P1, E1, 3A, 6A, 6G and N2). Some variability in concentrations of metals was observed in each core (Table 3-1 and Figures 4-31 and 4-32), mainly due to variations in amounts of fine-grained sediment. However, the coefficient of variation (CV) for metal/Al ratios averaged ~10% in each of the six cores for Ni, V, Zn, Fe, Cr, Ba, Co, Tl, Be, Pb, Sb and Cu (Table 4-2). Such uniform metal/Al ratios support long-term deposition of sediments with uniform composition and no identifiable impact from diagenesis for these metals. These conclusions are further supported below through detailed evaluation of cores from stations P1 and 6G and from data for river suspended sediments.

In Prudhoe Bay (station P1), concentrations of Al and Fe follow parallel trends down core (Figure 4-31). Variations in concentrations of Al and Fe in the core result from shifts in the fraction of sand, silt and clay deposited during a given time period. Vertical distributions for Ba, Pb, Cr, V and Zn (Figure 4-31), as well as Be, Cu, Ni, Sb and Tl, follow trends similar to those observed for Al and Fe with the CVs for the metal/Al ratios all <8%. These vertical profiles support long-term deposition of sediments with no discernible shifts in metal/Al ratios or anthropogenic inputs. Metal concentrations and the metal/Al ratios for Fe, Al, Pb, Cr, Zn in suspended sediments from the Sagavanirktok River are plotted at the top of each vertical profile in Figure 4-31 and are coincident with values found in the surficial layers of the core. This continuity, in conjunction with the vertical profiles, supports no discernible diagenetic impacts in the vertical distributions for Ag, Ba, Be, Co, Cr, Cu, Hg, Ni, Pb, Sb, Tl, V and Zn.

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 relative to other sections in the core (Figure 4-31). Coincident with elevated levels of TOC in the surface layer of sediment are increased concentrations of As/Al and slightly lower levels of Mn/Al (Figure 4-31). Furthermore, the Mn/Al ratios are enriched in the layers at ~20 cm where concentrations of TOC are high. Diagenetic impacts on Mn in sediments are well studied and can lead to a variety of perturbations in concentrations of Mn (Trefry and Presley 1982; Gobeil and others 1997). In the top 0.5 cm of the core from Prudhoe Bay, concentrations of Mn are about double levels found in subsequent layers to a depth of 15 cm, yet the Mn and Mn/Al levels in the top 0.5 cm of sediment are about 25% lower than in river suspended sediment. One possible explanation for this observation is that particles deposited in the sediment lose Mn via reductive dissolution and diffusion of dissolved Mn^{2+} from the sediments to the overlying water column (e.g., Gobeil and others 1997). The onset of this process in Prudhoe Bay occurs in the top layer of sediment and reaches completion at depths >1 cm. Such behavior (reducing conditions in the top 1 cm) seems inconsistent with a sedimentation rate of 0.1 cm/year and may reflect processes that occur in a stagnant, thin (<1 m-thick) layer of water trapped under 2 m of ice during 8 months of the year. A similar impact on As levels is observed in this core. The loss of As from the sediments is related to release of As from sediments to the overlying water during diagenetic remobilization under reducing conditions (Farmer and Lovell 1986). Overall, diagenetic effects alter the vertical distributions of Mn, As and, to some lesser degree, Cd, but none of the other metals studied are impacted.

At station 6G, on the Colville River delta, post-development sediments appears to be restricted to the top 3 cm of the sediment column. No discernible differences in metal/Al ratios are observed for all metals except Mn (Figure 4-32). Available data for suspended sediments from the Colville River show that concentrations of Fe, Al, Pb and Cr are higher than observed for sediments at station 6G; however, the metal/Al ratios are similar (Figure 4-32). Overall, no indications of anthropogenic inputs of metals are found in the core from station 6G and only concentrations of Mn are impacted by diagenesis.

Metal data from other cores in the area of Pole Island (station 3A) to Northstar Island, including stations 3A, L2, E1 and N2, show similar trends with uniform metal/Al ratios throughout the cores (Table 4-2). In some cases, the surficial layer of sediment could be quite old as demonstrated by undetectable levels of ^{137}Cs and excess ^{210}Pb. Concentrations of Mn, As and Cd show varying amounts of distortion due to diagenetic effects. Overall, concentrations of Ag, Ba, Be, Co, Cr, Cu, Hg, Ni, Pb, Sb, Tl, V and Zn in cores from these five sites are unimpacted by anthropogenic inputs or diagenesis.

4.2 Hydrocarbons and Metals in Organisms

4.2.1 Organics (Hydrocarbons)

Concentrations of PAH in organisms were low and were indicative of residues of sediment in the tissues. No inputs of Northstar related activities were discerned in the hydrocarbon distributions of the bivalves or amphipods. The GC/FID chromatogram, PAH distribution plot, and triterpane extracted ion chromatogram profile of a representative tissue sample (station 3A bivalve - *Astarte*) are shown for 1999, 2000, and 2002 in Figures 4-33, 4-34 and 4-35, respectively.

The GC/FID results show trace levels of terrigenous plant wax hydrocarbons in the n-C24 through n-C32 range, a pattern similar to the surficial sediments. The PAH distributions show trace levels of a mixture of petrogenic PAH (e.g., 2- and 3-ring PAH and alkyl PAH) and pyrogenic PAH (e.g., 4-, 5-, and 6-ring PAH), and perylene. The low levels of PAH found in the tissue samples result in “truncated” PAH patterns, where some of the higher alkylated PAH compounds are below the detection limit of the analytical method. Nonetheless, the pattern of PAH in the tissues is generally similar to the surficial sediments when the influence of detection limits is accounted for. The sample with the highest Total PAH concentration (1999 L04 - *Anonyx* at 80 μg/Kg) evidenced an enrichment of several pyrogenic PAH (i.e., phenanthrene, fluoranthene, and pyrene) that was not observed in any of the other tissue samples.

The S/Ts in the tissue samples were near the detection levels in most samples, making interpretation of the patterns more difficult. In some samples, the presence of interferences from the natural fats and oils of the tissue matrix were also encountered (large peaks in Figure 4-33). Nevertheless, the triterpane distributions in the tissue samples generally corresponded to the patterns observed in the sediments, with a predominance of both biogenic and recent organic matter triterpane markers. Overall, the organic data set for the tissue samples reveals the presence of trace levels of hydrocarbons, generally similar in distribution to the sediments, indicating a positive relationship between the background sediment hydrocarbons and the body burdens of the clams and amphipods.

There was limited overlap for stations where tissue samples were collected in 1999, 2000 and 2002, thus allowing only a precursory evaluation of temporal data trends. A comparison of the PAH data in the 1999, 2000, and 2002 tissues, where stations and organism type coincide, shows similar concentrations of Total PAH (Figure 4-36). At the four Northstar stations where organisms (*Anonyx)* were collected for at least two years, the Total PAH concentrations were also similar (Figure 4-36). Additional tissue data corresponding to the ANIMIDA sampling locations are clearly necessary to further evaluate the hydrocarbon relationships in the bivalves and amphipods, and their possible use as sentinel organisms for bioaccumulation of hydrocarbon contaminants.

Of the few stations with suspect sediment hydrocarbon content (i.e., stations L08, 5E, and 5D), corresponding biota samples were only collected at station L08. The clam (*Astarte*) samples collected at station L08 have hydrocarbon concentrations and distributions similar to the *Astarte* samples collected from stations 3A, 5H, and L09. Thus, the sediment anomaly observed at station L08 was not reflected in the associated biota tissue data.

4.2.2 Metals

Data from 1986, 1989, 1999, 2000 and 2002 are now available for Ba, Cd, Cr, Cu, Fe, Pb, V and Zn in amphipods (*Anonyx*) and clams (*Astarte*) from sites in the area of the BSMP that is being studied during the ANIMIDA program. These results provide a temporal perspective for monitoring trends in body burdens of selected metals over time. During 1999, 2000 and 2002, concentrations of 10 additional metals (Ag, Al, As, Be, Co, Hg, Mn, Ni, Sb and, Tl) were determined in the same two species of organisms to broaden the spectrum of analytes. One primary goal of the organism component of the study is to observe cumulative contaminant inputs from industrial activity in the coastal Beaufort Sea. Variability in concentrations of a given metal within or among years controls the sensitivity of that metal as a discriminator of contamination. In this regard, the discussion below focuses on variability in metal concentrations for amphipods and clams on a site-by-site and inter-annual basis.

Among the metals for which data are available for all four to five years, concentrations of Cu and Zn in the amphipod Anonyx are highest, yet, relatively uniform with average coefficients of variation (CV = [mean/standard deviation] x 100) of about 15% for both metals for the five different years (Figure 4-37). Levels of these two essential metals are controlled by osmoregulation within the organism and anomalous body burdens for these metals may imply a physiological imbalance. None is observed at this time. Concentrations of Pb, a non-essential metal, are low, yet, reasonably uniform with an average CV of ~20% for 1989, 1999 and 2000 (Figure 4-37). Higher variability (CV = 50%) was observed for Pb in 2002 (Figure 4-37). The importance of a low CV to the ANIMIDA program is that any changes that occur in metal concentrations in organisms over time must be statistically different from the baseline results. Thus, direct observation of a difference over time is directly related to the CV for a particular analyte.

The data for 1999, 2000 and 2002 for Ag, Al, As, Be, Co and Fe in *Anonyx* (Figure 4-38) as well as Hg, Mn, Sb and Tl (Figure 4-39) show marked similarity among years. Overall, the metal data for the amphipods provide a useful baseline for monitoring shifts in concentrations over time.

Mean concentrations of Ba, Cu, Pb, V and Zn in clams (*Astarte sp.*) sampled during 1986, 1989, 1999, 2000 and 2002 are relatively uniform (average CV<15%) during some years as discussed below (Figure 4-40). Such uniformity is encouraging with respect to using body burdens for metals as a long-term indicator of metal availability. However, the CV for a given metal in an individual year is sometimes large (>50%). Such variability limits statistical discrimination of changes in metal concentrations. For example, the CV for the six pooled samples of Astarte for 1989 was ~50% for Ba and Pb and 75% for Cd. In contrast, the CVs for the four-pooled samples of Astarte from 1999 were 15% for Ba, 9% for Pb and 17% for Cd. Some anomalous points that lead to high values for the CV can be partially explained, whereas others may be due to natural variability as described below.

Direct comparisons of metal levels in the few sediment samples where positive anomalies in metal concentrations were observed and metal levels in the biota are limited. However, no indication of links between metal levels in sediment and organisms were found. For example, an elevated Zn level was found in sediment at station 5H and higher Ba was found in sediment from station L08. However, no anomalous values for Zn or Ba were observed in clams *(Astarte)* from the respective stations.

One factor that sometimes introduces variability into concentrations of some elements in clams is the amount of sediment contained in the gut. Samples from this study were not depurated, nor were the guts removed. Therefore, any sediment that remained in the gut is incorporated into the value reported for a metal concentration for that organism; this may yield higher values for the CV. For example, the large CV for Ba in the 1989 data for *Astarte* (Figure 4-40) is partly due to a Ba level of 40.4 µg/g (overall mean was 24 µg Ba/g) in one sample from station 6D where the Fe concentration was 80% higher than the average for the other samples. If half of this Fe in the *Astarte* is due to sediment in the gut, then Ba associated with sediment can account for >40% of the Ba in the clam. The same sample from station 6D also contained V at levels almost double those in the other five samples and this excess V is most likely bound to sediment. The elements influenced by excess loading of sediment are those that are present at very low levels in the organism relative to the sediment. In this study, the metals most affected by sediment are Ba, Be, Co, Pb, Sb, Tl and V. For most of the remaining elements (Ag, As, Cd, Cu, Hg, Mn, and Zn), natural metal levels in the clam are high enough to minimize the influence of excess amounts of sediment.

Comparisons among the 1986, 1989, 1999, 2000 and 2002 data for metals in clams also are limited by geographical differences in sample location because *Astarte* were collected at only two common stations during 1989 and 1999 (stations 3A and 5H). However, four stations (L08, L09, 3A and 5H) were sampled during 1999 and 2000.

4.3 Caged Mussels and SPMDs

Transplanted, caged mussels and SPMDs were deployed in three replicate moorings adjacent to Northstar Island and three at a reference site to the east of the study area, as previously described in Section 2. This pilot study, performed during the summer 2002 field survey, represented the first known successful caged bivalve/SPMD deployments in this region.

4.3.1 SPMDs

Only hydrocarbon measurements were determined for the SPMDs, as metals do not readily diffuse into the SPMD membranes. The SPMDs from the reference site and Northstar showed no significant differences in most of the key PAH parameters measured. The total PAH concentrations in the SPMDs were low (470 – 540 ng/SPMD). An evaluation of the PAH distribution in the SPMD samples (Figure 4-43) reveals a composition of primarily petroleum PAH in both the Northstar and reference SPMDs, mixed with trace levels of pyrogenic PAH. The observed PAH distribution is similar to the documented PAH signature found in the sediments of the region. There is a slight enrichment of the 2-ring naphthalenes versus the 3-ring phenanthrenes and dibenzothiophenes, which indicates that, some of the more water-soluble 2-ring PAH may have diffused into the SPMD membranes directly from the water column in the dissolved phase. Whereas the primary mechanism of PAH assimilation into the lipid matrix of the device appears to have been direct diffusion from the suspended sediments in the water column.

The composition of combustion related or pyrogenic PAH from both the reference and Northstar SPMDs appears very similar (Figure 4-43) but it should be noted that there is an apparent significant increase in the pyrogenic PAH in the Northstar samples. However, the pyrogenic PAH are found at such trace levels in the SPMDs it is difficult to determine whether this result represents an actual trend or is simply an artifact of the trace PAH analysis in these samples.

4.3.2 Caged Mussels

4.3.2.1 Organics

The caged mussels from the Northstar and reference deployments showed no significant differences in most of the key hydrocarbon parameters measured. The PAH concentrations in the mussels were very low (13 – 17 ng/g total PAH), however, the concentrations were substantially higher than the pre-deployment reference levels indicating that the mussels bioaccumulated trace levels of hydrocarbons on a regional basis.

An evaluation of the PAH distribution in the mussel samples (Figure 4-44) reveals a similar composition of petroleum PAH in both the Northstar and reference mussels, mixed with perylene and lower levels of pyrogenic PAH. The observed PAH distribution is consistent with the known hydrocarbon background pattern found in the sediments, indicating the PAH were probably accumulated during the active filtering of water by the organisms. This is further supported when compared to the pre-deployment PAH distribution where perylene is absent.

The only source of perylene to the mussels is natural background, which is well documented in the region. Although only trace levels of combustion related pyrogenic hydrocarbons were found in all samples, it should be noted that the Northstar mussels had significantly higher levels than the reference mussels. This result appears to corroborate a similar trend in the associated SPMDs. However, whether the origin of the subtle change in pyrogenic hydrocarbons is associated with natural variability, Northstar Island activities, or is a result of a more widespread oil field phenomenon remains an area for future investigation.

4.3.1.2 Metals

No significant differences were observed between concentrations of metals in samples from the reference site in the coastal Beaufort Sea versus Northstar Island (Table 3-17). In fact, the mean values agreed within 5% for most metals. Some shifts in concentrations were observed between the predeployment site and the Beaufort Sea sites. For example, Ba in the mussels from the pre-deployment site was 6.5 µg/g relative to 18 µg/g in the Beaufort Sea. This difference is probably related to differences in ambient levels of dissolved Ba in the two systems and supports the contention that the organisms were actively filtering water. Similar shifts were observed for Be and Tl (Table 3-17).

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

Metal	ERL (μg/g)	ERM (μg/g)	Maximum value this study (μg/g)	Average Continental Crust (g/g)**	Sites with values >upper prediction interval (UPI)	Sites with values > UPI and >ERL
Ag	1.0	3.7	0.44	0.07	N13 (99) N14(99) N22 (00)	none
As	8.2	70	28.4	1.7	5D (99)*	5D (99)*
Cd	1.2	9.6	0.82	0.1	5D (99)*	none
Hg	0.150	0.710	0.200	0.04	5D (99)* N10 (00) N17 (00)	5D (99)*
Pb	46.7	218	22.3	14.8	5D (99)*	None
Zn	150	410	131	65	5H (99)	None

*One of three samples analyzed from the somewhat heterogeneous sediment from this site near West Dock.
**Wedepohl (1995).

Table 4-2. Summary of Results for Metal/Al Ratios and Related Coefficients of Variation (CV) in Sediment Cores

The sediment core samples were collected from the following locations: Prudhoe Bay (n = 29), Endicott Island (n = 13), Pole Island 3A (n = 10), Colville Delta (6A, n = 23; 6G, n = 14), Northstar Island (N2, 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 each of 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 ± 200	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

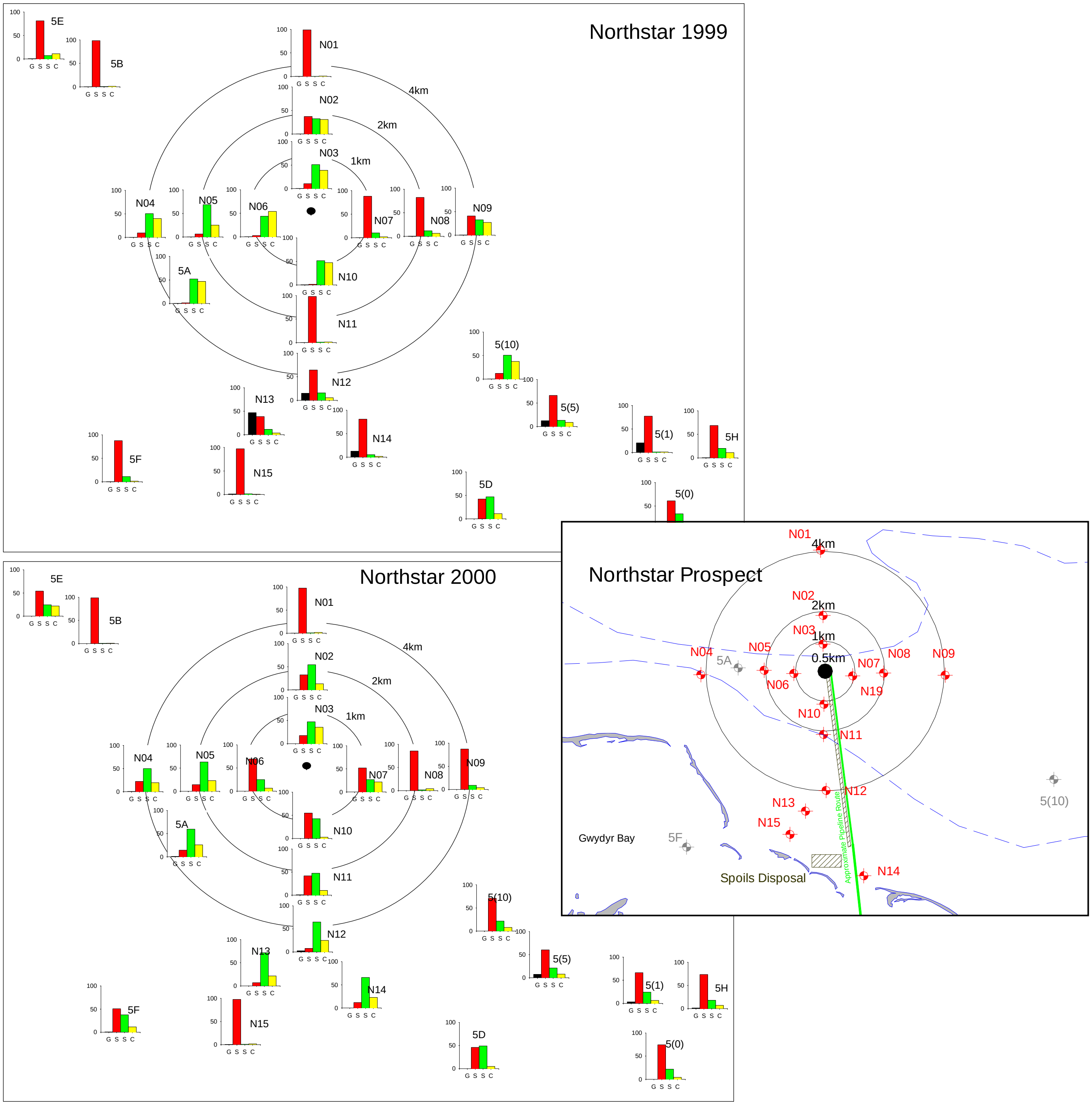
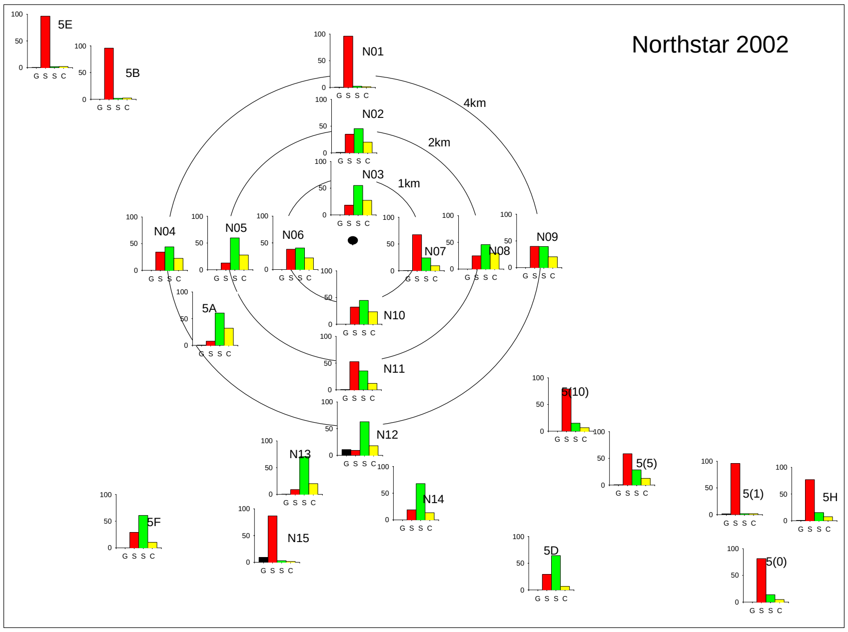


Figure 4-1. Map identifies sampling sites and histograms show grain size distribution as percent gravel (black bar), sand (red bar), silt (green bar) and clay (yellow bar) for sediment samples collected during 1999 and 2000



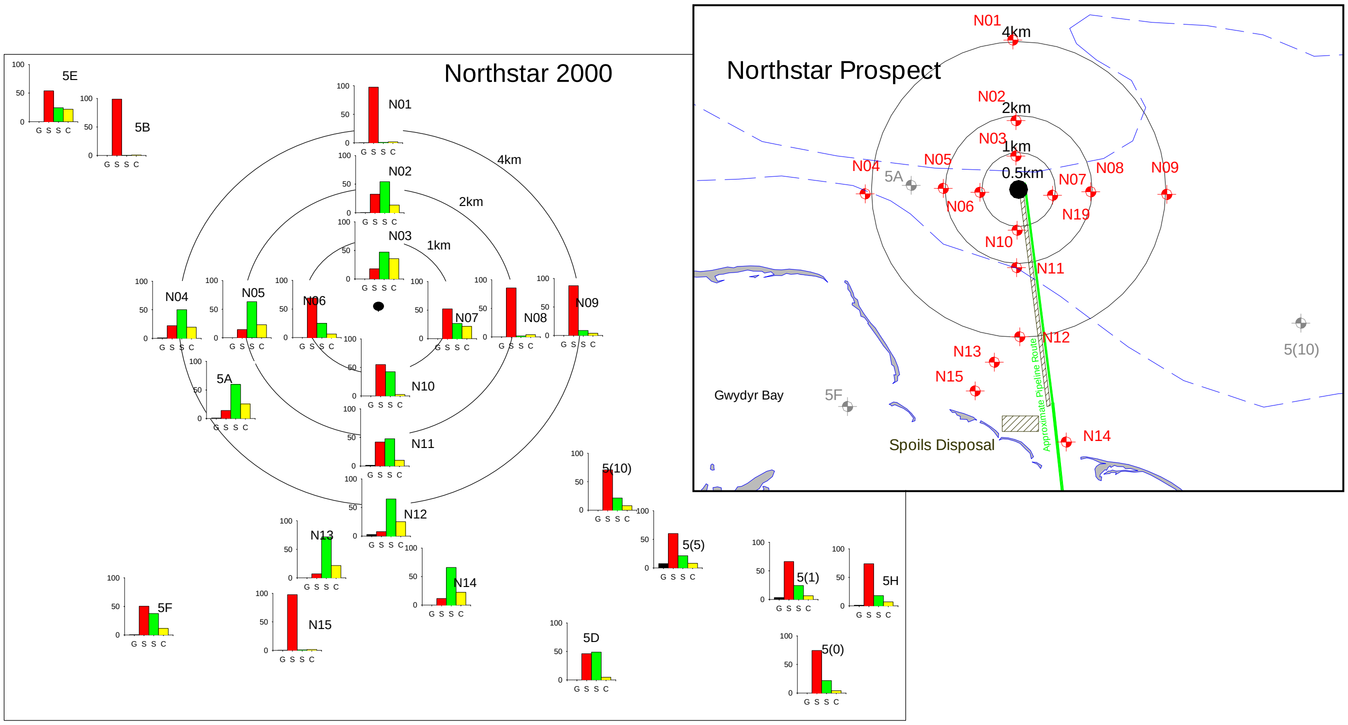


Figure 4-2. Map identifies sampling sites and histograms show grain size distribution as percent gravel (black bar), sand (red bar), silt (green bar) and clay (yellow bar) for sediment samples collected during 2002 and 2000

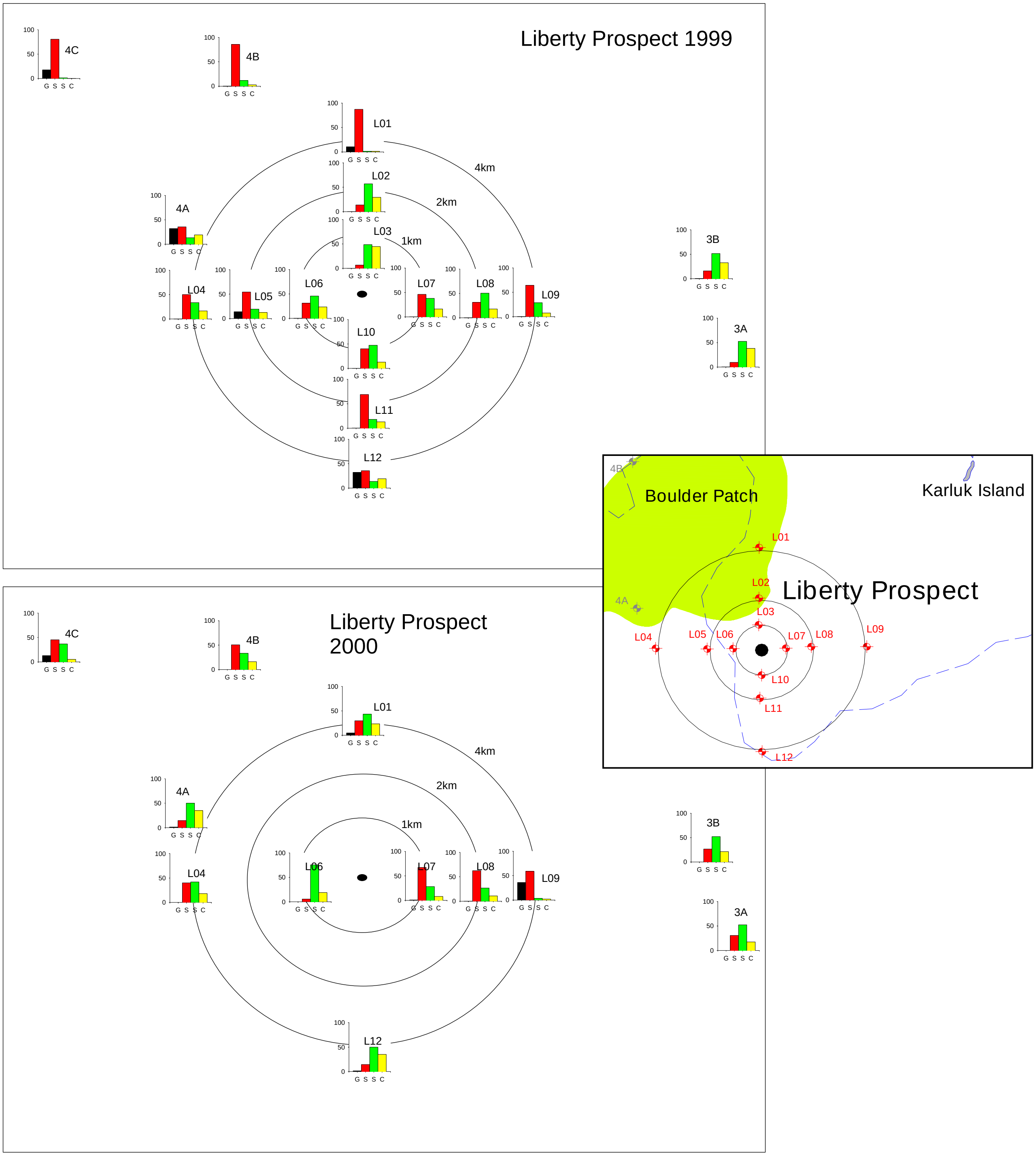


Figure 4-3. Map identifies sampling sites and histograms show grain size distribution as percent gravel (black bar), sand (red bar), silt (green bar) and clay (yellow bar) for sediment samples collected during 1999 and 2000

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

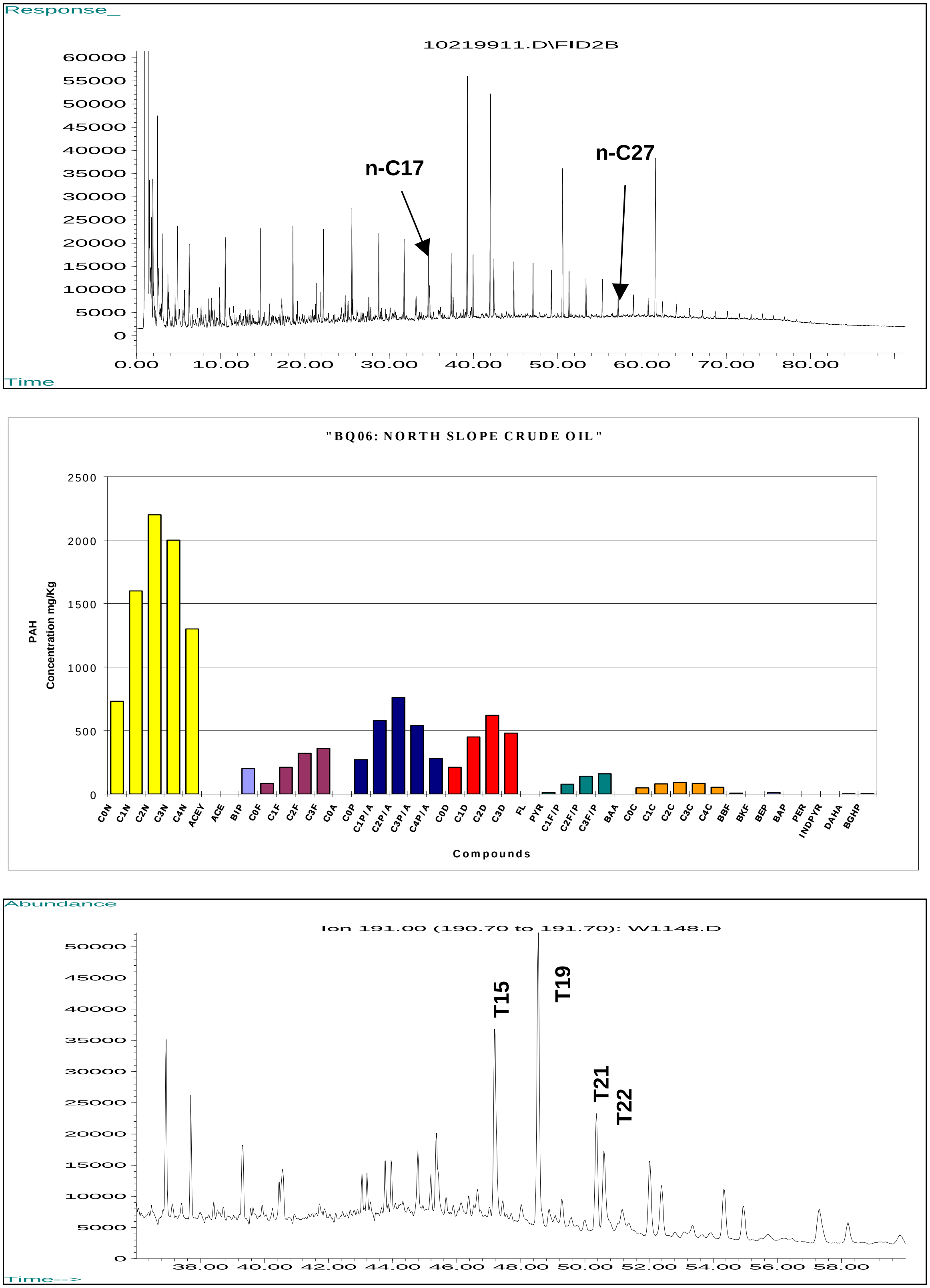


Figure 4-5. Northstar Oil – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

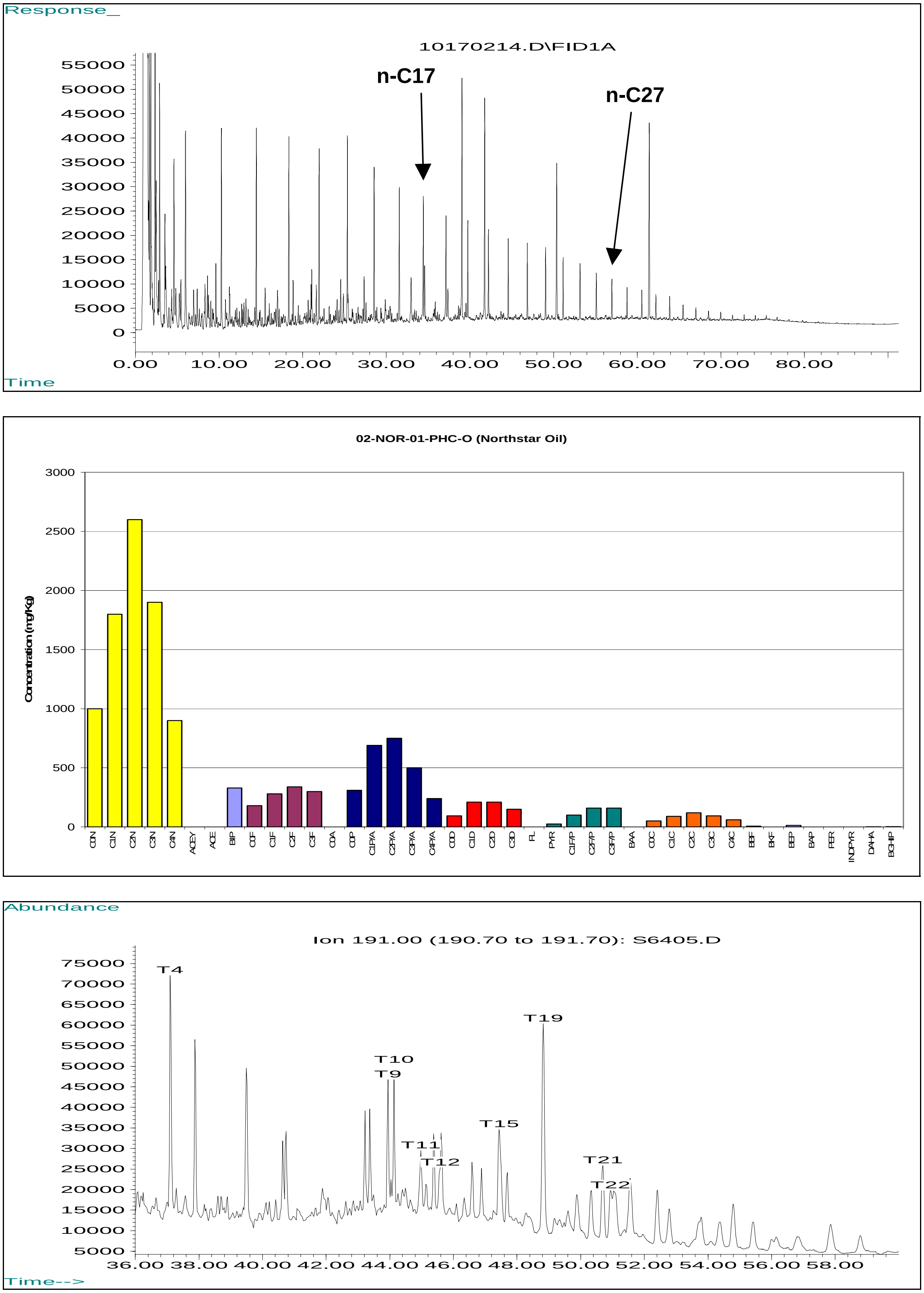


Figure 4-6. Colville River Sediment, Year 1999 – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

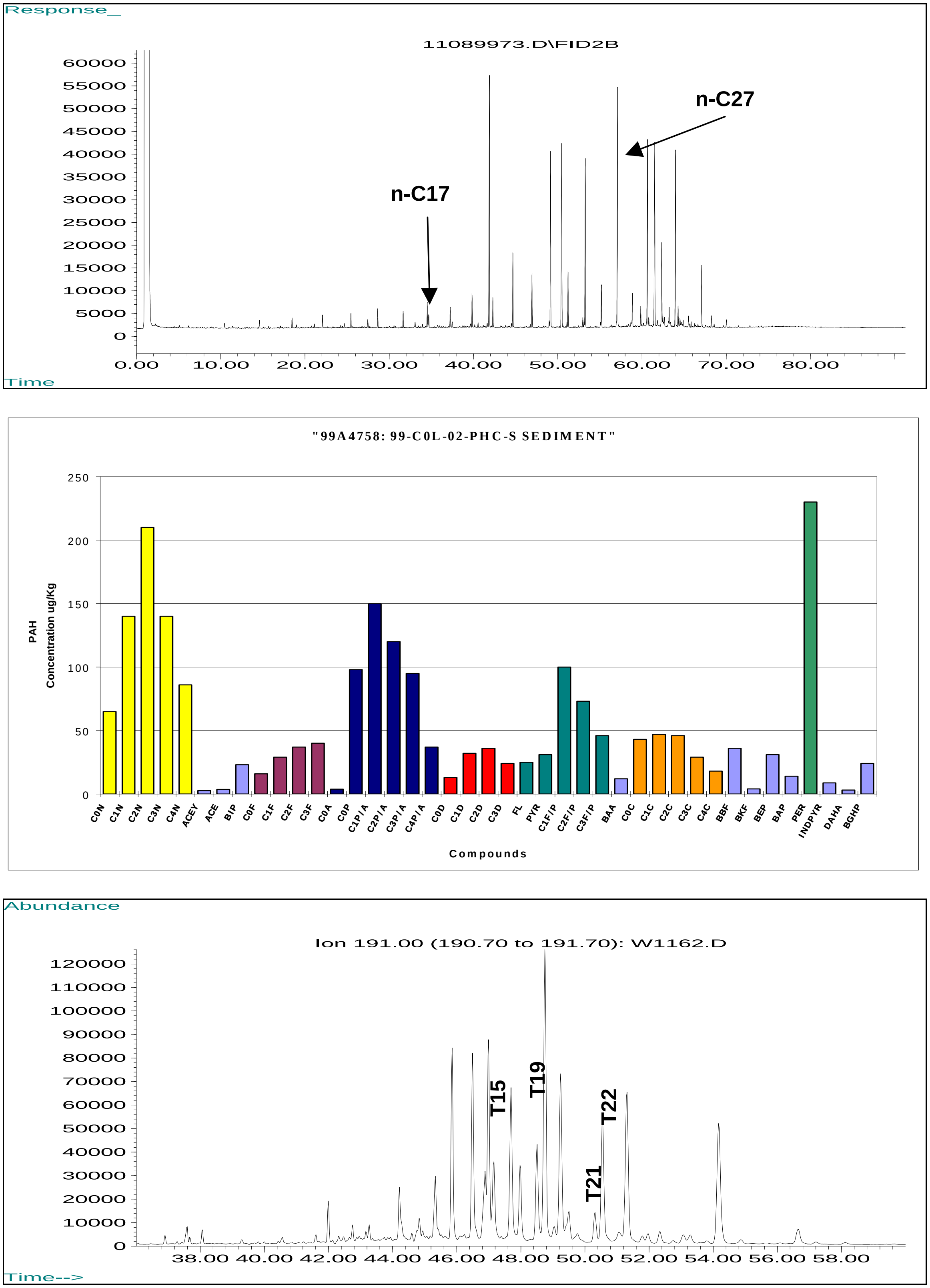


Figure 4-7. Northstar Station 6 Sediment, Year 1999 – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

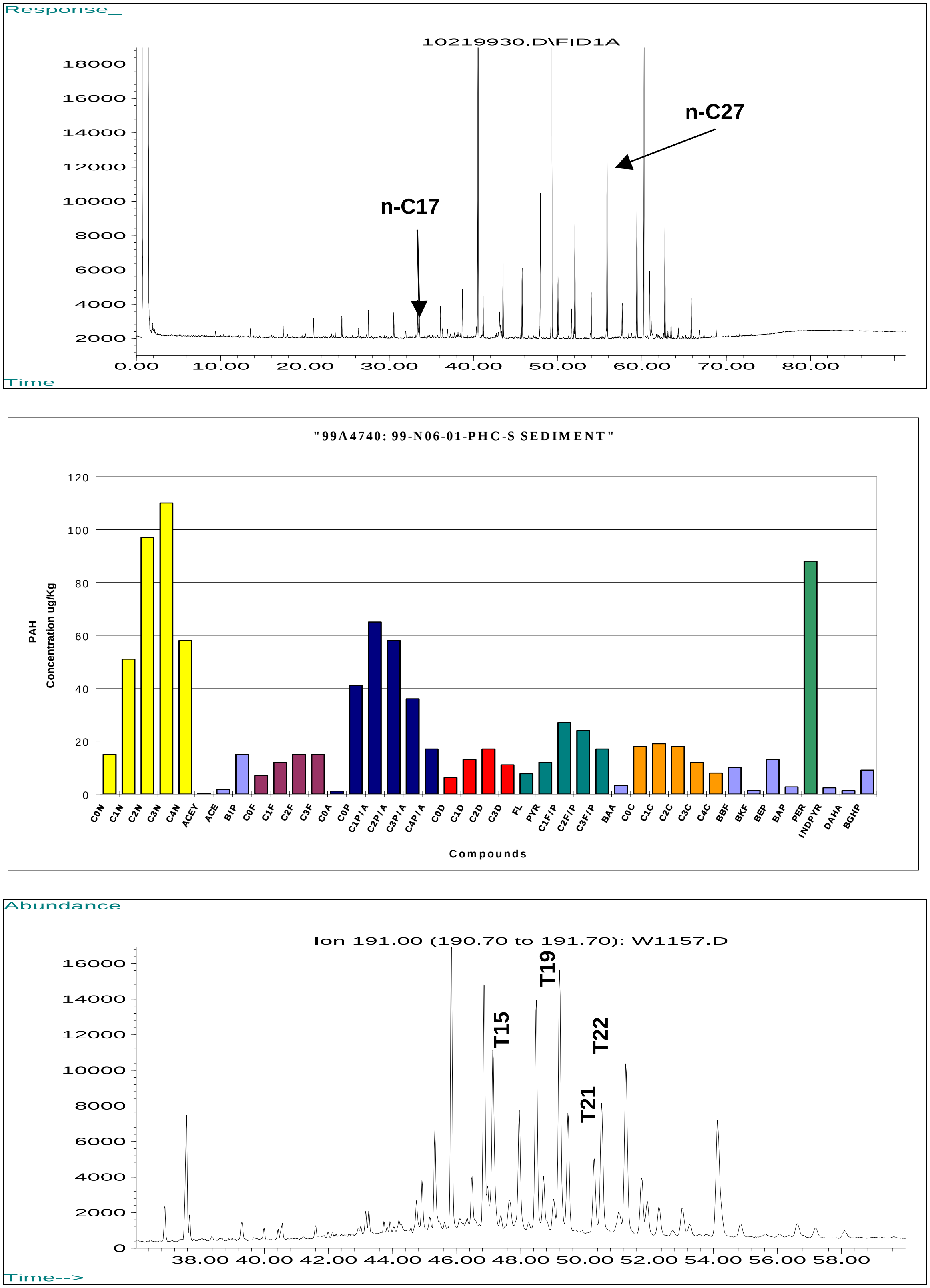
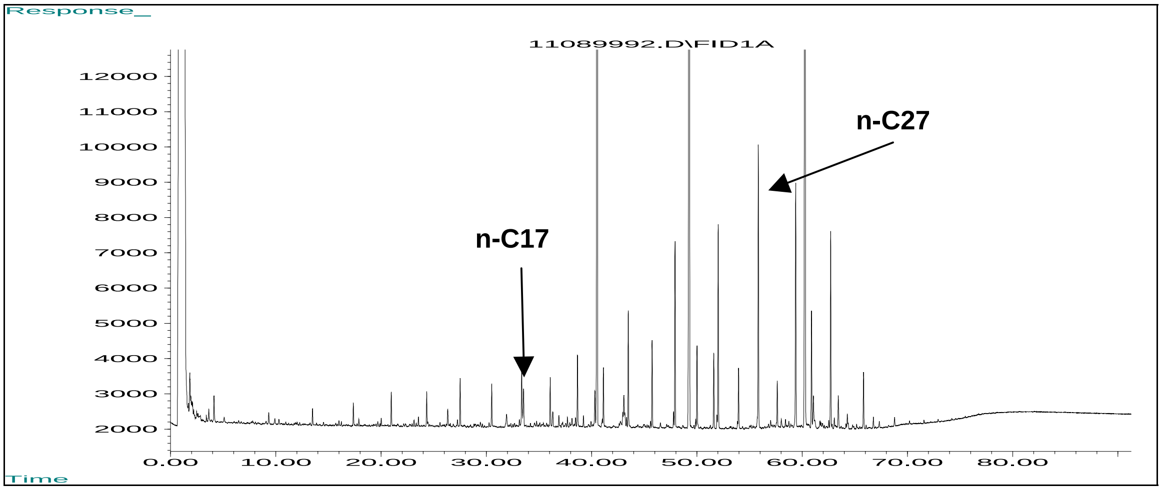
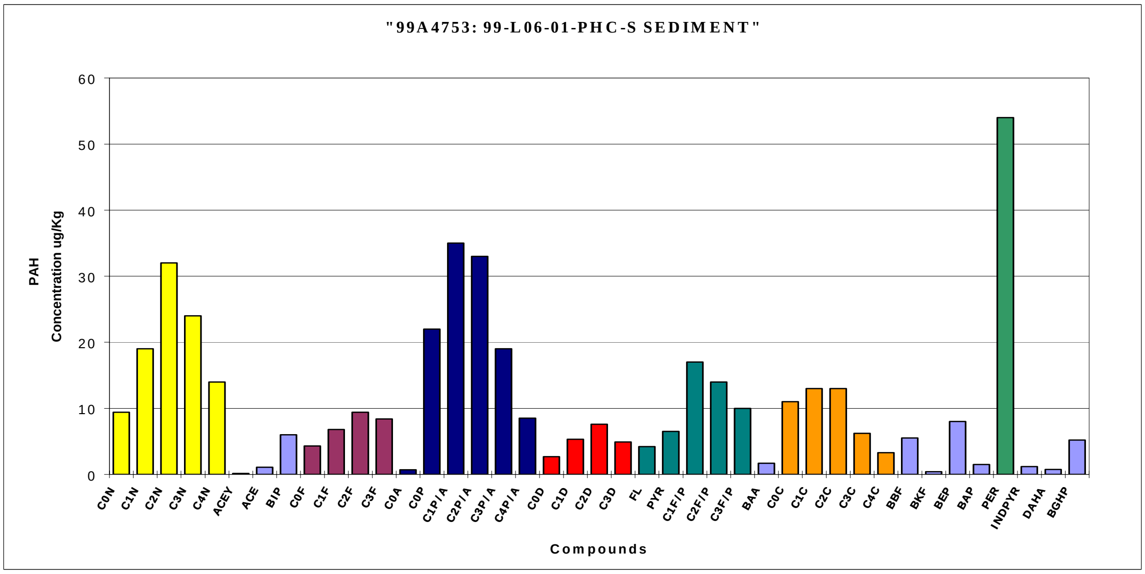


Figure 4-8. Liberty Station 6 Sediment, Year 1999 – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)





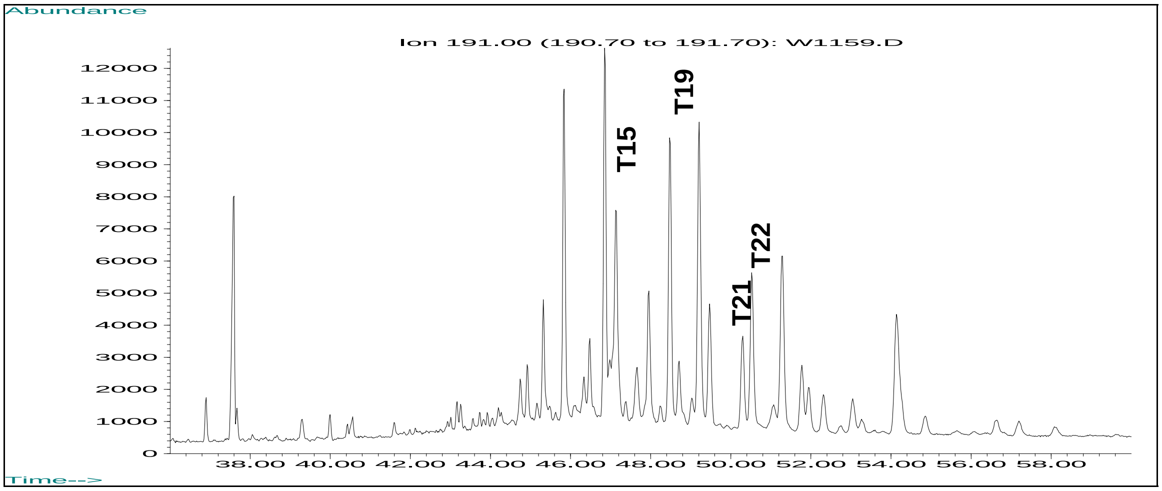


Figure 4-9. Station 3A Sediment, Year 1999 – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

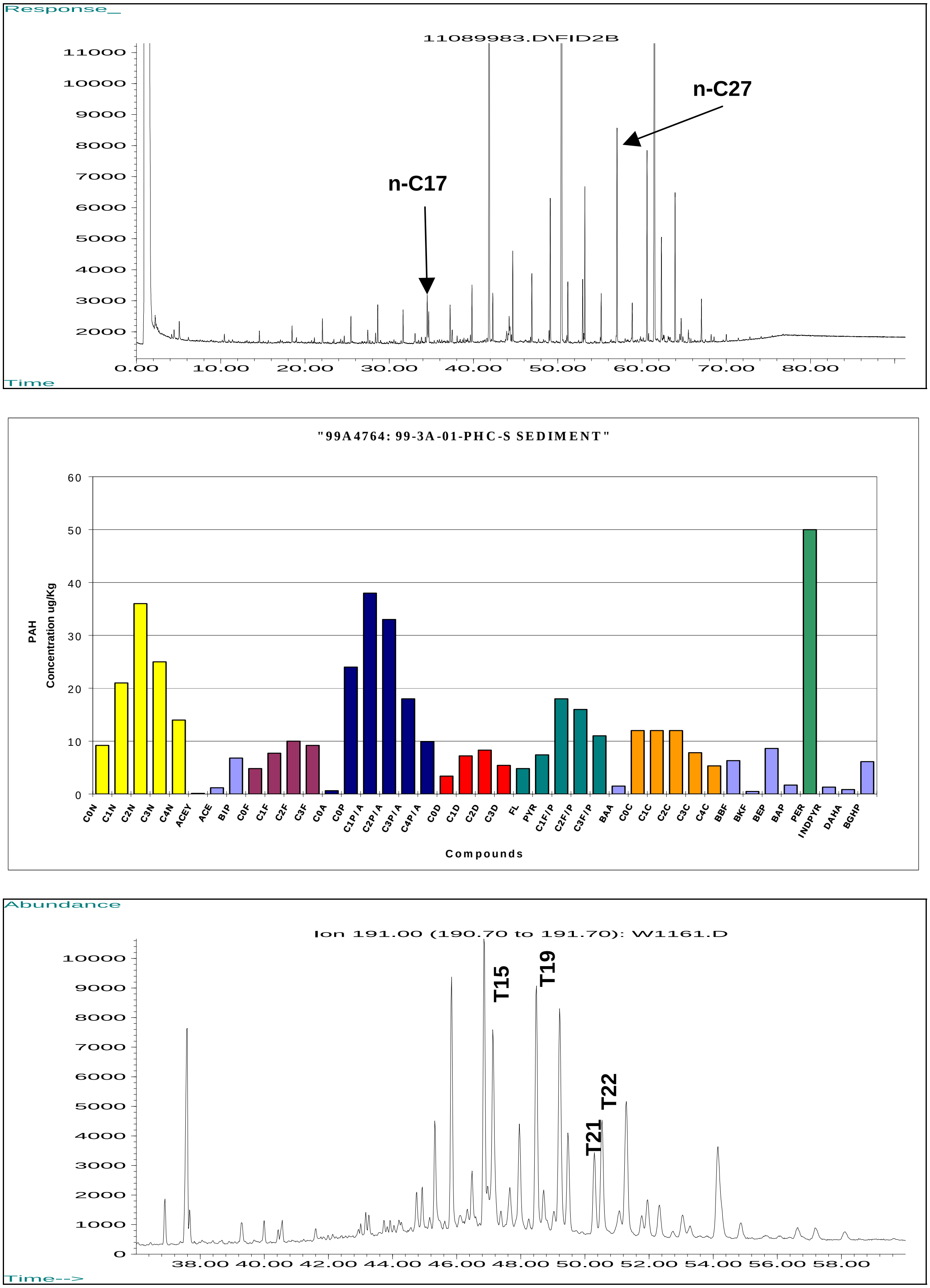


Figure 4-10. Station L08 Sediment, Year 1999 – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

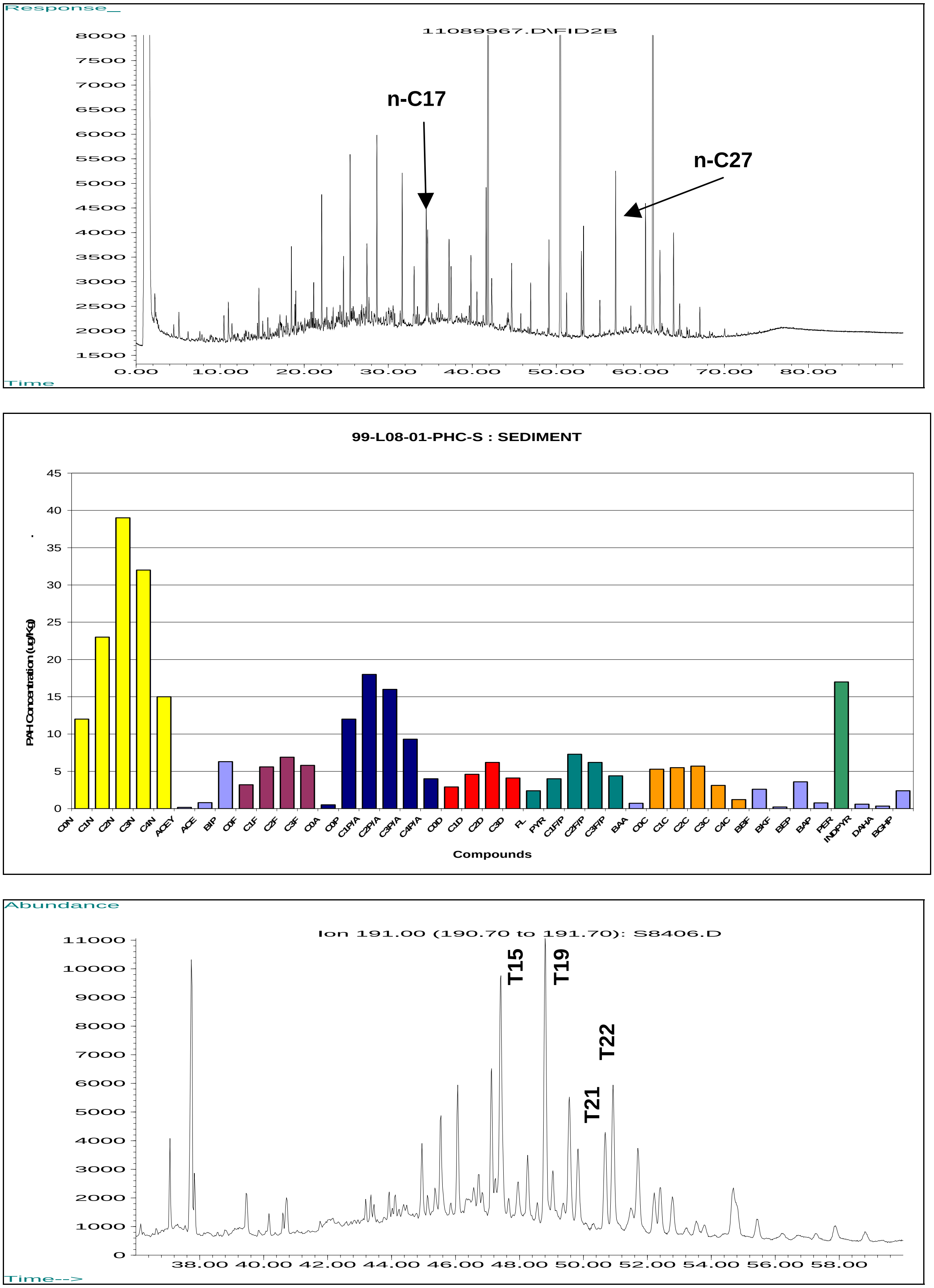


Figure 4-11. Station 5D Sediment, Year 1999 – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

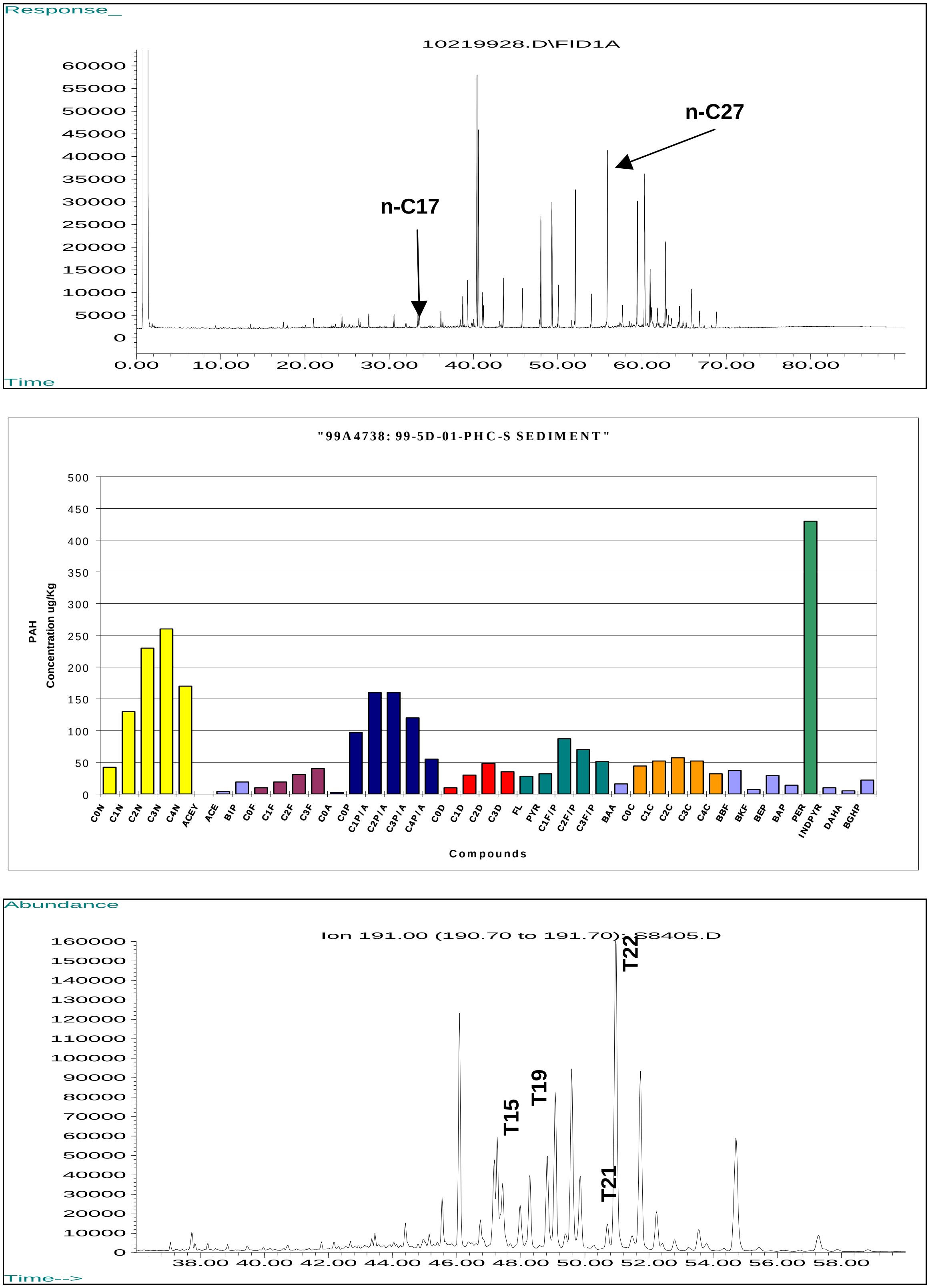


Figure 4-12. Northstar Station N06 Sediment, Year 2000 – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

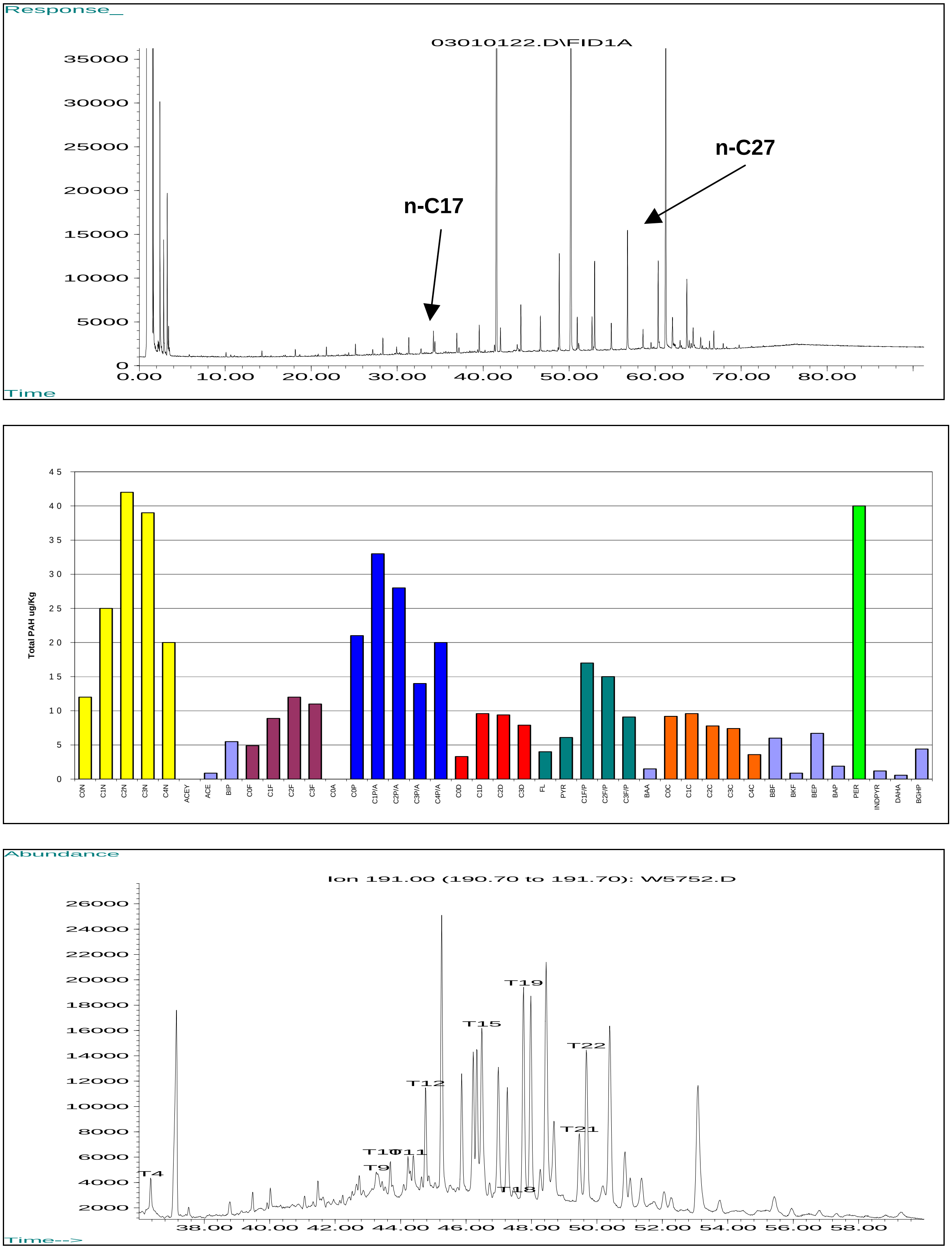


Figure 4-13. Liberty Station L08 (Rep 3) Sediment, Year 2000 – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

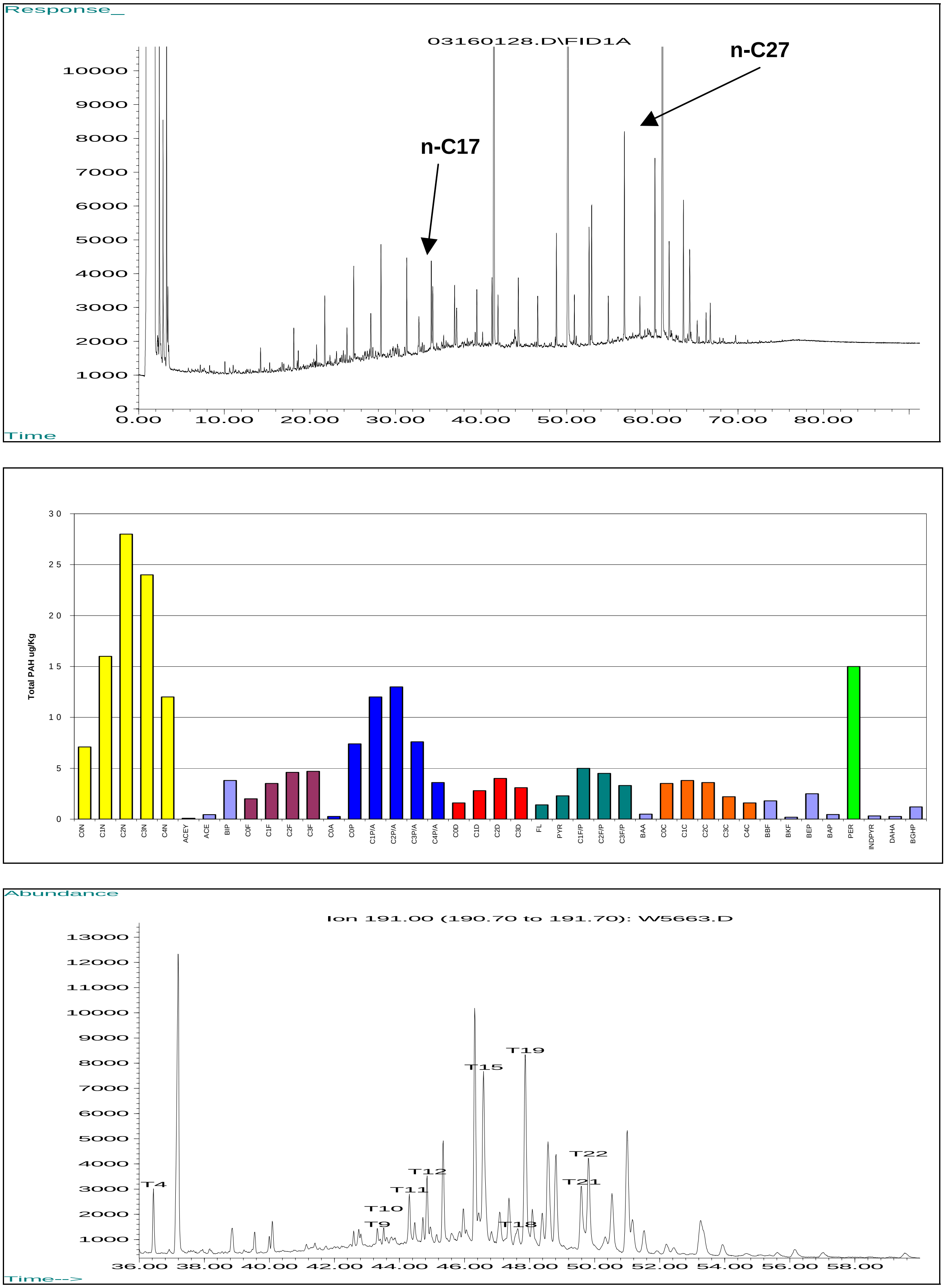


Figure 4-14. Northstar Station N06 Sediment, Year 2002 – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

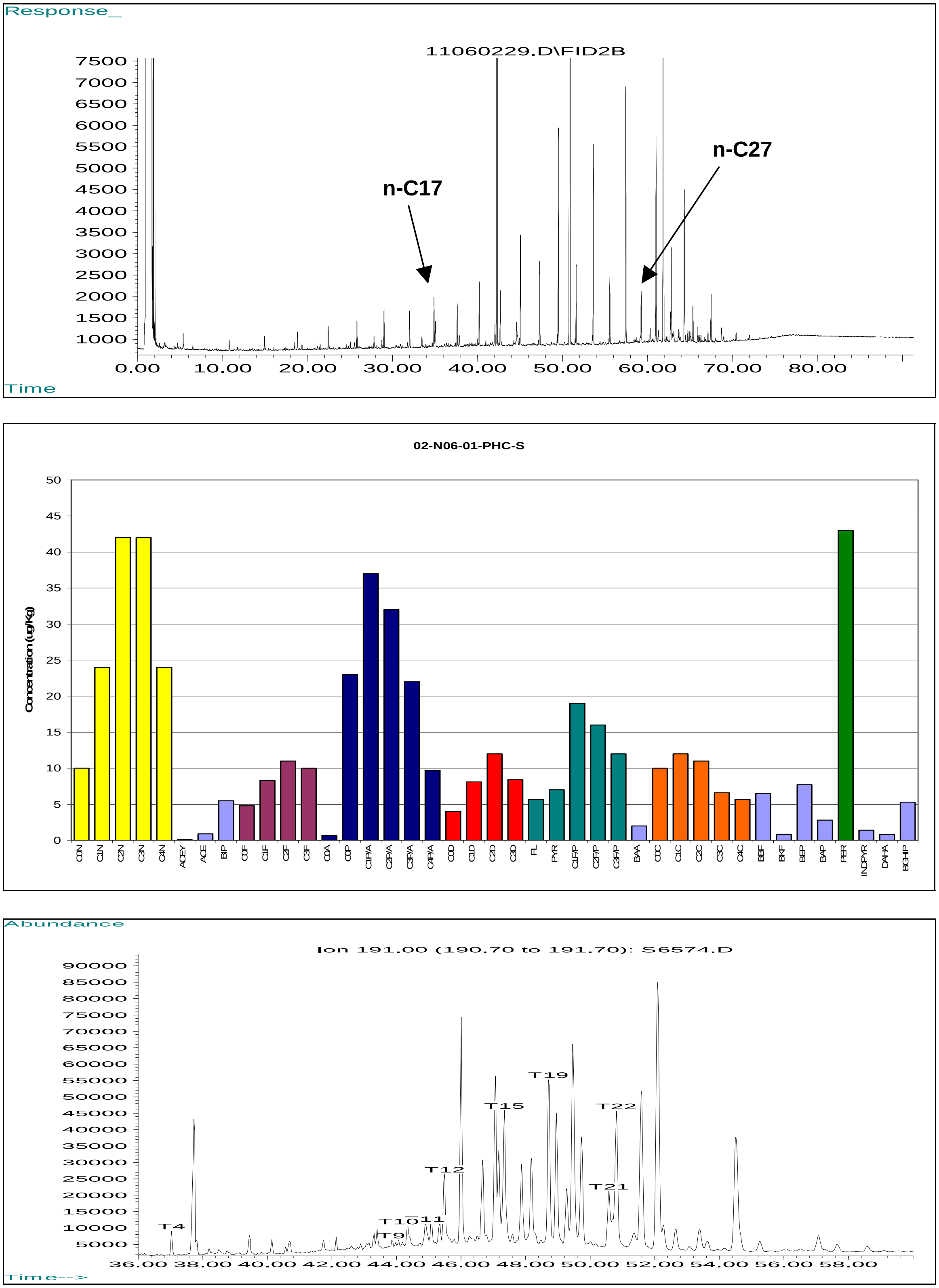
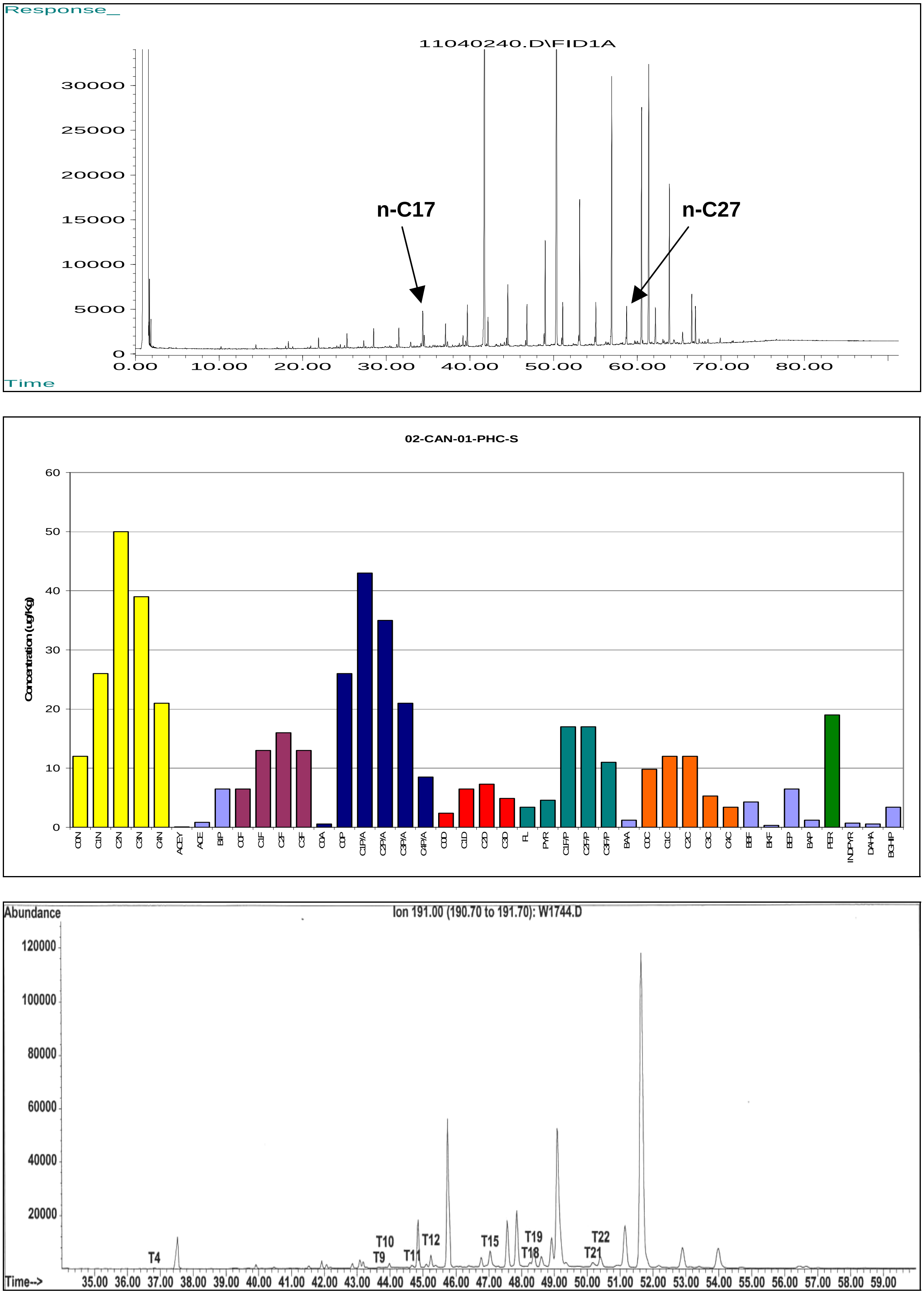


Figure 4-15. Canning River Sediment, Year 2002 – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)



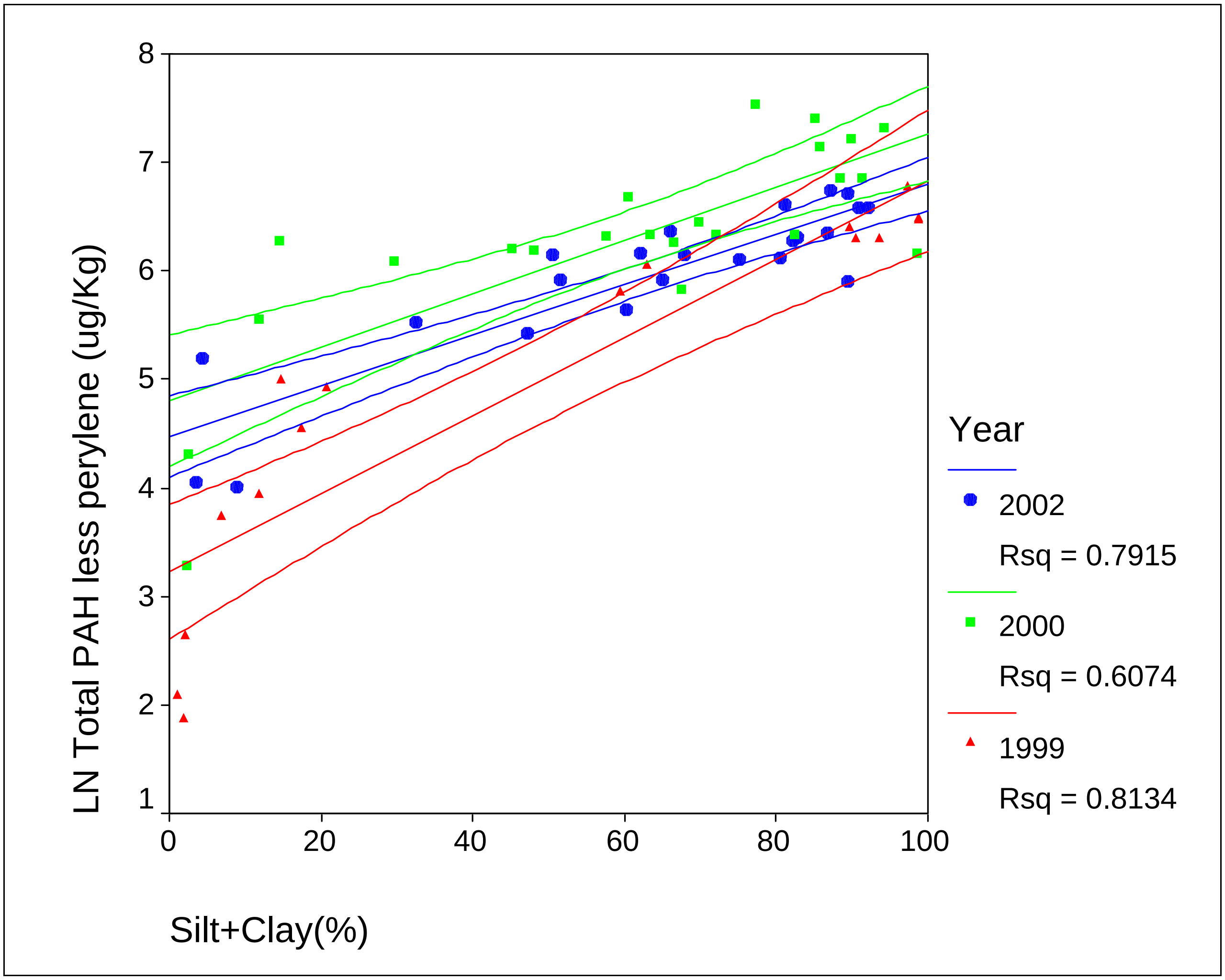


Figure 4-16. Scatterplot of Silt + Clay Results versus Total Polynuclear Aromatic Hydrocarbons Less Perylene for Northstar Surficial Sediment Samples in 1999, 2000, and 2002

The lines, Rsq, and 95% mean prediction intervals are from linear regression and related statistical calculations for Northstar stations by year.

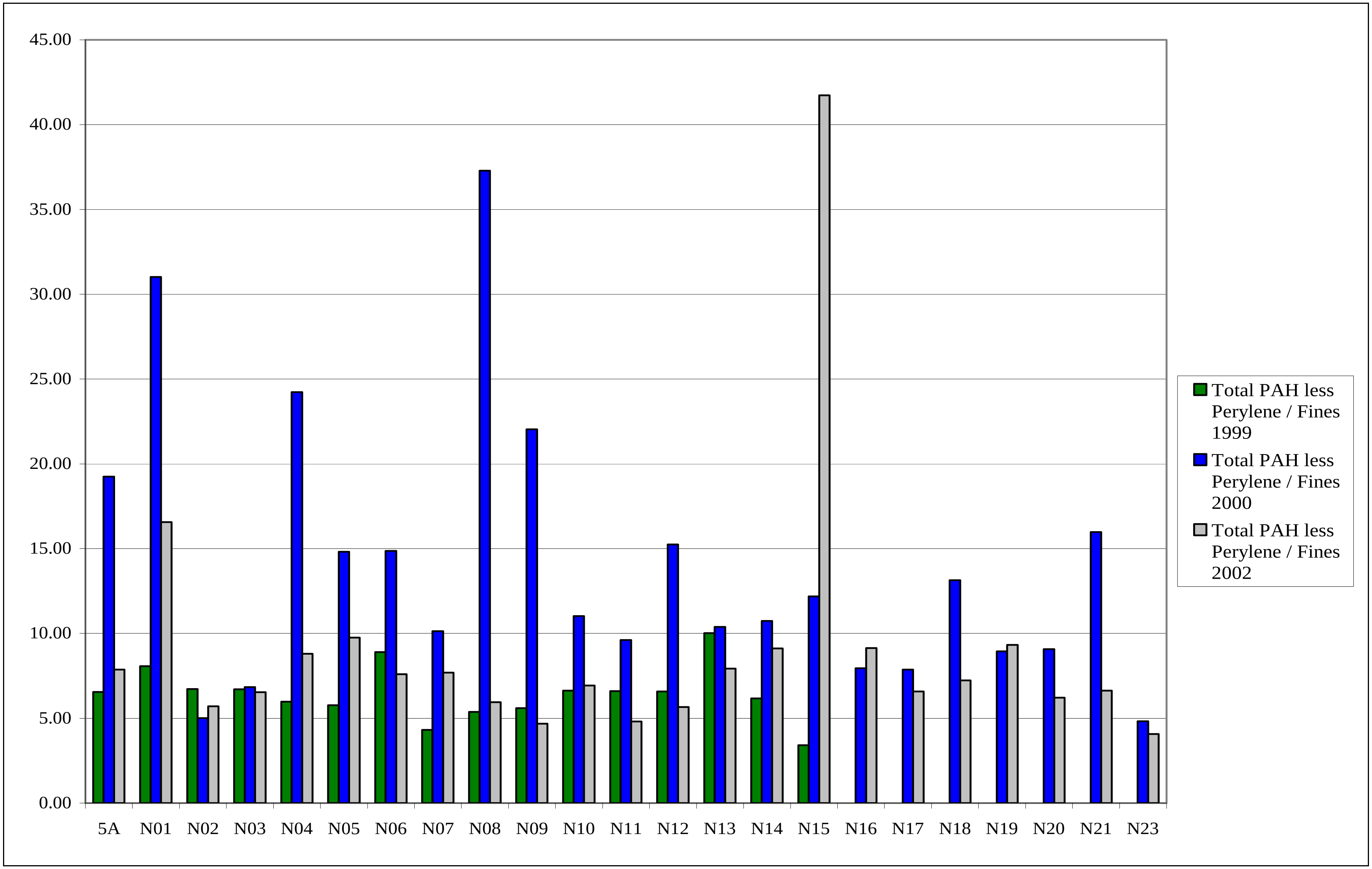


Figure 4-17. Total Polynuclear Aromatic Hydrocarbon less Perylene Concentrations normalized to Fines for all 1999, 2000, and 2002 Northstar stations

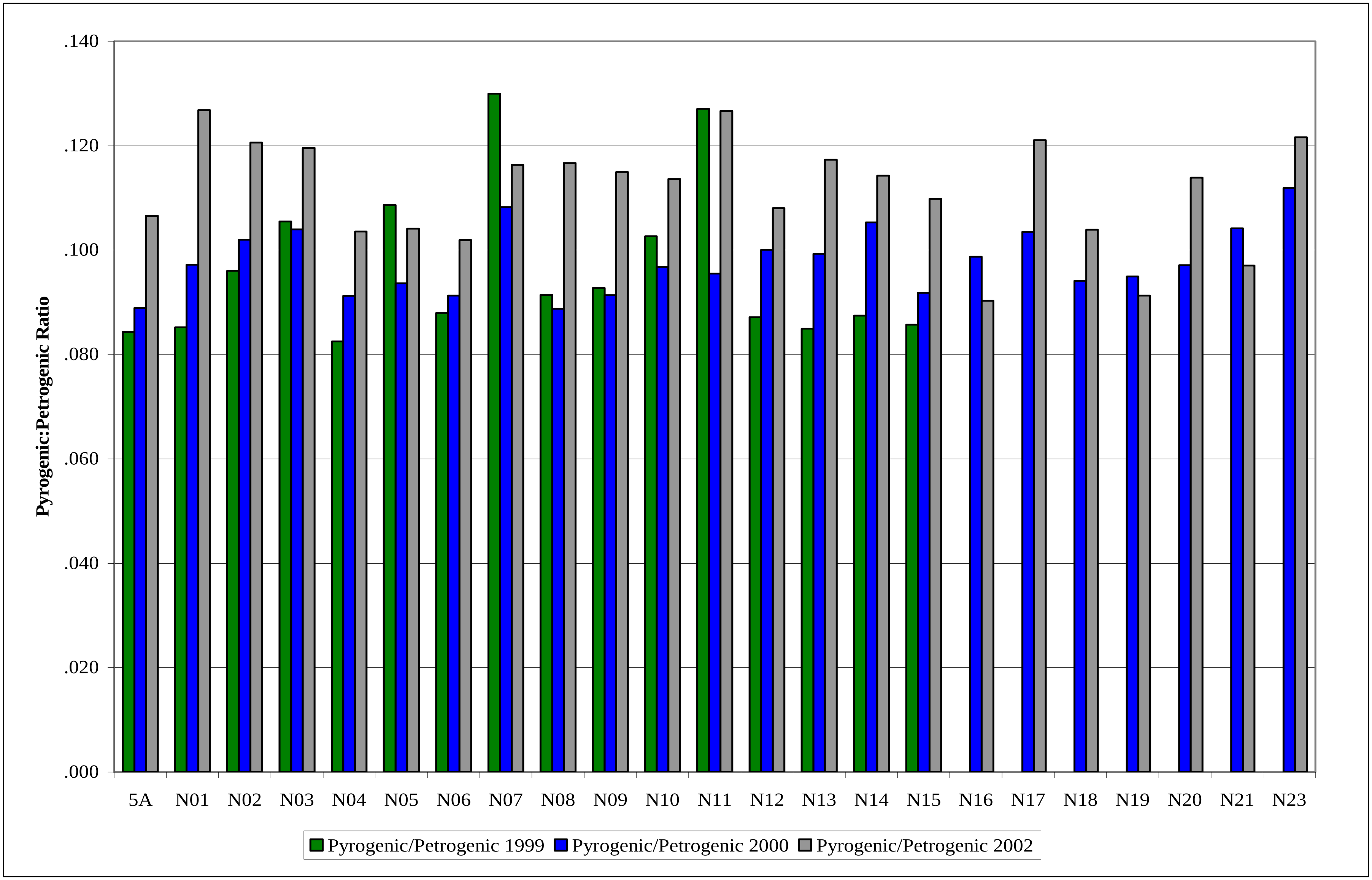


Figure 4-18. Pyrogenic:Petrogenic Ratios of Northstar Surficial Sediment Samples for 1999, 2000, and 2002

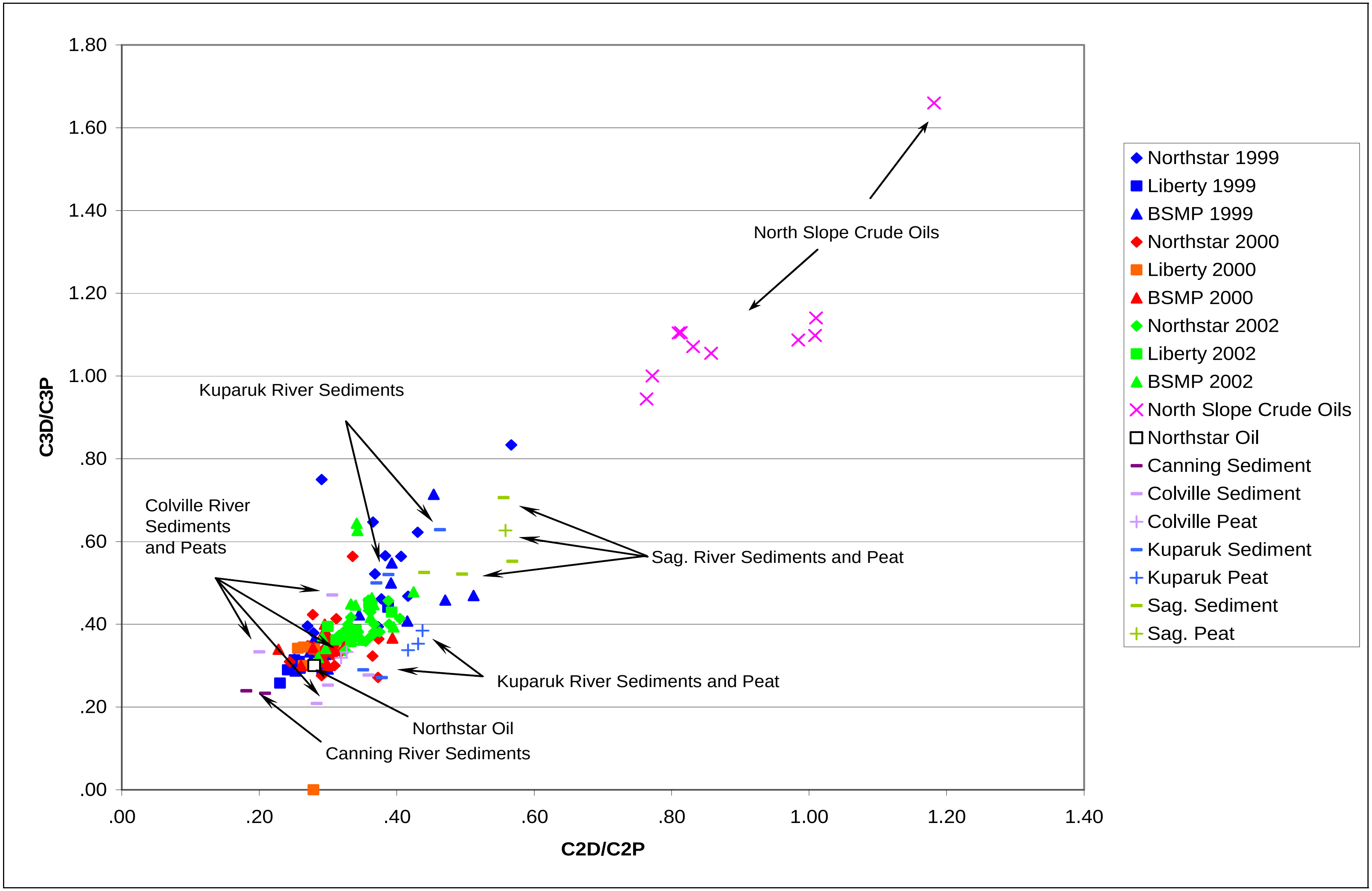


Figure 4-19. Double Ratio Source Plot of C2D/C2P vs C3D/C3P for BSMP, Liberty, Northstar, and River Sediment Samples for 1999, 2000, and 2002

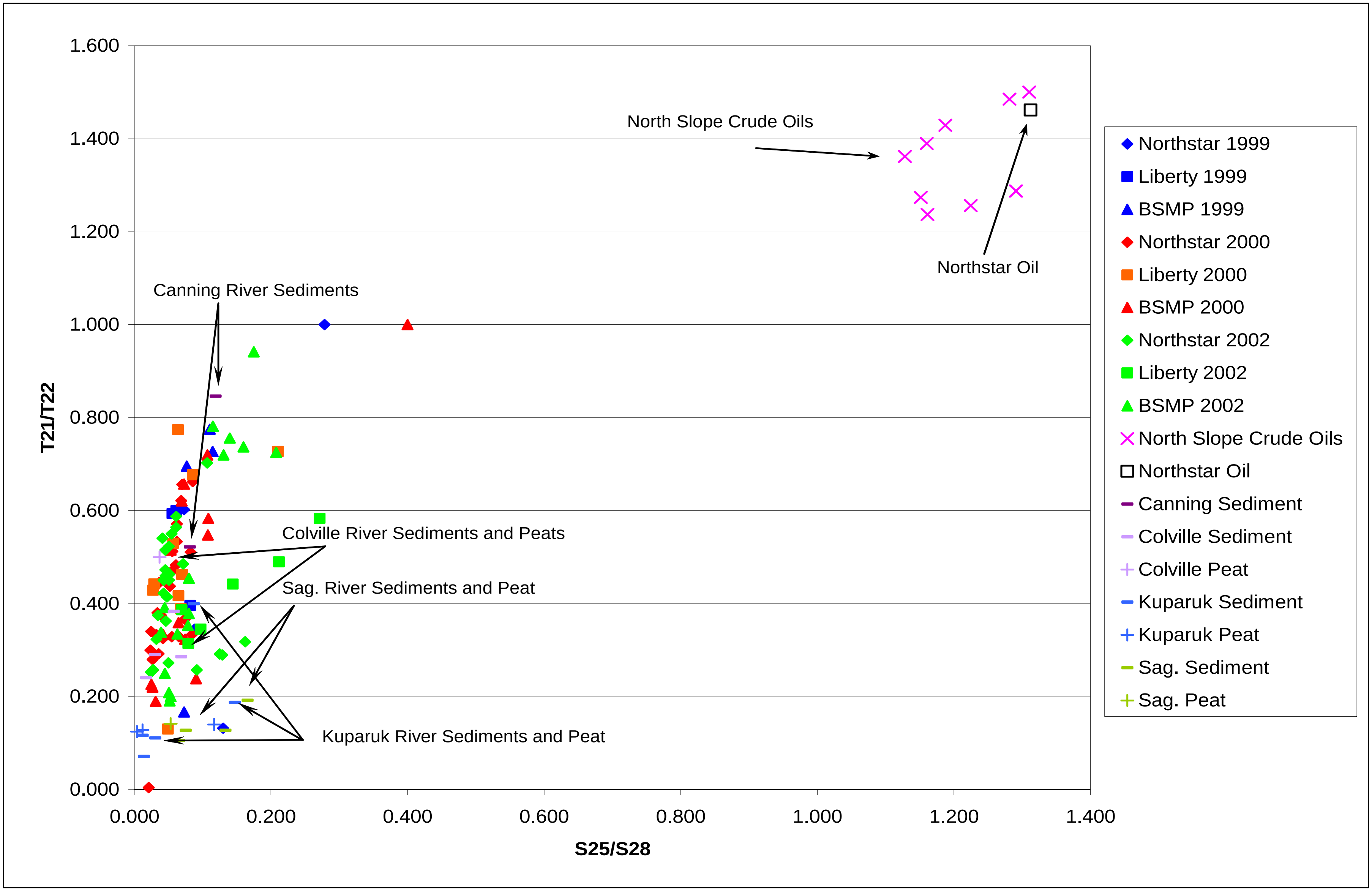


Figure 4-20. Double Ratio Source Plot of S25/S28 vs T21/T22 for BSMP, Liberty, Northstar, and River Sediment Samples for 1999, 2000, and 2002

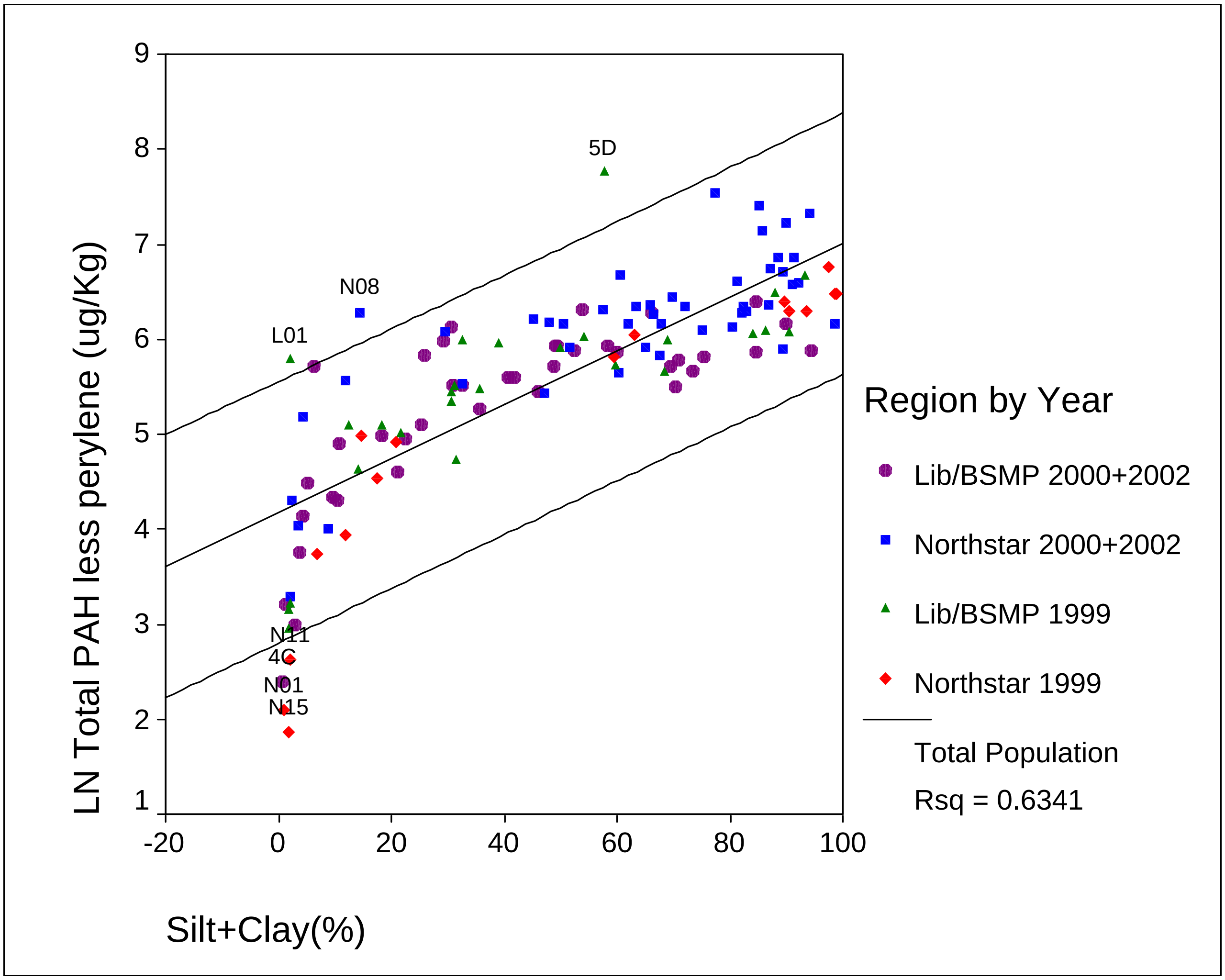


Figure 4-21. Regression Plot of Total PAH less Perylene versus Silt + Clay for all 1999, 2000, and 2002 Northstar, Liberty and BSMP Sediments

The lines, Rsq, and 95% individual prediction intervals are from linear regression.

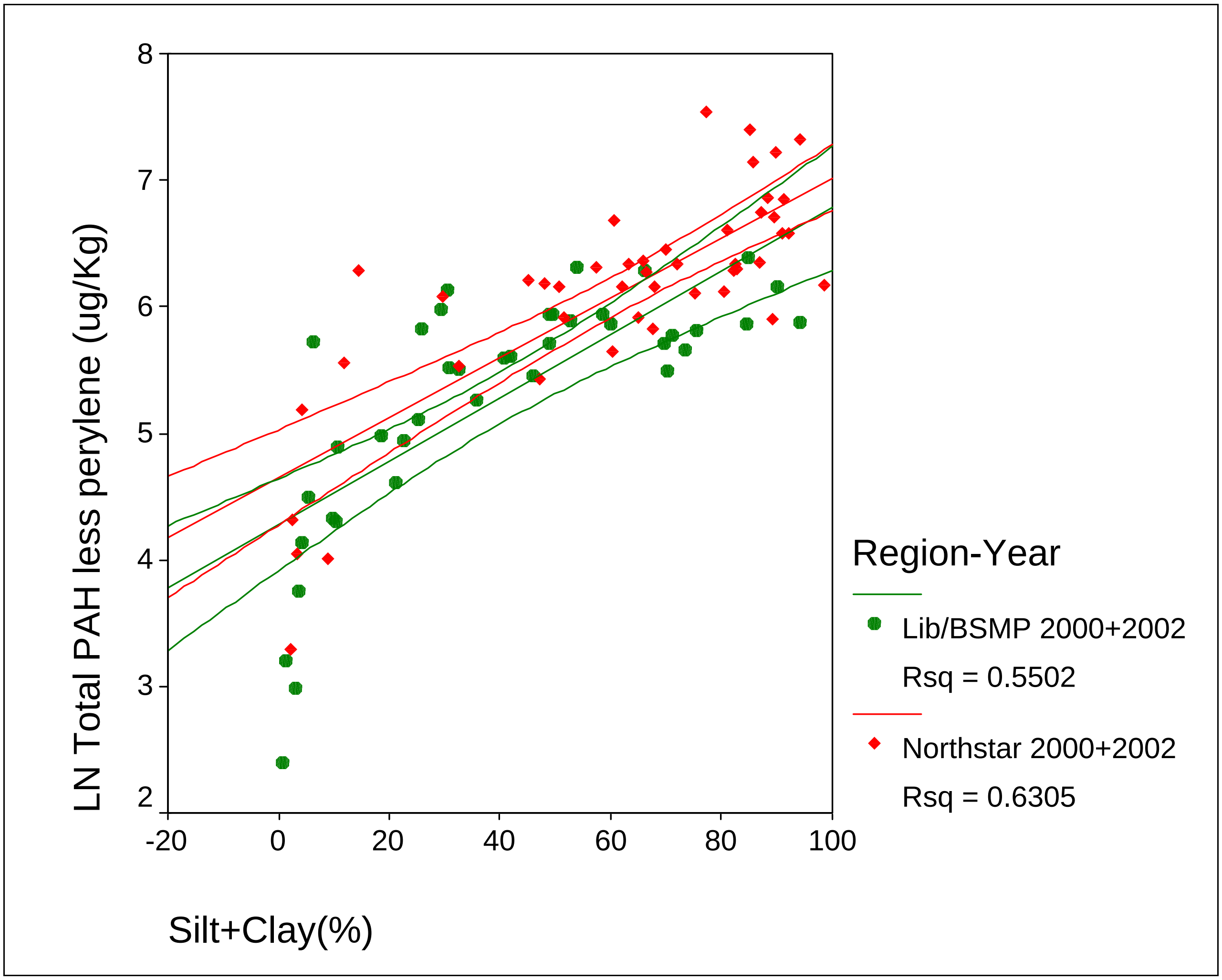


Figure 4-22. Regression Plot of LN Total PAH less Perylene versus Silt + Clay for all 2000 and 2002 Northstar, Liberty and BSMP Sediments

The lines, Rsq, and 95% prediction intervals are from linear regression and related statistical calculations

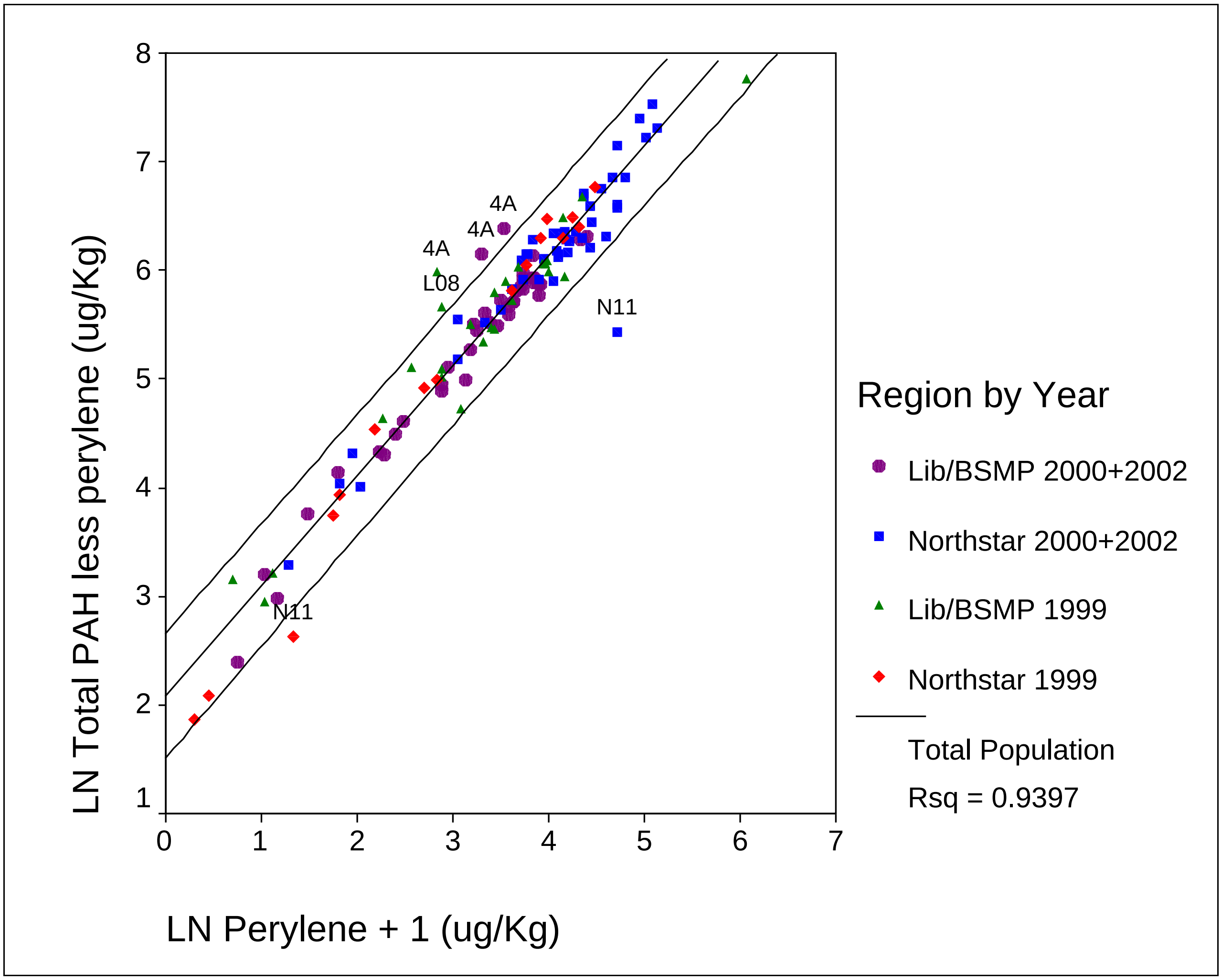


Figure 4-23. Regression Plot of Total PAH less Perylene versus Perylene for all 1999, 2000, and 2002 Northstar, Liberty and BSMP Sediments

The lines, Rsq, and 95% individual prediction intervals are from linear regression.

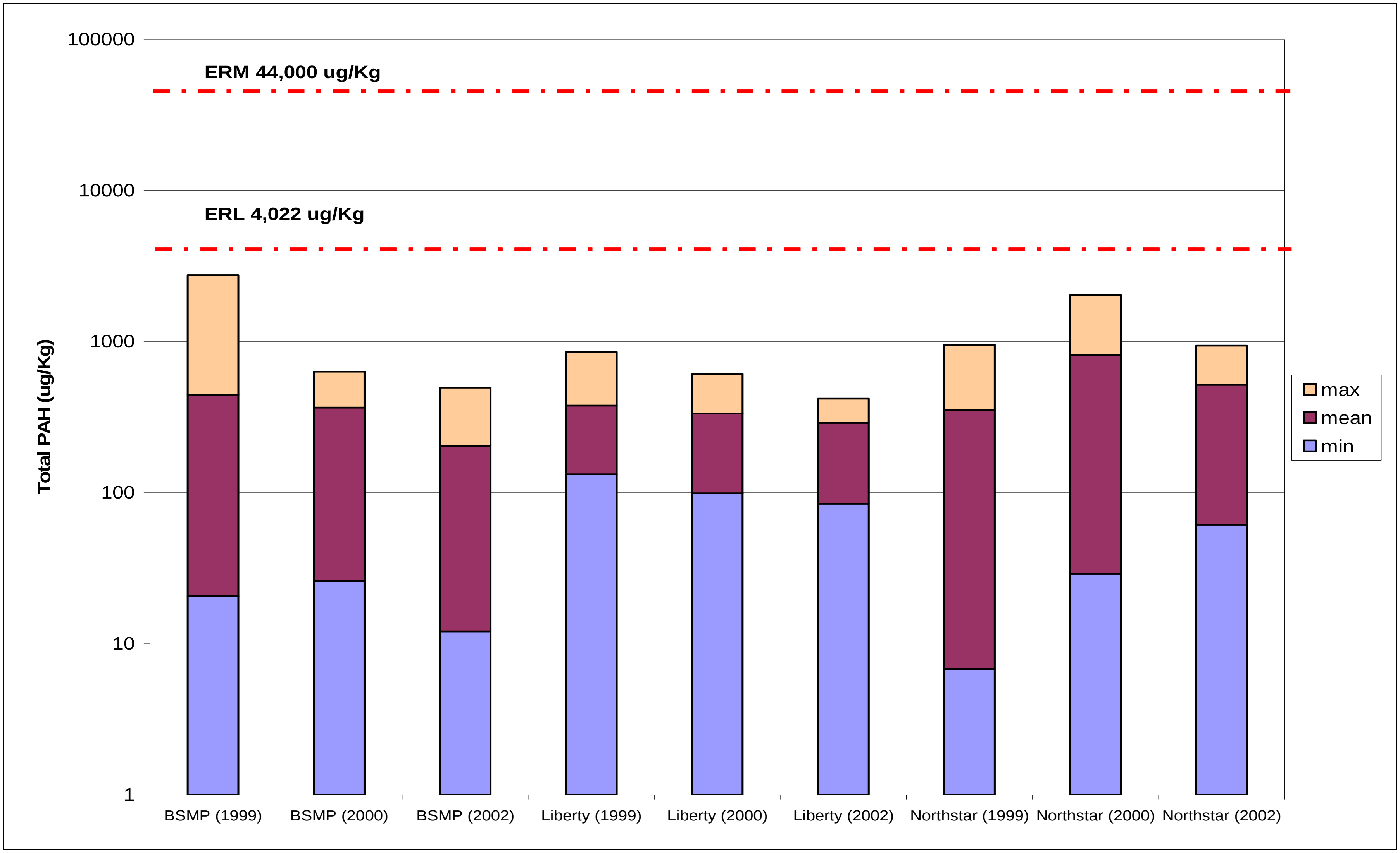


Figure 4-24. Comparison of Regional Mean 1999, 2000, and 2002 Total Polynuclear Aromatic Hydrocarbon Concentrations to Sediment Quality Criteria Effects Range-Low and Effects Range-Medium Values (Long et al., 1995) Note: y-axis is presented on a logarithmic scale.

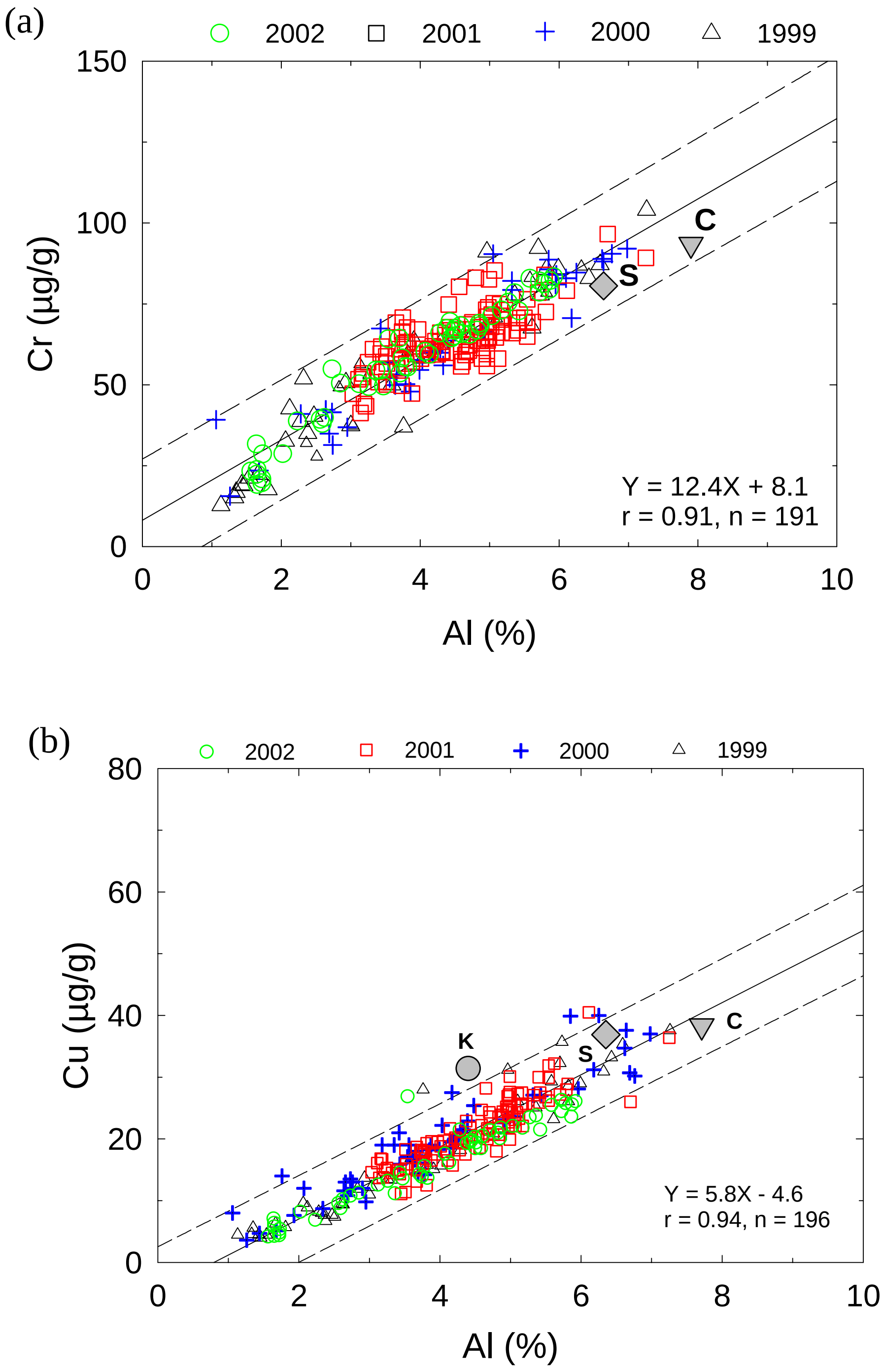


Figure 4-25. Concentrations of aluminum versus (a) chromium and (b) copper for sediment from the ANIMIDA study area

Equations are from linear regression calculations and r is the correlation coefficient. Dashed lines show the 99% prediction interval. Points marked with large letters are for suspended sediment from the Sagavanirktok (S), Kuparuk (K) and Colville (C) rivers. Data for sites identified on the graphs were not included in the regression calculations.

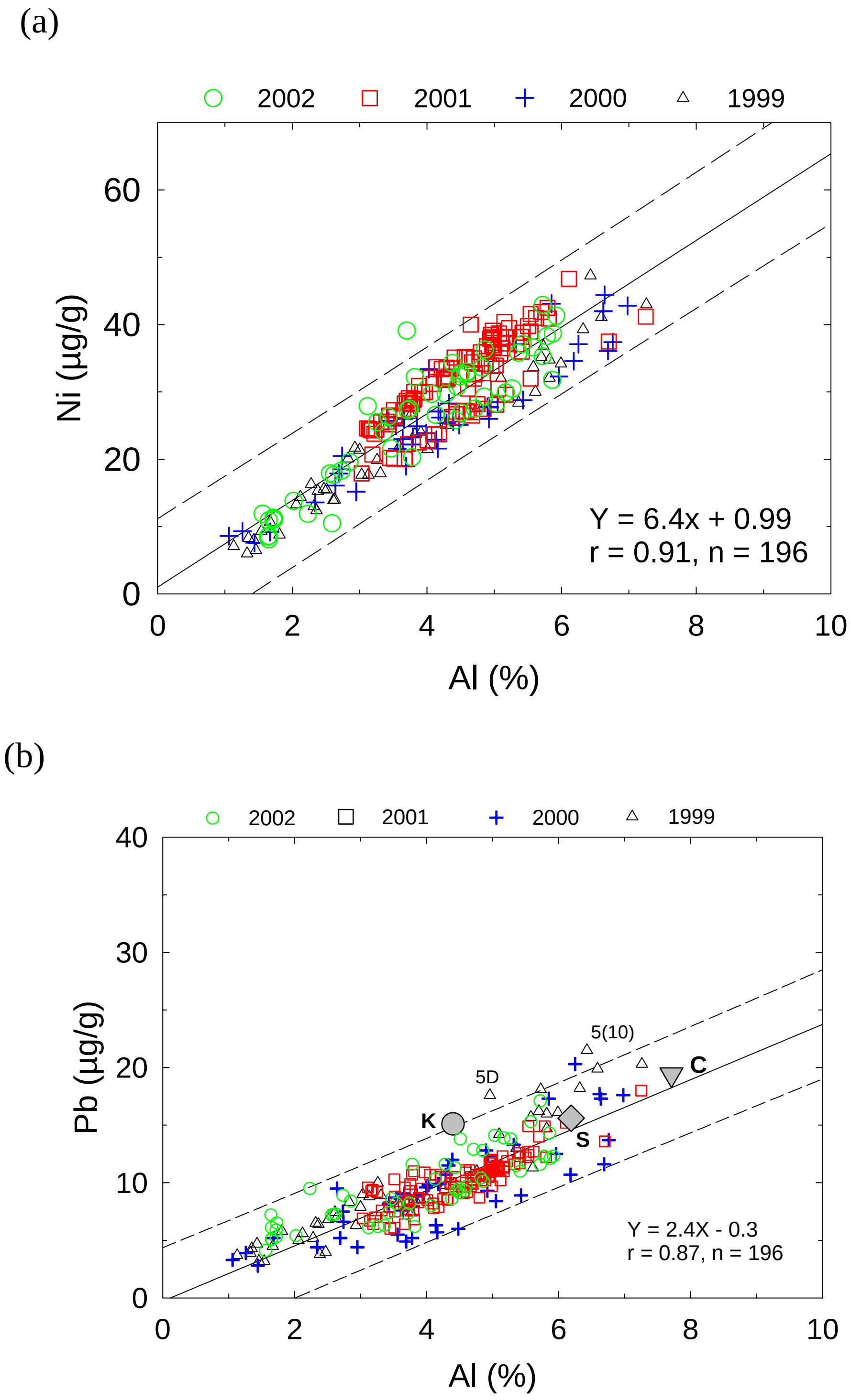


Figure 4-26. Concentrations of aluminum versus (a) nickel and (b) lead for sediment from the ANIMIDA study area

Equations are from linear regression calculations and r is the correlation coefficient. Dashed lines show the 99% prediction interval. Points marked with large letters are for suspended sediment from the Sagavanirktok (S), Kuparuk (K) and Colville (C) rivers. Data for sites identified on the graphs were not included in the regression calculations.

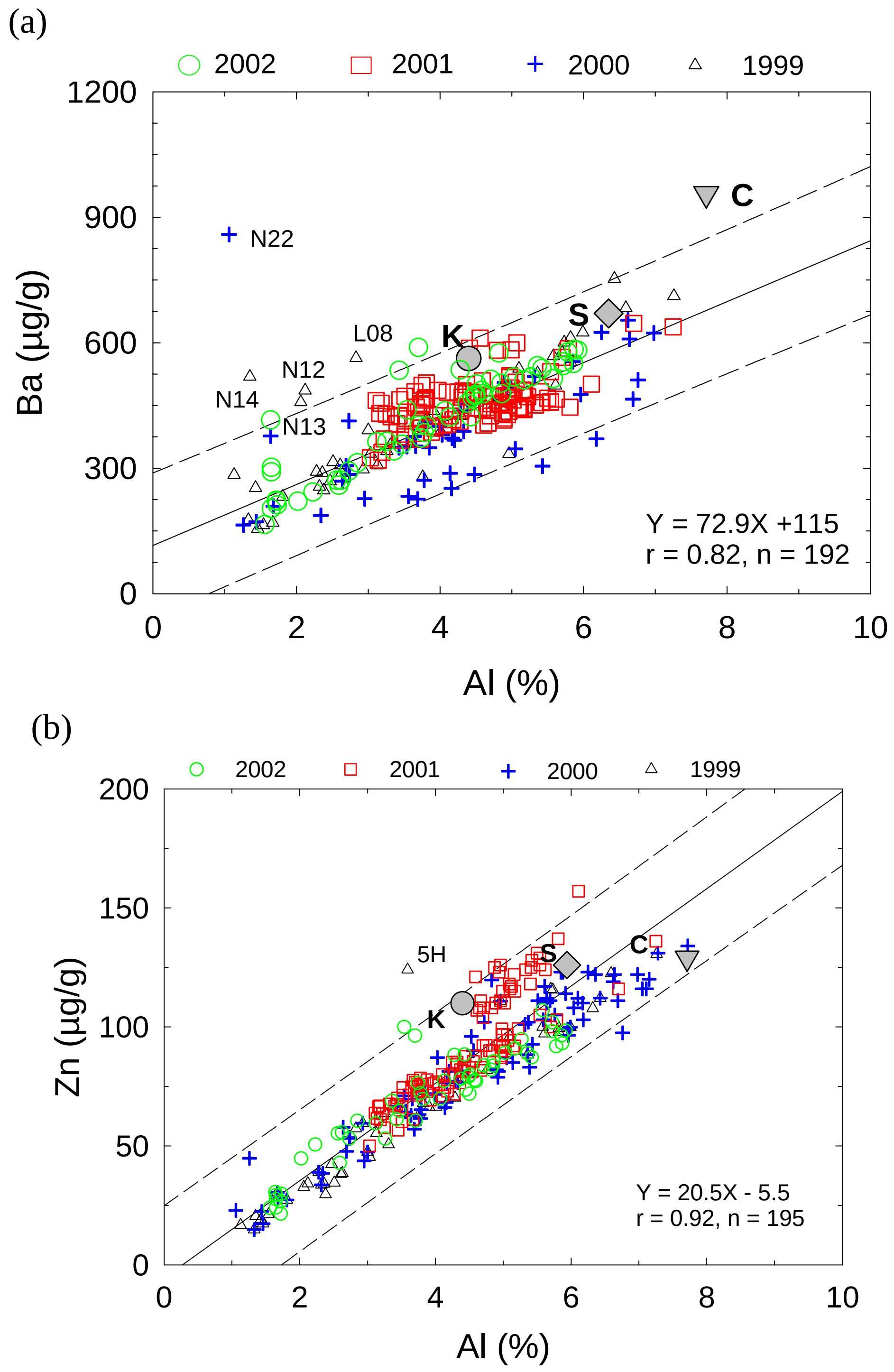


Figure 4-27. Concentrations of aluminum versus (a) barium and (b) chromium for sediment from the ANIMIDA study area

Equations are from linear regression calculations and r is the correlation coefficient. Dashed lines show the 99% prediction interval. Points marked with large letters are for suspended sediment from the Sagavanirktok (S), Kuparuk (K) and Colville (C) rivers. Data for sites identified on the graphs were not included in the regression calculations.

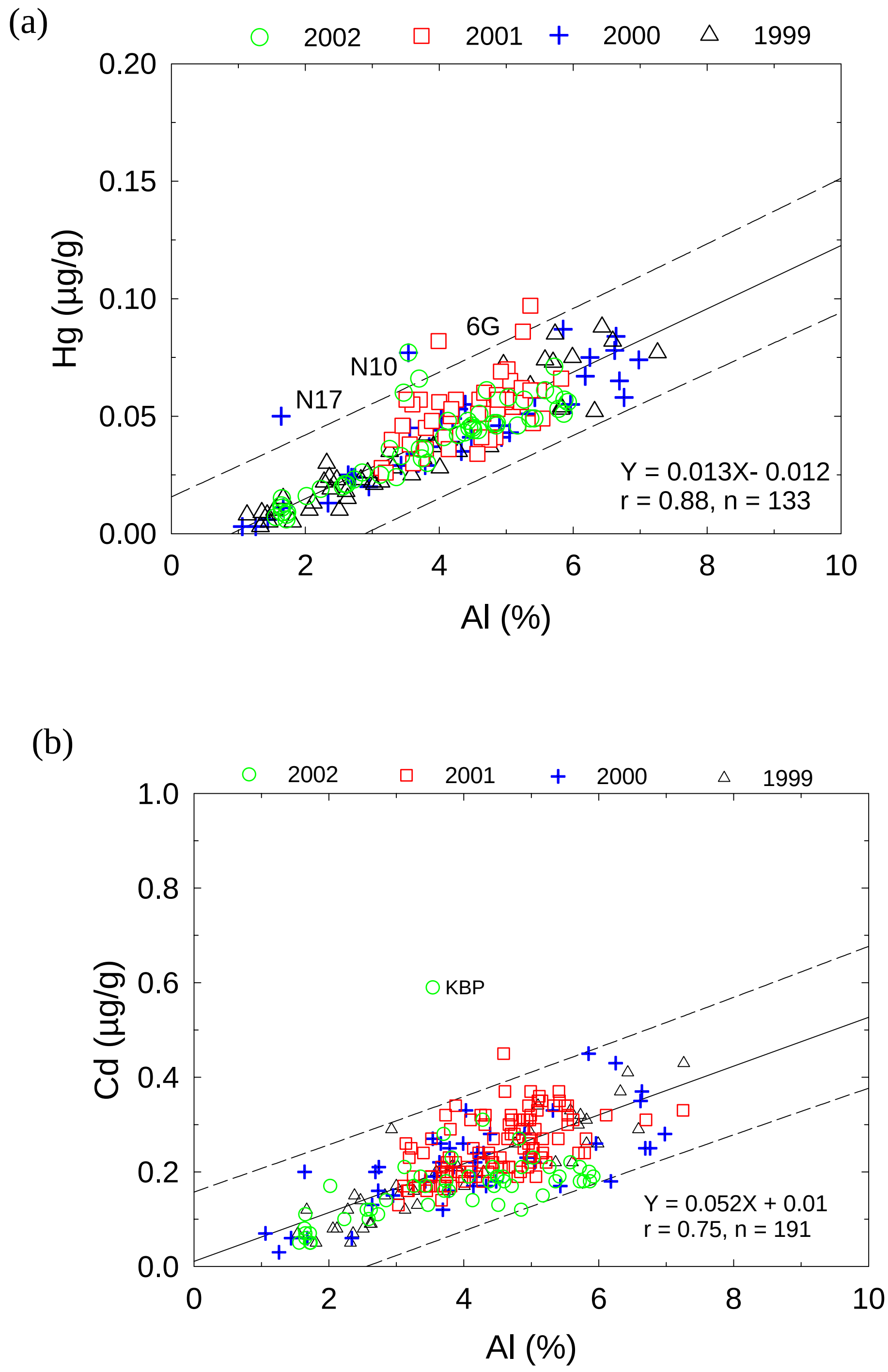


Figure 4-28. Concentrations of aluminum versus (a) mercury and (b) cadmium for sediment from the ANIMIDA study area

Equations are from linear regression calculations and r is the correlation coefficient. Dashed lines show the 99% prediction interval. Data for sites identified on the graphs were not included in the regression calculations.

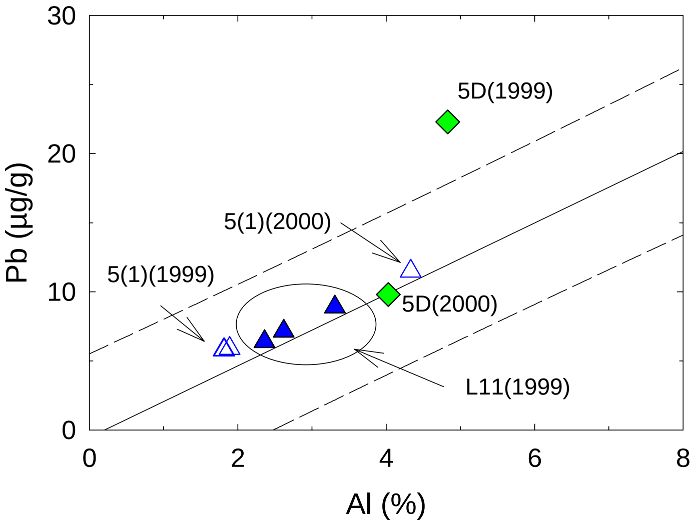


Figure 4-29. Concentrations of aluminum vs. lead in sediment

Dashed lines show the 99% prediction intervals developed for the entire data set.

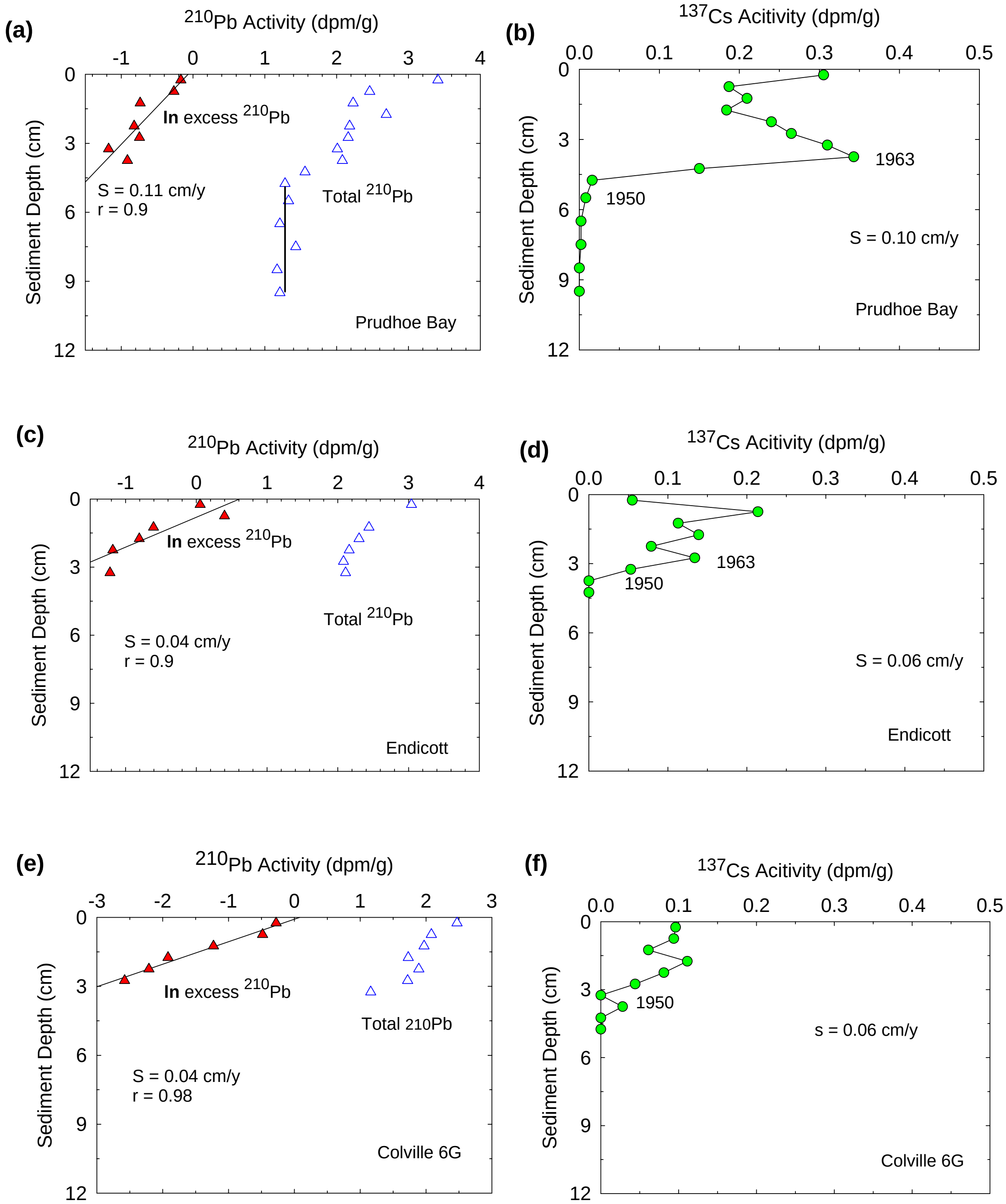


Figure 4-30. Vertical profiles for activities of excess ^{210}Pb, total ^{210}Pb and ^{137}Cs for sediment cores from sites in Prudhoe Bay (P1), near Endicott development (E1) and on the Colville River delta (6G)

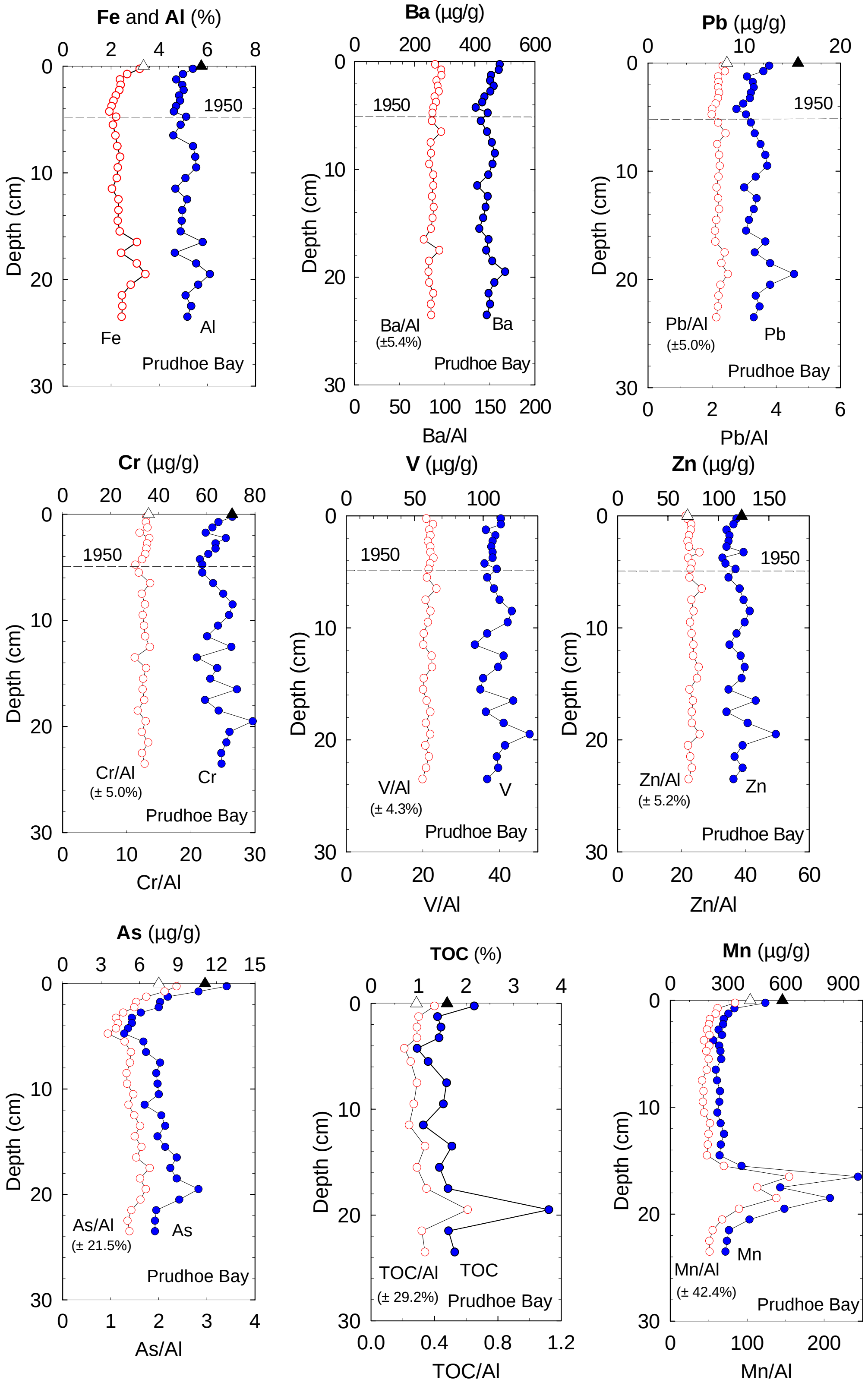


Figure 4-31. Vertical profiles for concentrations and ratios to Al in sediment core from Prudhoe Bay (station P1) for Fe and Al, Ba, Pb, Cr, V, Zn, As, total organic carbon (TOC), and Mn. Points marked with large letters on Pb, Cu, Cr, Zn and Ba graphs are for suspended sediment from the Sagavanirktok (S), Kuparuk (K) and Colville (C) rivers. Graphs with no line identifying a sediment age of 1950 (As, TOC and Mn) lack geochronological significance due post-depositional diagenesis/diffusion.

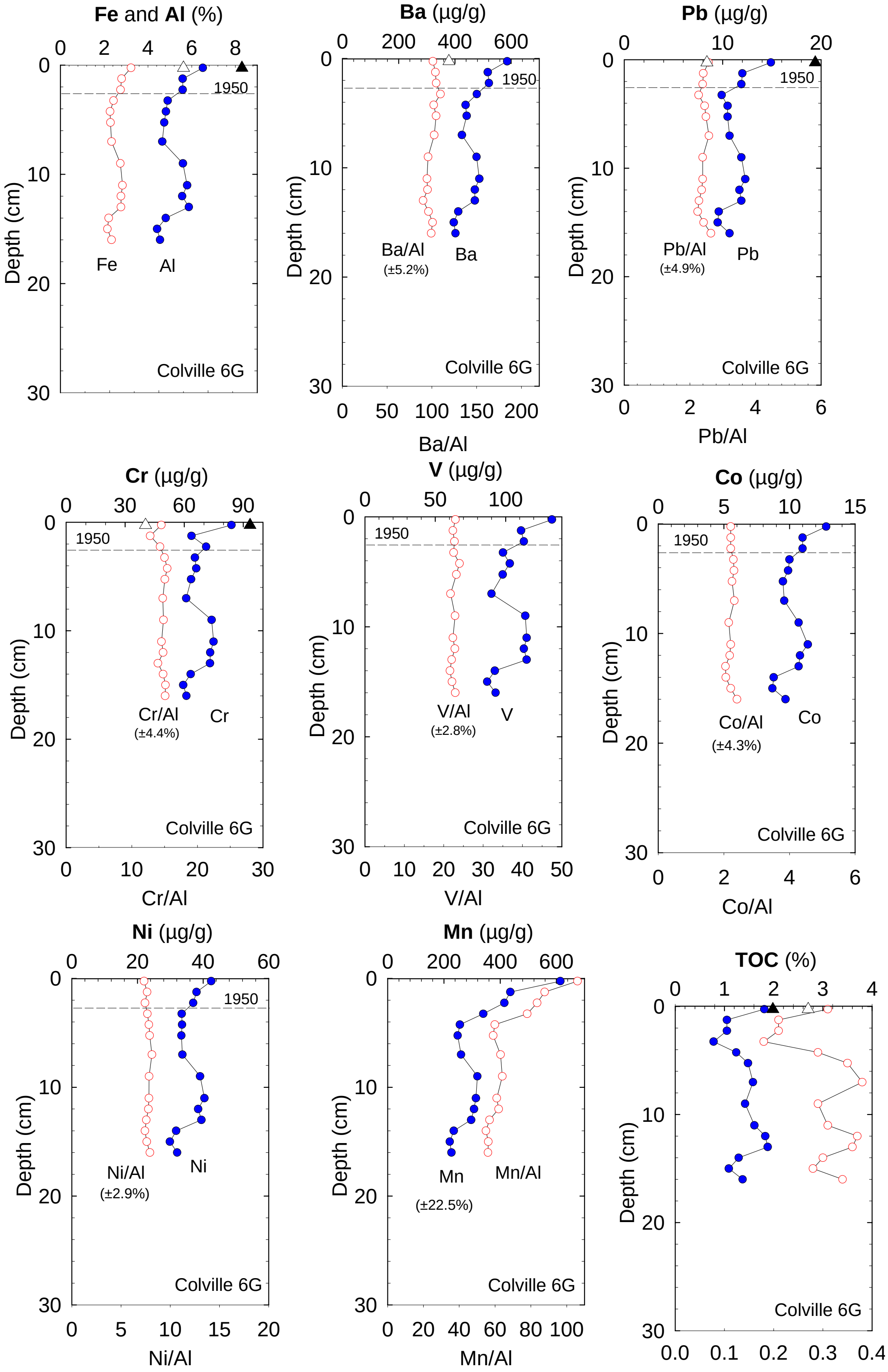


Figure 4-32. Vertical profiles for concentrations and ratios to Al in sediment core from Colville River delta (station 6G) for Fe and Al, Ba, Pb, Cr, V, Co, Ni, Mn , and total organic carbon (TOC). Points marked with large letters on Pb, Cu, Cr, Zn and Ba graphs are for suspended sediment from the Sagavanirktok (S), Kuparuk (K) and Colville (C) rivers. Graphs with no line identifying a sediment age of 1950 (As, TOC and Mn) lack geochronological significance due post-depositional diagenesis/diffusion.

Figure 4-33 Station 3A Astarte sp. Tissue, Year 1999 – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

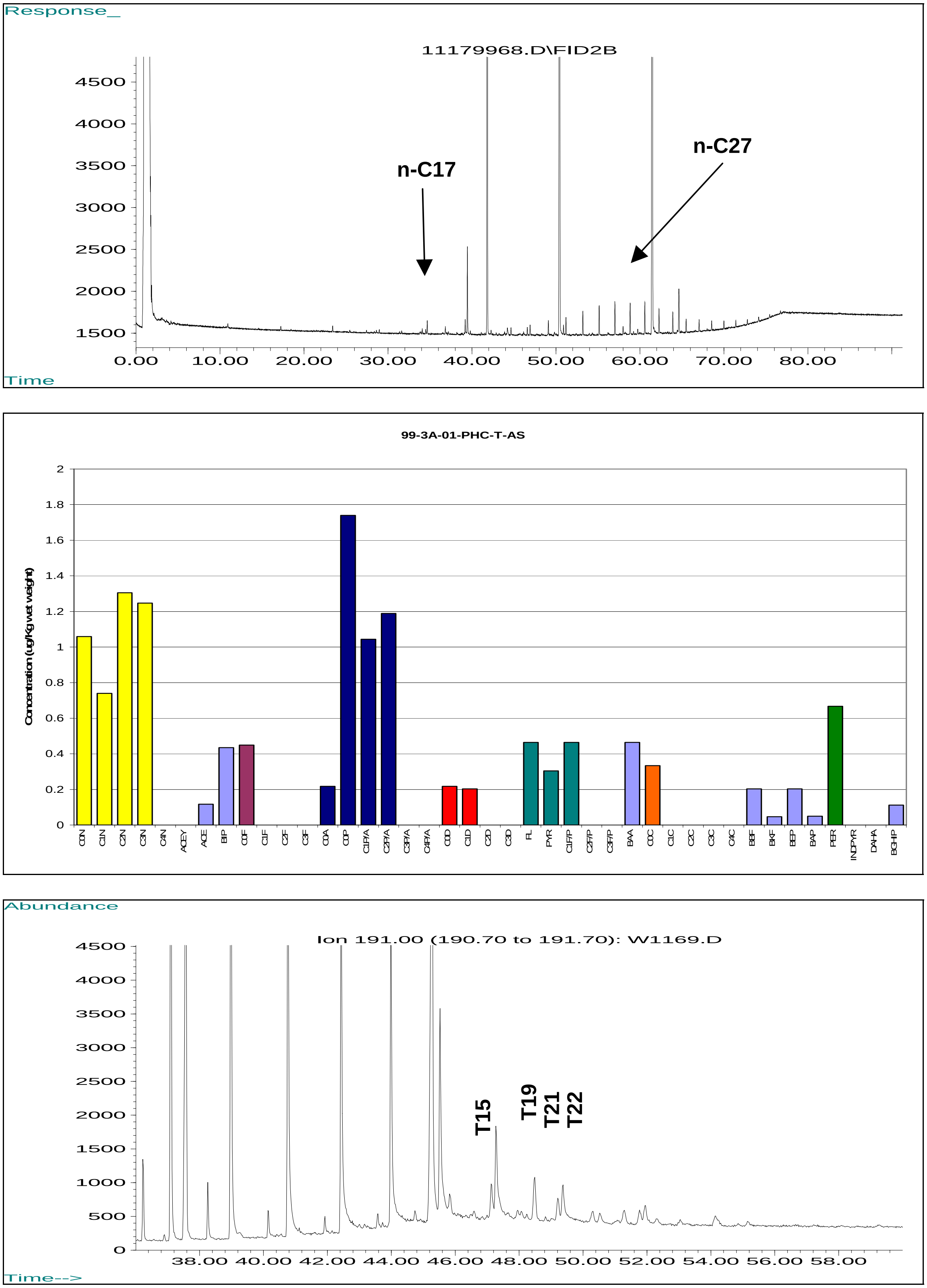


Figure 4-34. Station 3A Astarte sp. Tissue, Year 2000 – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)

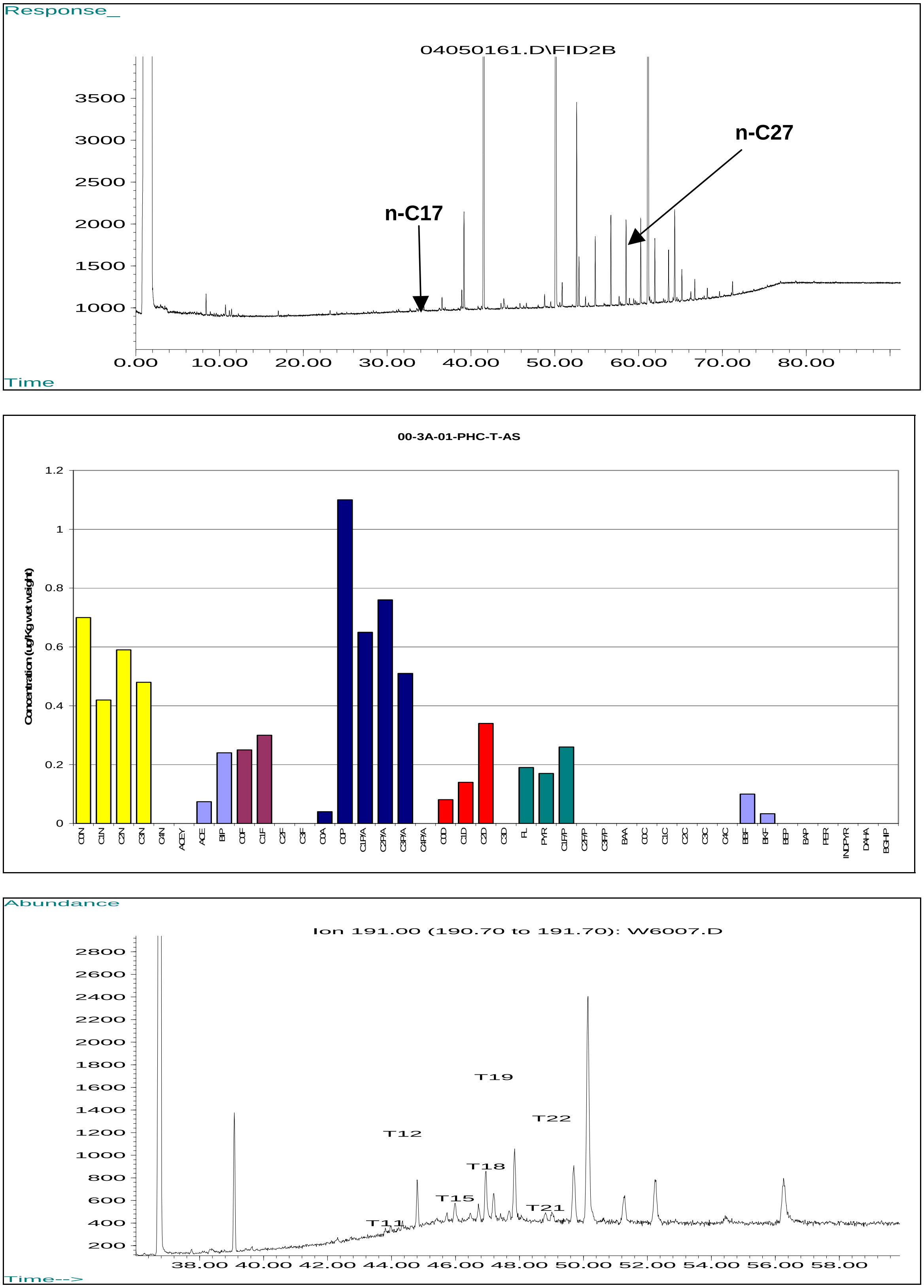
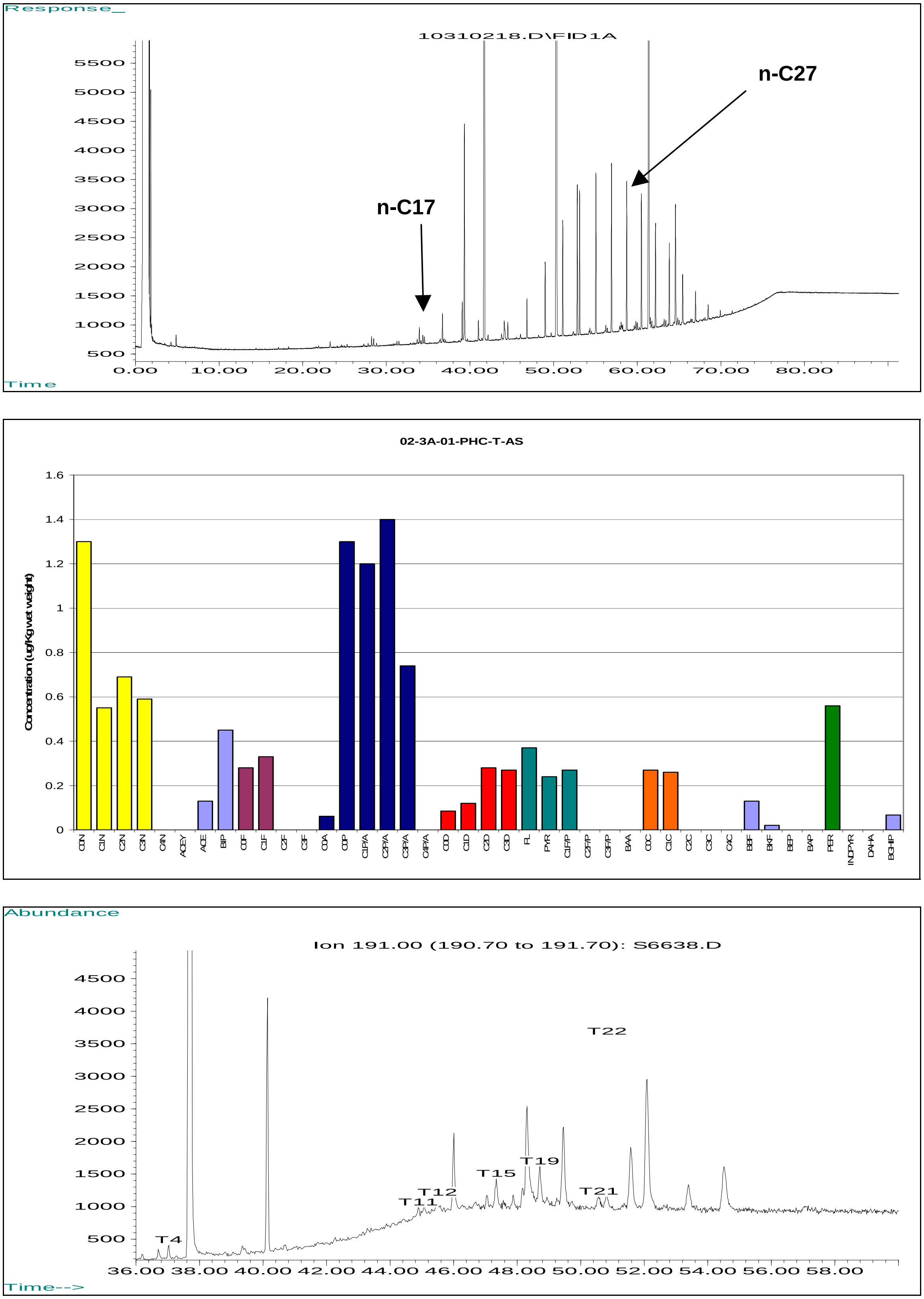


Figure 4-35 Station 3A Astarte sp. Tissue, Year 2002 – GC/FID Chromatogram (top), PAH Distribution Histogram (middle), Triterpane Ion Chromatogram (bottom)



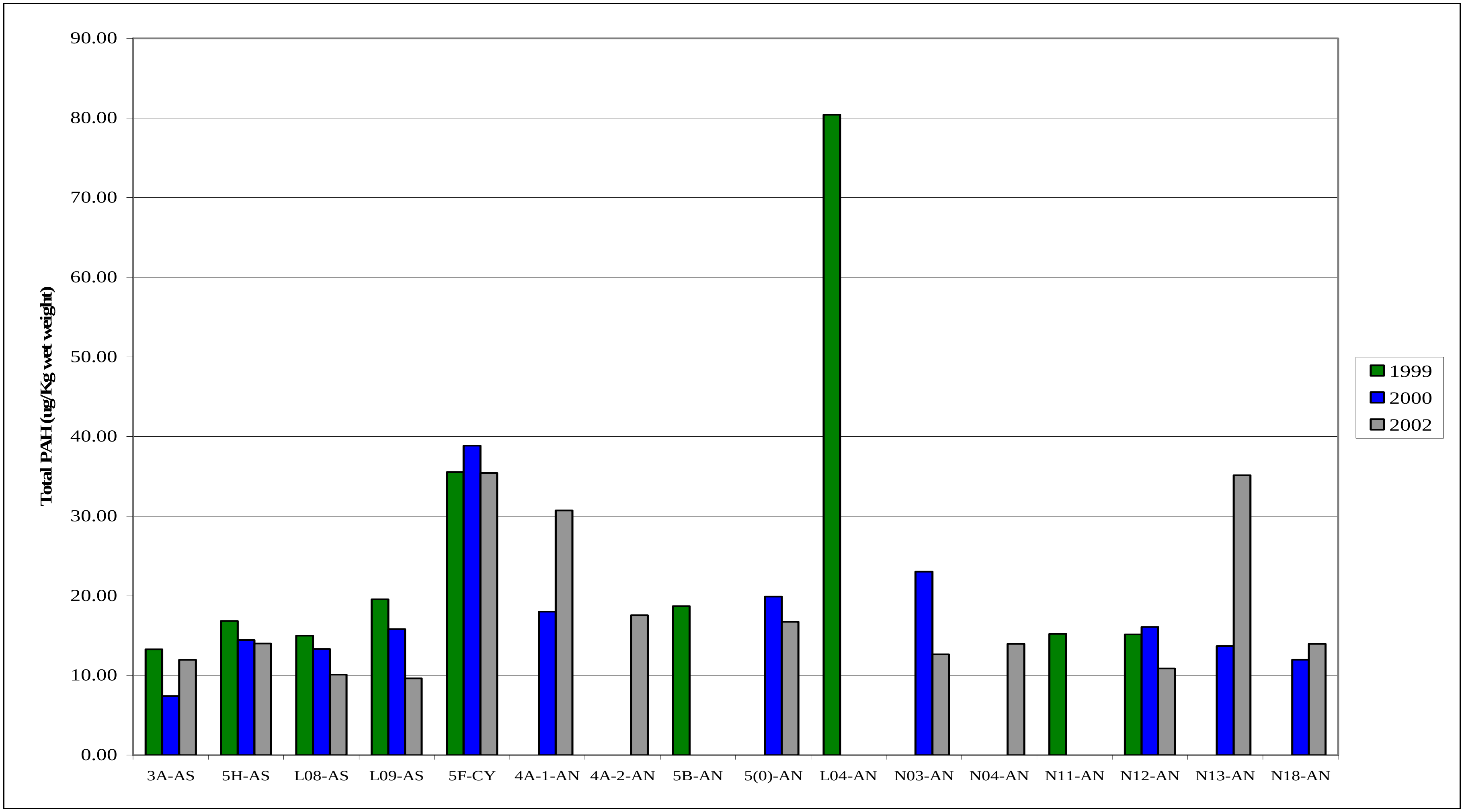


Figure 4-36. Total Polynuclear Aromatic Hydrocarbon Less Perylene Concentrations of Bivalves and Amphipods for BSMP, Liberty and Northstar Stations in 1999, 2000, and 2002

Sample suffix definitions – AN – Anonyx (clams), CY - Cyrtodaria (clams), AS – Astarte (amphipods)

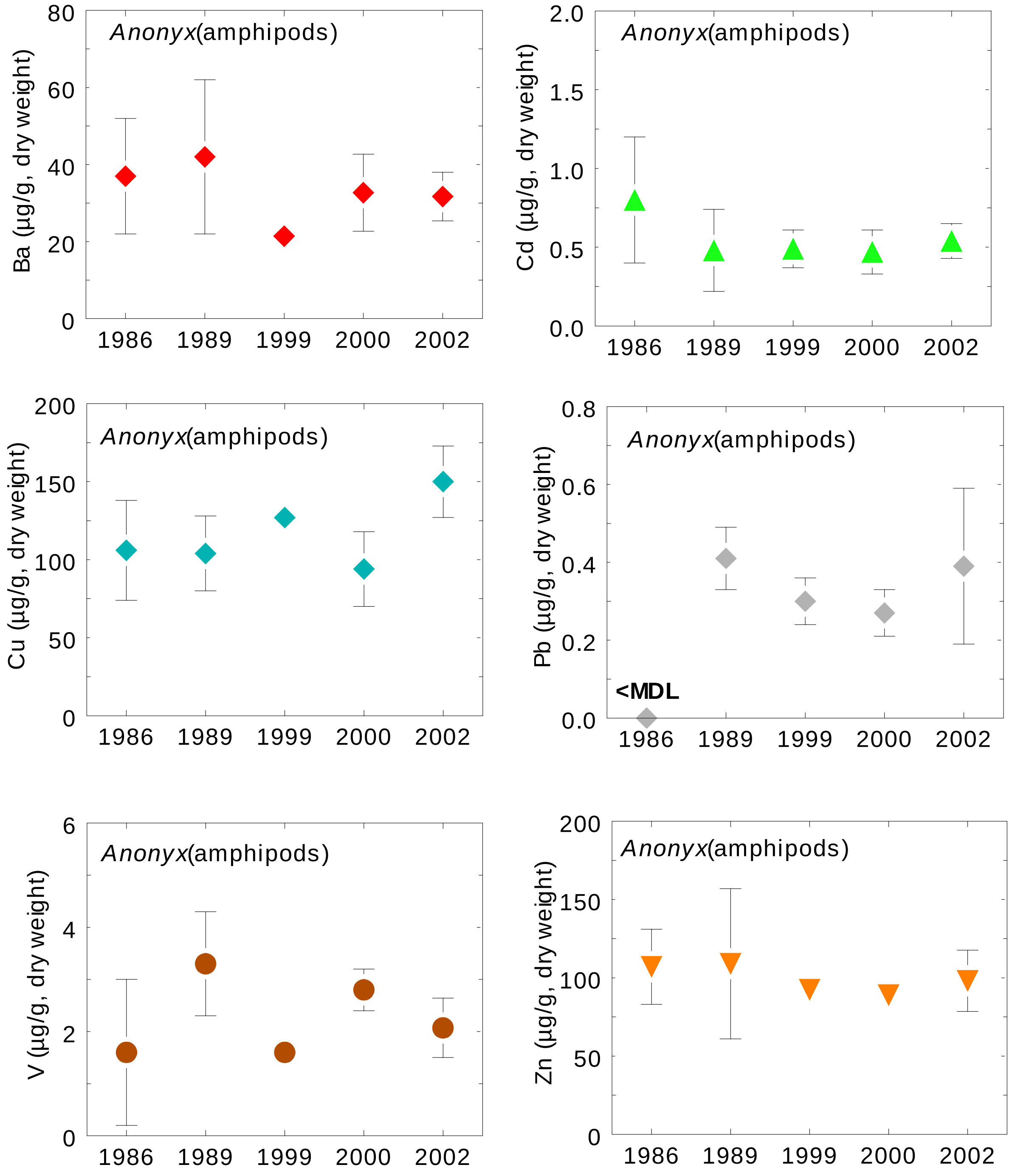


Figure 4-37. Mean concentrations (± standard deviation) of Ba, Cd, Cu, Pb, V and Zn in amphipods (Anonyx) collected from sites in the BSMP during 1986, 1989 and for ANIMIDA during 1999, 2000 and 2002.

In some cases the standard deviation is smaller than the marker**.**

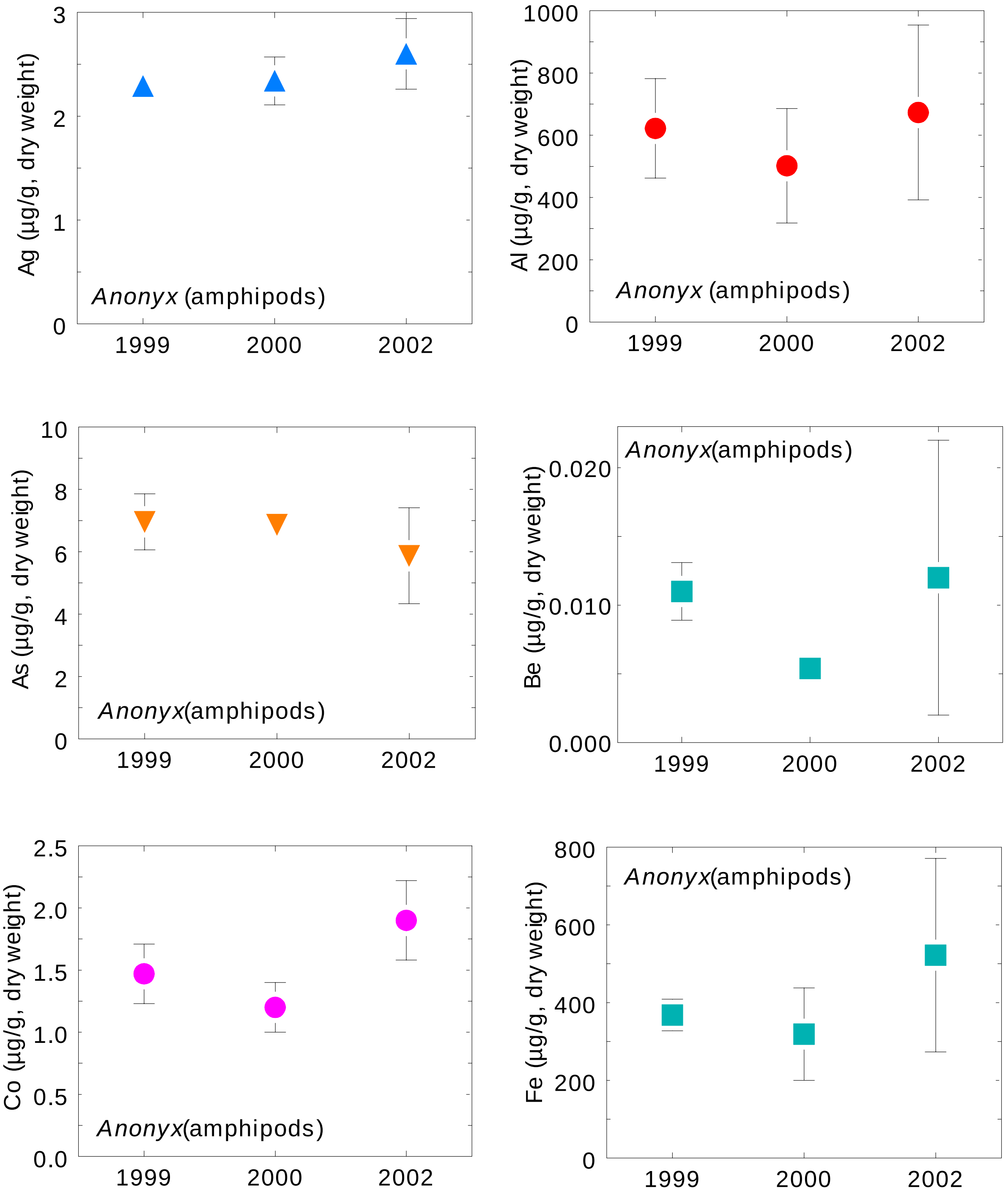


Figure 4-38. Mean concentrations (± standard deviation) of Ag, Al, As, Be, Co and Fe in amphipods (*Anonyx*) collected for ANIMIDA during 1999, 2000 and 2002.

In some cases the standard deviation is smaller than the marker

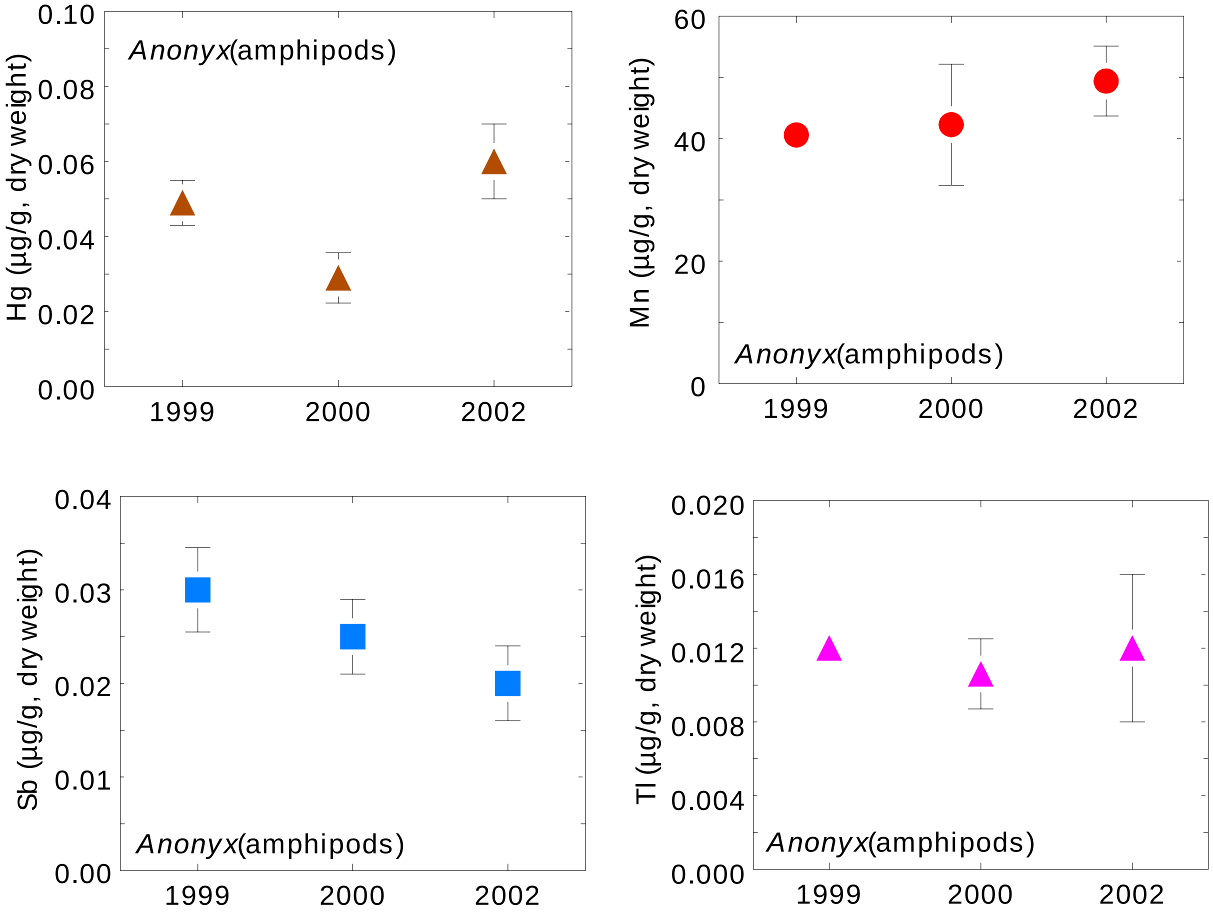


Figure 4-39. Mean concentrations (± standard deviation) of Hg, Mn, Sb and Tl in amphipods (*Anonyx*) collected for ANIMIDA during 1999, 2000 and 2002.

In some cases the standard deviation is smaller than the marker

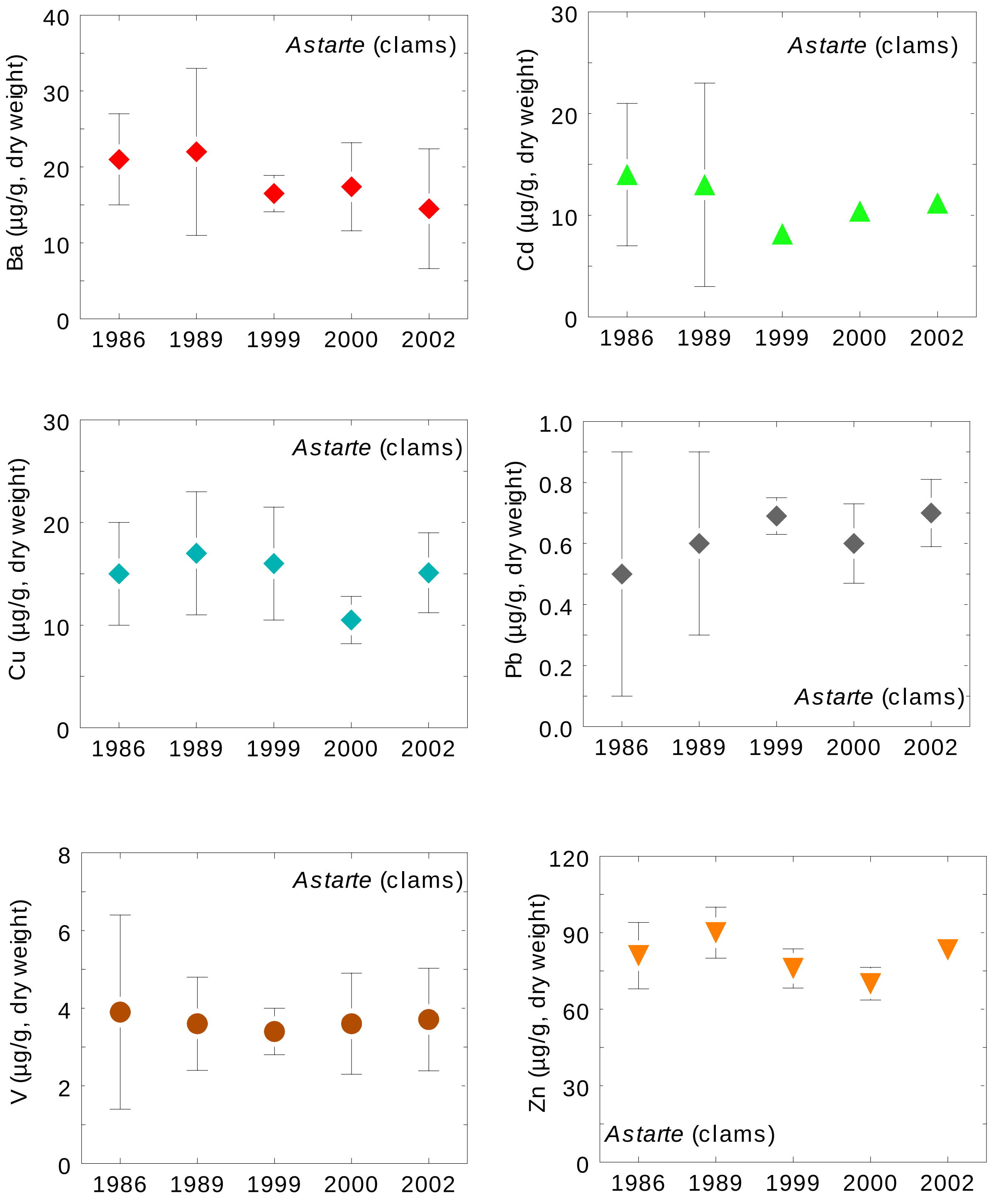


Figure 4-40. Mean concentrations (± standard deviation) of Ba, Cd, Cu, Pb, V and Zn in clams (*Astarte*) collected from sites in the BSMP during 1986, 1989 and for ANIMIDA during 1999, 2000 and 2002.

In some cases the standard deviation is smaller than the marker

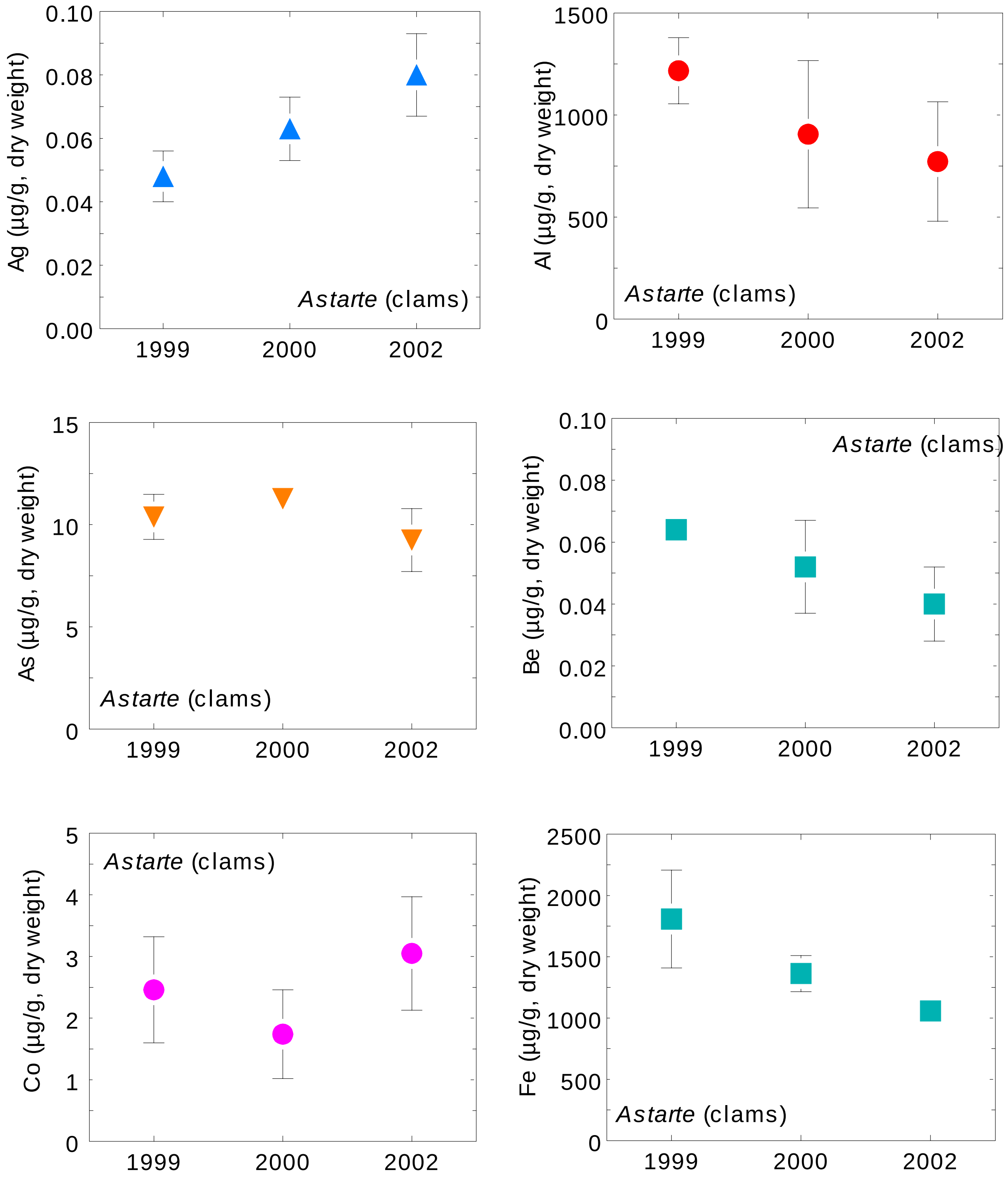


Figure 4-41. Mean concentrations (± standard deviation) of Ag, Al, As, Be, Co and Fe in clams (*Astarte*) collected for ANIMIDA during 1999, 2000 and 2002.

In some cases the standard deviation is smaller than the marker

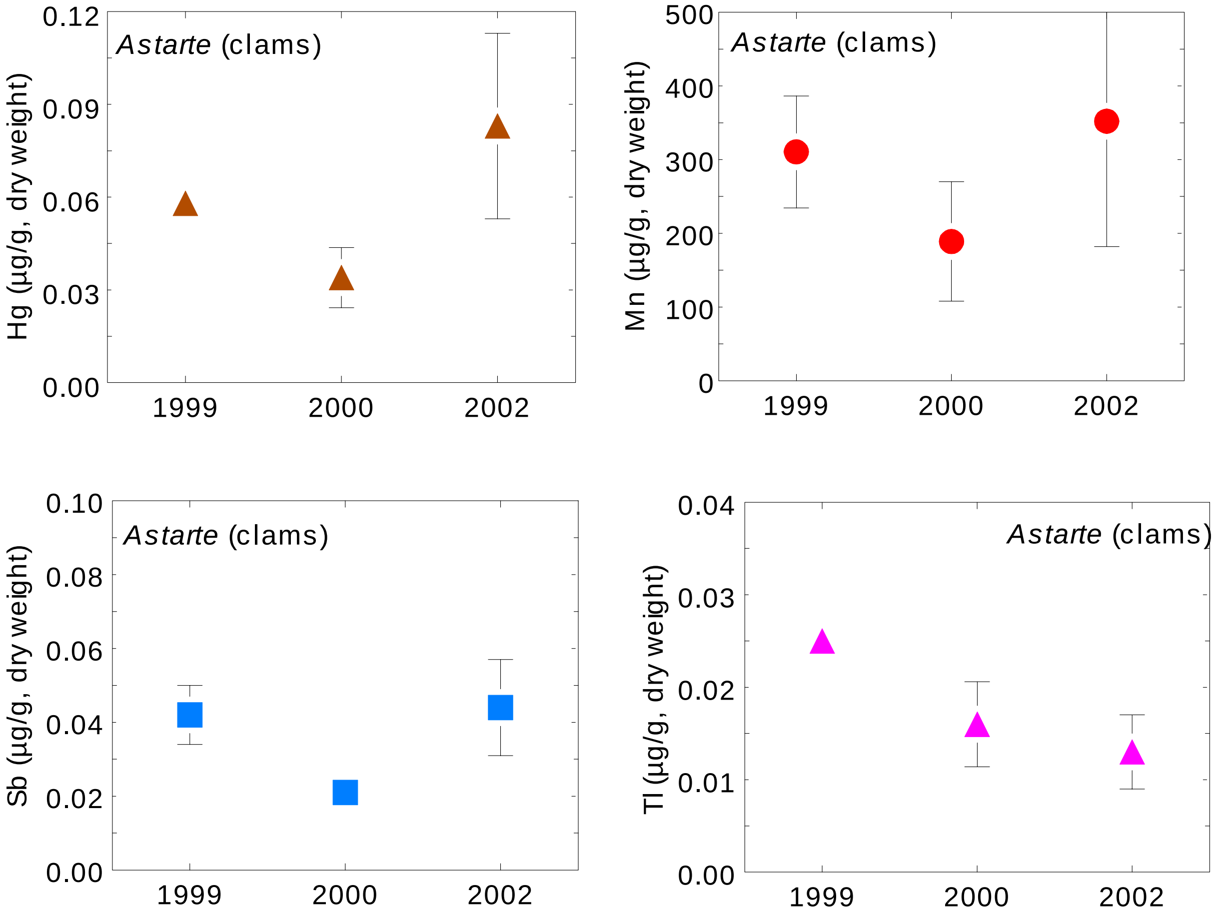
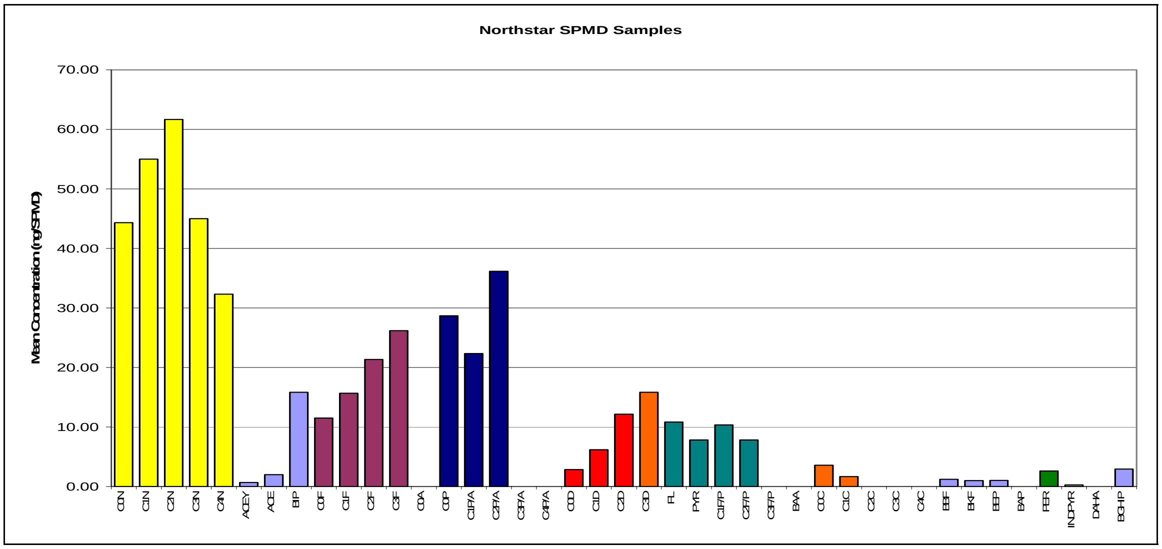
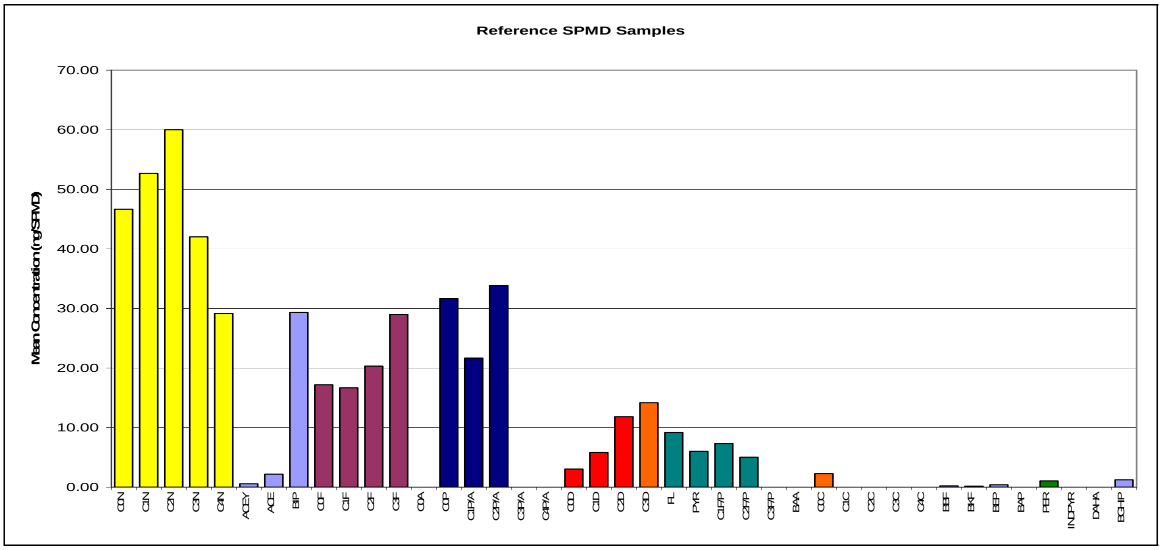


Figure 4-42. Mean concentrations (± standard deviation) of Hg, Mn, Sb and Tl in clams (*Astarte*) collected for ANIMIDA during 1999 and 2000.

In some cases the standard deviation is smaller than the marker

Figure 4-43. SPMD PAH Distribution Histograms, Northstar SPMDs (top), Reference SPMDs (middle), Field Blank SPMDs (bottom)





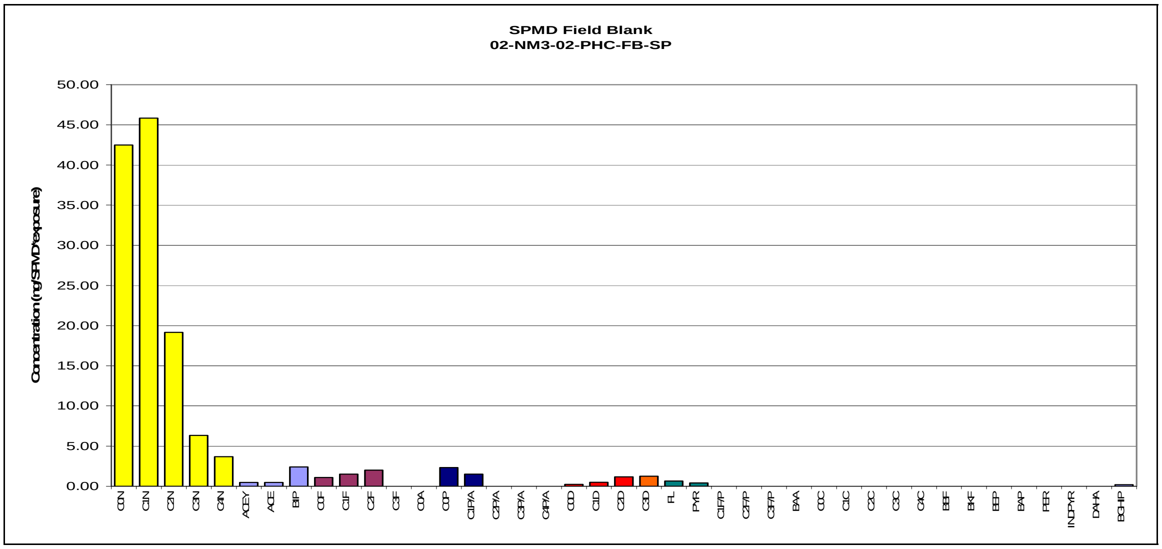
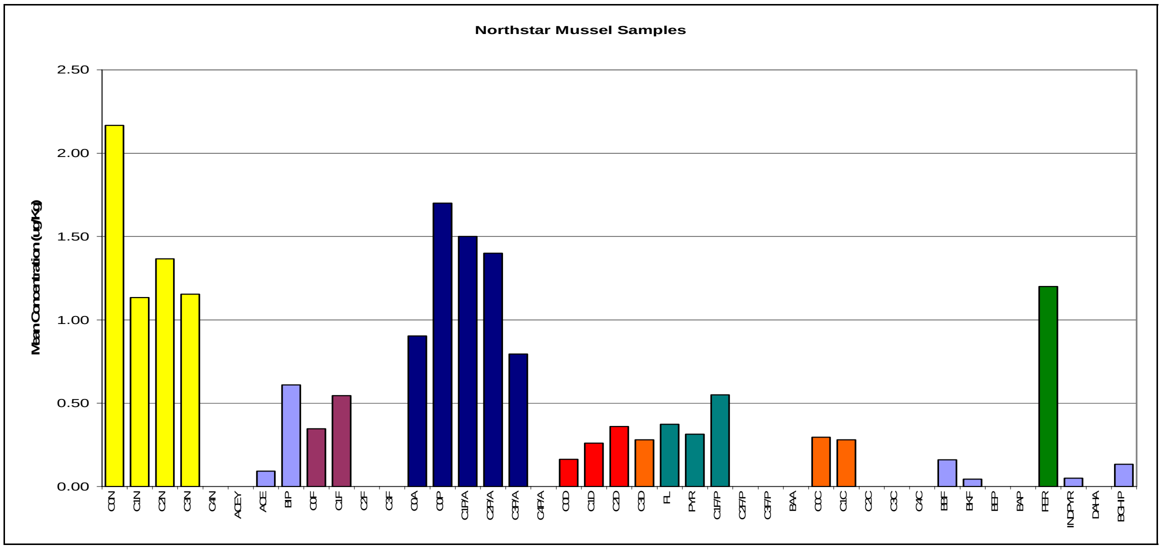
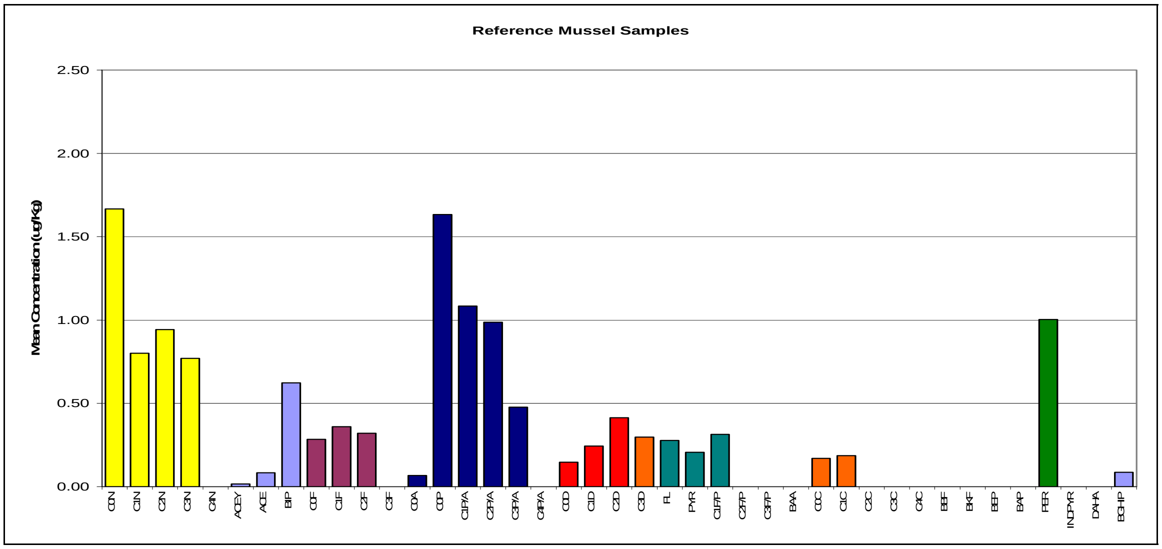
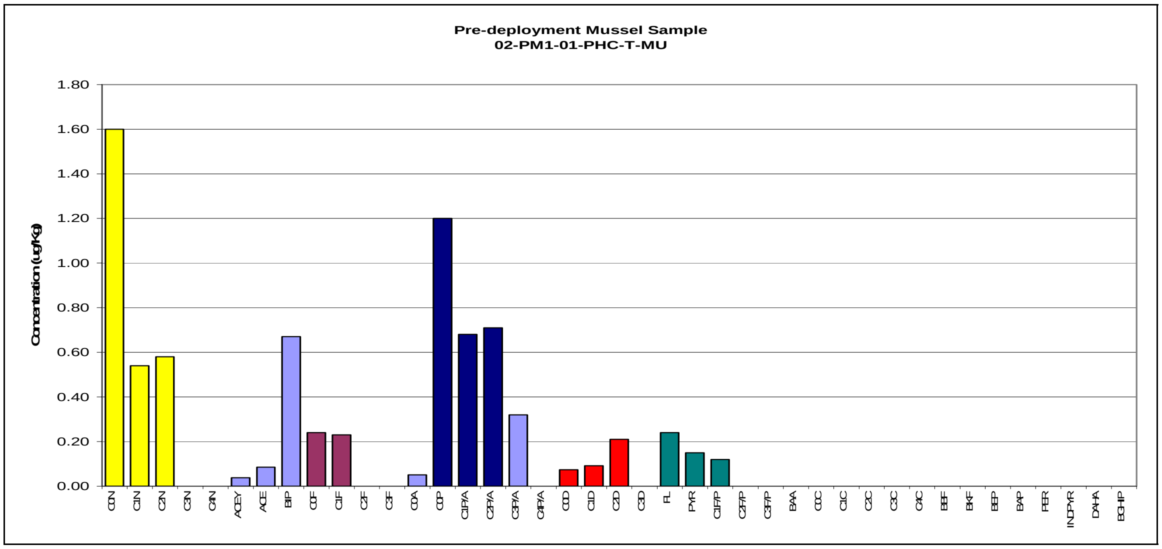


Figure 4-44. Mussel PAH Distribution Histograms, Northstar Mussels (top), Reference Mussels (middle), Pre-Deployment Blank Mussels (bottom)







5.0 Recommendations

Based on the results and interpretations of the sediment and biota samples collected under the ANIMIDA Phase I program and Task 2 of the ANIMIDA Phase II program, and with the potential development of the Liberty Prospect and new Beaufort Sea lease sales, there are a number of recommendations for future work in the ANIMIDA study area.

- Perform continued surface sediment and biota monitoring for hydrocarbons and metals in the Northstar Island area to assess potential impacts from Northstar productions activities.

- Collect and analyze sediments and biota for hydrocarbons and metals from new Liberty sediment stations to augment existing baseline information for Liberty and to assess potential impacts from Liberty development and production activities. This recommendation is based the assumption that Liberty Prospect will be developed from an alternative location.

- Perform continued surface sediment monitoring for hydrocarbons and metals at the wider regional BSMP study area stations (i.e., Cape Halkett to Griffin Point) to develop a comprehensive baseline of the area prior to exploration and development activities associated with new Beaufort Sea lease sales.

- Perform additional water column monitoring around Northstar and at reference areas with sensitive indicator organisms (i.e., transplanted caged mussels) and SPMDs.

- Collect and analyze additional offshore sediment cores for hydrocarbons and metals to further characterize the historical sediment record in the study area.

- Collect and analyze additional river sediment samples (e.g., McKenzie River, Colville Watershed) for metals and hydrocarbons to evaluate other regional sediment sources.

- Analyze additional North Slope field oils and seep oils/source rock/coal samples to enhance the differentiation of hydrocarbon sources.

- Continue use of the Double Ratio Plot of S25/S28 versus T21/T22 as a hydrocarbon source discrimination tool for the ANIMIDA study area.

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The Department of the Interior Mission

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

The Minerals Management Service Mission

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

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

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