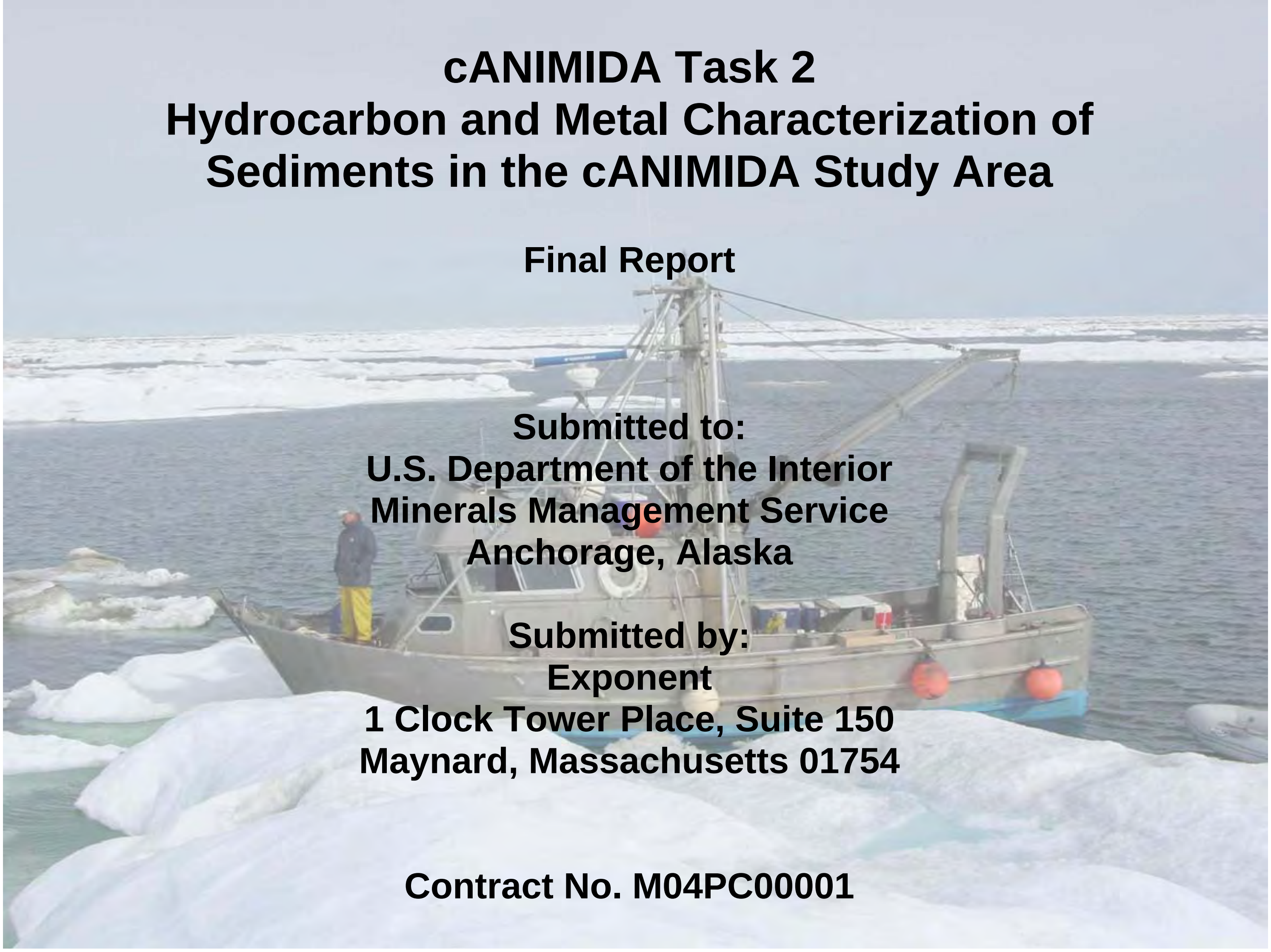
OCS Study MMS 2010-004



cANIMIDA Task 2
Hydrocarbon and Metal Characterization of Sediments in the cANIMIDA Study Area

Final Report

Submitted to:
U.S. Department of the Interior
Minerals Management Service
Anchorage, Alaska

Submitted by:
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Contract No. M04PC00001

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

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This study was funded by the U.S. Department of the Interior,
Minerals Management Service (MMS), Alaska Outer Continental Shelf Region,
Anchorage, Alaska, under Contract No. M04PC00001
as part of the MMS Alaska Environmental Studies Program.

February 2010

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Acronyms and Abbreviations

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
cANIMIDA	Continuation of ANIMIDA
cm	Centimeter
COC	Chain of Custody
CPI	Carbon Preference Index
CRM	Certified Reference Material
CV	Coefficient of Variation
CVAAS	Cold Vapor Atomic Absorption Spectrometry
%D	Percent Difference
DDW	Distilled, Deionized Water
dpm/g	Decompositions per Minute per Gram
DQO	Data Quality Objectives
DRO	Diesel Range Organics
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
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
H	Hypothesis
H_2O	Water
H_2SO_4	Sulfuric Acid
HCl	Hydrochloric Acid
$HClO_4$	Perchloric Acid
HF	Hydrogen Fluoride
HNO_3	Nitric Acid
ICP/MS	Inductively Coupled Plasma/Mass Spectrometry
ID	Inner Diameter
IRM	Instrument Reference Material
K-D	Kuderna-Danish
Kg	Kilogram
km	Kilometer

Acronyms and Abbreviations (continued)

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
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
NRC	National Research Council of Canada
OCS	Outer Continental Shelf
OCSLA	Outer Continental Shelf Lands Act
PAH	Polynuclear Aromatic Hydrocarbon
PB	Procedural Blank
Pb	Lead
PCB	Polychlorinated Biphenyl
ppm	Parts Per Million
Q	Question
QA	Quality Assurance
QAM	Quality Assurance Manual
QC	Quality Control
RF	Response Factor
RPD	Relative Percent Difference
rpm	Revolutions Per Minute
RSD	Relative Standard Deviation
S/T	Steranes/Triterpanes
SHC	Saturated Hydrocarbons
SIM	Selected Ion Monitoring
SOP	Standard Operating Procedure
SRM	Standard Reference Material
TALK	Total Alkanes
TOC	Total Organic Carbon
TPHC	Total Petroleum Hydrocarbons
µg	Microgram
µL	Microliter
µm	Micrometer
UCM	Unresolved Complex Mixture
URSGWC	URS Greiner Woodward Clyde
UPI	Upper Prediction Interval
USACE	United States Army Corps of Engineers
USAEDA	United States Army Engineering District, Alaska

Acronyms and Abbreviations (continued)

USDOI	United States Department of the Interior
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WBS	Work Breakdown Structure
yr	Year
ZGFAAS	Zeeman Graphite Furnace Atomic Absorption Spectrometry

Executive Summary

Overview

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 after a delay likely to be initiated at Liberty from an alternative location on the Endicott Satellite Drilling Island. 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.

In 1998, Minerals Management Service (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. The initial program, *Arctic Nearshore Impact Monitoring in the Development Area* (ANIMIDA), was 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 (Boehm et al., 2001b and Brown et al., 2005). Priorities were placed on characterizing the pre-construction environment and establishing a scientific basis for post-construction and production monitoring. Task Order 002 (Task 2) of the Continuation of Arctic Nearshore Impact Monitoring in Development Area (cANIMIDA) program continues the ANIMIDA sediment chemistry program.

Objectives

The cANIMIDA 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 cANIMIDA, are as follows:

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

Question 2. If concentrations of organic and/or metal chemicals of concern do increase in the environment as a result of the developments, do the increased concentrations exceed environmental quality guidelines (Effects Range-Lows [ERLs], Long et al., 1995)?

Question 3. What trends in the background levels of the chemicals of concern (i.e., anthropogenic-related organic and metal parameters) that are known to be associated with oil exploration, development, and production activities are seen in the historical sediment record, and do the concentrations of these chemicals increase as a result of these activities?

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

- Perform three annual field studies (fiscal years [FYs] 2004 to 2006) for the monitoring of sediment 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.

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

cANIMIDA Task 2 Study Design

To meet the objectives of the cANIMIDA 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 oil development projects. The elements of primary focus included:

- Hydrocarbons and associated polycyclic aromatic hydrocarbons (PAHs), and metals as primary contaminants of concern

- Sediment contamination

- Other natural and anthropogenic sources of chemicals of concern

The study design for cANIMIDA built on the ANIMIDA design (Boehm et al., 2001b and Brown et al., 2005) and involved:

- Design of a site-specific radial array sampling grid around the Northstar development
- Selection of area-wide stations that had previously been sampled as part of the MMS Beaufort Sea Monitoring Program (BSMP; Boehm et al., 1991) and ANIMIDA Programs
- Location and sampling of reference stations and regional sources.

Findings

As part of cANIMIDA, surficial sediment samples were collected from the cANIMIDA study area during the summers of 2004 through 2006 and sediment cores were collected in 2005 and 2006. All samples were analyzed for PAH, saturated hydrocarbons (SHC), steranes/triterpanes (S/T), metals, grain size, total organic carbon (TOC), and radionuclides for age-dating. This report also compares cANIMIDA results to surficial sediment sample data collected in 1999, 2000, and 2002 as part of the ANIMIDA Phase I (Boehm et al. 2001b) and Phase II (Brown et al., 2005).

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 cANIMIDA study area. Large changes in grain size distribution were first observed between 1999 and 2000 (Figure ES-1). During 1999, surficial sediment at stations N11-N14 was essentially all sand and gravel. In contrast, the 2000 samples from the same stations were dominated by silt and clay. 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 ES-1), both close to Northstar Island, much finer-grained particles were collected during 1999 than 2000. This shift may have resulted from inputs of coarser material at these stations 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.

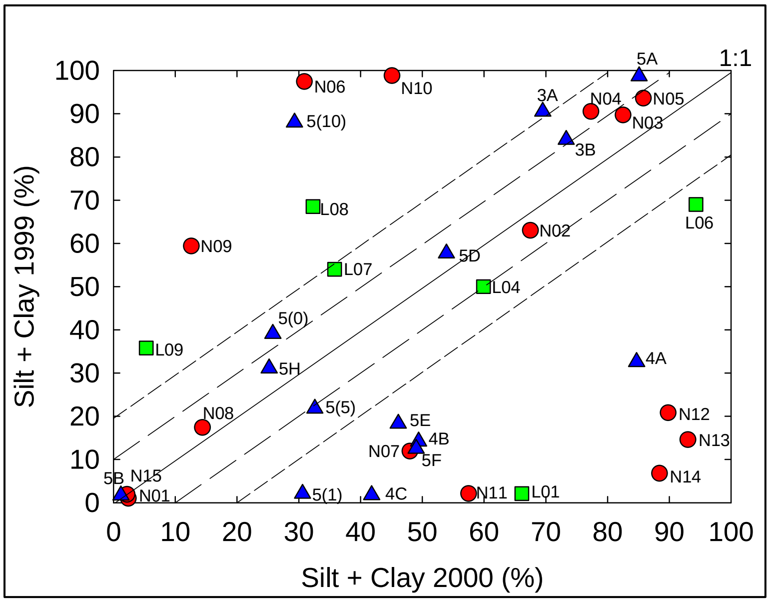


Figure ES-1. Values for silt + clay in surficial sediment from the coastal Beaufort Sea for 2000 versus 1999 with data from Northstar area (circles) Liberty Prospect (squares) and adjacent areas (triangles). Large and small dashed lines represent 90% and 80% deviation intervals from a 1:1 relationship between the two years, respectively. Solid line shows 1:1 relationship between 1999 and 2000 data. Dashed lines show interannual deviations of ±10 and ±20% for silt + clay.

The largest changes in grain size distribution observed during the ANIMIDA 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. Grain size distribution in 2004 - 2006 was different at several stations relative to 2002. More fine-grained sediment was observed in 2004 at stations 5B, 5D, N02 and N03 relative to 2002. In contrast, more gravel was collected at station N15 and more sand at station N11 in 2004. Collectively, the data from 1999-2006 show both abrupt and gradual movement of sediments in the Northstar area over time.

Previous shifts in grain size in the Liberty area were noted at station L01 where finer-grained sediment was collected during 2000 than during 1999 and at stations L08 and L09 where the opposite trend was found. Between 1999 and 2004, an increase in the amounts of fine-grained sediment has been observed at several stations including 4A, L07, L08 and 3A. The 2005 grain size data for the Liberty area shows increases in the coarser fractions at stations 4A and L08. The presence of a gravel (10.4%) and sand fraction (30.5%) at the deeper-water station L22 (29.2 m) suggests that ice-rafting may be a significant source of sediment to this location.

The most important finding derived from the grain size data is that sediments in many locations throughout the cANIMIDA study area are regularly shifting and that the sediment grain sizes found during one year may change prior to sampling during a subsequent year. Furthermore, the grain size distribution in surface sediments is very patchy from site to site. Thus, techniques that normalize sediment chemistry to account for differences in grain size have been used and radionuclide measurements have been made to determine that sediment collected during any given year is recent and not relict material.

Hydrocarbons. In contrast to a crude oil composition (Figure ES-2), the surficial sediments in the Northstar area and indeed for the whole region (e.g., Figure ES-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 ES-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 ES-4). Perylene was abundant in surficial sediments, often the most abundant single PAH compound in the overall PAH distribution. Perylene is not a contaminant associated with petroleum exploration and production activities, but is associated with biogenic sources of hydrocarbons in the Beaufort Sea.

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. The composition of the sediment hydrocarbons at Northstar is best summarized by a comparison of the pyrogenic to petrogenic PAH ratios in 1999, 2000, 2002 and 2004 – 2006 (Figure ES-4). A comparison for this ratio for all paired Northstar stations reveals no significant difference between years 1999 and 2000 indicating that there were no changes in sources 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 and 2004 show an increasing trend, which then decreases in 2005 and 2006. The comparisons of PAH data show a significant increase in the pyrogenic to petrogenic PAH ratio region-wide for years 2000 through 2004. A subsequent statistical analysis revealed that pyrogenic to petrogenic ratios for Northstar 2002 and Liberty/BSMP 2002 were not significantly different from each other, but that the ratios for Northstar 2004 were significantly greater than Liberty/BSMP 2004 and Northstar 2002. Also, the Northstar 2004 petrogenic PAH concentrations were significantly less than Northstar 2002 and Liberty/BSMP 2004 concentrations, while no significant differences were noted for pyrogenic PAHs between regions or years. These results suggest that the observed shift to a greater relative proportion of pyrogenic hydrocarbons in 2002 and 2004 could be the result of subtle increases in pyrogenic PAH; possibly related to Northstar area inputs (flaring, boat and vehicle traffic, etc). However, this shift in inputs is clearly variable (as shown by the decreased values in 2005 and 2006) and not currently of sufficient magnitude to result in a statistically significant increase in concentrations of PAH parameters. However, the observed potential of such a shift warrants continued sediment hydrocarbon monitoring in the area.

The observation that the Northstar 1999 sediments may be depleted in hydrocarbons relative to the other 1999, 2000, 2002, and 2004 - 2006 sediments is supported by a Total PAH less perylene versus silt + clay regression plot for all the 1999, 2000, 2002, and 2004 - 2006 sediment data. In this plot (Figure ES-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, 2002 and 2004 - 2006 samples. An analysis of the Northstar 2000, 2002, and 2004 – 2006 samples versus the BSMP and Liberty 2000, 2002, and 2004 - 2006 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 ES-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 2004 through 2006. No evidence of any inputs of Northstar-related petroleum hydrocarbons were observed in the surface sediments.

A comparison of the Total PAH from all cANIMIDA sediments from the study region in 1999, 2000, 2002, and 2004 - 2006 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. Additionally, potential toxicity of the PAHs in cANIMIDA sediments was evaluated using a more recent methodology; EPA's Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures (EPA, 2003). Based on this approach, if the sum of Equilibrium Partitioning Sediment Benchmark Toxic Units for "total PAHs" is less than or equal to 1.0, the PAH levels in the sediment is acceptable for the protection of benthic organisms. Toxic Unit values for the cANIMIDA Program sediments ranged from 0.01 to 0.7 for all samples collected, providing further evidence the concentrations of PAH present in the study area sediments are not likely to pose a risk to benthic organisms.

Figure ES-2. Northstar Oil – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).

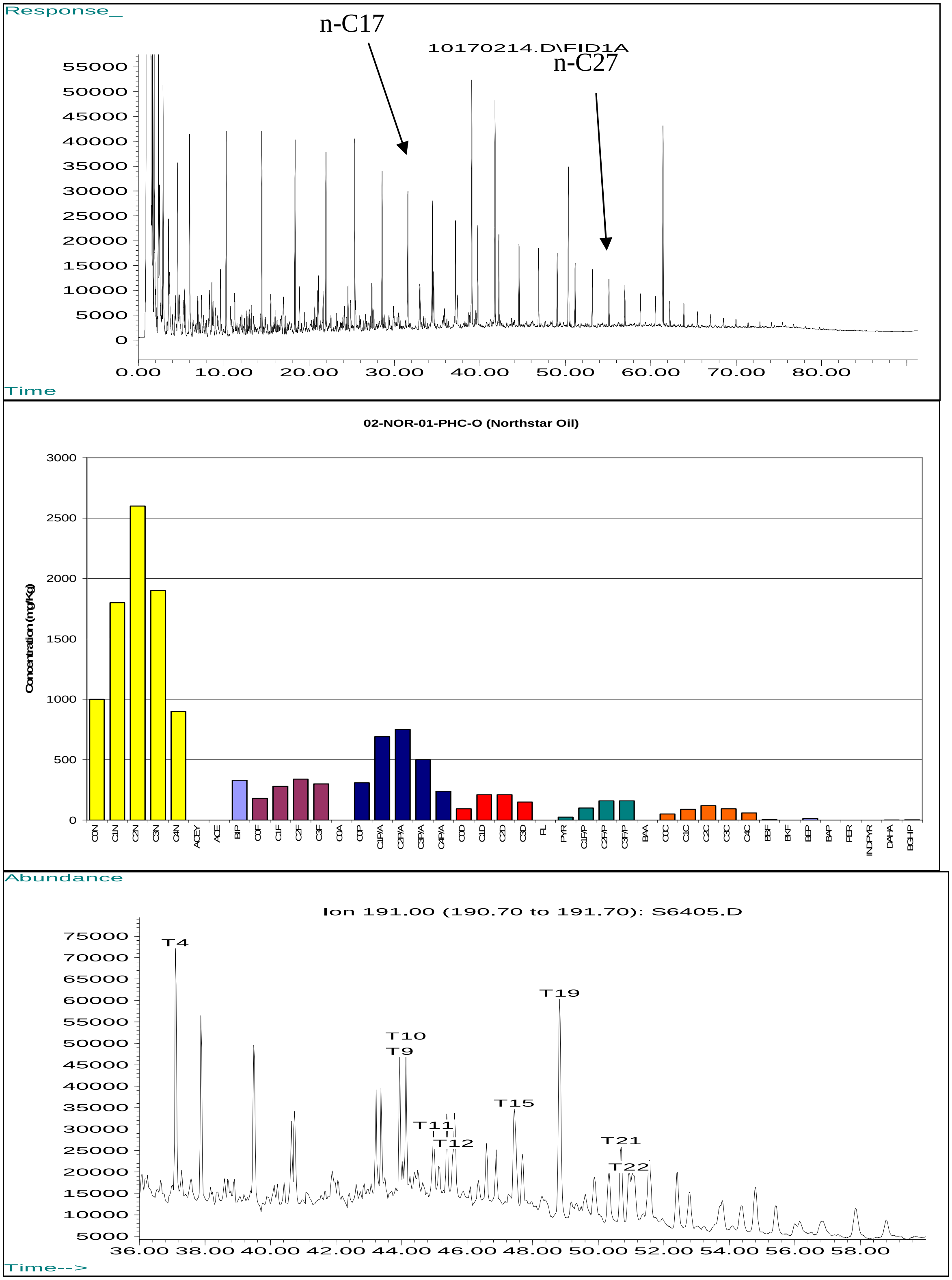
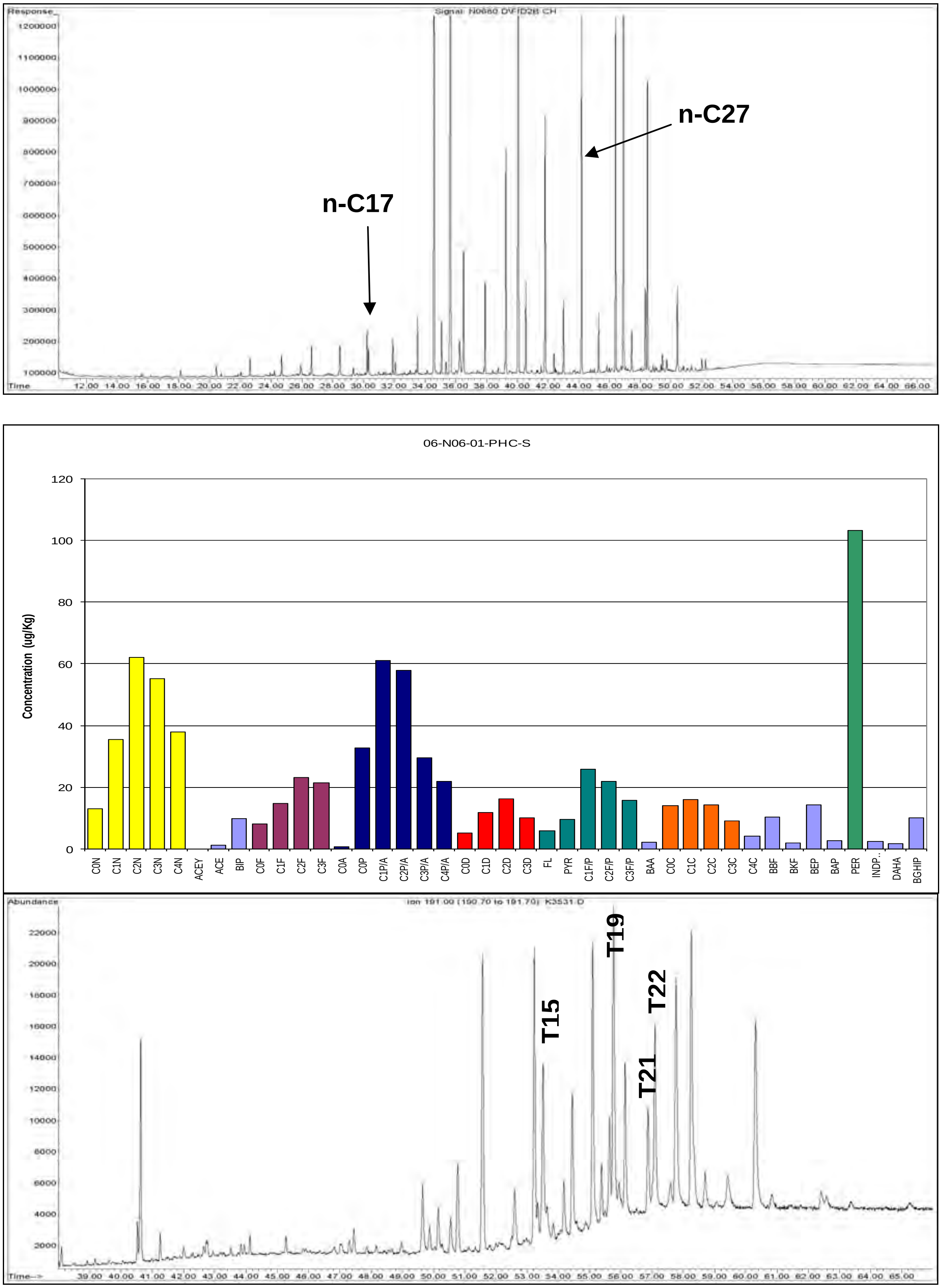


Figure ES-3. Station N06 Sediment, Year 2006 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).



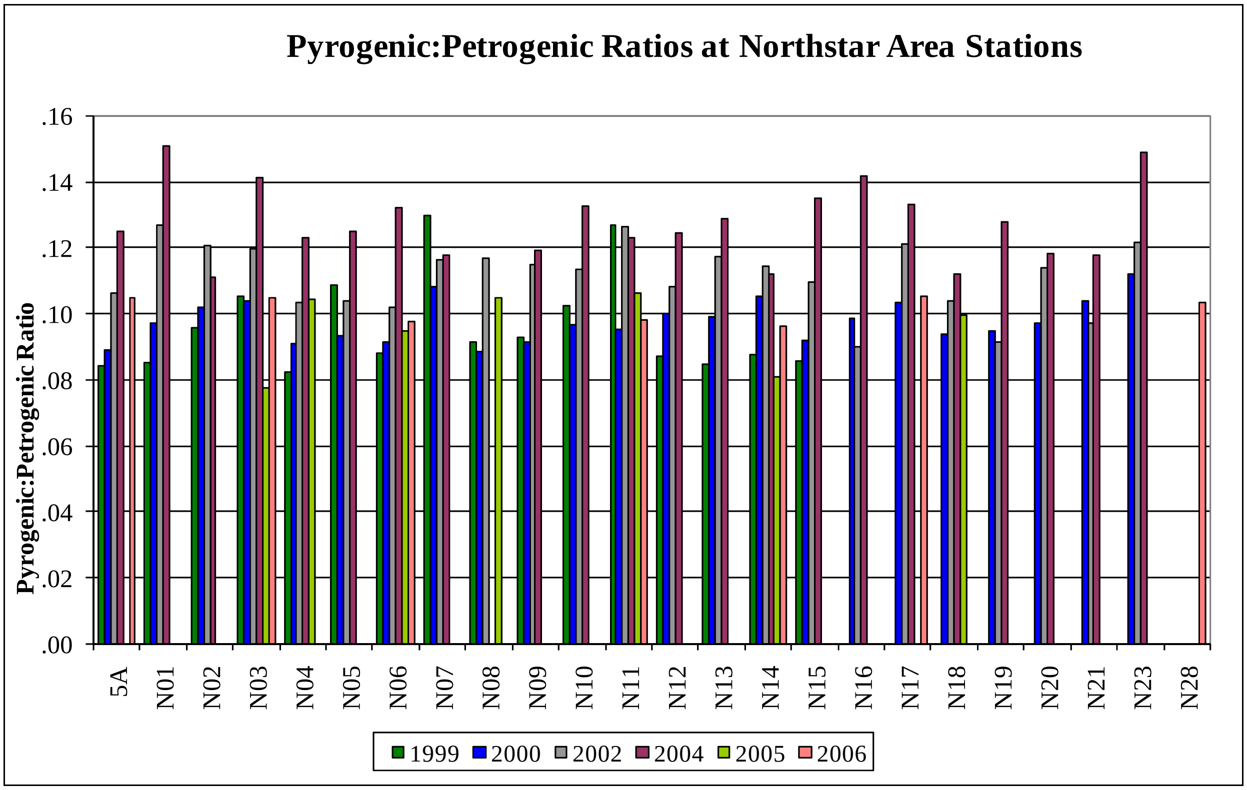


Figure ES-4. Pyrogenic:petrogenic ratios of Northstar surficial sediment samples for 1999 through 2006.

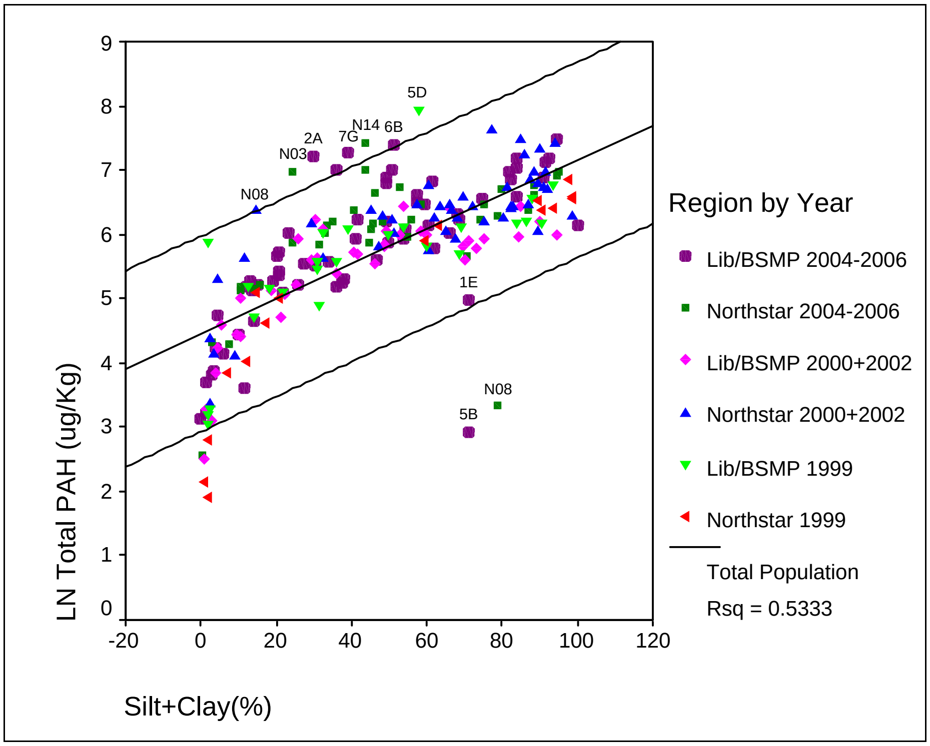


Figure ES-5. Regression plot of Total PAH less perylene versus silt + clay for all 1999 through 2006 Northstar, Liberty and BSMP sediments. The lines, Rsq, and 95% individual prediction intervals are from linear regression.

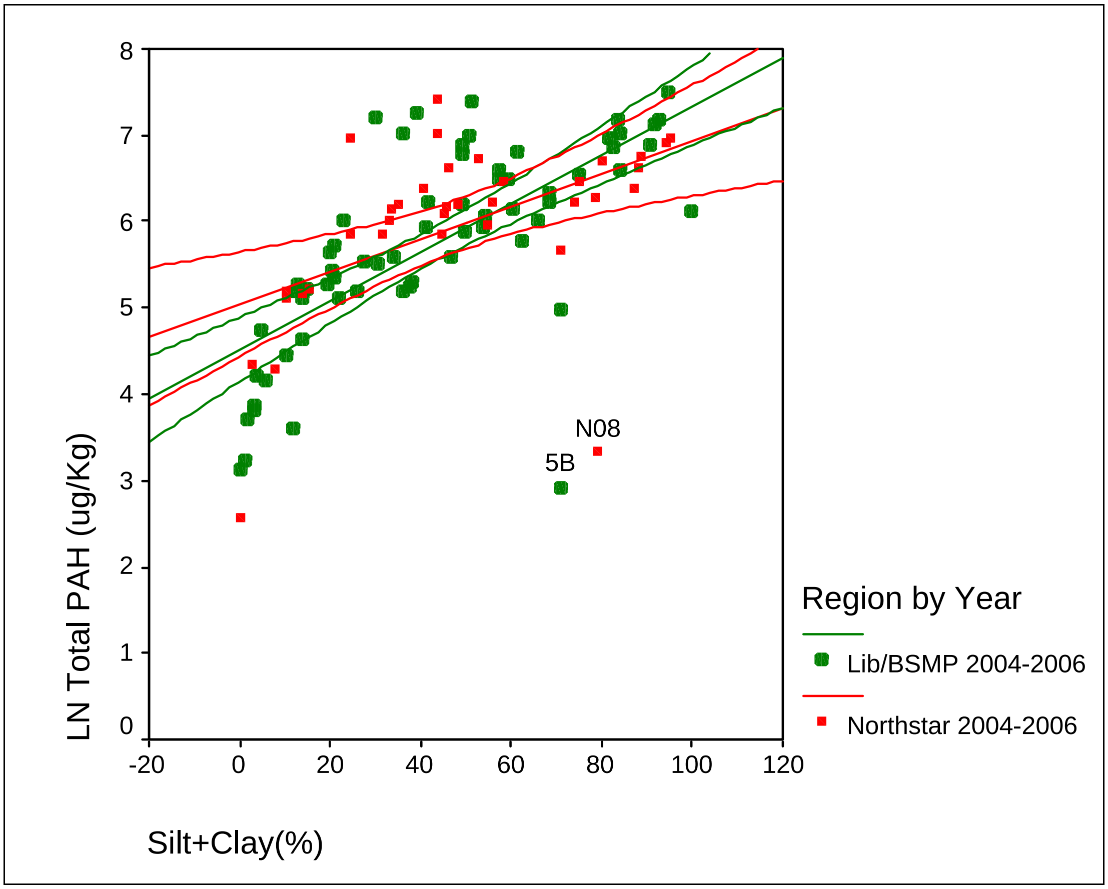


Figure ES-6. Regression plot of LN total PAH less perylene versus silt + clay for all 2004 through 2006 Northstar, Liberty and BSMP sediments. The lines and 95% mean regression prediction intervals are from linear regression and related statistical calculations.

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) 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. ANIMIDA metal data for 1999, 2000, 2001, and 2002 were used to produce a series of templates that can be used to identify possible metal contamination now and in the future. These templates were further tested with the cANIMIDA 2004 - 2006 data. For example, concentrations of Cr for 2004 - 2006 correlated well with Al (r = 0.99 for 2004 in Figure ES-7). The 2004 - 2006 data, with several noted exceptions for sites that had not previously been occupied during the ANIMIDA or cANIMIDA projects, plotted within the 99% prediction interval established previously using the 1999-2002 data from the Beaufort Sea (Trefry et al., 2003). The good linear fit for Al versus Cr is consistent with the mixing of relatively uniform composition, metal-rich aluminosilicate phases with metal-poor sand and shell. Thus, Cr levels in natural sediment from the Beaufort Sea are predicted to follow the trend presented in Figure ES-7. Graphs for Al versus Ba, Ni, Co, Cu, As, Cd and Sb also show strong linear relationships with few anomalous points from 2004 - 2006 that plot at more than ~10% above the upper prediction interval. In almost all cases anomalous results which were enriched in trace metals of concern were linked to historical exploration drilling activities from pre-1990, when drilling muds were discharged directly on the ice during the winter.

For example, Barium has been used historically as a sensitive indicator for the presence of petroleum drilling mud in sediment because barite (BaSO4) is such a common and distinctive additive. The graph for Al versus Ba for the 2004-2006 data shows 4 of 112 data points as positive anomalies on the Ba versus Al plot (Figure ES-8). Barium anomalies were previously reported for stations 7A and 7G in Harrison Bay for samples collected in 1989 and are consistent with exploratory drilling and drilling residues in the area. These sites had not been previously occupied during the ANIMIDA or cANIMIDA project. A detailed record of Ba contamination is described for the sediment core from station 7A below. Barium anomalies at stations N06 and 6H also may be due to minor remnants of drilling discharges.

Radionuclides. The cANIMIDA study area was described by Reimnitz and Barnes (1974) as a net erosional sedimentary environment during the Holocene. Naidu et al. (2001) and Trefry et al. (2003) reported difficulties in obtaining cores that could be aged dated using radionuclides that focus on the past 50-100 years. At best, sediment deposition in the cANIMIDA area has been patchy during the past century. Trefry et al. (2003) cautioned investigators to be sure that sediments collected for analysis of potential pollutants are representative of the most recent inputs. In this regard, surficial sediments from the 2004-2006 surveys were counted for the activities of excess ^{210}Pb and total ^{137}Cs (Figure ES-9). The pre-survey assumption was that surface sediments with low activities of excess ^{210}Pb (<0.5 dpm/g) or ^{137}Cs (<0.05 dpm/g) would contain very little silt or clay that had been recently or sufficiently well exposed to the water column or at the sediment-seawater interface to adsorb excess ^{210}Pb or ^{137}Cs. Therefore, such sediments would be less likely to contain recent material that had an anthropogenic contribution of metals or hydrocarbons. However, in some cases, sediments with low activities of excess ^{210}Pb and ^{137}Cs might be predominantly sand that had a naturally low affinity for these isotopes. Sediments that have intermediate levels of the two isotopes may be sandy or contain some mixture of old, recent and sandy sediments.

The radionuclide results for 2004, 2005 and 2006 samples indicate that during each of the three years, surface sediments with non-detectable amounts of excess ^{210}Pb (<0.05 dpm/g) and ^{137}Cs (<0.015 dpm/g) were found. In contrast, maximum values for excess ^{210}Pb of 2.8 dpm/g and ^{137}Cs of 0.20 dpm/g were observed. Collectively, the activities for ^{226}Ra (parent isotope to ^{210}Pb) correlated well with concentrations of Al (Figure ES-9a). This good relationship is consistent with higher amounts of ^{226}Ra in Al-rich clays. The y-intercept of 0.63 on the Al versus ^{226}Ra graph suggests that another Ra-bearing phase that contains little or no Al is present in the sediments. The relationship between Al and excess ^{210}Pb in surface sediments shows considerable scatter (Figure ES-9b). One explanation for the observed scatter is large differences in the accumulation rates and/or ages among the 112 samples of surface sediment. Samples with low amounts of excess ^{210}Pb (<0.5 dpm/g) and Al concentrations >3% are less likely to contain very much recent sediment relative to samples with excess ^{210}Pb >0.5 dpm/g and Al concentrations >3%. A weak, but observable trend of higher activity for excess ^{210}Pb in sediments with a higher activity of ^{137}Cs than was observed for the surface sediments, is consistent with increased adsorption of the two isotopes from water by more clay-rich (i.e., Al-rich) samples.

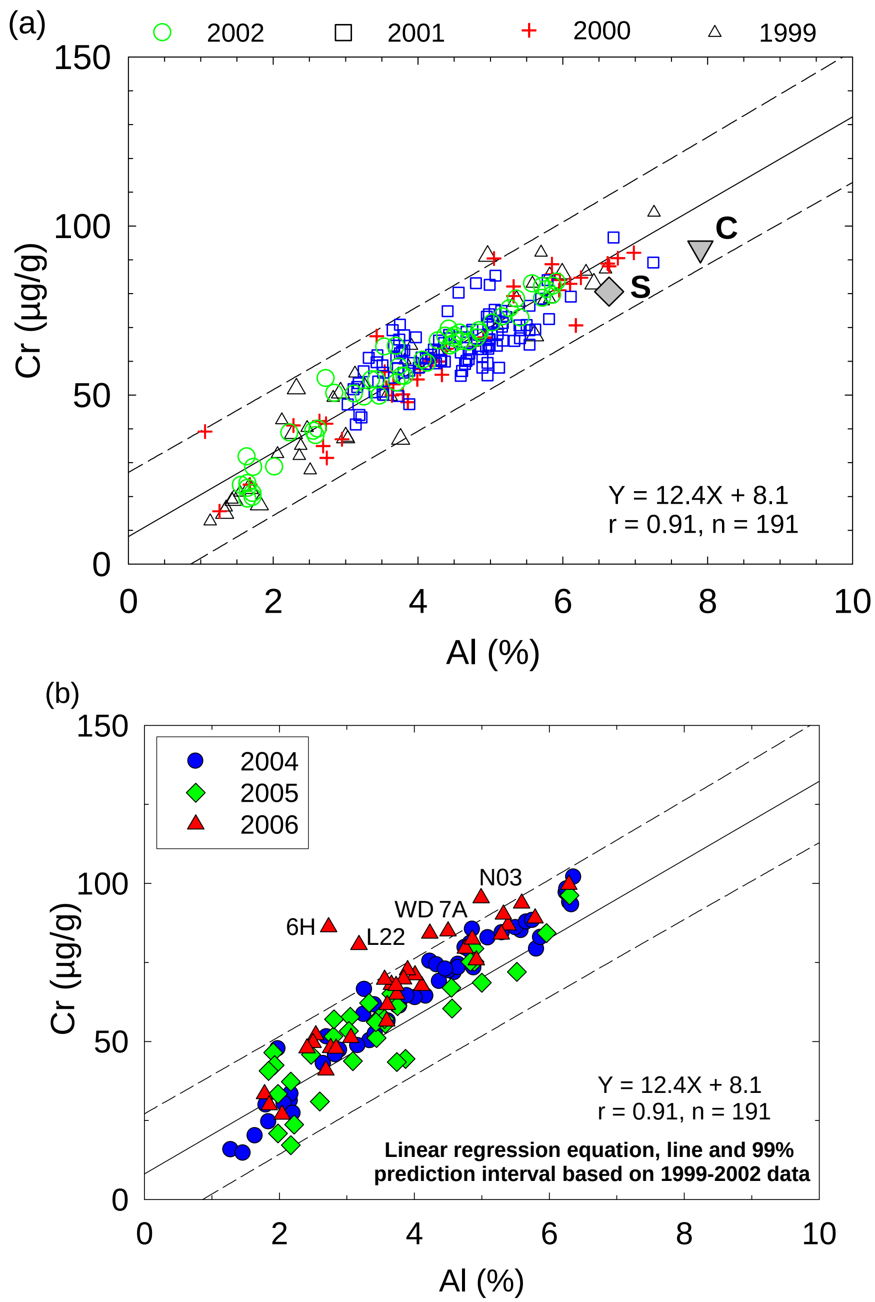


Figure ES-7. Concentrations of aluminum versus chromium for surface sediment from cANIMIDA study area collected in (a) 1999-2002 and (b) 2004-2006.

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) and Colville (C) Rivers. Data for sites identified on the graphs were not included in the regression calculations. Data for 2004-2006 were plotted with the prediction interval from the1999-2002 data.

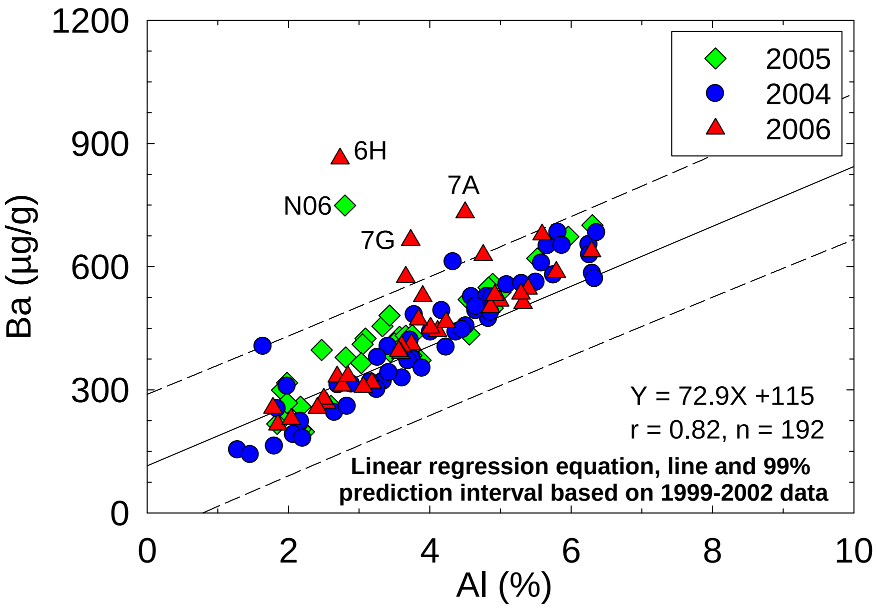


Figure ES-8. Concentrations of aluminum (Al) versus barium (Ba) for sediment from the cANIMIDA study area collected in 2004-2006.

Equations are from linear regression calculations and r is the correlation coefficient. Dashed lines show the 99% prediction interval. Data from 2004-2006 are plotted with prediction interval from 1999-2002 data.

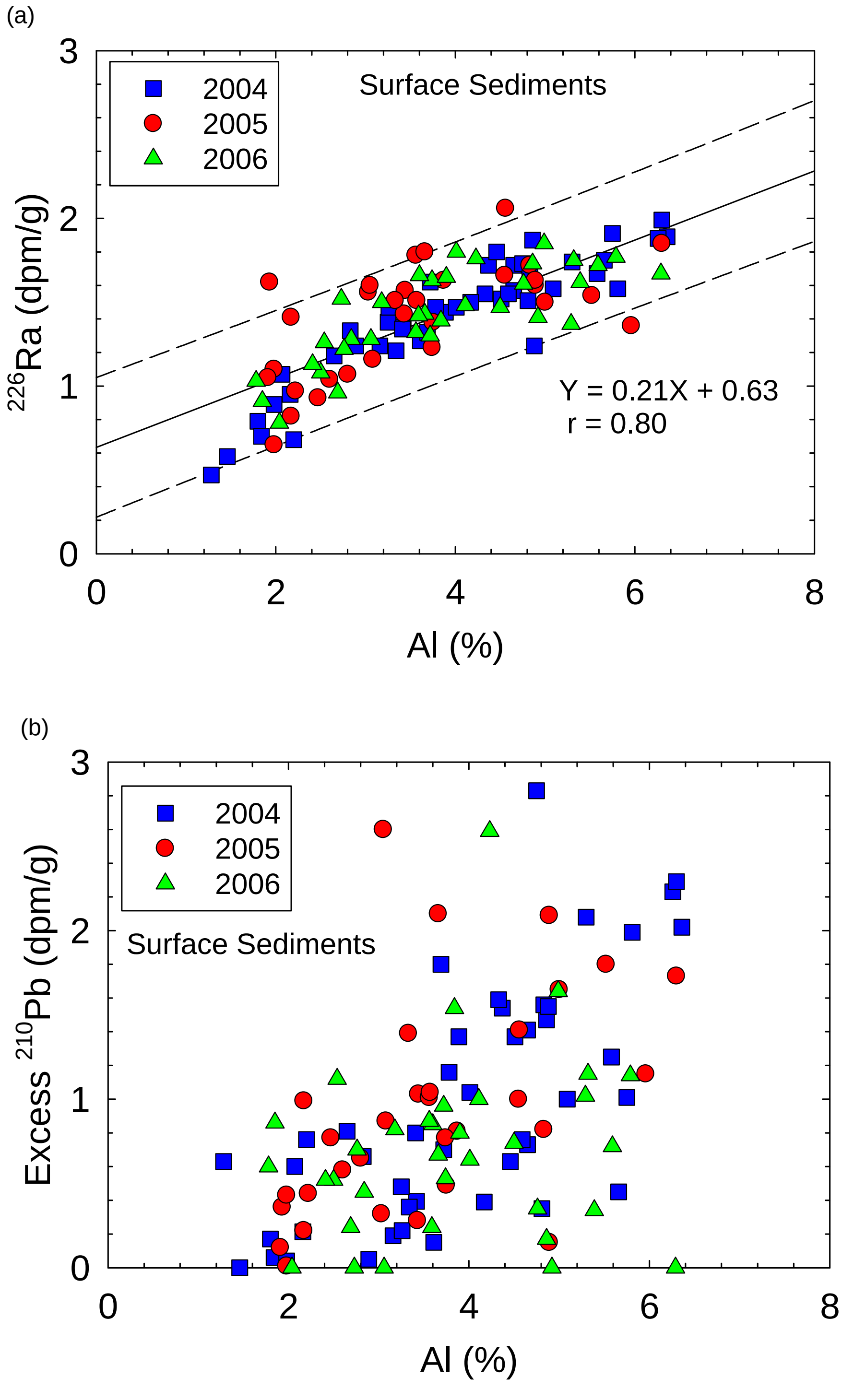


Figure ES-9. Concentrations of Al versus (a) activity of ^{226}Ra and (b) activity of excess ^{210}Pb for surface sediments from 2004-2006.

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

Temporal Trends of Hydrocarbons and Metals in Cores. The historical record of hydrocarbons and metal levels in sediments from the cANIMIDA study area was developed from 14 cores collected during 2005 and 2006. As in the ANIMIDA program, collection of sediment cores suitable for age-dating was complicated by bottom-fast ice, ice gouging, low net sediment accumulation rates, low activities of excess ^{210}Pb and ^{137}Cs, and storm-induced re-suspension 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 a few cores were viable for establishing a geochronology over the past 50 to 100 years using both ^{137}Cs and excess ^{210}Pb. In many instances, extremely low levels or no detectable amounts of excess ^{210}Pb or ^{137}Cs 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 and others, 2001) have encountered many of the same difficulties found during the cANIMIDA study. Based on inherent difficulties with area sediments, a primary goal of the geochronology effort for the cANIMIDA study was to collect some representative sediment that was deposited prior to the onset of development during the early 1970s and some sediments that were deposited post-development. Concentrations of trace metals and hydrocarbons were determined for a total of 81 samples from seven cores collected in 2005 (N26, PB1A, L17B, BP01, E01, 1C and 2A) and five cores collected in 2006 (N17, L22, 7A, 7C and 7E). Some variability in concentrations of hydrocarbons and metals was observed in each core, mainly due to variations in amounts of fine-grained sediment.

Forty-seven of 1296 metal concentrations (3.6% of the data points) plotted above the upper prediction intervals developed for the ANIMIDA study area. Thirty-five of the 47 data points were for sediments collected in Harrison Bay and 3 of the 47 data points were for station 2A in Camden Bay. Both Harrison Bay and Camden Bay are not part of the original ANIMIDA study area, but were part of the original Beaufort Sea Monitoring Program. The remaining 9 data points were from five different cores in different sediment layers and plot relatively close to the upper prediction interval and do not reveal any striking anomalies that can be clearly tied to anthropogenic sources.

Twenty of the 38 data points from outside the immediate cANIMIDA study area that plotted above the upper prediction interval were for Ba, 8 from Camden Bay and 12 from Harrison Bay. The Ba anomalies in Harrison Bay are found at depth in the core that can be best explained by the presence of barite residues from drilling muds. For example, a vertical profile for the Ba/Al ratio for the sediment core from station 7E shows that all 4 samples with significant Ba anomalies are between 2 and 10 cm in the 30-cm vertical section of sediment (Figure ES-10). The maximum anomaly dates to about 1988 ± 2 years. Drilling activity in the area of Harrison Bay sampled during 2006 is within the area of western Harrison Bay where drilling occurred in 1985 and 1986. Furthermore, samples collected in western Harrison Bay during 1989 had Ba anomalies in the top 2 cm of sediment The results for Ba in the core from station 7E (Figure ES-10) suggest that the peak concentration from the mid-1980s may have been preserved at this site. However, the sediments in the top 6 cm at station 7E contain high levels of TOC at 2-4%;

therefore, a diagenetic explanation for the observed Ba profile cannot be ruled out. More detailed study of the sediment column is needed to resolve natural from anthropogenic layers of Ba-rich sediment.

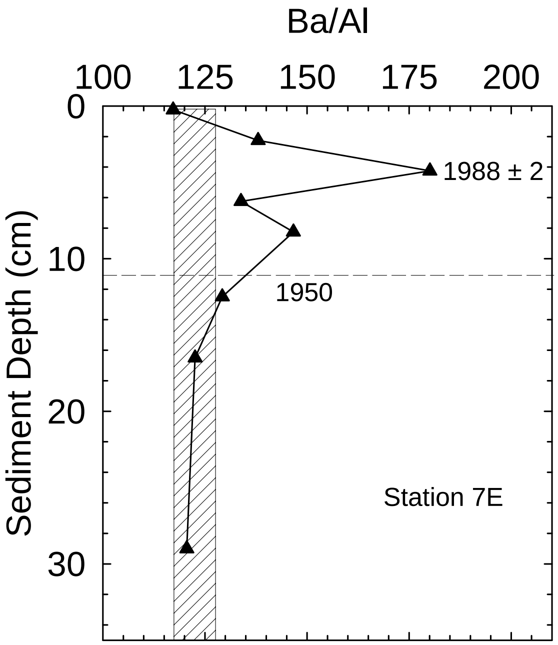


Figure ES-10. Vertical profile for the Ba/Al ratio (as ppm/%) in sediments from 2006 station 7E.

Shaded area shows background Ba/Al ratio (ppm vs. %) for study area. Dashed line shows deepest sample with detectable amounts of ^{137}Cs and thus dates to the early 1950s. Date of 1988 with error is from ^{137}Cs and excess ^{210}Pb data.

In general, comparisons of the core profiles for key diagnostic organic hydrocarbon parameters for all of the cores do not show any clear trends that would indicate an increase in petroleum hydrocarbons over time. The cores for which pre- and post-development dates can be established generally show uniform distributions of key parameters throughout the cores, with some variability in specific core sections. However the overall composition of the three classes of analytes analyzed (SHC, PAH and biomarkers) are similar throughout the cores and are consistent with the regional background hydrocarbon sources identified in the surface sediments.

In examining hydrocarbon trends in all of the cores, one technique developed in this study (discussed earlier) involves examining the relationship between the organic parameter of interest and perylene content. The natural background concentrations of organics in the study area have been shown to co-vary as a function of perylene content. 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. A plot of all the 2005 and 2006 sediment core data for total PAH minus perylene versus perylene is shown in Figure ES-11. In this plot a regression and 95% prediction intervals are shown for all data, where the regression defines the natural geological/geochemical background of all the sediments. The plot shows that most of the core samples fall within the 95% prediction intervals, indicating that the 2005 and 2006 core sediment samples are generally not different in Total PAH content from the historical natural background of the region.

Overall, the organic analyses of the sediment cores collected during 2005 and 2006 have provided an important historical perspective on hydrocarbons in the sediments from the study area. The results have shown that the concentrations and sources of hydrocarbons are generally uniformly consistent over the past 50 or more years and represent a regional background assemblage. For most organic hydrocarbon parameters, there are no significant increases (after geochemical normalization) of hydrocarbons in the sedimentary record post oil and gas development in the Prudhoe Bay area.

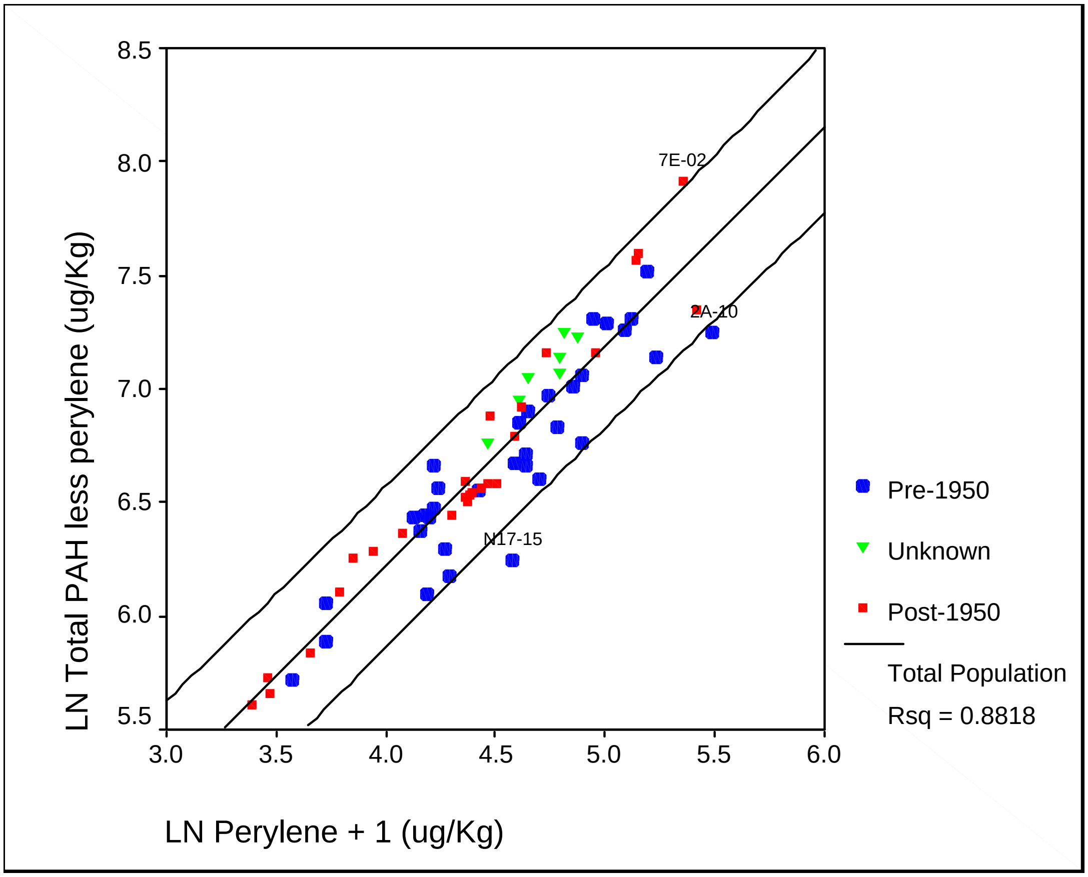


Figure ES-11. Regression plot of total PAH less perylene versus perylene for all 2005 through 2006 sediment core samples.

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

Summary

Overall, the results of the three years of cANIMIDA sampling along with ANIMIDA Phase I and II results indicate 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 spatial and temporal 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 expected to commence directional drilling at Liberty in 2010 from the Endicott satellite drilling island. 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. The initial program, *Arctic Nearshore Impact Monitoring in the Development Area* (ANIMIDA), was 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 (Brown et al., 2004). Priorities were placed on characterizing the pre-construction environment and establishing a scientific basis for post-construction and production monitoring. Task Order 002 of the Continuation of Arctic Nearshore Impact Monitoring in Development Area (cANIMIDA) program continues the ANIMIDA sediment chemistry program conducted under Task Order 002.

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 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 was originally 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 was 30 miles (~50 km) southeast of the proposed Northstar development and 7 miles (~12 km) from the Endicott Causeway. With recent advances in drilling technology, the Liberty development will now be directionally drilled from the Endicott satellite drilling island located at approximately 1.6 miles on 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 cANIMIDA 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, several wells are 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) and an Environmental Assessment for the extended reach drilling from Endicott in 2007 (USDOI, 2007). BPXA announced in July 2008 that they would proceed with development of the Liberty field using ultra-extended reach drilling from the Endicott field satellite drilling island. This approach greatly reduces the development logistics and potential environmental complexities associated with an offshore production island and pipeline as originally proposed. Drilling is expected to commence at Liberty in 2010.

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

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

1.5 Study Objectives

The primary objectives of the cANIMIDA program were 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 primary objective for cANIMIDA Task 2 was to characterize the sediments near ongoing and proposed offshore oil development related to potential contaminants and to serve as a continuation of the ANIMIDA organic and inorganic chemistry monitoring program. The specific objectives for Task 2 are listed below:

- Perform three annual or biannual field studies (fiscal years [FYs] 2004 to 2007) for the monitoring of sediment 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.

The results from ANIMIDA Task 2 sediment and biota sampling surveys indicated that no significant organic and metal contaminant inputs from Northstar were detected, and that any observed changes were well within the natural variability (Brown et al., 2004).

1.5.1 Task Order 2 Research Questions and Hypotheses

The objectives of the cANIMIDA program address a series of scientific questions concerning the potential impacts of the Northstar and Liberty developments. Each question can be turned into a testable hypothesis, which guides the design of the technical program. Three questions (Q) and hypotheses (H) applicable to Task Order 002 surficial sediments samples follow.

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

H1. The concentrations of organic (H1a) and metal (H1b) chemicals of concern 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 chemicals of concern do increase in the environment as a result of the developments, do the increased concentrations exceed environmental quality guidelines (Effects Range-Lows [ERLs], Long et al. 1995, Equilibrium Partitioning Sediment Benchmarks [ESBs], EPA 2003)?

H2. Concentrations of organic (H2a) and metal (H2b) chemicals of concern adjacent to the Northstar and/or Liberty developments do not pose an ecological risk to marine organisms as determined by sediment quality benchmarks.

Q3. What trends in the background levels of the chemicals of concern (i.e., anthropogenic-related organic and metal parameters) that are known to be associated with oil exploration, development, and production activities are seen in the historical sediment record, and do the concentrations of these chemicals increase as a result of these activities?

H3. The background level of chemical of concern in the historical sediment record show no trends associated with oil exploration, development, and production activities.

Incremental variations in hydrocarbons and metals are 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 samples of other representative sources (natural and anthropogenic) of these chemicals, so that sources can be fingerprinted and in turn detected and identified in sediments. All of these elements were built into this program. The design of this program 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	1997	Satellite[2]
Badami	Offshore	Oil	Onshore	1990	1998	Field
Eider	Offshore	Oil	Offshore	1998	1998	Satellite[1]
Tarn	Onshore	Oil	Onshore	1991	1998	Field
Tabasco	Onshore	Oil	Onshore	1992	1998	Satellite[2]
Midnight Sun	Onshore	Oil	Onshore	1998	1999	Satellite[4]
Alpine	Onshore	Oil	Onshore	1994	2000	Field
Northstar	Offshore	Oil	Offshore	1984	2001	Field
Aurora	Onshore	Oil	Onshore	1999	2001	Satellite[4]
NW Eileen/Borealis	Onshore	Oil	Onshore	1999	2001	Field
Polaris	Onshore	Oil	Onshore	1999	2001	Satellite
Meltwater	Onshore	Oil	Onshore	2000	2001	Pool
Palm	Onshore	Oil	Onshore	2001	2002	Pool
Orion	Onshore	Oil	Onshore	2000	2003	Satellite
Raven	Onshore	Oil	Onshore	?	2006	Pool
Fiord (CD 3)	Onshore	Oil	Onshore	1992	2006	Pool
Nanuq (CD 4)	Onshore	Oil	Onshore	1996	2006	Pool
Oooguruk	Offshore	Oil	Offshore	2003	2008	Pool

Source: USDOI, 2008

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.

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

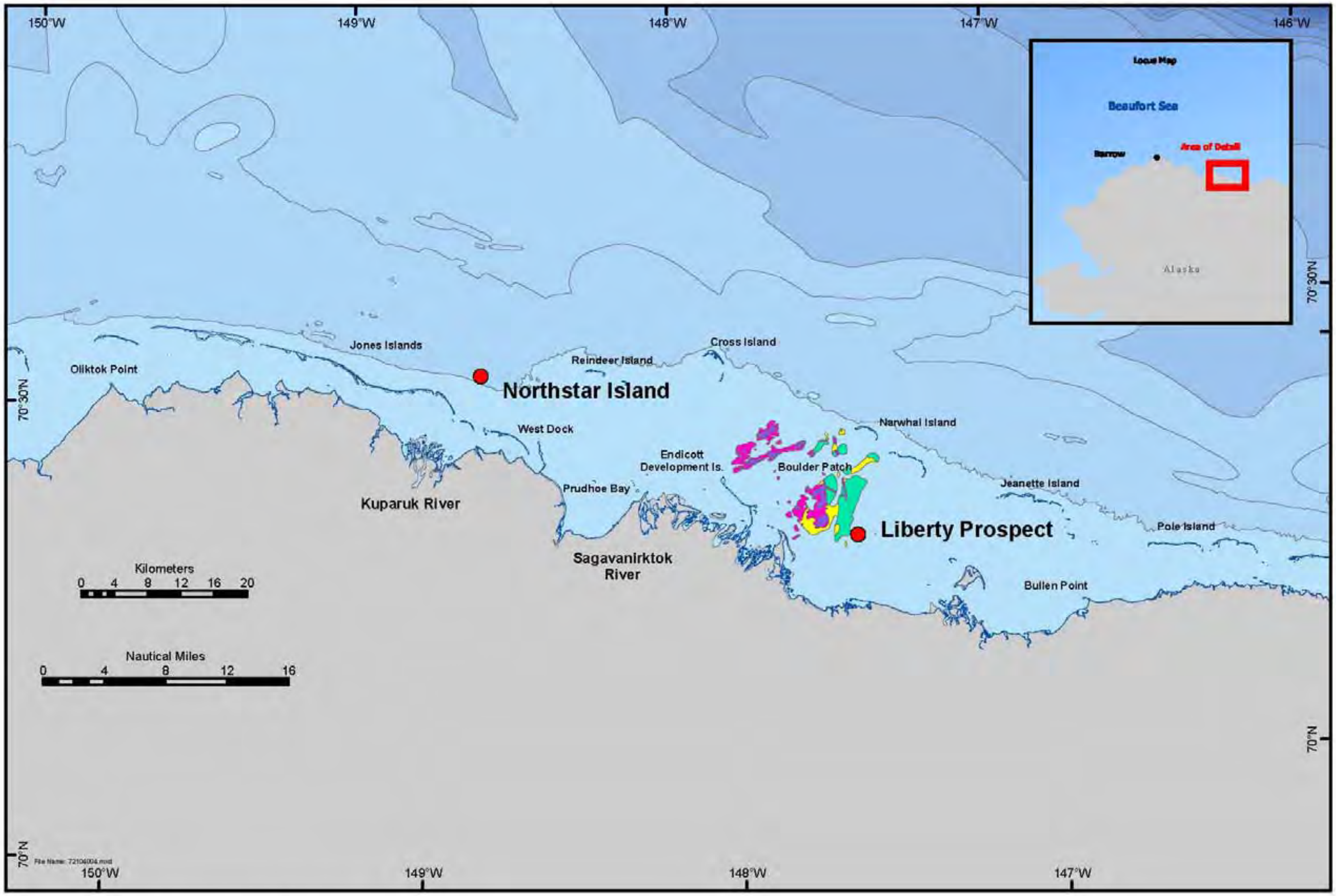


Figure 1-1. Map of the ANIMIDA study area.

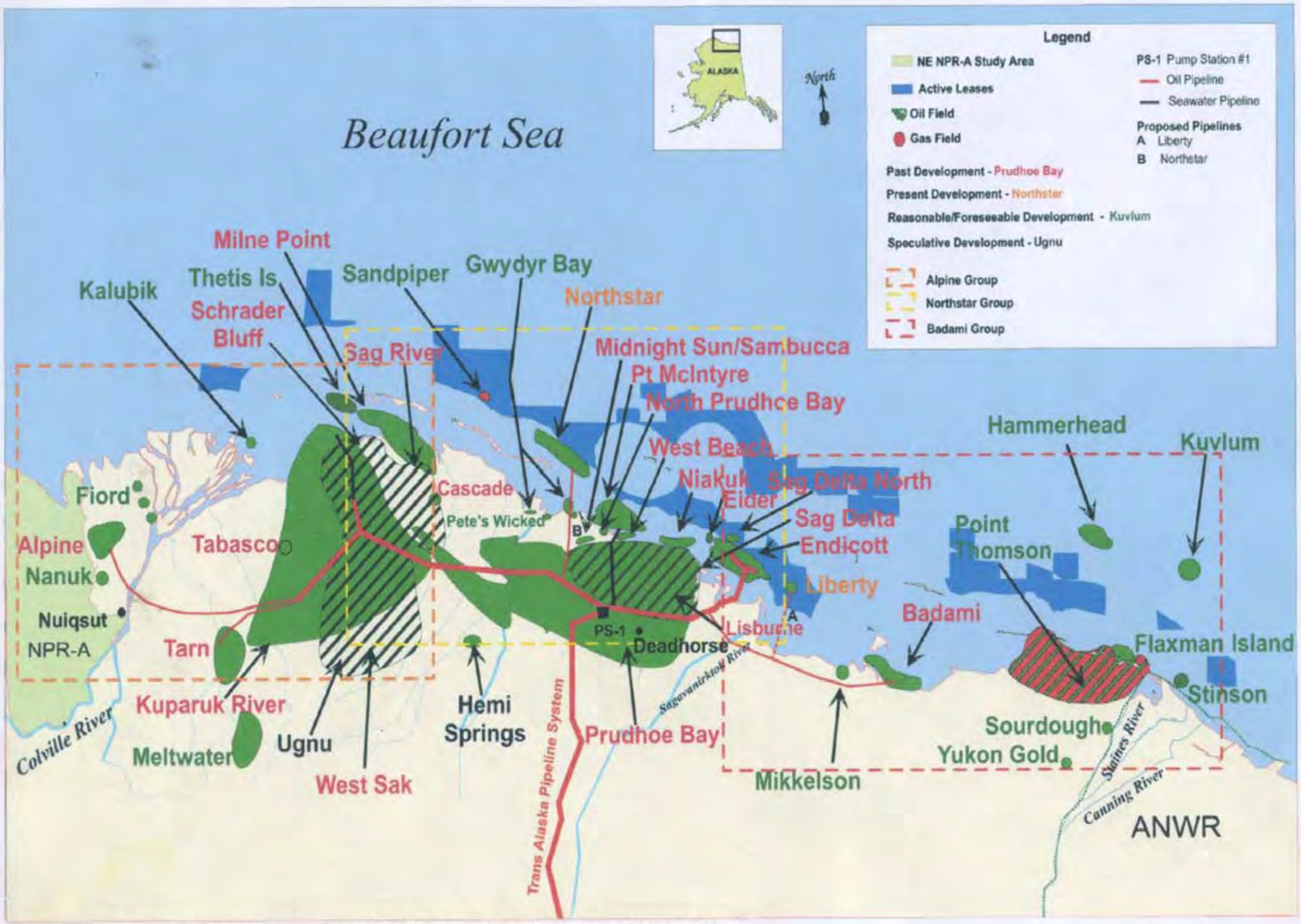
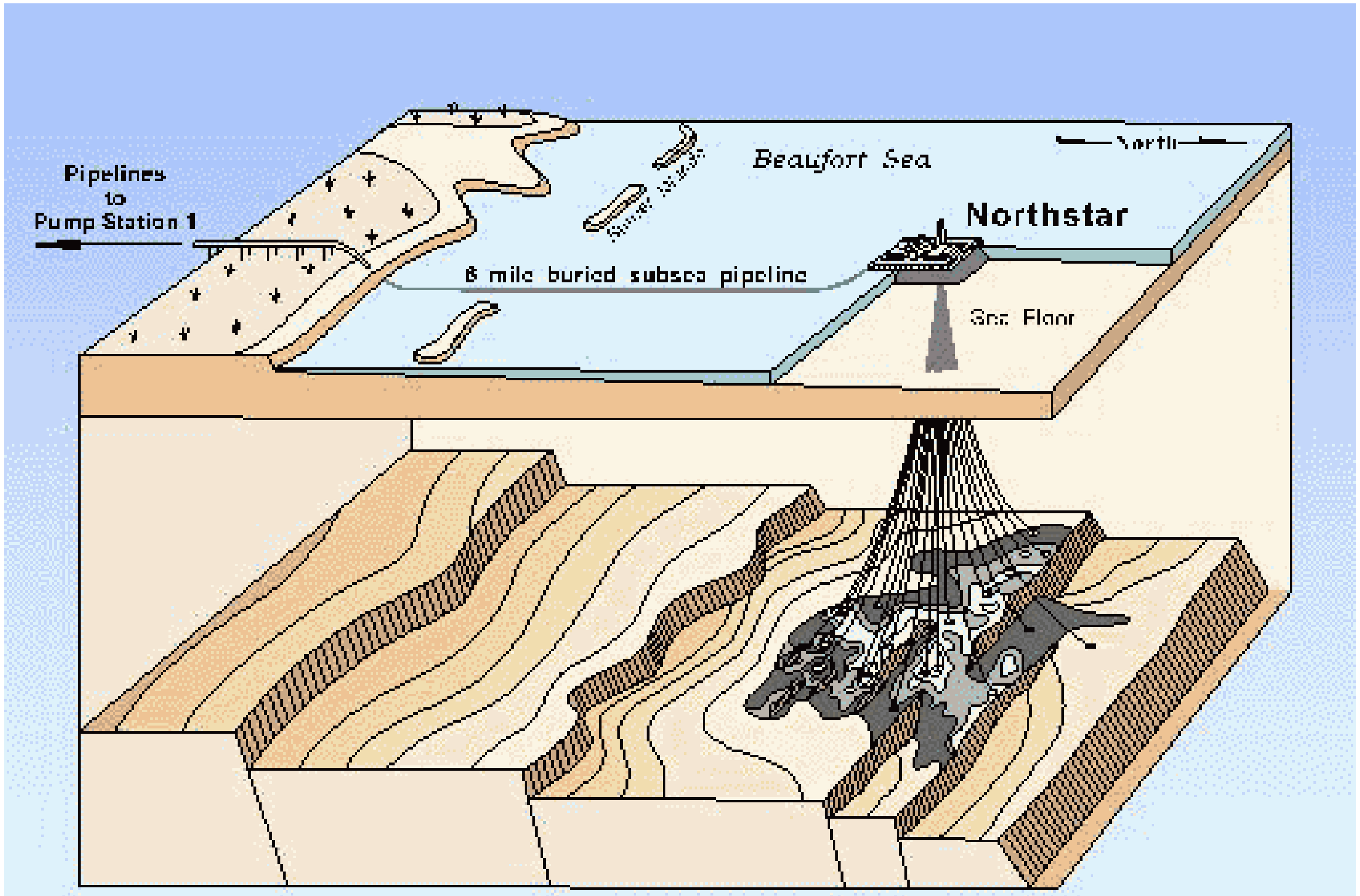


Figure 1-2. General Map of Onshore and Offshore Oil and Gas Development In the Study Areas

Source: USDOI, 2001

Figure 1-2. General map of onshore and offshore oil and gas development in the study areas.



Source: http://www.bp.com/alaska/index_nstar.htm

Figure 1-3. Schematic of BP's Northstar development.

2.0 Methods

This section and Appendix C describe the methods used in field sampling, field measurements, laboratory analyses, and data analyses.

2.1 Field Methods

2.1.1 Summer 2004 Survey

The summer 2004 field sampling was conducted from July 28 to August 27, 2004. The scientific crew, aboard the MMS *Vessel 1273*, collected samples for chemical and other analyses from the program study area. The field sampling and logistics plan (Battelle, 2004a) prepared for the summer 2004 field survey provides detailed explanations of the field methods for sample collection, equipment decontamination, and subsampling. Field sampling personnel from Battelle, Florida Institute of Technology (FIT), and Kinnetic Laboratories 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 operating conditions and logistic considerations. A detailed description of the activities conducted during the survey, including a log of the daily activities, is included in the Field Survey Report (Battelle, 2004b). 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. Task 2 surface sediment samples (0 to 1 centimeters [cm]) for hydrocarbon and metals chemistry were successfully collected from 47 offshore stations, including:

- 16 historic Beaufort Sea Monitoring Program (BSMP) stations,
- 22 historic Northstar Island and Northstar pipeline stations,
- 7 historic Liberty stations,
- new Liberty locations, and
- 1 crude oil source sample from Northstar.

A complete list of the sediment 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, and date of collection for each sample. Figure 2-1, a map of the cANIMIDA study area, shows the locations of the summer 2004 sampling stations. Additional daily survey and sampling station information is included in the 2004 station logs contained in the Summer 2004 Field Survey Report (Battelle, 2004b). Two stations were originally collected from incorrect positions [Stations 5(5) and L01] due to coordinate discrepancies, this error was noted while in the field and samples were later collected from the correct locations. The results for the two mis-positioned samples are reported but were not included in the data analyses.

2.1.2 Summer 2005 Survey

The summer 2005 field sampling was conducted from July 26 to August 14, 2005. The scientific crew, aboard the MMS *Vessel 1273*, collected samples for chemical and other analyses from the program study area. The field sampling and logistics plan (Battelle, 2005a) prepared for the summer 2005 field survey provides detailed explanations of the field methods for sample collection, equipment decontamination, and subsampling. Field sampling personnel from Battelle, FIT, and Kinnetic Laboratories 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 operating conditions and logistic considerations. A detailed description of the activities conducted during the survey, including a log of the daily activities, is included in the Field Survey Report (Battelle, 2005b). 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. Task 2 surface sediment samples (0 to 1 cm) for hydrocarbon and metals chemistry were successfully collected from 33 offshore stations, including:

- 18 historic and 1 new BSMP stations,
- 8 historic and 1 new Northstar Island stations,
- historic and 1 new Liberty stations,
- 1 historic and 1 new Prudhoe Bay stations,
- 1 historic Endicott station, and
- 1 new Boulder Patch station.

Task 2 sediment cores were collected from seven stations. Five to nine sediment depth segments were selected for chemical analysis from five of the seven sediment core stations for a total of 32 sediment core samples.

A complete list of the sediment 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, and date of collection for each sample. Figure 2-2, a map of the cANIMIDA study area, shows the locations of the summer 2005 sampling stations. Additional daily survey and sampling station information is included in the 2005 station logs contained in the Summer 2005 Field Survey Report (Battelle, 2005b).

2.1.3 Summer 2006 Survey

The summer 2006 field sampling was conducted from July 24 to August 12, 2006. The scientific crew, aboard the MMS *Vessel 1273,* collected samples for chemical and other analyses from the program study area. The field sampling and logistics plan (Battelle, 2006a) prepared for the summer 2006 field survey provides detailed explanations of the field methods for sample collection, equipment decontamination, and subsampling. Field sampling personnel from Battelle, FIT, and Kinnetic Laboratories participated in the survey. The scientific team and ship's captain (Mark Mertz - TEG Ocean Services) conducted the work on a 12- to 18-hour-a-day basis depending on operating conditions and logistic considerations. A detailed description of the activities conducted during the survey, including a log of the daily activities, is included in the Field Survey Report (Battelle, 2006b). 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. Task 2 surface sediment samples (0 to 1 cm) for hydrocarbon and metals chemistry were successfully collected from 34 offshore stations, including:

- 13 historic and 1 new BSMP stations,
- 6 historic and 2 new Northstar Island stations,
- historic and 4 new Liberty stations,
- 1 new McCovey station,
- 1 new West Dock station,
- 2 historic and 1 new Endicott station, and
- 1 historic Boulder Patch station.

Collected five source/peat material samples

Fourteen sediment cores were collected from seven stations. Six to eight sediment depth segments were selected for chemical analysis from five cores from Stations 7A, 7C, 7E, L22, and N17 for a total of 34 sediment core samples.

A complete list of the sediment sampling stations that were occupied and sampled in the study area is included in Table 2-3. Table 2-3 also provides the station identification, station type, latitude and longitude, and date of collection for each sample. Figure 2-3, a map of the cANIMIDA study area, shows the locations of the summer 2006 sampling stations. Additional daily survey and sampling station information is included in the 2006 station logs contained in the Summer 2006 Field Survey Report (Battelle, 2006b).

2.1.4 Field Sampling Procedures

Established and consistent sampling procedures were followed at each sampling station according to the Field Logistics and Sampling Plans for the 2004, 2005, and 2006 Field Surveys (Battelle, 2004a, 2005a, and 2006a).

Photodocumentation, station logs, and field notes were recorded during the field survey. The station logs for each sampling station are included in the Field Survey reports (Battelle, 2004b, 2005b, and 2006b). A copy of each Field Survey report is included in Appendix E. Each station log includes a description of the sampling location, observations, number and type(s) of samples collected, and comments.

2.1.4.1 Surface Sediment Sampling

Surficial 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 collection of 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 2-4.

2.1.4.2 Sediment Core Sampling

The sediment core sampling procedure included deployment of a dual-barrel gravity corer weighted with lead to allow “freefall” into the bottom to collect “side-by-side” cores for geochronology and chemistry. Polybutyrate core liners were placed within the metal barrels of the corer. After the cores were collected, the core liners were removed from the metal sleeves, sealed with plastic end caps and stored until returned to shore.

At an onshore facility, the cores were carefully extruded from the tops of the core liners and subsectioned as required for analysis. As each sediment interval was extruded, the edge of the core which has been in contact with the polybutyrate core liner was removed with a Teflon® spatula to prevent cross-contamination between sediment sections due to smearing during the extrusion. Then each section was sliced from the core using stainless-steel spatulas and transferred to the appropriate container.

One core was designated for trace metal determinations and geochronology (2005 and 2006) plus total organic carbon (2006). This core was sliced in 0.5-cm sections from 0-10 cm followed by 1-cm intervals from 10-20 cm and then 2-cm sections for the remainder of the core. The other core was used for organic contaminant determinations and grain size analysis (2005 and 2006) plus total organic carbon (2005). This core was sectioned in 2-cm intervals over its entire length.

2.2 Analytical Methods

Sample preparation and analysis methods are detailed in Appendix C of this report. General descriptions of these procedures are described in this section.

2.2.1 Grain Size and Total Organic Carbon

Grain size analyses were performed at FIT and were carried out using the classic method of Folk (1974) that includes a combination of wet sieving and pipette techniques. Total organic carbon (TOC) analyses were also performed at FIT and were determined using a combustion method described by Froelich (1980) for the analysis of organic carbon in marine sediments.

2.2.2 Organic Chemical Parameters

Analysis for organic contaminants was conducted by Battelle's environmental chemistry laboratory. The analyses were conducted in accordance with the laboratory's standard operating procedures (SOPs) and generally followed the same procedures used in previous ANIMIDA studies (Brown et al., 2005). Targeted compounds are listed in Tables 2-5, 2-6, and 2-7.

2.2.2.1 Saturated Hydrocarbons

Sediment samples were prepared using solvent extraction for the determination of organic chemical parameters. Saturated hydrocarbons (SHC) were determined by gas chromatography/flame ionization detection (GC/FID) based on United States Environmental Protection Agency (USEPA) Method 8015 (USEPA, 1993) and according to Battelle SOP No. 5-202-06, *Determination of Low Level Total Petroleum Hydrocarbon (Diesel Range Organics – DRO) and Individual Hydrocarbon Concentration in Environmental Samples.*

2.2.2.2 Polycyclic Aromatic Hydrocarbons and Biomarkers

Sediment samples were prepared using solvent extraction for the determination of organic chemical parameters. Polycyclic aromatic hydrocarbons (PAH) and geochemical biomarkers (steranes/triterpanes [S/T]) were determined by gas chromatography/mass spectrometry detection (GC/MS) according to Battelle SOP 5-157-08 *Identification and Quantification of Semi-volatile Organic Compounds by Gas Chromatography/Mass Spectrometry*, which is based on USEPA Method 8270 (USEPA, 1993) with modifications to expand the list of PAH (Table 2-6) and to lower detection limits using selected ion monitoring (SIM).

2.2.3 Inorganic Parameters

Analysis for inorganic parameters was conducted by FIT. The analyses were conducted in accordance with FIT's SOPs. The inorganic analytes for the sediment and source samples were trace and major metals. Target analytes and associated MDLs are listed in Tables 2-8a through 2-8c.

2.2.3.1 Trace and Major Metals Analysis in Sediment

Sediment samples were prepared using acid digestion for the determination of trace and major metals. Sediment samples and associated quality control samples 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 Tables 2-8a to 2-8c. All analytical techniques followed manufacturers' specifications and laboratory SOPs. 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 Radionuclides in Surface Sediment and Geochronology of Sediment Core

Surface sediment samples also were analyzed for excess ^{210}Pb and total ^{137}Cs in an effort to determine whether sediment at a particular location was recently deposited. Sediment core samples were sub-sectioned in 0.5-cm intervals in an effort to age-date the cores. Sediment samples were freeze-dried and ground to a fine powder. The samples were then set aside for at least 20 days to establish secular equilibrium and the activities of the various radionuclides were then determined by counting.

2.3 Quality Assurance/Quality Control

A quality assurance (QA) plan, which included quality control (QC) measures, was employed for the program. This section summarizes important aspects of this plan. QA/QC plan details are presented in Appendix C.

2.3.1 Quality Assurance

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 data quality objectives (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.

2.3.2 Quality Control

2.3.2.1 Field Quality Control

Equipment decontamination procedures were strictly followed during the sampling to minimize potential cross-contamination. The decontamination procedure included a physical scrub with soap and water, rinses with seawater and distilled water, and a rinse with isopropanol.

Field replicates were collected during the survey to assess the reproducibility and variability of the results.

Throughout the field surveys, field notes were maintained by the scientists in log books and on station logs. 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.

2.3.2.2 Laboratory Quality Control

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. DQOs for organics and metals are presented in Appendix C.

In the laboratory, samples were grouped together in batches of approximately 20 field samples for organic analyses or 40 field samples for metals analyses, plus associated QC samples. In general, the QC samples processed along with the sediment samples included procedural blanks, blank or matrix spikes (BS), and reference samples. Additional elements were added to the processing of the samples to monitor QC and to aid in the assessment of the data’s usability including balance calibration, solvent and standard checks, instrument calibrations and blanks, and duplicate sample analyses.

The laboratories maintained detailed records throughout the processing of the samples and all raw instrumental data were archived electronically. The final laboratory data packages contained sufficient detail so that an external audit could be performed. Laboratory reports were peer reviewed to ensure the DQOs were met, that the analyses met the program objectives, and that the data were accurate and defensible. The final laboratory data packages were reviewed prior to release of the final data.

2.4 Statistical Methods

Organic 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. Statistical analyses were carried out using the statistical program SPSS® 8.0. The datasets used in these analyses included the summer sediment sampling survey results from 1999, 2000, 2002, 2004, 2005 and 2006. 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. The summer 2002, 2004, 2005, and 2006 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 through 2006 field surveys. Several Liberty stations were only sampled during the summer 1999 survey and several were added for the summer 2004 survey. Additional Northstar stations were added for the summer 2000, 2002, and 2004 surveys. For the reported ANOVA models, only those stations sampled pre-construction and at least once post-construction were included in the analyses. The results for BSMP station 5D from the summer 1999 survey, BSMP station 5B from the summer of 2004 survey, and Northstar station N08 from the summer 2004 survey were severe outliers and thus were excluded from the statistical analyses. Results from stations 5D were not outliers in the other surveys but were excluded from the ANOVA model since the pre-construction result was an outlier. The S/T key parameters were not included in the statistical analyses due to limited pre-construction 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 oil or North Slope Crude oil, but is associated with biogenic sources of hydrocarbons 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 false discovery rates were controlled according to the Hochberg procedure (Benjamini and Hochberg, 1995).

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.

Table 2-1. MMS cANIMIDA Summer 2004 Sediment Sampling Stations

Sample ID	Station ID	Station Type	Latitude	Longitude	Date	Sediment Type	Comments
04-3A-01-PHC-S	3A	BSMP	70° 16.9327	147° 05.4570	30-Jul-04	Surface	
04-3B-01-PHC-S	3B	BSMP	70° 17.9035	147° 02.5445	30-Jul-04	Surface	
04-4A-01-PHC-S	4A	BSMP	70° 18.4539	147° 40.2372	3-Aug-04	Surface	Four grab attempts, 2 rejected; 2 used for sample (1 org, 1 met)
04-4B-01-SHC-S	4B	BSMP	70° 21.0155	147° 40.0320	3-Aug-04	Surface	
04-4C-01-PHC-S	4C	BSMP	70° 26.0898	147° 42.9757	3-Aug-04	Surface	
04-5(0)-01-PHC-S	5(0)	BSMP	70° 22.7435	147° 00.3850	3-Aug-04	Surface	
04-5(1)-01-PHC-S	5(1)	BSMP	70° 25.0763	148° 03.5628	5-Aug-04	Surface	
04-5(10)-01-PHC-S	5(10)	BSMP	70° 27.3238	148° 30.0676	8-Aug-04	Surface	
04-5(5)-01-PHC-S	5(5)	BSMP	70° 26.0820	147° 18.0805	3-Aug-04	Surface	
04-5(5a)-01-PHC-S	5(5a)	BSMP	70° 26.0079	148° 18.8205	8-Aug-04	Surface	Error in coordinates for 5(5). 5(5a) added at correct location.
04-5A-01-PHC-S	5A	BSMP	70° 29.6986	148° 46.0600	9-Aug-04	Surface	
04-5B-01-PHC-S	5B	BSMP	70° 34.8745	148° 55.1429	9-Aug-04	Surface	
04-5D-01-PHC-S	5D	BSMP	70° 24.4578	148° 33.5676	8-Aug-04	Surface	
04-5E-01-PHC-S	5E	BSMP	70° 38.3621	149° 16.3576	9-Aug-04	Surface	
04-5F-01-PHC-S	5F	BSMP	70° 26.4946	148° 49.5346	9-Aug-04	Surface	
04-5H-01-PHC-S	5H	BSMP	70° 22.2280	147° 47.8581	2-Aug-04	Surface	
04-L01-01-PHC-S	L01	Liberty	70° 17.9321	148° 40.0906	2-Aug-04	Surface	
04-L01A-01-PHC-S	L01A	Liberty	70° 18.9281	147° 33.9044	11-Aug-04	Surface	Error in coordinates for L01. L01A added at correct location.
04-L04-01-PHC-S	L04	Liberty	70° 17.0604	147° 40.0976	2-Aug-04	Surface	
04-L06-01-PHC-S	L06	Liberty	70° 16.9242	147° 34.0839	2-Aug-04	Surface	Field Triplicate
04-L06-02-PHC-S	L06	Liberty	70° 16.9242	147° 34.0839	2-Aug-04	Surface	Field Triplicate
04-L06-03-PHC-S	L06	Liberty	70° 16.9242	147° 34.0839	2-Aug-04	Surface	Field Triplicate
04-L07-01-PHC-S	L07	Liberty	70° 16.7760	147° 32.0016	2-Aug-04	Surface	
04-L08-01-PHC-S	L08	Liberty	70° 16.7007	147° 30.3426	2-Aug-04	Surface	
04-L09-01-PHC-S	L09	Liberty	70° 16.5705	147° 27.2041	2-Aug-04	Surface	
04-L17-01-PHC-S	L17	Liberty	70° 23.6088	147° 32.9282	3-Aug-04	Surface	New station added in Liberty area.
04-L18-01-PHC-S	L18	Liberty	70° 18.3738	147° 45.6664	3-Aug-04	Surface	New station added in Liberty area.
04-N01-01-PHC-S	N01	Northstar	70° 31.6679	148° 41.4653	8-Aug-04	Surface	
04-N02-01-PHC-S	N02	Northstar	70° 30.5390	148° 41.3394	7-Aug-04	Surface	
04-N03-01-PHC-S	N03	Northstar	70° 30.0202	148° 41.4901	7-Aug-04	Surface	
04-N04-01-PHC-S	N04	Northstar	70° 29.6787	148° 48.0977	9-Aug-04	Surface	

Table 2-1. MMS cANIMIDA Summer 2004 Sediment Sampling Stations (continued)

Sample ID	Station ID	Station Type	Latitude	Longitude	Date	Sediment Type	Comments
04-N05-01-PHC-S	N05	Northstar	70° 29.6337	148° 44.6996	7-Aug-04	Surface	
04-N06-01-PHC-S	N06	Northstar	70° 29.5591	148° 43.2685	7-Aug-04	Surface	Field Triplicate
04-N06-02-PHC-S	N06	Northstar	70° 29.5591	148° 43.2685	7-Aug-04	Surface	Field Triplicate
04-N06-03-PHC-S	N06	Northstar	70° 29.5591	148° 43.2685	7-Aug-04	Surface	Field Triplicate
04-N07-01-PHC-S	N07	Northstar	70° 29.5703	148° 40.0925	6-Aug-04	Surface	
04-N08-01-PHC-S	N08	Northstar	70° 29.4281	148° 38.3250	6-Aug-04	Surface	
04-N09-01-PHC-S	N09	Northstar	70° 29.3405	148° 35.1494	6-Aug-04	Surface	
04-N10-01-PHC-S	N10	Northstar	70° 29.0187	148° 41.7696	6-Aug-04	Surface	
04-N11-01-PHC-S	N11	Northstar	70° 28.4650	148° 42.0122	6-Aug-04	Surface	Large rocks at target, station moved.
04-N12-01-PHC-S	N12	Northstar	70° 27.3503	148° 42.1061	6-Aug-04	Surface	
04-N13-01-PHC-S	N13	Northstar	70° 26.9832	148° 43.5749	9-Aug-04	Surface	
04-N14-01-PHC-S	N14	Northstar	70° 25.9829	148° 40.3584	9-Aug-04	Surface	
04-N15-01-PHC-S	N15	Northstar	70° 26.7197	148° 44.5858	9-Aug-04	Surface	
04-N16-01-PHC-S	N16	Northstar	70° 29.9089	148° 42.3907	7-Aug-04	Surface	Thin layer of flock over stiff clay. Small volume of sample collected.
04-N17-01-PHC-S	N17	Northstar	70° 29.8177	148° 40.3584	6-Aug-04	Surface	Fine flock over stiff clay.
04-N18-01-PHC-S	N18	Northstar	70° 29.0908	148° 42.2610	6-Aug-04	Surface	
04-N19-01-PHC-S	N19	Northstar	70° 29.1251	148° 40.5610	6-Aug-04	Surface	
04-N20-01-PHC-S	N20	Northstar	70° 27.9697	148° 41.6865	6-Aug-04	Surface	
04-N21-01-PHC-S	N21	Northstar	70° 26.8124	148° 41.7302	9-Aug-04	Surface	
04-N23-01-PHC-S	N23	Northstar	70° 29.3749	148° 41.9297	6-Aug-04	Surface	

Table 2-2: MMS cANIMIDA Summer 2005 Sediment Sampling Stations

Sample ID	Station ID	Station Type	Latitude	Longitude	Date	Sediment Type	Comments
05-1A-01-PHC-S	1A	BSMP	70° 01.6023	144° 32.8494	07-Aug-05	Surface	
05-1B-01-PHC-S	1B	BSMP	70° 04.1803	144° 47.5640	07-Aug-05	Surface	
05-1C-01-PHC-S	1C	BSMP	70° 09.1850	145° 01.3962	07-Aug-05	Surface	
05-1C-01-PHC-S-C	1C-01	BSMP	70° 09.1850	145° 01.3962	07-Aug-05	Core	
05-1C-02-PHC-S-C	1C-02	BSMP	70° 09.1850	145° 01.3962	07-Aug-05	Core	
05-1C-03-PHC-S-C	1C-03	BSMP	70° 09.1850	145° 01.3962	07-Aug-05	Core	
05-1C-04-PHC-S-C	1C-04	BSMP	70° 09.1850	145° 01.3962	07-Aug-05	Core	
05-1C-05-PHC-S-C	1C-05	BSMP	70° 09.1850	145° 01.3962	07-Aug-05	Core	
05-1C-06-PHC-S-C	1C-06	BSMP	70° 09.1850	145° 01.3962	07-Aug-05	Core	
05-1C-07-PHC-S-C	1C-07	BSMP	70° 09.1850	145° 01.3962	07-Aug-05	Core	
05-1C-10-PHC-S-C	1C-10	BSMP	70° 09.1850	145° 01.3962	07-Aug-05	Core	
05-1C-15-PHC-S-C	1C-15	BSMP	70° 09.1850	145° 01.3962	07-Aug-05	Core	
05-1D-01-PHC-S	1D	BSMP	70° 05.6494	144° 05.3693	07-Aug-05	Surface	
05-1E-01-PHC-S	1E	BSMP	70° 06.1382	143° 46.5326	07-Aug-05	Surface	
05-2A-01-PHC-S	2A	BSMP	70° 00.5031	145° 05.7580	08-Aug-05	Surface	
05-2A-01-PHC-S-C	2A-01	BSMP	70° 00.5031	145° 05.7580	08-Aug-05	Core	
05-2A-02-PHC-S-C	2A-02	BSMP	70° 00.5031	145° 05.7580	08-Aug-05	Core	
05-2A-03-PHC-S-C	2A-03	BSMP	70° 00.5031	145° 05.7580	08-Aug-05	Core	
05-2A-04-PHC-S-C	2A-04	BSMP	70° 00.5031	145° 05.7580	08-Aug-05	Core	
05-2A-05-PHC-S-C	2A-05	BSMP	70° 00.5031	145° 05.7580	08-Aug-05	Core	
05-2A-10-PHC-S-C	2A-10	BSMP	70° 00.5031	145° 05.7580	08-Aug-05	Core	
05-2A-15-PHC-S-C	2A-15	BSMP	70° 00.5031	145° 05.7580	08-Aug-05	Core	
05-2B-01-PHC-S	2B	BSMP	70° 04.0493	145° 12.3790	08-Aug-05	Surface	
05-2C-01-PHC-S	2C	BSMP	70° 09.8125	145° 20.1312	07-Aug-05	Surface	
05-2D-01-PHC-S	2D	BSMP	70° 03.6074	145° 19.3016	08-Aug-05	Surface	
05-2E-01-PHC-S	2E	BSMP	70° 12.9076	146° 11.7098	06-Aug-05	Surface	
05-2F-01-PHC-S	2F	BSMP	70° 10.2610	146° 02.0765	06-Aug-05	Surface	
05-2G-01-PHC-S	2G	BSMP	70° 06.0654	145° 32.5651	08-Aug-05	Surface	
05-2H-01-PHC-S	2H	BSMP	70° 04.8725	145° 03.4209	08-Aug-05	Surface	
05-3A-01-PHC-S	3A	BSMP	70° 16.9268	147° 05.4828	30-Jul-05	Surface	
05-3B-01-PHC-S	3B	BSMP	70° 17.9819	147° 02.2393	30-Jul-05	Surface	

Table 2-2. MMS cANIMIDA Summer 2005 Sediment Sampling Stations (continued)

Sample ID	Station ID	Station Type	Latitude	Longitude	Date	Sediment Type	Comments
05-4A-01-PHC-S	4A	BSMP	70° 18.4483	147° 40.3106	30-Jul-05	Surface	
05-4B-01-PHC-S	4B	BSMP	70° 21.0517	147° 40.0062	30-Jul-05	Surface	
05-5(1)-01-PHC-S	5(1)	BSMP	70° 25.0151	148° 03.4548	09-Aug-05	Surface	
05-5(5)-01-PHC-S	5(5)	BSMP	70° 18.8060	148° 23.2290	09-Aug-05	Surface	
05-BP01-01-PAC-S-0-1	BP01	Boulder Patch	70° 20.7485	147° 32.9140	01-Aug-05	Surface	
05-BP01-01-PHC-S-C	BP01-01	Boulder Patch	70° 20.7485	147° 32.9140	01-Aug-05	Core	
05-BP01-02-PHC-S-C	BP01-02	Boulder Patch	70° 20.7485	147° 32.9140	01-Aug-05	Core	
05-BP01-03-PHC-S-C	BP01-03	Boulder Patch	70° 20.7485	147° 32.9140	01-Aug-05	Core	
05-BP01-04-PHC-S-C	BP01-04	Boulder Patch	70° 20.7485	147° 32.9140	01-Aug-05	Core	
05-BP01-05-PHC-S-C	BP01-05	Boulder Patch	70° 20.7485	147° 32.9140	01-Aug-05	Core	
05-BP01-06-PHC-S-C	BP01-06	Boulder Patch	70° 20.7485	147° 32.9140	01-Aug-05	Core	
05-L07-01-PHC-S	L07	Liberty	70° 16.7876	147° 31.0398	30-Jul-05	Surface	
05-L08-01-PHC-S	L08	Liberty	70° 16.6976	147° 30.2128	30-Jul-05	Surface	
05-N03-01-PHC-S	N03	Northstar	70° 30.0139	148° 41.4768	10-Aug-05	Surface	
05-N04-01-PHC-S	N04	Northstar	70° 29.6879	148° 48.1382	04-Aug-05	Surface	Core attempt unsuccessful at this location.
05-N06-01-PHC-S	N06	Northstar	70° 29.5199	148° 43.2428	04-Aug-05	Surface	
05-N08-01-PHC-S	N08	Northstar	70° 29.4106	148° 38.3036	04-Aug-05	Surface	
05-N11-01-PHC-S	N11	Northstar	70° 28.4375	148° 41.9479	04-Aug-05	Surface	
05-N11-02-PHC-S	N11	Northstar	70° 28.4375	148° 41.9479	04-Aug-05	Surface	
05-N14-01-PHC-S	N14	Northstar	70° 26.0127	148° 40.4733	04-Aug-05	Surface	
05-N18-01-PHC-S	N18	Northstar	70° 29.0884	148° 42.2224	04-Aug-05	Surface	
05-N26-01-PHC-S	N26	Northstar	70° 37.4202	148° 24.1883	10-Aug-05	Surface	
05-N26-01-PHC-S-C	N26-01	Northstar	70° 37.4202	148° 24.1883	10-Aug-05	Core	
05-N26-02-PHC-S-C	N26-02	Northstar	70° 37.4202	148° 24.1883	10-Aug-05	Core	
05-N26-03-PHC-S-C	N26-03	Northstar	70° 37.4202	148° 24.1883	10-Aug-05	Core	
05-N26-04-PHC-S-C	N26-04	Northstar	70° 37.4202	148° 24.1883	10-Aug-05	Core	
05-N26-05-PHC-S-C	N26-05	Northstar	70° 37.4202	148° 24.1883	10-Aug-05	Core	

Table 2-2. MMS cANIMIDA Summer 2005 Sediment Sampling Stations (continued)

Sample ID	Station ID	Station Type	Latitude	Longitude	Date	Sediment Type	Comments
05-PB1-01-PHC-S	PB1	Prudhoe	70° 18.7944	148° 23.1992	10-Aug-05	Surface	Core attempt unsuccessful at this location.
05-PB1A-01-PHC-S	PB1A	Prudhoe	70° 19.9592	148° 21.3937	10-Aug-05	Surface	
05-PB1A-01-PHC-S-C	PB1A-01	Prudhoe	70° 19.9592	148° 21.3937	10-Aug-05	Core	
05-PB1A-02-PHC-S-C	PB1A-02	Prudhoe	70° 19.9592	148° 21.3937	10-Aug-05	Core	
05-PB1A-03-PHC-S-C	PB1A-03	Prudhoe	70° 19.9592	148° 21.3937	10-Aug-05	Core	
05-PB1A-04-PHC-S-C	PB1A-04	Prudhoe	70° 19.9592	148° 21.3937	10-Aug-05	Core	
05-PB1A-05-PHC-S-C	PB1A-05	Prudhoe	70° 19.9592	148° 21.3937	10-Aug-05	Core	
05-E01-01-PHC-S-0-1	E01-0-1	Sag - near mouth	70° 21.1003	147° 56.0895	01-Aug-05	Surface	

Table 2-3. MMS cANIMIDA Summer 2006 Sediment Sampling Stations

Sample ID	Station ID	Station Type	Latitude	Longitude	Date	Sediment Type	Comments
06-4A-01-PHC-S	4A	BSMP	70°18.4578	147°40.1781	28, 29-Jul-06	Surface	
06-5(1)-01-PHC-S	5(1)	BSMP	70°24.9899	148°03.4663	27-Jul-06	Surface	
06-5(5)-01-PHC-S	5(5)	BSMP	70°26.0927	148°18.1566	31-Jul-06	Surface	
06-5A-01-PHC-S	5A	BSMP	70°29.6996	148°46.1128	6, 7-Aug-06	Surface	
06-6A-01-PHC-S	6A	BSMP	70°32.2000	149°57.7200	3, 4-Aug-06	Surface	
06-6B-01-PHC-S	6B	BSMP	70°33.3611	150°24.6255	1, 2, 3-Aug-06	Surface	
06-6D-01-PHC-S	6D	BSMP	70°44.9300	150°28.5100	03-Aug-06	Surface	
06-6F-01-PHC-S	6F	BSMP	70°40.1641	151°12.1239	2, 3-Aug-06	Surface	
06-6G-01-PHC-S	6G	BSMP	70°31.4000	149°54.6000	03-Aug-06	Surface	
06-6H-01-PHC-S	6H	BSMP	70°29.6753	150°14.5986	01-Aug-06	Surface	
06-7A-01-PHC-S	7A	BSMP	70°37.6525	152°09.8789	02-Aug-06	Surface	
06-7A-01-PHC-SC	7A-01	BSMP	70°37.6525	152°09.8789	02-Aug-06	Core	
06-7A-02-PHC-SC	7A-02	BSMP	70°37.6525	152°09.8789	02-Aug-06	Core	
06-7A-03-PHC-SC	7A-03	BSMP	70°37.6525	152°09.8789	02-Aug-06	Core	
06-7A-04-PHC-SC	7A-04	BSMP	70°37.6525	152°09.8789	02-Aug-06	Core	
06-7A-05-PHC-SC	7A-05	BSMP	70°37.6525	152°09.8789	02-Aug-06	Core	
06-7A-07-PHC-SC	7A-07	BSMP	70°37.6525	152°09.8789	02-Aug-06	Core	
06-7A-09-PHC-SC	7A-09	BSMP	70°37.6525	152°09.8789	02-Aug-06	Core	
06-7C-01-PHC-SC	7C-01	BSMP	70°54.8501	152°00.3010	02-Aug-06	Core	
06-7C-02-PHC-SC	7C-02	BSMP	70°54.8501	152°00.3010	02-Aug-06	Core	
06-7C-03-PHC-SC	7C-03	BSMP	70°54.8501	152°00.3010	02-Aug-06	Core	
06-7C-04-PHC-SC	7C-04	BSMP	70°54.8501	152°00.3010	02-Aug-06	Core	
06-7C-05-PHC-SC	7C-05	BSMP	70°54.8501	152°00.3010	02-Aug-06	Core	
06-7C-10-PHC-SC	7C-10	BSMP	70°54.8501	152°00.3010	02-Aug-06	Core	
06-7C-15-PHC-SC	7C-15	BSMP	70°54.8501	152°00.3010	02-Aug-06	Core	
06-7E-01-PHC-S	7E	BSMP	70°43.5819	152°04.3662	02-Aug-06	Surface	
06-7E-01-PHC-SC	7E-01	BSMP	70°43.5819	152°04.3662	02-Aug-06	Core	
06-7E-02-PHC-SC	7E-02	BSMP	70°43.5819	152°04.3662	02-Aug-06	Core	
06-7E-03-PHC-SC	7E-03	BSMP	70°43.5819	152°04.3662	02-Aug-06	Core	
06-7E-04-PHC-SC	7E-04	BSMP	70°43.5819	152°04.3662	02-Aug-06	Core	
06-7E-05-PHC-SC	7E-05	BSMP	70°43.5819	152°04.3662	02-Aug-06	Core	

Table 2-3. MMS cANIMIDA Summer 2006 Sediment Sampling Stations (continued)

Sample ID	Station ID	Station Type	Latitude	Longitude	Date	Sediment Type	Comments
06-7E-07-PHC-SC	7E-07	BSMP	70°43.5819	152°04.3662	02-Aug-06	Core	
06-7E-09-PHC-SC	7E-09	BSMP	70°43.5819	152°04.3662	02-Aug-06	Core	
06-7E-15-PHC-SC	7E-15	BSMP	70°43.5819	152°04.3662	02-Aug-06	Core	
06-7G-01-PHC-S	7G	BSMP	70°38.9050	151°53.6441	2, 3 Aug-06	Surface	
06-BP01-01-PHC-S	BP01	Boulder Patch	70°20.7490	147°32.9140	28, 29 Jul; 9 Aug-06	Surface	
06-COL-03-01-PHC-P	COL-03	Other	70°23.9847	150°28.9083	03-Aug-06	Peat	Coleville River
06-E01-01-PHC-S	E01	Other	70°21.1034	147°56.1035	27 Jul; 9 Aug-06	Surface	
06-E02-01-PHC-S	E02	Other	70°21.0539	147°58.2819	28-Jul-06	Surface	
06-EI01-01-PHC-P	EI01	Other	70°34.8687	151°59.2539	02-Aug-06	Peat	Eskimo Island
06-Kup-01-PHC-P	Kup	Other	70°19.5355	149°00.1299	28-Jul-06	Peat	Kuparuk River
06-L03-01-PHC-S	L03	Liberty	70°17.3384	147°33.2819	28, 29 Jul-06	Surface	
06-L08-01-PHC-S	L08	Liberty	70°16.7030	147°30.2990	28, 29 Jul; 9 Aug-06	Surface	
06-L19-01-PHC-S	L19	Liberty	70°18.6216	147°49.3156	27, 28 Jul-06	Surface	
06-L20-01-PHC-S	L20	Liberty	70°15.4461	147°43.9446	27-Jul-06	Surface	
06-L21-01-PHC-S	L21	Liberty	70°13.7169	147°38.2051	27-Jul-06	Surface	
06-L22-01-PHC-S	L22	Liberty	70°29.2491	147°16.4027	30-Jul-06	Surface	
06-L22-01-PHC-SC	L22-01	Liberty	70°29.2491	147°16.4027	30-Jul-06	Core	
06-L22-02-PHC-SC	L22-02	Liberty	70°29.2491	147°16.4027	30-Jul-06	Core	
06-L22-03-PHC-SC	L22-03	Liberty	70°29.2491	147°16.4027	30-Jul-06	Core	
06-L22-04-PHC-SC	L22-04	Liberty	70°29.2491	147°16.4027	30-Jul-06	Core	
06-L22-05-PHC-SC	L22-05	Liberty	70°29.2491	147°16.4027	30-Jul-06	Core	
06-L22-14-PHC-SC	L22-14	Liberty	70°29.2491	147°16.4027	30-Jul-06	Core	
06-M01-01-PHC-S	M01	McCovey	70°30.7602	148°27.3847	31-Jul-06	Surface	
06-N03-01-PHC-S	N03	Northstar	70°30.0020	148°41.5700	5, 6, 7 Aug-06	Surface	
06-N03-02-PHC-S	N03	Northstar	70°30.0020	148°41.5700	5, 6, 7 Aug-06	Surface	
06-N06-01-PHC-S	N06	Northstar	70°29.5360	148°43.1940	05-Aug-06	Surface	
06-N11-01-PHC-S	N11	Northstar	70°28.4295	148°41.9090	5, 6, 7 Aug-06	Surface	
06-N14-01-PHC-S	N14	Northstar	70°26.0060	148°40.4290	4, 5, 6 Aug-06	Surface	
06-N17-01-PHC-SC	N17-01	Northstar	70°29.8717	148°40.2850	31-Jul-06	Core	
06-N17-02-PHC-SC	N17-02	Northstar	70°29.8717	148°40.2850	31-Jul-06	Core	
06-N17-03-PHC-SC	N17-03	Northstar	70°29.8717	148°40.2850	31-Jul-06	Core	

Table 2-3. MMS cANIMIDA Summer 2006 Sediment Sampling Stations (continued)

Sample ID	Station ID	Station Type	Latitude	Longitude	Date	Sediment Type	Comments
06-N17-04-PHC-SC	N17-04	Northstar	70°29.8717	148°40.2850	31-Jul-06	Core	
06-N17-05-PHC-SC	N17-05	Northstar	70°29.8717	148°40.2850	31-Jul-06	Core	
06-N17-15-PHC-SC	N17-15	Northstar	70°29.8717	148°40.2850	31-Jul-06	Core	
06-N28-01-PHC-S	N28	Northstar	70°29.5230	148°41.5252	5, 6 Aug-06	Surface	
06-PI01-01-PHC-P	PI01	Other (Pingok Island)	70°33.3634	149°28.2316	04-Aug-06	Peat	Pingok Island, one of the Jones Islands
06-Sag-01-PHC-P	Sag	Other (Sagavanirktok River)	70°00.0748	148°40.0873	28-Jul-06	Peat	Sagavanirktok River
06-SDI-1-01-PHC-S	SDI01	Other (SDI)	70°19.5860	147°52.3960	27 Jul; 9 Aug-06	Surface	
06-WD01-01-PHC-S	WD01	Other (West Dock)	70°23.8470	148°31.4233	6, 8 Aug-06	Surface	West Dock

Table 2-4. 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	Battelle
Sediment	Metals, TOC, radiochemistry	Plastic jar	Frozen -20°C	Florida Institute of Technology
Sediment	Grain Size	Plastic bag	Stored at 4°C	Florida Institute of Technology

Table 2-5. 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 2-6. 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			
C2-Naphthalenes	C2N	A/2	Chrysene	C0C	B/3
C3-Naphthalenes	C3N	A/2	C1-Chrysenes	C1C	B/3
C4-Naphthalenes	C4N	A/2	C2-Chrysenes	C2C	B/3
			C3-Chrysenes	C3C	B/3
Acenaphthylene	ACEY	A/2	C4-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
C1-Fluorenes	C1F	A/2	Benzo[e]pyrene	BEP	B/4
C2-Fluorenes	C2F	A/2	Benzo[a]pyrene	BAP	B/4
C3-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
C1-Phenanthrenes/Anthracenes	C1P/A	A/3			
C2-Phenanthrenes/Anthracenes	C2P/A	A/3			
C3-Phenanthrenes/Anthracenes	C3P/A	A/3			
C4-Phenanthrenes/Anthracenes	C4P/A	A/3			
Dibenzothiophene	C0D	A/3			
C1-Dibenzothiophenes	C1D	A/3	Surrogate Compounds		
C2-Dibenzothiophenes	C2D	A/3	Naphthalene-d8	D8N	A/1
C3-Dibenzothiophenes	C3D	A/3	Acenaphthene-d10	D10ACE	A/2
			Phenanthrene-d10	D10PH	A/3
Fluoranthene	FLANT	A/3	Benzo(a)pyrene-d12	D12BAP	B/4
Pyrene	PYR	A/3			
C1-Fluoranthenes/Pyrenes	C1F/P	A/3	Internal Standard		
C2-Fluoranthenes/Pyrenes	C2F/P	A/3	Fluorene-d10	D10F	A
C3-Fluoranthenes/Pyrenes	C3F/P	A/3	Chrysene-d12	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 2-7. 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 2-8a. Summary of Instrumental Methods and Method Detection Limits for Metal Analysis of Sediment (2004)

2004 Sediments		
Metal	Method	MDLs (µg metal/g dry sediment)
Ag – silver	ZGFAAS	0.007
Al – aluminum	FAAS	10
As – arsenic	ZGFAAS	0.1
Ba – barium	FAAS	22
Be – beryllium	ZGFAAS	0.003
Cd – cadmium	ZGFAAS	0.003
Co – cobalt	ZGFAAS	0.04
Cr – chromium	FAAS	3
Cu – copper	FAAS	2
Fe – iron	FAAS	10
Hg – mercury	CVAAS	0.001
Mn – manganese	FAAS	2
Ni – nickel	FAAS	0.5
Pb – lead	ZGFAAS	0.03
Sb – antimony	ZGFAAS	0.05
Tl – thallium	ZGFAAS	0.03
V – vanadium	FAAS	10
Zn – zinc	FAAS	0.5
Grain Size	Sieve and Pipet	---
TOC	Shimadzu Carbon System	0.03%

Notes:
CVAAS = Cold Vapor Atomic Absorption Spectrometry
FAAS = Flame Atomic Absorption Spectrometry
GFAAS = Graphite Furnace Atomic Absorption Spectrometry
MDL = Method Detection Limit
ZGFAAS = Zeeman Graphite Furnace Atomic Absorption Spectrometry

Table 2-8b. Summary of Instrumental Methods and Method Detection Limits for Metal Analysis of Sediment (2005)

2005 Sediments		
Metal	Method	MDLs (µg metal/g
Ag – silver	ZGFAAS	0.007
Al – aluminum	FAAS	10
As – arsenic	ZGFAAS	0.08
Ba – barium	FAAS	22
Be – beryllium	ZGFAAS	0.003
Cd – cadmium	ZGFAAS	0.003
Co – cobalt	ZGFAAS	0.04
Cr – chromium	FAAS	3
Cu – copper	FAAS	2
Fe – iron	FAAS	10
Hg – mercury	CVAAS	0.001
Mn – manganese	FAAS	2
Ni – nickel	FAAS	0.08
Pb – lead	ZGFAAS	0.03
Sb – antimony	ZGFAAS	0.05
Tl – thallium	ZGFAAS	0.03
V – vanadium	FAAS	10
Zn – zinc	FAAS	0.5
Grain Size	Sieve and Pipet	---
TOC	Shimadzu Carbon System	0.04%

Notes:
CVAAS = Cold Vapor Atomic Absorption Spectrometry
FAAS = Flame Atomic Absorption Spectrometry
GFAAS = Graphite Furnace Atomic Absorption Spectrometry
MDL = Method Detection Limit
ZGFAAS = Zeeman Graphite Furnace Atomic Absorption Spectrometry

Table 2-8c. Summary of Instrumental Methods and Method Detection Limits for Metal Analysis of Sediment (2006)

	2006 Sediments	
Metal	Method	MDLs (µg metal/g dry sediment)
Ag – silver	ICP-MS	0.007
Al – aluminum	FAAS	10
As – arsenic	ICP-MS	0.02
Ba – barium	ICP-MS	0.01
Be – beryllium	ICP-MS	0.009
Cd – cadmium	ICP-MS	0.001
Co – cobalt	ZGFAAS	0.001
Cr – chromium	FAAS	1
Cu – copper	FAAS	2
Fe – iron	FAAS	10
Hg – mercury	CVAAS	0.001
Mn – manganese	FAAS	2
Ni – nickel	ICP-MS	0.004
Pb – lead	ICP-MS	0.002
Sb – antimony	ICP-MS	0.001
Tl – thallium	ICP-MS	0.001
V – vanadium	FAAS	10
Zn – zinc	FAAS	0.5
Grain Size	Sieve and Pipet	---
TOC	Shimadzu Carbon System	0.04

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

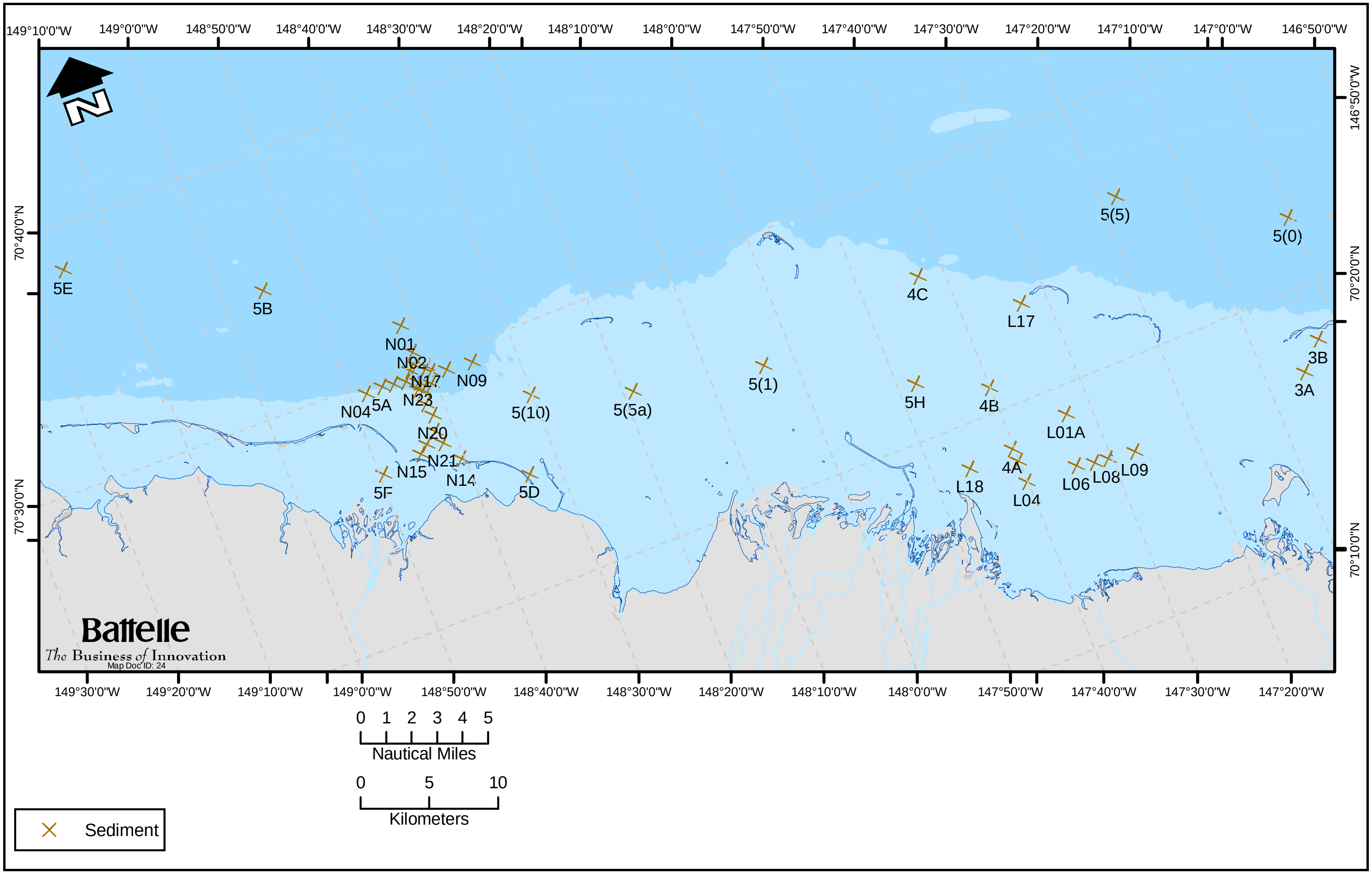


Figure 2-1. Summer 2004 cANIMIDA sampling locations.

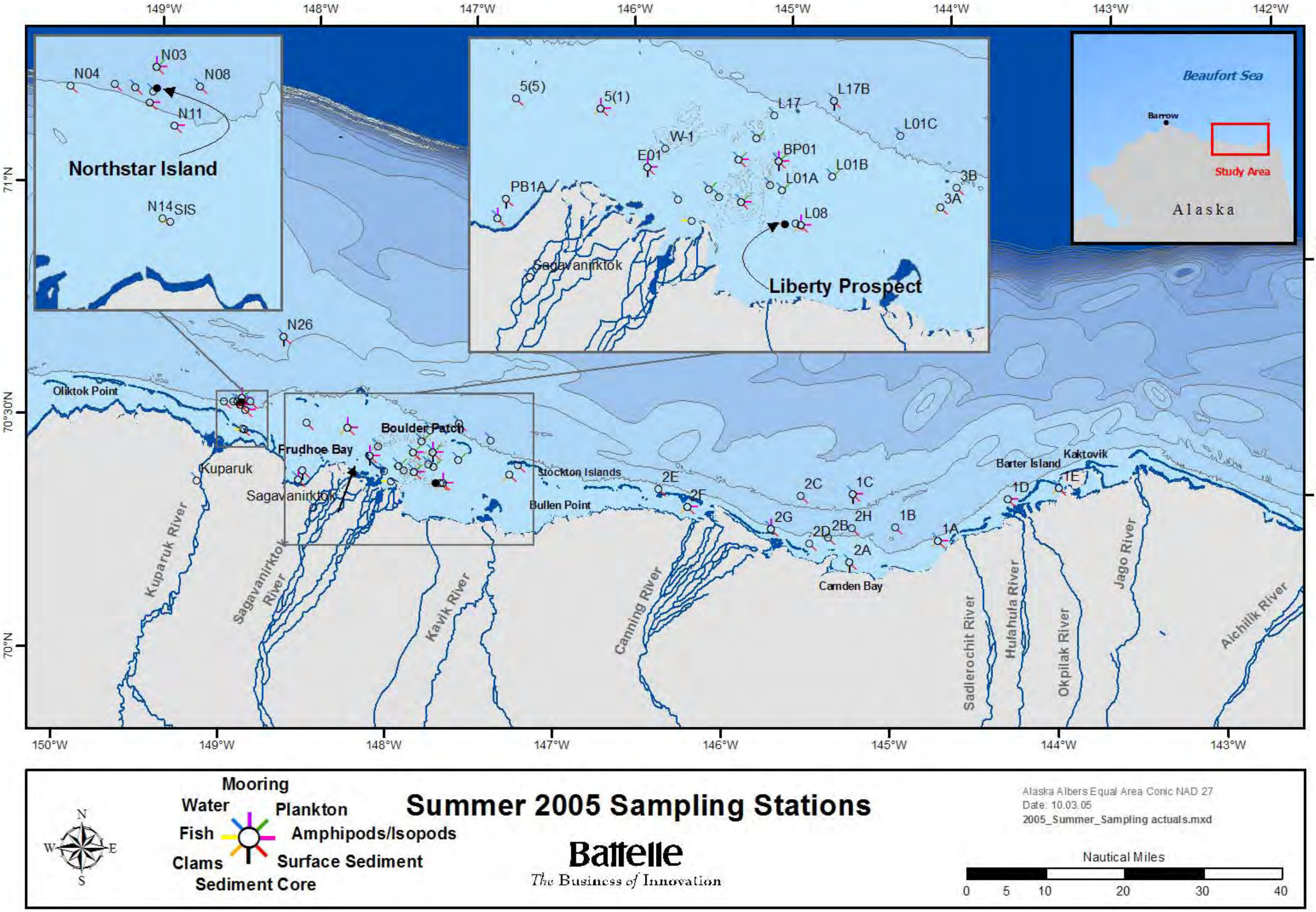


Figure 2-2. Summer 2005 cANIMIDA sampling locations.

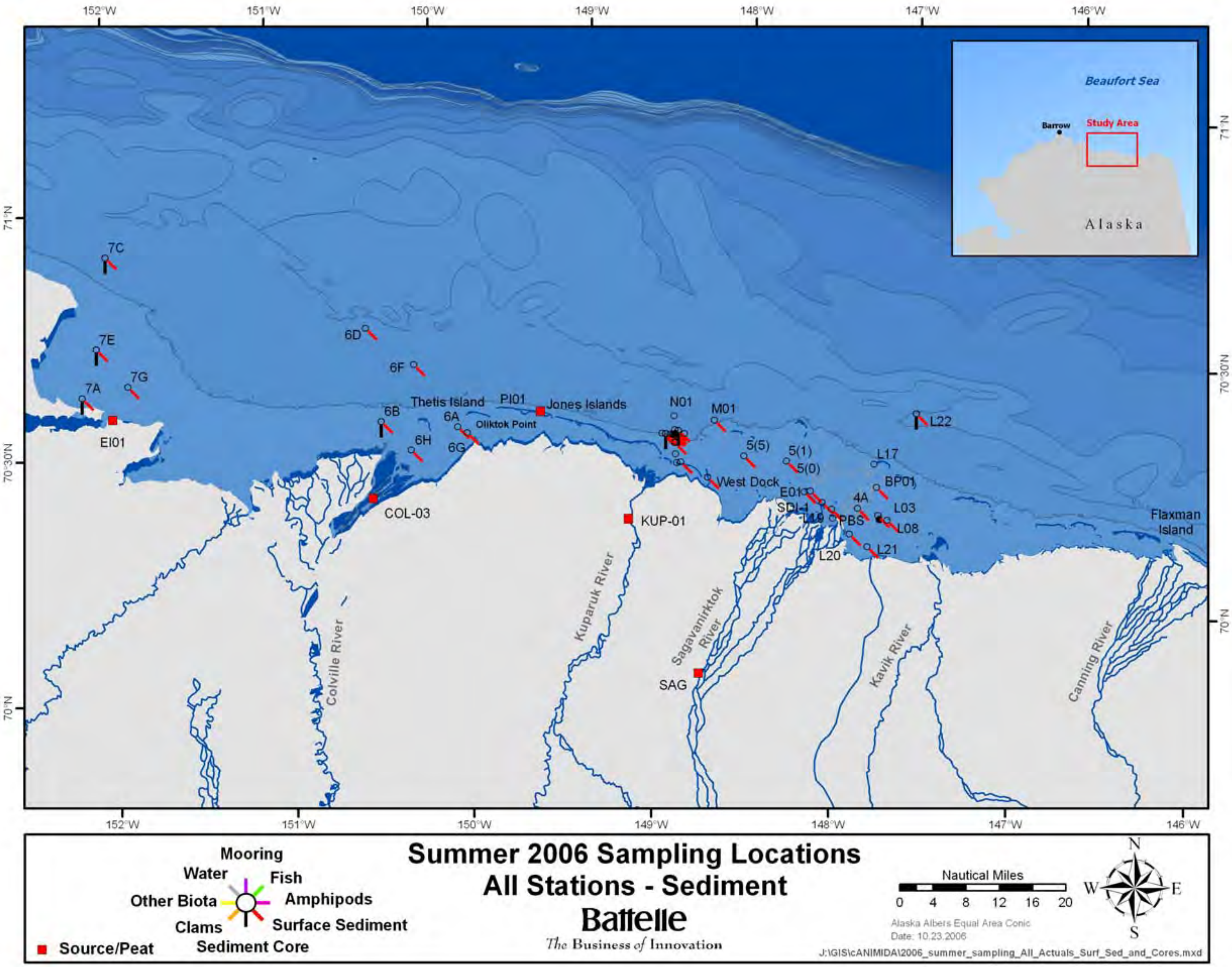


Figure 2-3. Summer 2006 cANIMIDA sampling locations.

3.0 Results

The results and general trends in the TOC, grain size, organic, and inorganic data from the surficial sediment and sediment core samples collected during the summer 2004, 2005, and 2006 cANIMIDA field surveys are presented in this section. The results from the ANIMIDA field surveys (1999-2002) are presented in separate reports (Brown et al., 2004 and Boehm et al., 2001b) and are discussed as appropriate in this report for comparison with the 2004 though 2006 results.

During 2004, surface sediment samples were collected from the Northstar (n = 23 locations), Liberty (n = 9 locations) and BSMP stations from 3A to 5H and 5(0) to 5(10) (n = 16). Then, during 2005, samples were collected at eastern BSMP stations 1A to 2H (n = 13) along with a more limited number of samples from Northstar (n = 7), Liberty (n = 5) and the 2004 BSMP sites (n = 6). In 2006, sediments were collected from western BSMP stations 6A to 7G (n = 10) along with a more limited number of samples from Northstar (n = 7), Liberty (n = 10) and the 2004 BSMP sites (n = 4). This sampling strategy provided a suite of samples that extended from Camden Bay to Harrison Bay with repeated focus on the Northstar and Liberty areas. Sediment cores were collected at seven locations during both the 2005 (1C, 2A, BP01, E01, L17B, PB1A and N26) and 2006 (6B, 7A, 7C, 7E, N05, N17 and L22) field surveys. The cANIMIDA collection scheme greatly extended the original ANIMIDA study area to both the east and the west.

3.1 Surficial Sediment Results

3.1.1 General Chemical and Physical Measurements

3.1.1.1 Total Organic Carbon (TOC) and Grain Size

Surficial sediments from each station were analyzed for TOC and grain size (percent gravel, sand, silt and clay). The TOC values for surficial sediments ranged from 0.02% in the sandy sediment in shallow water (1.8 m) at station L21 near the mouth of the Sagavanirktok River to 6.4% in a peat-bearing sample from station N14 (Tables 3-1 through 3-4 and Appendix A). The overall mean value for TOC of 0.77 ± 0.77% for 2004-2006 was not significantly different ($p<0.01$) to the means from 1999-2002 of 0.91 ± 0.86%. Considerable patchiness was 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 other Beaufort Sea data. For example, Carsola (1954) reported a range of TOC values from 0.2-1.2 % for Beaufort Sea sediments.

The grain size results (Tables 3-1 through 3-4 and Appendix A) show similar variability to that described above for TOC. Gravel content (>2 mm) ranged from 0% at 68 of 112 surface samples locations to 61% at station N15, located adjacent to Stump Island and 46% above the pipeline just south of Northstar Island. Likewise, the clay content (<0.002 mm) varies from <1% at several locations to ~50% at station 4A. The highest clay content in the 1999-2002 (ANIMIDA) data set also was 50% at station 4A. 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.

Across the extended study area of the cANIMIDA program, sediment sampled during 2004, 2005 and 2006 averaged 47%, 40% and 50% silt + clay, respectively, (Table 3-1) relative to values for silt + clay that averaged 43% in 1999, 52% in 2000 and 50% in 2002. Similarly, concentrations of Al, an indicator of clay content, averaged 3.8% in 2004, 3.6% in 2005 and 3.8% in 2006, relative to 3.6% in 1999, 4.1% in 2000, and 3.8% in 2002. Despite having similar mean values for TOC, silt + clay, and Al, from year to year, the standard deviations within a given year are large (Table 3-1), thus no significant differences in mean values for TOC, silt + clay, or Al have been observed among years for 1999-2006.

Based on the 2004 grain size data, a few general trends were observed. Gravel was found at >2% of the total sediment mass in 10 samples. Three samples contained >10% gravel (22.5% at N04, 61% at N15 and 45.7% at N23). Station N23 is near the pipeline from Northstar Island that was backfilled with gravel and station N15 is close the gravel-rich Stump Island (Figure 3-1). Sediment to the east of Northstar Island at stations N07 and N09 was rich in sand, as was the case at stations N01, N02 and N03 north of the island and station N11 south of Northstar Island (Figure 3-1). An area containing more silt and clay follows along a southeast to northwest line to the south and west of Northstar Island. The sediment at stations 5F and 5D that are in the transport pathway of the Kuparuk River contained 84% and 100% silt + clay, respectively (Figure 3-1). Comparison of the 2004 grain size data with the 1999-2002 data in Section 4 considers temporal and spatial trends in more detail.

In 2005, at Northstar stations N04, N05, N06 and N08, an increase in the sand fraction was observed relative to 2004 (Figures 3-1 and 3-2). In contrast, the stations sampled within 4 km of Northstar in 2006 contained a larger fraction of silt and clay than found in 2005. Stations N14, 5(5) and 5(1) had similar grain size distribution in 2004, 2005 and 2006 (Figures 3-1, 3-2, and 3-3).

In the area of the Liberty Prospect during 2004, the highest amounts of sand were recovered at nearshore Stations L17 and L18 (Figure 3-4) and more offshore at Stations L01, 4B and 4C (Figure 3-5). A patch of mostly silt and clay was found to the east and west of the proposed site for the Liberty Prospect (Figure 3-4). With limited repetition of stations during 2005 and 2006, no clear trends were observed. However, the sand fraction in the Liberty area averaged 44%, 40% and 59% for years 2004, 2005 and 2006, respectively (Figures 3-4, 3-5, and 3-6). Sediments at the new coastal stations (L19, L20 and L21) sampled in 2006 were predominantly sand. Once again, some interesting interannual trends are discussed 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 (the sum of all target parent and alkyl PAHs), total petroleum hydrocarbons (TPHC; the sum of the resolved and unresolved saturated hydrocarbons n-C9 through n-C40), and total S/T (the sum of the sterane and triterpane target compounds). The data for each of these summary parameters are presented on a dry-weight basis and results for field replicates are presented as the mean value with the standard deviation in parentheses. The results are separated into three regional groupings: BSMP stations (Table 3-2), Northstar stations (Table 3-3), and Liberty stations (Table 3-4). Within this report and with the associated data analyses, BSMP station 5A was designated as a Northstar station based on its 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 historic ANIMIDA and BSMP program data, are provided in Table 3-6. 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 ranged from 1.1 to 57 mg/kilogram (mg/Kg) during the summer 2006 survey, 0.2 to 38 mg/kilogram (mg/Kg) during the summer 2005 survey, and 1.0 to 33 mg/Kg during the summer 2004 survey. Outliers of 100 mg/Kg at Station N14 in 2005 and 85 mg/Kg at Station N08 in 2004 were detected, and may have been influenced by the entrainment of recent organic material (i.e., peat). The TPHC concentrations at Stations N08 and N14 ranged from 0.6 to 24 mg/Kg in 1999, 2000, and 2002. A TPHC measurement of 230 mg/Kg was noted for the 2006 Eskimo Island peat sample.

The mean TPHC concentrations for the three regions (Northstar, Liberty, and BSMP) were 10, 7.2, and 12 mg/Kg (Table 3-2 through 3-4), respectively in the summer 2006 survey; 17, 15, 8.0 mg/Kg in the summer 2005 survey; and 16, 17, and 8.5 in the summer 2004 survey. Overall, the levels of TPHC measured during the summer 2004 through 2006 surveys are within the range of values reported from previous studies of the region and other Alaskan coastal areas (Table 3-7).

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 through 2006 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 interaction effects were noted (Tables 3-11 and 3-12).

The composition of SHCs in the river sediment 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 sediment (Figure 4-6), Northstar station 6 (Figures 4-8 through 4-13), and BSMP station 3A (Figures 4-18 and 19). Also, the composition of the SHCs in surficial sediments in 2000, 2002, 2004, 2005, and 2006 are 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 through 2006 (Figures 4-8 through 4-13).

3.1.2.2 Polynuclear Aromatic Hydrocarbons

Concentrations of Total PAH in surficial sediments ranged from 25 to 1,800 micrograms/Kg (µg/Kg) during the summer 2006 survey, 31 to 1,600 micrograms/Kg (µg/Kg) during the summer 2005 survey, and 13 to 1,100 µg/Kg during the summer 2004 survey.

The mean Total PAH concentrations for the three regions (Northstar, Liberty, and BSMP) were 640, 280, and 750 µg/Kg (Tables 3-2 through 3-4), respectively in the summer 2006 survey; 560, 710, and 430 µg/Kg in the summer 2005 survey, and 460, 640, and 310 µg/Kg in the summer 2004 survey. Overall, the levels of PAH measured during the summer 2004 through 2006 surveys are within the range of values reported from previous studies of the region and other Alaskan coastal areas (Table 3-7).

An increase in the mean regional concentration of Total PAH at Northstar was noted between the 1999 pre-construction measurements and the combined 2000 through 2006 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*construction interaction effects were noted (Tables 3-11 and 3-12).

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, 2002, 2004, and 2005 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, 2002, 2004, and 2005 (Figures 4-8 through 4-12).

3.1.2.3 Steranes and Triterpanes

Concentrations of Total S/T in surficial sediments from the ranged from 3.3 to 173 µg/Kg during the summer 2006 survey, 2.1 to 98 µg/Kg during the summer 2005 survey, and 1.8 to 110 µg/Kg during the summer 2004 survey. One outlier at 660 µg/Kg was detected at Station N14 in 2005.

The mean Total S/T concentrations for the three regions (Northstar, Liberty, and BSMP) were 55, 34, and 65 µg/Kg (Tables 3-2 through 3-4), respectively, in the summer 2006 survey; 99, 85, and 32 µg/Kg in the summer 2005 survey, and 54, 52, and 31 µg/Kg in the summer 2004 survey. Overall, the levels of Total S/Ts measured during the summer 2004 through 2006 surveys are within the range of values reported from previous studies of the region and other Alaskan coastal areas (Table 3-7).

3.1.3 Metals

All surficial sediments, (top 1 cm) were analyzed for total concentrations of Ag, Al, As, Ba, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Sn, Tl, V and Zn (Table 3-1 and Appendix A). Concentrations of all metals show a high degree of patchiness throughout the study area as previously described for TOC and grain size (Tables 3-2 through 3-4). However, metal concentrations do vary in response to variations in grain size and TOC as will be discussed below. The highest concentrations of metals were found in Al-rich (>6% Al) sediments from stations N03, N17, L06, L07, and 7C (Tables 3-8 through 3-10). These maximum concentrations are within natural limits for the area as discussed in Section 4.

During 2004, sediment was collected from 22 stations in the Northstar area, eight more than during 1999. Several of the additional stations were sited close to the island and along the pipeline. The lowest metal concentrations were found in sandy sediment at stations N01, N09, N11, and N15 (Table 3-9). In accordance with the grain size distribution, the highest levels of metals occurred at stations N04, N05, N12, N13, N21 and N23 where silty sediment was present (Table 3-9). Concentrations of Fe, Zn, Cu, Cr and Ni were slightly elevated in the gravel-rich, Al-poor sediment from the top of the pipeline (Station N23). In the immediate area of Liberty Prospect, no clear trends in grain size or metal distribution were observed. Highest metal levels were found at Stations L06 and L07 and the lowest metal values were observed at station L01 (Table 3-10).

The patchwork of metal concentrations throughout the study area can be normalized by ratioing metal values to either Al or Fe and thereby removing variations in metal concentrations that result from differences in grain size, TOC and/or mineralogy. For example, Figure 3-7a shows a strong, positive relationship between Al and grain size data for 1999-2002, expressed as percent (silt+clay). The Al versus grain size data for 2004-2006 (Figure 3-7b) plot well with the prediction intervals from the 1999-2002 data. 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 for 2004-2006 correlated well with Al levels (Figure 3-8a). The 2004-2006 data are plotted in Figure 3-8a with the prediction interval from the 1999-2002 data. Six of the 112 data points on the graph for Al versus Fe plotted above the upper prediction interval from the 1999-2002 data (Figure 3-8a). These six samples appear to contain an enriched Fe phase and will be discussed in more detail below.

Only an example of a metal/Al plot for V is given in this section to show the effectiveness of the normalization process (Figure 3-8b). Even though individual metal concentrations are extremely variable from site to site, these differences in absolute concentrations can be almost completely 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 3-8b show the natural trend (i.e., V/Al ratio) for area sediments. The 2004-2006 data for V and Al are plotted with the prediction interval for the 1999-2002 data (Figure 3-8b) to help further validate the previously established trend. Positive deviations from a prediction interval constructed around the regression line such as in Figure 3-8b can often be related to anthropogenic inputs of that metal. The two of 112 data points on the Al versus V graph that plot above the upper prediction interval are most likely due to natural processes. This concept is outlined below. Then, an overall detailed evaluation of likely sites with metal contamination is presented in Section 4.

With respect to the Fe anomalies, station L22 was sited at the deepest water depth (29.2 m) in either the ANIMIDA or cANIMIDA programs and a small amount of additional iron oxide on these fine-grained offshore particles was most likely responsible for the high Fe concentration in Figure 3-8a. The presence of an enriched iron oxide in the sediment from station L22 is supported by enrichment of V (Figure 3-8b) as well as for As and Cr. These three metals exist as oxyanions in seawater and are readily adsorbed by freshly precipitated iron oxides that form at river mouths Semmler, 2006). Thus, as future studies are carried out, this observation will need to be further checked and included in evaluations of sediment contamination. Perhaps an enriched iron oxide phase also fits the data from station N03 (e.g., V enrichment at station N03, Figure 3-8b) as well as stations 6G and 6H near the mouth of the Colville River. In contrast with observations for stations L22, N03, 6G and 6H, the observed Fe enrichment for stations N14 and WDK (Figure 3-8a) is accompanied by enrichment Ag, As, Cd, Co, Cu, Ni, Pb, Hg and Zn is believed to be due to the presence of trace amounts of naturally occurring sulfide minerals. A detailed evaluation of this explanation is developed in Section 4. A similar observation was made for nearby station 5D in 1999 and no explanation for that anomaly was presented at that time. Finding and addressing these anomalies in the Al versus metal plots is important to future use of these plots to identify anthropogenic metal contamination.

Detailed identification of possible metal contamination in surface sediments, along with evaluation of possible adverse biological impacts from any contamination will be presented in the discussion (Section 4).

3.1.4 Radionuclides

The cANIMIDA study area was described by Reimnitz and Barnes (1974) as a net erosional sedimentary environment during the Holocene. Naidu et al. (2001) and Trefry et al. (2003) reported difficulties in obtaining cores that could be aged dated using radionuclides that focus on the past 50-100 years. At best, sediment deposition in the cANIMIDA area has been patchy during the past century. Trefry et al. (2003) cautioned investigators to be sure that sediments collected for analysis of potential pollutants are representative of the most recent inputs. In this regard, surficial sediments from the 2004-2006 surveys were counted for the activities of excess ^{210}Pb and total ^{137}Cs (Figure 3-9a). The pre-survey assumption was that surface sediments with low activities of excess ^{210}Pb (<0.5 dpm/g) or ^{137}Cs (<0.05 dpm/g) would contain very little silt or clay that had been recently or sufficiently well exposed to the water column or at the sediment-seawater interface to adsorb excess ^{210}Pb or ^{137}Cs. Therefore, such sediments would be less likely to contain recent material that had an anthropogenic contribution of metals or hydrocarbons. However, in some cases, sediments with low activities of excess ^{210}Pb and ^{137}Cs might be predominantly sand that had a naturally low affinity for these isotopes. Sediments that have intermediate levels of the two isotopes may be sandy or contain some mixture of old, recent and sandy sediments.

The results for 2004, 2005 and 2006 are presented in Tables 3-13 through 3-15. During each of the three years, surface sediments with non-detectable amounts of excess ^{210}Pb (<0.05 dpm/g) and ^{137}Cs (<0.015 dpm/g) were found (Tables 3-13 through 3-15). In contrast, maximum values for excess ^{210}Pb of 2.8 dpm/g and ^{137}Cs of 0.20 dpm/g were observed (Tables 3-13 through 3-15). Collectively, the activities for ^{226}Ra (parent isotope to ^{210}Pb) correlated well with concentrations of Al (Figure 3-9a and Pb). This good relationship is consistent with higher amounts of ^{226}Ra in Al-rich clays. The y-intercept of 0.63 on the Al versus ^{226}Ra graph (Figure 3-9a) suggests that another Ra-bearing phase that contains little or no Al is present in the sediments.

The relationship between Al and excess ^{210}Pb in surface sediments shows considerable scatter (Figure 3-9b). One explanation for the observed scatter is large differences in the accumulation rates and/or ages among the 112 samples of surface sediment. Samples with low amounts of excess ^{210}Pb (<0.5 dpm/g) and Al concentrations >3% are less likely to contain very much recent sediment relative to samples with excess ^{210}Pb >0.5 dpm/g and Al concentrations >3%. The pertinent isotope information for each is listed in Tables 3-13 through 3-15. A weak, but observable trend of higher activity for excess ^{210}Pb in sediments with a higher activity of ^{137}Cs than was observed for the surface sediments is consistent with increased adsorption of the two isotopes from water by more clay-rich (i.e., Al-rich) samples (Figure 3-10).

3.1.5 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” was tested. The results of the statistical analyses are presented in the Tables 3-11 to 3-12.

In Tables 3-11 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 or LN perylene). 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 through 2006. A positive (or negative) effect along with a significant *p*-value (*p*-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 through 2006) 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 rates for these tests were 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 through 2006) even after adjusting for grain size. However, when the data are adjusted for log-normal (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 Sediment Core Results

3.2.1 General Chemical and Physical Measurements

3.2.1.1 Total Organic Carbon (TOC) and Grain Size

Sampling locations for sediment cores were based on the presence of fine-grained sediments as well as specific locations such as revisiting the 1989 sites in Harrison Bay (7A, 7C, 7E). Thus, the average fraction of silt + clay for the 2005-2006 sediment cores was ~70% relative to ~44% for the surface sediments (Table 3-16). The highest average silt + clay content of 88% was found for the core from station 7C (2006) and the lowest average silt + clay content was 43% from BP01 (2005). Station 7C is located ~55 km from the mouth of the Colville River in western Harrison Bay and station BP01 is located in the general area of the Boulder Patch. The most fine-grained layer in all of the cores with 95% silt + clay was at 18-20 cm in the core from station 7C. The coarsest grained sample, with only 28% silt + clay was at 28-30 cm in the core from station N17. The coarse sample from station N17 contained some peat that distorted the grain size distribution.

Concentrations of TOC averaged 1.1% for the 2005-2006 sediment cores relative to 0.9 % for the surface samples (Table 3-16). Both these averages show again the generally low organic matter content for sediments from the study area. The highest average TOC value was 2.1% for the core from station 7E in western Harrison Bay and the lowest average TOC was 0.46% for the core from station N26 located about 0.2 km northeast of Northstar Island. The most TOC-rich layer was from station 7E at 3.88% (2-4 cm) and the lowest TOC value of 0.34% was for station N26 (2-4 cm).

3.2.2 Organics

Concentrations of organics were determined for 32 samples from 5 sediment cores in 2005 (Cores 1C, 2A, BP01, N26, and PB1A) and for 34 samples from 5 sediment cores in 2006 (Cores 7A, 7C, 7E, L22, and N17). Each core was sectioned into 2-cm layers. Organic parameter results for the sediment core samples are summarized in Table 3-5. The summary results include Total PAH, TPHC, Total S/T, the percent of the fine grain-size fraction (the sum of the silt + clay grain-size fraction), and the ratio of pyrogenic PAHs to petrogenic PAHs. The results are separated into groupings by core locations with results listed in order of sample depth.

Descriptions of key diagnostic parameters, which are useful in describing the overall organics dataset are provided in Table 3-6. Vertical core profiles of 6 key parameters for each core are included in Figures 3-11 through 3-20. As discussed later, only two of the core samples (Cores PB1A and N26) yielded geochronology results that allowed accurate determination of sedimentation rates, and thus estimates of deposition dates (Table 3-17). According to the age-dating results for these cores, pre-development sediment is clearly present at depths > 2.5 cm and post-development (since 1970) sediment would most likely be found in the top 2 cm of the sediment column. The complete organics data, including concentrations for individual PAH, SHC, and S/T target compounds, are included in Appendix B.

3.2.2.1 Saturated Hydrocarbons

Concentrations of TPHC in the summer 2005 and 2006 sediment core samples ranged from 3.8 to 42 mg/Kg. TPHC concentrations in the summer 2001 sediment core samples ranged from 3.2 to 31 mg/Kg.

The composition of SHCs through the depth of all the sediment cores was generally similar, indicating a common TPHC source relationship between pre-1970 and post-1970 sediments. For example, similar patterns are noted in the GC/FID chromatograms for the top and bottom segment (pre-1970 and post-1970) sediments from cores N26 (Figures 4-21 and 4-22) and 1C (Figures 4-23 and 4-24).

Overall, the levels of TPHC measured during the 2005 and 2006 sediment core surveys are within the range of values reported from previous studies of the region and other Alaskan coastal areas (Table 3-7).

3.2.2.2 Polynuclear Aromatic Hydrocarbons

Concentrations of Total PAH in the summer 2005 and 2006 sediment core samples ranged from 300 to 2,950 μg/Kg.

As noted with the SHC composition, the composition of Total PAH in the pre-1970 and post-1970 sediments was similar, indicating a common PAH source relationship. For example, similar patterns are noted in the PAH histograms for the top and bottom segments (pre-1970 and post-1970) sediments from cores N26 (Figures 4-21 and 4-22) and 1C (Figures 4-23 and 4-24).

Overall, the levels of PAH measured during the 2005 and 2006 sediment core surveys are within the range of values reported from previous studies of the region and other Alaskan coastal areas (Table 3-7).

3.2.2.3 Steranes and Triterpanes

Concentrations of Total S/T in the summer 2005 and 2006 sediment core samples ranged from 13 to 200 μg/Kg.

As noted with the SHC composition, the composition of triterpanes in the pre-1970 and post-1970 sediments was similar, indicating a common triterpane source. For example, similar patterns are noted in the triterpane EICPs for the top and bottom segments (pre-1970 and post-1970) sediments from cores N26 (Figures 4-21 and 4-22) and 1C (Figures 4-23 and 4-24).

Overall, the levels of Total S/T measured during the 2005 and 2006 sediment core surveys are within the range of values reported from previous studies of the region and other Alaskan coastal areas (Table 3-7).

3.2.3 Metals

Concentrations of trace metals were determined for 47 samples from all seven cores collected in 2005 (stations 1C, 2A, BP01, E01, L17B, PB1A and N26) and for 34 samples from 5 cores collected in 2006 (stations 7A, 7C, 7E, L22 and N17). Each core was sectioned into 0.5- and 2.0-cm thick layers. The average Al concentration for all sediments from cores was 31% greater than found for the 2005-2006 surface sediments. Similarly greater averages were found for Ba, Co, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Tl, V and Zn in the cores than the surface sediments. These differences are directly related to naturally higher metal concentrations in the more clay-rich (i.e., more aluminosilicate rich) sediments in the cores.

Some variability in concentrations of metals was observed in most cores (Figures 3-FIT9-20), mainly due to shifts in the relative amounts of fine-grained sediment. However, the vertical profiles for metals/Al for most metals in most cores show a relatively uniform trend because Al concentrations were relatively uniform with increasing depth in each core (Figures 3-21 through 3-32). The metals data are evaluated with respect to possible contamination and for temporal trends in Section 4.

3.2.4 Geochronology of Sediment Cores

The historical record of sediment deposition was investigated using the vertical distribution of the activities of ^{137}Cs and excess ^{210}Pb in sediment cores collected at seven locations in 2005 (1C, 2A, BP01, E01, L17B, PB1A and N26) and seven locations in 2006 (6B, 7A, 7C, 7E, L22, N05 and N17). As previously reported (Weiss and Naidu, 1986; Naidu et al., 2001; Trefry et al., 2003), efforts to reconstruct recent geochronology for sediments in the cANIMIDA study area have been complicated by the impacts of bottom-fast ice, ice gouging, low net accumulation rates, low activities of ^{137}Cs and excess ^{210}Pb, and storm-induced resuspension and transport of sediment offshore in deeper water. In the ANIMIDA study, only 3 of 11 cores provided reliable geochronologies for excess ^{210}Pb (i.e., $r>0.9$ for log normalized excess ^{210}Pb versus depth); however, a decrease to non-detectable values for ^{137}Cs was found in each core that identified layers of sediment that pre-dated the early 1950s (Brown et al., 2003). Based on previous results and aware of inherent difficulties, the primary goal of the geochronology portion of the cANIMIDA study was to be able to differentiate layers in sediment cores that were most likely deposited prior the late 1960s and early 1970s relative to layers of sediment that were most likely deposited during the subsequent post-development period.

Among the 14 cores collected for this study, between 2 and 4 cores provided reliable results for excess ^{210}Pb according the conditions specified above, depending on whether selected points (e.g., sand layers) were not included in the regression analysis for excess ^{210}Pb. A decrease in activities of ^{137}Cs to non-detectable values was observed for all 14 cores and a reasonable identification of sediment layers that were deposited during pre-development versus post-development could be made in most cases. This simplified division can be used to help test the null hypothesis that no contaminant inputs have been deposited at a given site since development began in 1970. Table 3-17 summarizes sedimentation rates and provides a calculated depth that most likely coincides with 1950, a year that pre-dates the presence of ^{137}Cs on Earth. In the worst case, comparison of concentrations of potential contaminants in sediments from above and below the ~1950 horizon provided information needed to determine whether contaminants have been deposited since development began.

The vertical profiles for ^{137}Cs, total ^{210}Pb and log normalized excess ^{210}Pb for all 14 cores are presented in Figures 3-33 through 3-36. In some instances, such as 2006 stations N05 and N17, only a few samples were analyzed because no detectable ^{137}Cs and very low values for excess ^{210}Pb were observed at the top of the core.

Sedimentation rates for the 14 cores ranged from <0.02 cm/yr at stations E01, L22, N05 and N17 (Table 3-17) to 0.3 cm/yr at station 1C in Camden Bay (Table 3-17). The mean sedimentation rate for the 13 stations (using 0.02 cm/yr for four stations and excluding station 7C) was 0.10 ± 0.08 cm/yr.

3.3 Quality Control Results

Laboratory and field QC samples were analyzed to assess precision, accuracy, and representativeness of the sample preparation and analytical procedures. The number and type of laboratory and field QC samples was based on the total number of field samples and as specified in Battelle SOPs and the Field Sampling and Logistics Plans (Battelle 2004a, 2005a, and 2006a). For this program, the following field and laboratory QC samples and measures were used to evaluate accuracy, precision, and representativeness of the analytical data: field replicates, surrogate recoveries, procedural blanks, blank spike samples, matrix spike samples, laboratory duplicates, standard reference materials, and/or oil reference standards.

This section provides a general summary 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. Quality control result details are presented in Appendix D of this report.

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

3.3.1 Field Quality Control

Field replicate samples were collected to assess overall precision and representativeness of the sampling and analytical efforts. The results for the field QC sample analyses are presented in

Appendices A and B, along with the associated environmental samples. A summary of these results is provided in this section and detailed discussion is provided in Appendix D.

3.3.2 Organic Laboratory Quality Control

The results for the organic QC samples and measures are presented in Appendix B, along with the results for the associated environmental samples. A summary of these results is provided in the following section and detailed discussion is provided in Appendix D.

The majority of the quality control samples prepared and analyzed along with the organic analysis samples met the DQOs and acceptance limits presented in Appendix C and Tables C-1 through C-2. Minor quality control exceedances included low surrogate recoveries, trace level blank contamination, low and high blank spike recoveries, laboratory duplicate precision exceedances, low SRM recoveries, and high control oil recoveries. These minor data quality exceedances did not adversely affect the quality or usability of the organic data.

The results for one sample were considered to be unusable due to severe quality control exceedances. Sample 04-N08-01-PHC-S had very low recoveries (<10%) for all four surrogates. The PAH results for this sample were outliers when assessed against the complete dataset, thus, this sample was considered an outlier and not used for statistical evaluation of the data or presented in graphics.

3.3.3 Metals Laboratory Quality Control

The results for the metal QC samples and measures are presented in Appendix A, along with the results for the associated environmental samples. A summary of these results is provided in the following section and detailed discussion is provided in Appendix D.

All of the quality control samples prepared and analyzed along with the metal analysis samples met the DQOs and acceptance limits presented in Appendix C and Table C-3. All metal results, as reported by FIT, are usable for project objectives and statistical analyses.

Table 3-1. Summary Data for Total 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 2004	Mean ± Std. Dev. (n = 47)	0.09 ±0.03	3.83 ±1.35	10.3 ±3.4	410 ±143	1.0 ±0.5	0.17 ±0.07	8.3 ±2.5	61.4 ±21.7	18.2 ±8.2	2.27 ±0.73
Surface Sediment 2005	Mean ± Std. Dev. (n = 31)	0.10 ±0.08	3.55 ±1.24	10.2 ±4.4	426 ±142	0.9 ±0.3	0.19 ±0.15	7.7 ±2.4	54.1 ±18.6	17.1 ±9.8	2.01 ±0.63
Surface Sediment 2006	Mean ± Std. Dev. (n = 34)	0.14 ±0.03	3.82 ±1.20	10.7 ±3.8	458 ±158	1.1 ±0.3	0.21 ±0.09	9.0 ±2.6	67.9 ±19.7	18.2 ±7.7	2.45 ±0.73
All data 2004-2006	Range	0.03-0.44	1.3-6.3	4.7-24.9	142-863	0.4-3.6	0.03-0.77	3.6-13.8	14.7-100	3.9-46.2	0.9-3.7
All data 1999-2002	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 2004	Mean ± Std. Dev. (n = 47)	0.043 ±0.021	324 ±110	25.0 ±8.2	9.3 ±3.6	0.41 ±0.15	0.29 ±0.12	88.7 ±35.2	73.8 ±26.7	0.60 ±0.48	47.2 ±34.6
Surface Sediment 2005	Mean ± Std. Dev. (n = 31)	0.037 ±0.023	291 ±105	25.7 ±9.4	10.1 ±3.5	0.39 ±0.16	0.28 ±0.10	74.9 ±29.0	64.8 ±25.2	0.93 ±1.24	40.1 ±29.9
Surface Sediment 2006	Mean ± Std. Dev. (n = 34)	0.038 ±0.017	341 ±116	27.7 ±8.7	10.5 ±3.6	0.50 ±0.13	0.37 ±0.13	92.1 ±33.4	73.3 ±22.7	0.98 ±0.65	49.6 ±31.5
All data 2004-2006	Range	0.003-0.113	100-633	6.9-45.8	4.3-20.1	0.14-0.82	0.0.05-0.64	25.2-155	15.1-136	0.02-6.42	0.1-100
All data 1999-2002	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. Table of Concentrations for Selected Organic Parameters and Grain Size in BSMP Sediment Samples

Station	Total PAH (μg/Kg)	Total PHC (mg/Kg)	Total S/T (μg/Kg)	TOC (%)	Silt+Clay (%)
BSMP - 2004					
3A	460	9.8	37	0.87	60
3B	470	11	35	0.81	--
4A	1100	15	49	0.77	82
4B	85	3.6	5.7	0.30	10
4C	40	1.3	4.0	0.22	1.6
5(0)	200	6.8	18	0.91	38
5(1)	23	1.1	2.5	0.04	0.1
5(10)	130	8.0	26	0.16	--
5(5)	250	8.2	35	0.43	30
5B	18	4.5	1.8	0.08	71
5D	459	25	90	0.54	100
5E	190	1.7	20	0.05	13
5F	720	17	91	0.61	84
5H	230	5.9	20	0.30	21
2004 Mean (SD)	310 (300)	8.5 (6.8)	31 (29)	0.44 (0.32)	43 (35)
BSMP – 2005					
1A	190	3.6	31	0.92	38
1B	100	1.6	11	0.18	14
1C	430	11	56	0.50	54
1D	36	0.56	2.4	--	12
1E	150	8.2	40	1.7	71
2A	1400	20	68	0.91	30
2B	68	0.39	4.6	0.12	4.0
2C	500	10	72	0.50	68
2D	45	0.23	2.1	0.18	3.1
2E	64	0.54	5.4	0.60	5.9
2F	280	2.5	13	0.61	20
2G	1300	14	44	1.5	84
2H	270	2.9	30	0.40	34
3A	700	9.0	49	0.91	75
3B	560	10	41	0.80	68
4A	410	38	24	0.65	23
4B	170	1.4	11	0.49	14
5(1)	48	0.30	3.2	0.05	3.3
5(5)	370	5.4	37	0.87	41
BP01	250	3.8	19	0.60	27
E01	1200	17	62	0.84	92
PB1	180	1.6	13	--	--
PB1A	1100	20	98	--	--
2005 Mean (SD)	430 (430)	8.0 (9.2)	32 (26)	0.67 (0.43)	37 (29)

Table 3-2 continued. Table of Concentrations for Selected Organic Parameters and Grain Size in BSMP Sediment Samples

Station	Total PAH (μg/Kg)	Total PHC (mg/Kg)	Total S/T (μg/Kg)	TOC (%)	Silt+Clay (%)
BSMP - 2006					
4A	370	5.1	19	0.65	54
5(1)	180	3.1	12	0.46	26
5(5)	190	3.6	16	0.75	19
6A	1300	22	120	1.5	93
6B	1600	17	74	0.81	52
6D	1100	11	78	0.74	51
6F	180	2.0	14	0.68	12
6G	970	19	130	2.1	49
6H	120	1.1	12	0.08	4.6
7A	910	10	90	0.76	61
7E	1800	26	170	2.2	94
7G	1400	19	120	0.81	39
BP01	290	5.6	19	0.80	48
E01	220	3.9	14	0.28	18
E02	1200	26	130	2.8	61
M01	92	1.3	8.0	0.62	6.3
SDI	420	10	29	1.0	60
WD01	1100	27	120	2.8	81
COL (Peat)	740	47	83	--	--
EI01 (Peat)	120	230	87	--	--
KUP (Peat)	110	57	35	--	--
PI01 (Peat)	13	8.7	3.0	--	--
SAG (Peat)	290	25	41	--	--
2006 Mean (SD)[1]	750 (580)	12 (9.3)	65 (55)	1.1 (0.81)	46 (28)
BSMP 1999 - 2002 Mean (SD)	340 (420)	6.6 (7.8)	27 (20)	0.81 (1.4)	39 (29)

Note[1] - Peat samples were not included in the average sediment concentrations.

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

Station	Total PAH (μg/Kg)	Total PHC (mg/Kg)	Total S/T (μg/Kg)	TOC (%)	Silt+Clay (%)
Northstar – 2004					
5A	500	5.4	56	0.76	56
N01	73	4.9	7.5	0.07	7.6
N02	480	3.3	35	0.38	46
N03	1100	25	110	0.46	24
N04	490	5.1	47	1.2	48
N05	540	11	52	0.33	79
N06[1]	830 (28)	19 (0.89)	81 (1.8)	0.39	53
N07	180	1.0	18	0.12	16
N08	28	85	100	0.41	79
N09	170	12	18	0.14	14
N10	860	23	100	0.48	89
N11	76	5.6	7.5	0.05	2.7
N12	250	9.6	24	1.7	--
N13	580	21	68	0.88	87
N14	650	15	78	0.57	58
N15	13	1.2	2.0	0.04	0.40
N16	650	15	59	0.29	75
N17	750	25	100	0.55	88
N18	470	7.0	53	0.92	34
N19	350	9.8	31	0.98	24
N20	380	8.1	40	1.4	55
N21	350	10	31	0.29	31
N23	760	30	100	0.63	46
2004 Mean (SD)	460 (290)	15 (17)	53 (24)	0.58 (0.45)	45 (29)
Northstar – 2005					
N03	950	14	59	--	--
N04	180	2.9	12	0.11	10
N06	410	6.6	32	0.20	33
N08	350	5.0	27	0.51	45
N11	490	7.2	38	0.44	--
N11	72	0.60	6.7	--	--
N14	1600	100	660	6.4	44
N18	590	9.0	38	0.83	41
N26	290	1.6	25	--	--
2005 Mean (SD)	560 (480)	17 (33)	99 (210)	1.4 (2.4)	34 (14)
Northstar – 2006					
5A	500	5.6	43	0.70	42
N03	1100	22	90	1.4	95
N03	1000	15	81	1.2	94
N06	810	11	68	0.95	80
N11	510	8.8	49	0.76	74
N14	170	1.2	13	0.23	10
N28	440	6.3	39	1.1	45
2006 Mean (SD)	640 (330)	10 (6.7)	55 (27)	0.91 (0.38)	63 (32)
Northstar 1999-2002 Mean (SD)	**610 (440)**	**11 (7.0)**	**63 (41)**	**0.97 (0.72)**	**58 (33)**

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. Table of Concentrations for Selected Organic Parameters and Grain Size in Liberty Sediment Samples

Station	Total PAH (μg/Kg)	Total PHC (mg/Kg)	Total S/T (μg/Kg)	TOC(%)	Silt+Clay(%)
3.3.4 Liberty - 2004					
L01	430	7.3	43	0.47	--
L04	490	12	35	0.69	49
L06[1]	960 (88)	23 (6.9)	71 (9.4)	1.6	82
L07	980	25	85	2.4	91
L08	740	26	88	1.1	57
L09	410	13	36	0.97	66
L17	270	9.3	21	0.65	47
L18	880	18	62	0.47	49
2004 Mean (SD)	640 (280)	17 (7.2)	52 (24)	1.0 (0.65)	63 (17)
3.3.5 Liberty - 2005					
L07	1100	23	140	1.6	84
L08	310	7.8	30	0.28	21
2005 Mean (SD)	710 (580)	15 (11)	85 (77)	0.94 (0.93)	52 (45)
3.3.6 Liberty - 2006					
L03	330	6.0	24	1.2	62
L08	360	13	38	0.79	50
L19	160	3.4	10	0.43	22
L20	180	3.4	13	0.41	15
L21	25	2.0	3.3	0.020	1.2
L22	650	16	60	0.81	59
2006 Mean (SD)	280 (220)	7.2 (5.7)	25 (21)	0.60 (0.40)	35 (26)
Liberty – 1999 to 2002 Mean (SD)	340 (170)	7.3 (4.1)	34 (15)	0.67 (0.30)	47 (26)

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. Table of Concentrations for Selected Organic Parameters and Grain Size in Sediment Core Samples.

Core Station - Year/ Depth (cm)	Total PAH (μg/Kg)	TPHC (mg/Kg)	Total S/T (μg/Kg)	Silt+Clay (%)	Pyrogenic/ Petrogenic (ratio)
1C – 2005					
2	760	13	77	68	0.11
4	820	14	81	71	0.12
6	770	13	78	63	0.12
8	810	13	78	68	0.12
10	780	14	77	71	0.12
12	790	14	81	68	0.12
14	750	13	75	70	0.12
20	790	14	82	70	0.12
30	890	15	94	71	0.12
Mean (SD)	790 (42)	14 (0.78)	80 (5.7)	69 (2.6)	0.12 (0.00)
2A – 2005					
2	1400	24	64	91	0.08
4	980	20	66	39	0.08
6	700	23	79	59	0.07
8	1060	18	47	63	0.07
10	1200	20	60	67	0.08
20	1600	38	160	90	0.10
30	1400	42	190	92	0.09
Mean (SD)	1200 (320)	26 (9.5)	95 (56)	72 (20)	0.08 (0.01)
BP01 – 2005					
2	300	4.8	21	33	0.09
4	340	4.3	21	31	0.08
6	320	4.4	20	36	0.09
8	380	5.0	24	35	0.09
10	400	6.2	21	52	0.08
12	340	3.9	13	70	0.09
Mean (SD)	350 (38)	4.7 (0.80)	20 (3.8)	43 (15)	0.09 (0.00)
N26 – 2005					
2	590	7.1	44	71	0.10
4	490	6.4	39	35	0.11
6	570	7.2	42	39	0.10
8	850	11	62	58	0.10
10	780	9.8	56	57	0.10
Mean (SD)	660 (150)	8.3 (2.1)	49 (9.8)	52 (15)	0.10 (0.00)
PB1A – 2005					
2	1100	23	85	36	0.07
4	1300	30	94	91	0.07
6	1000	18	64	95	0.08
8	880	16	51	--	0.08
10	840	14	56	93	0.08
Mean (SD)	1000 (180)	20 (6.3)	70 (19)	79 (28)	0.08 (0.00)

Table 3-5 (continued). Table of Concentrations for Selected Organic Parameters and Grain Size in Sediment Core Samples.

Core Station - Year/ Depth (cm)	Total PAH (μg/Kg)	TPHC (mg/Kg)	Total S/T (μg/Kg)	Silt+Clay (%)	Pyrogenic/ Petrogenic (ratio)
7A – 2006					
2	638	7.3	39	38	.104
4	808	9.7	50	55	.105
6	1047	14	73	68	.101
8	1177	16	75	64	.104
10	1580	24	115	77	.104
14	1608	21	118	88	.104
18	1665	23	125	84	.108
Mean (SD)	1200 (410)	16 (6.5)	85 (34)	68 (17)	0.10 (0.002)
7C – 2006					
2	1252	16	75	78	.107
4	1524	26	86	88	.108
6	1508	21	87	88	.108
8	1299	20	85	86	.108
10	953	13	56	92	.106
20	1143	16	60	95	.105
30	1387	27	89	91	.107
Mean (SD)	1300 (200)	20 (5.0)	77 (13)	88 (5.7)	0.11 (0.001)
7E – 2006					
2	1423	23	107	77	.086
4	2946	34	204	67	.071
6	2155	42	182	53	.091
8	2108	25	137	58	.086
10	1780	25	110	74	.102
14	1096	19	82	47	.102
18	1625	22	106	67	.108
30	2016	27	127	84	.107
Mean (SD)	1900 (560)	27 (7.4)	130 (41)	66 (13)	0.094 (0.013)
L22 – 2006					
2	467	7.9	36	48	.124
4	684	13	54	60	.127
6	692	16	55	65	.130
8	648	14	55	65	.134
10	690	13	54	69	.132
28	713	15	59	64	.131
Mean (SD)	650 (92)	13 (2.8)	52 (8.3)	62 (7.4)	0.13 (0.004)
N17 – 2006					
2	922	12.5	54	85	.105
4	999	14.4	61	89	.115
6	512	9.2	36	66	.112
8	552	10.1	37	73	.113
10	615	10.0	36	76	.107
30	611	20.1	85	28	.101
Mean (SD)	700 (200)	13 (4.1)	51 (20)	70 (22)	0.11 (0.005)

Table 3-6. 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 3-6 (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 3-7. 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[g] (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 – 1.1	0.9 – 69	0.009 – 0.087
Average (Range) Concentrations for ANIMIDA Study Area Sediment Cores[c]	0.54 (0.28 – 2.0)	9.0 (3.2 – 31)	0.059 (0.021 – 0.22)
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 – 0.18)
Average (Range) Concentrations for cANIMIDA Study Area Surficial Sediments[f]	0.46 (0.013 – 1.6)	13 (0.39 – 104)	0.050 (0.002 – 0.66)
Average (Range) Concentrations for cANIMIDA Study Area Sediment Cores[f]	0.82 (0.30 – 1.6)	15 (3.8 – 42)	0.066 (0.013 – 0.19)

[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.
[e] Brown et al., 2005.
[f] Results from this study.
[g] Total PHC concentrations for the ANIMIDA and cANIMIDA studies included saturated hydrocarbons only, while Total PHC concentrations for the other studies included saturated and aromatic hydrocarbons.

NA – not applicable.

Table 3-8. Table of Concentrations of Selected Metals in BSMP Sediment Samples

Station	Al (%)	Ba (µg/g)	Hg (µg/g)	Pb (µg/g)	Cd (µg/g)
BSMP 2004 (2002)					
2A	4.65 (4.71)	503 (512)	0.056 (0.061)	12.8 (12.9)	0.18 (0.17)
3B	4.37 (5.03)	441 (518)	0.061 (0.058)	11.8 (14.1)	0.17 (0.23)
4A	4.46 (4.28)	447 (535)	0.056 (0.042)	11.7 (11.6)	0.23 (0.31)
4B	2.07 (2.02)	191 (221)	0.023 (0.016)	5.4 (5.4)	0.19 (0.17)
4C	1.80 (1.56)	163 (165)	0.011 (0.007)	5.2 (4.1)	0.04 (0.05)
5H	2.65 (2.85)	245 (313)	0.025 (0.026)	6.9 (8.4)	0.19 (0.14)
5(0)	3.89 (3.12)	353 (363)	0.052 (0.025)	10.5 (6.1)	0.19 (0.21)
5(1)	1.46 (1.72)	142 (223)	0.006 (0.006)	5.3 (5.3)	0.03 (0.07)
5(5)	5.84 (3.47)	668 (357)	0.052 (0.060)	14.7 (8.6)	0.11 (0.13)
5(10)	2.83 (2.62)	260 (271)	0.029 (0.021)	6.9 (7.3)	0.16 (0.12)
5A	4.01 (5.42)	441 (538)	0.055 (0.049)	11.6 (11.0)	0.19 (0.19)
5B	1.28 (1.72)	154 (221)	0.003 (0.008)	4.2 (5.9)	0.05 (0.05)
5D	3.25 (3.64)	301 (371)	0.036 (0.029)	7.3 (6.9)	0.23 (0.20)
5E	2.20 (1.65)	182 (203)	0.015 (0.009)	6.5 (5.1)	0.03 (0.06)
5F	3.61 (4.38)	329 (455)	0.045 (0.043)	8.5 (8.6)	0.21 (0.18)
2004 Mean (SD)	3.72 (2.22)	321 (154)	0.035 (0.020)	8.6 (3.3)	0.15 (0.07)
BSMP 2005					
1A	3.44	393	0.045	8.7	0.14
1B	2.60	261	0.016	7.1	0.09
1C	5.00	538	0.035	11.4	0.11
1D	3.87	372	0.017	9.7	0.05
1E	4.56	435	0.036	14.5	0.13
2A	3.56	398	0.043	9.8	0.17
2B	2.22	198	0.009	6.0	0.05
2C	5.52	620	0.047	12.9	0.11
2D	2.17	204	0.008	6.3	0.06
2E	1.89	227	0.019	5.6	0.19
2F	3.03	365	0.031	7.3	0.24
2G	3.66	432	0.063	12.2	0.43
2H	3.74	383	0.025	10.4	0.10
3A	4.83	549	0.052	12.5	0.20
3B	4.55	520	0.050	11.8	0.17
4A	3.43	481	0.019	10.6	0.19
4B	1.98	268	0.020	6.3	0.19
5(1)	1.98	317	0.011	6.9	0.04
5(5)	3.75	433	0.037	10.1	0.19
BP01	2.17	259	0.028	5.2	0.11
E01	4.89	499	0.059	11.5	0.35
2005 Mean (SD)	3.47 (1.14)	388 (122)	31.9 (16.7)	9.4 (2.8)	0.16 (0.10)

Table 3-8 (continued). Table of Concentrations of Selected Metals in BSMP Sediment Samples

Station	Al (%)	Ba (µg/g)	Hg (µg/g)	Pb (µg/g)	Cd (µg/g)
BSMP 2006					
4A	3.59	389	0.028	8.9	0.24
5A	3.06	307	0.026	6.4	0.46
6A	5.32	511	0.056	12.7	0.28
6B	5.29	534	0.046	11.6	0.18
6D	4.92	531	0.041	12.4	0.15
6F	2.84	333	0.020	5.7	0.10
6G	3.56	394	0.056	14.7	0.17
6H	2.73	863	0.013	7.8	0.11
7A	4.40	732	0.040	11.5	0.16
7C	6.29	637	0.059	16.0	0.19
7E	5.59	678	0.066	15.2	0.33
7G	3.73	665	0.037	11.2	0.15
5(1)	2.69	332	0.023	8.3	0.14
5(5)	2.76	310	0.028	6.9	0.16
BP01	3.60	407	0.035	8.7	0.22
E01	2.41	256	0.022	6.0	0.13
2006 Mean (SD)	3.92 (1.22)	492 (180)	0.037 (0.016)	10.2 (3.4)	0.20 (0.09)

Table 3-9: Table of Concentrations for Selected Metals in Northstar Sediment Samples

Station	Al (%)	Ba (µg/g)	Hg (µg/g)	Pb (µg/g)	Cd (µg/g)
Northstar 2004 (2002)					
N01	1.84 (1.73)	254 (212)	0.010 (0.009)	5.1 (6.5)	0.04 (0.05)
N02	3.72 (4.51)	421 (501)	0.038 (0.044)	9.1 (13.8)	0.17 (0.13)
N03	6.30 (5.42)	584 (537)	0.070 (0.055)	16.1 (14.2)	0.22 (0.17)
N04	4.17 (4.13)	493 (422)	0.058 (0.048)	10.3 (10.3)	0.19 (0.14)
N05	3.78 (5.78)	483 (578)	0.042 (0.053)	8.6 (12.3)	0.15 (0.18)
N06	4.59 (4.85)	527 (503)	0.051 (0.046)	11.0 (12.8)	0.19 (0.12)
N08	5.30 (4.45)	559 (469)	0.056 (0.045)	10.4 (9.3)	0.21 (0.17)
N09	2.89 (3.71)	314 (402)	0.023 (0.036)	4.5 (7.3)	0.15 (0.16)
N10	5.50 (4.49)	562 (473)	0.065 (0.046)	12.3 (9.5)	0.22 (0.19)
N11	1.98 (2.73)	309 (293)	0.012 (0.023)	3.8 (8.9)	0.09 (0.11)
N12	4.75 (4.86)	506 (478)	0.051 (0.047)	10.9 (10.1)	0.17 (0.21)
N13	4.83 (5.58)	474 (514)	0.065 (0.061)	9.0 (15.3)	0.26 (0.22)
N14	4.23 (5.72)	404 (545)	0.049 (0.059)	9.2 (11.6)	0.23 (0.21)
N15	1.64 (1.65)	406 (302)	0.004 (0.015)	6.5 (6.1)	0.07 (0.11)
N12	4.75 (4.86)	506 (478)	0.051 (0.047)	10.9 (10.1)	0.17 (0.21)
N17	6.25 (5.27)	654 (518)	0.063 (0.057)	13.3 (13.8)	0.21 (0.21)
N21	3.26 (4.43)	379 (423)	0.030 (0.048)	5.3 (11.3)	0.16 (0.21)
N23	5.66 (4.82)	651 (575)	0.068 (0.047)	15.7 (10.4)	0.31 (0.27)
2004 Mean (SD)	4.19 (1.43)	471 (113)	0.045 (0.021)	9.6 (3.6)	0.18 (0.07)
Northstar 2005					
N4	1.91	299	0.016	5.4	0.09
N5	4.89	558	0.050	12.7	0.23
N6	2.80	749	0.027	8.9	0.14
N8	3.54	421	0.032	8.1	0.18
N11	3.09	425	0.029	9.3	0.13
N14	2.93	395	0.113	16.5	0.75
N18	3.33	455	0.039	10.0	0.28
2005 Mean (SD)	3.21 (0.90)	472 (144)	0.044 (0.032)	10.1 (3.6)	0.26 (0.23)
Northstar 2006					
N3	5.39	552	0.048	16.0	0.29
N6	4.76	628	0.054	13.7	0.26
N11	3.74	411	0.049	9.3	0.23
N14	1.78	256	0.013	4.3	0.09
N17	4.86	501	0.056	12.6	0.21
N27	5.39	546	0.058	14.2	0.25
N28	4.11	443	0.041	9.9	0.23
2006 Mean (SD)	4.19 (1.26)	477 (121)	0.046 (0.015)	11.4 (3.9)	0.22 (0.06)

Table 3-10. Table of Concentrations of Selected Metals in Liberty Sediment Samples

Station	Al (%)	Ba (µg/g)	Hg (µg/g)	Pb (µg/g)	Cd (µg/g)
Liberty 2004 (2002)					
L01	2.16 (2.59)	220 (259)	0.022 (0.021)	4.3 (7.2)	0.10 (0.10)
L04	3.69 (3.78)	371 (385)	0.048 (0.036)	8.3 (11.6)	0.18 (0.16)
L06-1	4.86 (4.58)	489 (486)	0.066 (0.044)	9.6 (9.3)	0.23 (0.19)
L06-2	6.36	683	0.082	13.9	0.23
L07	5.75 (4.07)	580 (437)	0.097 (0.041)	18.1 (8.0)	0.36 (0.19)
L08	4.33 (3.43)	612 (534)	0.061 (0.033)	13.7 (7.4)	0.21 (0.17)
L09	4.51 (2.23)	456 (243)	0.064 (0.019)	15.1 (9.5)	0.19 (0.10)
2004 Mean (SD)	4.52 (1.37)	487 (157)	0.063 (0.024)	11.8 (4.7)	0.21 (0.08)
Liberty 2005					
L7	6.30	701	0.097	20.1	0.38
L8	2.47	397	0.026	7.2	0.12
L17B	5.96	673	0.047	14.8	0.13
2005 Mean (SD)	4.90 (2.11)	590 (168)	0.057 (0.036)	14.0 (6.5)	0.21 (0.15)
Liberty 2006					
L3	4.01	451	0.040	14.2	0.28
L8	3.66	575	0.032	10.9	0.22
L19	2.54	268	0.025	6.0	0.21
L20	2.50	278	0.018	7.2	0.16
L21	2.04	229	0.004	5.5	0.04
L22	3.18	317	0.036	12.2	0.17
2006 Mean (SD)	2.99 (0.76)	368 (143)	0.026 (0.015)	9.3 (3.6)	0.18 (0.08)

Table 3-11. Statistical Model Result Summary with Silt + Clay Covariate

Performed on data from 36 stations sampled pre-construction and sampled at least once post-construction (includes Northstar stations N01 through N15; Liberty stations L01, L03, L04, L06, L07, L08, and L09; and BSMP stations 3A, 3B, 4A, 4B, 4C, 5(0), 5(1), 5(5), 5(10), 5A, 5B, 5E, 5F, and 5H). Model includes Station as a factor nested within Region and Year as a factor nested within Construction. Silt+clay was included in the model as a covariate when the dependant variable was reported as a concentration. Outliers were excluded from the analysis.

Key Parameter (dependant variable)				**Silt+Clay Covariate**		**Northstar Effect**		**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**
LN Total PAH (µg/Kg)	**0.848**	**0.000**	4.508	**0.022**	**0.000**	**-1.917**	**0.000**	-0.067	0.763	**0.859**	**0.000**
LN Total PAH less perylene (µg/Kg)	**0.847**	**0.000**	4.409	**0.022**	**0.000**	**-1.891**	**0.000**	-0.080	0.715	**0.852**	**0.000**
LN Perylene (µg/Kg)	**0.859**	**0.000**	2.247	**0.021**	**0.000**	**-1.592**	**0.000**	0.048	0.237	**0.746**	**0.000**
LN Petrogenic PAH (µg/Kg)	**0.848**	**0.000**	4.293	**0.022**	**0.000**	**-1.807**	**0.000**	-0.092	0.667	**0.834**	**0.000**
LN Pyrogenic PAH (µg/Kg)	**0.859**	**0.000**	2.109	**0.020**	**0.000**	**-1.444**	**0.000**	-0.125	0.499	**0.718**	**0.000**
LN TPHC (mg/Kg)	**0.747**	**0.000**	1.044	**0.017**	**0.000**	**-0.861**	**0.022**	-0.147	0.470	**0.516**	**0.006**
LN LALK (mg/Kg)	**0.851**	**0.000**	-1.816	**0.018**	**0.000**	**-0.839**	**0.004**	0.039	0.801	**0.480**	**0.001**
LN TALK (mg/Kg)	**0.824**	**0.000**	-0.456	**0.022**	**0.000**	**-1.249**	**0.002**	0.001	0.994	**0.818**	**0.000**
LN Isoprenoids (mg/Kg)	**0.873**	**0.000**	-2.564	**0.012**	**0.000**	**-0.455**	**0.009**	-0.141	0.137	**0.343**	**0.000**
LN TOC (%)	**0.745**	**0.000**	-1.491	**0.018**	**0.000**	**-1.345**	**0.009**	-0.094	0.625	0.126	0.612
N/P	**0.414**	**0.001**	0.926			**0.595**	**0.002**	-0.225	0.034[1]	-0.061	0.522
Pyrogenic PAH/ Petrogenic PAH	**0.636**	**0.000**	0.101			-0.006	0.463	0.002	0.605	-0.0003	0.949
C2D/C2P	**0.576**	**0.000**	0.291			**0.149**	**0.000**	**-0.072**	**0.000**	-0.008	0.588
C3D/C3P	**0.520**	**0.000**	0.346			**0.237**	**0.000**	-0.054	0.094	**-0.111**	**0.000**
LALK/TALK	**0.407**	**0.004**	0.191			-0.006	0.906	0.033	0.181	-0.005	0.844
C16/(C15+C17)	0.334	0.067	0.322			--	--	--	--	--	--
Pristane/Phytane	0.325	0.110	2.223			--	--	--	--	--	--
CPI	**0.639**	**0.000**	4.486			**-2.393**	**0.003**	0.441	0.312	0.434	0.272

Note[1] – This result was considered to be not significant when controlling the false discovery rate (Benjamini and Hochberg, 1995).

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

Performed on data from 36 stations sampled pre-construction and sampled at least once post-construction (includes Northstar stations N01 through N15; Liberty stations L01, L03, L04, L06, L07, L08, and L09; and BSMP stations 3A, 3B, 4A, 4B, 4C, 5(0), 5(1), 5(5), 5(10), 5A, 5B, 5E, 5F, and 5H). Model includes Station as a factor nested within Region and Year as a factor nested within Construction. Perylene (log-transformed) was included in the model as a covariate. Outliers were excluded from the analysis.

Key Parameter (dependant variable)				**LN Perylene Covariate**		**Northstar Effect**		**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**
LN Total PAH less perylene (µg/Kg)	**0.977**	**0.000**	2.156	**1.008**	**0.000**	-0.299	0.066	-0.140	0.094	0.104	0.183
LN Petrogenic PAH (µg/Kg)	**0.977**	**0.000**	2.067	**0.998**	**0.000**	-0.235	0.143	-0.153	0.065	0.095	0.222
LN Pyrogenic PAH (µg/Kg)	**0.982**	**0.000**	0.108	**0.904**	**0.000**	-0.036	0.770	-0.168	0.010[1]	0.047	0.433
LN TPHC (mg/Kg)	**0.832**	**0.000**	-0.517	**0.713**	**0.000**	0.230	0.467	-0.162	0.323	-0.022	0.886
LN LALK (mg/Kg)	**0.940**	**0.000**	-3.409	**0.734**	**0.000**	0.276	0.144	0.017	0.859	-0.068	0.453
LN TALK (mg/Kg)	**0.949**	**0.000**	-2.585	**0.961**	**0.000**	0.250	0.256	-0.033	0.771	0.098	0.355
LN Isoprenoids (mg/Kg)	**0.930**	**0.000**	-3.569	**0.477**	**0.000**	0.239	0.074	-0.153	0.028[1]	-0.010	0.870
LN TOC (%)	**0.781**	**0.000**	-2.997	**0.709**	**0.000**	-0.429	0.382	-0.238	0.165	-0.353	0.139

Note[1] –This result was considered to be not significant when controlling the false discovery rate (Benjamini and Hochberg, 1995).

Table 3-13. Summary Data for 2004 for Radionuclides and Aluminum in Surface Sediment from the Coastal Beaufort Sea

Sample Identification	Excess Pb-210 (dpm/g)	Ra-226 (dpm/g)	Cs-137 (dpm/g)	Al (%)
3A 2004	0.73	1.57	0.082	4.65
3B 2004	1.54	1.72	0.036	4.37
4A-1 2004	0.63	1.80	0.075	4.46
4B 2004	0.59	1.07	<0.01	2.01
4C 2004	0.17	0.79	<0.01	1.80
5(0) 2004	1.37	1.44	0.100	3.89
5(1) 2004	0.00	0.58	<0.01	1.46
5(5) 2004	1.99	1.58	0.085	5.81
5(5A) 2004	0.39	1.35	0.044	3.42
5(10) 2004	0.66	1.33	<0.01	2.83
5A 2004	1.04	1.47	0.075	4.01
5B 2004	0.63	0.47	0.010	1.28
5D 2004	0.48	1.38	0.066	3.25
5E 2004	0.76	0.68	<0.01	2.20
5F 2004	0.15	1.27	0.084	3.61
5H 2004	0.81	1.18	0.038	2.65
L01 2004	0.21	0.95	0.011	2.16
L01A 2004	1.41	1.72	0.11	4.65
L04 2004	1.80	1.32	0.044	3.69
L06 #1 2004	1.47	1.87	0.13	4.86
L06 #2 2004	2.02	1.89	0.20	6.36
L06 #3 2004	2.23	1.88	0.19	6.26
L07 2004	1.01	1.91	0.16	5.75
L08 2004	1.59	1.55	0.11	4.33
L09 2004	1.37	1.52	0.082	4.51
L17 2004	0.36	1.21	0.035	3.34
L18 2005	0.19	1.24	0.028	3.16
N01 2004	0.06	0.70	<0.01	1.84
N02 2004	0.70	1.62	0.038	3.72
N03 2004	2.29	1.99	0.11	6.30
N04 2004	0.39	1.50	0.066	4.17
N05 2004	1.16	1.47	0.045	3.78
N06 #1 2004	0.76	1.55	0.057	4.59
N06 #2 2004	1.25	1.67	0.095	5.58
N06 #3 2004	1.00	1.58	0.093	5.09
N08 2004	2.08	1.74	0.13	5.30
N09 2004	0.05	1.24	0.033	2.89
N11 2004	0.04	0.89	0.011	1.98
N12 2004	2.83	1.73	0.19	4.75
N13 2004	1.56	1.65	0.16	4.83
N16 2004	0.35	1.51	0.060	4.81
N18 2004	0.80	1.34	0.056	3.41
N20 2004	1.55	1.24	0.090	4.88
N21 2004	0.22	1.47	0.033	3.26
N23 2004	0.45	1.75	0.12	5.66

Table 3-14. Summary Data for 2005 for Radionuclides and Aluminum in Surface Sediment from the Coastal Beaufort Sea

Sample ID	Excess Pb-210 (dpm/g)	Ra-226 (dpm/g)	Cs-137 (dpm/g)	Al (%)
1A 2005	1.03	1.57	0.061	3.44
1B 2005	0.58	1.04	0.031	2.60
1C 2005	1.65	1.50	0.066	5.00
1D 2005	0.81	1.63	0.004	3.87
1E 2005	1.41	2.06	0.032	4.56
2A 2005	1.01	1.78	0.053	3.56
2B 2005	0.44	0.97	<0.01	2.22
2C 2005	1.80	1.54	0.082	5.52
2D 2005	0.22	0.82	0.003	2.17
2E 2005	0.36	1.62	0.009	1.93
2F 2005	0.32	1.56	0.018	3.03
2G 2005	2.10	1.80	0.16	3.66
2H 2005	0.77	1.23	0.060	3.74
3A 2005	0.82	1.72	0.064	4.83
3B 2005	1.00	1.66	0.058	4.55
4A 2005	0.28	1.43	0.019	3.43
4B 2005	0.43	1.10	0.007	1.98
5(1) 2005	0.01	0.65	0.008	1.98
5(5) 2005	0.49	1.38	0.034	3.75
BP01 2005	0.99	1.41	0.003	2.17
E01 2005	2.09	1.60	0.12	4.89
L07 2005	1.73	1.85	0.13	6.30
L08 2005	0.77	0.93	0.011	2.47
L17B 2005	1.15	1.36	0.055	5.96
N04 2005	0.12	1.05	0.012	1.91
N05 2005	0.15	1.63	0.032	4.89
N06 2005	0.65	1.07	0.044	2.80
N08 2005	1.04	1.51	0.015	3.57
N11 2005	0.87	1.16	0.033	3.08
N14 2005	2.60	1.60	0.026	3.05
N18 2005	1.39	1.51	0.043	3.33

Table 3-15. Summary Data for 2006 for Radionuclides and Aluminum in Surface Sediment from the coastal Beaufort Sea

Sample ID	Excess Pb-210 (dpm/g)	Ra-226 (dpm/g)	Cs-137 (dpm/g)	Total Pb-210 (dpm/g)	Al (%)
N03 R1	1.64	1.85	<0.015	3.49	4.99
N03 R2	1.14	1.77	<0.015	2.91	5.79
N06	0.35	1.61	<0.015	1.96	4.76
N11	0.53	1.63	<0.015	2.16	3.74
N14	0.60	1.03	<0.015	1.63	1.78
N17	0.17	1.73	<0.015	1.90	4.86
N27	0.34	1.62	<0.015	1.96	5.39
N28	1.00	1.48	0.061	2.48	4.11
West Dock	2.59	1.76	0.064	4.35	4.23
M01	0.86	0.91	<0.015	1.77	1.85
L03	0.64	1.8	<0.015	2.44	4.01
L08	0.67	1.43	0.033	2.10	3.66
L19	1.12	1.26	<0.015	2.38	2.54
L20	0.52	1.08	<0.015	1.60	2.50
L21	0.00	0.78	<0.015	0.78	2.04
L22	0.82	1.5	<0.015	2.32	3.18
E01	0.52	1.13	<0.015	1.65	2.41
E02	0.80	1.65	0.125	2.45	3.90
SDI-1	1.54	1.39	0.029	2.93	3.84
BP01	0.85	1.66	0.014	2.51	3.60
4A	0.24	1.42	<0.015	1.66	3.59
5A	0.00	1.28	<0.015	1.28	3.06
6A	1.15	1.75	0.037	2.90	5.32
6B	1.02	1.37	0.035	2.39	5.29
6D	0.00	1.41	<0.015	1.41	4.92
6F	0.45	1.28	<0.015	1.73	2.84
6G	0.87	1.32	0.035	2.19	3.56
6H	0.00	1.52	<0.015	1.52	2.73
7A	0.74	1.47	<0.015	2.21	4.50
7C	0.00	1.67	<0.015	1.67	6.29
7E	0.72	1.72	<0.015	2.44	5.59
7G	0.96	1.3	<0.015	2.26	3.72
5(1)	0.24	0.96	<0.015	1.20	2.69
5(5)	0.70	1.22	0.016	1.92	2.76

Table 3-16. Summary Data for Total Metals, Total Organic Carbon (TOC), and Grain Size in Sediment Cores 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 (%)
Sediment Cores 2005-2006	Mean ± Std. Dev. (n = 81)	0.11 ±0.04	4.81 ±1.09	10.3 ±3.6	590 ±152	1.1 ±0.3	0.22 ±0.10	10.3 ±2.45	76.7 ±15.5	21.8 ±5.1	2.73 ±0.55
Surface Sediment 2005-2006	Mean ± Std. Dev. (n = 64)	0.12 ±0.06	3.67 ±1.21	10.3 ±3.9	441 ±151	1.0 ±0.3	0.20 ±0.12	8.3 ±2.6	60.9 ±20.0	17.3 ±8.4	2.21 ±0.70

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 (%)
Sediment Cores 2005-2006	Mean ± Std. Dev. (n = 81)	0.048 ±0.016	319 ±83	33.0 ±6.6	12.2 ±2.6	0.58 ±0.13	0.42 ±0.07	101 ±22.4	87.6 ±14.4	1.1 ±0.7	69.5 ±16.8
Surface Sediment 2005-2006	Mean ± Std. Dev. (n = 64)	0.037 ±0.020	315 ±113	26.4 ±8.8	10.2 ±3.5	0.45 ±0.15	0.32 ±0.12	82.9 ±31.5	68.4 ±23.6	0.90 ±0.91	43.6 ±32.2

Table 3-17. Summary Data for Age-Dated Sediment Cores from the Coastal Beaufort Sea

Year	Core	Core Length (cm)	Water Depth (m)	Depth for 1950 (cm)	^{137}Cs sed. rate (cm/yr)	Excess ^{210}Pb sed. rate (cm/yr)
2005	1C	54	22.2	16.5	0.30	unreliable (0.7, r = 0.78*)
	2A	52	4.1	10	0.12	unreliable (0.18, r = 0.56)
	BP01	10	6.6	9.5	0.17	unreliable (0.13, r = 0.76)
	E01	21	3.7	1	<0.01	unreliable
	L17B	30	20.9	6	0.10	unreliable
	PB1A	42	3.0	3.5	0.06	0.09 (r = 0.91)
	N26	17	23.9	6.5	0.11	0.07 (r = 0.98)
2006	6B	42	5.5	~2.5	0.05	unreliable
	7A	19	2.1	4.5	0.08	unreliable
	7C	42	13.8	?	?	unreliable
	7E	32	2.7	11.5	0.20	unreliable (0.25, r = 0.59)
	L22	36	29.2	1	<0.02	unreliable
	N05	14	11.2	1	<0.02	unreliable
	N17	46	11.9	1	<0.02	unreliable

Figure 3-1. Histograms showing grain size distribution as percent gravel (black bar), sand (red bar), silt (green bar) and clay (yellow bar) for sediment samples collected during 2004 in the Northstar area.

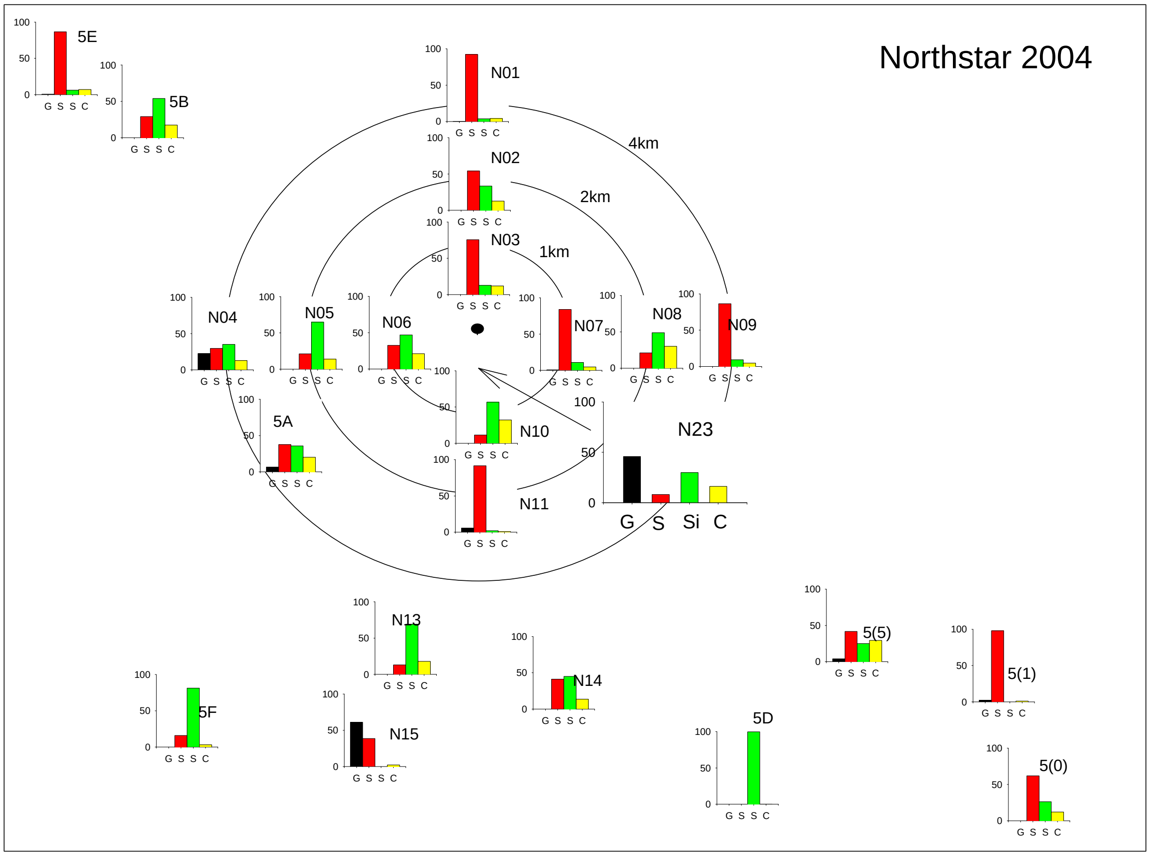


Figure 3-2. Histograms showing grain size distribution as percent gravel (black bar), sand (red bar), silt (green bar) and clay (yellow bar) for sediment samples collected during 2005 in the Northstar area.

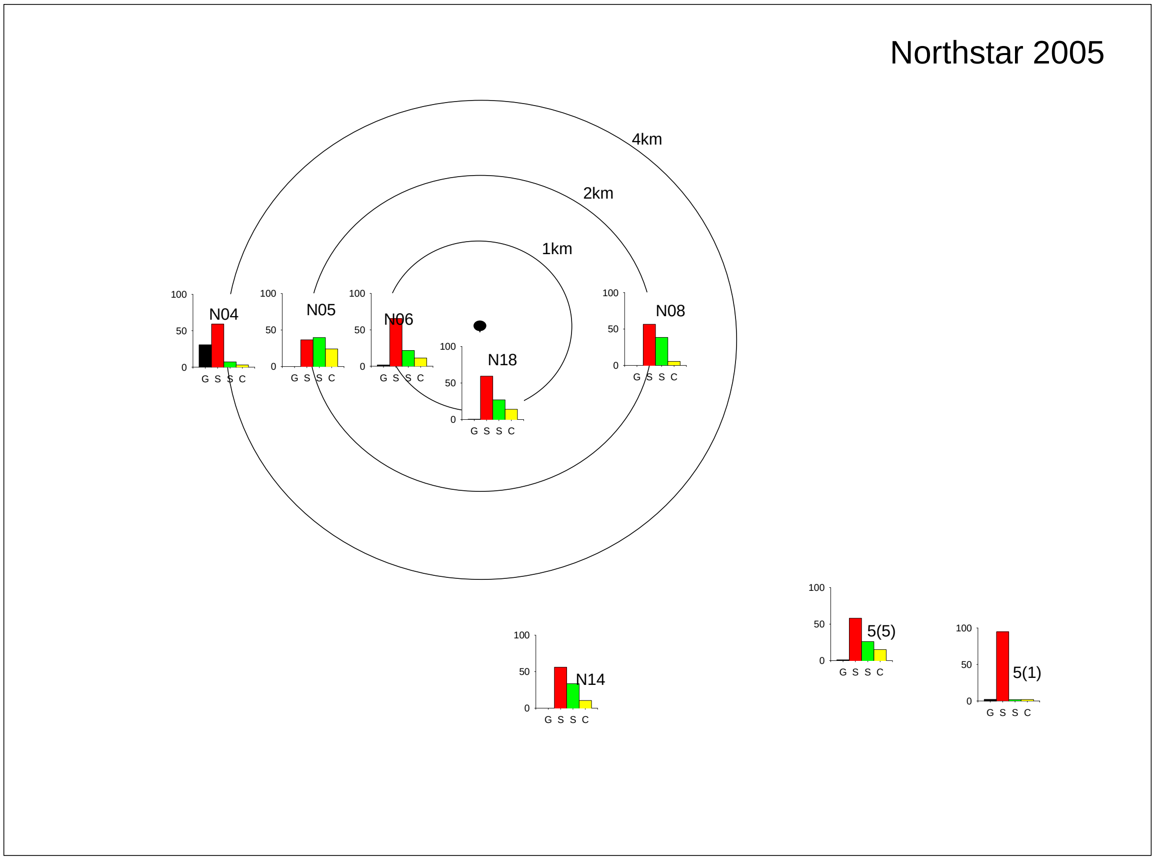


Figure 3-3. Histograms showing grain size distribution as percent gravel (black bar), sand (red bar), silt (green bar) and clay (yellow bar) for sediment samples collected during 2006 in the Northstar area.

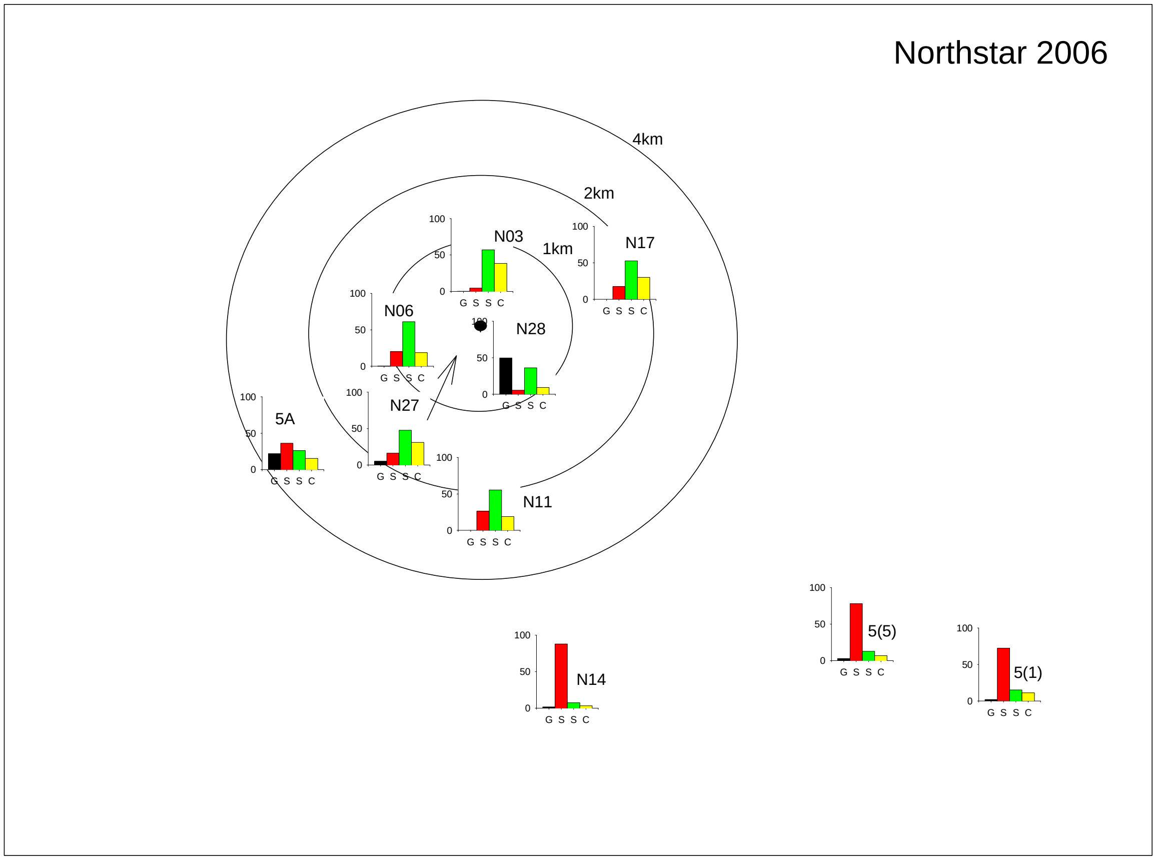


Figure 3-4. Histograms showing grain size distribution as percent gravel (black bar), sand (red bar), silt (green bar) and clay (yellow bar) for sediment samples collected during 2004 in the Liberty area.

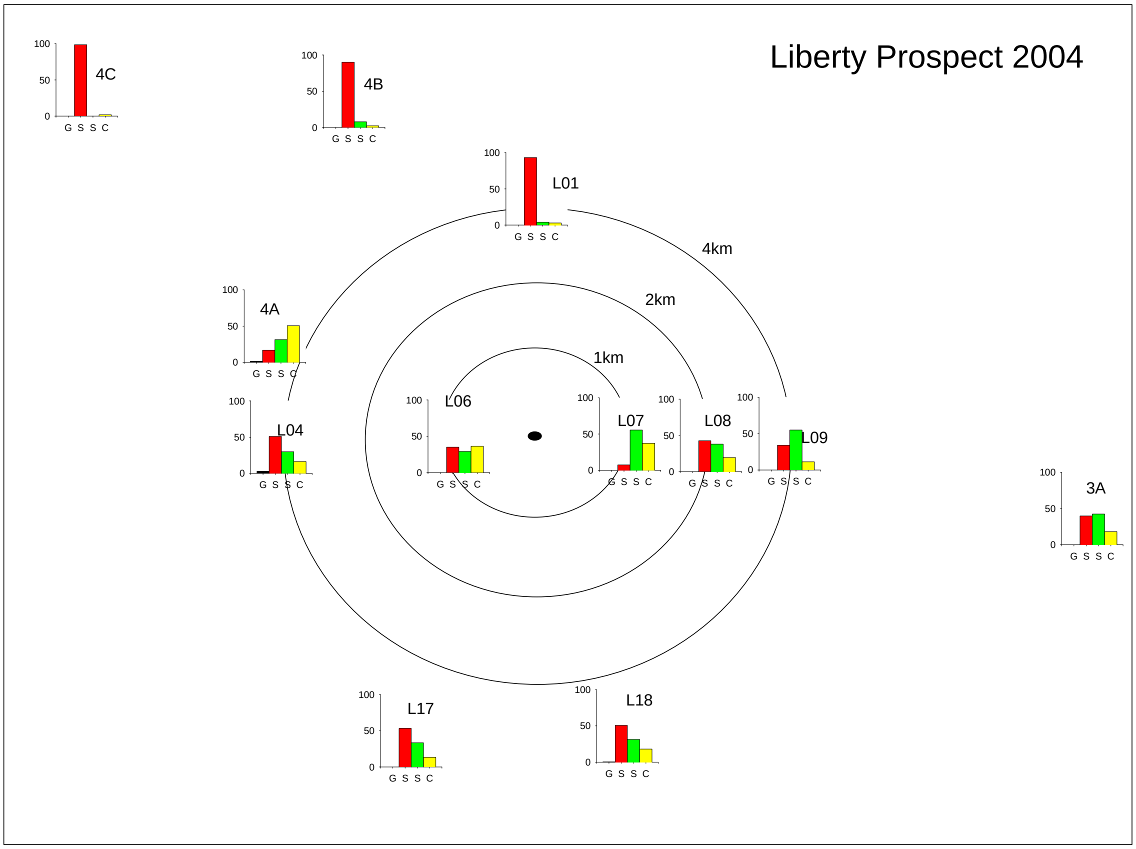


Figure 3-5. Histograms showing grain size distribution as percent gravel (black bar), sand (red bar), silt (green bar) and clay (yellow bar) for sediment samples collected during 2005 in the Liberty area.

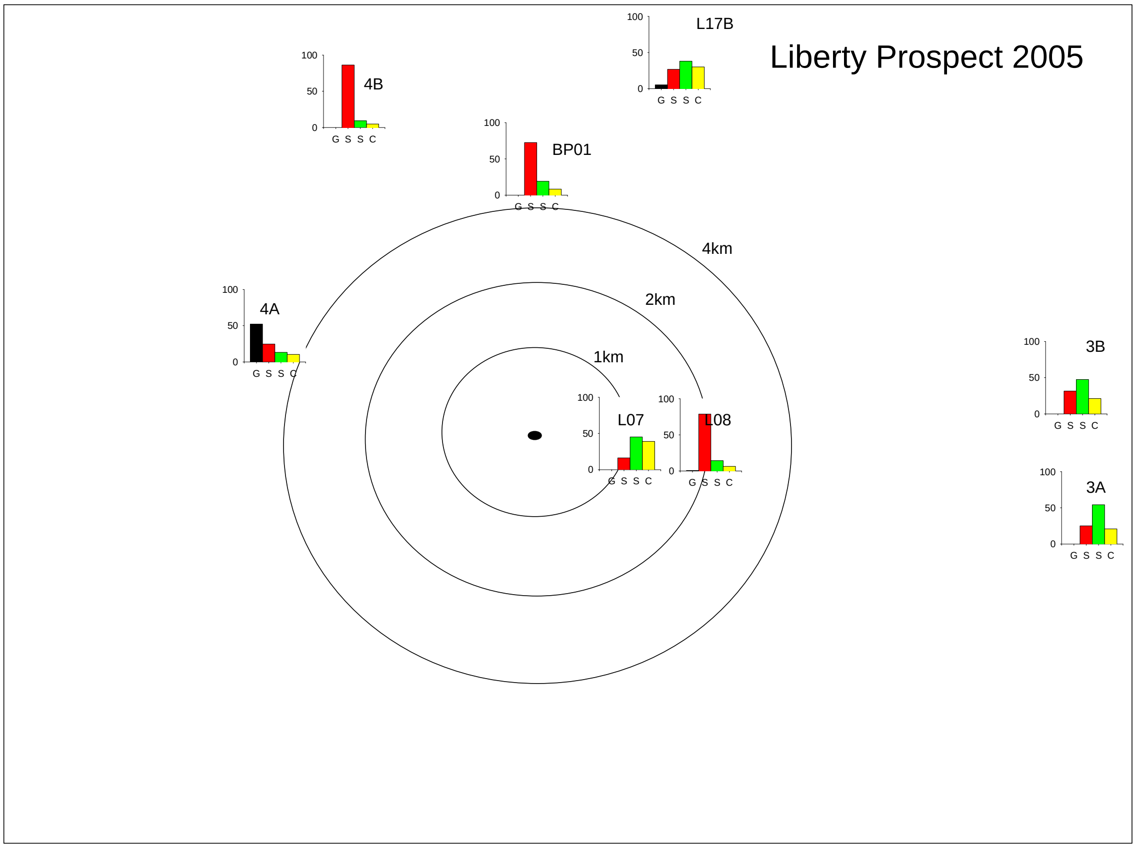


Figure 3-6. Histograms showing grain size distribution as percent gravel (black bar), sand (red bar), silt (green bar) and clay (yellow bar) for sediment samples collected during 2006 in the Liberty area.

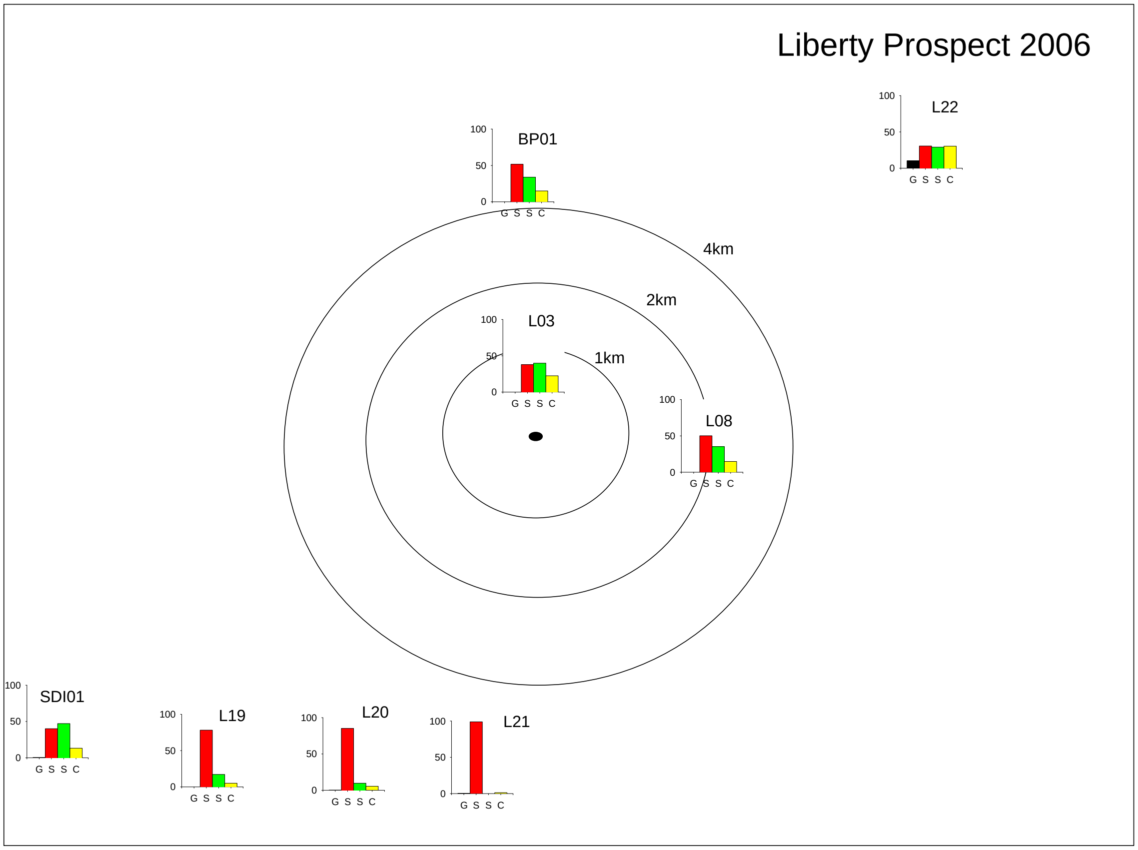


Figure 3-7. Concentrations of Al versus Silt + Clay for surface sediments from all stations sampled during (a) 1999-2002 and (b) 2004-2006.

The line and correlation coefficient (r) are from linear regression calculations. Data from 2004-2006 are plotted with prediction interval from the 1999-2002 data.

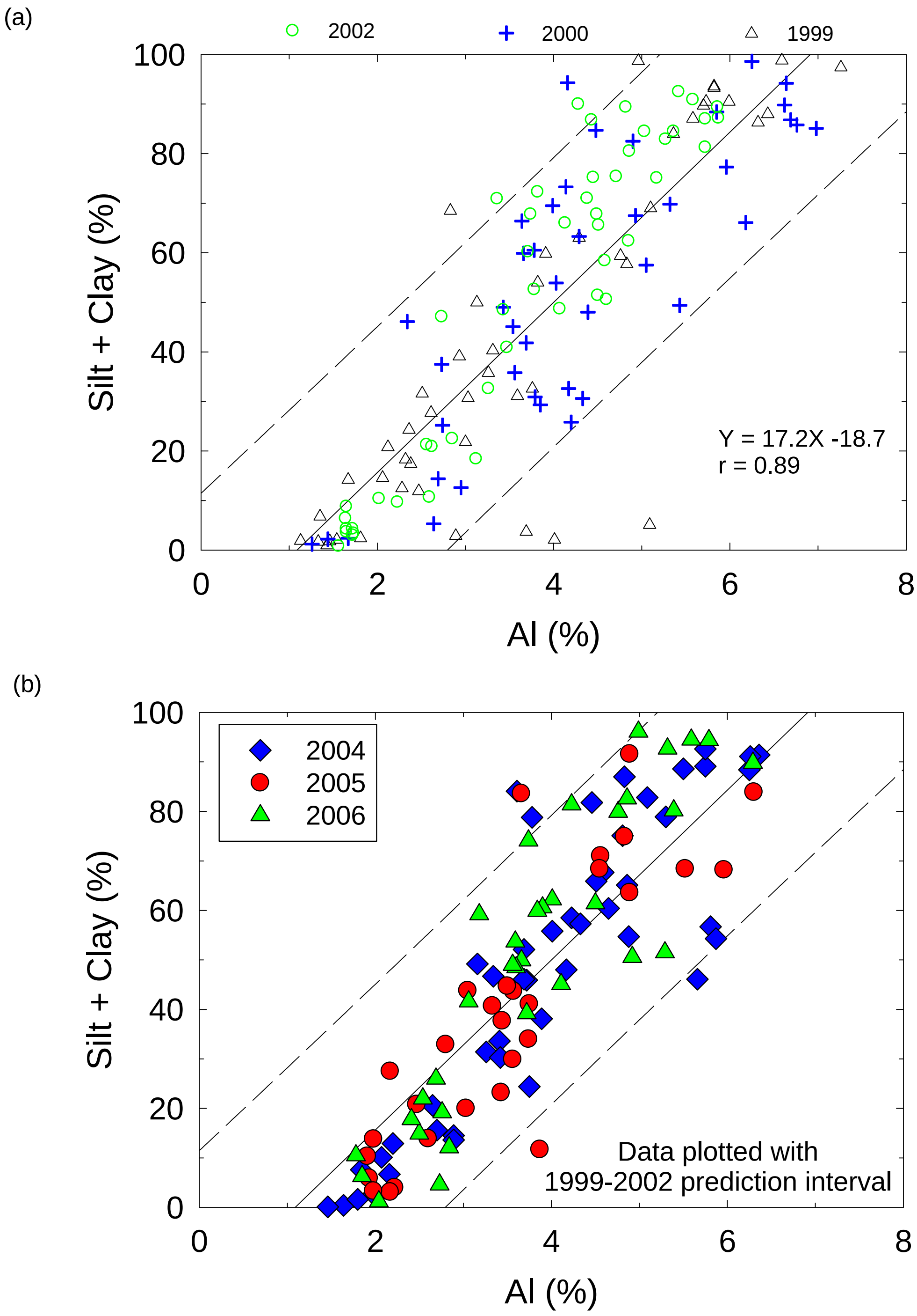


Figure 3-8. Concentrations of Al versus (a) Fe and (b) V for surface sediments from 2004-2006.

The lines, equations, correlation coefficients (r) and 99% prediction intervals are from linear regression and related statistical calculations. Data from 2004-2006 are plotted with prediction interval from the 1999-2002 data.

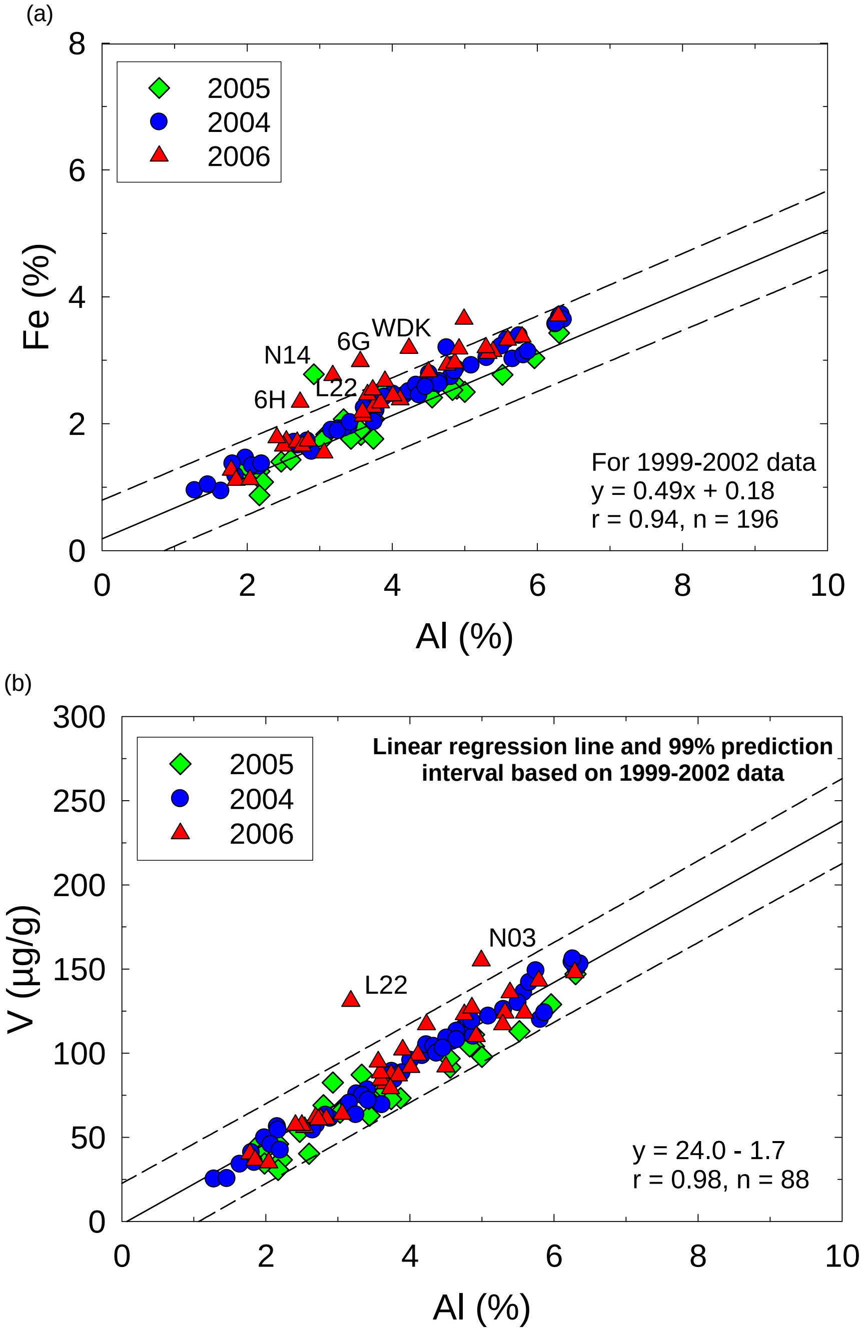


Figure 3-9. Concentrations of Al versus (a) activity of ^{226}Ra and (b) activity of excess ^{210}Pb for surface sediments from 2004-2006.

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

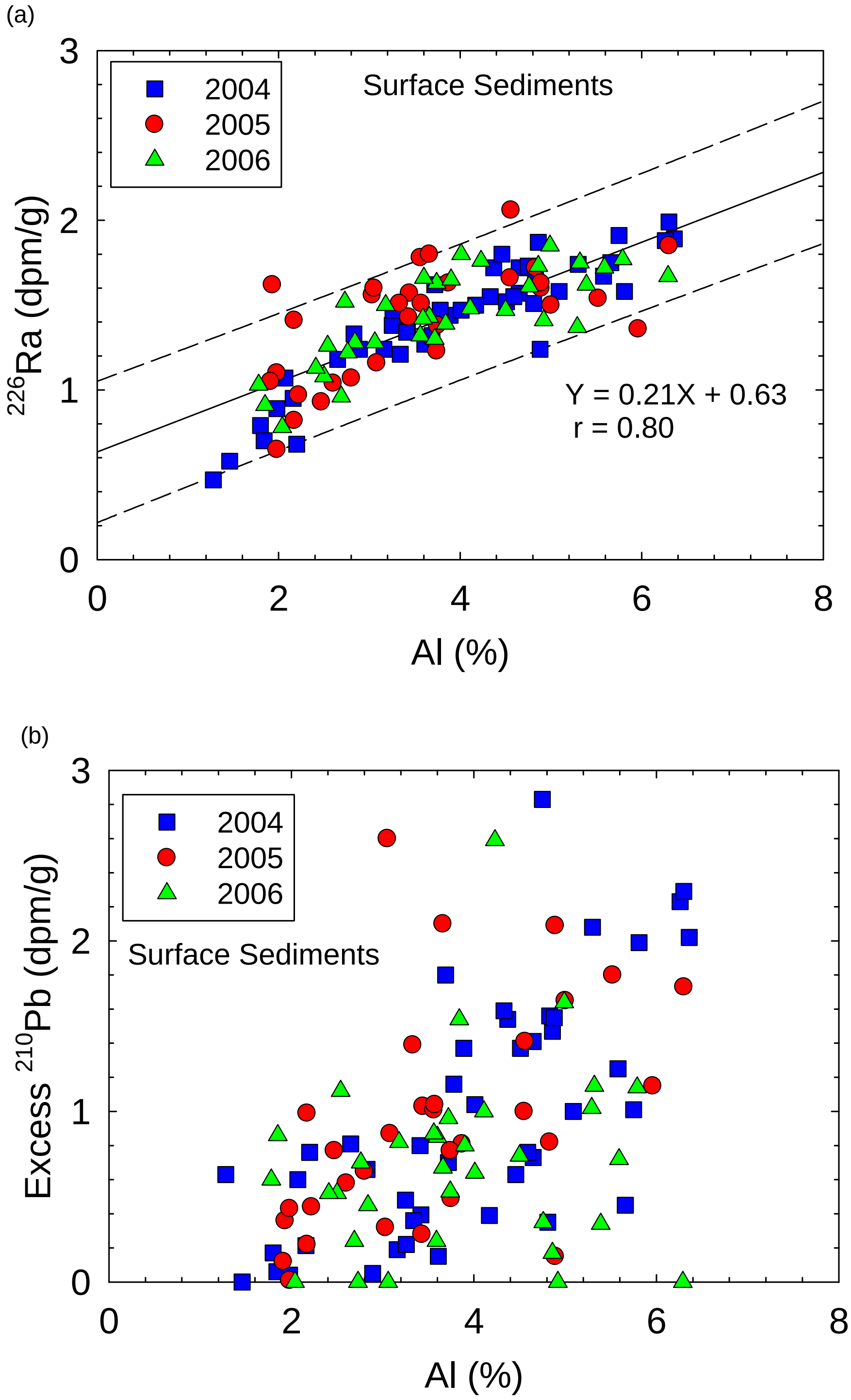
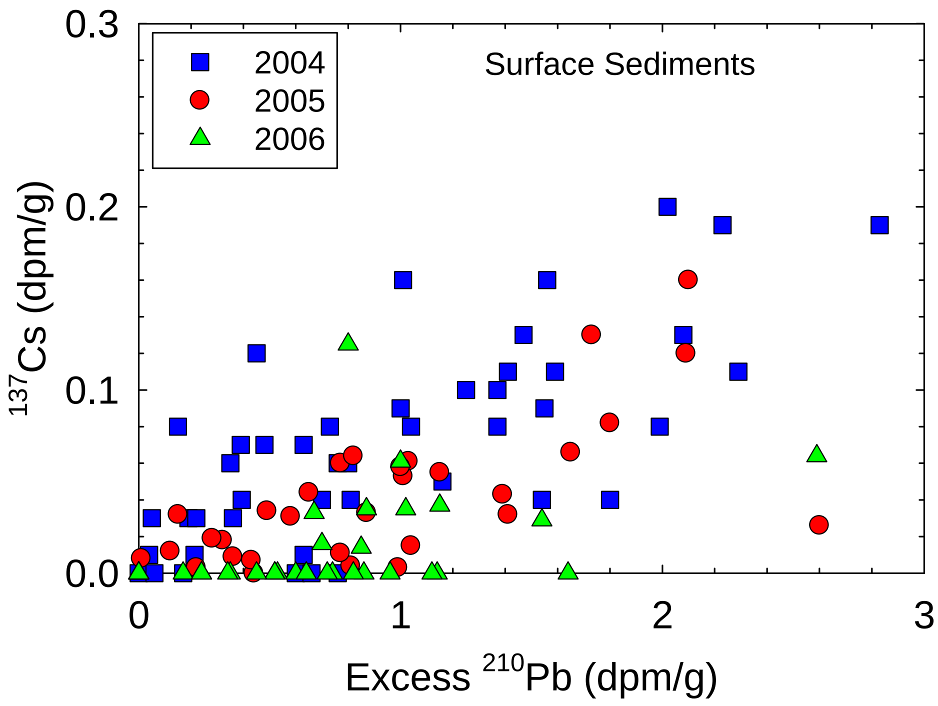


Figure 3-10. Activities of ^{137}Cs versus activities of excess ^{210}Pb for surface sediments from 2004-2006.



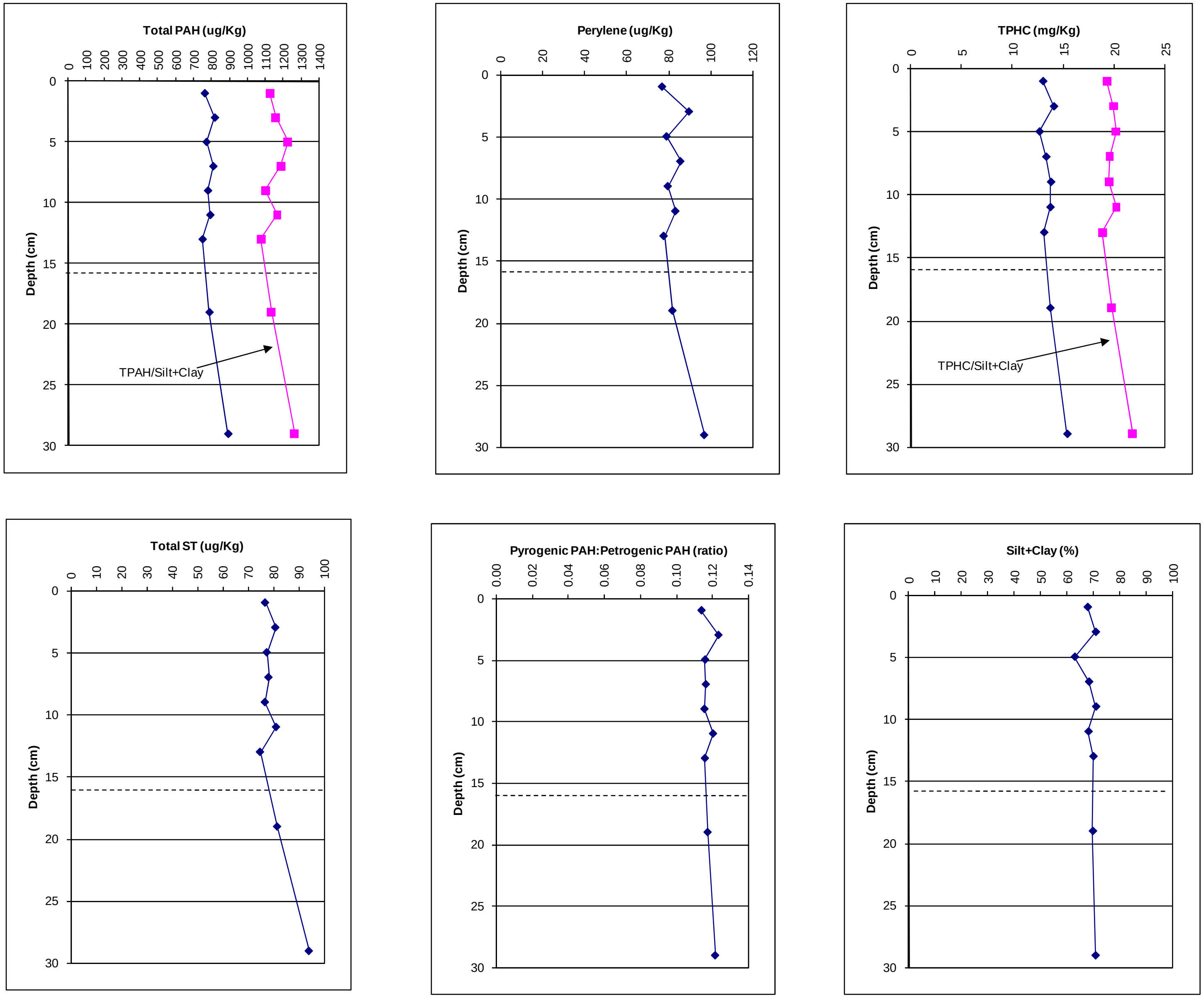


Figure 3-11. Sediment core profiles for Station 1C – 2005 (dashed line shows depth in sediment that corresponds to Year 1950).

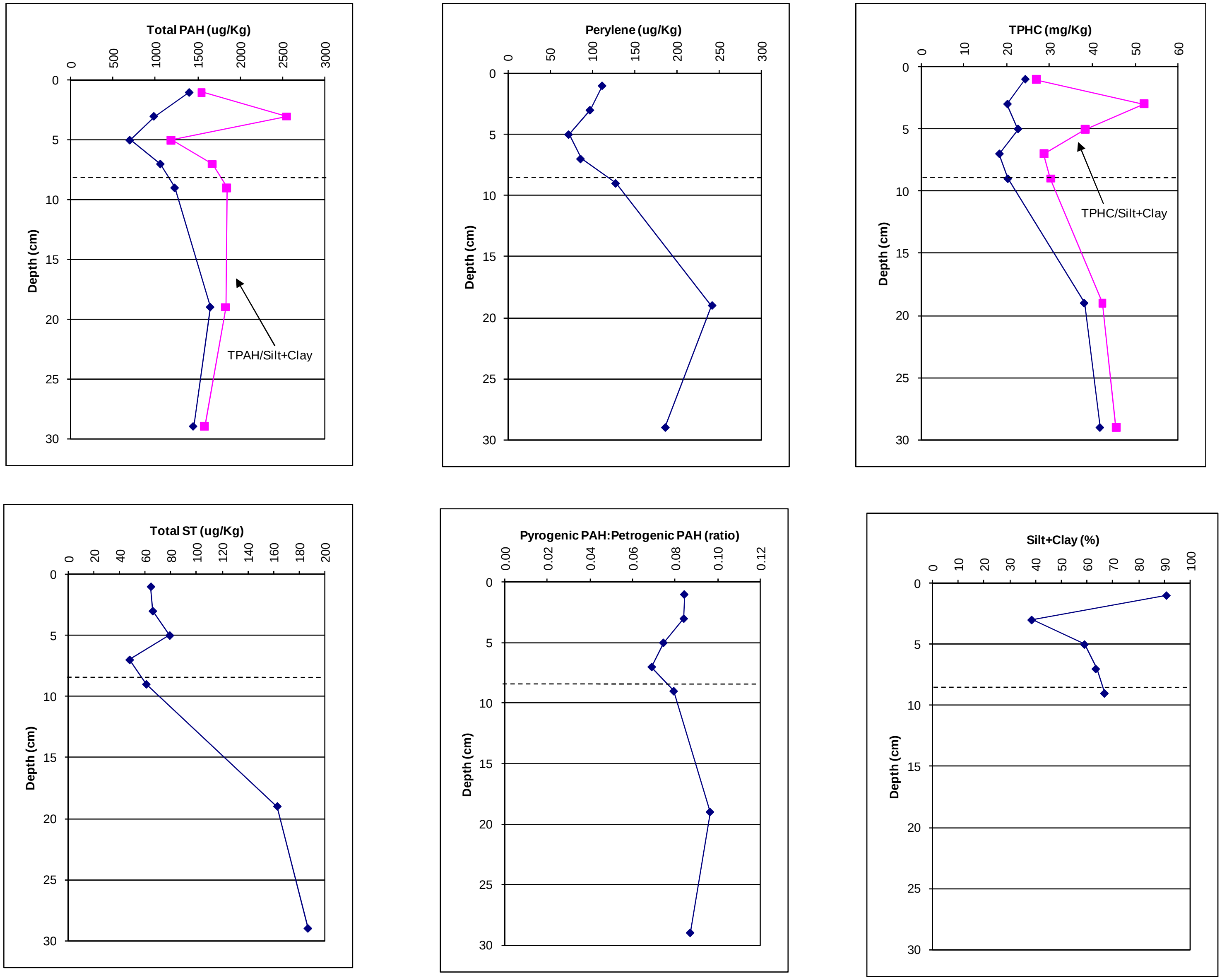


Figure 3-12. Sediment core profiles for Station 2A – 2005 (dashed line shows depth in sediment that corresponds to Year 1950).

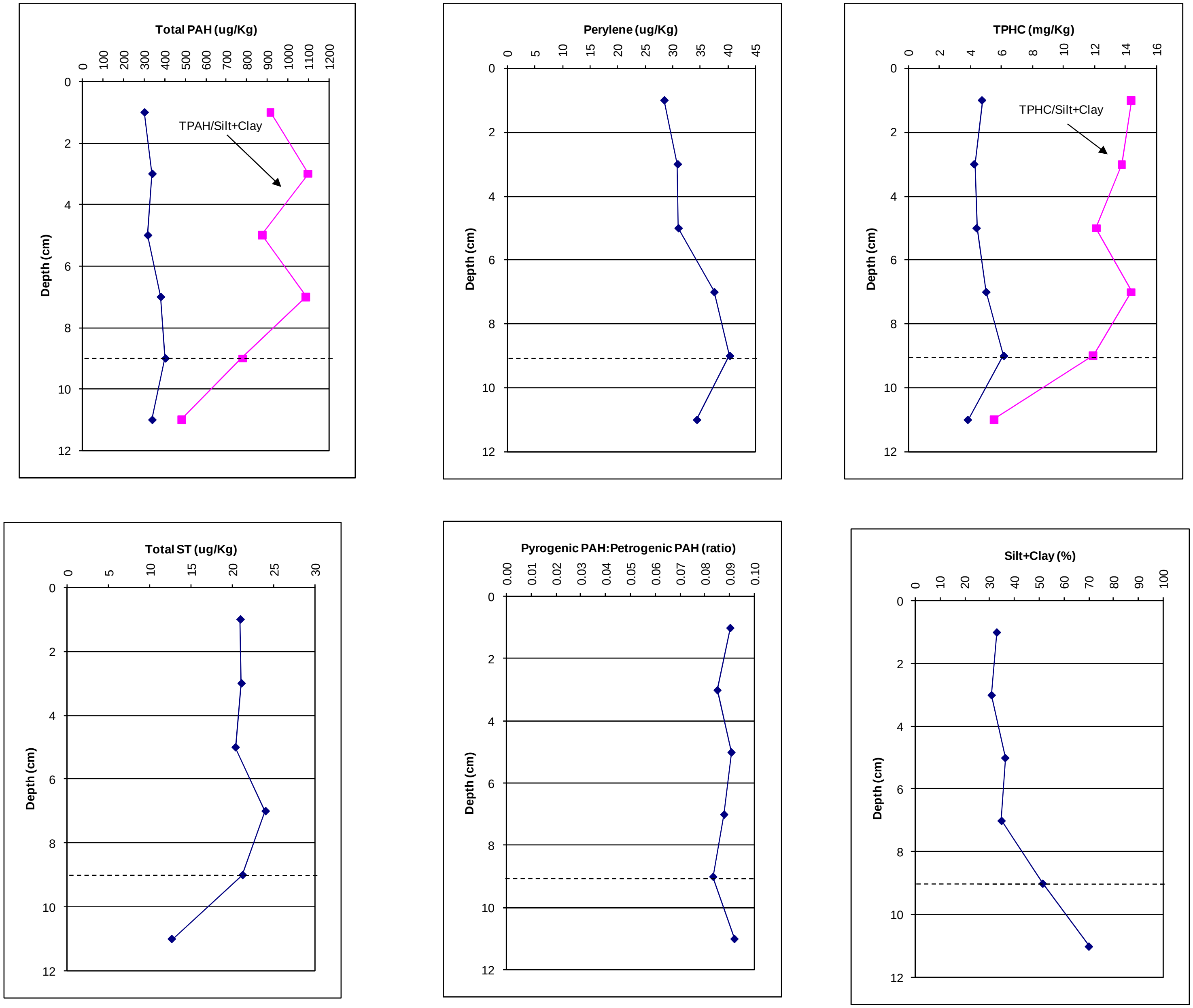


Figure 3-13. Sediment core profiles for Station BP01 – 2005 (dashed line shows depth in sediment that corresponds to Year 1950).

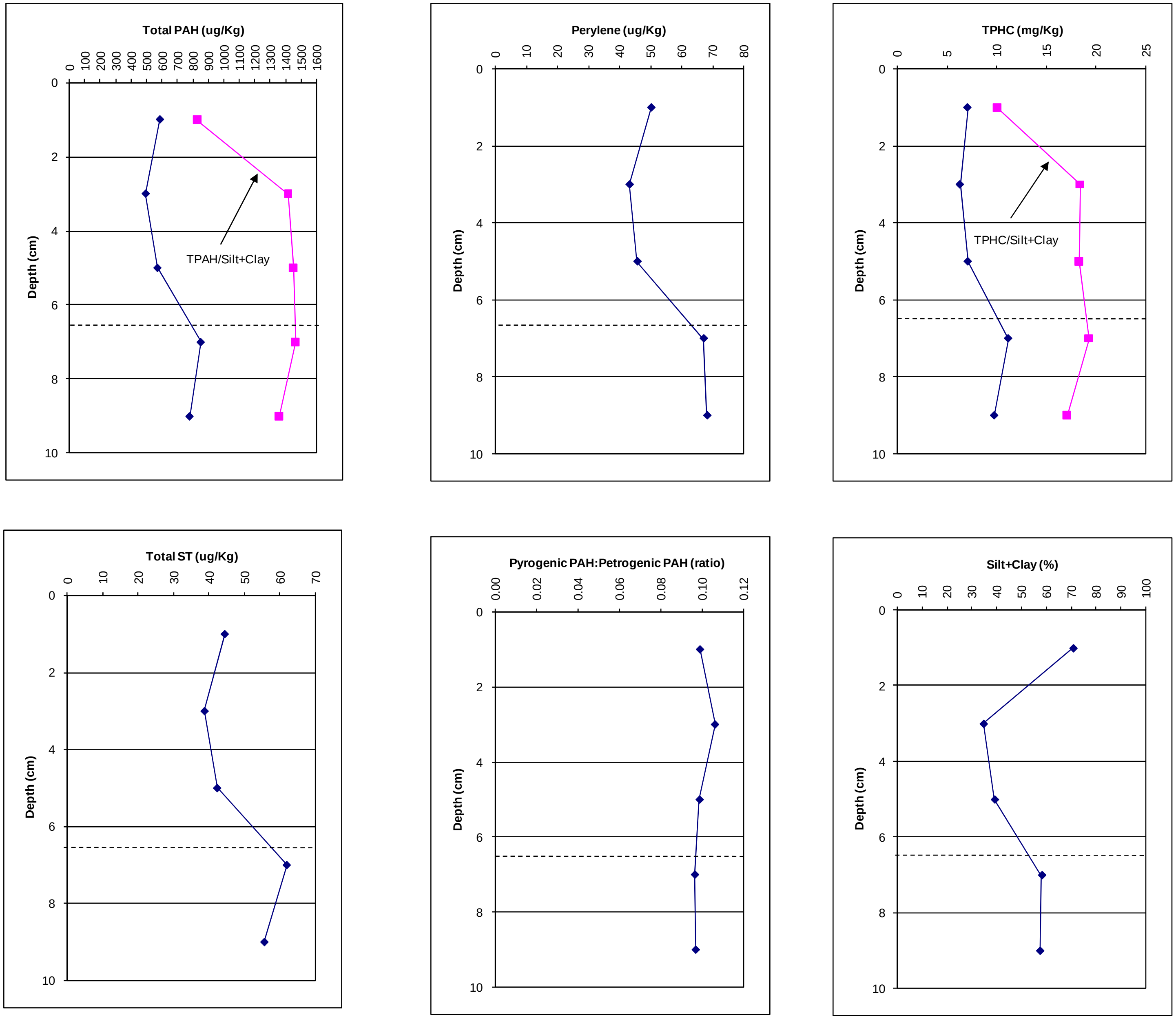


Figure 3-14. Sediment core profiles for Station N26 – 2005 (dashed line shows depth in sediment that corresponds to Year 1950).

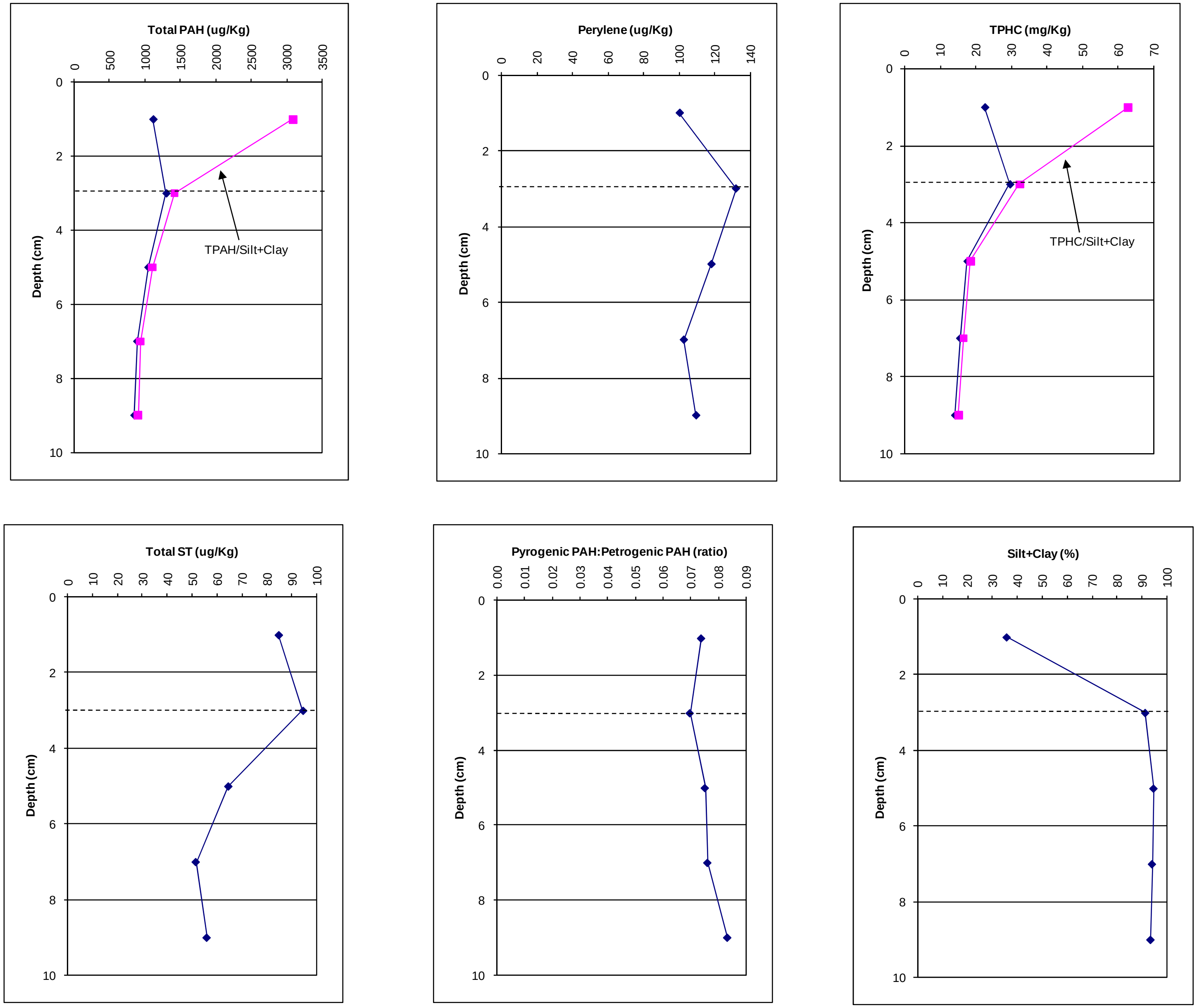


Figure 3-15. Sediment core profiles for Station PB01 – 2005 (dashed line shows depth in sediment that corresponds to Year 1950).

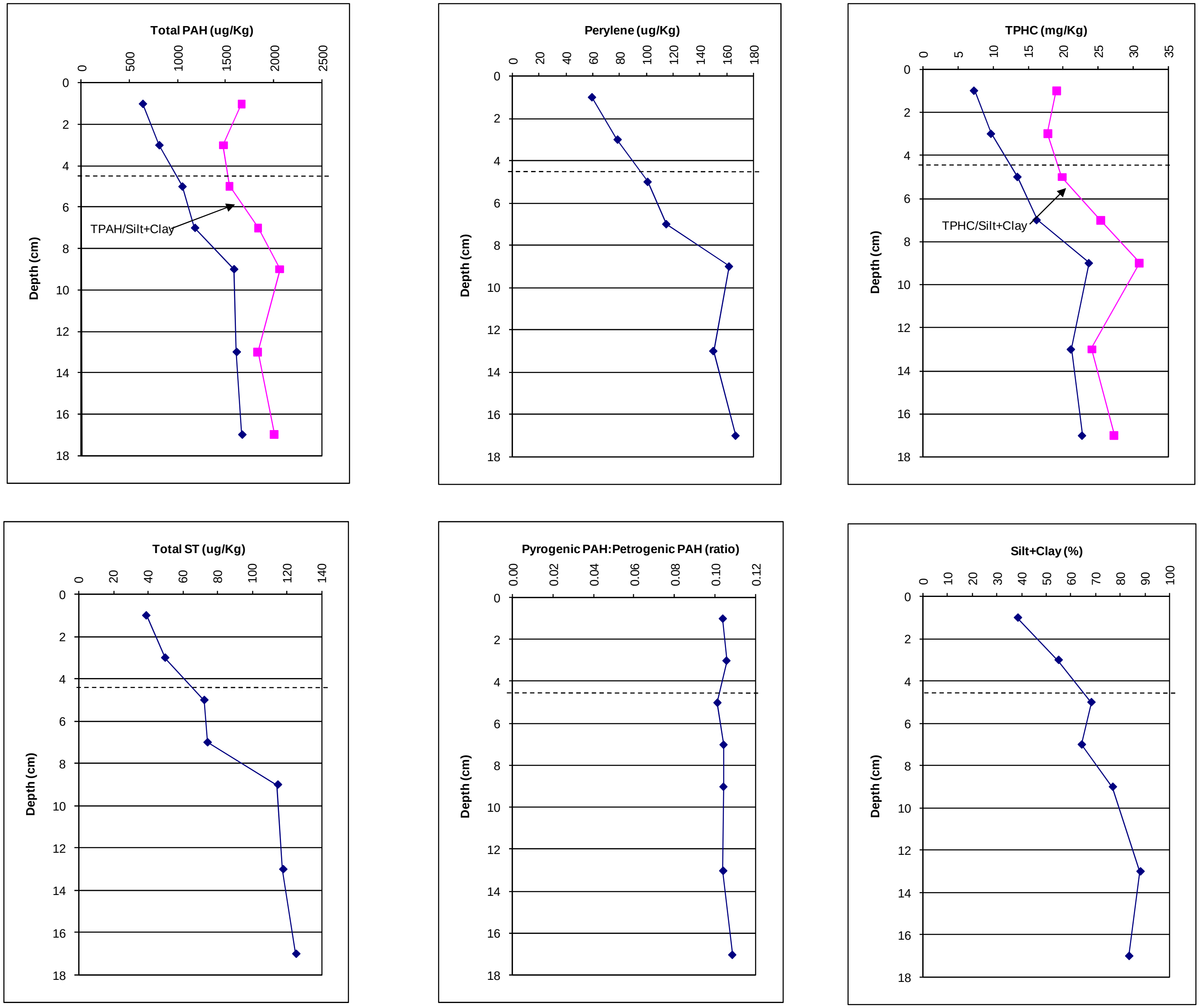


Figure 3-16. Sediment core profiles for Station 7A – 2006 (dashed line shows depth in sediment that corresponds to Year 1950).

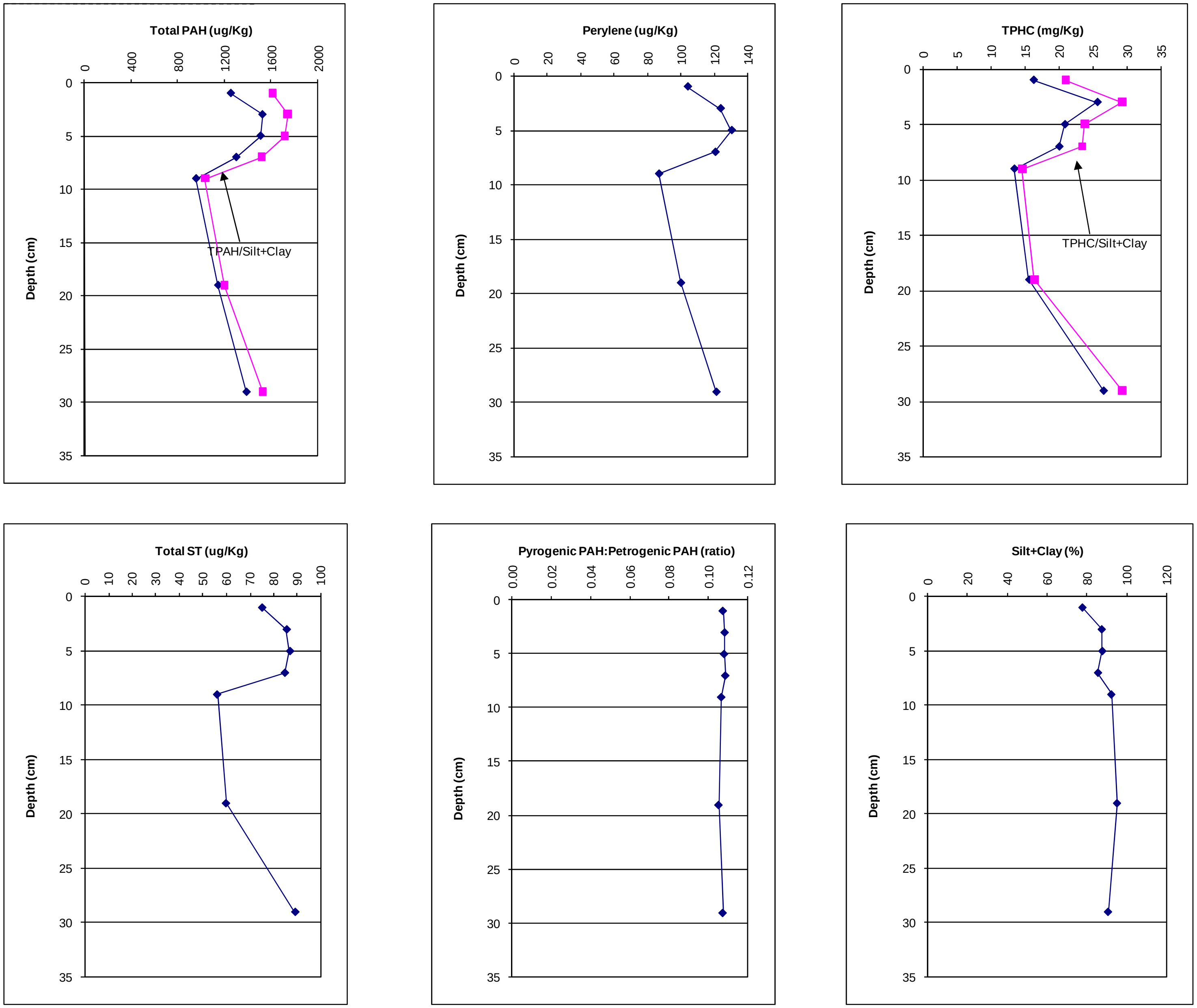


Figure 3-17. Sediment core profiles for Station 7C – 2006 (accurate geochronology could not be determined).

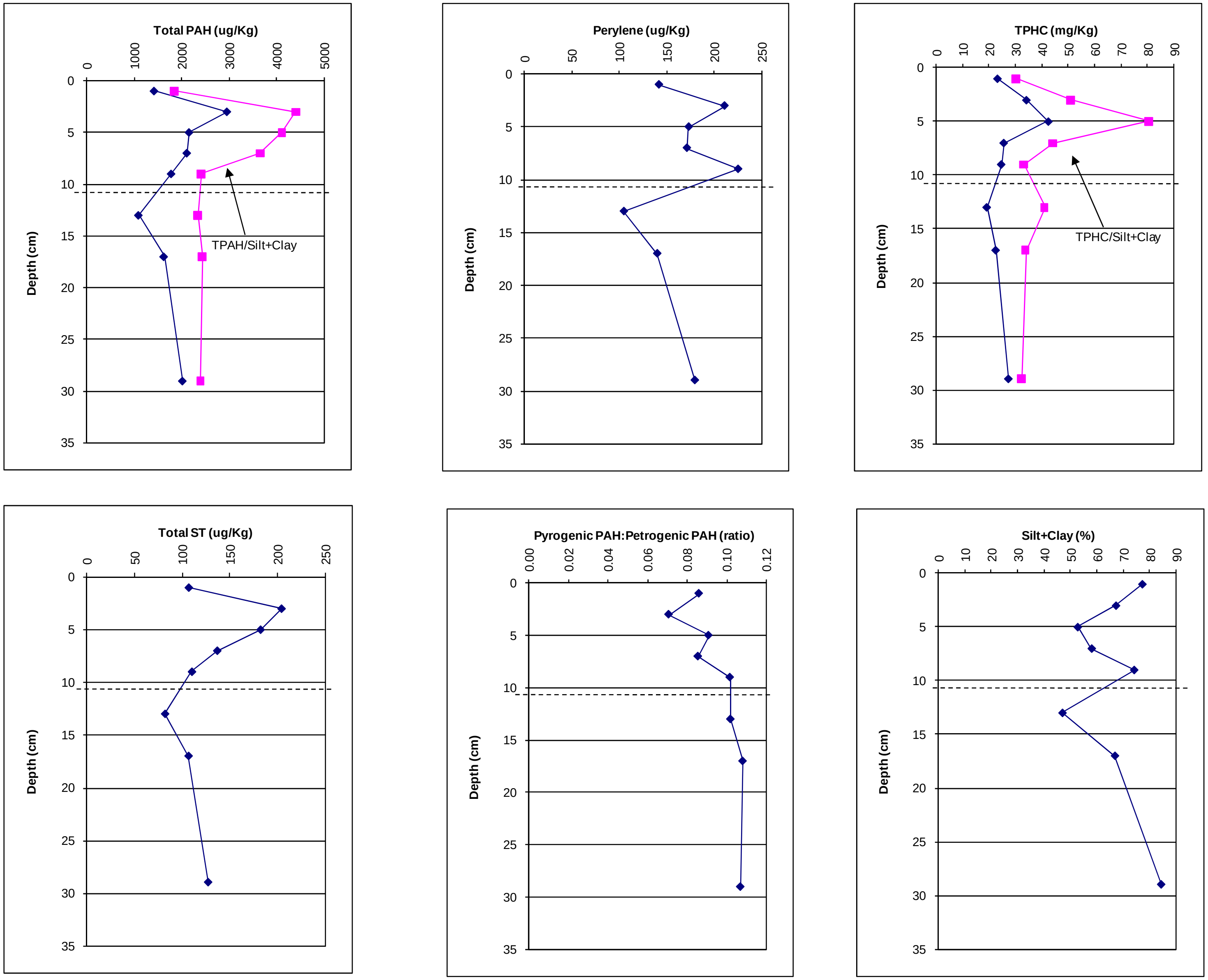


Figure 3-18. Sediment core profiles for Station 7E – 2006 (dashed line shows depth in sediment that corresponds to Year 1950).

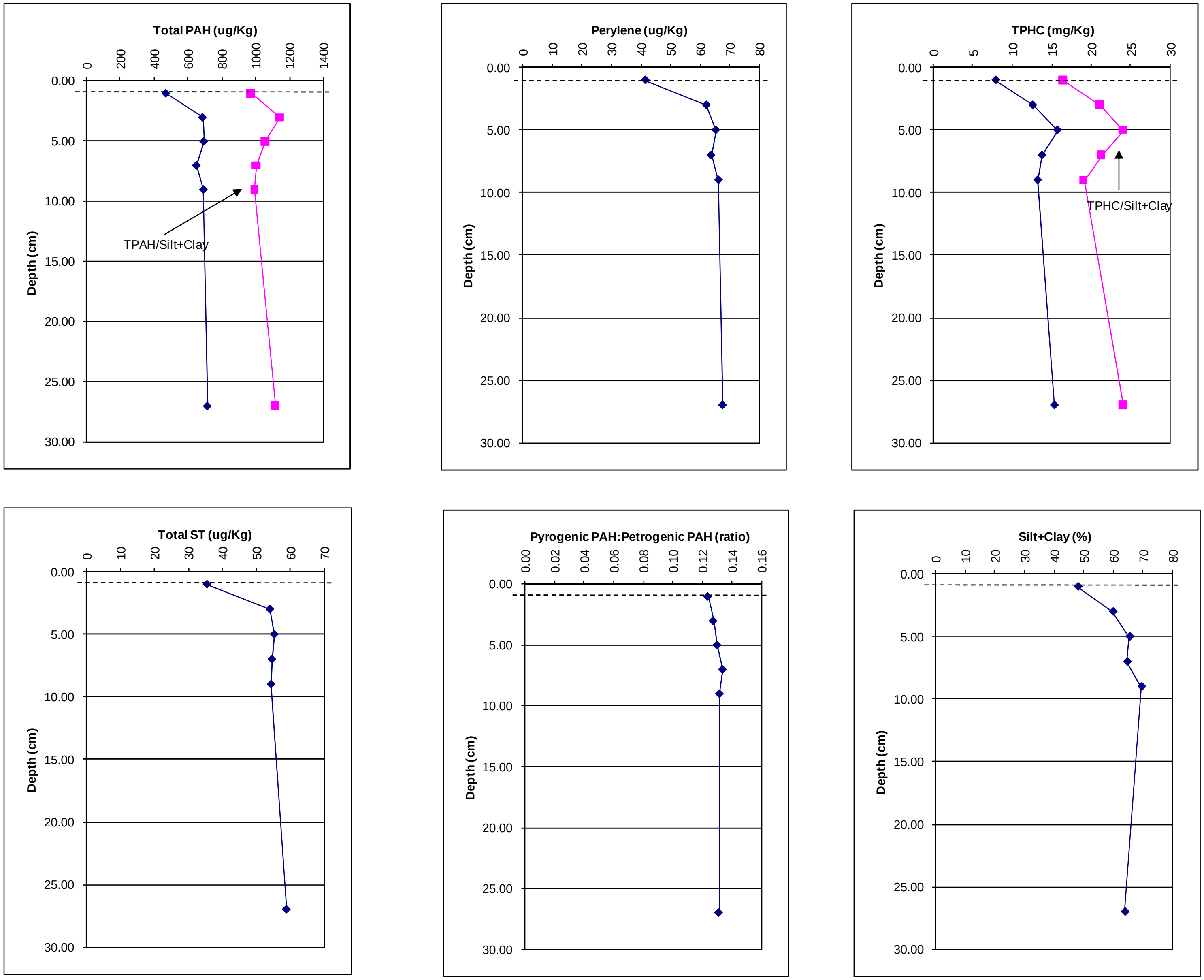


Figure 3-19. Sediment core profiles for Station L22 – 2006 (dashed line shows depth in sediment that corresponds to Year 1950).

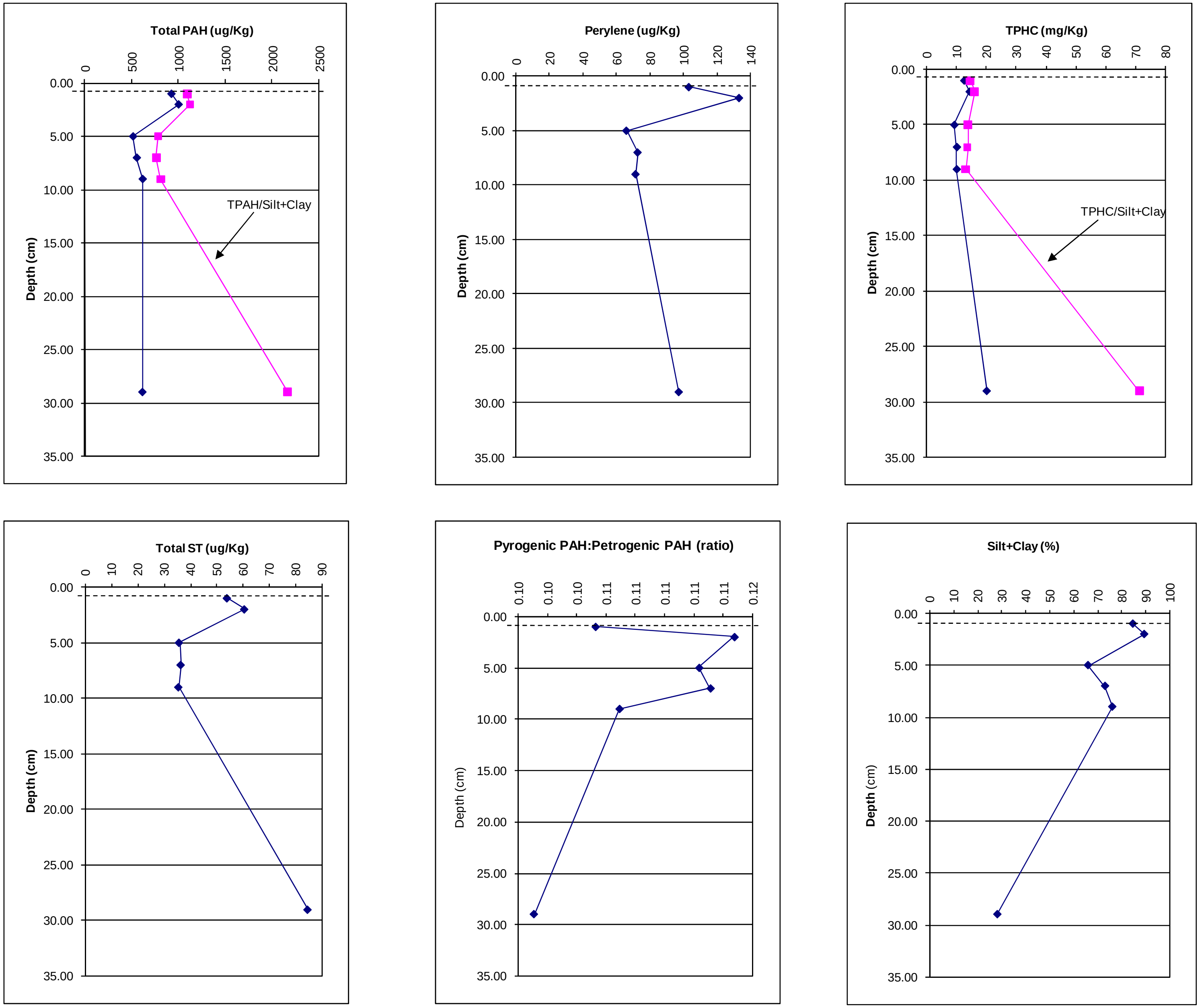


Figure 3-20. Sediment core profiles for Station N17 – 2006 (dashed line shows depth in sediment that corresponds to Year 1950).

Figure 3-21. Vertical profiles for metals and metal/Al ratios for in sediments from station L17B sampled during 2005. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

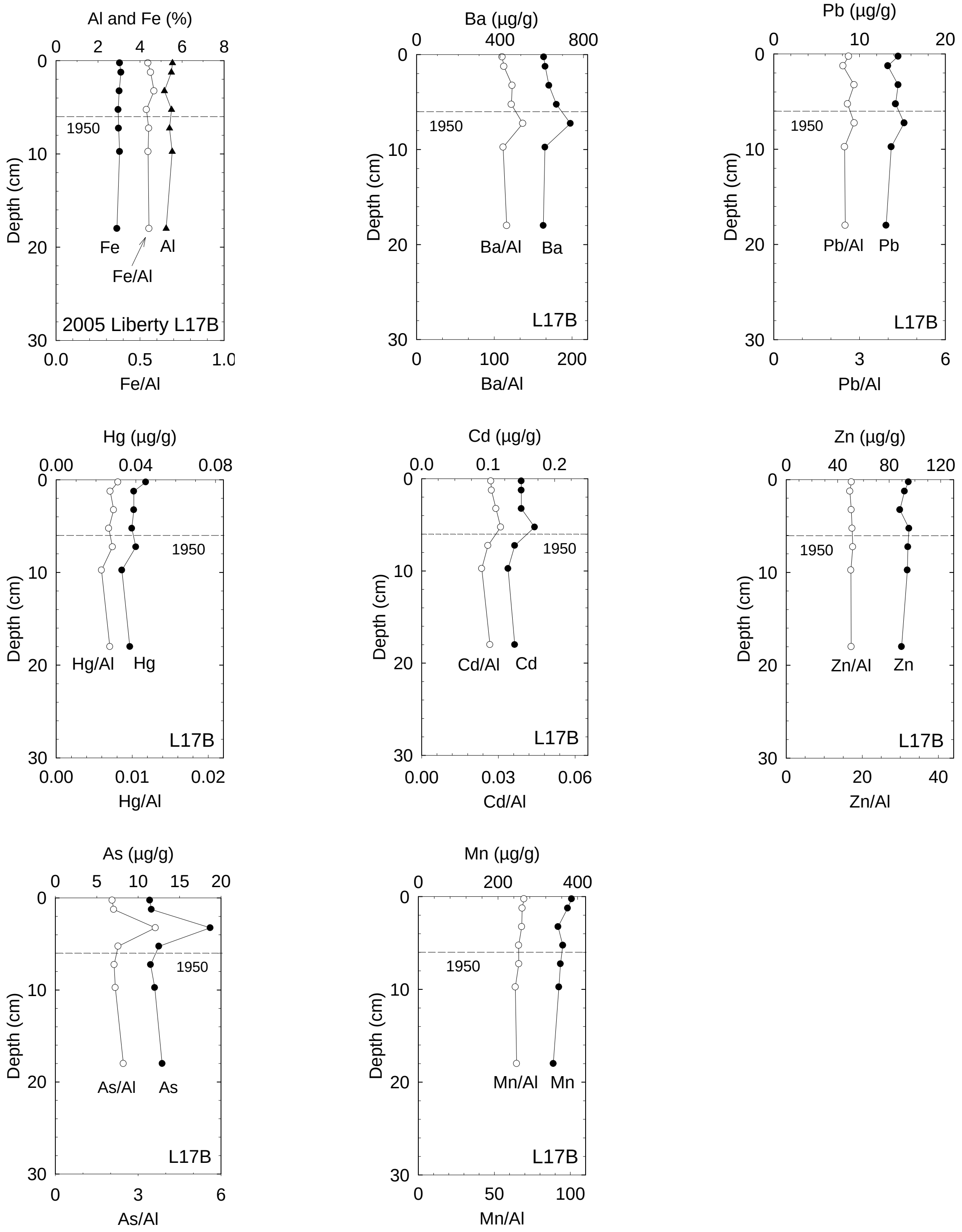


Figure 3-21 (cont.). Vertical profiles for metals and metal/Al ratios for in sediments from station L17B sampled during 2005. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

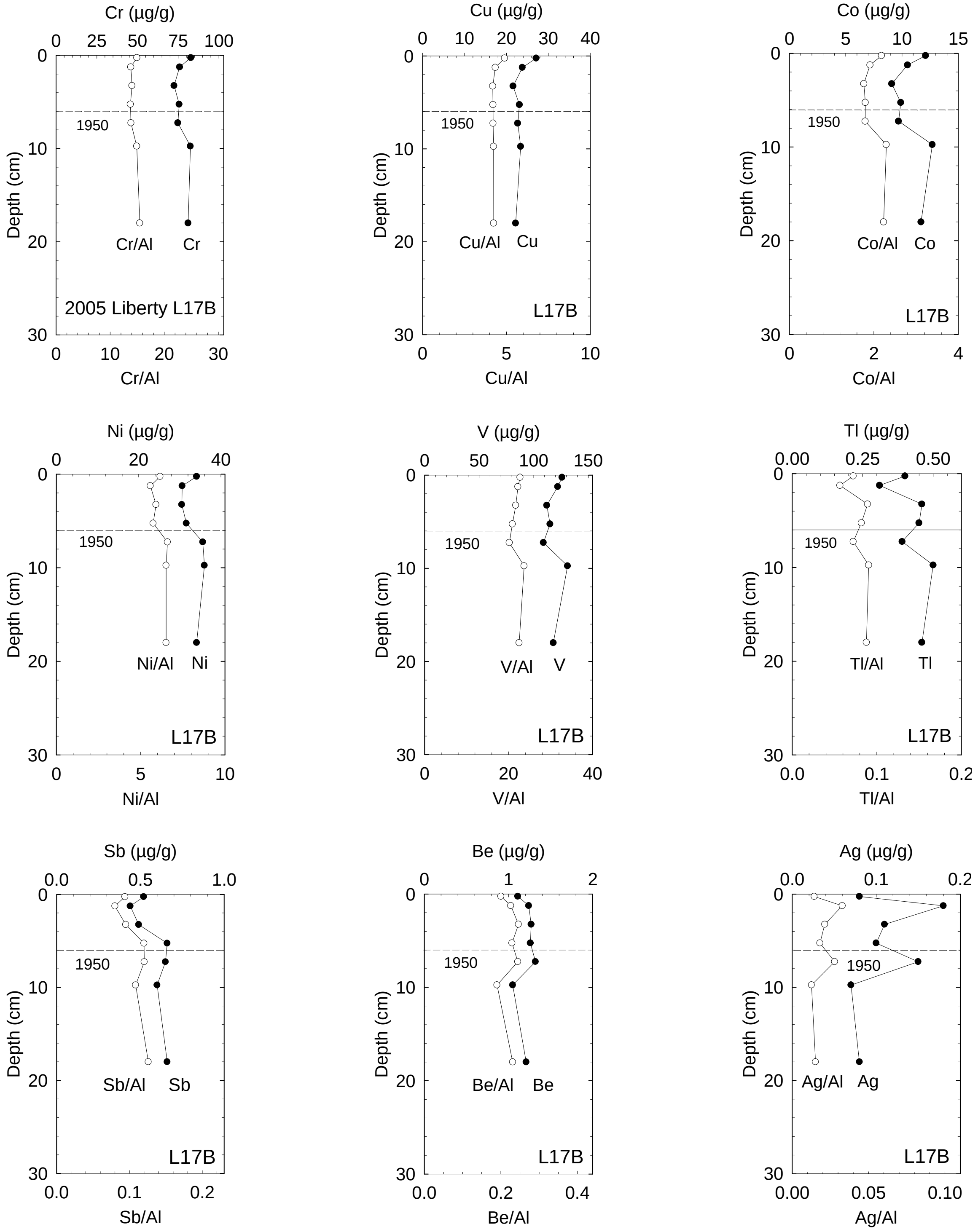


Figure 3-22. Vertical profiles for metals and metal/Al ratios for in sediments from station 1C sampled during 2005. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

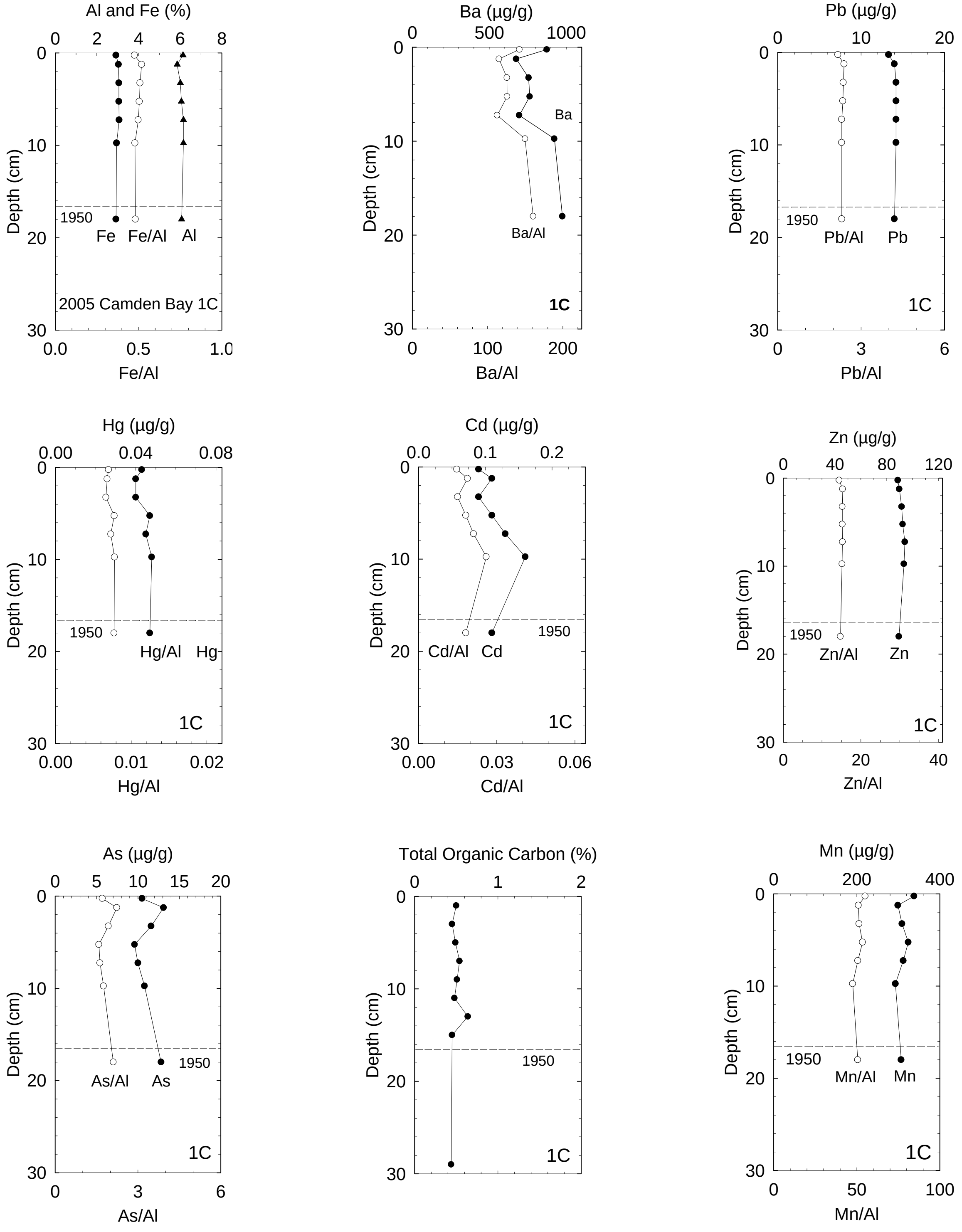


Figure 3-22 (cont.). Vertical profiles for metals and metal/Al ratios for in sediments from station 1C sampled during 2005. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

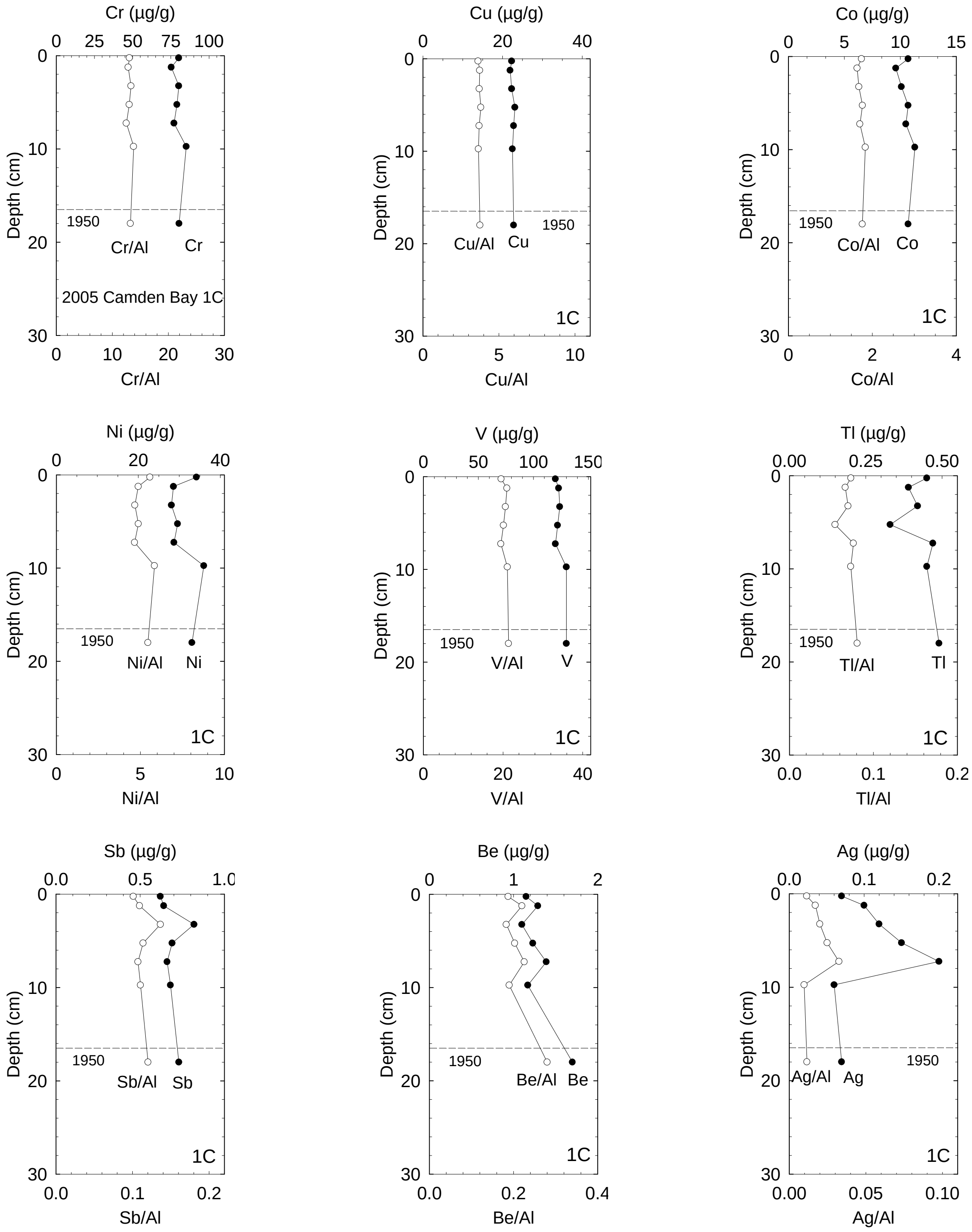


Figure 3-23. Vertical profiles for metals and metal/Al ratios for in sediments from station 2A sampled during 2005. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

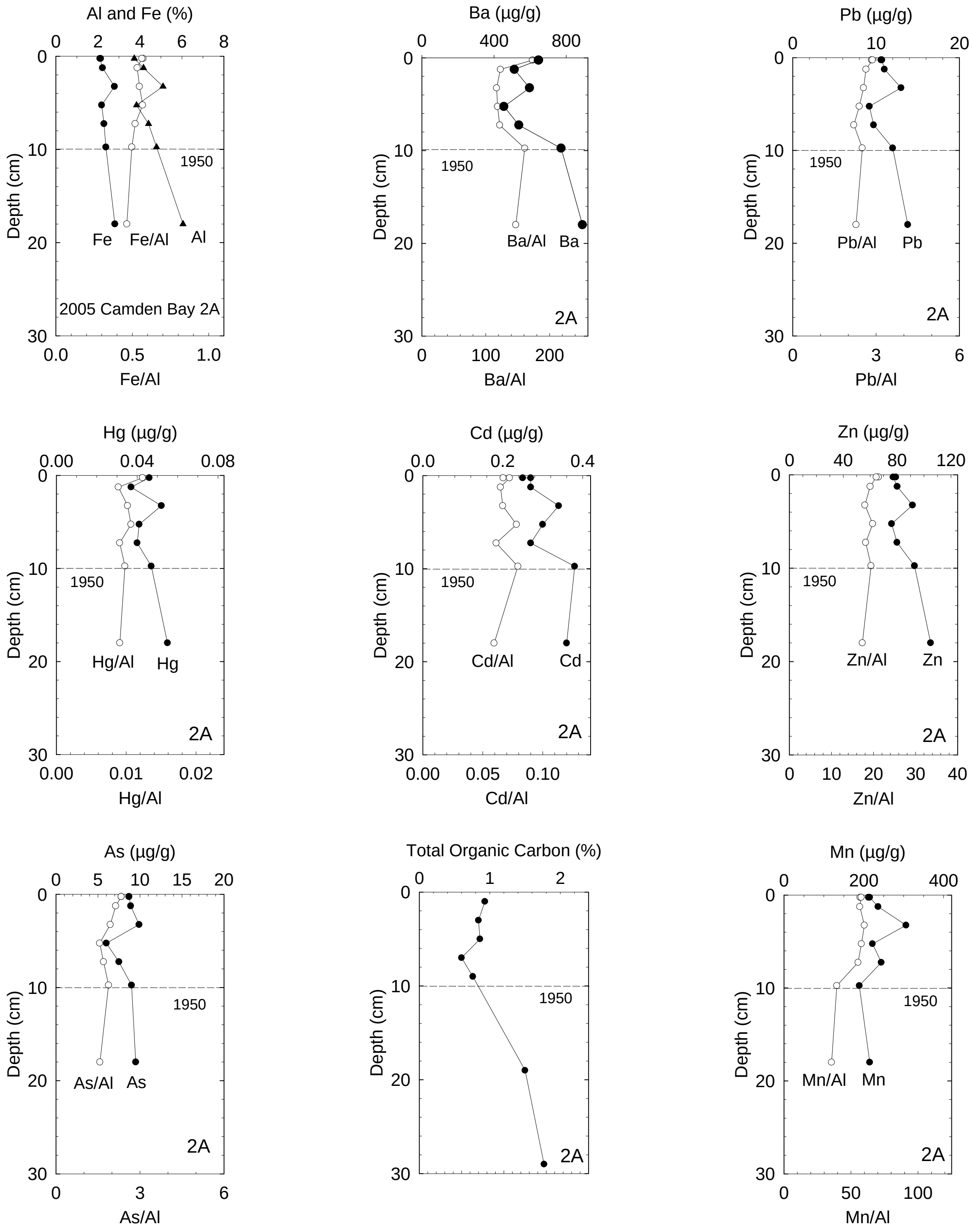


Figure 3-23 (cont.). Vertical profiles for metals and metal/Al ratios for in sediments from station 2A sampled during 2005. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

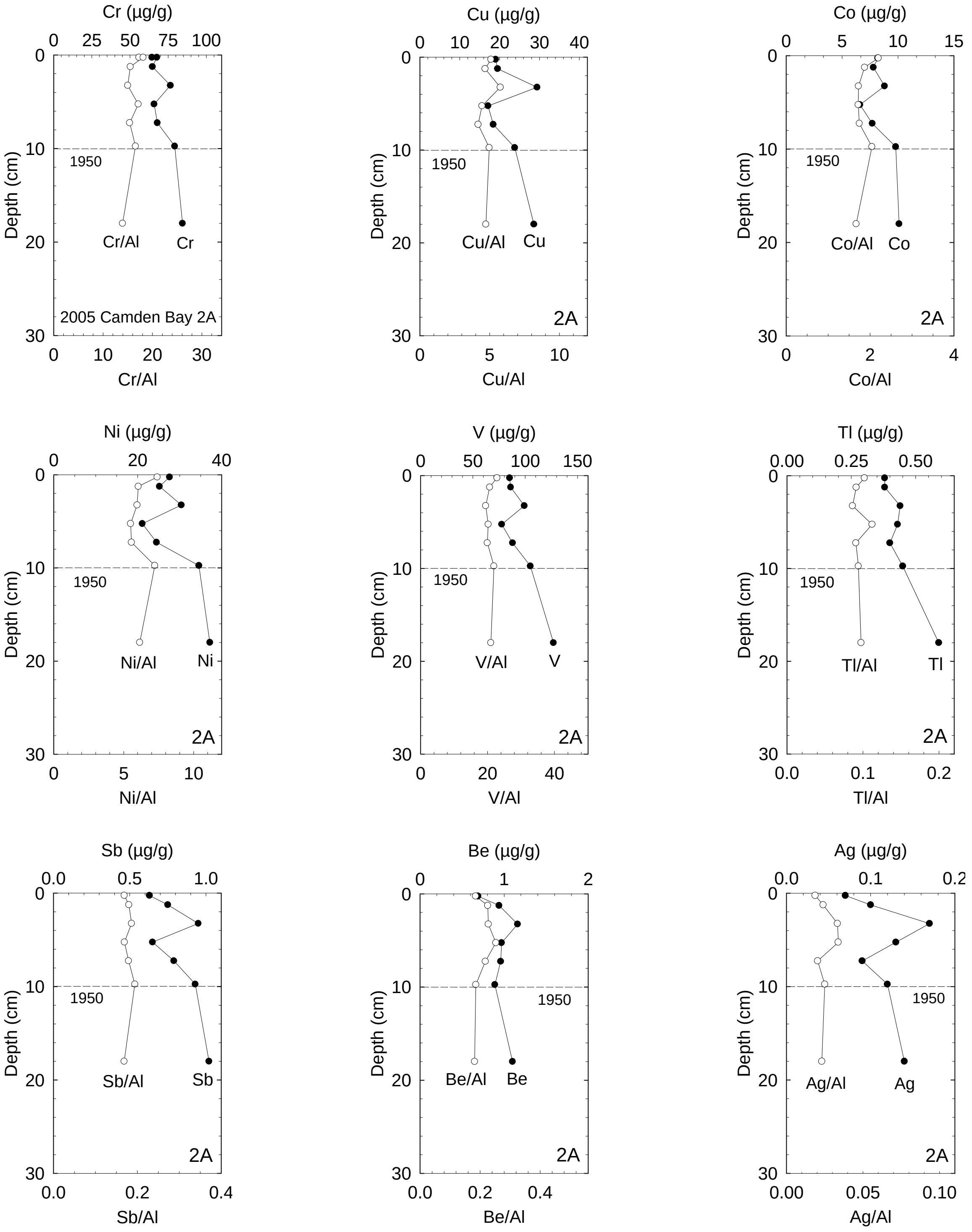


Figure 3-24. Vertical profiles for metals and metal/Al ratios for in sediments from station BP01 sampled during 2005. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

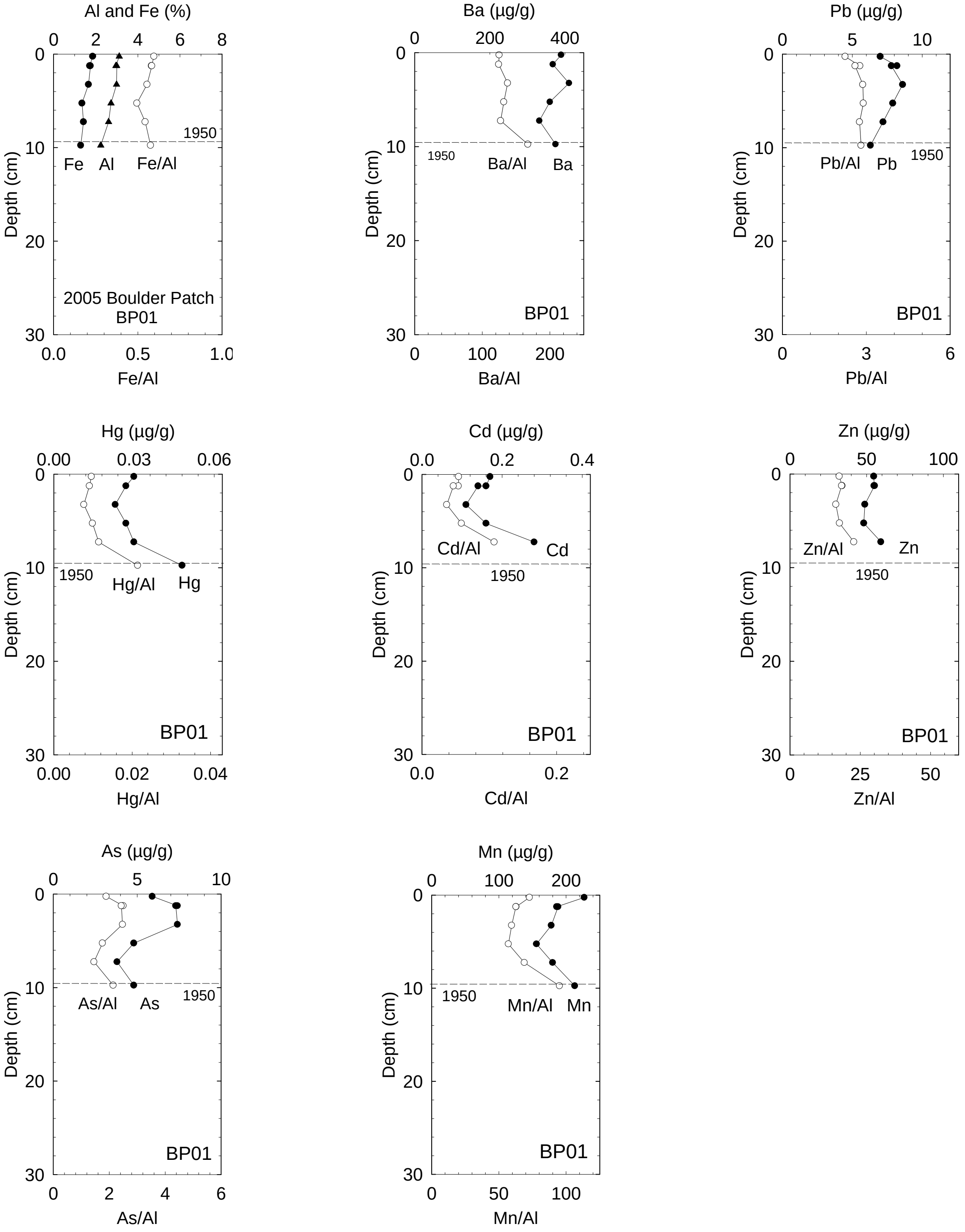


Figure 3-24 (cont.). Vertical profiles for metals and metal/Al ratios for in sediments from station BP01 sampled during 2005. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

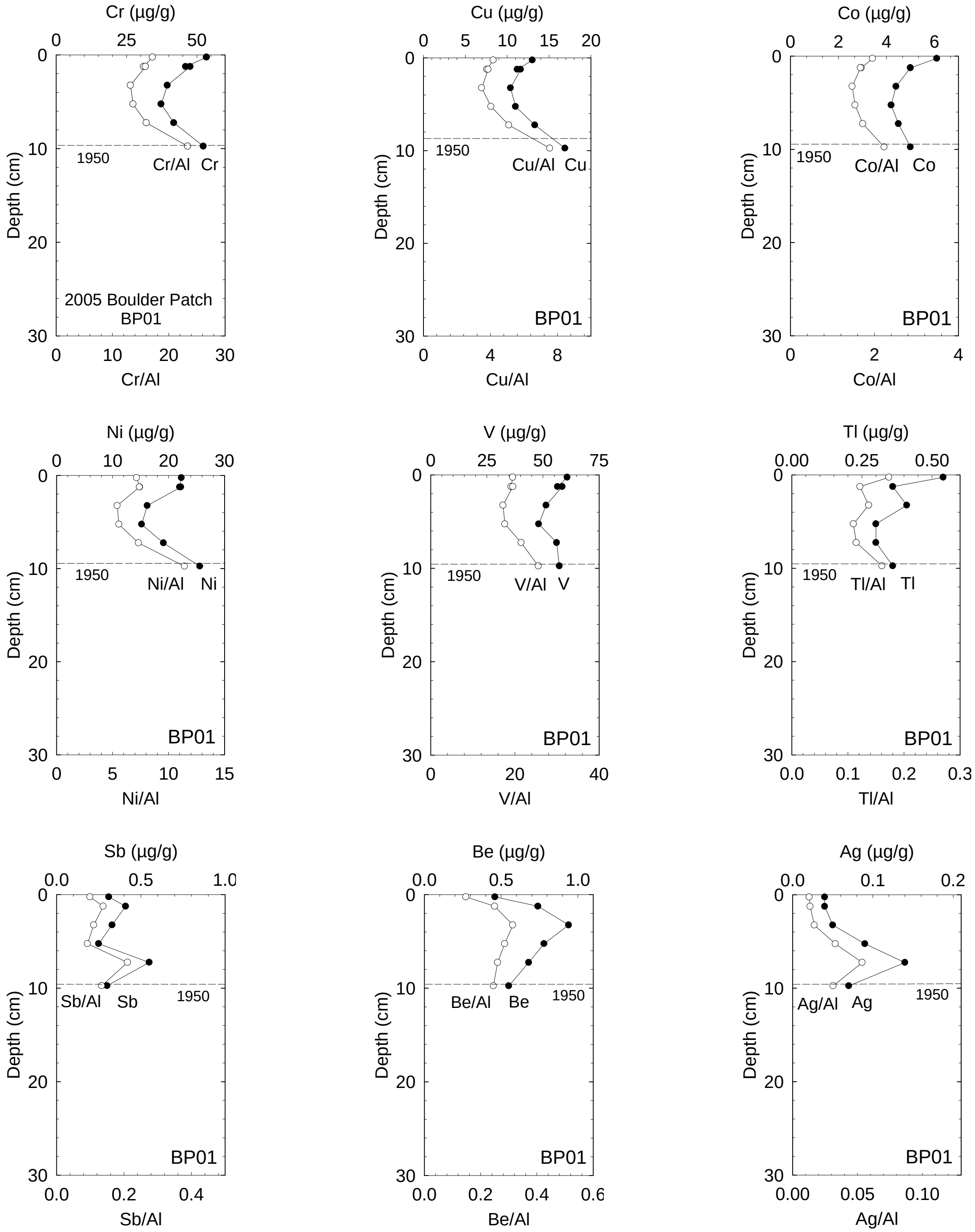


Figure 3-25. Vertical profiles for metals and metal/Al ratios for in sediments from station E01 sampled during 2005. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

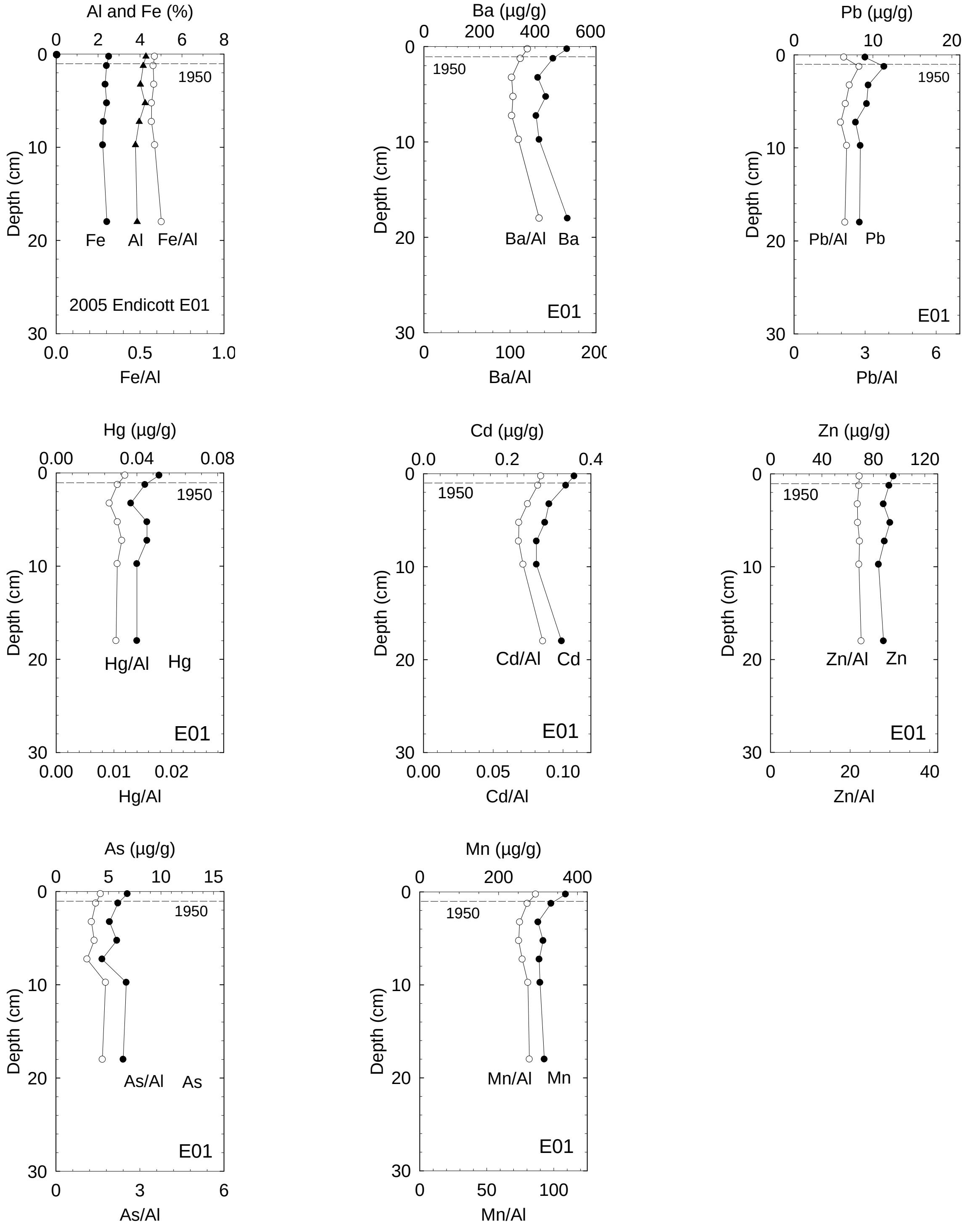


Figure 3-25 (cont.). Vertical profiles for metals and metal/Al ratios for in sediments from station E01 sampled during 2005. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

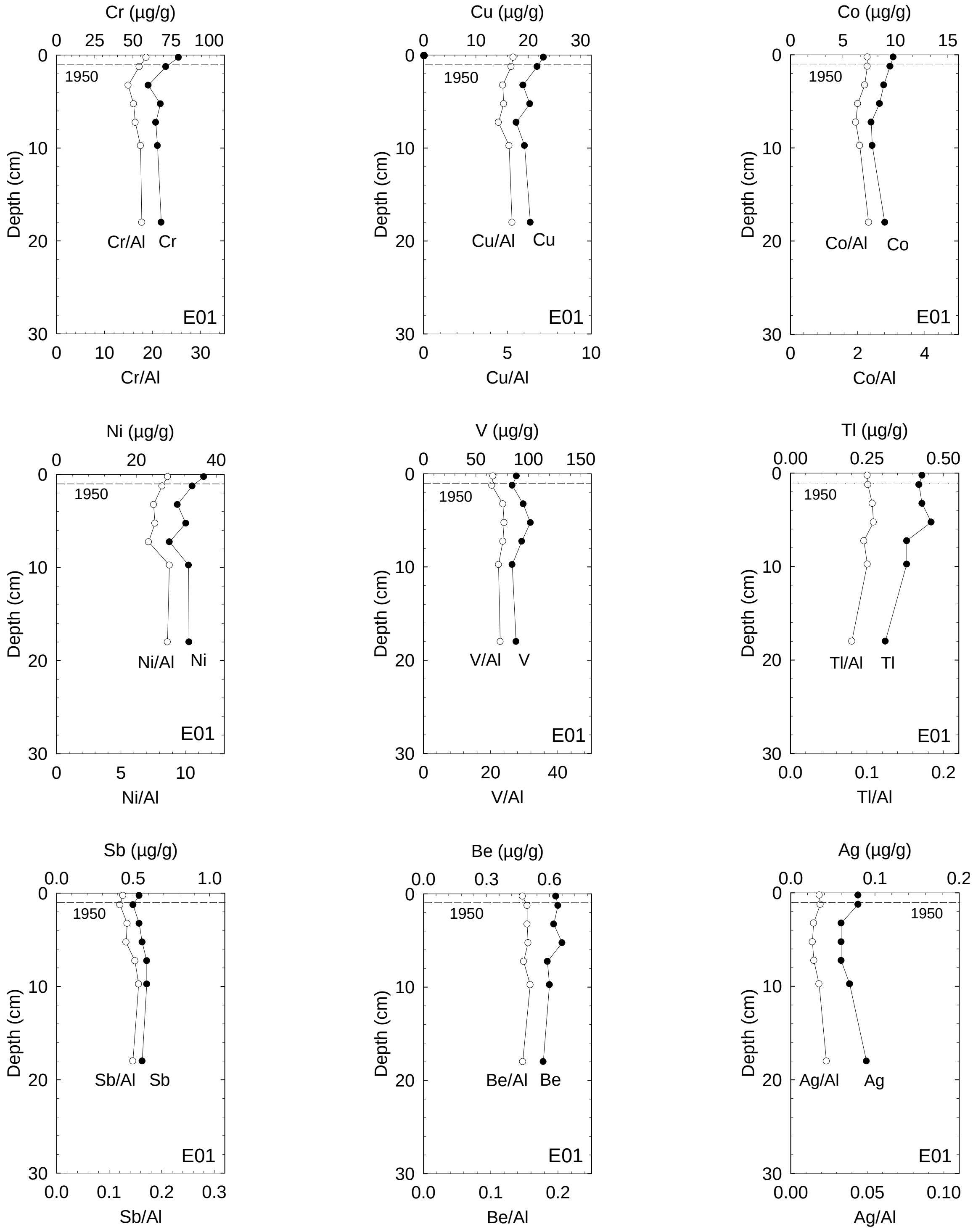


Figure 3-26. Vertical profiles for metals and metal/Al ratios for in sediments from station PB1A sampled during 2005. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

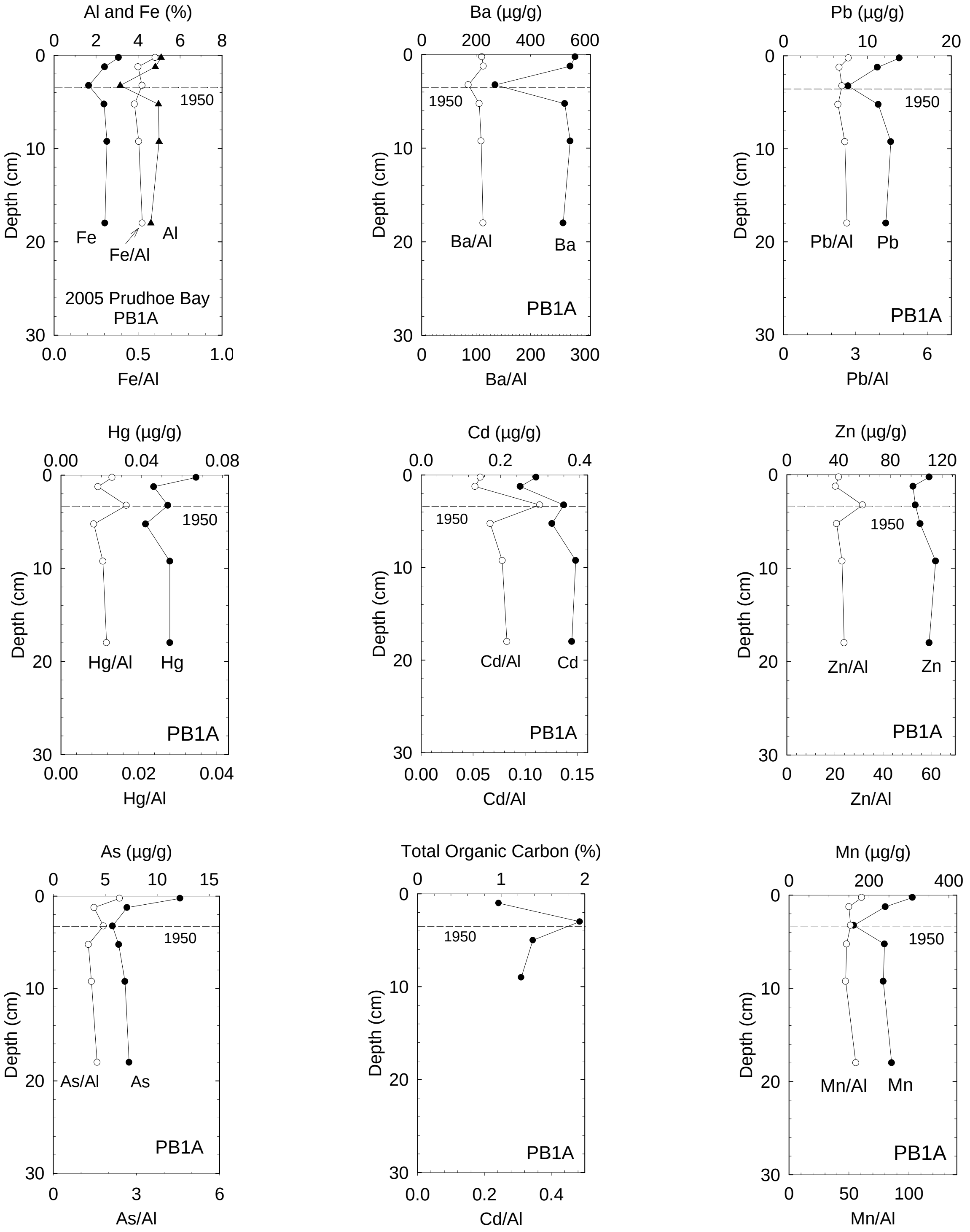


Figure 3-26 (cont.). Vertical profiles for metals and metal/Al ratios for in sediments from station PB1A sampled during 2005. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

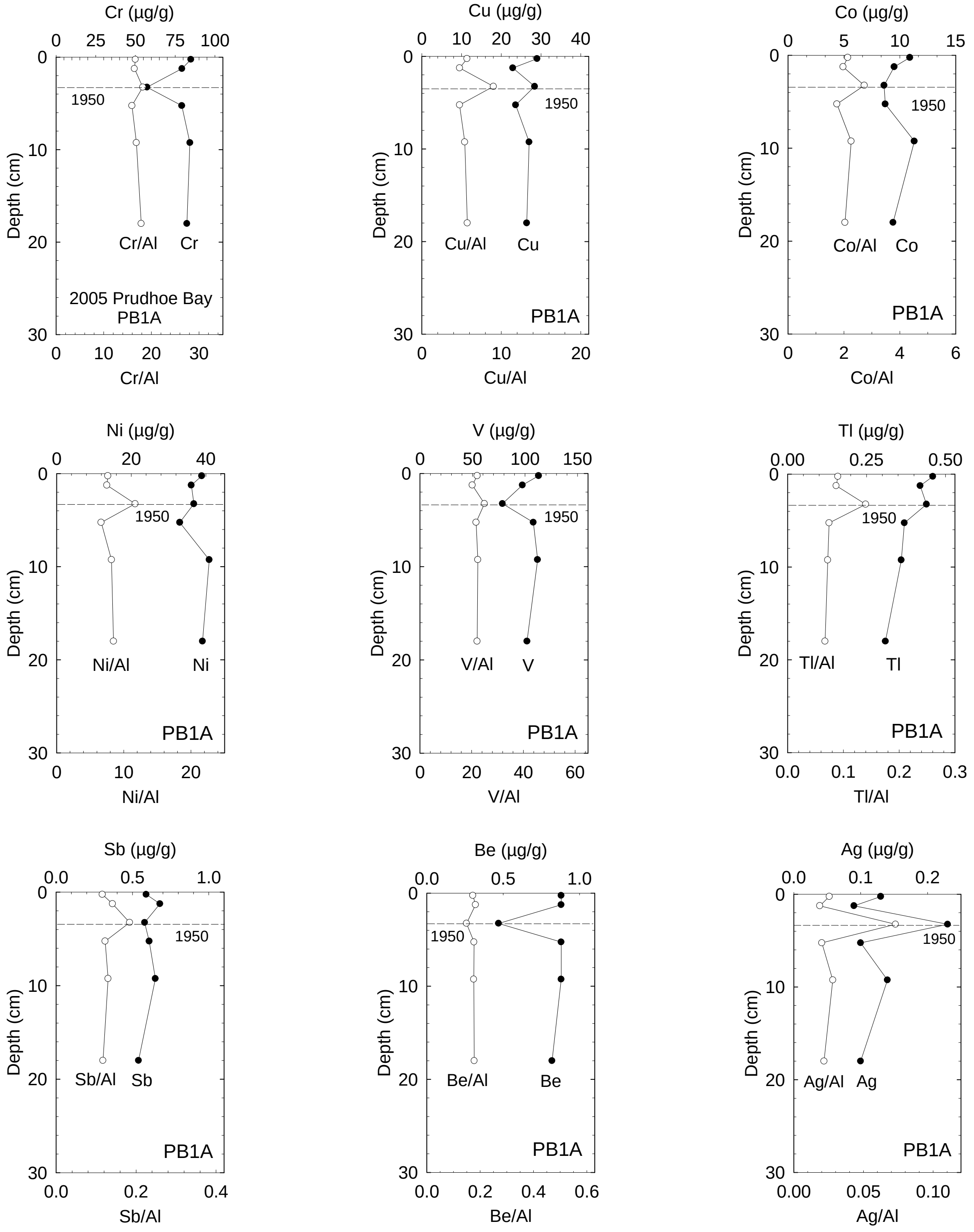


Figure 3-27. Vertical profiles for metals and metal/Al ratios for in sediments from station N26 sampled during 2005. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

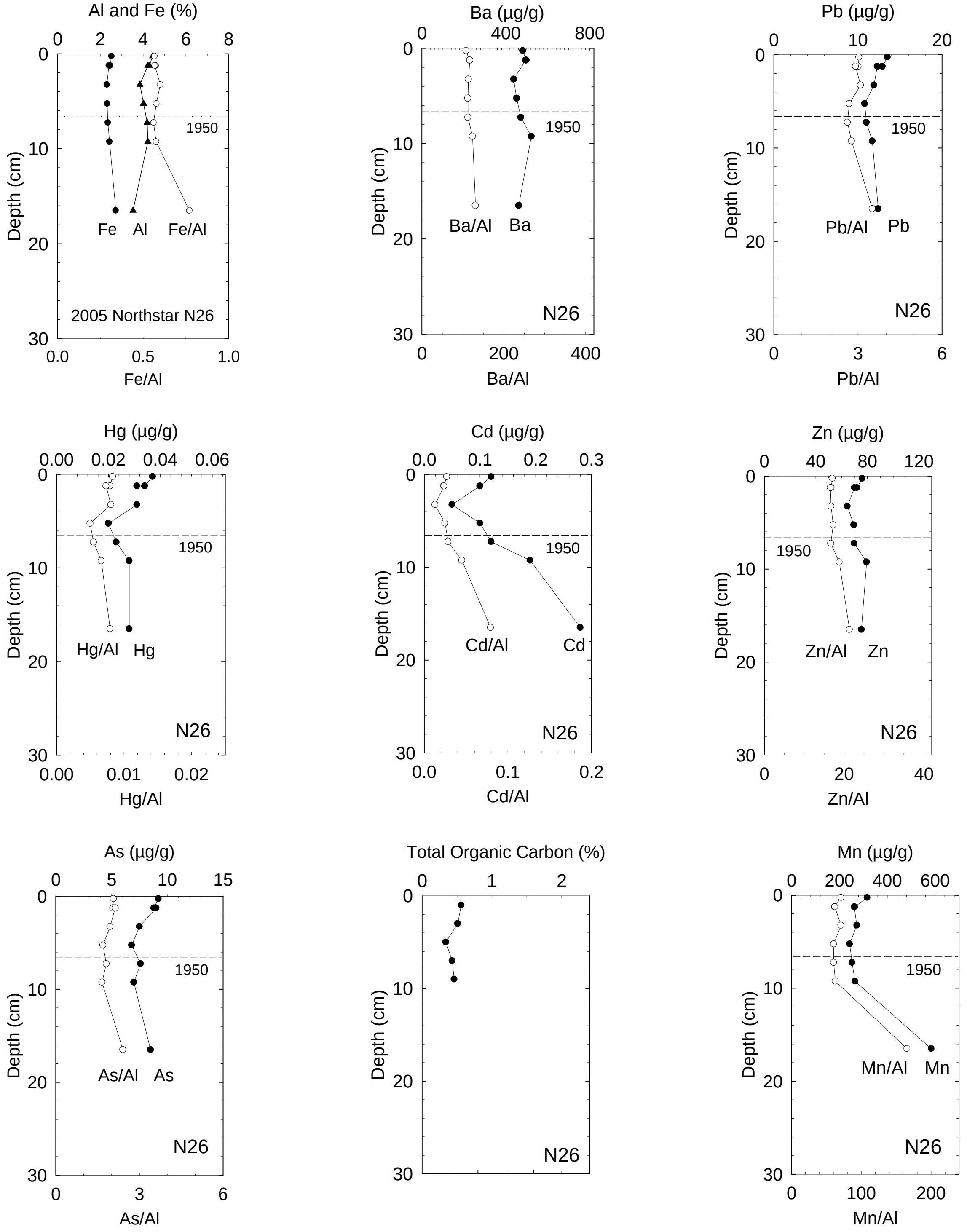


Figure 3-27 (cont.). Vertical profiles for metals and metal/Al ratios for in sediments from station N26 sampled during 2005. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

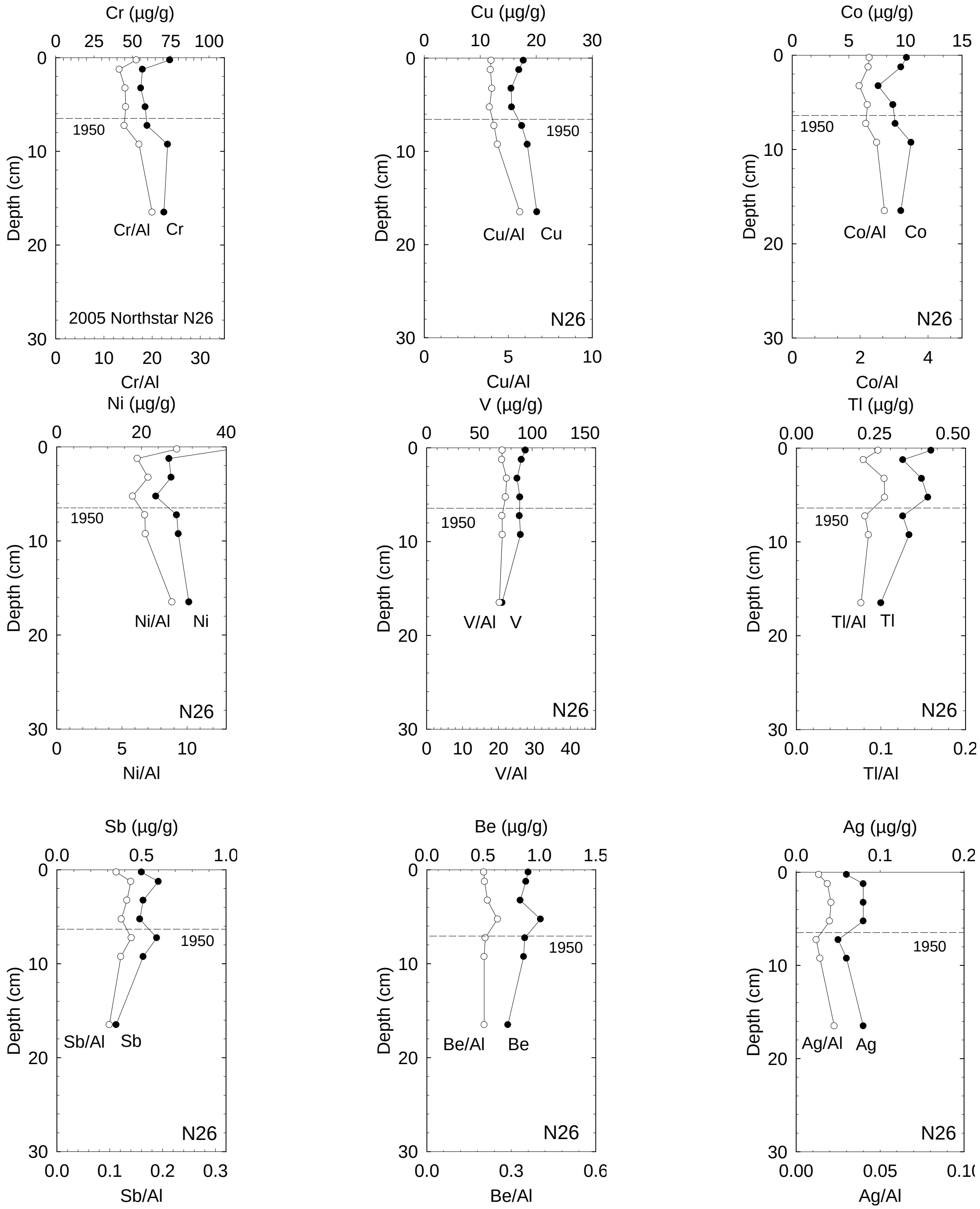


Figure 3-28. Vertical profiles for metals and metal/Al ratios for in sediments from station N17 sampled during 2006. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

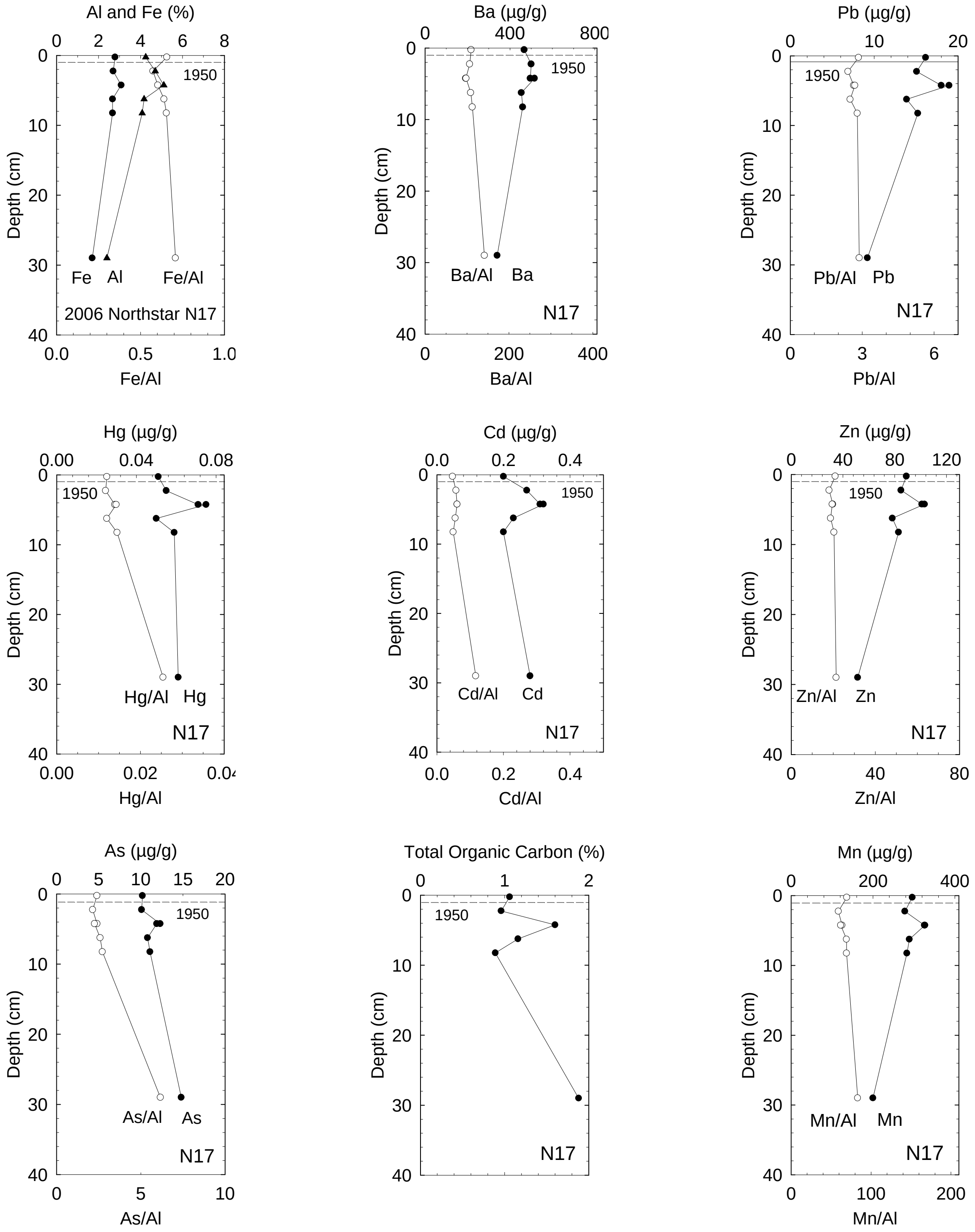


Figure 3-28 (cont.). Vertical profiles for metals and metal/Al ratios for in sediments from station N17 sampled during 2006. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

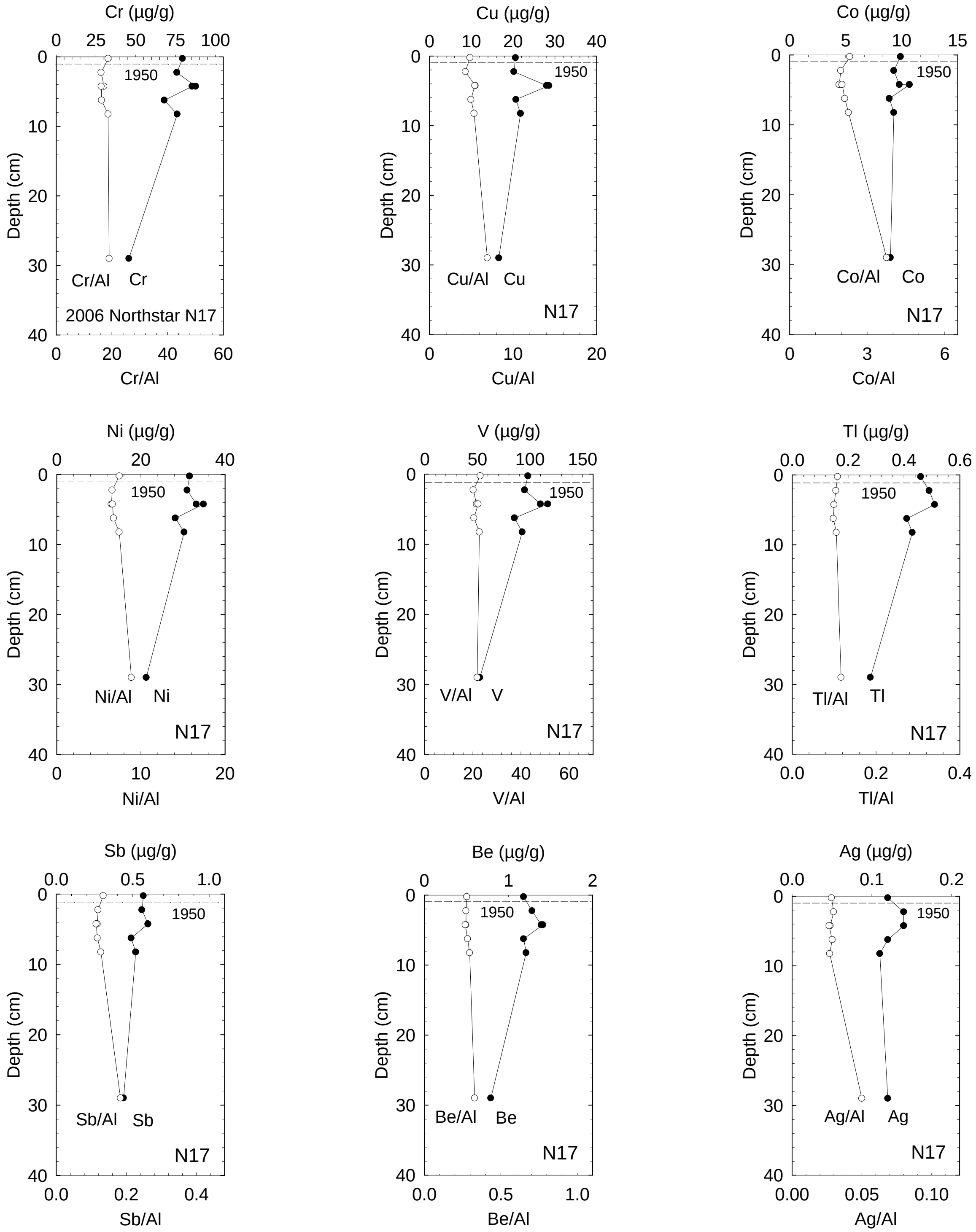


Figure 3-29. Vertical profiles for metals and metal/Al ratios for in sediments from station L22 sampled during 2006. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

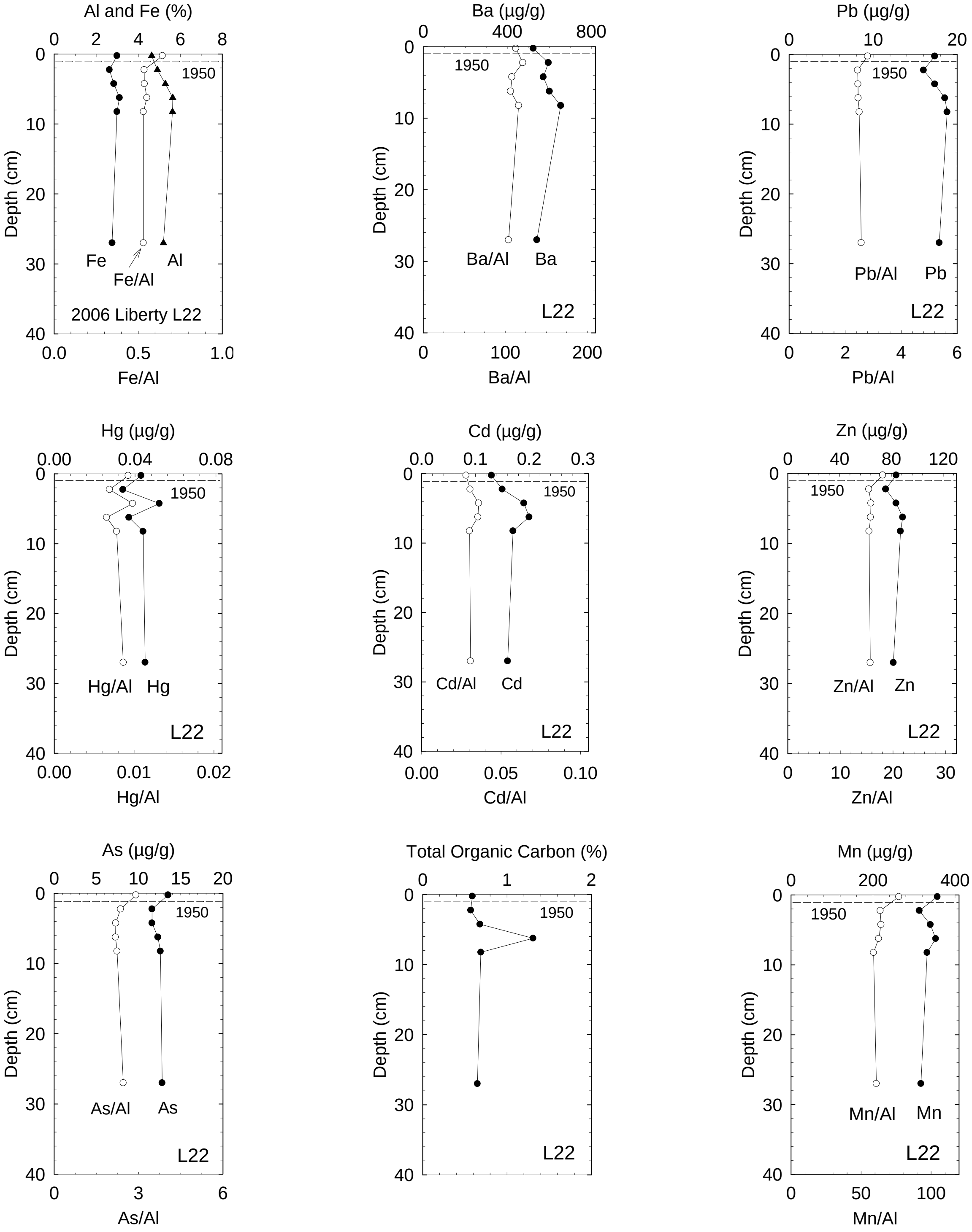
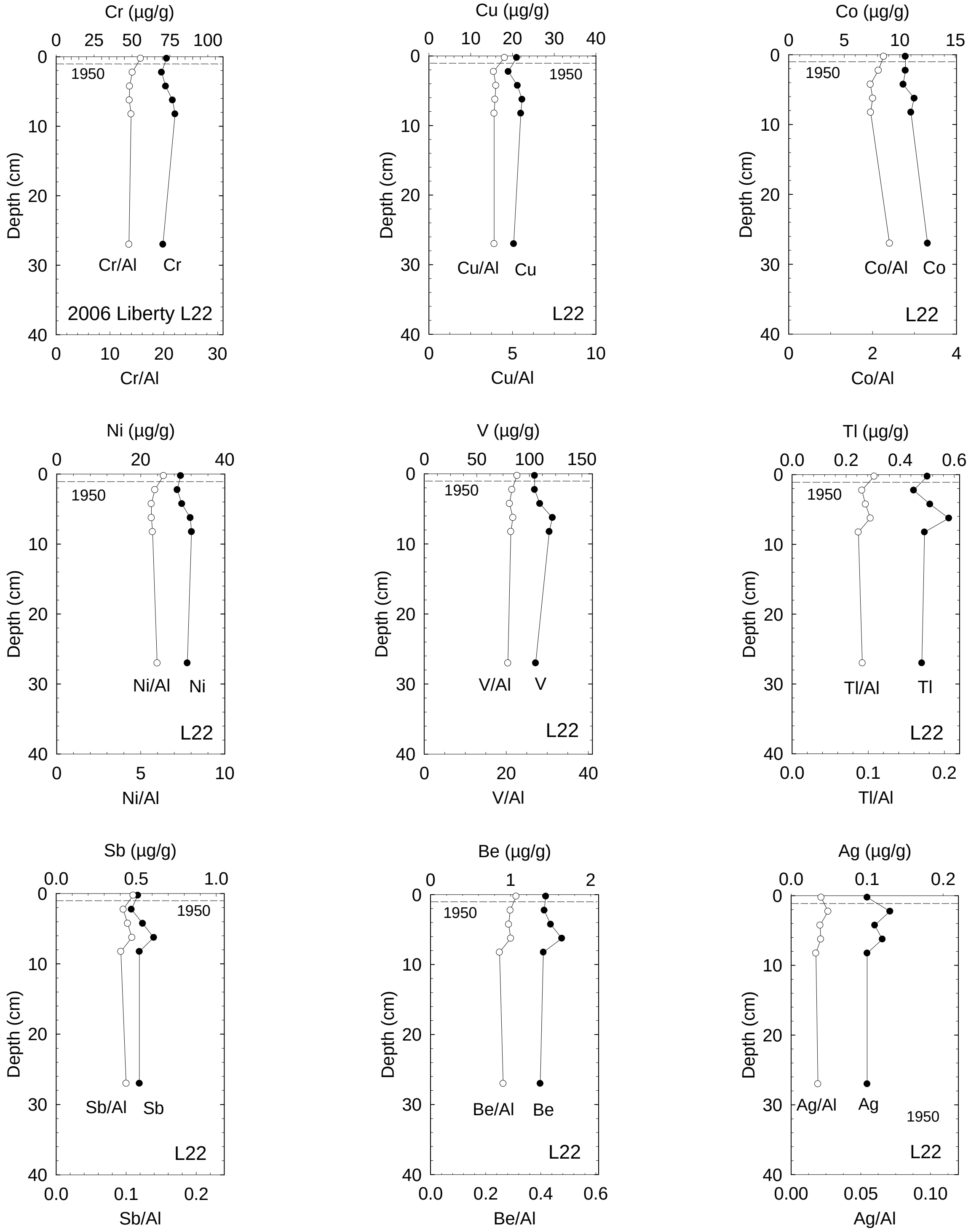


Figure 3-29 (cont.). Vertical profiles for metals and metal/Al ratios for in sediments from station L22 sampled during 2006. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.



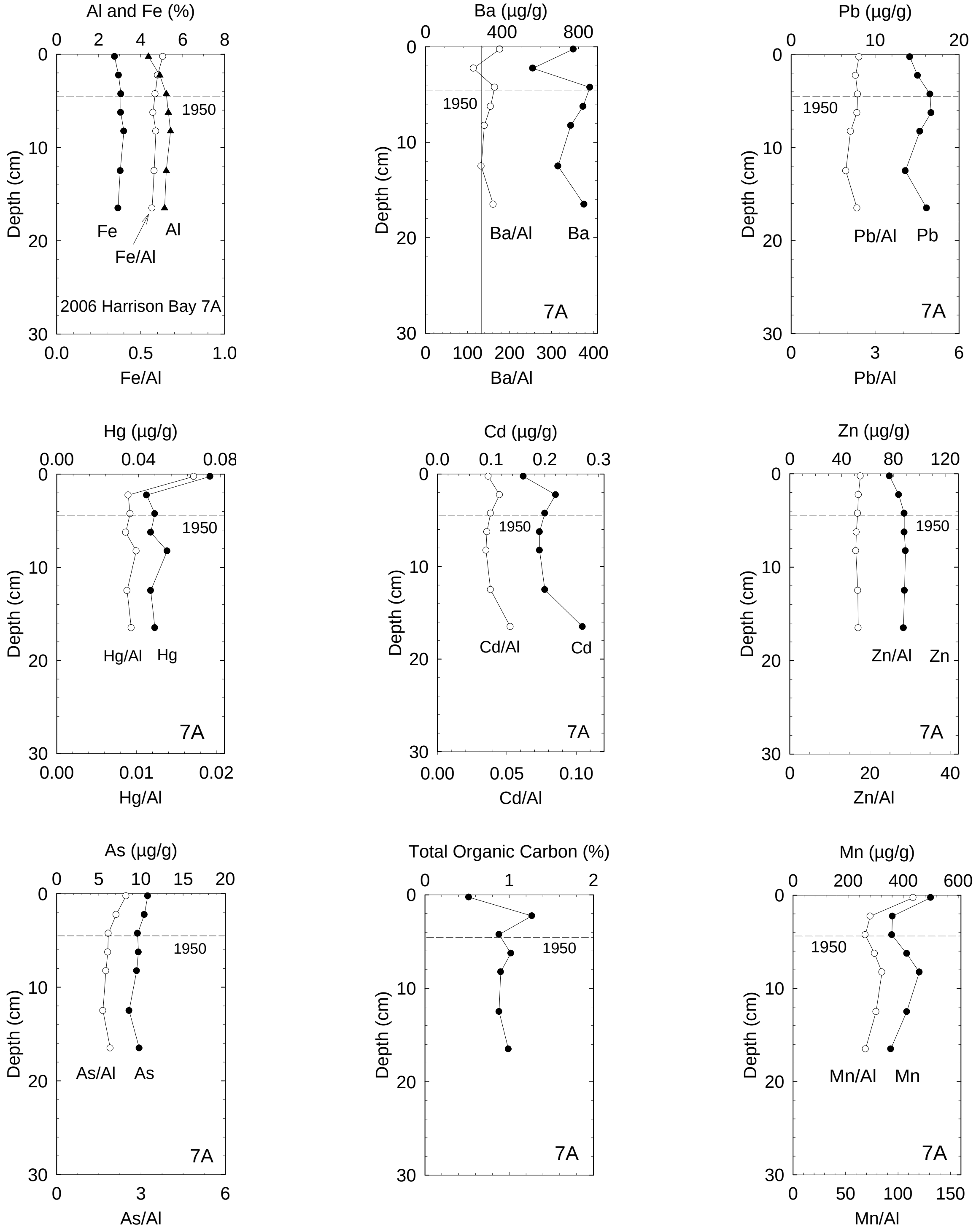


Figure 3-30. Vertical profiles for metals and metal/Al ratios for in sediments from station 7A sampled during 2006. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

Figure 3-30 (cont.). Vertical profiles for metals and metal/Al ratios for in sediments from station 7A sampled during 2006. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

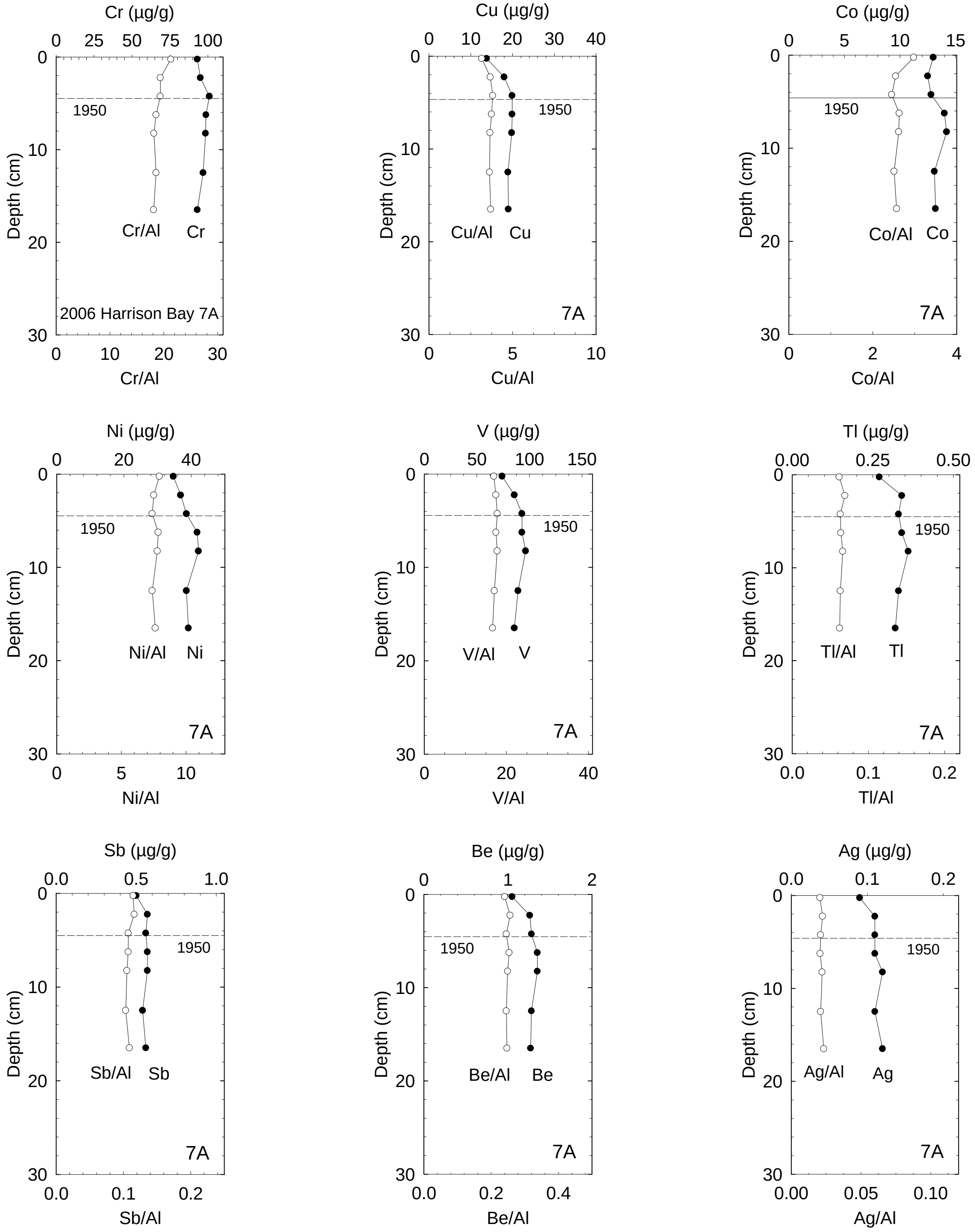


Figure 3-31. Vertical profiles for metals and metal/Al ratios for in sediments from station 7C sampled during 2006. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

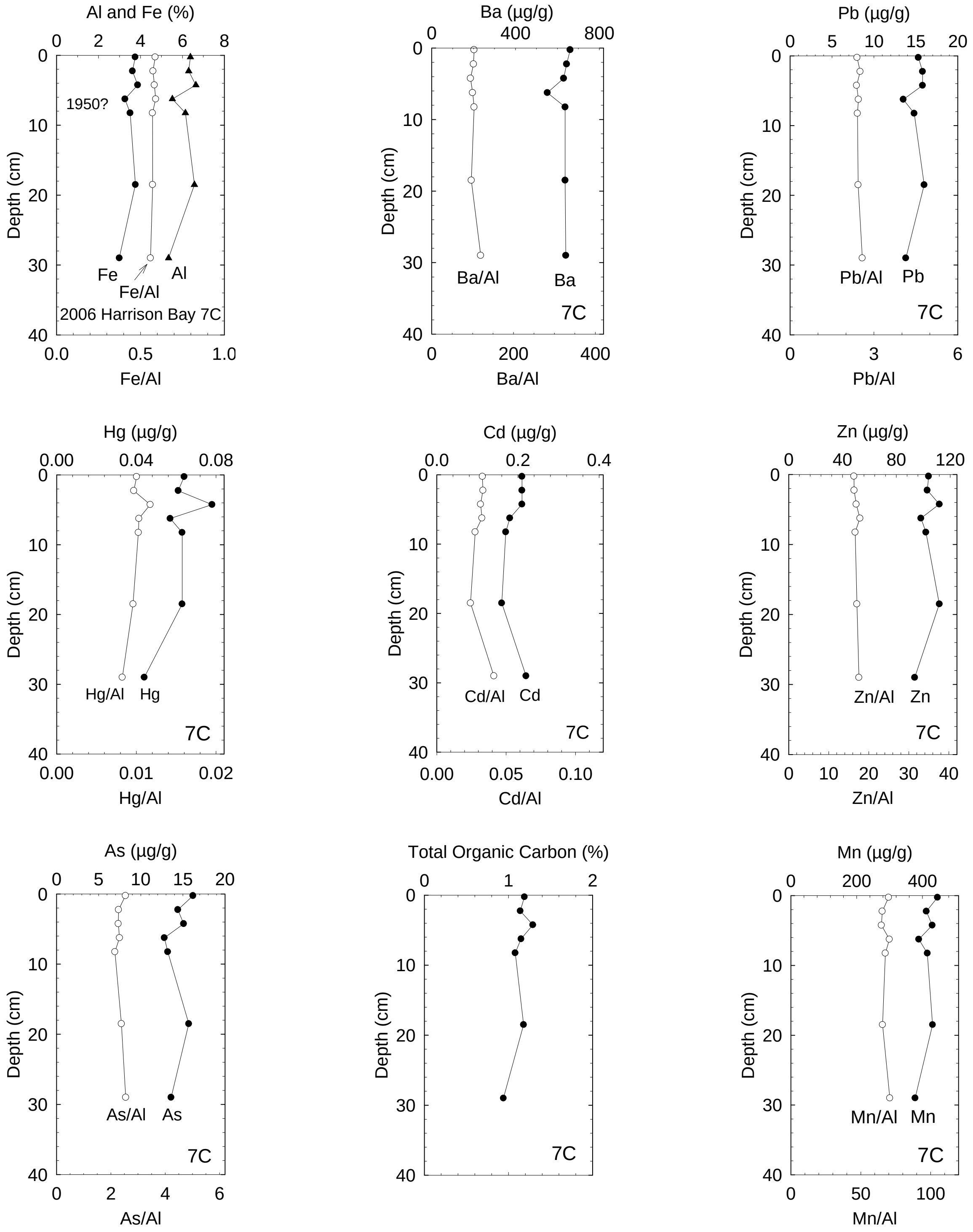


Figure 3-31 (cont.). Vertical profiles for metals and metal/Al ratios for in sediments from station 7C sampled during 2006. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

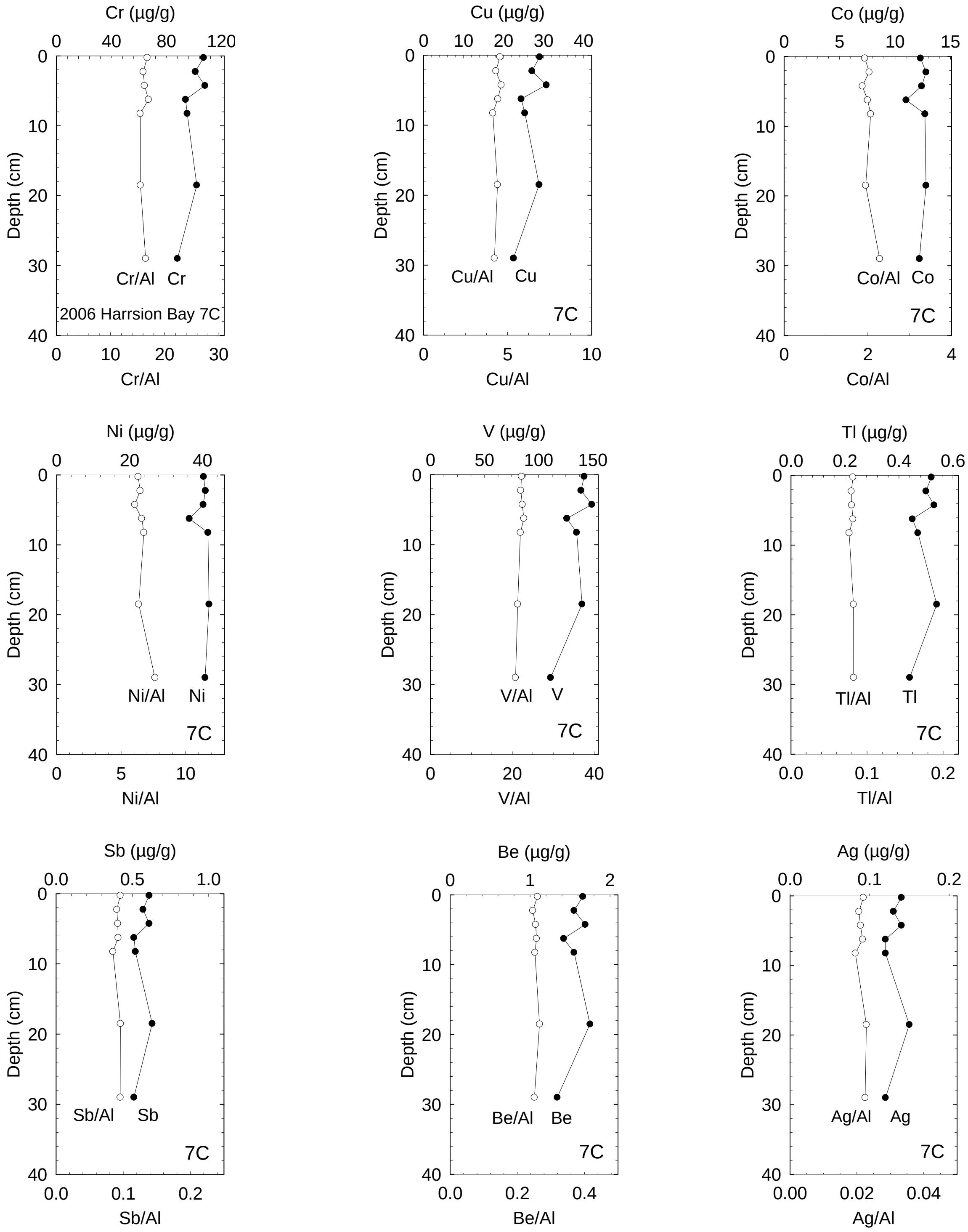


Figure 3-32. Vertical profiles for metals and metal/Al ratios for in sediments from station 7E sampled during 2006. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

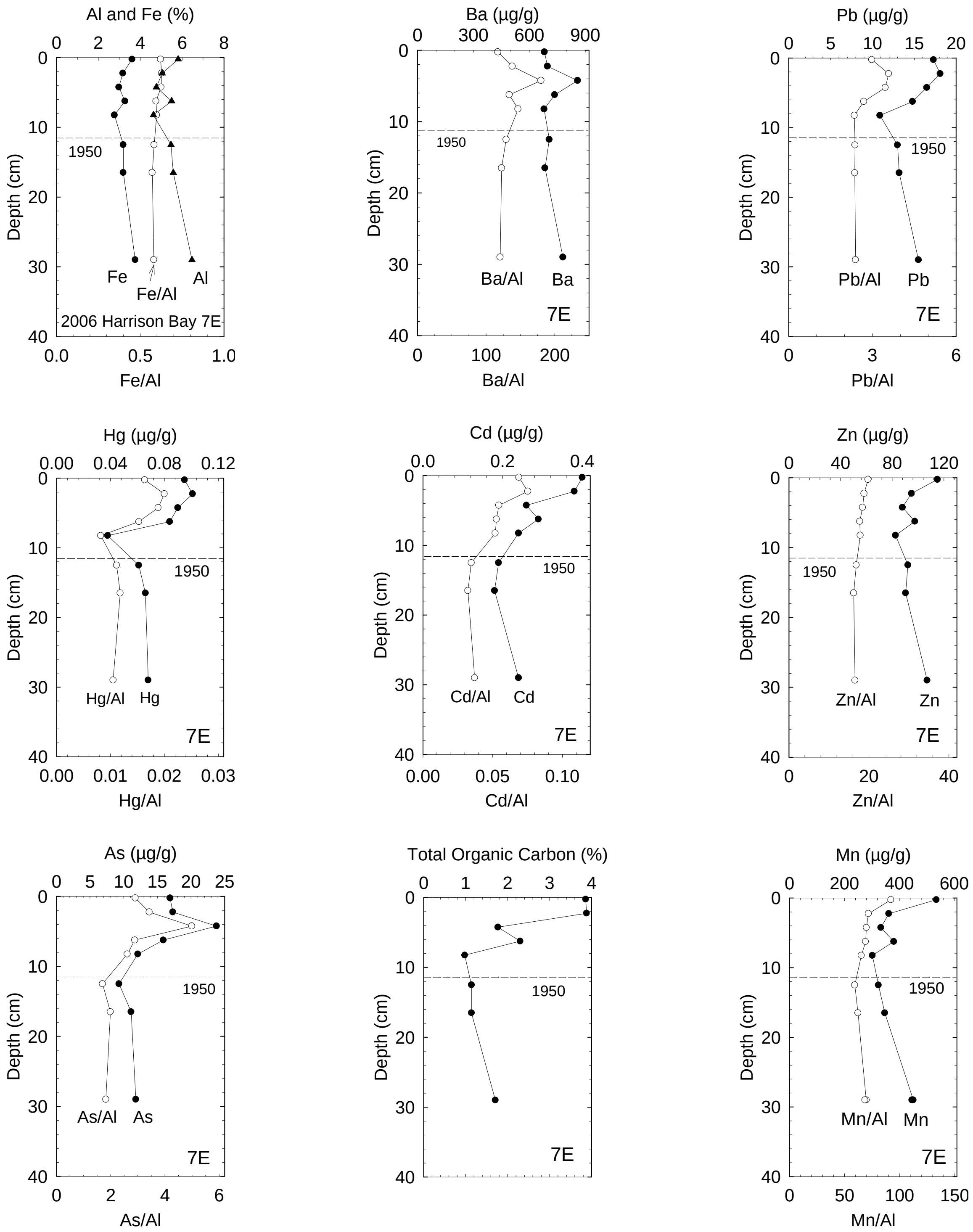


Figure 3-32 (cont.). Vertical profiles for metals and metal/Al ratios for in sediments from station 7E sampled during 2006. Dashed line shows depth in sediment that corresponds with 1950 based on sediment geochronology.

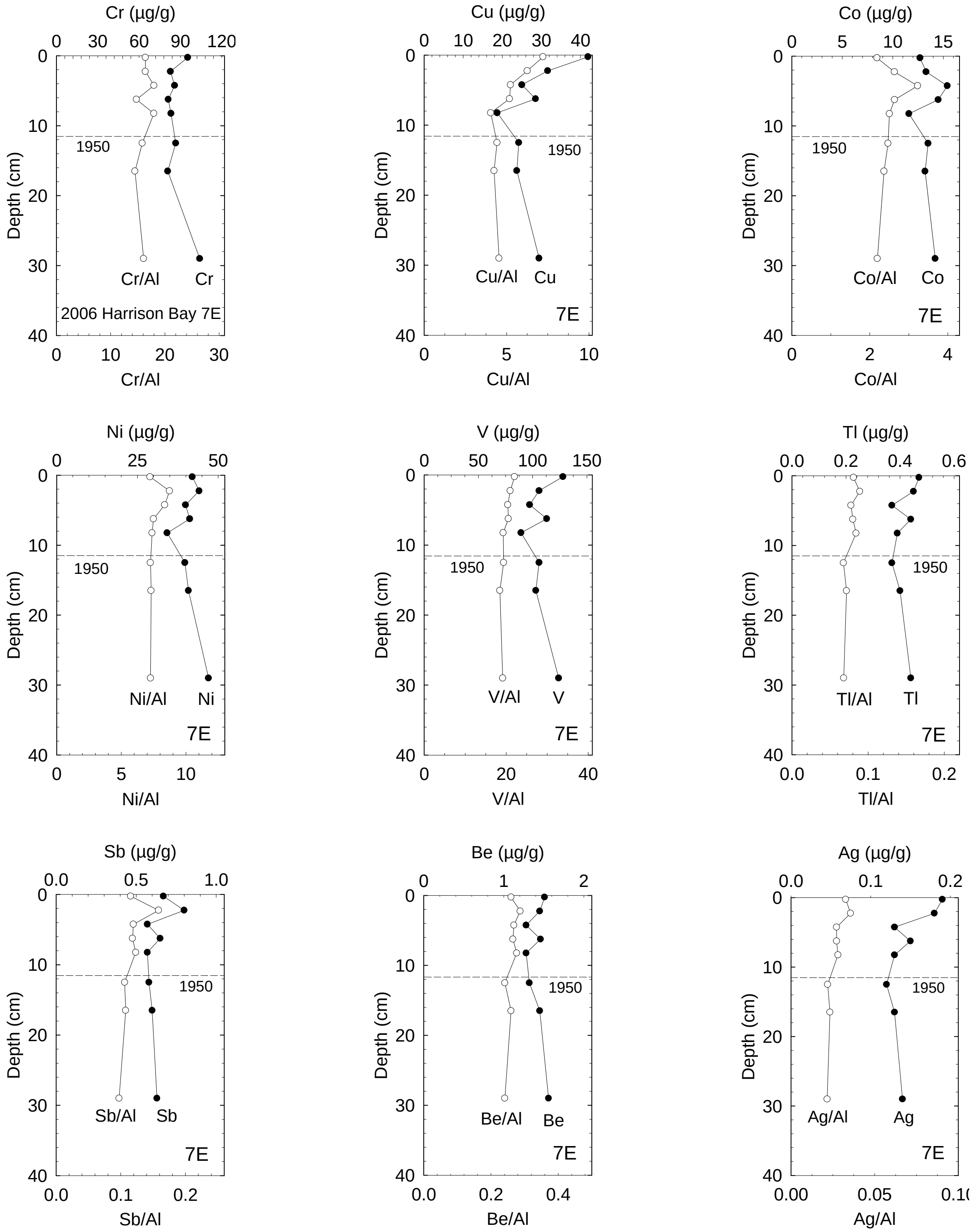


Figure 3-33. Vertical profiles for activities of ^{137}Cs, total ^{210}Pb, and excess ^{210}Pb for sediments core from stations 1C, 2A and BP01 collected during 2005.

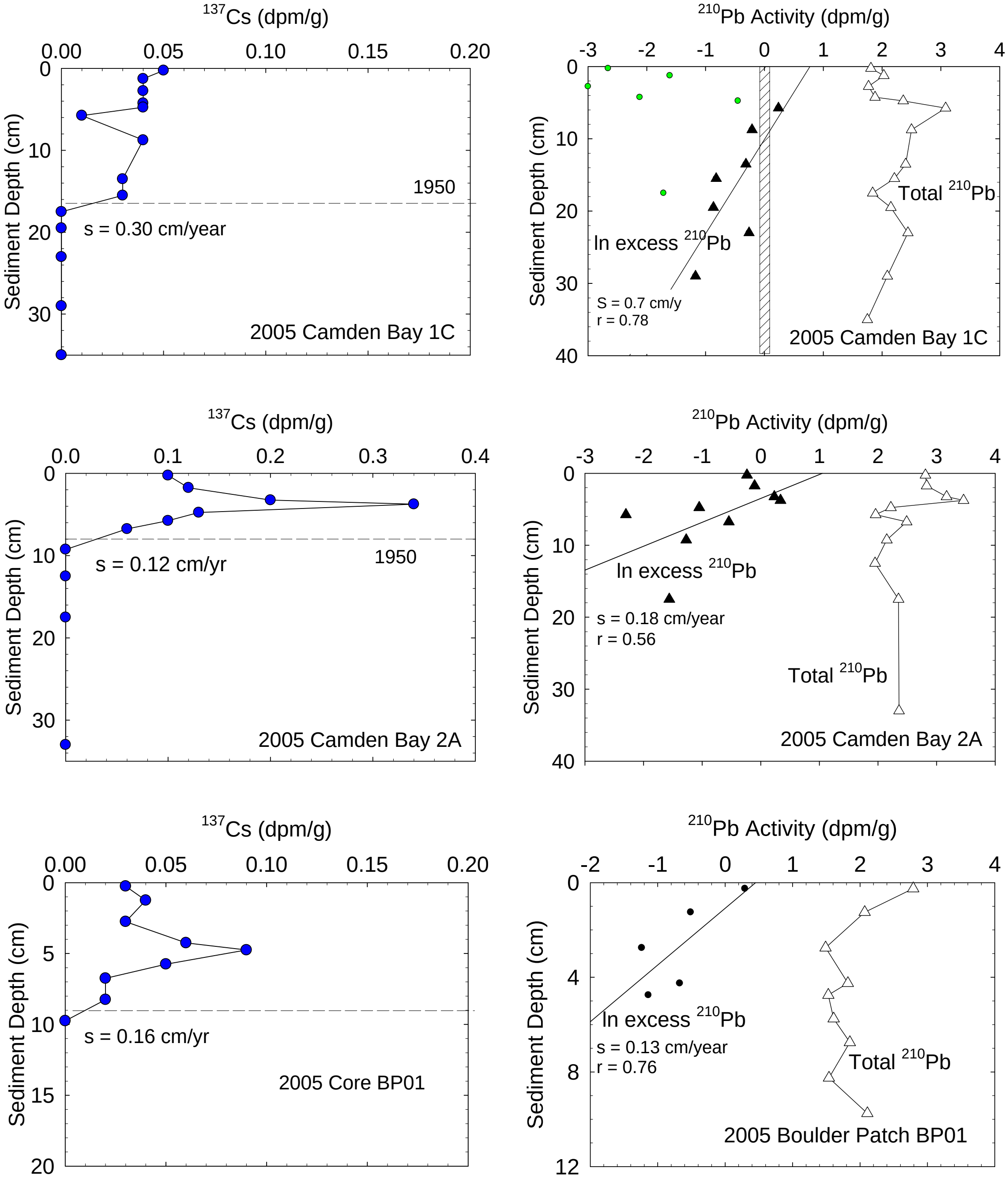


Figure 3-34. Vertical profiles for activities of ^{137}Cs, total ^{210}Pb, and excess ^{210}Pb for sediments core from stations E01, L17B and PB1A collected during 2005.

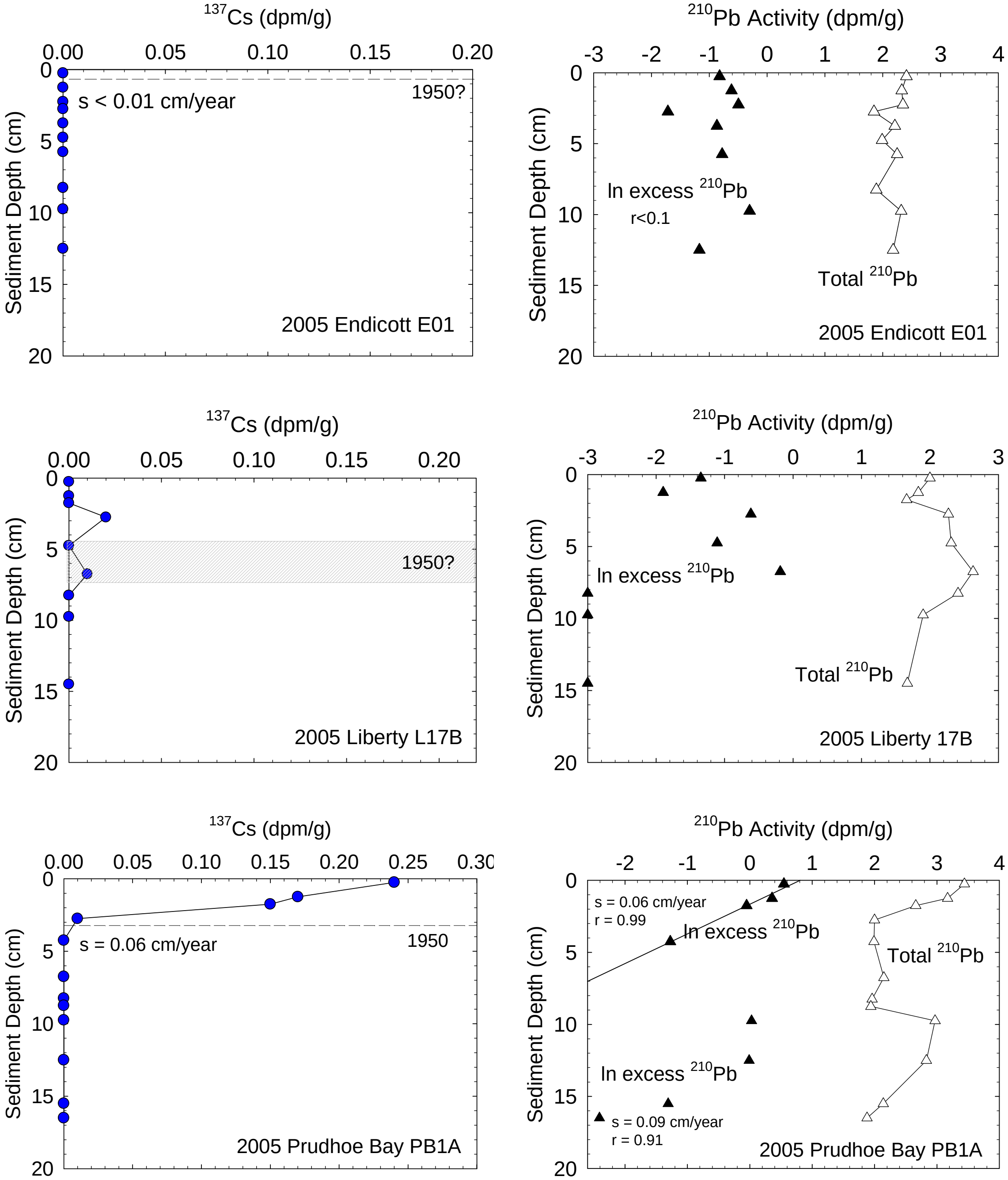


Figure 3-35. Vertical profiles for activities of ^{137}Cs, total ^{210}Pb, and excess ^{210}Pb for sediments core from station N26 sampled during 2005 and stations 6B and 7A collected during 2006.

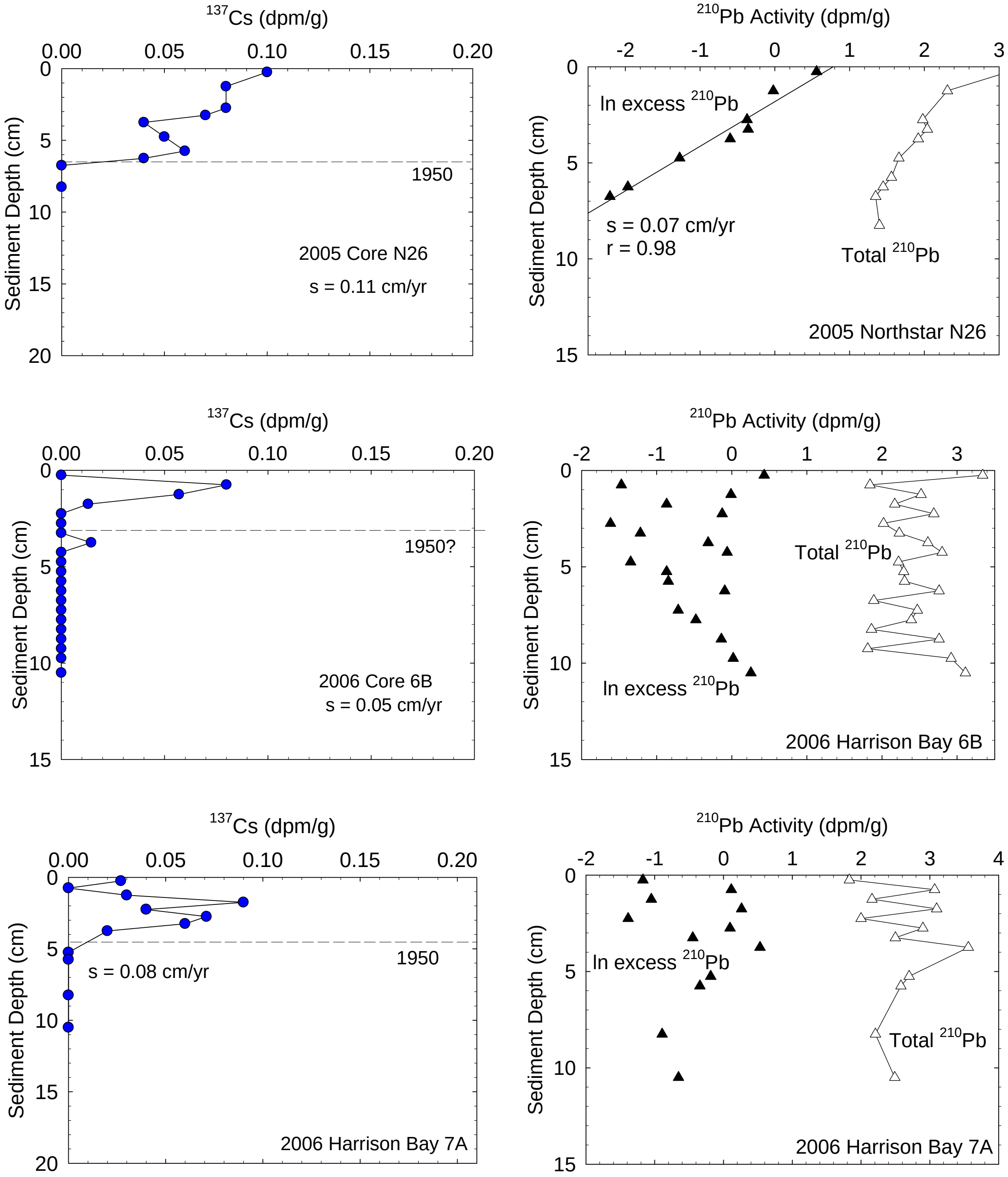
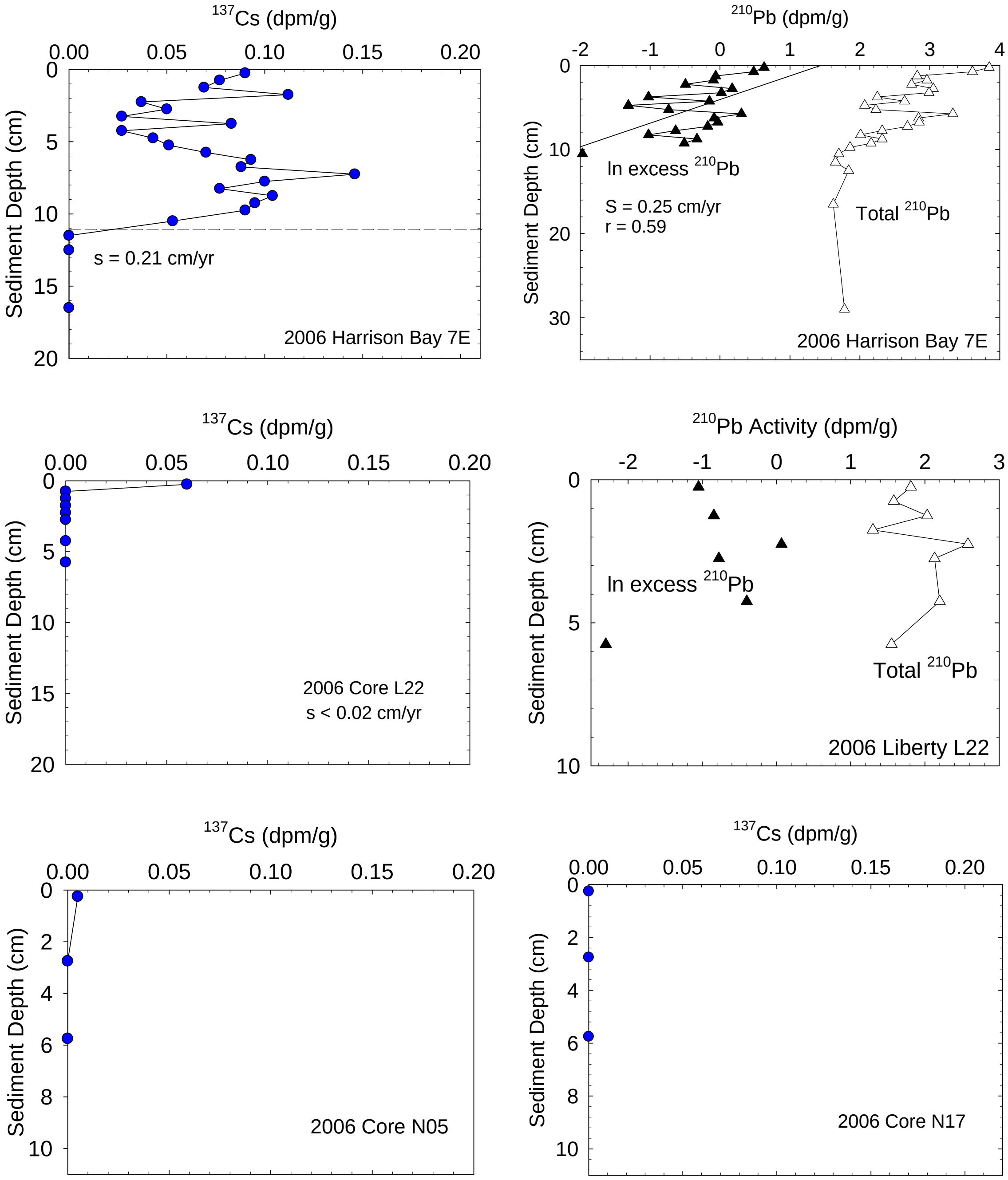


Figure 3-36. Vertical profiles for activities of ^{137}Cs, total ^{210}Pb, and excess ^{210}Pb for sediments core from stations 7E and L22 collected during 2006 and ^{137}Cs for stations N05 and N17 sampled during 2006.



4.0 Discussion

In this section, the results for sediment grain size, radionuclides, trace metals and organic substances from the cANIMIDA study area during 2004-2006 are discussed with respect to trends since the 1999-2002 ANIMIDA study (Brown et al., 2004) and possible contamination of sediments with metals or organic substances.

4.1 Surficial Sediments

4.1.1 Grain Size

Inter-annual shifts in the texture of surficial sediment have been observed throughout the cANIMIDA study area. Large changes in grain size distribution were first observed in the ANIMIDA program between 1999 and 2000 (Figure 4-1). For example, 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 from these same stations 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 were less than observed between 1999 and 2000 (Figures 4-1 and 4-2). During 2002, much less sand was found at stations N06, N07, N08 and N09 than during 2000; most likely because fine-grained sediment introduced to that area during river runoff had not yet been moved farther offshore. In contrast, sand has dominated at stations N01, 5B and N15 from 1999-2002.

Grain size distribution in 2004 was different at several stations relative to 2002 (Figure 4-2). More fine-grained sediment was observed in 2004 at stations 5B, 5D, N02 and N03 relative to 2002. In contrast, more gravel was collected at station N15 and more sand at station N11 in 2004 (Figure 4-2). Results for 2005 from the Northstar area (Figure 3-2) show increases in sand at most of the stations relative to 2004 with further increases in sand at stations N06, N14 and 5(5) in the 2006 samples (Figure 3-3). In contrast, marked increases in silt + clay were observed at stations N03 and N06 relative to 2004 and/or 2005. Thus, the Northstar area appears have a dynamic sedimentary environment, an observation that is consistent with difficulties in finding sediment cores with a useful record of sediment geochronology based on attempts at stations N02 and N15 (ANIMIDA) and N05 and N17 (cANIMIDA). A reliable geochronology was obtained for station N26 (2005); however, this station was located ~15 km northeast of

Northstar Island at a water depth of ~24 m relative to depths of ~12 m in the immediate area of Northstar Island.

Previous shifts in grain size in the Liberty area were noted at station L01 where finer-grained sediment was collected during 2000 than during 1999 and at stations L08 and L09 where the opposite trend was found. Between 1999 and 2004, an increase in the amounts of fine-grained sediment has been observed at several stations including 4A, L07, L08 and 3A (Figure 4-3). The 2005 grain size data for the Liberty area shows increases in the coarser fractions at stations 4A and L08 (Figure 3-5). The presence of a gravel (10.4%) and sand fraction (30.5%) at the deeper-water station L22 (29.2 m) suggests that ice-rafting may be a significant source of sediment to this location (Figure 3-6).

One key observation from the grain size data is that sediments in many locations throughout the cANIMIDA study area are regularly shifting and that the sediment grain sizes found during one year may change prior to sampling during a subsequent year. Furthermore, the grain size distribution in surface sediments is very patchy from site to site. Thus, techniques that normalize sediment chemistry to account for differences in grain size have been used and radionuclide measurements have been made to determine that 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 through 2006 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 3-7), 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 4-12. 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)
- Canning River sediment – 2002 (Figure 4-7)
- Station N06 – Northstar sediment – 1999 (Figure 4-8)
- Station N06 – Northstar sediment – 2000 (Figure 4-9)
- Station N06 – Northstar sediment – 2002 (Figure 4-10)
- Station N06 – Northstar sediment – 2004 (Figure 4-11)
- Station N06 – Northstar sediment – 2005 (Figure 4-12)

- Station N06 – Northstar sediment – 2006 (Figure 4-13)
- Station L08 – Liberty sediment – 1999 (Figure 4-14)
- Station L08 – Liberty sediment – 2000 (Figure 4-15)
- Station L08 – Liberty sediment – 2005 (Figure 4-16)
- Station L08 – Liberty sediment – 2006 (Figure 4-17)
- Station 3A – BSMP sediment station near Stockton Islands – 1999 (Figure 4-18)
- Station 3A – BSMP sediment station near Stockton Islands – 2005 (Figure 4-19)
- Station 2A – BSMP sediment station in West Camden Bay – 2005 (Figure 4-20)

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 Saturated Hydrocarbons

In general, the surficial sediments (GC/FID chromatograms in Figures 4- 8 through 4-20) 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). Two sediment samples have CPI ratios of less than two (5B [2004] and N15 [2004]). The lower CPI ratios at stations 5B and N15 are due to low SHC concentrations (i.e., trace levels), combined with corresponding low TOC, which contribute to CPI ratio uncertainty and potential inaccuracy.

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 4-20). This characteristic petroleum alkane signature in the sediments has been well documented by previous studies in the region (Boehm et al., 1987; Steinhauer and Boehm, 1992; Boehm et al., 1990; Brown et al., 2004). In 1999, an unresolved complex mixture (UCM) characteristic of diesel fuel hydrocarbon was noted in the GC/FID chromatogram for the surface sediment sample collected at station L08. The diesel fuel pattern was somewhat 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 and a visible but less pronounced diesel signature in the other two replicates. The diesel fuel pattern was identified in the 2005 L08 sample and was either not present or at trace levels in the L08 samples collected in 2002, 2004 and 2006. The absence of a similar diesel fuel signature in samples from adjacent stations and the 2002, 2004 and 2006 samples suggest a very limited or patchy area of sediment contamination. These results warrant continued evaluation and monitoring in future field surveys.

4.1.2.2 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 and the regional peat samples, often the most abundant single PAH compound in the overall PAH distribution (Figures 4-8 through 4-20). 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 and 1991).

The variations in PAH composition of representative surficial sediments from the region in 1999, 2000, 2002, and 2004 - 2006 are shown in the PAH distribution plots in Figures 4-6 through 4-20. 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 (Figures 4-6 and 4-7) and peat, 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, 2000, 2004 and 2005 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 and 2006 samples 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 and 2004, the PAH concentration at 5E (260 and 190 ug/Kg, respectively) was comparable to the levels in 1999, 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 but present at moderate levels in 2004, 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 appears to be depleted in PAH versus SHC, relative to the regional petroleum hydrocarbon background present in other sediments, suggesting an alternate hydrocarbons source in 1999 (e.g., coal or peat).

4.1.2.3 Triterpanes

In general, the triterpane distributions in the sediment samples are indicative of a petroleum pattern (Figures 4-6 through 4-20), 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) and other unnamed triterpanes (the large peaks which elute prior to T15 and in the 45- to 47-minute range – Peters and Moldowan, 1993). 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 surficial 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. 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 (Figure 4-6) and peat 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 4-8 through 4-13). This similarity suggests that there is a strong link between Colville River hydrocarbon sources – mostly erosional inputs of regional shales, coal, 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 4-6) 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, identified in the 2006 Sagavanirktok peat sample (SAG-01), 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, 2002, 2004 - 2006], N20 and N21

[2002], 5D [1999, 2000, 2002 and 2004], and 5F [2000, 2002, 2004 and 2005] 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 is of particular interest, since the high SHC and PAH concentrations indicate hydrocarbon contamination at this station. The observed T22 pattern indicates that coal particles, possibly from the Kuparuk River, may be one of the sources of the hydrocarbon enrichment.

Several surficial sediment samples have distinctly different triterpane distributions. Stations 5E [1999, 2000 and 2002], 5B [2000 and 2002], and L08 [1999 and 2005] (Figures 4-14 and 4-16) 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 suggests that the observed petroleum contamination at L08 is a complex mixture of hydrocarbons including diesel and heavier hydrocarbons such as heavy 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.

4.1.2.4 Sediment Quality Guidelines

An established technique of evaluating the significance of the measured sediment hydrocarbons to overall ecological risk of the region involves comparisons to sediment quality guidelines or benchmarks. 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 and cANIMIDA sediments from the study region in 1999 through 2006 to the ERL and ERM criteria is shown in Figure 4-21. None of the Total PAH concentrations determined in this study exceed the ERL. 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 sum of the C1-naphthalenes value at station 2G in 2005 (109 µg/Kg), station 6B in 2006 (123 µg/Kg), and station 7E in 2006 (90 µg/Kg) were slightly higher than the ERL value listed for the single 2-methylnaphthalene isomer (70 µg/Kg). However, the value at this station 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 ecological risk to marine organisms in the area.

Potential toxicity of the PAHs present in cANIMIDA sediments was further evaluated using a more recent methodology; EPA's Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures (EPA 2003, http://www.epa.gov/nheerl/publications/files/PAHESB.pdf). Based on this approach, if the sum of Equilibrium Partitioning Sediment Benchmark Toxic Units (ΣESBTUFCV) for "total PAHs" is less than or equal to 1.0, the concentration of the mixture of PAHs in the sediment is acceptable for the protection of benthic organisms. ΣESBTUFCV values were calculated for each sediment sample (with reported TOC values) with values ranging up to 0.01 to 0.7. The ESB approach provides another line of evidence the concentrations of PAH present in the cANIMIDA sediments throughout the study area are not likely to pose a risk to benthic organisms.

4.1.2.5 Temporal and Spatial Trends

In examining the spatial trends (variability between stations), one technique involves examining the relationship between the organic parameter of interest and percent silt + clay or TOC content. 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 (pre-construction) 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 the radial sampling design around the prospect and regional BSMP station coverage. As noted earlier, statistical analyses of the 1999 through 2006 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 post-1999 sediments (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, 2002, and 2004 - 2006 Northstar stations (Figure 4-22). In this plot the regression lines and 95% prediction intervals do not overlap, indicating a significant increase in PAH at Northstar in 2000, 2002, and 2004 - 2006 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 and 2004 - 2006, but still generally higher than 1999 (Figure 4-23). Station N15 in 2002 and 2004 and N11 in 2004 appear to be outliers on this plot due to a very low %fines result (4.3%, 0.4%, 2.7%, respectively). The concentration of Total PAH (less perylene) at Station N03 in 2004 appears elevated as compared to previous years, however, the concentration of perylene at this station is also correspondingly higher indicating the source of PAH at this station is from the regional background.

However, a closer examination of the PAH data show that although Northstar concentrations increased post-construction (2000, 2002, and 2004 - 2006 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, 2002 and 2004 - 2006. A comparison for this ratio for all paired Northstar stations (Figure 4-24) 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 and 2004 show an increasing trend (Figure 4-24) which then decreases in 2005 and 2006. The statistical comparisons of PAH data (Table 3-11) show a significant increase in the pyrogenic to petrogenic PAH ratio region-wide for years 2000 through 2004. A subsequent ANOVA revealed that pyrogenic to petrogenic ratios for Northstar 2002 and Liberty/BSMP 2002 were not significantly different from each other, but that the ratios for Northstar 2004 were significantly greater than Liberty/BSMP 2004 and Northstar 2002. Also, the Northstar 2004 petrogenic PAH concentrations (with perylene as a covariate) were significantly less than Northstar 2002 and Liberty/BSMP 2004 concentrations, while no significant differences were noted for pyrogenic PAHs between regions or years. These results suggest that the observed shift to a greater relative proportion of pyrogenic hydrocarbons in 2002 and 2004 could be the result of a subtle increase in pyrogenic PAH; possibly related to Northstar area inputs (flaring, boat and vehicle traffic, etc.) However, this shift in inputs is clearly variable (as shown by the decreased values in 2005 and 2006) and not currently of sufficient magnitude to result in a statistically significant increase in concentrations of PAH parameters. However, the observed potential of such a shift warrants continued sediment hydrocarbon monitoring in the area.

In 2005 and 2006, only eight of the 23 previously sampled Northstar stations were sampled for surficial sediments. The differences in the pyrogenic to petrogenic ratio for this subset of Northstar stations were evaluated; the 2005 - 2006 pyrogenic to petrogenic ratio was not significantly different from 1999 or 2000 ratios but was significantly lower than the 2002 and 2004 ratios. However, it is uncertain if this reduction in the pyrogenic to petrogenic ratio was throughout the Northstar region due to the limited Northstar sampling in 2005 and 2006.

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 ANIMIDA and cANIMIDA surficial sediments and source samples (Figure 4-25) reveals that the source composition of PAH in the Northstar 2000, 2002, and 2004 - 2006 sediments is in the same range as the 1999, 2000, 2002, and 2004 - 2006 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 4-25). 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 4-26, 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 in the sediments versus the crude oils and provides another 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 sediments is further supported by a Total PAH less perylene versus silt + clay regression plot for all the 1999, 2000, 2002, and 2004 - 2006 sediment data. In this plot (Figure 4-27) 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 sediment 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, 2002 and 2004 samples versus the BSMP and Liberty 2000, 2002, and 2004 samples resulted in no significant difference for all bulk hydrocarbon parameters and most of the diagnostic ratios. The results of this analysis are further illustrated by a PAH regression plot (Figure 4-28) which shows overlap between the regression lines and 95% prediction intervals (i.e., no significant difference) for the Northstar, BSMP, and Liberty sediments for 2004 - 2006.

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 which resulted in a positive Northstar and Northstar/Construction effect (i.e., a significant increase in these parameters associated with Northstar; Table 3-11). 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 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; Figure 4-4 and 4-5), 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 4-29, $R^2 = 0.93$) 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 six stations fall outside the prediction intervals (4A – all years but 2005, L08 in 1999, N11 – two years, 1A in 2005, 2G in 2005, N14 in 2005 and 6B in 2006). Sediments from stations N11 and N14 appear to be slightly enriched in perylene, possibly due to the proximity to the Kuparuk River, which contains sediments rich in perylene. Station 1A sediments also appear to be enriched in perylene. Station 4A and 2G 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 after 1999 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). However, subsequent analysis of “source material” from the Kuparuk river gravel mine (borrow pit) revealed results similar to the previously analyzed Kuparuk River sediments.

The most likely explanation of the three is that the Northstar surface sediments were depleted in hydrocarbons in 1999. The organic analyses and resulting statistical comparisons of the 1999, 2000, 2002, and 2004 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 six-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, 2002, and 2004 - 2006 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 and regional distribution.

4.1.3 Metals

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 cANIMIDA study were obtained for surface sediments collected during 2004, 2005 and 2006. Metal data also are available for sediment cores collected during 2005 and 2006. The patchwork of metal concentrations described in the Results section can be normalized reasonably well by plotting metal values versus concentrations of the major element Al. Concentrations of trace metals generally correlate well with concentrations of Al because concentrations of both Al and most metals are very low in quartz sand or carbonate shell material and much higher in fine-grained aluminosilicates. Aluminum is rarely introduced by anthropogenic activities and is present at percent levels in most sediment relative to part per million (ppm) levels for trace metals. Thus, for this study, Al provided a valuable normalization tool that incorporated the metal controlling variables of grain size, organic carbon content and mineralogy. In the ideal case (e.g., Figure 3-8), a good linear correlation will be observed between concentrations of a trace metal and Al. Significant, positive deviations from this linear trend, as explained in more detail below, can be used to identify metal contamination. Plots of trace metal concentrations versus Al have been used in various forms for many years to identify sediment metal contamination (e.g., Bruland et al., 1974; Trefry et al., 1985; Schropp et al., 1990).

As a product of the ANIMIDA program, Trefry et al. (2003) used metal data for 1999-2002 from the coastal Beaufort Sea to produce a series of metal versus Al plots that will be used in this report as templates for identifying possible metal contamination or deviations from previous observations. A linear regression and a 99% prediction interval were calculated for each of the metal versus Al plots using the 1999-2002 data. However, these templates were developed without sediments from Camden Bay (the 1 and 2 series of stations) or from Harrison Bay (the 7 series of stations) or from a deeper water station (L22) because these areas were not sampled during the ANIMIDA study (1999-2002). In the paragraphs below, the metals data for 112 surface sediments studied during the cANIMIDA program (2004-2006) will be evaluated to identify possible metal contamination. No large anomalies in metal concentrations on the metal/Al plots or high metal values were observed during this study. However, 44 of 1792 metal concentrations (~2.5% of the data points) in surface sediments plotted above the upper prediction intervals on the respective metal versus Al graphs (Table 4-1). Eleven of these anomalies are believed to be due to the presence of a trace amount of a natural metal sulfide mineral (stations N14 and N15) as discussed in detail below. A similar anomaly was observed at nearby station 5D in 1999 and no explanation for this anomaly was given at that time. An additional 16 anomalies were found outside the cANIMIDA study area, either far to the west in Harrison Bay or to the east in Camden Bay. Thus, a total of about 17 minor anomalies on the metal versus Al graphs (0.9% of data points) were identified in the cANIMIDA area; these results also will be discussed in more detail below. In a subsequent section, the metal data will be evaluated with respect to possible adverse biological effects.

A plot of Al versus Cr from the ANIMIDA program (Figure 4-30a) shows the strong positive relationship observed for the 1999-2002 data. The good linear fit for Al versus Cr in Figure 4-30a is consistent with mixing of relatively uniform composition, metal-rich aluminosilicate phases with metal-poor sand and shell. Chromium concentrations in natural sediment from the ANIMIDA study area are predicted to follow the trend presented in Figure 4-30a. Concentrations of Cr for 2004 and 2005 correlated well with Al (r = 0.94) and all of the 2004 and 2005 data plotted within the 99% prediction interval established previously using the 1999-2002 data (Figure 4-30b).

Sediments from five stations (7A, 6H, N03, WD and L22) sampled during 2006 had Cr concentrations that plotted above the upper 99% prediction interval on Figure 4-30b with a maximum total Cr concentration among these five stations of 89 μg/g at station N03. Concentrations of Cr were previously reported to be elevated at station 7A in Harrison Bay (Boehm et al., 1990; Trefry et al., 2003) and were elevated throughout the sediment core collected during 2006 at station 7A, as described below. Station 6 H was not sampled during

1984-1989 or 1999-2006; however, the station is located in a nearshore location in the eastern reaches of Harrison Bay that is similar setting to station 7A. Crecelius et al. (1991) noted elevated levels of Cr in eastern Harrison Bay (BSMP stations 7A, 7B and 7G) and western Camden Bay (BSMP station 2E) with a maximum total Cr value in that study also at 89 µg/g. At an extreme, Snyder-Conn et al. (1990) previously found Cr levels as high as 331 µg/g adjacent to a mud discharge near Cross Island. This extreme value is most likely due to the presence of a chromium lignosulfonate additive in the drilling mud (Snyder-Conn et al., 1990). This additive is no longer used in drilling mud mixtures. Thus, the 2006 Cr anomalies may be from relict anthropogenic inputs; additional discussion about station 7A follows in the section on sediment cores. For reference, the Cr/Al ratio for suspended sediments from the Colville River (Figure 4-30a) does not support elevated Cr levels in sediment carried into Harrison Bay from upland locations.

Concentrations of Fe also were elevated at stations 6H, N03, WD, and L22 (Figure 3-8), four of the same stations where Cr concentrations plotted above the upper prediction interval on Figure 4-30b. Station L22, at a water depth of 29 m, was most distant from land and in the deepest water sampled during either the ANIMIDA or cANIMIDA studies. Based on results for Fe (Figure 3-8a), V (Figure 3-8b) and As (Figure 4-31c), the observed Cr enrichment in sediment from station L22 is believed to be related to scavenging by fine-grained iron oxides, a natural phenomenon. Anomalies for Fe, V and Cr also were found for 2006 station N03 (water depth 12.3 m, located ~1 km north of Northstar Island) and these anomalies also may be a natural phenomenon. The slight Cr enrichment (<10% above upper prediction interval with total Cr of 84.2 µg/g) in the sample from West Dock (WD) is noteworthy from the perspective of recommending resampling in the busy area of West Dock in the future.

Only one anomalous point was observed on the Ni versus Al plot for 2004-2006 (Figure 4-32a). The Ni anomaly was for 2005 station N14. Anomalies also were found for Fe, Hg, Ag, Zn, Cd, Pb, Cu, Co and As for 2005 station N14 (Figure 3-8 and 4-32). Station N14, located in 3.7 m of water adjacent to the western end of Stump Island, also was sampled in 1999, 2000, 2002, 2004 and 2006. Small anomalies only for Ag (1999) and Cu (2000) had been previously observed for station N14. However, at station 5D, located at a water depth of 1.6 m near the eastern end of Stump Island, anomalies for the same 10 metals were identified in one of three samples collected in 1999 sample (pre-Northstar development). No anomalies were found at station 5D in sediments collected during 2000, 2002 and 2004.

The absolute values for each of the anomalies for stations N14 (2005) and 5D (1999) were calculated by taking the measured metal concentration and subtracting the concentration calculated for a given metal using the measured Al concentration with the linear regression equations for the 1999-2002 metal versus Al plots. These data are presented in Table 4-2 and plotted in Figure 4-33). A strong positive relationship (r = 0.99) was observed between the concentrations of excess metals for station N14 versus 5D (Figure 4-33). No anomalies were identified for Ba, Be, Cr, Mn, Sb, Tl or V in the sediments from station N14 (2005) or 5D (1999). The 10 metals with positive anomalies on the metal versus Al plots for station N14 are commonly found to occur together in Fe-rich sulfide minerals (Bendel et al., 1993; Halbach et al., 1998). Conversely, the metals with no observed positive anomalies are not commonly found in Fe-sulfide deposits (Bendel et al., 1993; Halbach et al., 1998). The excess metal concentrations calculated from the positive metal anomalies on the metal versus Al plots were extrapolated to pyrite with average of 45% Fe and the resulting values are in reasonable agreement with published values for the various trace metals in pyrite (Table 4-2). Thus, the metal anomalies are believed to be due to the presence of a minor amount (1.5-2.5%) of naturally occurring iron sulfide in the sediments from stations N14 (2005) and 5D (1999). The source of the anomalies for 10 different metals is not believed to be due to a manufactured alloy because the levels of impurities are higher than expected in typical Fe, Cu or Zn alloys. At present, the observed metal anomalies in 2 out 244 surface sediments collected between 1999 and 2006 seems to be explained by the presence of minor amounts naturally occurring iron sulfides near Stump Island. Sand and gravel islands, like Stump Island, are natural deposition sites for heavy minerals such as pyrite. No other similar sites were sampled during the cANIMIDA project to replicate this finding. This pyrite observation does challenge users of metal versus Al plots to be alert to possible, and most likely occasional, incorporation of some naturally occurring mineral in a sediment sample.

Only the data point for station N14 (2005) was anomalous on the Ni versus Al graph (Figure 4-32a); however, more than one point was above the upper prediction limit for each of the other metals that were enriched at station N14 (2005). For Ag, the sample from station N15 (2004) also was enriched (Figure 4-32b). Station N15 is sited in shallow water (2.4 m) adjacent to Egg Island, just west of Stump Island. The anomaly for Ag at station N15 (2004) is small relative to the anomaly at station N14 (2005). Thus, if the presence of a trace sulfide mineral is responsible for the very small Ag anomaly, no detectable anomalies would be found for the other related metals.

A minor anomaly for Hg was observed at station L07 (2004, Figure 3-32c). Small Cu anomalies also were observed at station L07 for 2004 and 2005 (Figure 4-31a). Brown et al. (2004) reported petroleum contamination at nearby station L08 and suggested that it may be a remnant of past drilling in the area. The trace metal anomalies plot at <10% above the upper prediction interval and are considered to be consistent with the statistical boundaries of a 99% prediction interval.

A Zn anomaly for the 2004 sample from station N01, located 4 km north of Northstar Island, is unique for that location; however, the absolute concentration of Zn at 93.9 μg/g is well below typical concentrations of Zn at other locations in the study area (Figure 4-34a). In addition to the various anomalies described above, three additional anomalies were found for Cd, one for Pb, one for Cu, two for Co and one for As (Table 4-1). During the ANIMIDA study (1999-2002), a few minor anomalies in concentrations of Pb and Hg were observed and one data point each for Zn, Ag and Be plotted above the respective upper prediction intervals. One anomalous data point for Be and none for Sb were found in the 2004-2006 samples. None of these scattered points follow any trends that are simple or seem to be of concern at this point. As in the past, these anomalies will be followed up during any future sampling. An overview of possible metal contamination in the cANIMIDA area will be presented in the Conclusions.

Barium has been used historically as a sensitive indicator for the presence of petroleum drilling mud in sediment because barite ($BaSO_4$) is such a common and major ingredient (e.g., Chow et al., 1978). The graph for Al versus Ba for the 2004-2006 data shows 4 of 112 data points as positive anomalies on the Ba versus Al plot (Figure 4-35a). Barium anomalies were previously reported for stations 7A and 7G by Trefry et al. (2003) for samples collected in 1989 and are consistent with exploratory drilling and drilling residues in the area (Snyder-Conn et al., 1990; Crecelius et al., 1991). A detailed record of Ba contamination is described for the sediment core from station 7A below. Barium anomalies at stations N06 and 6H also may be due to minor remnants of drilling discharges. The largest observed anomaly of 549 µg/g at 2006 station 5H [anomaly = 863 µg/g – (2.73% Al (72.9) + 115) = 549 µg/g] is equivalent to a residue of 0.1% barite from drilling mud with 53% Ba (Trefry et al., 2007).

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. For general use, the guidelines have been applied as follows: adverse biological effects are "rarely" observed when metal levels are <ERL, "occasionally" observed when contaminants are present at levels between the ERL and ERM and "frequently" observed when concentrations are >ERM.

Six (Ag, As, Cd, Hg, Pb and Zn) of the 16 metals investigated during this study have been assigned realistic ERL and ERM concentrations by Long et al. (1995). These guidelines are continuingly evolving as demonstrated by the extensive efforts of Field et al. (1999) to validate values for Hg, Pb and Zn. Some difficulties still exist with ERL values for Cr, Cu and Ni as the values for the ERL (Long et al., 1995) are lower than typical continental crust (Wedepohl, 1995) and are thus not discussed here. Overall, the sediment quality data should be used primarily as guidelines at this time. No concentrations of any of the six metals exceed their respective values for the ERM (Table 4-1). Therefore, adverse biological effects are not expected to be a frequent occurrence at any station in the study area as the result of trace metals. Furthermore, no concentrations of the six metals from this study in 2004 exceeded the respective values for the ERL (Table 4-1) and thus adverse biological effects from these six metals would be rare.

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.

4.2 Sediment Cores

The summer 2005 - 2006 field sampling programs successfully obtained core samples suitable for age dating from nine of ten stations (Figures 2-2 and 2-3). In this section of the report the results of the sediment core analyses will be further evaluated for general trends and relationships, and comparisons of the pre- and post-development results will be discussed.

4.2.1 Geochronology

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

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

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

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

4.2.1.1 Geochronology of Hydrocarbons

The hydrocarbon dataset for the core sediments from 2005 and 2006 include SHC, PAH, and S/T data from ten core samples collected. As noted previously, nine of the cores have reliable deposition rates and detailed geochronology. All ten cores were all analyzed for organic parameters to further expand our knowledge of the historical record of hydrocarbons in the study area. Even though we cannot accurately estimate the historical timeframe of some of these sediments, we do know that they primarily represent pre-development (i.e., pre-1970) sediment levels and are likely much older. These data are assessed in part by using a suite of key diagnostic parameters and ratios (Table 3-6) that are useful in describing hydrocarbon trends in the marine environmental (Boehm et al., 2001a; Brown et al., 2002).

To facilitate the presentation and discussion of the organics data, GC/FID chromatograms from the SHC analysis, PAH distribution plots, and triterpane extracted ion chromatogram profiles (EICPs) for representative core samples and selected source samples are presented in Figures 4-4 through 4-7 and Figures 4-36 through 4-39. 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)
- Canning River sediment – 2002 (Figure 4-7)
- Station N26 (0-2 cm) – Northstar sediment core station - 2005 (Figure 4-36)
- Station N26 (8-10 cm) – Northstar sediment core station - 2005 (Figure 4-37)
- Station 1C (0-2 cm) – BSMP sediment core station - 2005 (Figure 4-38)
- Station 1C (28-30 cm) – BSMP sediment core station - 2005 (Figure 4-39)

Saturated Hydrocarbons

In general, the sediments in the core samples (GC/FID chromatograms in Figures 4-36 through 4-39) exhibit a mixture of primarily terrestrial biogenic hydrocarbons and lower levels of petroleum hydrocarbons (Figure 4-4 shows a North Slope Crude Oil for reference). This assemblage is clearly dominated by plant wax normal (i.e., straight-chain) alkanes in the n-C27 through n-C33 carbon range. This is further demonstrated by carbon preference index (CPI) values that range from 4.6 to 6.9 for all sediment core samples, which is characteristic of sediments influenced by terrigenous plant inputs (Wakeham and Carpenter, 1976; Boehm, 1984).

Traces of lower molecular weight alkanes (LALK; n-C9 through n-C20 alkanes), indicative of petroleum sources, are visible as more minor components relative to the plant wax alkanes in the core sediments and in the Colville River sample for comparison (Figures 4-6 and 4-36 through 4-39). This natural "background" petroleum alkane signature in the sediments has been well documented by previous studies in the region, including earlier ANIMIDA work (Boehm et al., 1987; Steinhauer and Boehm, 1992; Boehm et al., 1990; Boehm et al., 2001b; Brown et al., 2002).

Polynuclear Aromatic Hydrocarbons

The PAH distributions for the core sediments show that the PAHs are primarily of a combined fossil fuel origin (i.e., petroleum and coal) and lesser contributions of pyrogenic or combustion-related compounds (e.g., 4-, 5-, and 6-ring PAHs), with a somewhat variable biogenic component (perylene). The petrogenic PAHs account for approximately 90 percent of the Total PAH less perylene throughout the core samples. Perylene was abundant in the core sediments, and often the most abundant single PAH compound in the overall PAH distribution (Figures 4-36 through 4-39). Perylene is a naturally occurring PAH formed during early diagenesis in sediments from biological source precursors (Wakeham and Farrington, 1980; Wakeham et al., 1980). Perylene has also been shown to increase with depth in sediment cores, as historical diagenesis increases (with time) in deeper core sections (Wakeham and Farrington, 1980). It may also be found in crude oil at very trace concentrations. Perylene was generally found at comparable concentrations in the Northstar and BSMP surficial sediments, but several cores show a clear trend in increasing perylene concentrations with depth (e.g., core 7A – Figure 3-16), likely a product of early diagenesis in the deeper sediments.

The PAH distributions are generally similar in all the cores at surface and at depth, and are characterized by the presence of a full suite of petroleum PAHs similar to the PAH distribution seen in the North Slope Crude oil. As noted previously, perylene dominates the overall PAH distribution as one of the most abundant individual PAHs in the samples. Perylene is found at equal or greater relative abundance in the river sediments and peat (Figure 4-6 and 4-7), which supports the relationship of the rivers as a source of the hydrocarbons in the nearshore sediments, as noted previously for the SHCs. Low levels of 4-, 5-, and 6-ring combustion PAHs are also present, but are generally only a minor component of the overall PAH composition in the sediments.

Triterpanes

In general, the triterpane distributions in the sediment core samples are indicative of a petroleum source (Figures 4-36 through 4-39), 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 the core sediment samples are composed of a mixture of these characteristic petroleum triterpanes, along with recent organic or biogenic markers such as diploptene (the large peak to the right of the T21 and T22 doublet) and other unnamed triterpanes. In addition, the relative abundance of T22 at greater levels than T21 in most samples provides further evidence of substantial recent organic matter inputs to the sediments.

The triterpane distributions of the Colville River (Figure 4-6), Sagavanirktok River, and Kuparuk River sediments have recent organic matter and petroleum hydrocarbon triterpane patterns with some similarities to those observed in the sediment samples. This similarity suggests that there is a strong link between the river hydrocarbon sources – mostly erosional inputs of regional rock (shale) coal, peat, etc. (i.e., natural background) and the sediments over time.

Comparisons of Hydrocarbons over Time

The key diagnostic organic parameters (Table 3-6) calculated for sediment core sections are important in examining the historical trends of hydrocarbons in the sediment record. As discussed earlier, reliable geochronology could be established for nine sediment cores Comparisons of selected key diagnostic parameters in the form of core profiles (Figures 3-11 through 3-20), in conjunction with simple statistical treatments, allow an assessment of pre- and post-development hydrocarbon trends over time.

In general, comparisons of the core profiles for key diagnostic organic parameters for all of the cores do not show any clear trends that would indicate an increase in petroleum hydrocarbons over time. The core profile from stations 7C where geochronology could not be established (likely representing a historical pre-development record) is generally uniform and shows little variability of the hydrocarbon parameters over time. The cores for which pre- and post-development dates can be established generally show uniform distributions of key parameters throughout the cores, with some variability in specific core sections. However the overall composition of the three classes of analytes analyzed (SHC, PAH and biomarkers) are all similar throughout the cores and are consistent with the regional background hydrocarbon sources identified in the surface sediments (Figures 4-36 – 4-39).

In examining hydrocarbon trends in all of the cores, one useful technique (discussed earlier) involves examining the relationship between the organic parameter of interest and TOC content or alternatively, the percent silt plus clay or perylene content. The natural background concentrations of organics in the study area have been shown to co-vary as a function of perylene content. 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. A plot of all the 2005 and 2006 sediment core data for total PAH minus perylene versus perylene is shown in Figure 4-40. In this plot a regression and 95% prediction intervals are shown for all data, where the regression defines the natural geological/geochemical background of all the sediments. The plot shows that most of the core samples fall within the 95% prediction intervals, indicating that the 2005 and 2006 core sediment samples are generally not different in Total PAH content from the historical natural background of the region.

Another evaluation of the sources of PAH in the core samples was performed using a dibenzothiophene-to-phenanthrene source ratio plot, which has been used earlier is this study to investigate PAH sources. An examination of the source plot for all the 2001, 2005 and 2006 core sediments and additional source samples (i.e., field oils, river sediments and peat) is shown in Figure 4-41, and reveals that the source compositions of PAH in the core samples are generally similar (i.e., the data points cluster together on the plot) with some variability that can be attributed to local riverine source influences. For example, data points from core 2A (just east of the Canning River delta) tend to cluster below and to the left of the main grouping of data points and near the Canning River sediment data.

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]) of all the 2001, 2005 and 2006 core samples and sources samples (Figure 4-42) shows that the core data fall well within the range defined by the cluster of all of the surface sediment samples from the area (Figure 4-26). This provides further evidence that the sediment core data are representative of the regional hydrocarbon background, and do not indicate any substantial influence from post-development anthropogenic hydrocarbon inputs from the Prudhoe Bay area.

Overall, the organic analyses of the sediment cores collected during 2005 and 2006 have provided an important historical perspective on hydrocarbons in the sediments from the study area. The results have shown that the concentrations and sources of hydrocarbons are generally uniformly consistent over the past 50 or more years and represent a regional background assemblage. For most organic hydrocarbon parameters, there are no significant increases (after geochemical normalization) of hydrocarbons in the sedimentary record post oil and gas development in the Prudhoe Bay area.

4.2.1.2 Sediment deposition and the temporal distribution of sediment metals

The historical record of metal levels in sediments from the cANIMIDA study area was developed from 14 cores collected during 2005 and 2006. As in the ANIMIDA program, collection of sediment cores suitable for age-dating was 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 a few cores were viable for establishing a geochronology over the past 50 to 100 years using both ^{137}Cs and excess ^{210}Pb. In many instances, extremely low levels or no detectable amounts of excess ^{210}Pb (<0.2 dpm/g) or ^{137}Cs (<0.02 dpm/g) were found, even in the top 0.5 cm of sediment. Such observations are consistent with previous reports that characterize this coastal area as a net erosional environment (Reimnitz and Wolf 1998).

As reported earlier, past efforts to reconstruct recent geochronology for coastal sediments from this nearshore area of the Beaufort Sea (Weiss and Naidu, 1986; Naidu and others, 2001) have encountered many of the same difficulties found during the cANIMIDA study. Based on these difficulties with area sediments, a primary goal of the geochronology effort for the cANIMIDA 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 sediments that were deposited post-development.

Concentrations of trace metals were determined for a total of 81 samples from seven cores collected in 2005 (N26, PB1A, L17B, BP01, E01, 1C and 2A) and five cores collected in 2006 (N17, L22, 7A, 7C and 7E). Some variability in concentrations of metals was observed in each core, mainly due to variations in amounts of fine-grained sediment. Forty-seven of 1296 metal concentrations (3.6% of the data points) plotted above the upper prediction intervals developed for the ANIMIDA study area (Table 4-3). Thirty-five of the 47 data points were for sediments collected in Harrison Bay (the 7 series of stations) and 3 of the 47 data points were for station 2A in Camden Bay. Both Harrison Bay and Camden Bay are not part of the original ANIMIDA study area, but were part of the original Beaufort Sea Monitoring Program. The remaining 9 data points were from five different cores in different sediment layers: (1) station PB1A at 3-3.5

cm for Ag, Cd, Cu and Ni, (2) station L17B at 3-3.5 cm for As, (3) station N17 at 28-30 cm for As and Hg, (4) station N26 at 16-17 cm for Fe, and (5) station BP01 at 9.5-10 cm for Zn (Table 4-1 and Figures 4-43 through 4-47). These 9 data points plot relatively close to the upper prediction interval and do not reveal any striking anomalies that can be clearly tied to anthropogenic sources. The anomalies in the PB1A core from Prudhoe Bay may well be linked with a trace sulfide mineral as described previously for the more discernible anomalies at stations N14 (2005) and 5D (1999).

Twenty of the 38 data points from outside the immediate cANIMIDA study area that plotted above the upper prediction interval were for Ba, 8 from Camden Bay and 12 from Harrison Bay (Table 4-1). The expanded scale graph (Figure 4-48) shows that the highest Ba anomalies in Camden Bay were at 19-20 cm for both stations 1C and 2A with generally lower anomalies toward the top of each core. Based on the ^{137}Cs data, depths below 17 cm at station 1C and below 9 cm at station 2A were deposited prior to 1950 (Figure 3-23). The data for excess ^{210}Pb are scattered in each core; however, they support a pre-1950 date for the 19-20 cm sections of the cores. At station 2A, but not 1C, the concentration of TOC is >1.5% below 18 cm in the core. In the core from station 1C, the TOC is about 0.5% throughout the core (Figures 3-22 and 3-23). The source of the Ba anomalies is not clear at this time; however, diagenetic remobilization, diffusion and reprecipitation of Ba within the sediment column have been observed in sediments (e.g., McManus et al., 1994; Torres et al., 1995). Such a process complicates the identification of drilling mud residues and requires additionally support for such determinations as described below for Harrison Bay.

In contrast with the observations in Camden Bay, the Ba anomalies in Harrison Bay (Figure 4-49) are found at depth in the core that can be best explained by the presence of barite residues from drilling muds. For example, a vertical profile for the Ba/Al ratio for the sediment core from station 7E shows that all 4 samples with significant Ba anomalies are between 2 and 10 cm in the 30-cm vertical section of sediment (Figure 4-50). The maximum anomaly of 396 µg/g [anomaly = 859 µg/g – (4.77% Al (72.9) + 115) = 396 µg/g] dates to about 1988 ± 2 years (Figure 4-50). This anomaly is equivalent to a residue of 0.08% barite from drilling mud with 53% Ba (Trefry et al., 2007). Drilling activity in the area of Harrison Bay sampled during 2006 is within the area of western Harrison Bay where drilling occurred in 1985 and 1986. Furthermore, samples collected in western Harrison Bay during 1989 had Ba anomalies in the top 2 cm of sediment for stations 7A and 7G. The sediment at station G was hard and not penetrable for coring in 2006; therefore, cores were collected at stations 7A, 7C and 7E. The results for Ba in the core from station 7E (Figure 4-50) suggest that the peak concentration from the mid-1980s may have preserved at this site. However, the sediments in the top 6 cm at station 7E contain high levels of TOC at 2-4%; therefore, a diagenetic explanation for the observed Ba profile can not be ruled out. More detailed study of the sediment column is needed to resolve natural from anthropogenic layers of Ba-rich sediment.

Table 4-1. Sites with metal values for surface sediments above the upper prediction interval (UPI) on metal versus aluminum plots and values for Effects Range Low (ERL) and Effects Range Median (ERM) from Long et al. (1995) with results from this study.

Metal	Sites with Values>UPI (of n = 112 samples)	Maximum (this study) (µg/g)	ERL (µg/g)	ERM (µg/g)	Maximum (this study) (µg/g)	Sites with Values>UPI and >ERL
Ag	[N14, 2005] [N15, 2004]	0.44	1.0	3.7	0.44	None
As	**2005 (L07)** **2006 (6G, 7G)** [N14, 2005]	24.9	(8.2)*	70	24.9	**2005 (L07)** **2006 (6G, 7G)***
Ba	**2005 (N06)** **2006 (6H,7A,7G)**	863	None	None	863	N/A
Be	**2004 (5E)** [N15, 2005]	3.6	None	None	3.6	N/A
Cd	**2005 (2G)** **2006 (5A,E02)** [N14, 2005]	0.77	1.2	9.6	0.77	None
Co	**2006 (7A,7G)** [N14, 2005]	13.8	None	None	13.8	N/A
Cr	**2006 (6H,7A,N03,WD,L22)**	99.6	(81)*	370	99.6	(several)*
Cu	**2004 and 2005 (L07)** **2006 (WD)** [N14, 2005]	46.2	(34)*	270	46.2	Three*
Fe	**2004 (N12)** **2006(6G,6H,N03,WD,L22)** [N14, 2005]	3.7%	None	None	3.7%	N/A
Hg	**2004 (L07)** [N14, 2005]	0.113	0.150	0.710	0.113	None
Ni	[N14, 2005]	45.8	(20.9)*	51.6	45.8	[N14, 2005]*
Pb	**2006(6G)** [N14, 2005]	20.1	46.7	218	20.1	None
Sb	None	0.82	None	None	0.82	N/A
Tl	None	0.64	None	None	0.64	N/A
V	**2006(N03,L22)**	155	None	None	155	N/A
Zn	**2005(N01)** [N14, 2005]	136	150	410	136	None

Table 4-2. Concentrations of excess metal in sediments from stations N14 (2005) and 5D (1999) with extrapolated values to pyrite (FeS_2) and reported values for metals in pyrite.

Metal	Excess at Station N14 (µg/g)	Extrapolated Concentration In FeS_2 for N14 (µg/g)*	Excess at Station 5D (µg/g)	Extrapolated Concentration In FeS_2 for 5D (µg/g)*	Typical Values in FeS_2 (µg/g)**
Hg	0.087	3.4	0.150	9.6	-
Ag	0.33	13	0.32	21	25-40
Cd	0.59	23	0.55	35	-
Co	6.8	270	9.5	610	200-600
Pb	9.9	390	10.0	640	100-700
As	15.0	590	16.6	1,070	100-600
Ni	23.4	920	16.5	1,060	-
Cu	33.4	1,310	23.5	1,510	1000-10,000
Zn	44	1,720	26	1,670	1,000-4,000
Fe	11,500	450,000	7,000	450,000	380,000-480,000

* Based on 45% Fe in pyrite.
** from Bendel et al. (1993), Halbach et al. (1998)

Table 4-3. Sites with metal values for sediment cores above the upper prediction interval on metal versus aluminum plots and values for Effects Range Low (ERL) and Effects Range Median (ERM) from Long et al. (1995) with results from this study. Asterisks point out metals with unreliable values for ERL as explained in text.

Metal	Sites with Values>UPI (of n = 81 samples)	Maximum (this study (µg/g)	ERL (µg/g)	ERM (µg/g)	Maximum (this study (µg/g)	Sites with Values>UPI and >ERL
Ag	2005, PB1A, 3-3.5 cm	0.23	1.0	3.7	0.44	None
As	**2005 (L17B 3-3.5 cm)** **2006 (7E 4-4.5 cm)**	23.8	(8.2)*	70	24.9	**2005 (L07)** **2006 (6G, 7G)**
Ba	**2005, 1C, 5 of 7 depths** **2005, 2A, 3 of 7 depths** **2006, 7A, 6 of 7 depths** **2006, 7C, 6 of 8 depths**	975	None	None	863	N/A
Be	**None**	1.8	None	None	3.6	N/A
Cd	2005, PB1A 3-3.5 cm	0.40	1.2	9.6	0.77	None
Co	**2006, 7A, 0-0.5cm** **2006, 7E 4-4.5 cm**	15.4	None	None	13.8	N/A
Cr	**2006, 7A, 6 of 7 depths**	108	(81)*	370	99.6	(several)*
Cu	**2005, PB1A, 3-3.5 cm** **2006, 7E 0.0.5 cm**	41.9	(34)*	270	46.2	
Fe	**2005, N26, 16-17 cm**	3.9%	None	None	3.7%	N/A
Hg	**2006, 7E, 3 of 8 depths**	0.101	0.150	0.710	0.113	None
Ni	2005, PB1A, 3-3.5 cm	47.0	(20.9)*	51.6	45.8	
Pb	**2006, 7E, 2 of 8 depths**	18.1	46.7	218	20.1	None
Sb	**2005, 2A, 3 of 7 depths**	1.02	None	None	0.82	N/A
Tl	**None**	0.82	None	None	0.64	N/A
V	**None**	149	None	None	155	N/A
Zn	**2005, BP01, 9.5-10 cm**	112	150	410	136	None

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.

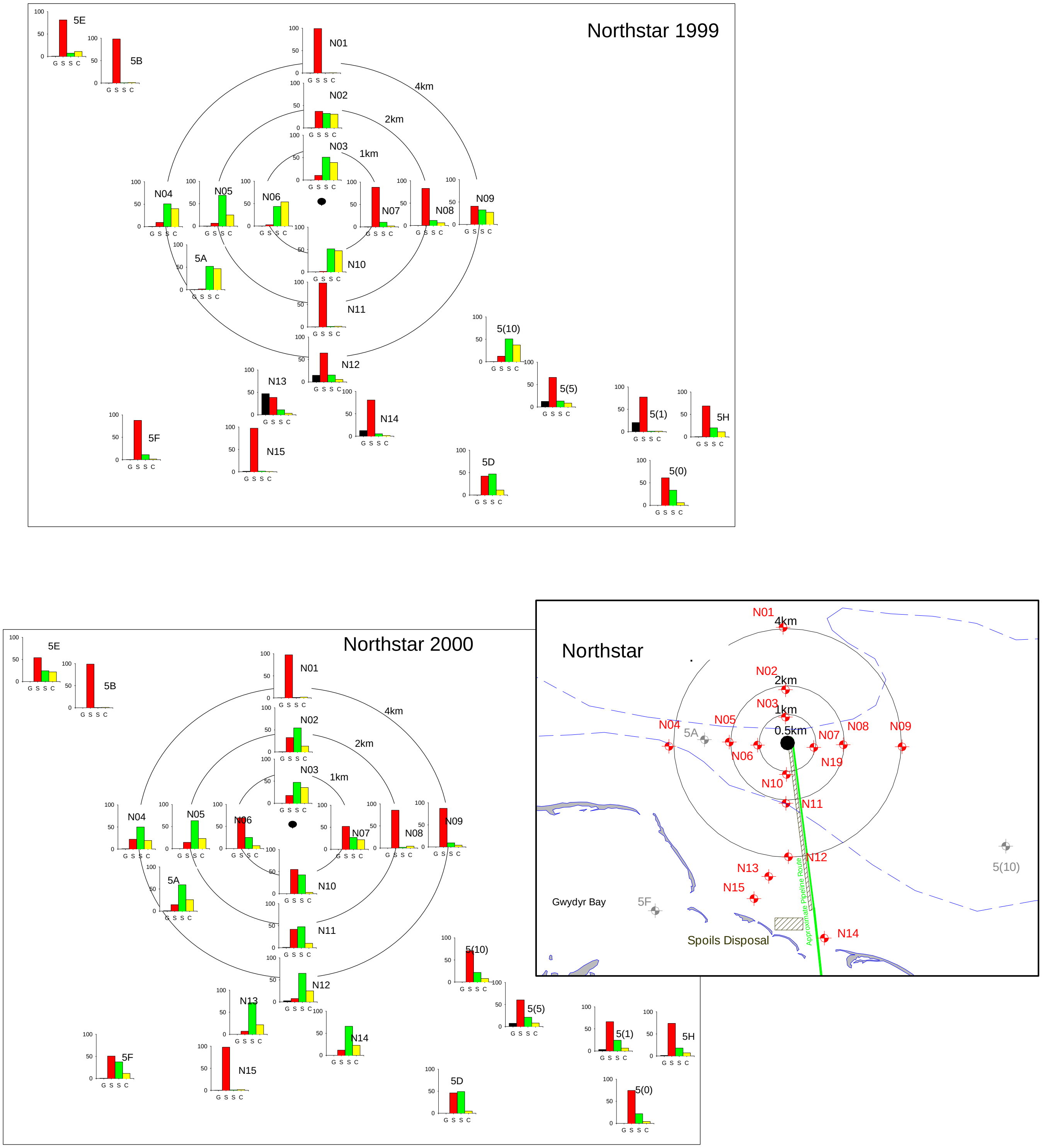


Figure 4-2. Map identifies sampling sites and histograms show grain size distribution as percent gravel (black bar), sand (red bar), silt (green bar) and clay (yellow bar) for sediment samples collected during 2004 and 2002.

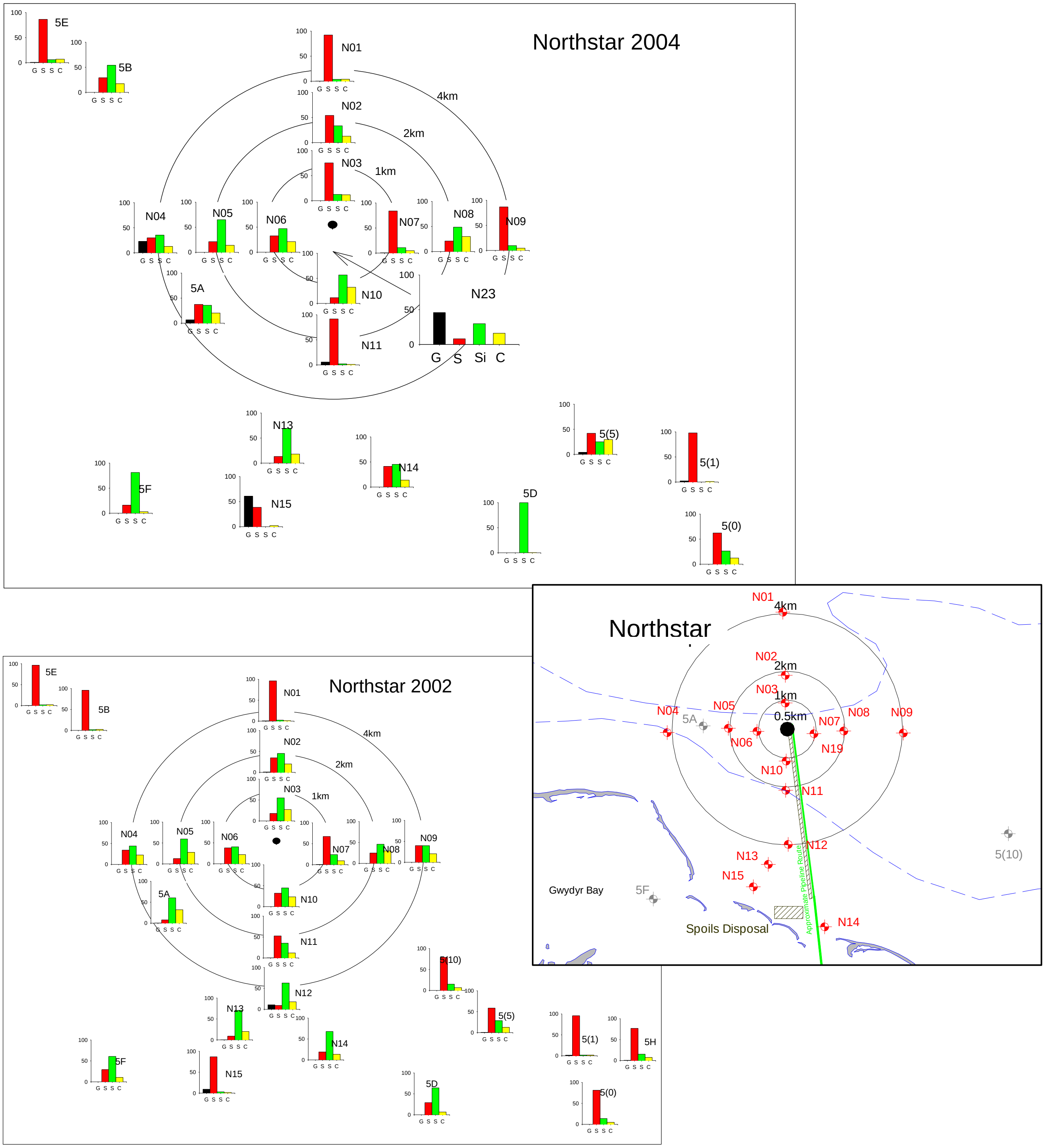


Figure 4-3. Map identifies sampling sites and histograms show grain size distribution as percent gravel (black bar), sand (red bar), silt (green bar) and clay (yellow bar) for sediment samples collected during 2004 and 1999.

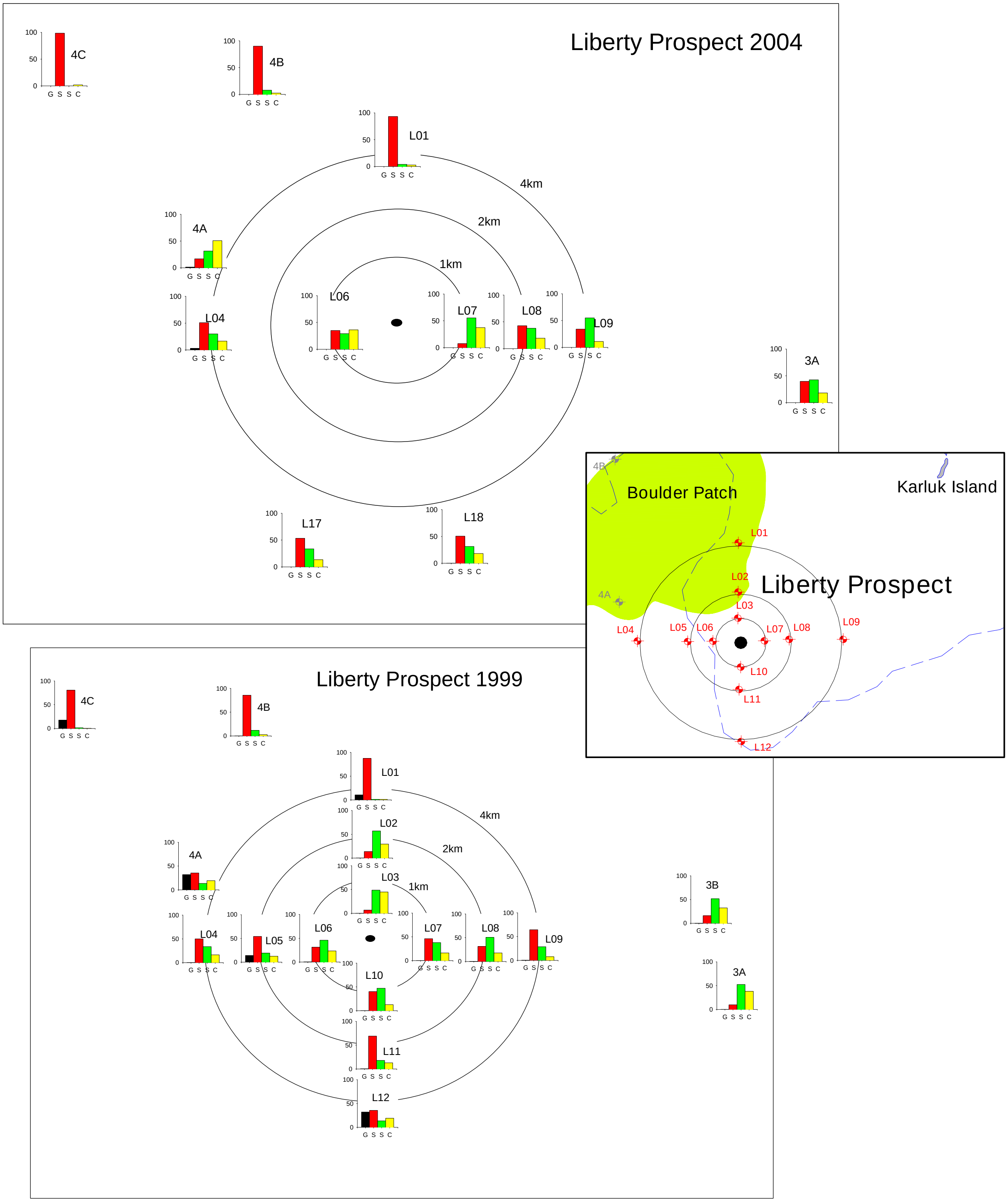


Figure 4-4. North Slope Crude Oil – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).

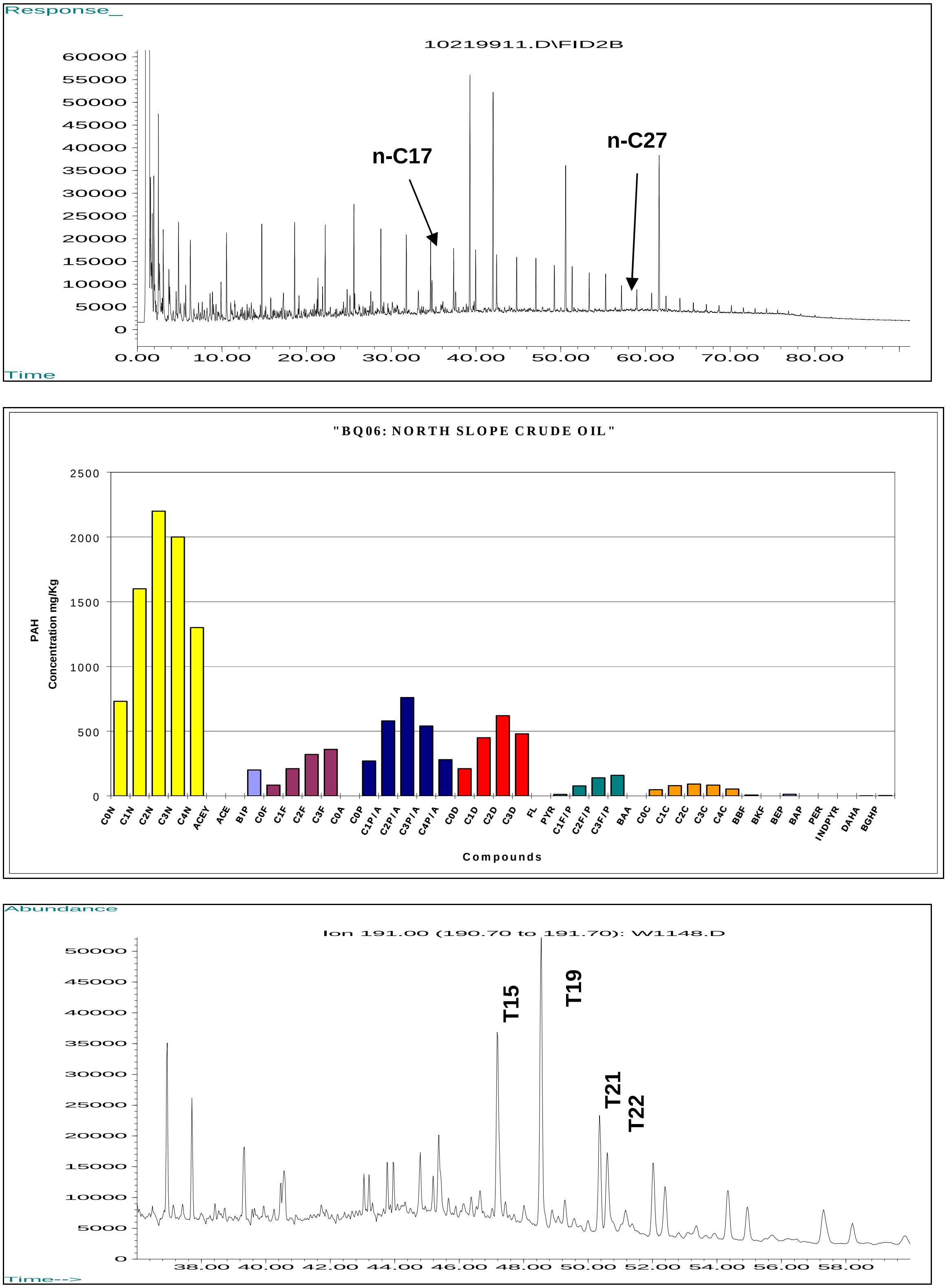


Figure 4-5. Northstar Oil – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).

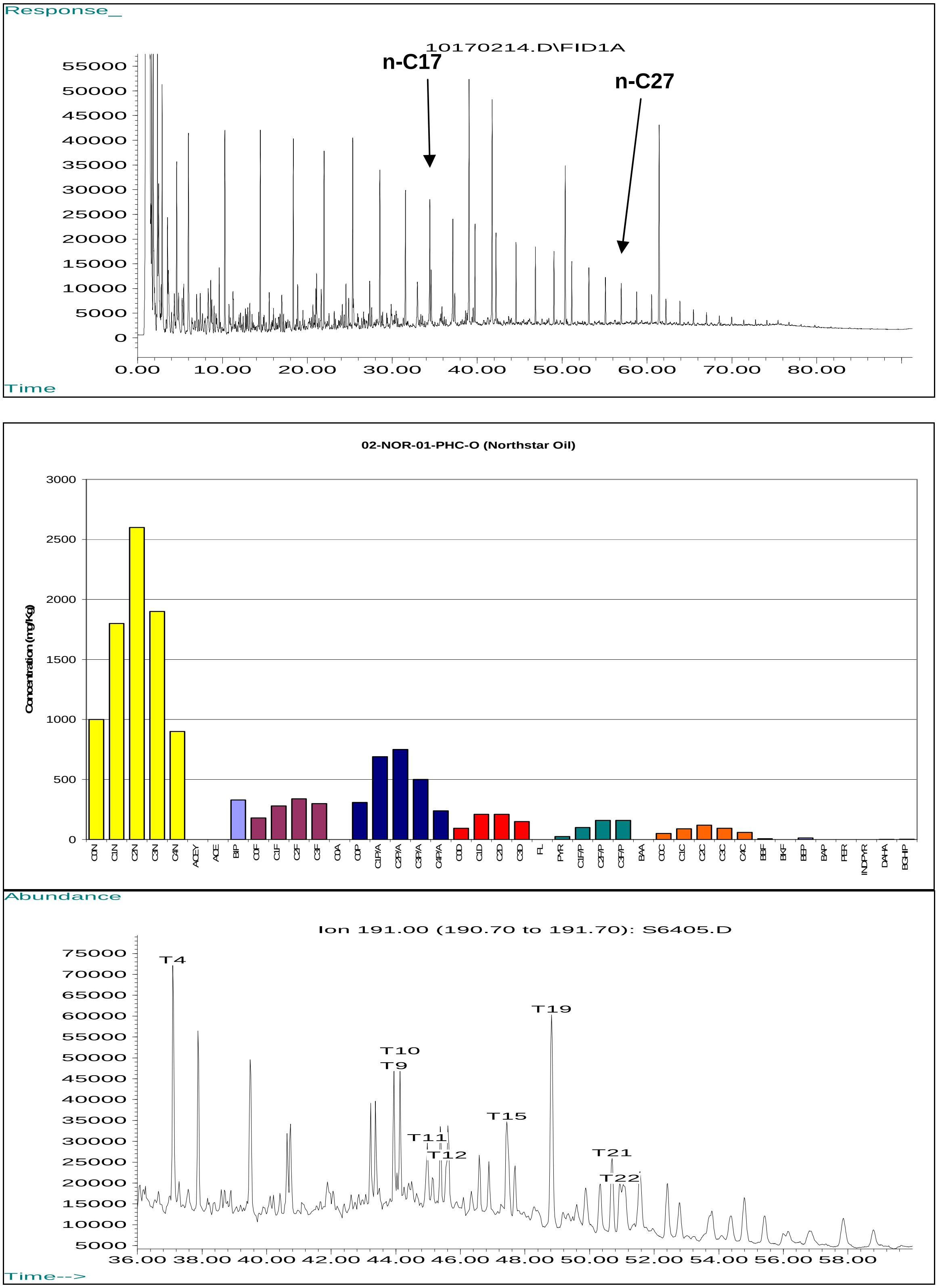


Figure 4-6. Colville River Sediment, Year 1999 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).

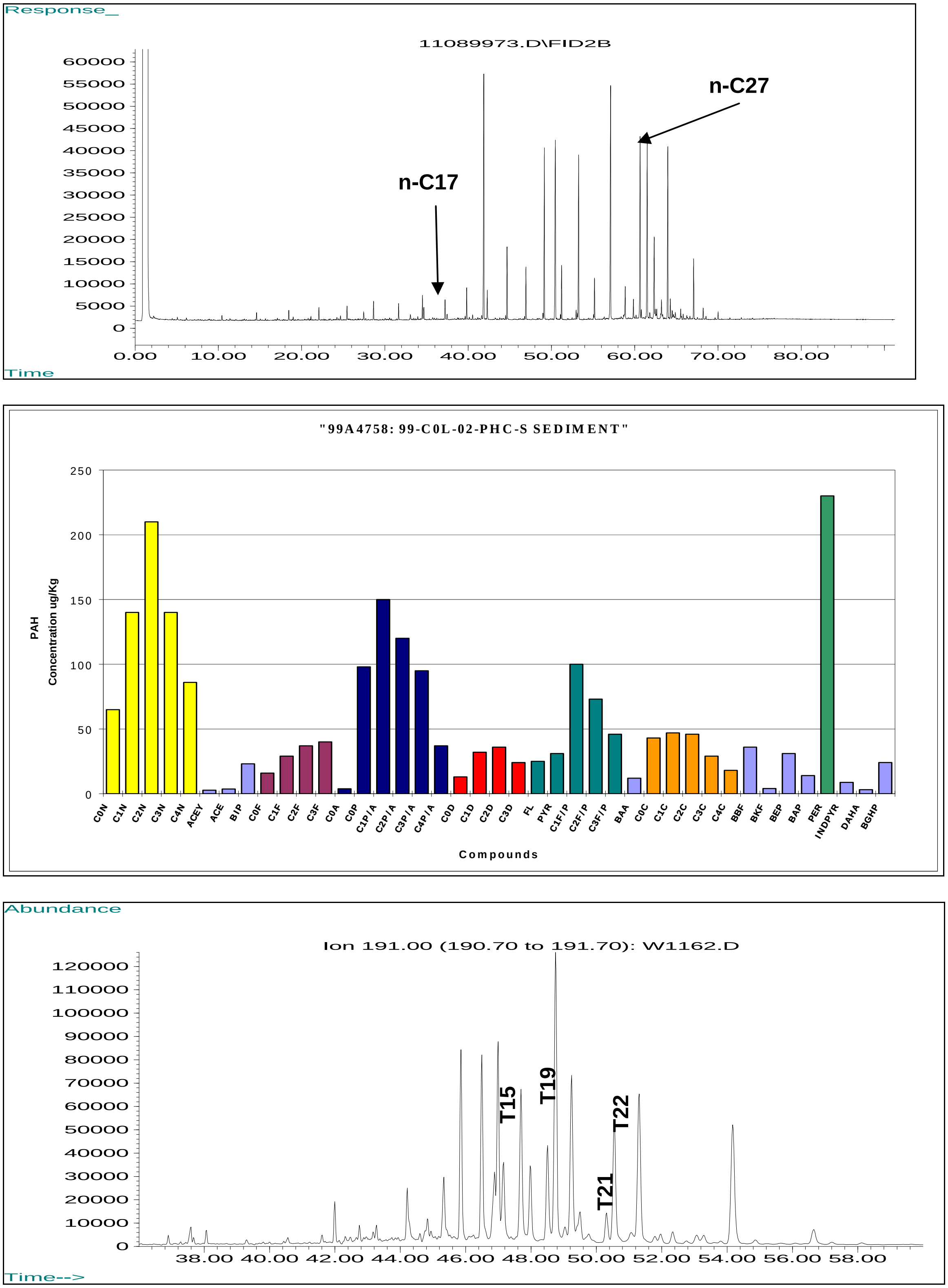


Figure 4-7. Canning River Sediment, Year 2002 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).

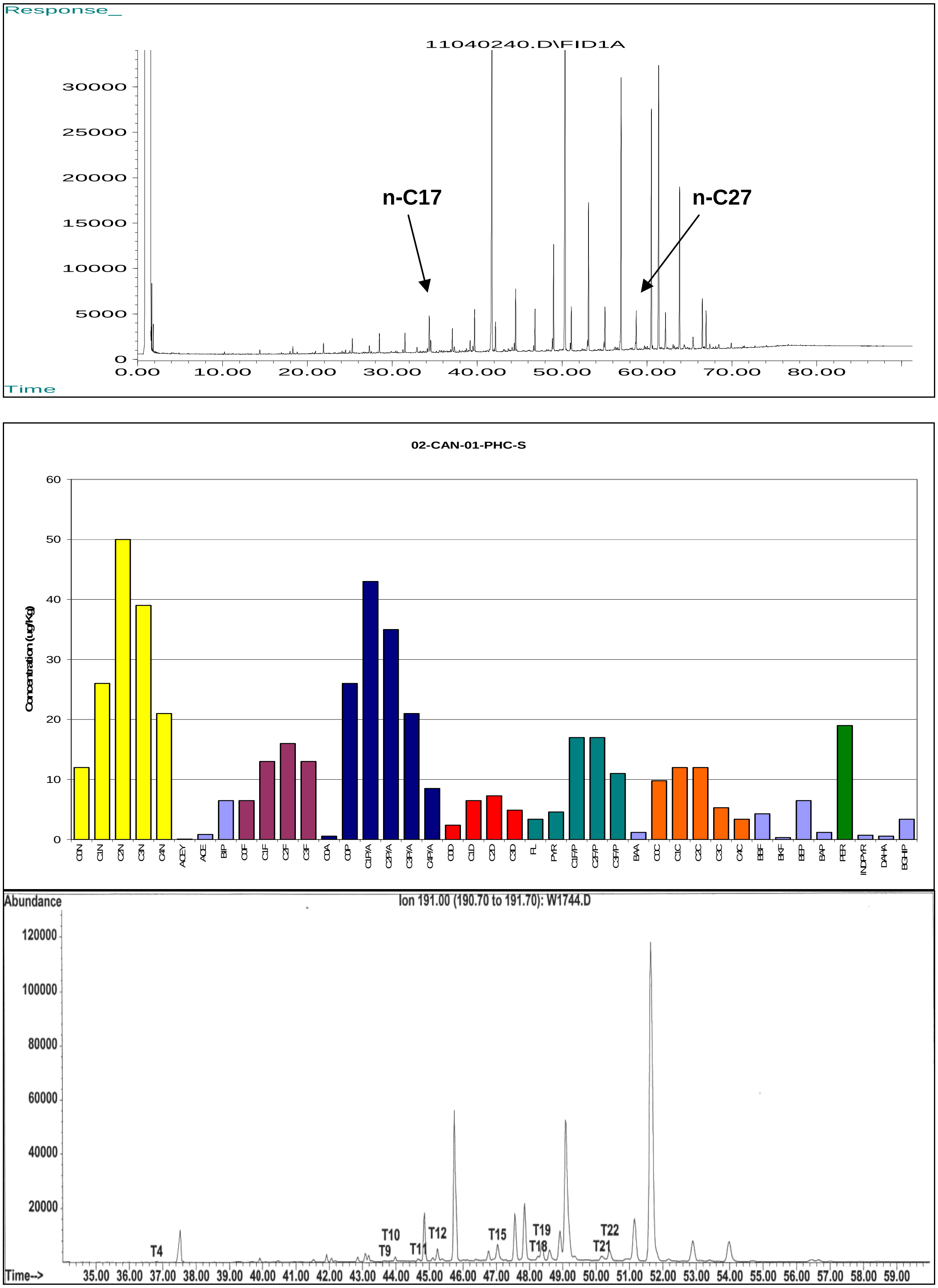


Figure 4-8. Northstar Station 6 Sediment, Year 1999 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).

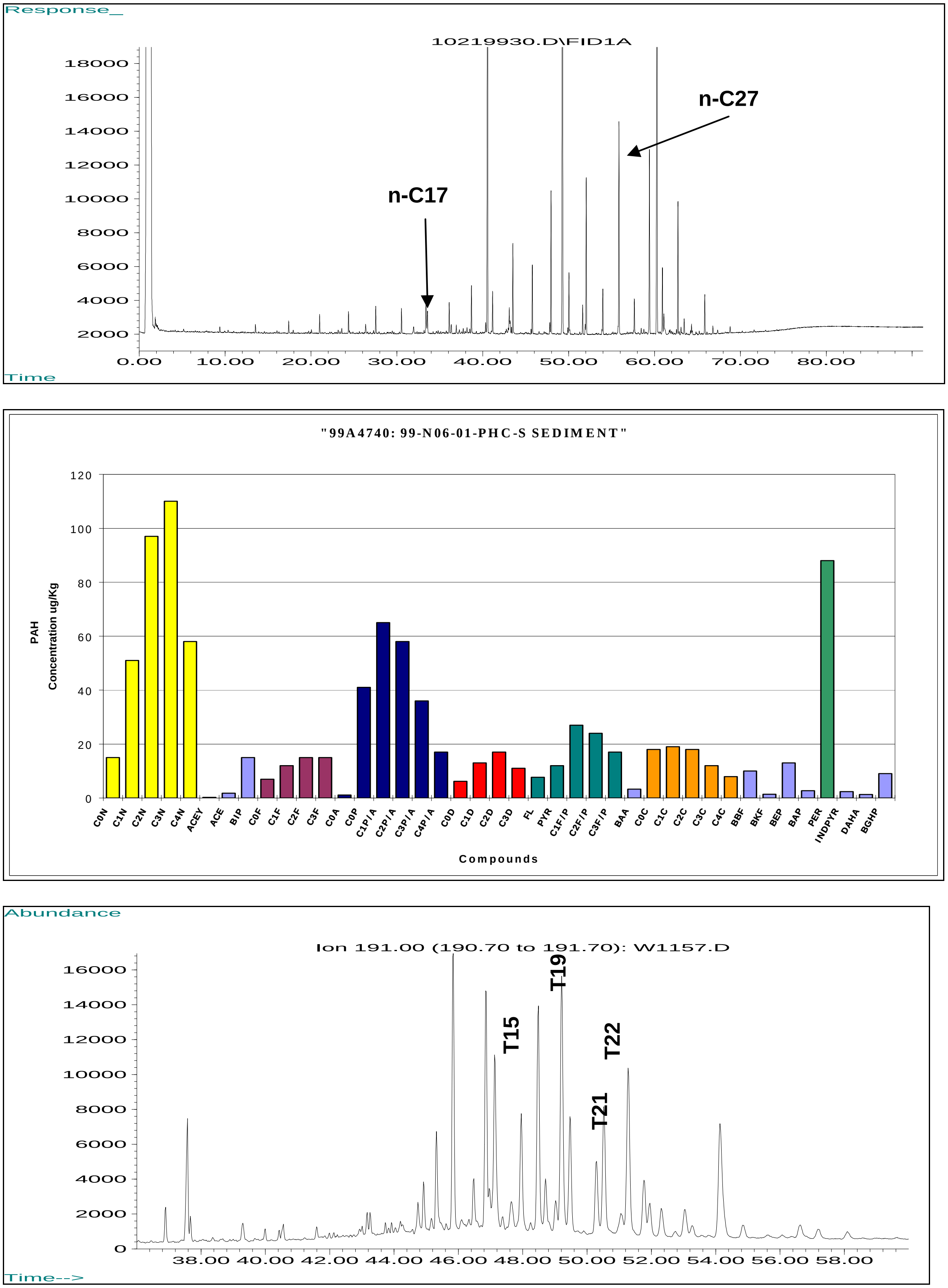
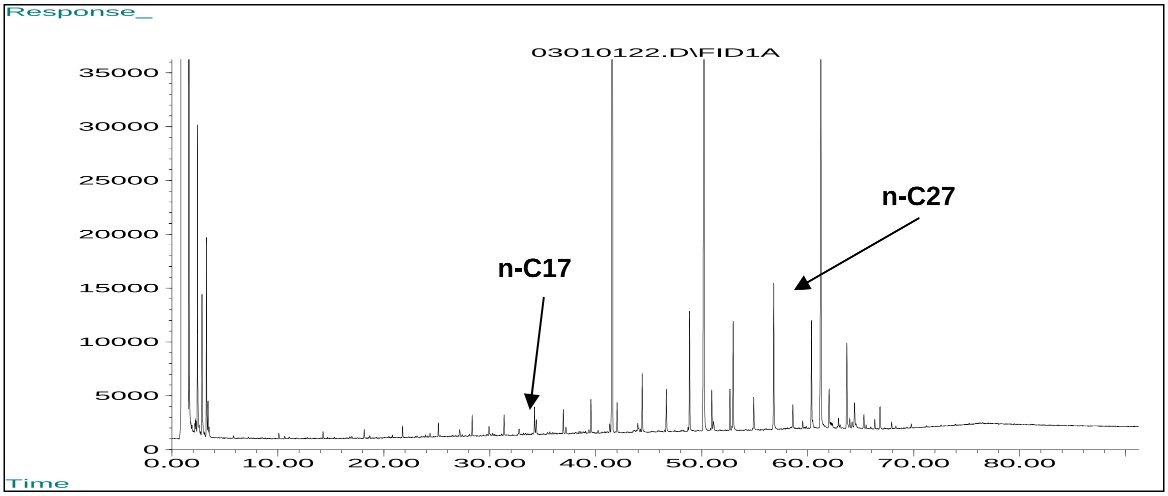
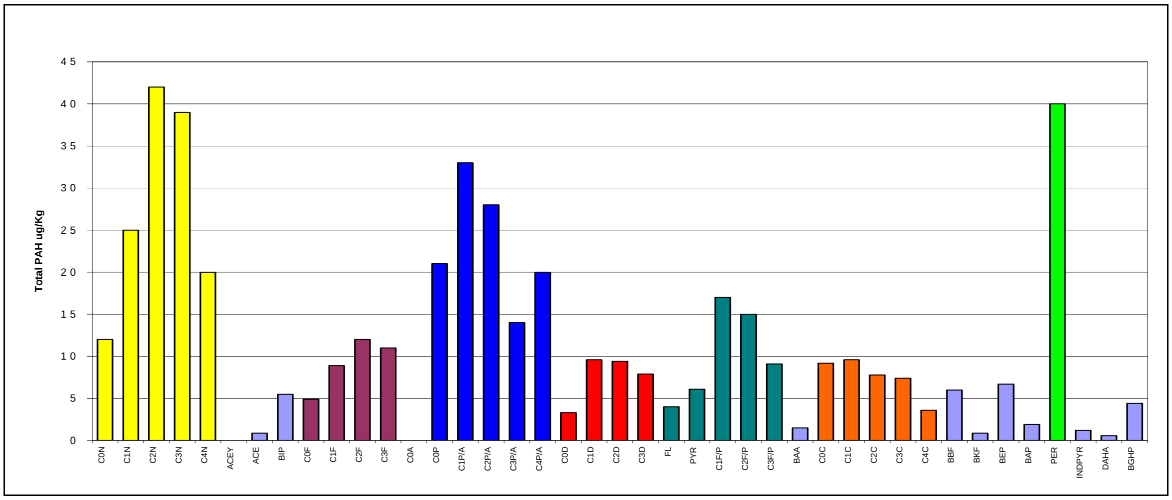


Figure 4-9. Northstar Station N06 Sediment, Year 2000 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).





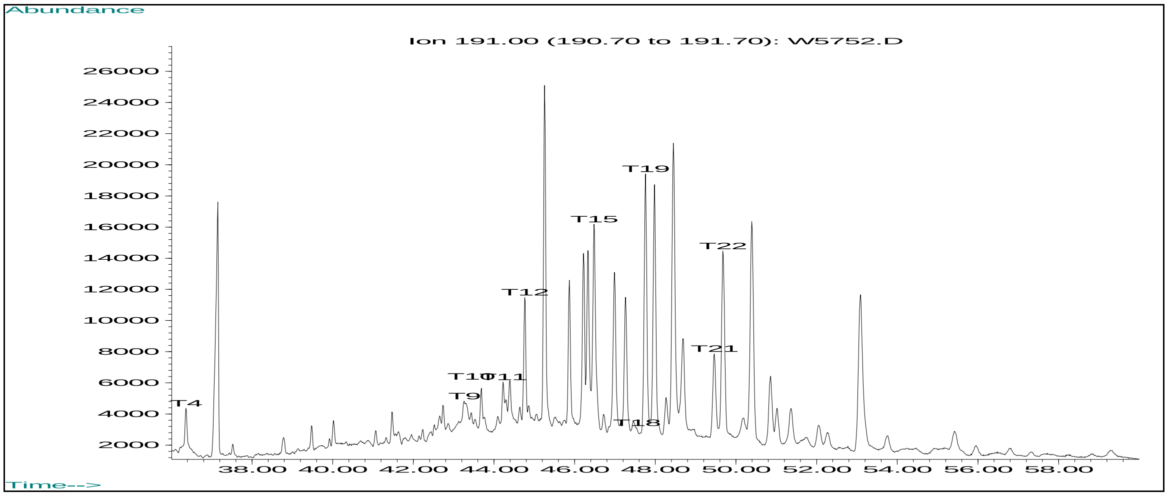


Figure 4-10. Northstar Station N06 Sediment, Year 2002 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).

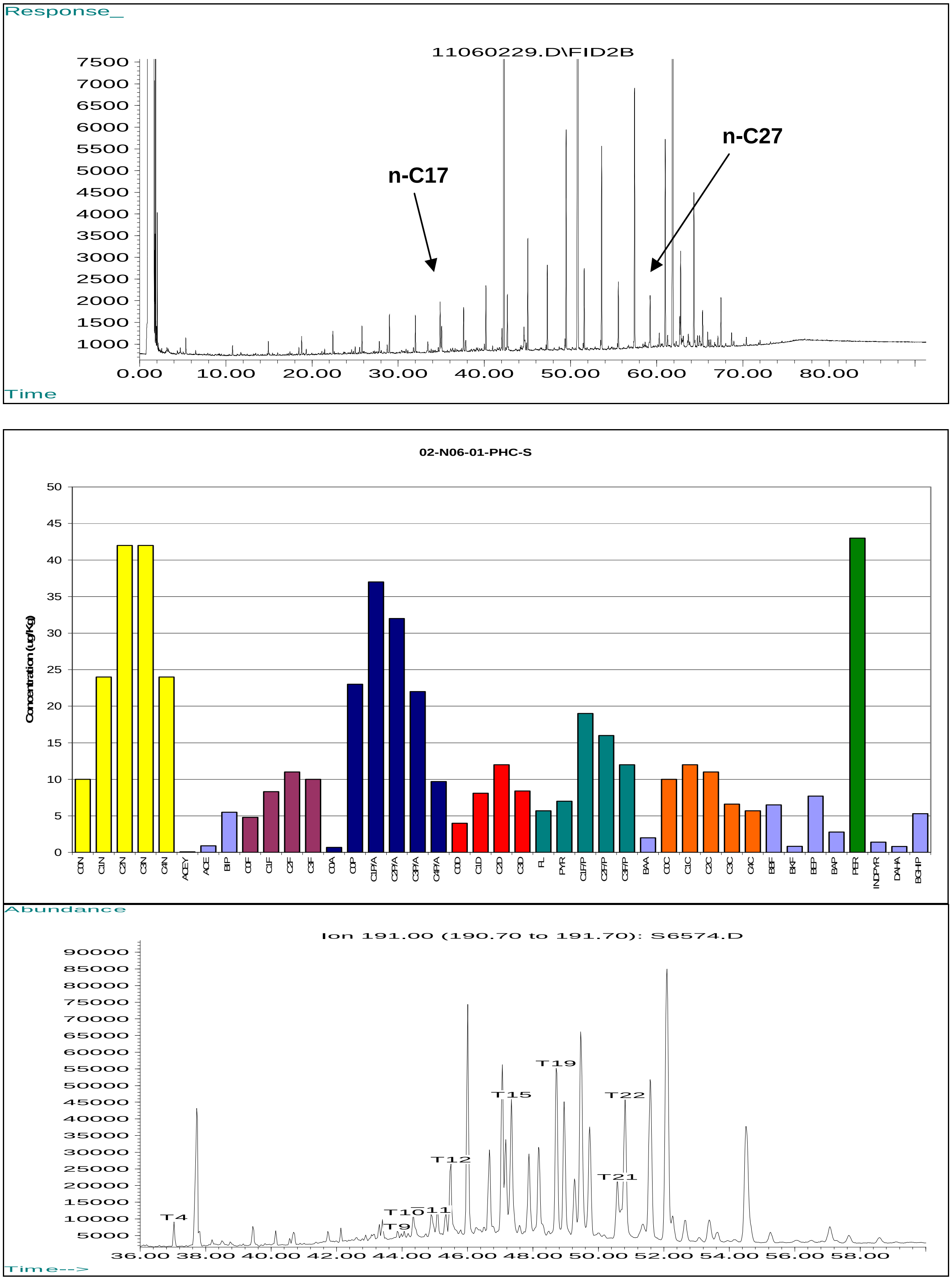


Figure 4-11. Northstar Station N06 Sediment, Year 2004 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane Ion chromatogram (bottom).

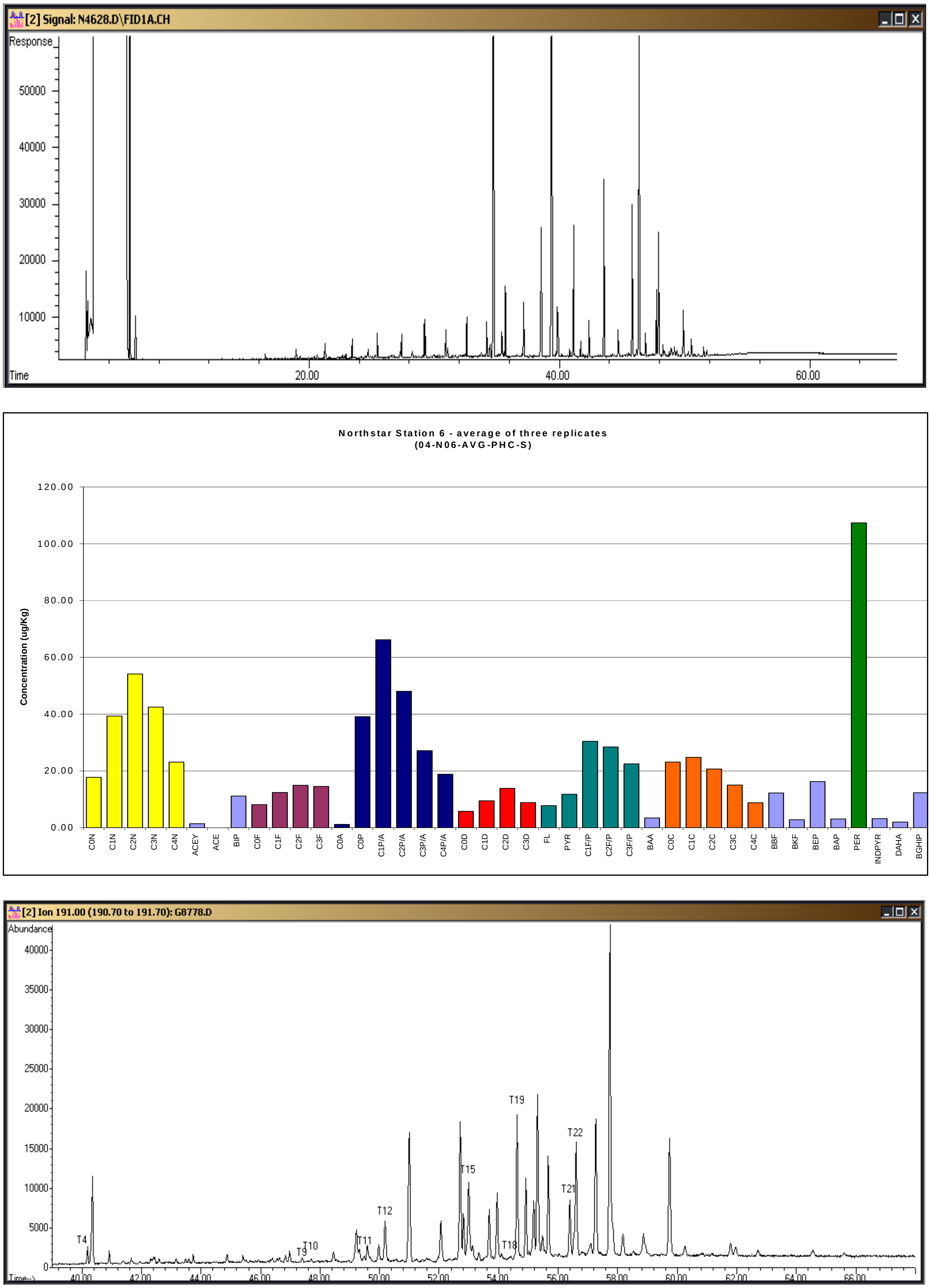
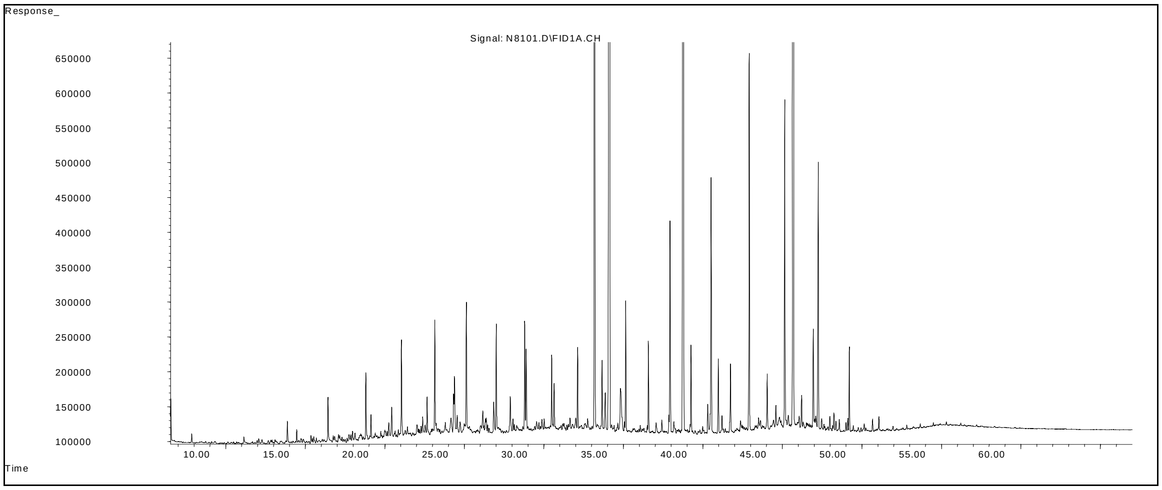
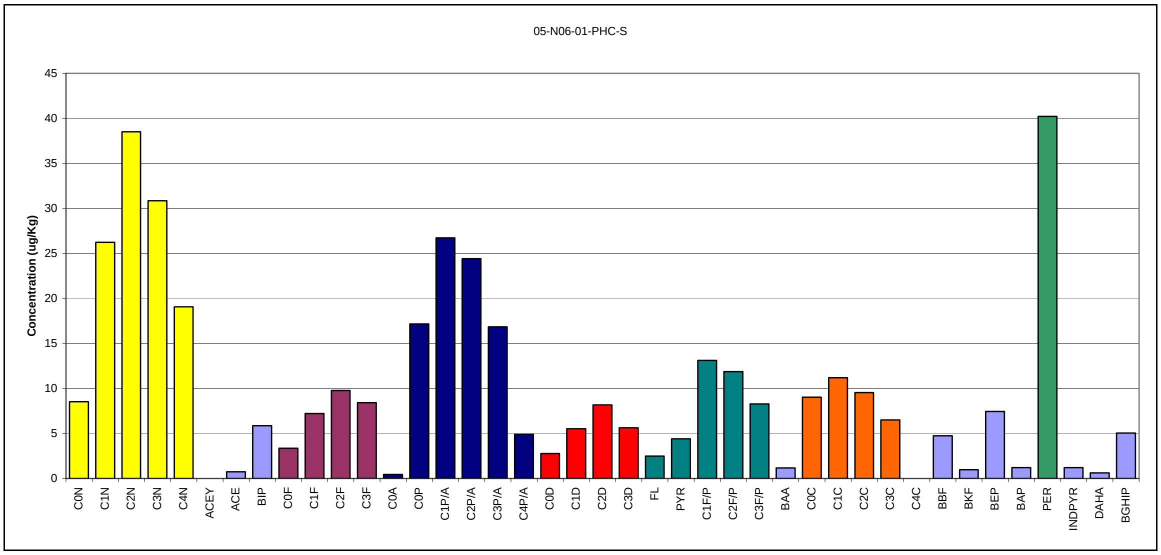


Figure 4-12. Northstar Station N06 Sediment, Year 2005 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).





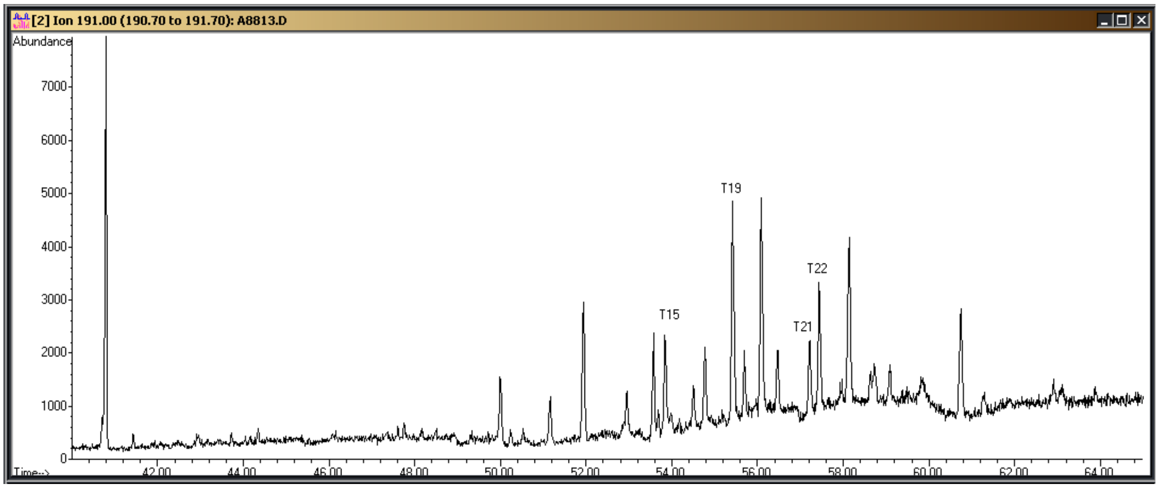


Figure 4-13. Station N06 Sediment, Year 2006 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).

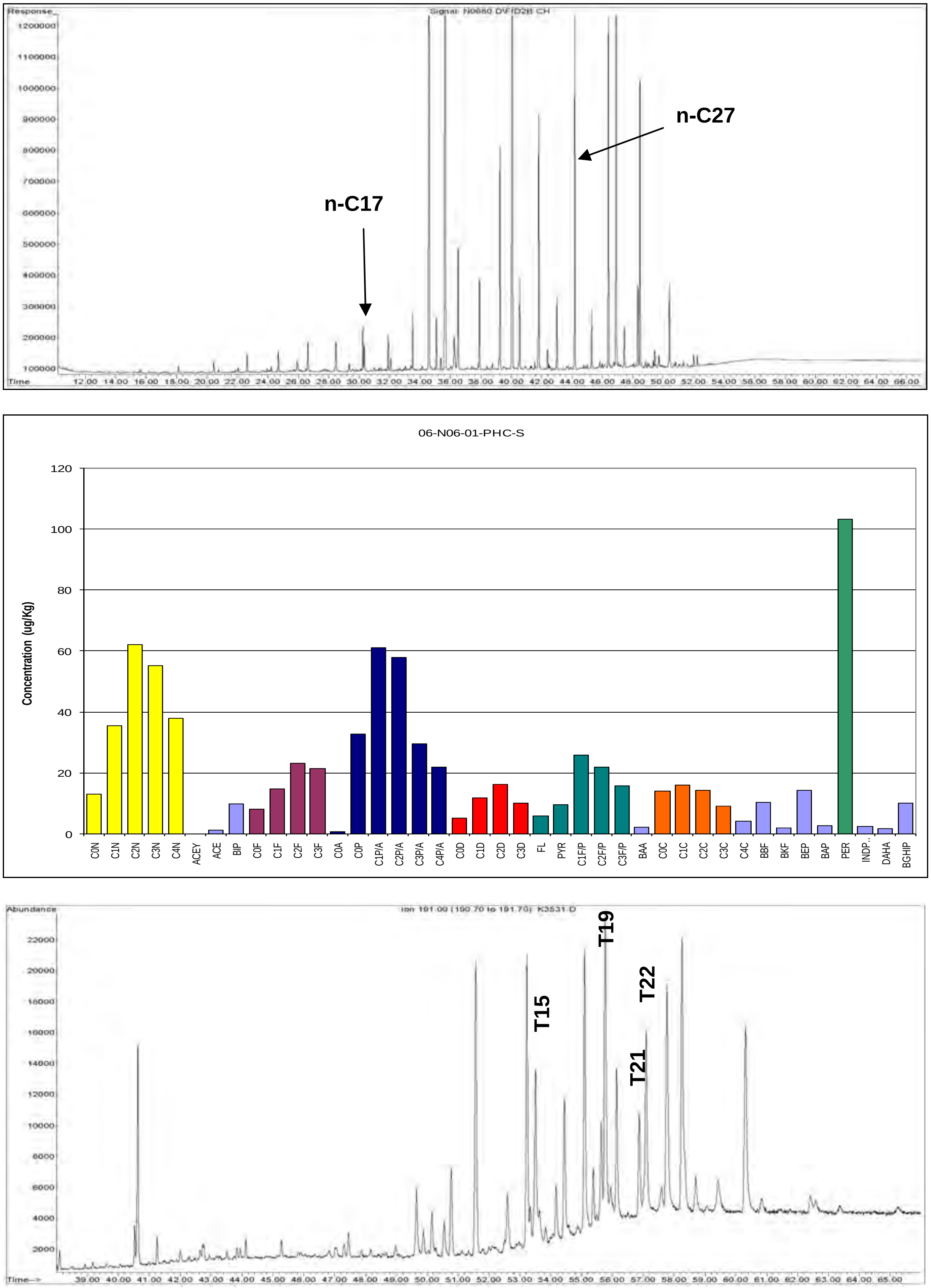


Figure 4-14. Station L08 Sediment, Year 1999 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).

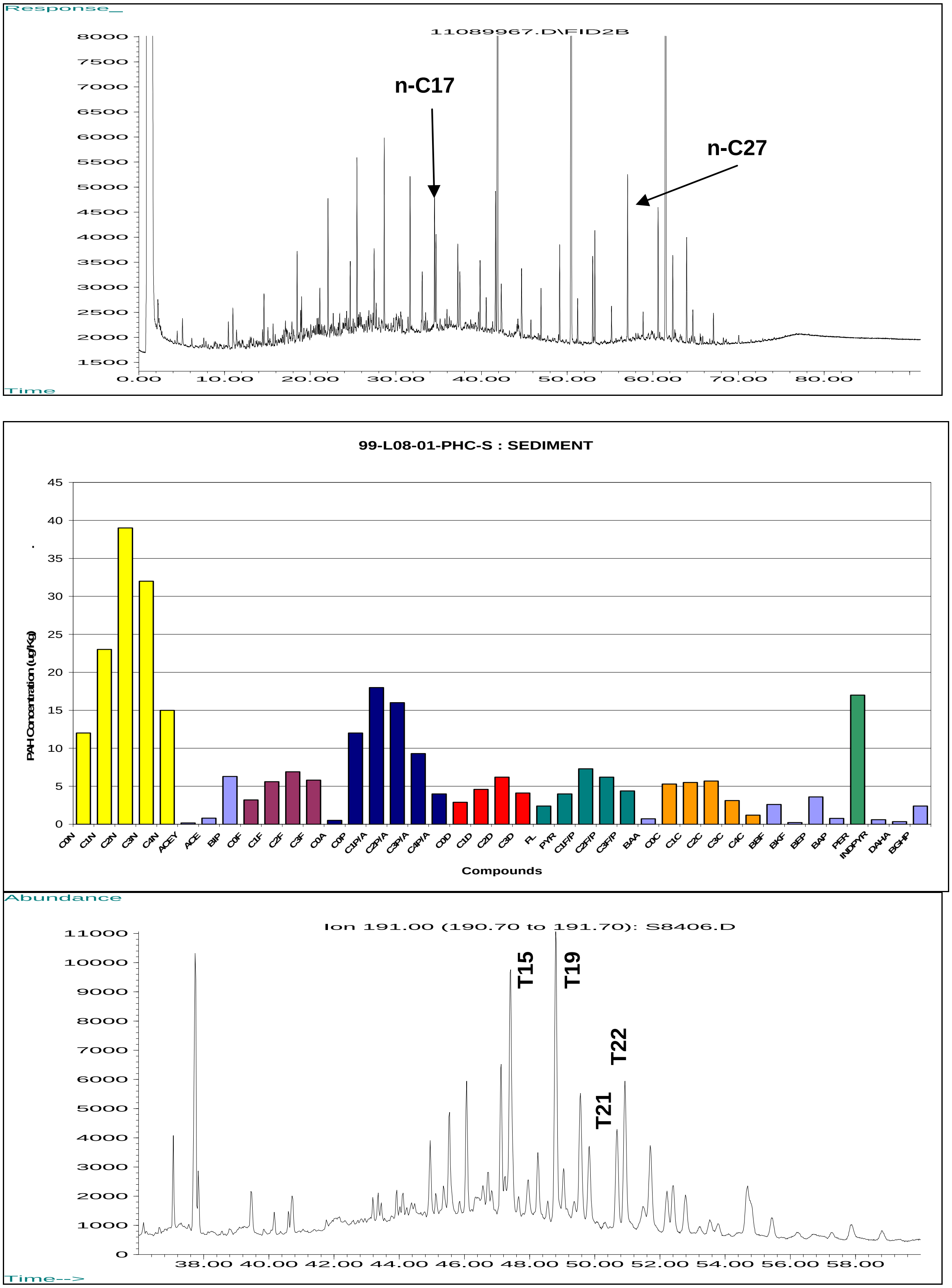


Figure 4-15. Liberty Station L08 (Rep 3) Sediment, Year 2000 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).

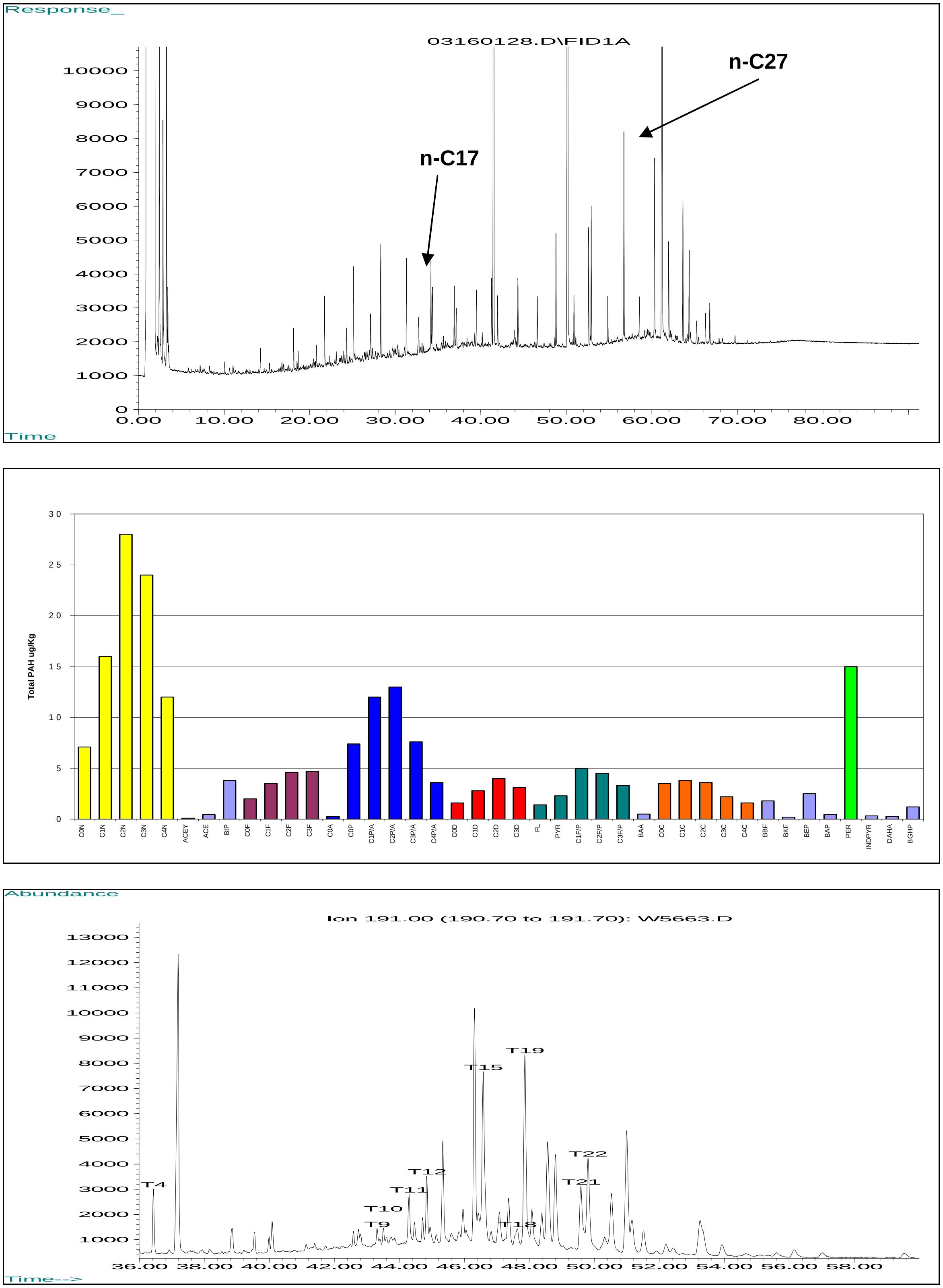


Figure 4-16. Liberty Station L08 Sediment, Year 2005 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).

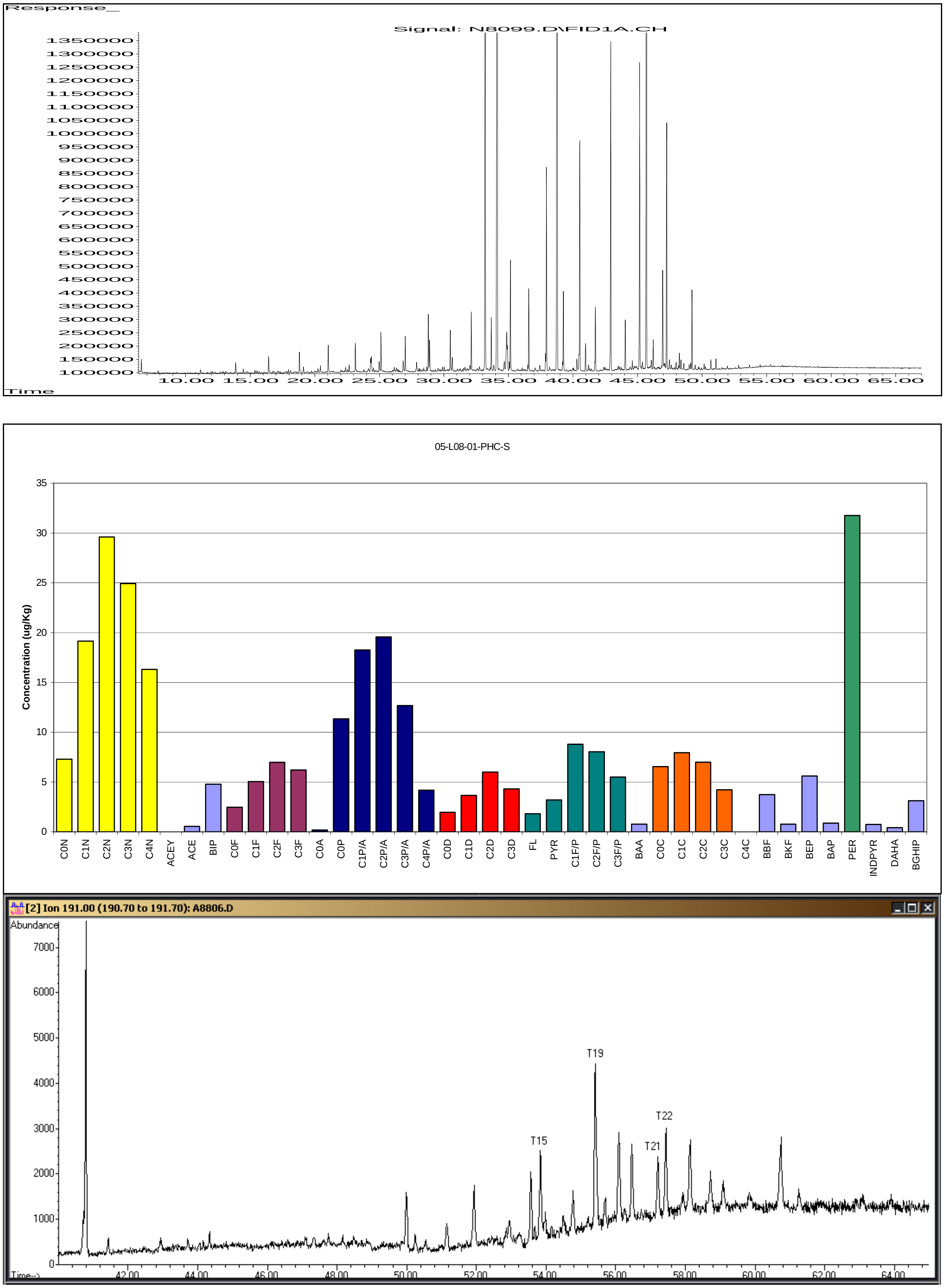
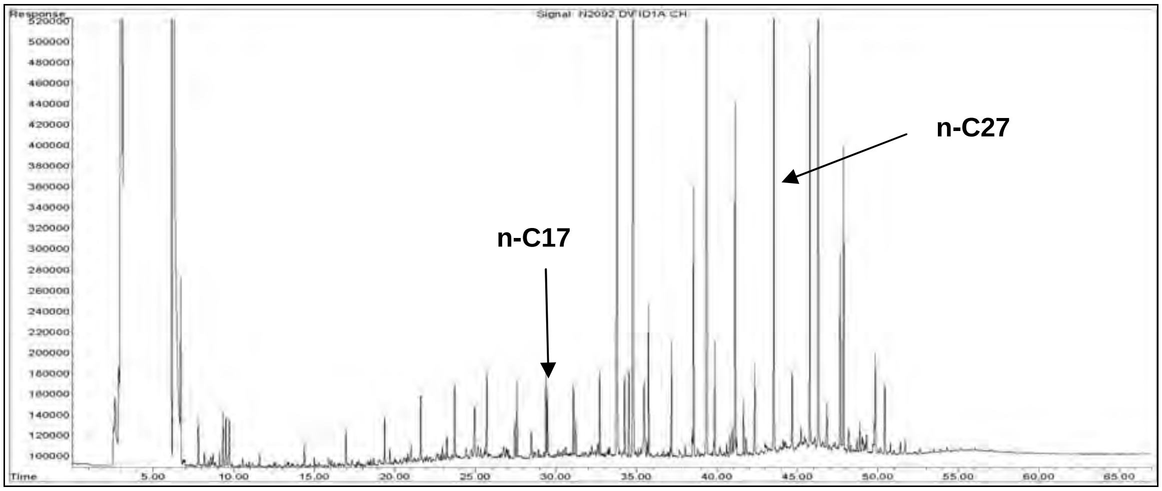
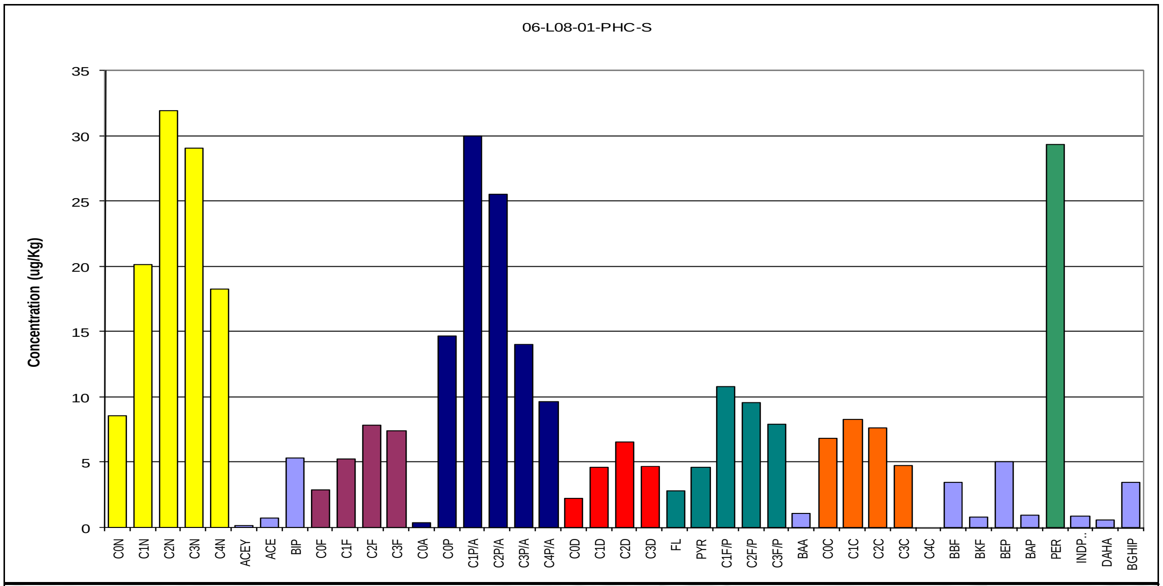


Figure 4-17. Station L08 Sediment, Year 2006 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).





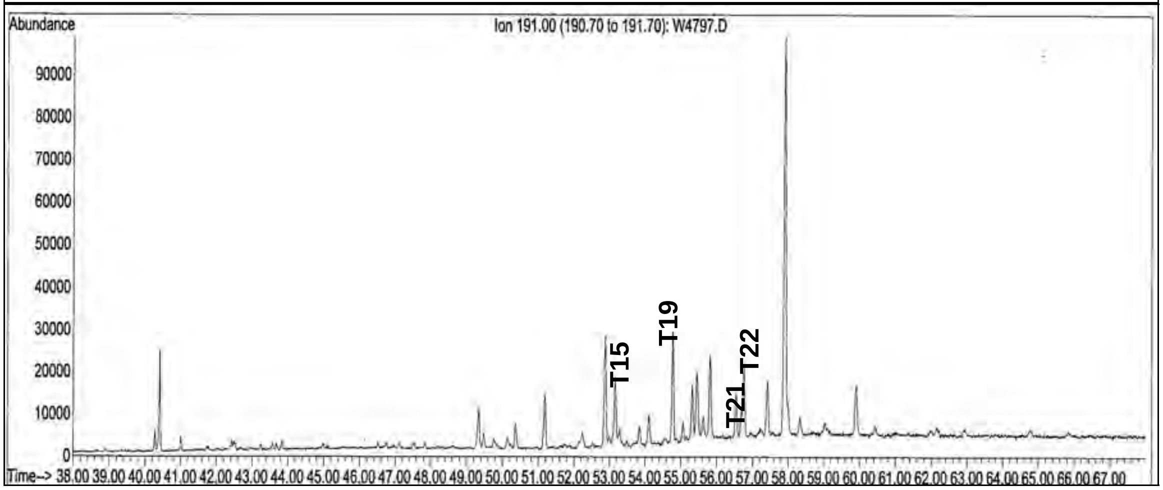


Figure 4-18. Station 3A Sediment, Year 1999 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).

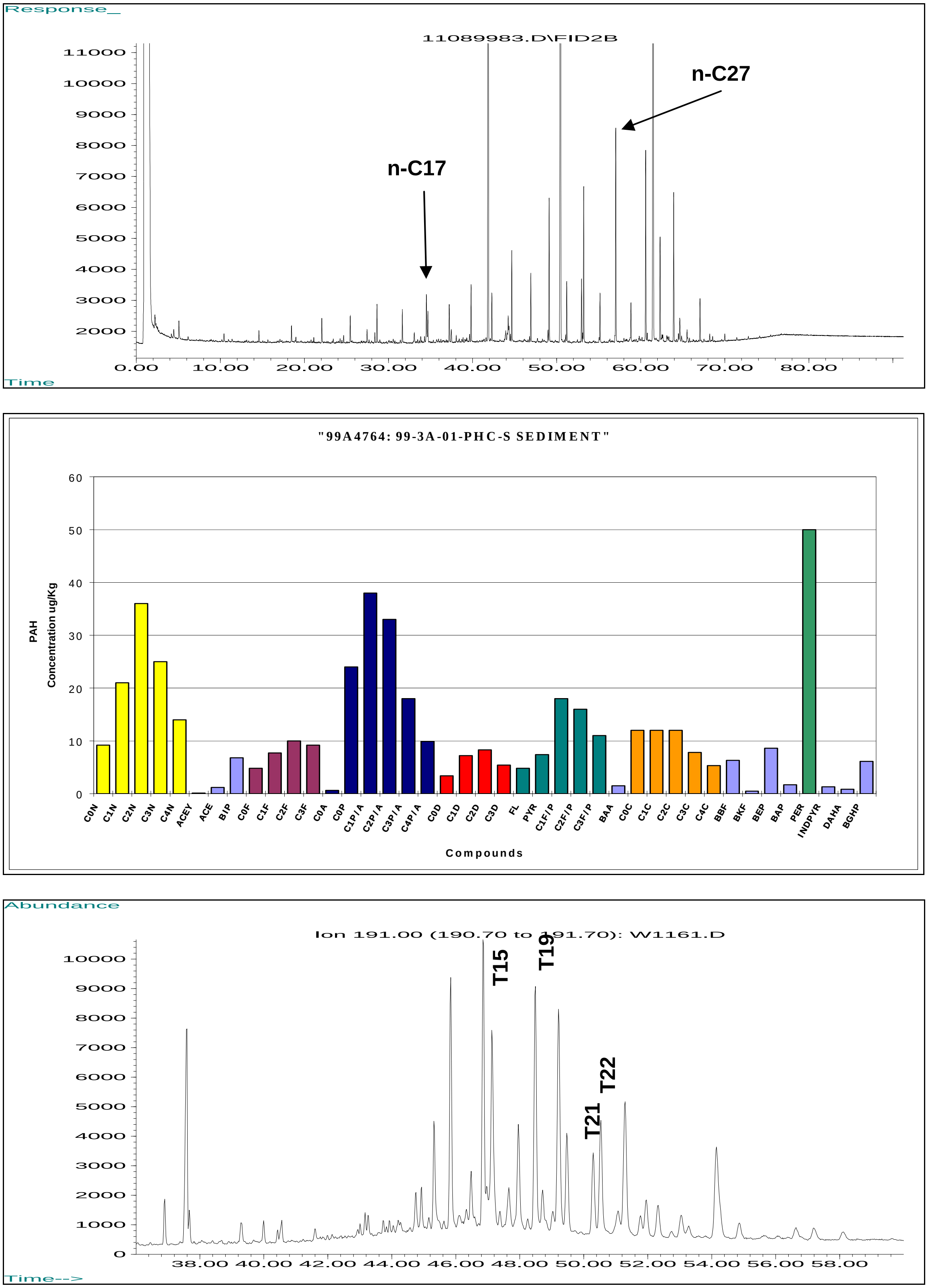


Figure 4-19. Station 3A Sediment, Year 2005 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).

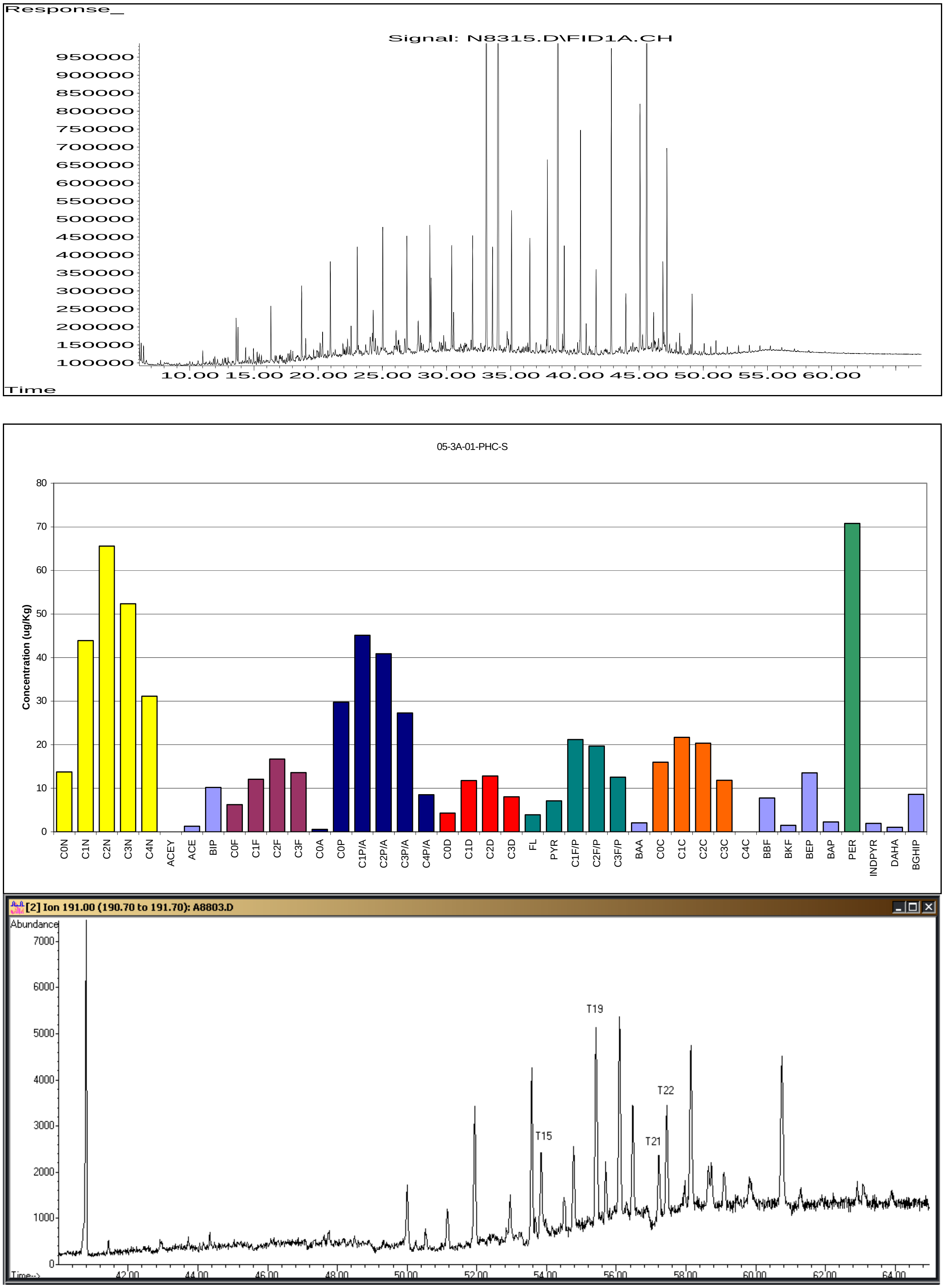
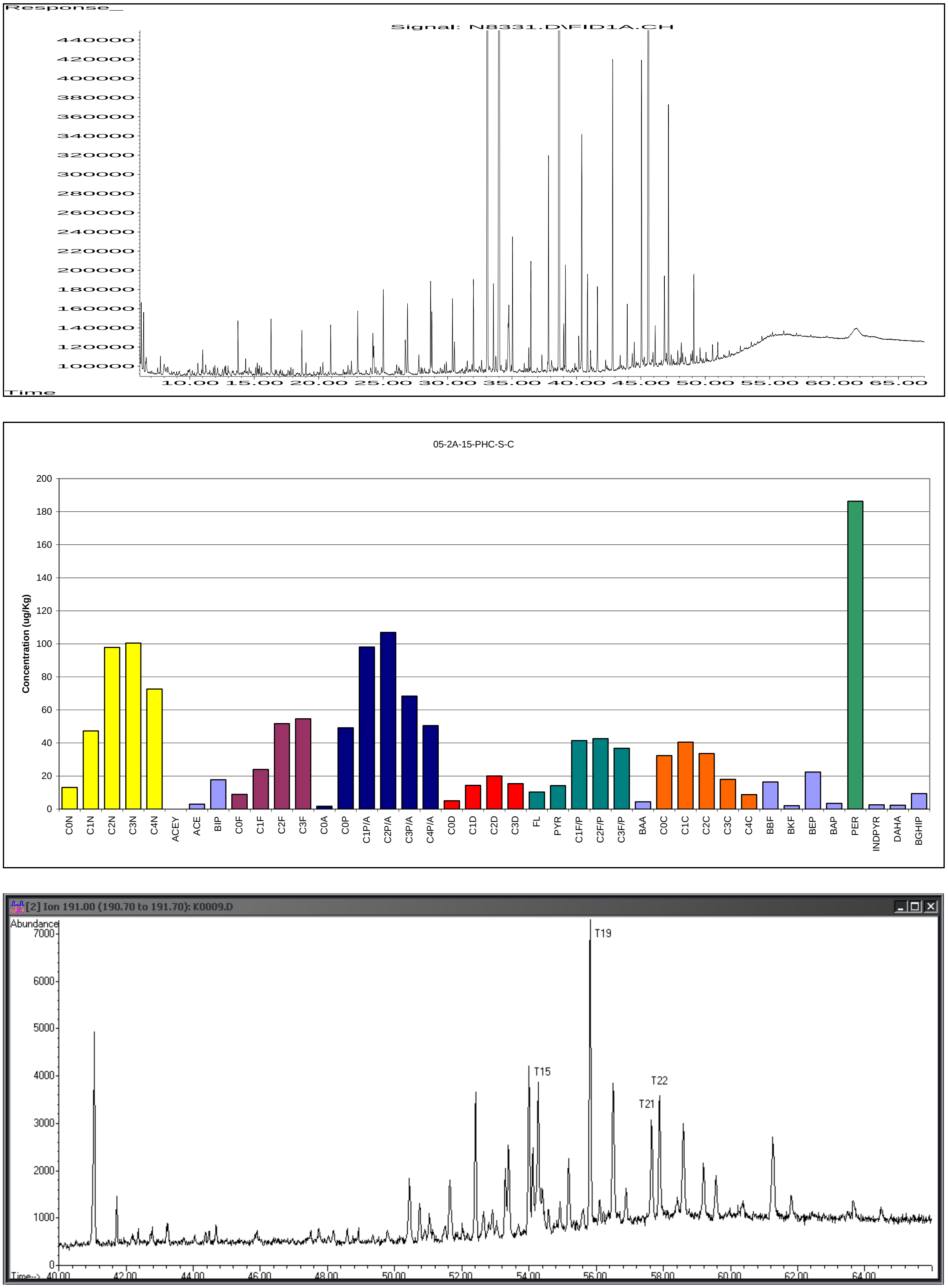


Figure 4-20. Station 2A Sediment, Year 2005 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).



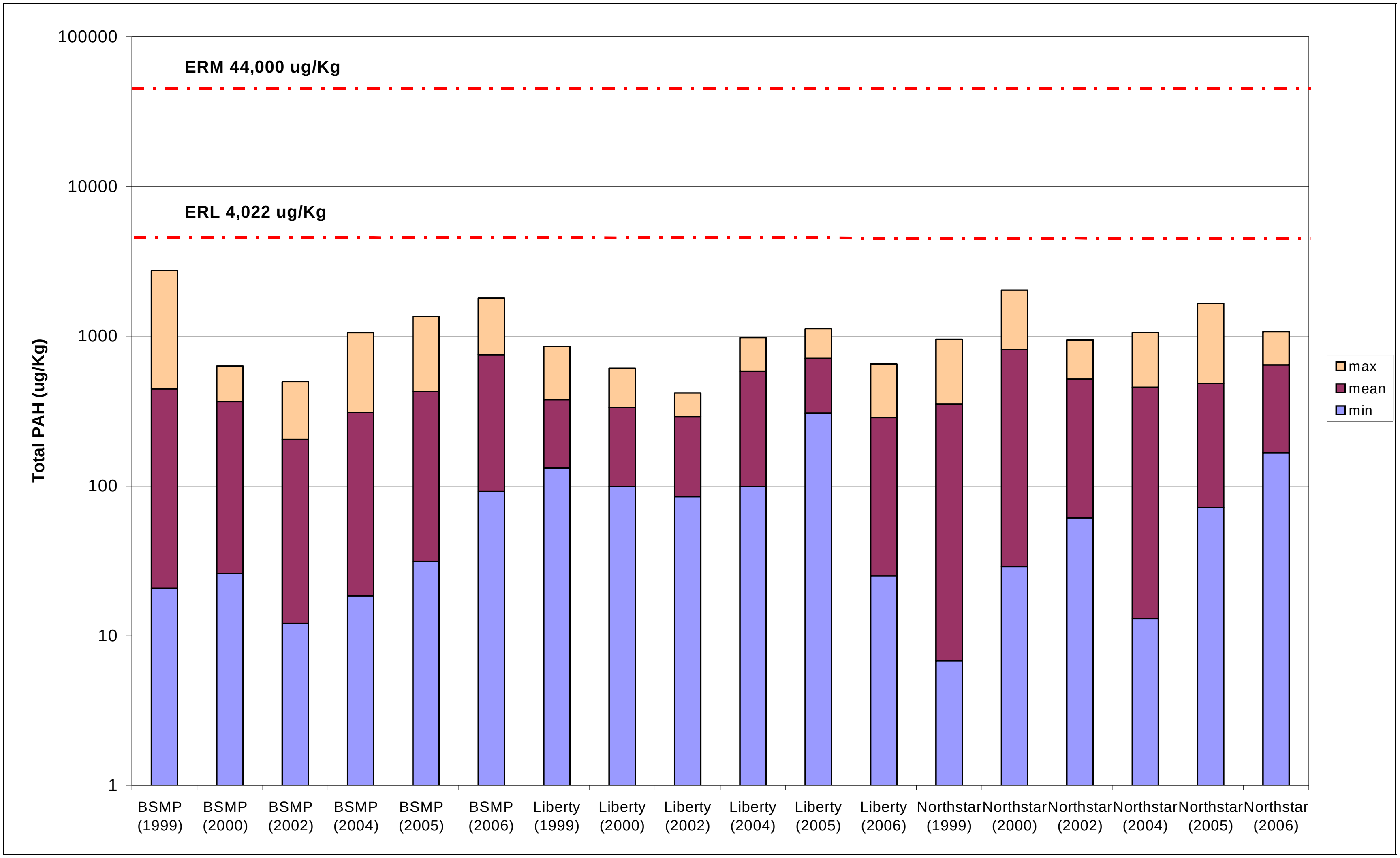
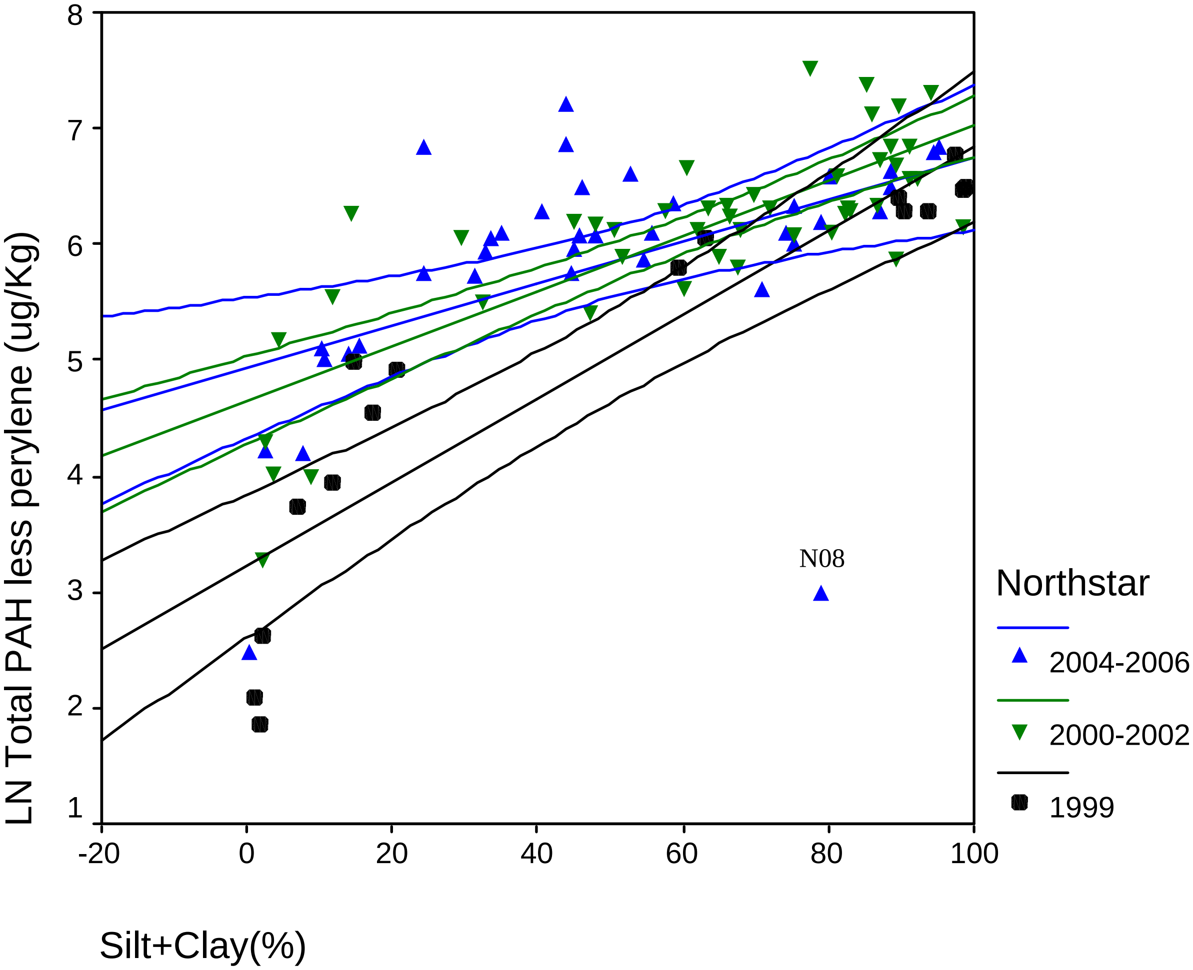


Figure 4-21. Comparison of regional minimum, maximum, and mean concentrations by year for total polynuclear aromatic hydrocarbon concentrations to sediment quality guidelines effects range-low and effects range-medium values (Long et al., 1995). Note: y-axis is presented on a logarithmic scale.

Figure 4-22. Scatterplot of silt + clay results versus total polynuclear aromatic hydrocarbons less perylene for Northstar surficial sediment samples in 1999 through 2006.

The lines, Rsq, and 95% mean prediction intervals are from linear regression and related statistical calculations for Northstar stations by year. Station N08 from year 2004 was an outlier and was excluded from this graph.



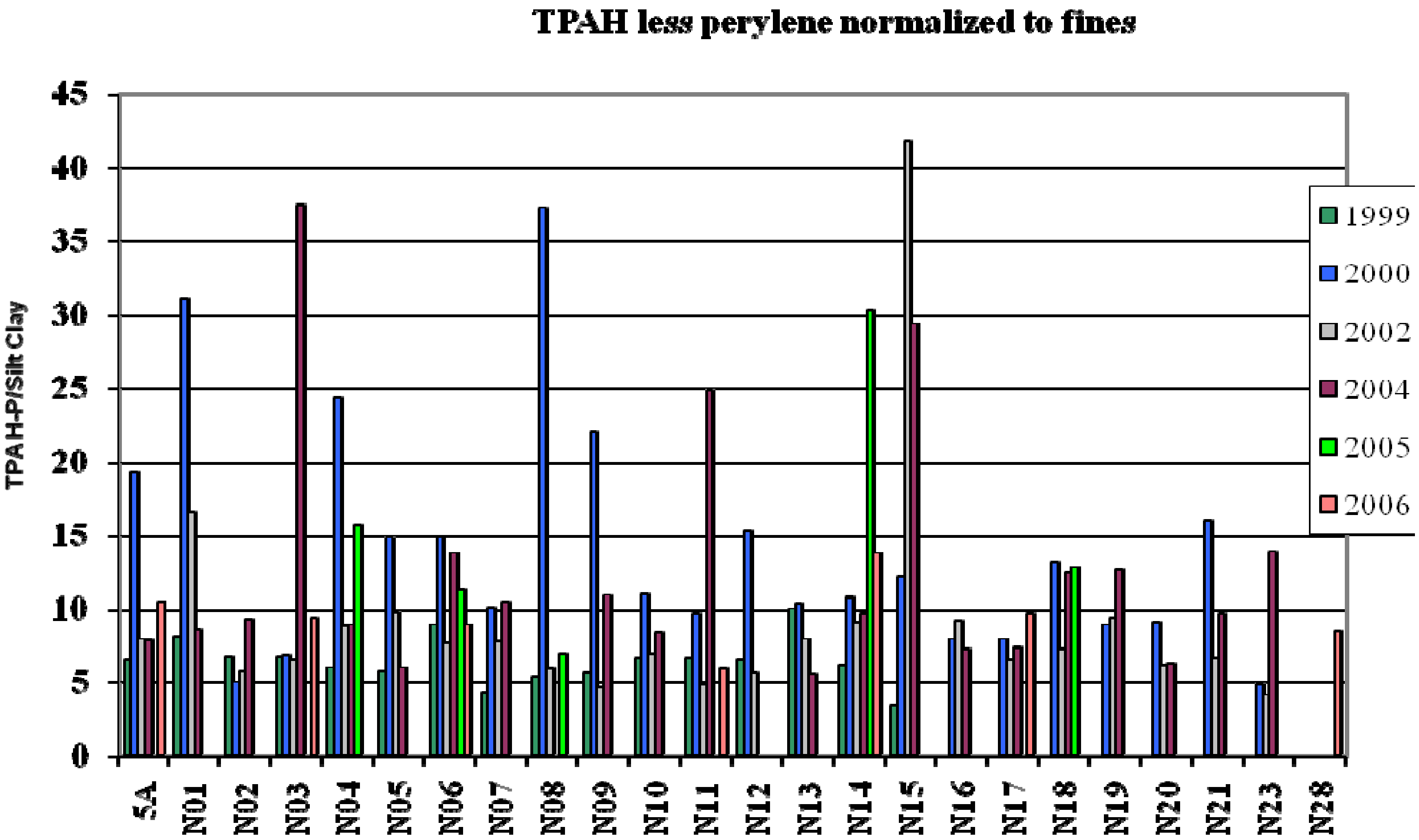


Figure 4-23. Total polynuclear aromatic hydrocarbon (TPAH) less perylene concentrations normalized to fines for all 1999 through 2006 Northstar stations.

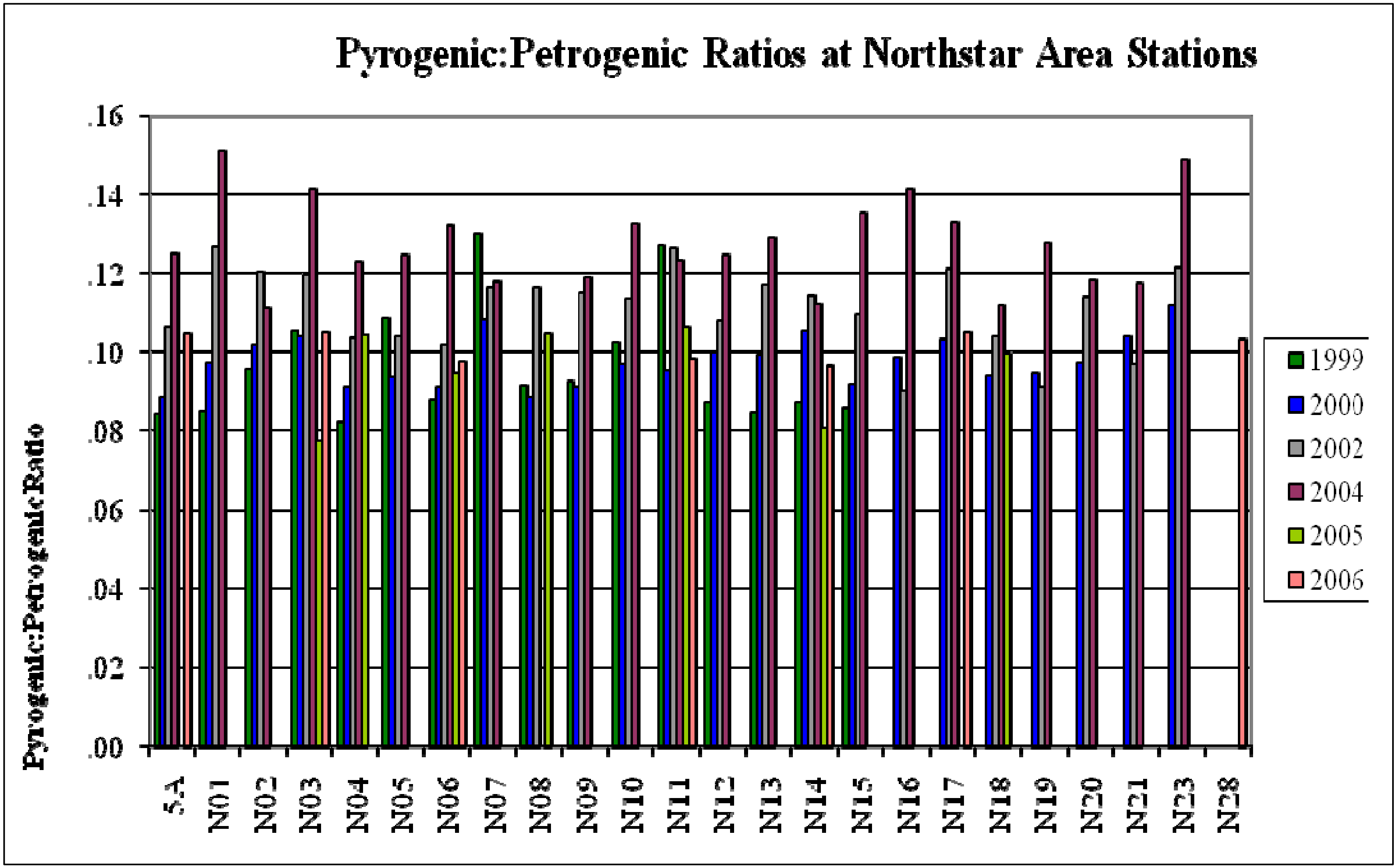


Figure 4-24. Pyrogenic:petrogenic ratios of Northstar surficial sediment samples for 1999 through 2006.

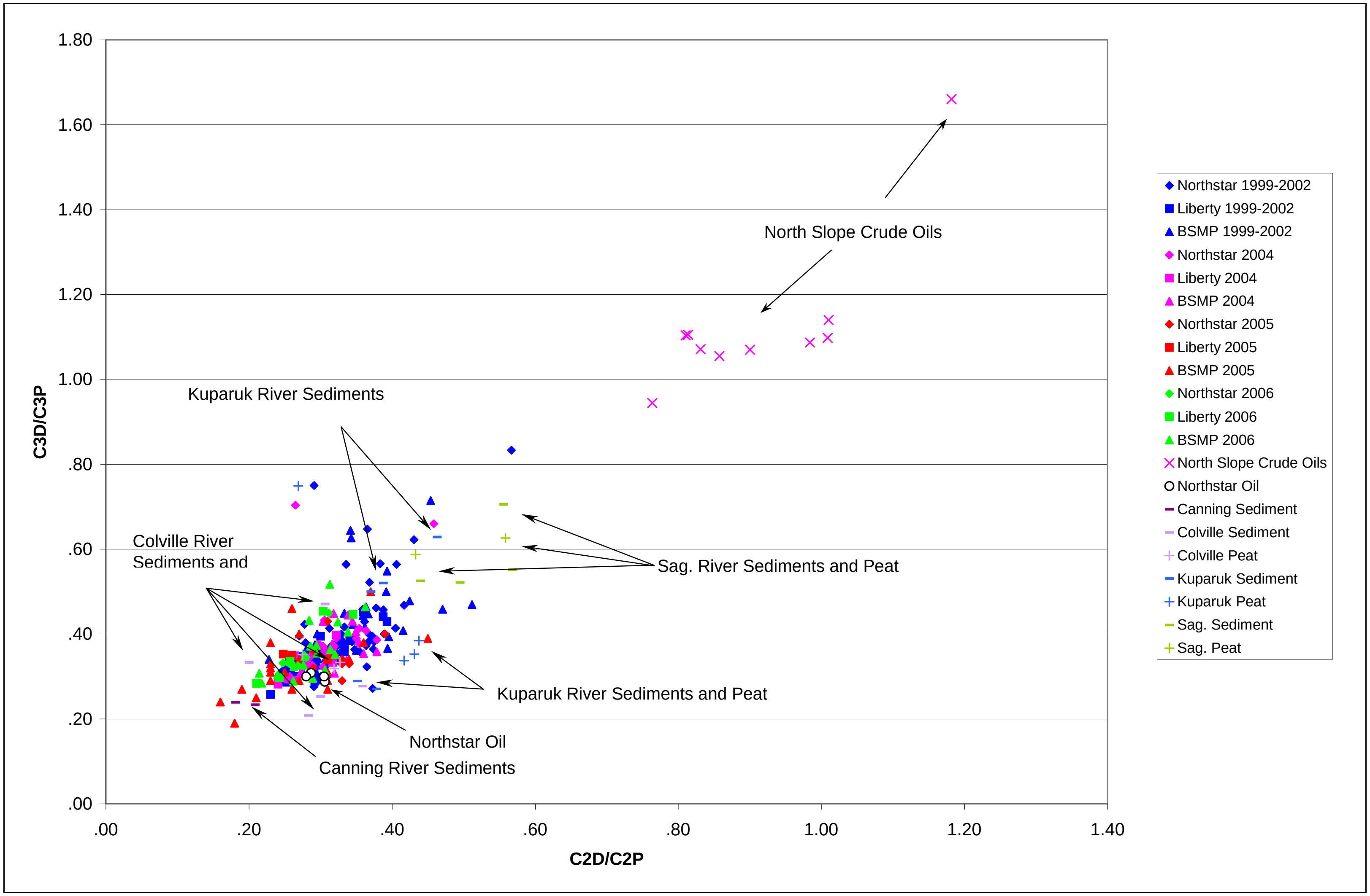


Figure 4-25. Double ratio source plot of C2D/C2P versus C3D/C3P for BSMP, Liberty, Northstar, and River sediment samples for 1999 through 2006.

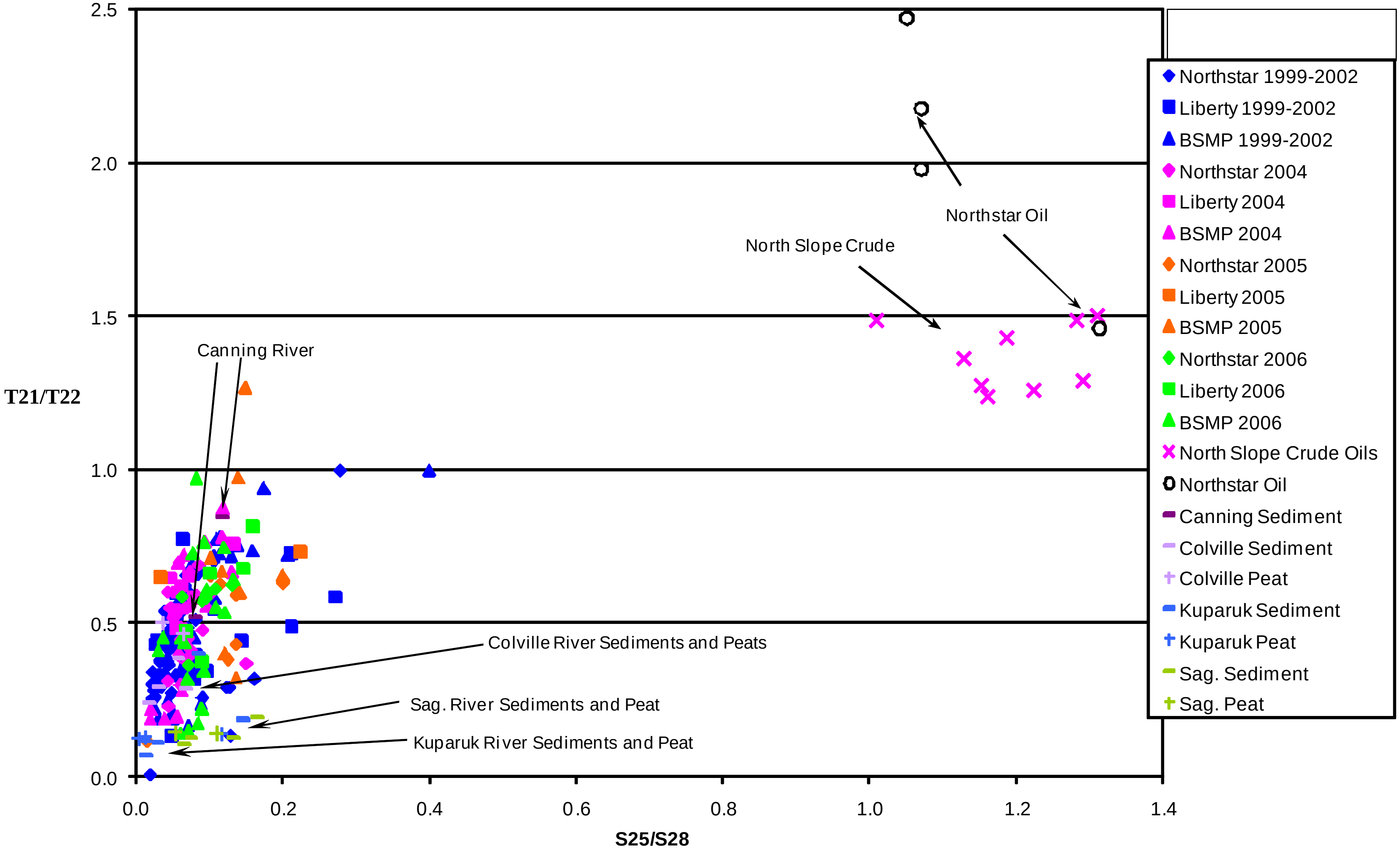


Figure 4-26. Double ratio source plot of S25/S28 versus T21/T22 for BSMP, Liberty, Northstar, and River sediment samples 1999 through 2006.

Figure 4-27. Regression plot of total PAH less perylene verus silt + clay for all 1999 through 2006 Northstar, Liberty and BSMP sediments.

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

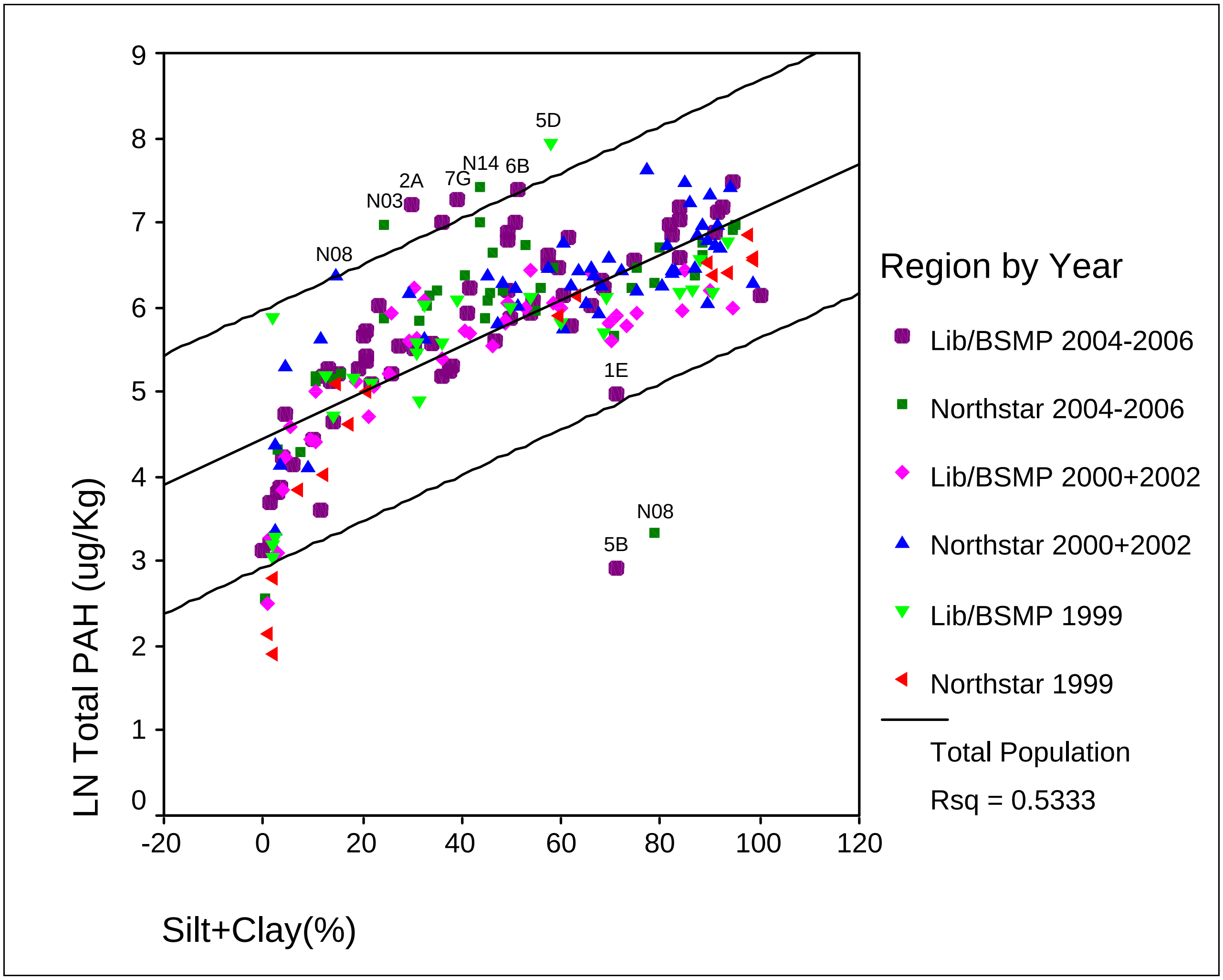


Figure 4-28. Regression plot of LN total PAH less perylene versus silt + clay for all 2004 through 2006 Northstar, Liberty and BSMP sediments.

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

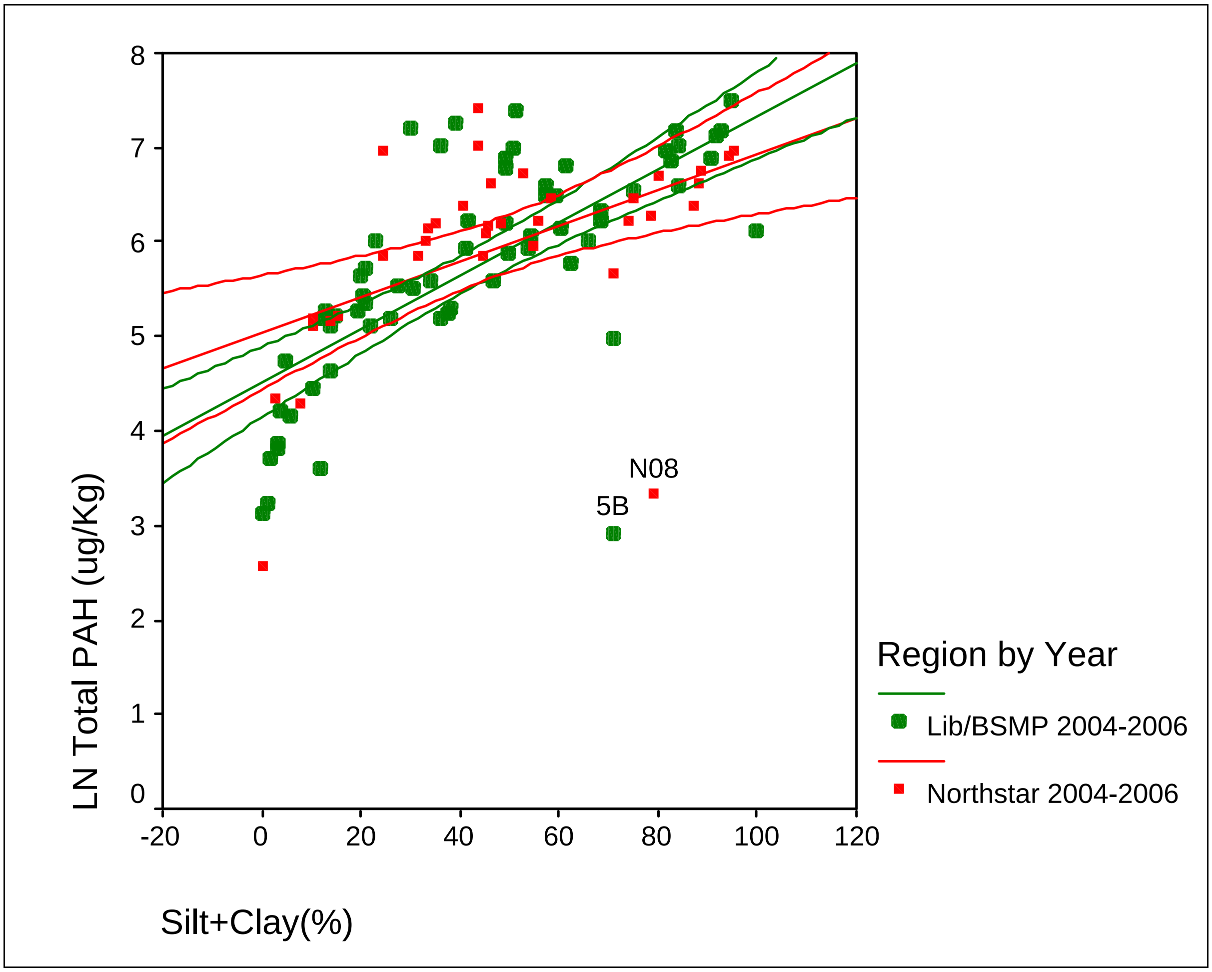


Figure 4-29. Regression plot of Total PAH less perylene versus perylene for all 1999 through 2006 Northstar, Liberty and BSMP sediments.

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

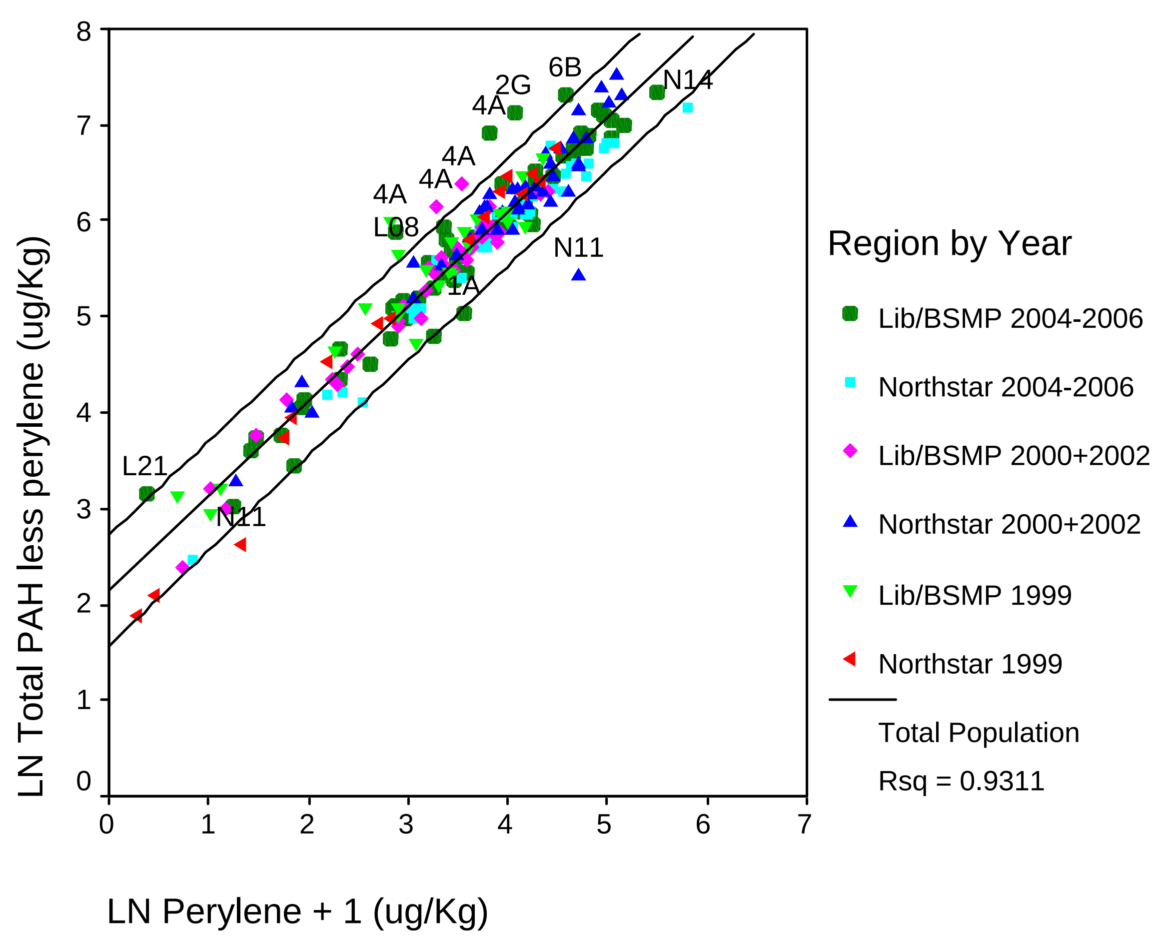


Figure 4-30. Concentrations of aluminum versus chromium for surface sediment from the cANIMIDA study area collected in (a) 1999-2002 and (b) 2004-2006.

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) and Colville (C) Rivers. Data for sites identified on the graphs were not included in the regression calculations. Data for 2004-2006 were plotted with the prediction interval from the 1999-2002 data.

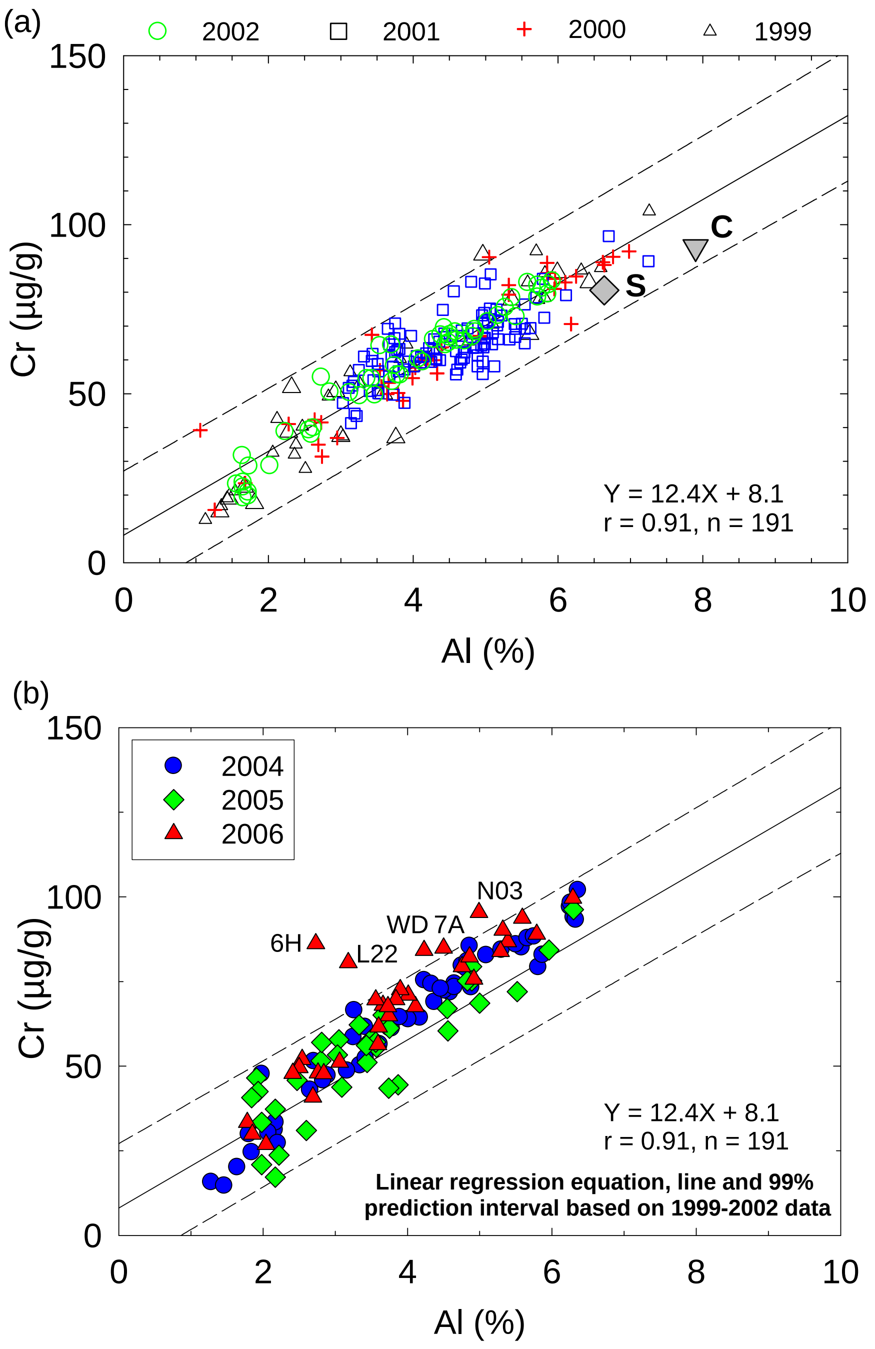


Figure 4-31. Concentrations of aluminum versus (a) copper, (b) cobalt and (c) arsenic for sediment from the cANIMIDA study area collected in 2004-2006.

Equations are from linear regression calculations and r is the correlation coefficient. Dashed lines show the 99% prediction interval. Data from 2004-2006 are plotted with prediction interval from 1999-2002 data.

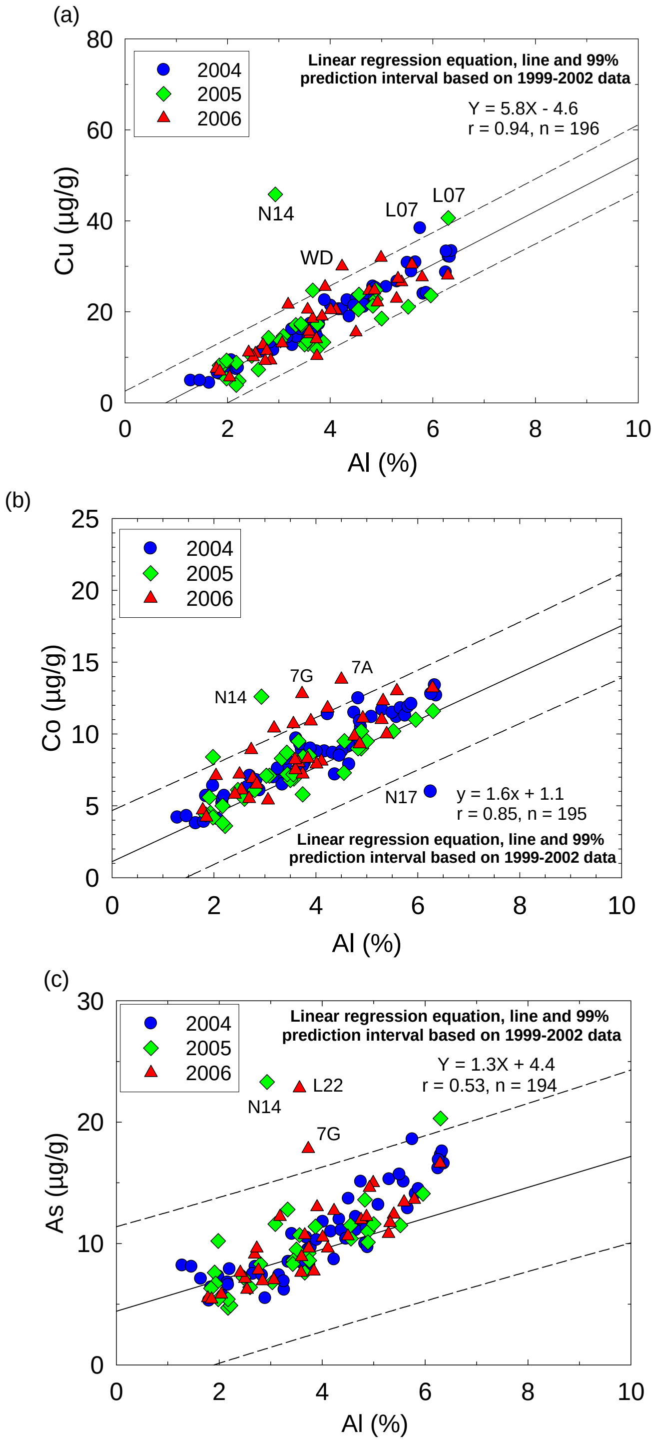


Figure 4-32. Concentrations of aluminum versus (a) nickel, (b) silver and (c) mercury for sediment from the cANIMIDA study area collected in 2004-2006.

Equations are from linear regression calculations and r is the correlation coefficient. Dashed lines show the 99% prediction interval. Data from 2004-2006 are plotted with prediction interval from 1999-2002 data.

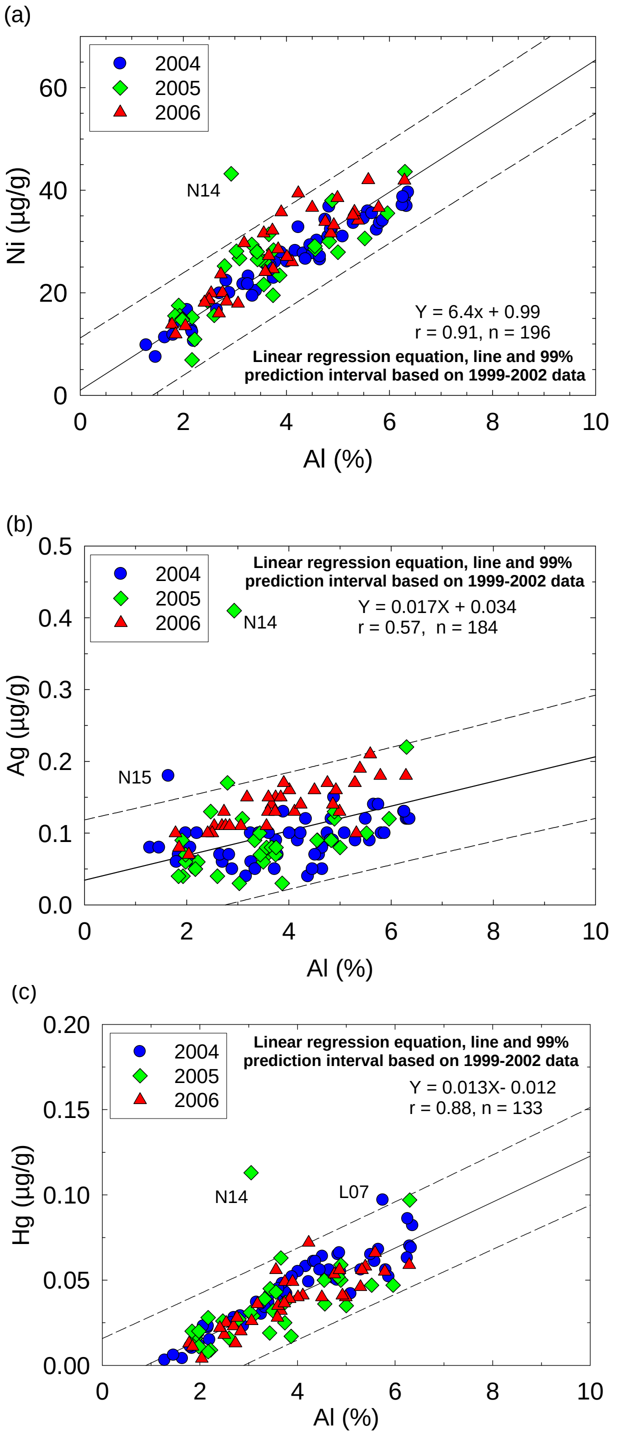


Figure 4-33. Concentrations of excess metals for sediment from 1999 station 5D versus 2005 station N14.

Concentrations of the excess metals for stations N14 (2005) and 5D (1999) were calculated by taking the measured metal concentration and subtracting the concentration calculated for a given metal using the measured Al concentration with the linear regression equations for the 1999-2002 metal versus Al plots. The dashed line shows the 1:1 correspondence between the data for 1999 Station 5D and 2005 Station N14.

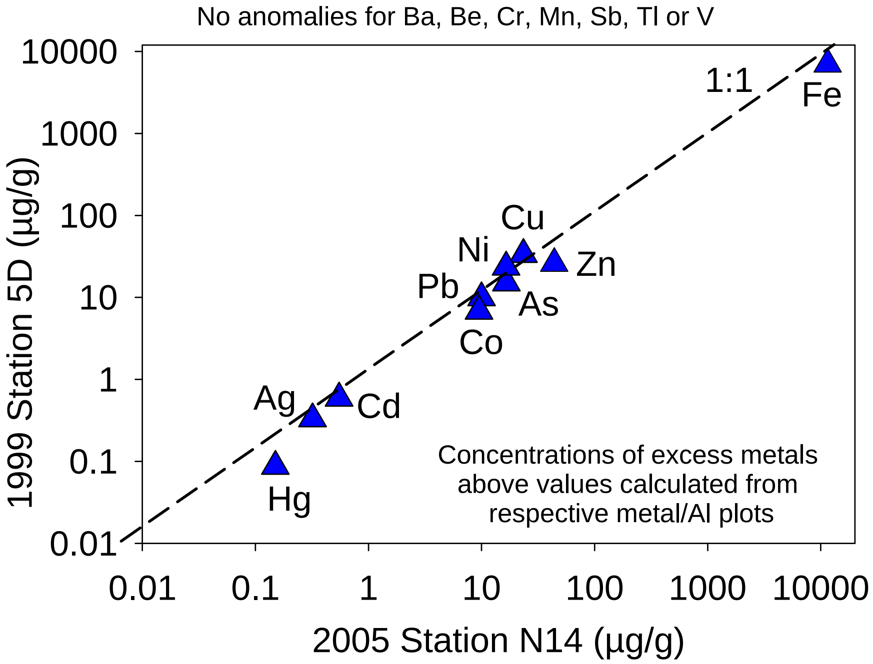


Figure 4-34. Concentrations of aluminum versus (a) zinc, (b) cadmium and (c) lead for sediment from the cANIMIDA study area collected in 2004-2006.

Equations are from linear regression calculations and r is the correlation coefficient. Dashed lines show the 99% prediction interval. Data from 2004-2006 are plotted with prediction interval from 1999-2002 data.

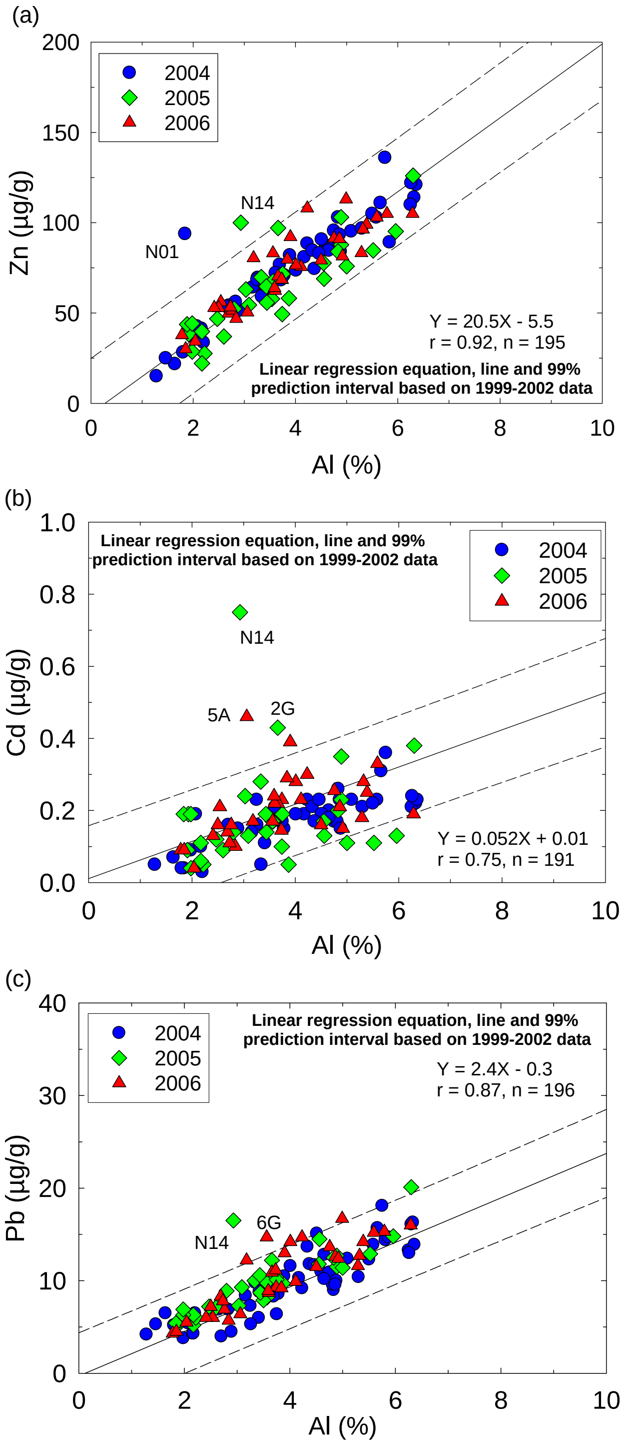


Figure 4-35. Concentrations of aluminum versus (a) barium, (b) antimony and (c) beryllium for sediment from the cANIMIDA study area collected in 2004-2006.

Equations are from linear regression calculations and r is the correlation coefficient. Dashed lines show the 99% prediction interval. Data from 2004-2006 are plotted with prediction interval from 1999-2002 data.

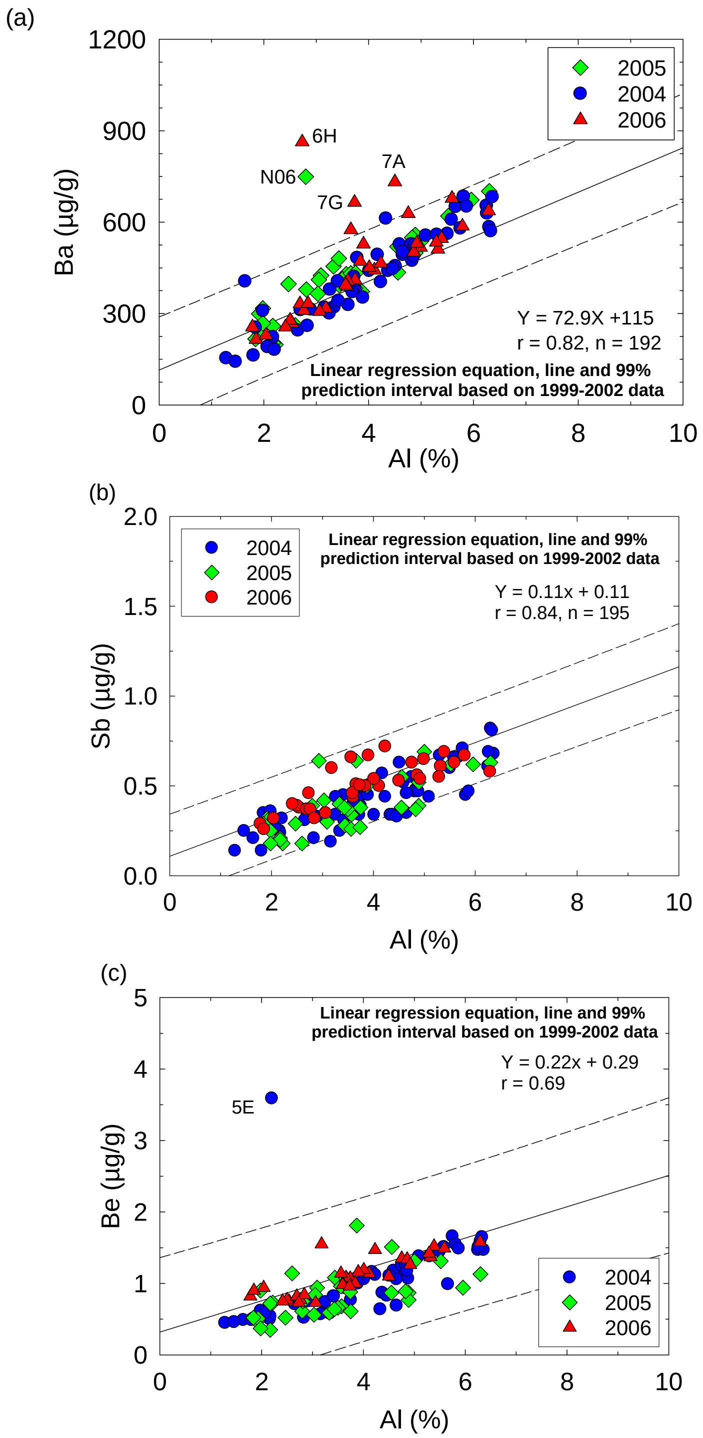
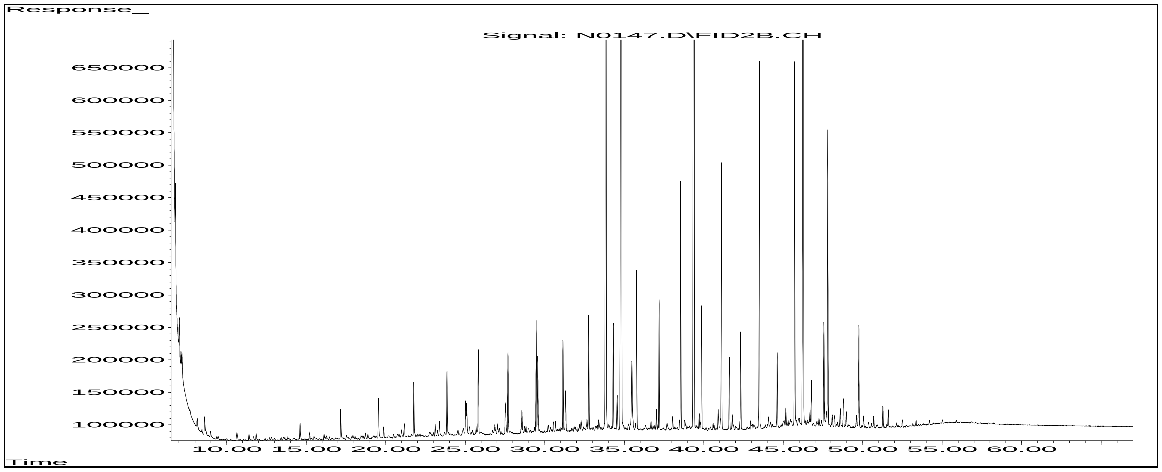
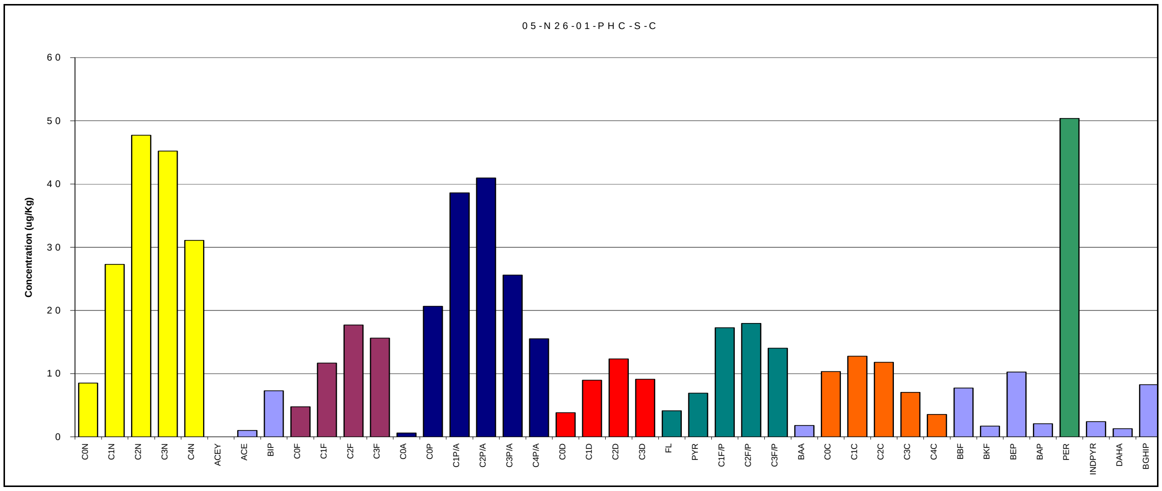


Figure 4-36. Sediment Core N26 Interval 0-2 cm, Year 2005 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).





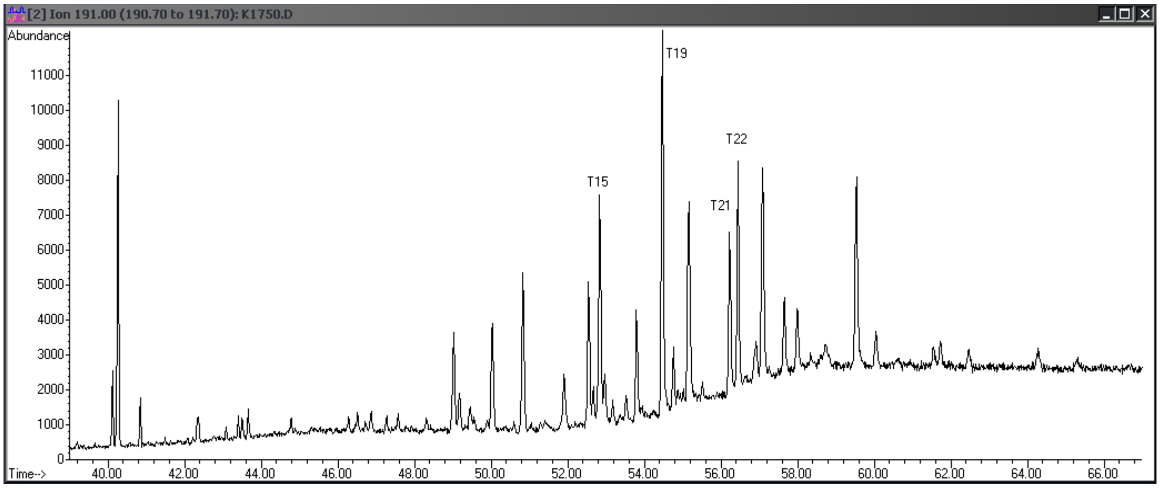


Figure 4-37. Sediment Core N26 Interval 8-10 cm, Year 2005 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).

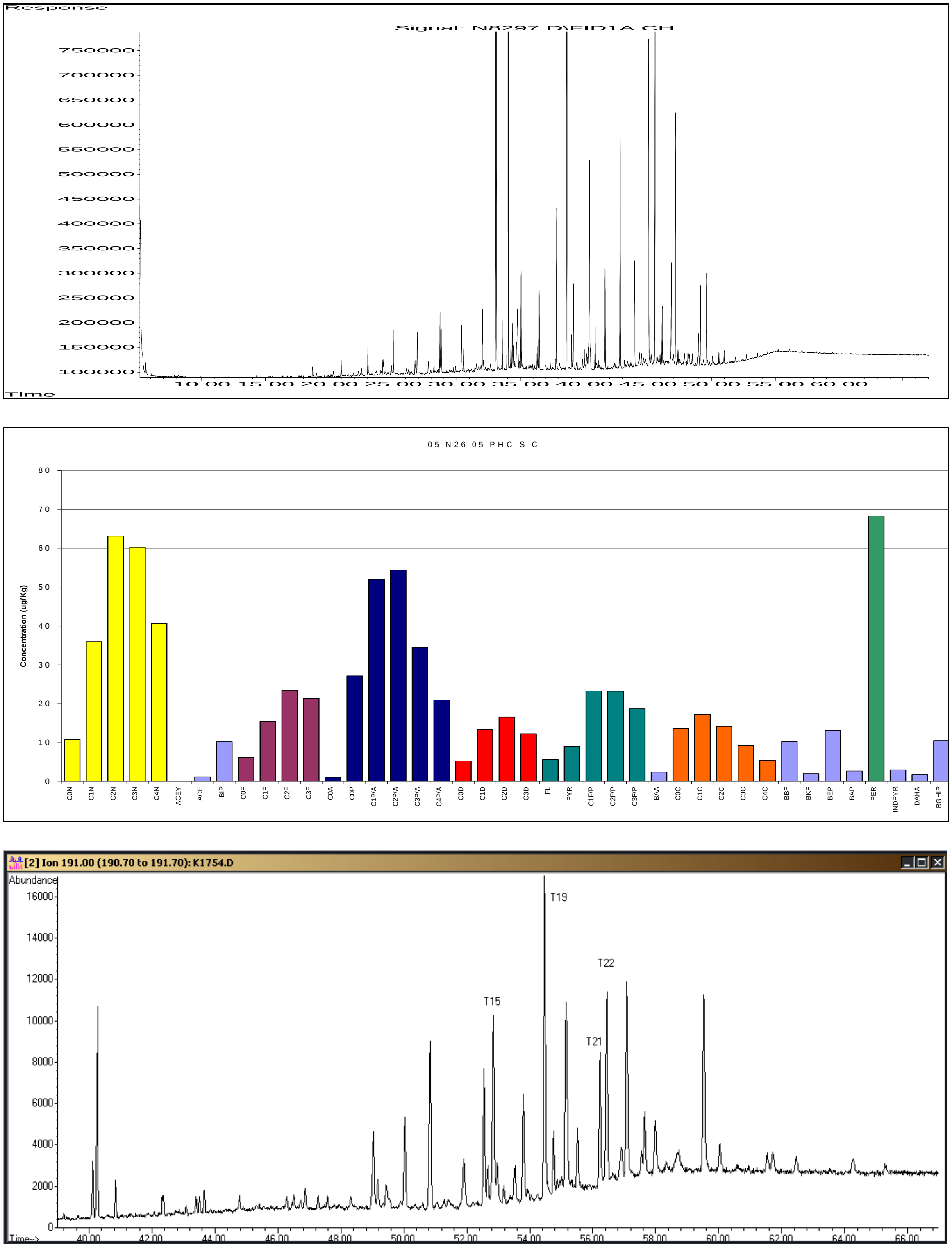
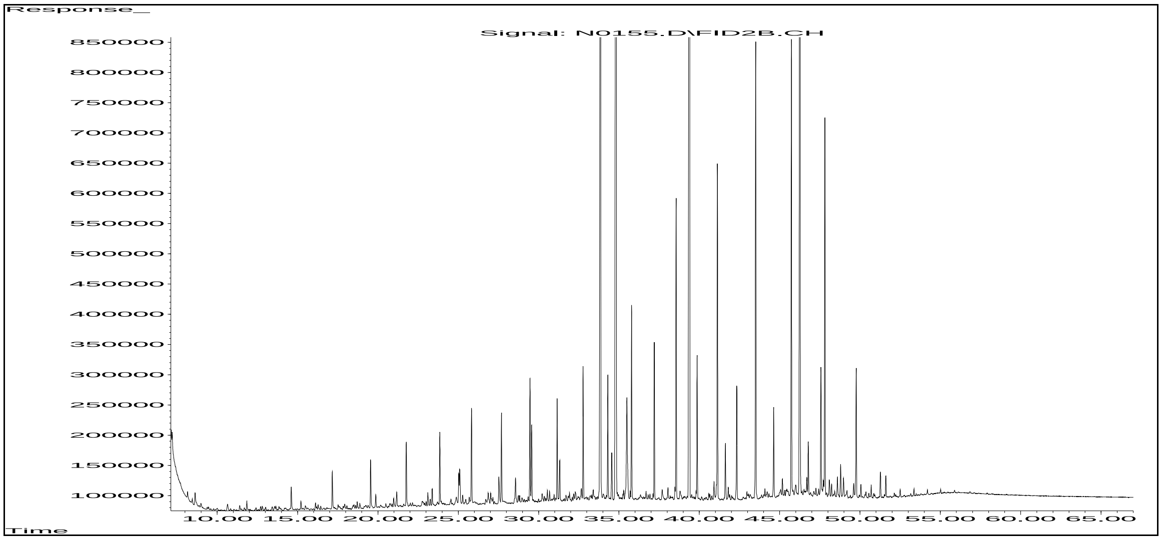
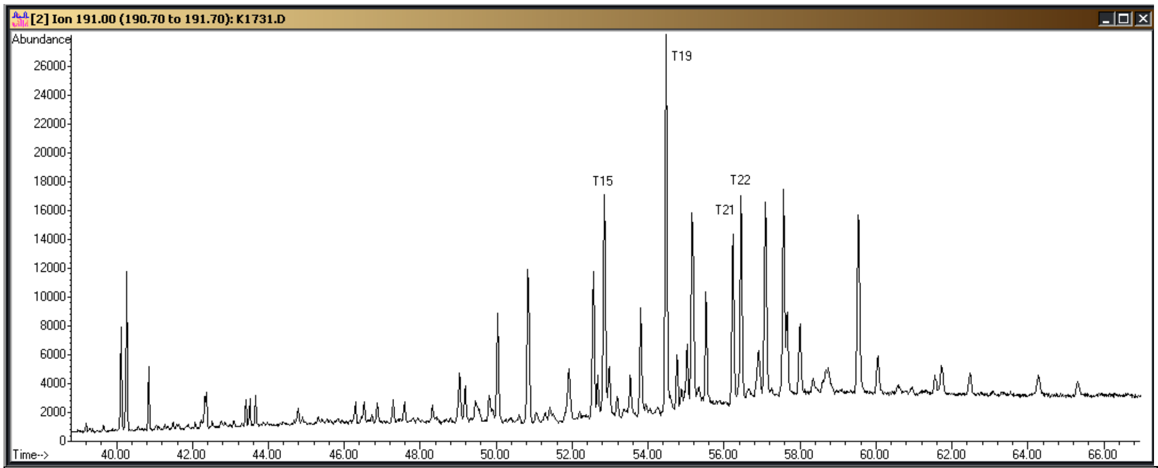


Figure 4-38. Sediment Core 1C Interval 0-2 cm, Year 2005 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).

Figure 4-39. Sediment Core 1C Interval 28-30 cm, Year 2005 – GC/FID chromatogram (top), PAH distribution histogram (middle), triterpane ion chromatogram (bottom).





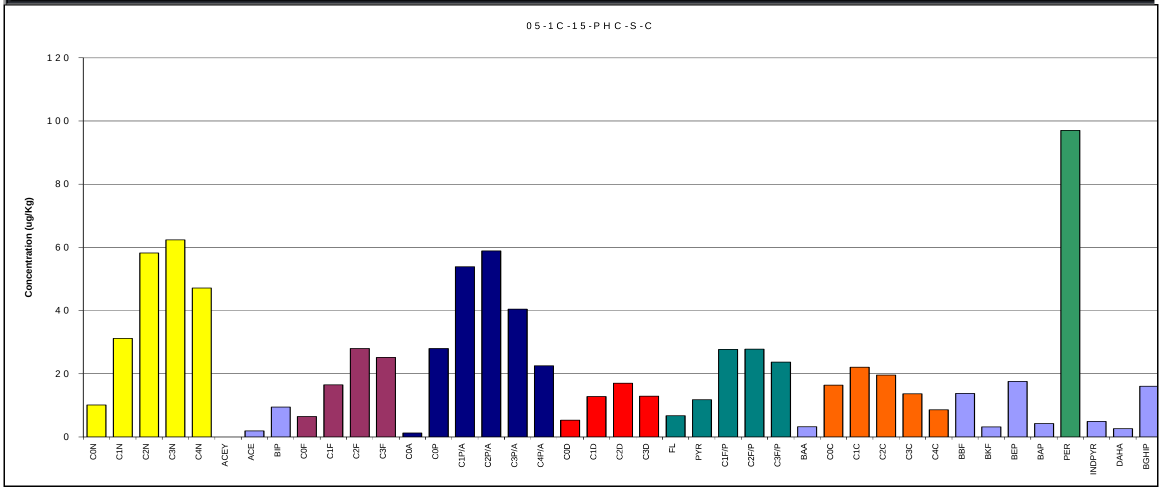
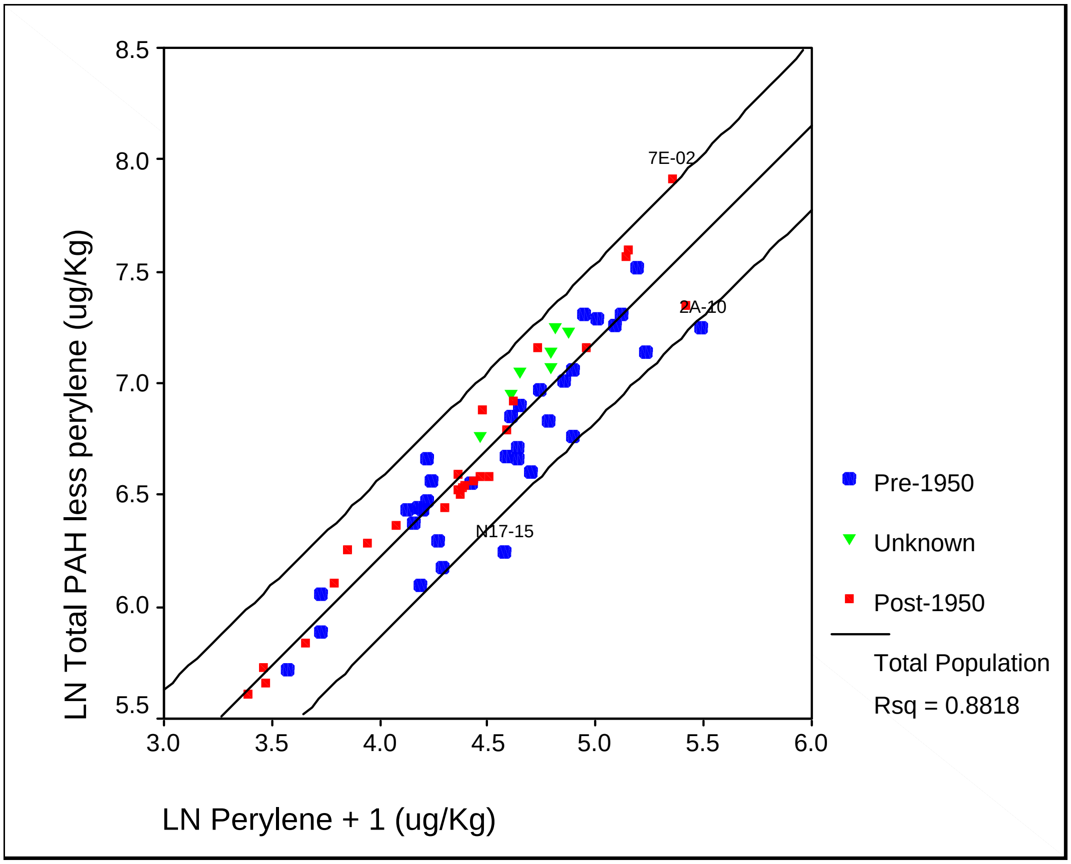


Figure 4-40. Regression plot of Total PAH less perylene versus perylene for all 2005 through 2006 sediment core samples.

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



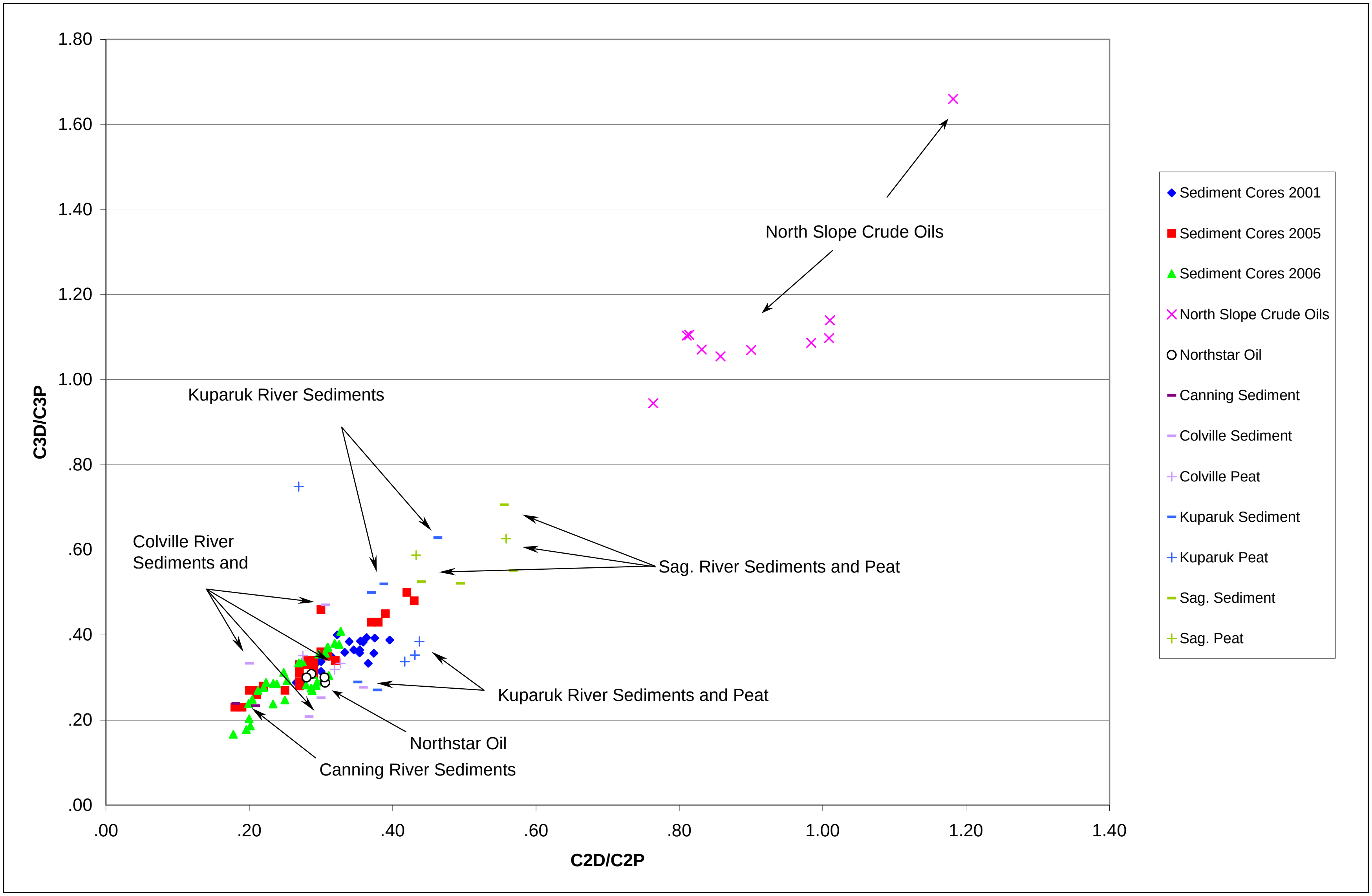


Figure 4-41. Double ratio source plot of C2D/C2P versus C3D/C3P for 2001, 2005, and 2006 sediment core samples.

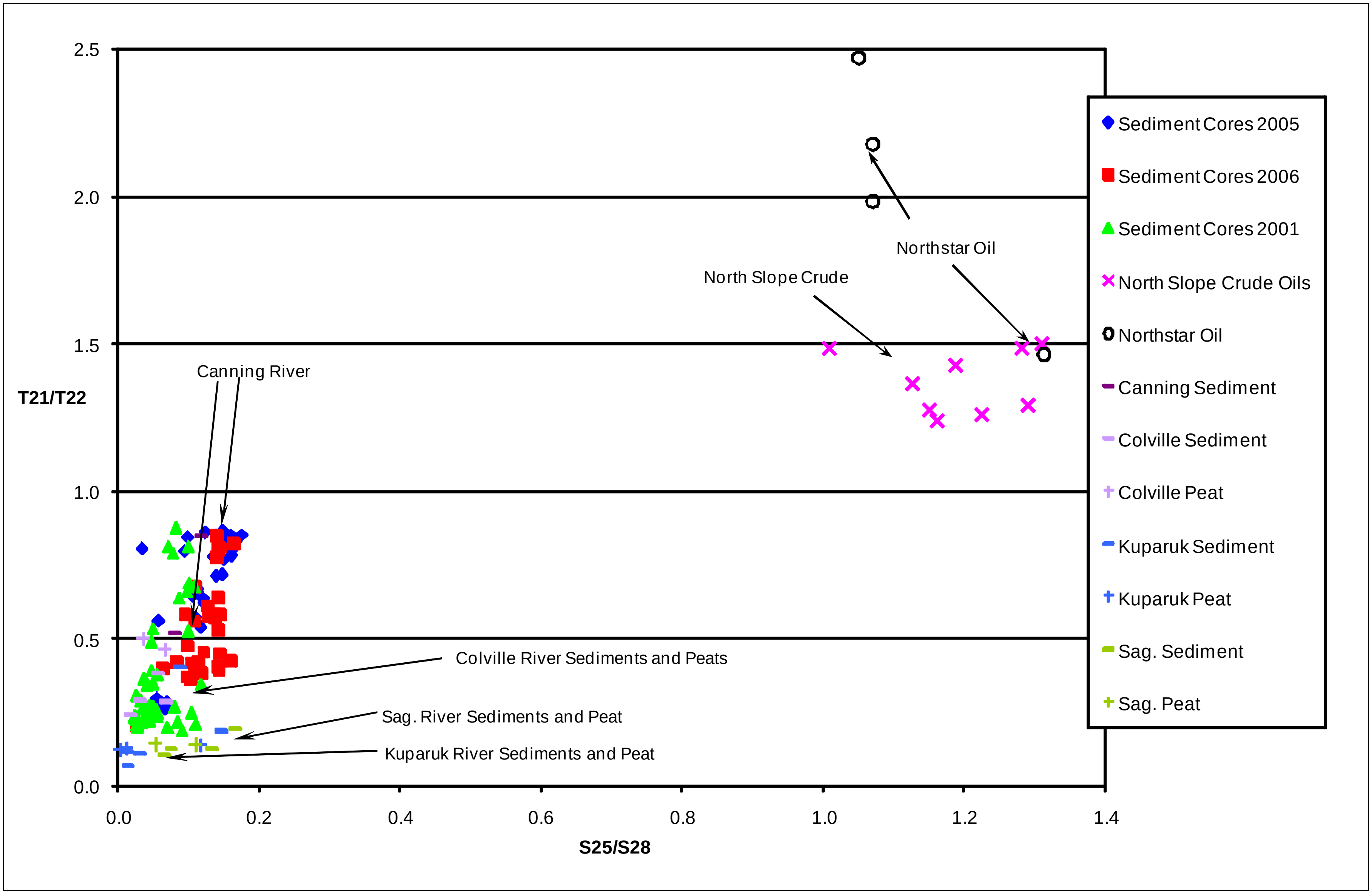


Figure 4-42. Double ratio source plot of S25/S28 versus T21/T22 for 2001, 2005, and 2006 sediment core samples.

Figure 4-43. Concentrations of aluminum versus (a) iron, (b) vanadium and (c) beryllium for sediment from the cANIMIDA study area collected in 2004-2006.

Equations are from linear regression calculations and r is the correlation coefficient. Dashed lines show the 99% prediction interval. Data from 2004-2006 are plotted with the regression lines and prediction intervals from 1999-2002 data.

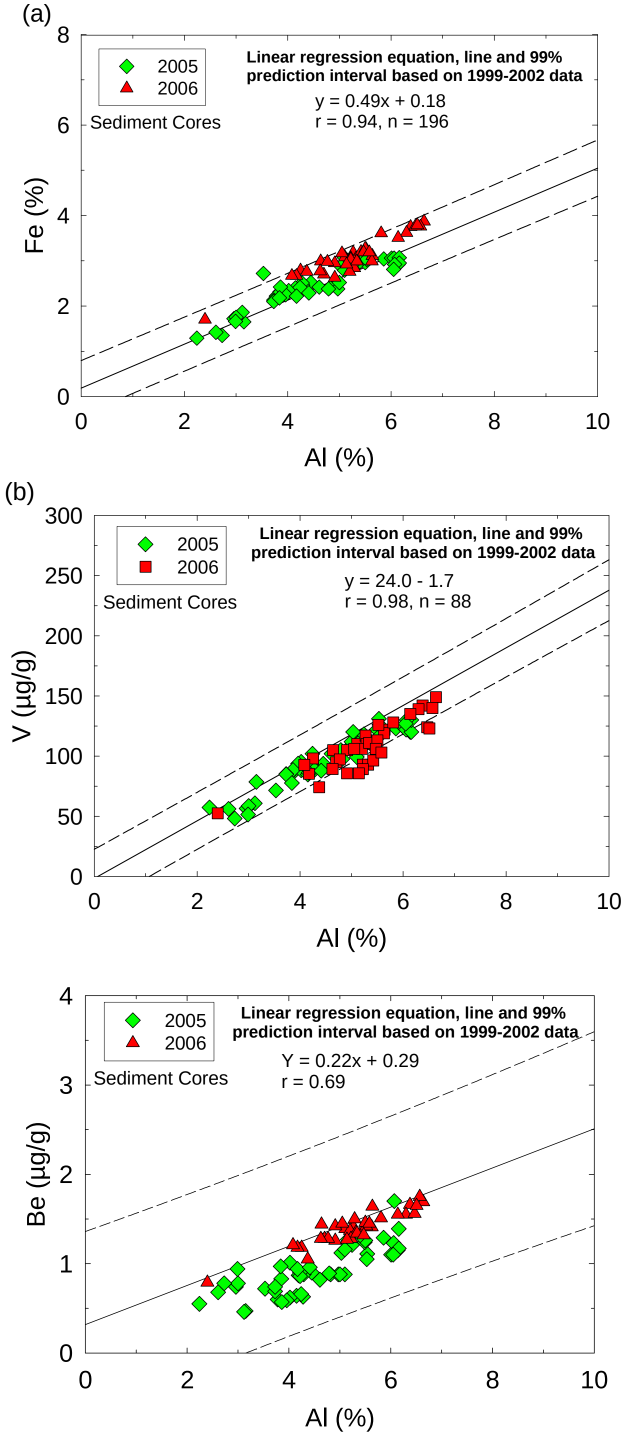


Figure 4-44. Concentrations of aluminum versus (a) nickel, (b) copper and (c) cobalt for sediment from the cANIMIDA study area collected in 2004-2006.

Equations are from linear regression calculations and r is the correlation coefficient. Dashed lines show the 99% prediction interval. Data from 2004-2006 are plotted with the regression lines and prediction intervals from 1999-2002 data.

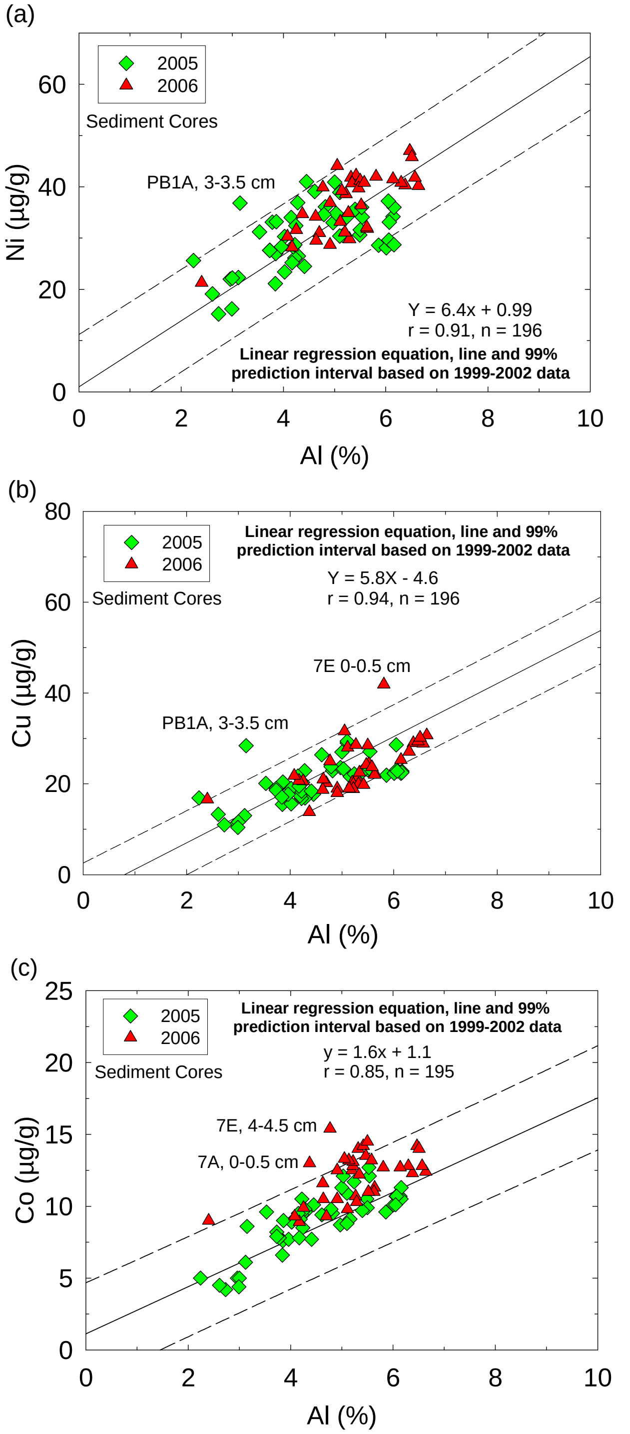


Figure 4-45. Concentrations of aluminum versus (a) zinc, (b) silver and (c) cadmium for sediment from the cANIMIDA study area collected in 2004-2006.

Equations are from linear regression calculations and r is the correlation coefficient. Dashed lines show the 99% prediction interval. Data from 2004-2006 are plotted with the regression lines and prediction intervals from 1999-2002 data.

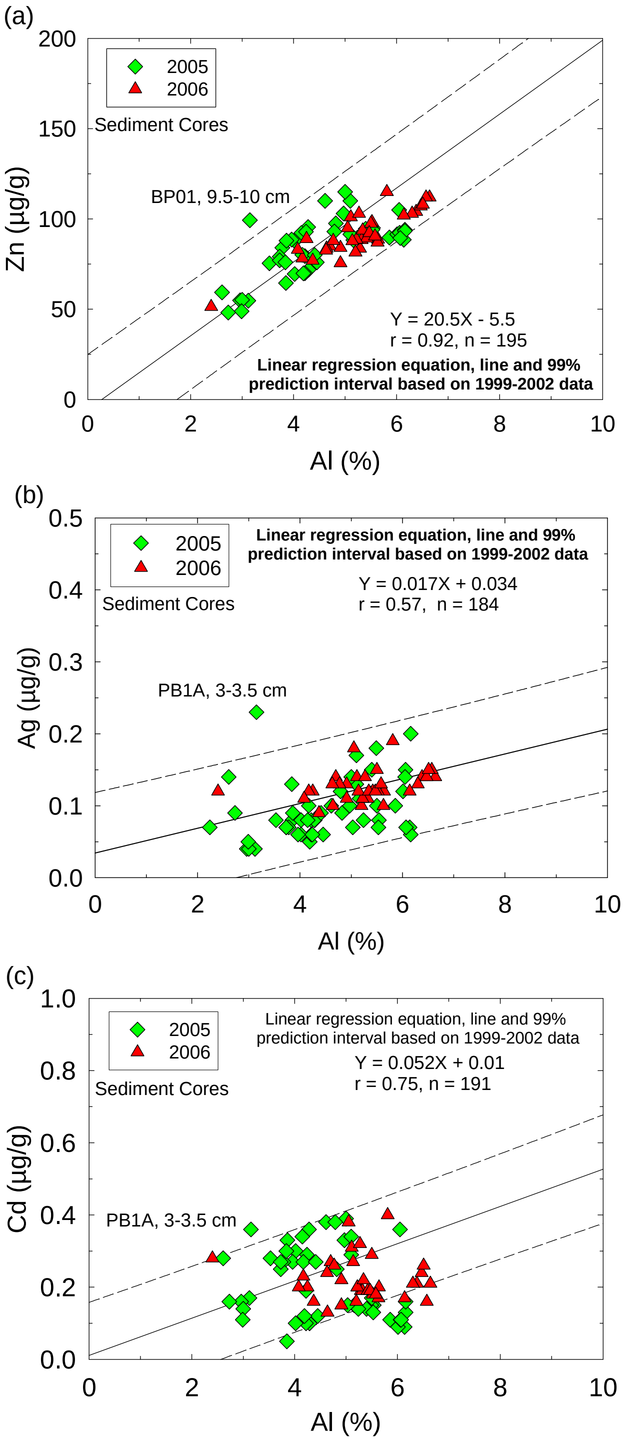


Figure 4-46. Concentrations of aluminum versus (a) lead, (b) mercury and (c) arsenic for sediment from the cANIMIDA study area collected in 2004-2006.

Equations are from linear regression calculations and r is the correlation coefficient. Dashed lines show the 99% prediction interval. Data from 2004-2006 are plotted with the regression lines and prediction intervals from 1999-2002 data.

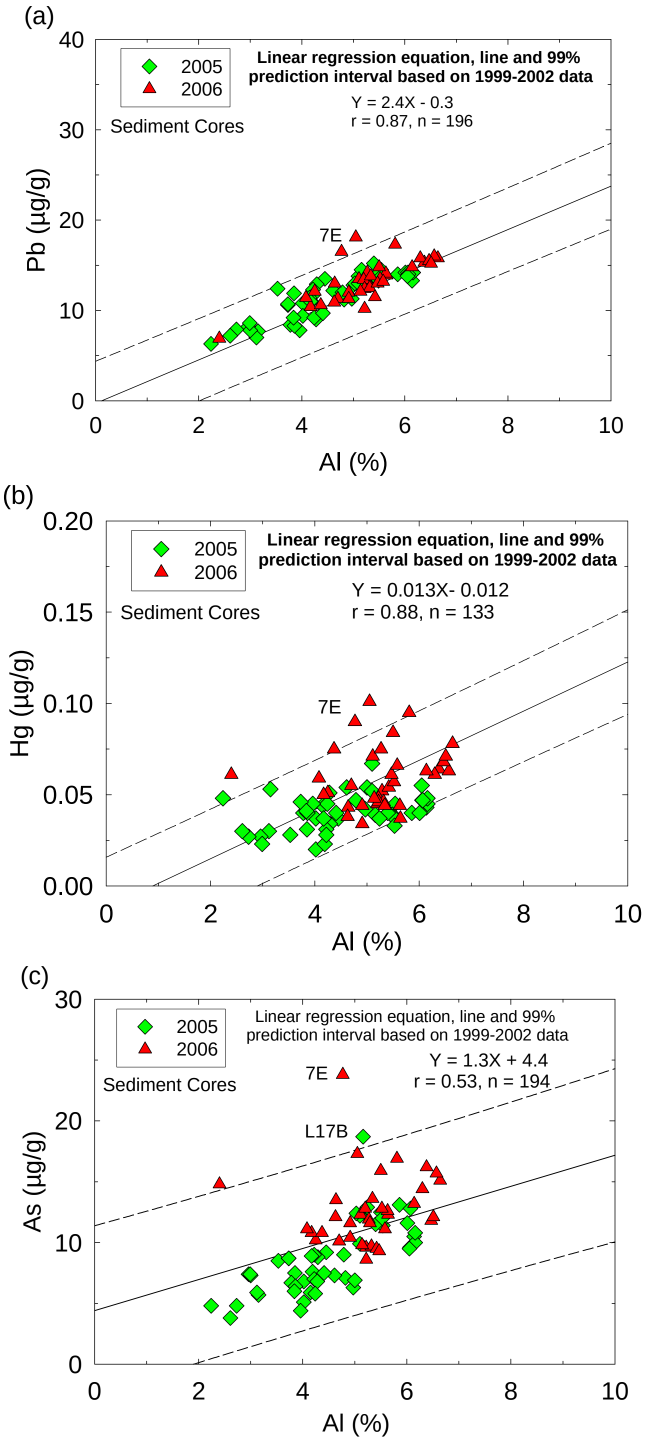


Figure 4-47. Concentrations of aluminum versus (a) antimony, (b) thallium and (c) chromium for sediment from the cANIMIDA study area collected in 2004-2006.

Equations are from linear regression calculations and r is the correlation coefficient. Dashed lines show the 99% prediction interval. Data from 2004-2006 are plotted with the regression lines and prediction intervals from 1999-2002 data.

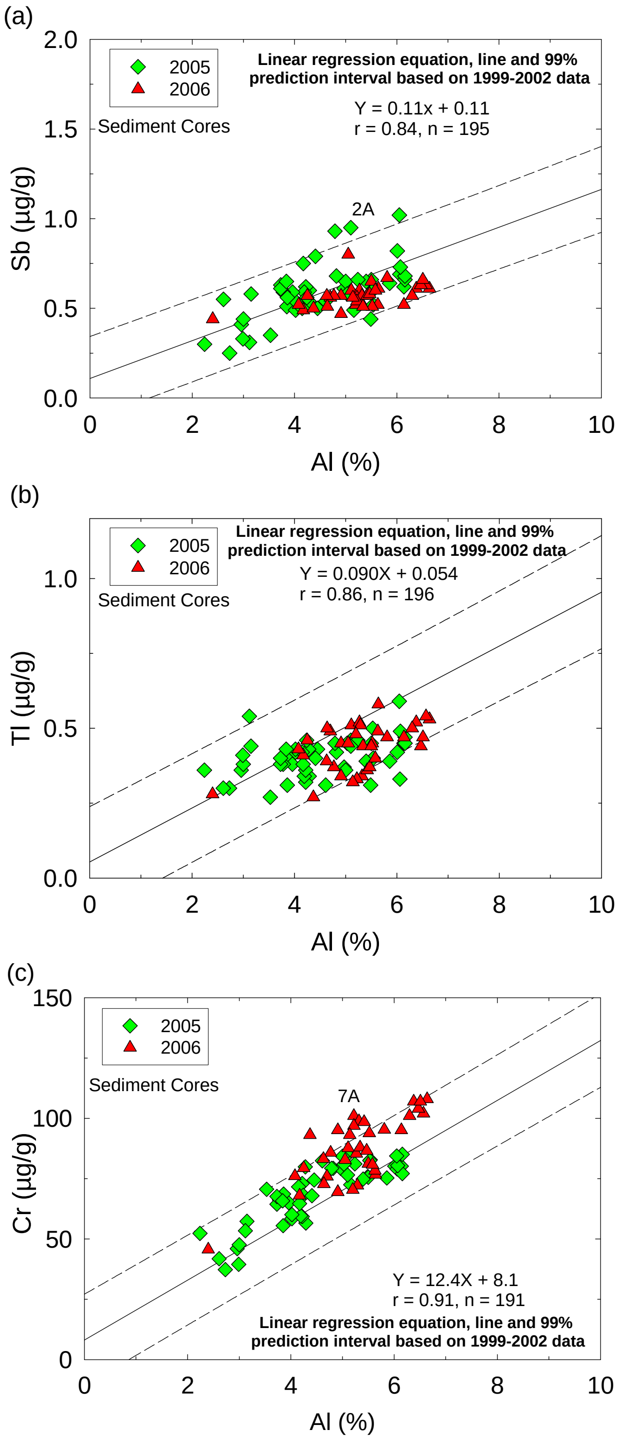


Figure 4-48. Concentrations of aluminum versus barium for (a) all sediment core samples from 2005 and 2006 and (b) 2005 samples that plotted above the upper prediction interval. Shaded rectangle in (a) is expanded in (b).

Equation is from linear regression calculations and r is the correlation coefficient. Dashed lines show the 99% prediction interval. Data from 2004-2006 are plotted with the regression lines and prediction intervals from 1999-2002 data.

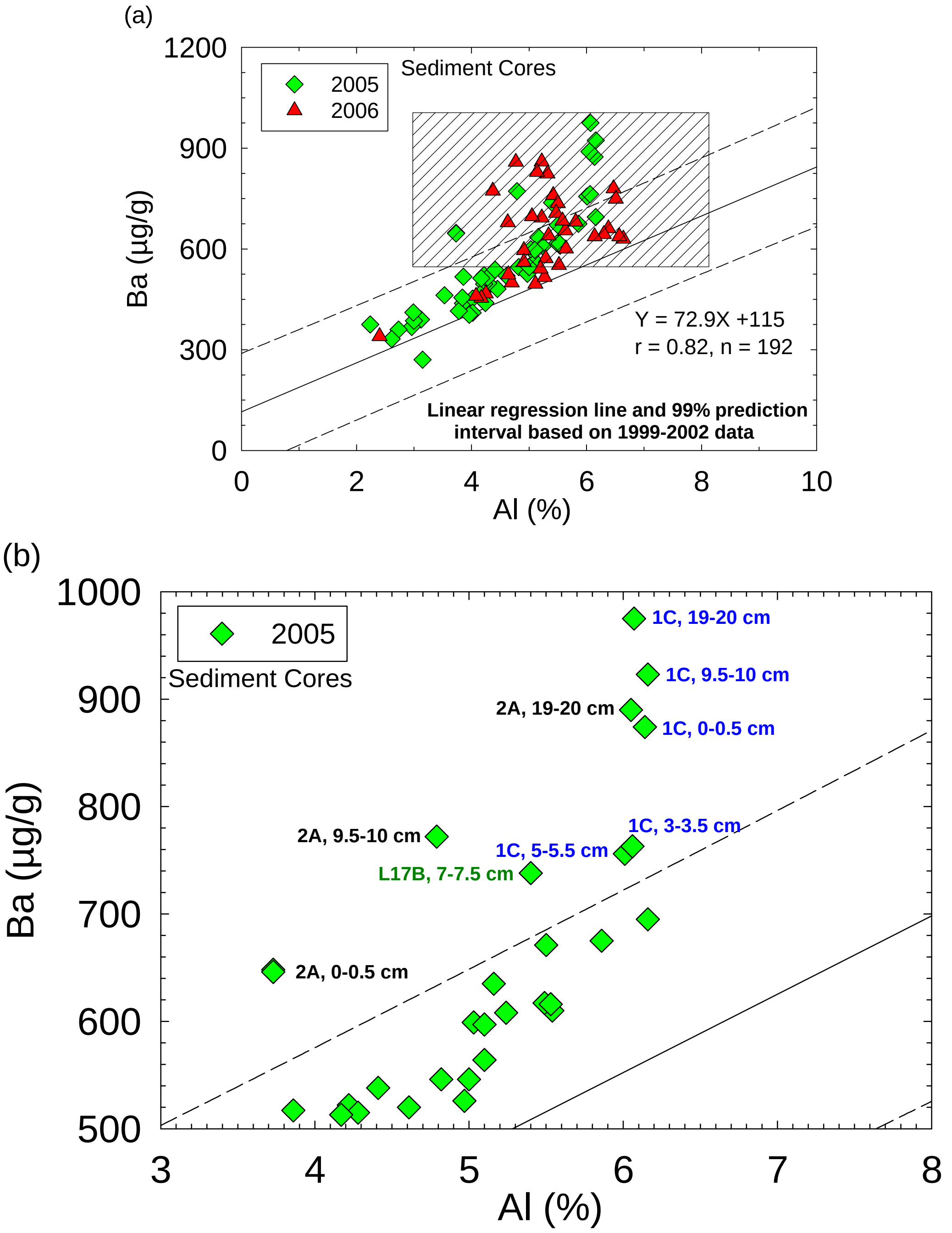


Figure 4-49. Concentrations of aluminum versus barium for (a) all sediment core samples from 2005 and 2006 and (b) 2006 samples that plotted above the upper prediction interval. Shaded rectangle in (a) is expanded in (b).

Equation is from linear regression calculations and r is the correlation coefficient. Dashed lines show the 99% prediction interval. Data from 2004-2006 are plotted with the regression lines and prediction intervals from 1999-2002 data.

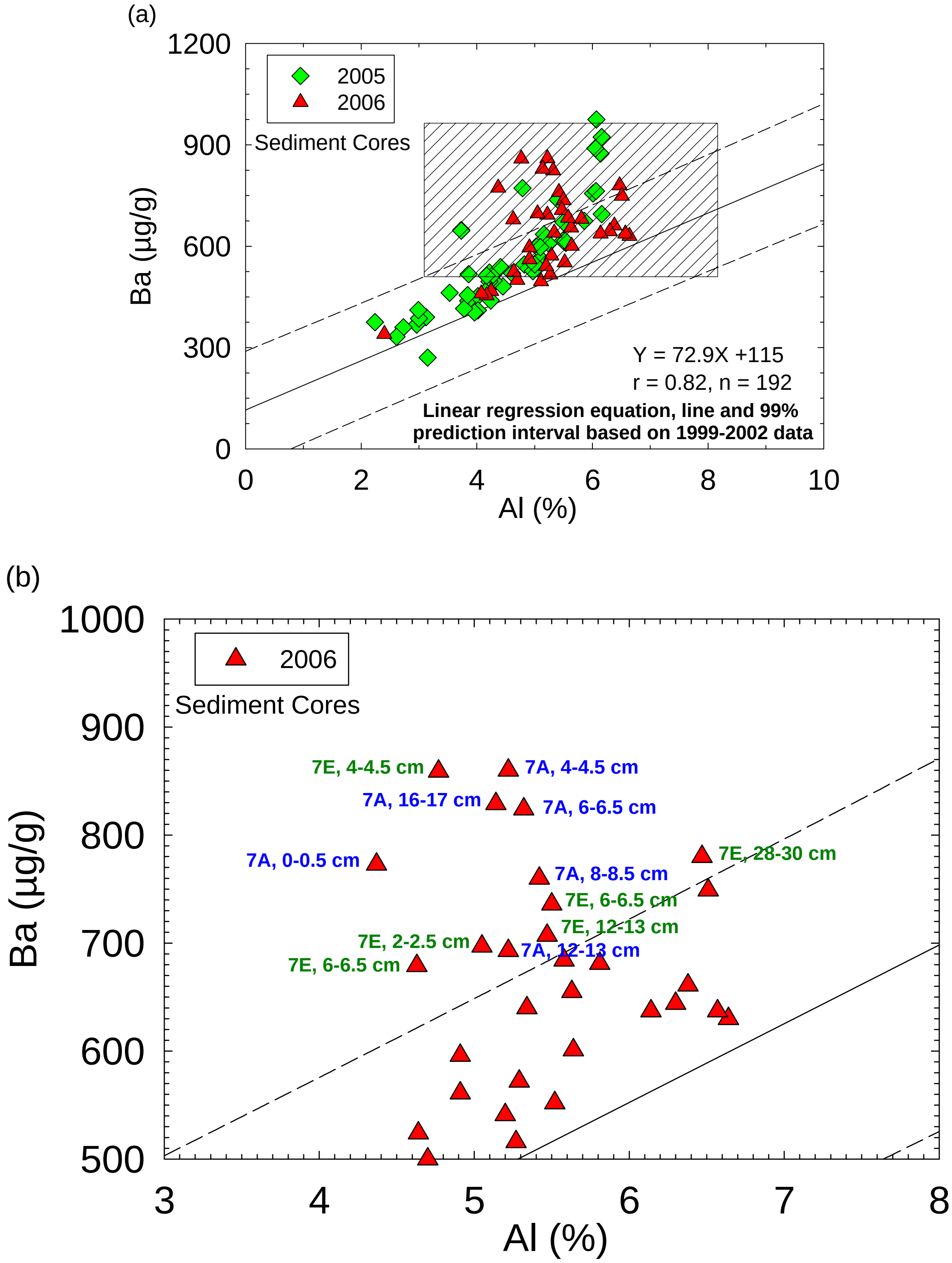
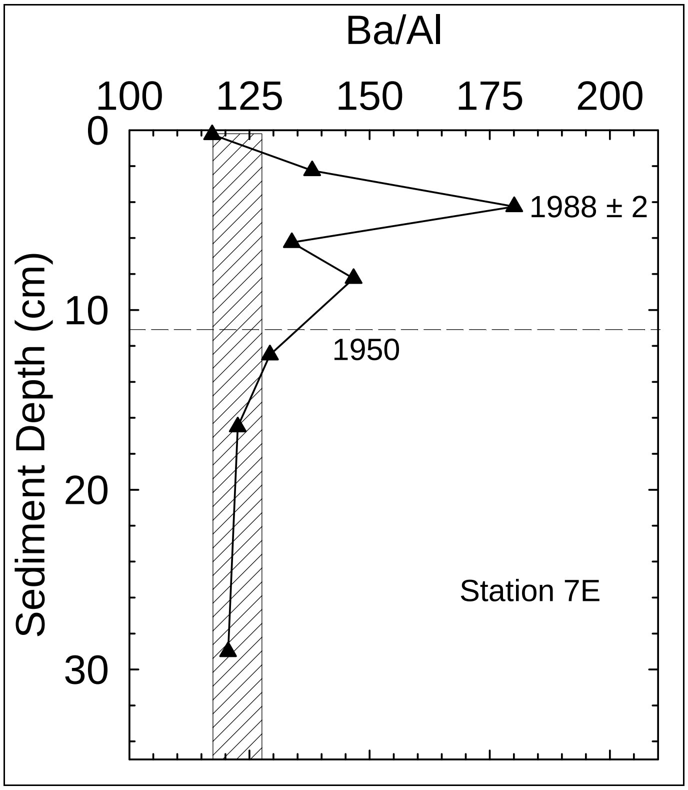


Figure 4-50. Vertical profile for the Ba/Al ratio in sediments from 2006 station 7E.

Shaded area shows background Ba/Al ratio (ppm vs. %) for study area. Dashed line shows deepest sample with detectable amounts of ^{137}Cs and thus dates to the early 1950s. Date of 1988 with error is from ^{137}Cs and excess ^{210}Pb data.



5.0 Recommendations

Based on the results and interpretations of the sediment samples collected under the ANIMIDA program (1999 – 2002) and the cANIMIDA program (2004 - 2006), there are a number of recommendations for future work in the study area.

- Continue to analyze surface sediments for hydrocarbon and metals to monitor potential impacts of regional petroleum development activities. However based on our current understanding of this dynamic near-shore coastal area, a monitoring interval of 3 to 5 years is reasonable. However, new offshore or near-shore development activities should be considered in any future monitoring efforts.
- Future sediment monitoring programs should consider including the following elements:
- Continue to perform focused surface sediment monitoring for hydrocarbons and metals in the Northstar Island and West Dock area to assess potential future impacts from Northstar production activities.
- Collect and analyze sediments for hydrocarbons and metals from new Liberty sediment stations in the Sagavanirtok River delta area, to augment existing baseline information for Liberty and to assess potential impacts from future Liberty development and production activities. This recommendation is based the assumption that Liberty Prospect will be developed from an alternative “onshore” location at the Endicott Satellite Drilling Island.
- 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 exploration activities (i.e, Camden Bay) and lease sales.
- Collect and analyze additional river sediment samples (e.g., McKenzie River, North East Brooks Range 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 to use Double Ratios of S25/S28 versus T21/T22 as a hydrocarbon discrimination tool and metal to Al ratios to assess metals inputs to the ANIMIDA study area.
- Analyze surface sediment and cores for radionuclides to better delineate areas of recent sediment deposition.
- Collect and analyze additional offshore sediment cores for hydrocarbons and metals to further characterize the historical sediment record in the 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.