FINAL REPORT

Environmental Studies in the Chukchi Sea 2008: Chemical Characterization

Volume 1

Service Contract No. 68393.0-SA-AKR

August 2010

Prepared for
ConocoPhillips Alaska Inc.
P. O. Box 100360
Anchorage, AK 99501

Shell Exploration & Production
3601 C Street, Suite 1000
Anchorage, AK 99503

Prepared by
Battelle Memorial Institute
Exponent Inc.
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PRINCIPAL AUTHORS

Lead Author

Jerry M. Neff
Neff & Associates LLC
20 Templewood Drive
Duxbury, MA 02332
781-837-3879
neffjm@comcast.net

Co-Authors

Gregory S. Durell
Battelle
397 Washington Street
Duxbury, MA 02332
781-952-5233
durell@battelle.org

John H. Trefry
Florida Institute of Technology
150 West University Blvd.
Melbourne, FL 32901
321-674-7305
jtrefry@fit.edu

John S. Brown
Exponent, Inc.
1 Clock Tower Place, Suite 150
Maynard, Massachusetts 01754
978-461-4602
jsbrown@exponent.com

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EXECUTIVE SUMMARY

The Chukchi Sea Lease Sale 193 Planning Area is located off the northwest coast of Alaska. The Chukchi Sea is a shallow embayment of the Arctic Ocean with water depths in most of the lease sale area ranging from 29 m to approximately 80 m, with water depths in a small area of the northeast corner of the lease area extending to about 3,000 m (MMS, 2007). About 80% of the planning area lies between the 30 and 90 m isobaths. The Burger and Klondike survey areas are located about 120 km northwest of Wainwright, AK, in 40 to 50 m of water (Figure ES-1).

Five exploratory wells were drilled between 1989 and 1991 in blocks leased in Chukchi Sea Sales 97 and 109 (Table ES-1). Exploratory wells were drilled in the Klondike and Burger survey areas during the summer and fall of 1989 and discovered gas, condensate, and crude oil resources. ConocoPhillips Alaska, Inc. (CPAI) and Shell Exploration and Production (Shell E&P) submitted bids for lease blocks in the Burger and Klondike survey areas in the February 6, 2008 Chukchi Sea Lease Sale 193. CPAI is managing a scientific field survey program in these two survey areas on behalf of both CPAI and Shell E&P. The field program will provide baseline (pre-drilling) information on the physical, chemical, biological, and oceanographic environment, including assessment of zooplankton and benthic biological communities, and distribution and concentrations of chemicals associated with offshore oil and gas operations (metals and hydrocarbons) in the Klondike and Burger survey areas. An assemblage of bottom-founded acoustic recorders were also placed within the areas to capture calls from vocalizing marine mammals and to record sound from ambient conditions (currents, ice, etc).

The objective of the Chemical Characterization Program component of the Chukchi Sea Environmental Studies Program is to determine baseline (pre-exploration and development) concentrations of metals and hydrocarbons in sediments and tissues of zooplankton and benthic invertebrates in the study areas and how distribution and concentrations of these chemicals may be being influenced by inter-annual environmental changes. This report summarizes the results of the Chemical Characterization Program for 2008.

Sediments and invertebrates were sampled at 65 stations in the Burger (34 stations) and Klondike (31 stations) survey areas, 900 km^2 squares in 40 to 50 m of water (Figure ES-1). Five of the stations in each survey area were at the historic drill sites. A total of 80 sediment samples were analyzed for hydrocarbons and metals. A total of 79 marine invertebrate samples also were analyzed for hydrocarbons and metals (Table ES-2).

Sediment and tissue samples were analyzed for four hydrocarbon types: total petroleum hydrocarbons (TPH), total and individual resolved saturated hydrocarbons (SHC), total and individual sterane and triterpane petroleum biomarkers (S/T), and total and individual polycyclic aromatic hydrocarbons (PAH) (Table ES-3). The PAH analyses included 42 parent PAH and alkyl-PAH isomer groups. Lipids also were measured in tissues to aid the data interpretation. Twelve metals were analyzed in sediment and tissue samples: silver (Ag), arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), lead (Pb), selenium (Se), and zinc (Zn) (Table ES-3). Aluminum (Al) also was analyzed in sediment samples as an aid to normalizing metals concentrations to the clay mineral fraction of sediments. Grain size, total organic carbon (TOC), and carbonate were also measured in sediment samples.

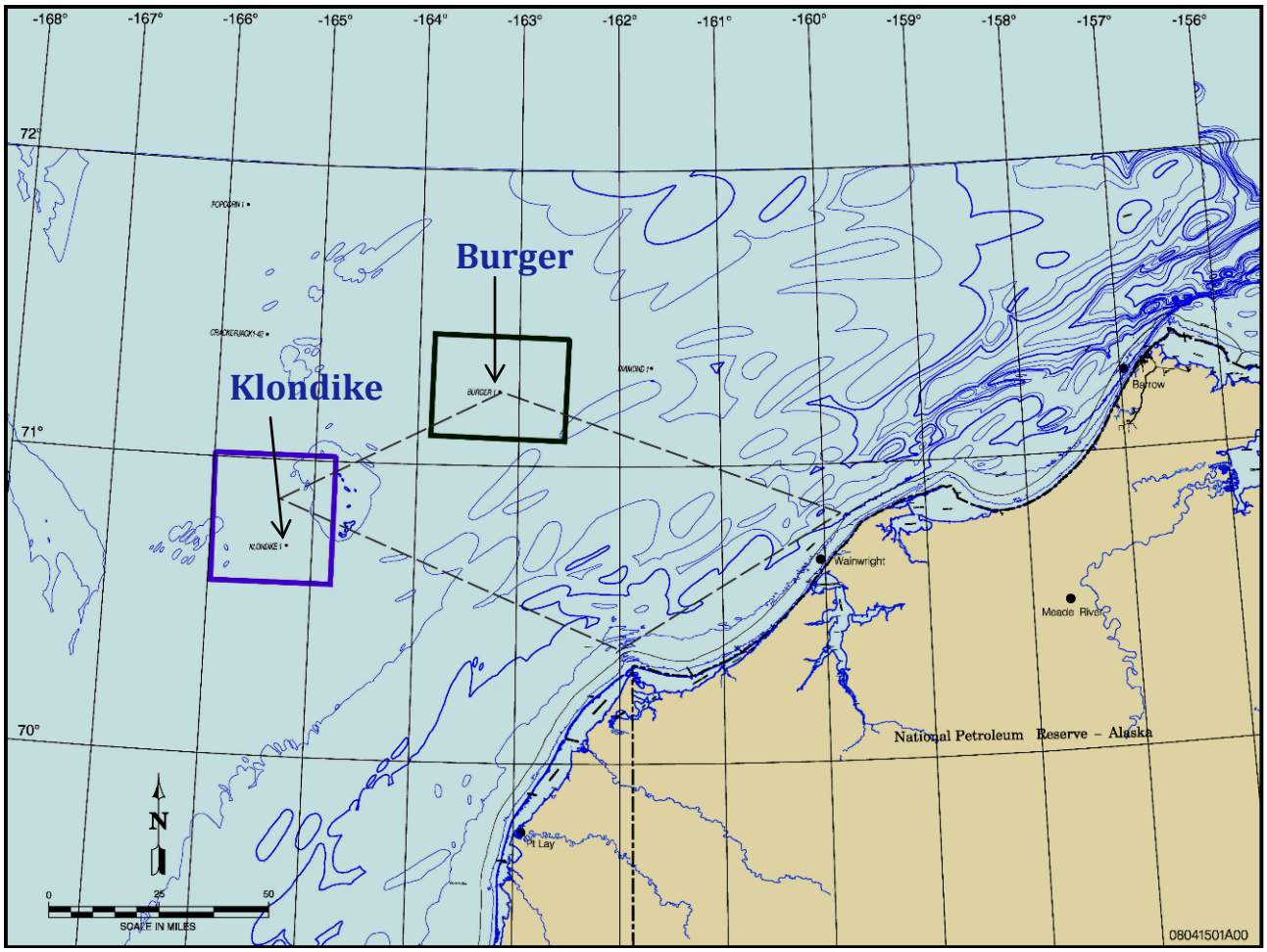

Figure ES-1. The Chukchi Sea study area showing the locations of the Burger and Klondike survey areas and the locations of two exploratory wells drilled in 1989.

Table ES-1. Chronological order of exploratory wells drilled to date on the Federal outer continental shelf of the U.S. Chukchi Sea. Data from BOEMRE, Alaska OCS Region, Anchorage, AK.

Prospect	Spud Date[a]	Water Depth (meters)	Drilling Unit
Klondike	7/9/89	43	Explorer III Drillship
Burger	9/22/89	45	Explorer III Drillship
Popcorn	10/14/89	44	Explorer III Drillship
Crackerjack	9/23/90	42	Explorer III Drillship
Diamond	9/7/91	46	Explorer III Drillship

[a] Date drilling began.

Table ES-2. Numbers of sediment and marine invertebrate tissue samples collected and number analyzed (in parentheses) at the Burger and Klondike survey areas in 2008.

Sample	Burger	Klondike	Total
Sediment	60 (39)	59 (41)	119 (80)[a]
Amphipods	9 (9)	1 (1)[b]	10 (10)
Crabs	16 (9)[b]	16 (9)	32 (18)
Clams	36 (17)	10 (6)[b]	46 (13)
Worms	10 (9)[b]	24 (9)[b]	34 (18)
Zooplankton	14 (5)	12 (5)[3]	26 (10)
Total	145 (88)	122 (71)	267 (149)

[a] Includes 13 samples of subsurface sediment layers (2 – 12 cm below sediment surface) from three sediment cores collected at the two historic drill sites.
[b] Hydrocarbons, but not metals, were analyzed in some tissue samples because insufficient tissue mass.

Table ES-3. Summary of chemical and physical analyses of sediment and marine invertebrate tissue samples.

Parameter	Sediment	Invertebrate Tissue
Hydrocarbons and Lipids		
Parent and Alkylated PAH (PAH)	X	X
Petroleum Biomarkers (S/T)	X	X
Saturated Hydrocarbons (SHC)	X	X
Total Petroleum Hydrocarbons (TPH)	X	X
Total Lipids		X
Metals and Ancillary Parameters		
Ag, Al, As, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Pb, Se, Zn	X	
Ag, As, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Pb, Se, Zn		X
Grain Size	X	
Total Organic Carbon (TOC) and Carbonate	X	

Sediment grain size was quite variable from station to station and also between the Burger and Klondike survey areas. Gravel ranged from 0 to 61%, sand from 14 to 96%, silt from 4 to 64% and clay ranged from 0 to 36% in all samples. The hydrocarbons and metals in sediments are associated primarily with the silt + clay (mud) fraction, which usually also contains most of the TOC. The Burger survey area contained more fine-grained sediments than the Klondike area, with a mean value for mud of 53% for the Burger sediments compare to 40% for Klondike sediments. Fine-grained sediments with ≥60% mud in both areas were located farthest from the coast. Fine-grained sediment from river runoff and coastal erosion settles slowly and often is transported offshore by prevailing water currents, whereas coarse-grained sands and gravel settle rapidly and usually are deposited in nearshore areas. However, this distribution of sediment texture is continually modified by frequent storm winds from the northeast, particularly in the open-water season, causing sediment resuspension and bed transport, and the strong prevailing northward water currents from the Bering Straits through the Herald Valley, Central Channel, and Barrow Canyon, that carries fine-grained sediments, primarily from the Yukon River (Ortiz et al. (2009) and redistributes them throughout the area (Weingartner, 2008). The Burger and Klondike survey areas lie between the Central Channel and the Barrow Canyon. Thus, there is no obvious relationship between water depth, which ranges from 38 to 45 m, and grain size in the two areas.

The range of TOC concentrations in surface sediments was 0.12 to 1.54% (a 13-fold range), with a lower average of 0.73 % in sediments from the Klondike area relative to 0.95% for sediments from the Burger area. Subsurface sediments from cores collected at the two historic drill sites contained slightly higher mean TOC concentrations (1.01%). TOC in Chukchi Sea sediments is adsorbed to mud sediment particles or associated with particulate organic carbon (POC), derived from terrestrial plant matter and marine plankton detritus, and is an important source of nutrition for the benthic community (Moran et al., 2005; Chen et al., 2006; Magen et al., 2010).

Hydrocarbon concentrations and distributions are variable in surface sediments throughout the Burger and Klondike survey area, with higher concentrations in some surface and subsurface sediments at the historic drill sites at Klondike and Burger (Table ES-4). TPH concentrations in surface sediments from fixed and random background stations span a 39-fold range, reflecting the mixed, primarily biogenic, sources of this complex mixture of primarily saturated hydrocarbons and related wax esters and fatty acids from a mixed marine and terrestrial origin. ∑SHC, total PAH (TPAH) and S/T concentrations in surface sediments are less variable (≈ 10-fold range) and distributions are similar. A large fraction of the hydrocarbons in sediments at background stations in the two survey areas probably is derived from deposition of particulate organic carbon (POC) from surface waters (Moran et al., 2005). The concentrations of all the hydrocarbon types measured as part of this study are well within the range of the non-toxic background concentrations reported by other studies in Alaskan and other Arctic coastal and shelf sediments.

Surface and subsurface sediments from the two historic drill sites contain higher concentrations of all hydrocarbon types, particularly TPAH and total S/T, than the surface sediments from the other stations. The center stations at the historic drill sites have the highest hydrocarbon concentrations, with TPAH concentrations in core samples ranging from 470 to 650 µg/kg and 636 to 3,082 µg/kg, at Burger and Klondike, respectively. The concentrations dissipate notably away from the center. The highest concentrations are in the surface (0 to -2 cm) samples. These data suggest that the increment in hydrocarbon concentrations is from historic drilling activities. Similar elevated PAH concentrations have been observed in sediments at former drill sites in the Alaskan and Canadian Beaufort Sea and in nearshore surface sediments throughout the Arctic (Neff, 2010). The PAH are derived primarily from organic-rich geologic strata penetrated by the drill. The organic layers contain peat eroded from the vast Holocene deposits on the North Slope, kerogen-containing shales, and soft coal that is carried to the coastal waters of the Arctic Ocean in runoff. Additional PAH are from the sandstone in the oil- and gas-bearing strata penetrated by the drill. These hydrocarbons are in the cuttings discharged to the ocean during exploratory drilling. PAH in kerogens and peat are highly refractory to dissolution and biodegradation, accounting for their persistence in surface sediments for two decades and their low bioavailability to benthic marine animals.

A few subsurface sediments from the drill sites also contained elevated concentrations of barium, a well-known indicator of drilling mud and cuttings accumulation on the sea floor. Highest concentrations of Ba in the sediment core at the Klondike drill site are in the upper 6 cm (~ 2,000 µg/g), and concentrations decrease slightly with depth to 1,650 µg/g at -12 cm. Barium concentrations at all levels in the core are four- to five-fold higher than concentrations in surface sediments from fixed and random stations in the Burger and Klondike survey areas. The excess barium in the sediment cores undoubtedly was derived from the barite (barium sulfate) used as a

weighting agent in the drilling muds used to drill the wells. Barite occurs naturally in the mud fraction of marine sediments and has a very low aqueous solubility and is not toxic to marine organisms (Neff, 2010).

Table ES-4. Range of hydrocarbon concentrations in surface sediments and tissues of marine invertebrates from fixed and random stations in the Burger and Klondike survey areas and in surface and subsurface sediments from stations at the two historic drill sites. Concentrations are µg/kg dry wt (parts per billion).

Hydrocarbon Type[a]	Sample Type	Burger Survey Area	Klondike Survey Area
		Fixed and Random Stations	
Total Petroleum Hydrocarbons (TPH)	Sediment	2,430 – 18,000	461 – 15,300
	Clam	4,690 – 129,000	79,800
	Amphipod	3,150 – 38,400	33,700
	Crab	1,450 – 8,010	885 – 19,800
	Worm	3,400 – 130,000	4,720 – 133,000
	Zooplankton	113,000 – 361,000	291,000 – 888,000
Total Resolved SHC (∑SHC)	Sediment	963 – 3,920	371 – 4,010
	Clam	1,020 – 3,230	1,720 – 8,830
	Amphipod	1,050 – 12,600	6,340
	Crab	500 – 3,980	794 – 14,200
	Worm	3,110 – 19,900	2,410 – 6,480
	Zooplankton	27,000 – 143,000	90,800 – 449,000
Total Steranes/ Triterpanes (S/T)	Sediment	7.18 – 28.4	2.94 – 23.7
	Clam	0 – 15.4	0 – 8.76
	Amphipod	0 – 5.43	25.8
	Crab	3.71 – 5.83	5.10 – 17.8
	Worm	13.3 – 75.2	14.5 – 28.8
	Zooplankton	13.0 – 40.5	134 – 459
Total Polycyclic Aromatic Hydrocarbons (TPAH)	Sediment	121 – 482	47.2 - 451
	Clam	26.7 – 204	70.6 - 355
	Amphipod	32.2 – 45.8	84.8
	Crab	22.7 – 99.9	30.5 – 69.8
	Worm	154 – 302	133 - 315
	Zooplankton	75.7 – 92.1	140 - 360

Table ES-4. Range of hydrocarbon concentrations in surface sediments and tissues of marine invertebrates from fixed and random stations in the Burger and Klondike survey areas and in surface and subsurface sediments from stations at the two historic drill sites. Concentrations are µg/kg dry wt (parts per billion), continued.

Hydrocarbon Type[a]	Sample Type	Burger Survey Area	Klondike Survey Area
		Historic Drill Site Stations	
TPH	Sediment	1,870 – 22,200	4,040 – 22,200
∑SHC	Sediment	1,980 – 3,440	1,840 – 5,600
S/T	Sediment	16.0 – 52.2	13.6 – 79.7
TPAH	Sediment	253 – 650	265 – 3,080

[a] TPH – total petroleum hydrocarbons, the sum of resolved and unresolved, primarily saturated hydrocarbons in the n-C_9 through n-C_{40} range. ∑SHC: the sum of individual resolved saturated hydrocarbons (38 n-alkanes and isoprenoids). S/T – the sum of 17 steranes and triterpanes – a source indicator (petroleum biomarker) for complex hydrocarbon assemblages. TPAH – the sum of 42 parent and alkylated polycyclic aromatic hydrocarbon isomers.

Concentrations of different hydrocarbon types are variable in tissues of marine invertebrates collected at the Burger and Klondike survey areas (Table ES-4). The variability in concentrations of hydrocarbons in tissues of benthic invertebrates may be related to variability among stations in the concentrations of mud and TOC in surface sediments. Concentrations of the different hydrocarbon types are higher in some of the marine invertebrate taxa from the Klondike area than in those from the Burger area. Because hydrocarbons tend to bind more strongly to fine particles and organic coatings on sediment particles, and samples from Burger contain slightly higher mud (52.9 ± 17.2%) and TOC (0.95 ± 0.26%) concentrations than surface sediments from Klondike (40.4 ±17.3% mud and 0.73 ± 0.31% TOC), it is likely that the hydrocarbons in Burger sediments are less bioavailable than those in Klondike sediments.

Zooplanktons collected in surface waters at both survey areas contain higher concentrations of TPH, ∑SHC, and S/T than the benthic invertebrates; the range of TPAH concentrations is similar in all marine invertebrates sampled. This is further confirmation that POC is an important source of hydrocarbons in sediments and marine invertebrates. The POC in the Chukchi Sea is derived primarily from primary production in surface waters, and is composed of a complex mixture, including saturated hydrocarbons and fatty acids, and steranes/triterpanes of biological origin (Moran et al., 2005).

Concentrations of TPAH vary by a factor of about 10 in surface sediments and clam tissues collected in the two survey areas. TPAH concentrations in the other invertebrate taxa are less variable (2.3 to 4.7-fold), reflecting the ability of marine crustaceans and polychaete worms to rapidly excrete accumulated PAH.

Hydrocarbons usually are bioaccumulated by benthic invertebrates (e.g., clams, worms, amphipods, and crabs) primarily from hydrocarbons desorbing from the hydrocarbon reservoir in the fine-grained sediment fraction and from ingestion of food items. Thus, there should be a relationship between concentrations of hydrocarbons in benthic marine invertebrates and in the sediments on or in which they reside. There is little relationship between the concentrations of ∑SHC, total S/T, and TPAH in tissues of benthic invertebrates and the sediments where they

reside (Table ES-4). If these invertebrates were bioaccumulating hydrocarbons from sediments, concentrations in tissues should be higher than those in the sediments. Only SHC concentrations tend to be higher in tissues of amphipods and crabs than in sediments. Much of the SHC is pristane, which these crustaceans bioaccumulate from zooplankton, particularly calanoid copepods that biosynthesize this isoprenoid. These results indicate that TPAH and S/T in surface sediments at Burger and Klondike, including surface sediment from the historic drill sites, have a very low bioavailability to benthic clams, crustaceans, and worms residing in the sediments. Zooplankton, particularly those collected in the Klondike survey area, contain higher concentrations of SHC and S/T than the benthic invertebrates do. These hydrocarbons probably are biogenic. Most of the TPH in invertebrate tissues also is biogenic.

The TPH, PAH, SHC, and S/T in sediments and invertebrate tissues in the Burger and Klondike survey areas of the Chukchi Sea come from a variety of sources [e.g., shoreline erosion, diagenic terrestrial plant material (i.e., peat and kerogen), aquatic plant (mainly phytoplankton) material, natural petroleum hydrocarbon sources (oil seeps, and coal in runoff from rivers and coastal erosion), and long-range atmospheric transport and deposition) (Valette-Silver et al. 1999)]. Overall, the levels of hydrocarbons measured in the Chukchi Sea study areas are within the range reported from previous studies of other Arctic, including Alaskan, continental shelf areas.

The sediment alkane assemblage is dominated by odd-carbon-number alkanes, indicative of a regional hydrocarbon background of terrestrial plant origin. The higher concentration of low molecular weight alkanes and the bimodal distribution of alkanes in the chromatograms for sediments from the historic drill sites at Burger and particularly Klondike indicate a mixture of natural background biogenic and petrogenic hydrocarbons. The PAH assemblage in drill site sediments is dominated by alkyl naphthalenes, phenanthrenes, and fluoranthenes/pyrenes, indicative of a petrogenic source, probably peat and kerogen-rich shale deposits that cover the North Slope tundra (Mull, 1995; Jones and Yu, 2010). The sources of the hydrocarbons in sediments at these historic drilling sites, dominated by higher than background concentrations of TPAH, and total S/T, probably is mixture of regional background hydrocarbons and shallow peat/kerogen layers drilled during the former exploratory drilling operations.

Although concentrations of PAH, SHC, and S/T are lower in most benthic invertebrates than in the sediments in which they reside, these hydrocarbons probably are bioaccumulated from the small amounts desorbing from the sediments, or from ingestion of organisms and organic detritus in sediments. Zooplankton probably bioaccumulate hydrocarbons from ingestion of organic particles, including other zooplankton and organic detritus (POC). Since PAH, and other hydrocarbons do not biomagnify in marine food chains, trophic transfer is inefficient and hydrocarbon concentrations do not reach high concentrations in upper trophic level marine animals, such as fish, bowhead and beluga whales, seals, walrus, and polar bears.

PAH are the hydrocarbons of greatest concern with respect to toxicity of oil residues in the marine environment. Concentrations of total and individual PAH in surface sediments and the tissues of benthic marine invertebrates and zooplankton collected throughout the Burger and Klondike survey areas were well below concentrations known to be toxic to marine organisms, including those from Arctic seas (Neff, 2010). Thus, there is no risk to the Chukchi Sea marine ecosystem from the levels of petroleum hydrocarbons in the Burger and Klondike survey areas.

All sediment concentrations of Ag, Al, Cd, Cr, Fe, Mn and Zn were clearly at background values. Therefore, the sources of these metals in the sediments of the Chukchi Sea are natural and most likely include runoff of soils via rivers, coastal erosion, and transport and deposition with suspended sediments by ocean currents. Concentrations of Ba in sediments were elevated above background values by greater than a factor of 3 at three of the 63 stations sampled. These three stations were in the vicinity of the historic drill sites in the Burger and Klondike survey areas, where drilling mud and cuttings were discharged in the sea in 1989. The probable source of this Ba is from barite (barium sulfate), the dominant insoluble solid in most drilling muds. Concentrations of Pb were enriched in only two of the Ba-rich sediment samples and concentrations of Cu and Hg were slightly enhanced in sediments at only one of the stations where sediments contained elevated Ba concentrations. These Pb, Cu and Hg enrichments are small; thus, it is difficult to pinpoint an exact source; however, it may be due to minor enrichment in the drilling mud, particularly the barite, or in drill cuttings. Metals associated with drilling mud barite and drill cuttings are in extremely insoluble forms, usually metal sulfides, and are toxicologically inert (Neff, 2008).

Comparison of metal concentrations between marine invertebrates from the Burger and Klondike areas was limited to crabs, with nine data points for each area, and worms, with nine data points from Burger and six data points from Klondike. No *Macoma* clams were collected from the Klondike area and only two samples of *Astarte* clams and zooplankton were collected from the Klondike area. Concentrations of As, Cd, Hg and Mn were significantly higher in crabs from the Klondike area than in those from the Burger area. These differences may be due to differences in metal concentrations in the water column or in their foods. Concentrations of Ba and Cr were significantly higher in worms from the Klondike area than the Burger area. Ba and Cr, which usually are present in sediments as highly insoluble sulfate and hydroxy minerals, often are present in tissues of benthic invertebrates at concentrations lower than those in sediments. However, the maldanid polychaetes sampled in this study contained sediments in the gut and this probably was the source of these metals in the worms.

A geographic comparison can be made for the clam *Astarte* from the 2008 survey in the Chukchi Sea because a sizeable data set is available for the Beaufort Sea for several years between 1986 and 2006. The results show that concentrations of As, Ba, Cr, Cu, Fe, Hg, Pb and Zn in *Astarte* from the Chukchi Sea are not significantly different from values determined for the Beaufort Sea. However, clams from the Chukchi Sea contain significantly higher concentrations of Cd and lower concentrations of Mn than clams from the Beaufort Sea and this trend is most likely due to natural conditions. Cd enters the Chukchi and Beaufort Seas in upwelled deep water from the offshore shelf and slope. Chukchi Sea clams were collected from deeper water than those in the Beaufort Sea. The bioavailability of sediment Mn depends on sediment redox conditions, which may be different in the Chukchi and Beaufort Seas.

No concentrations of any of the five metals (Ag, Cd, Hg, Pb and Zn) in all sediments from the 2008 survey of the Chukchi Sea exceeded their respective risk-based sediment guideline concentrations for marine invertebrates, and none of the metals were present in higher than normal concentrations in Chukchi Sea marine invertebrates. Therefore, there is a very low risk of adverse biological effects from metals in Chukchi Sea sediments.

1.0 INTRODUCTION

1.1. Study Area

The Chukchi Sea Lease Sale 193 Planning Area (Planning Area) is located off the northwest coast of Alaska. The Planning Area extends from near Point Barrow (156ºW longitude) in the east to the boundary with Russian waters at 169ºW longitude and from near Point Hope (68º20'N latitude) in the south, northward to 75ºN latitude and lies entirely above the Arctic Circle (66º 33' 39"N) in the Arctic geographic zone.

The Chukchi Sea Planning Area is a shallow embayment of the Arctic with water depths within the Lease Sale Area ranging from 30 m to approximately 50 m. About 80% of the planning area lies between the 30 and 90 m isobaths. The Burger and Klondike survey areas are located about 120 km northwest of Wainright, AK, in 40 to 50 m of water (Figure 1-1).

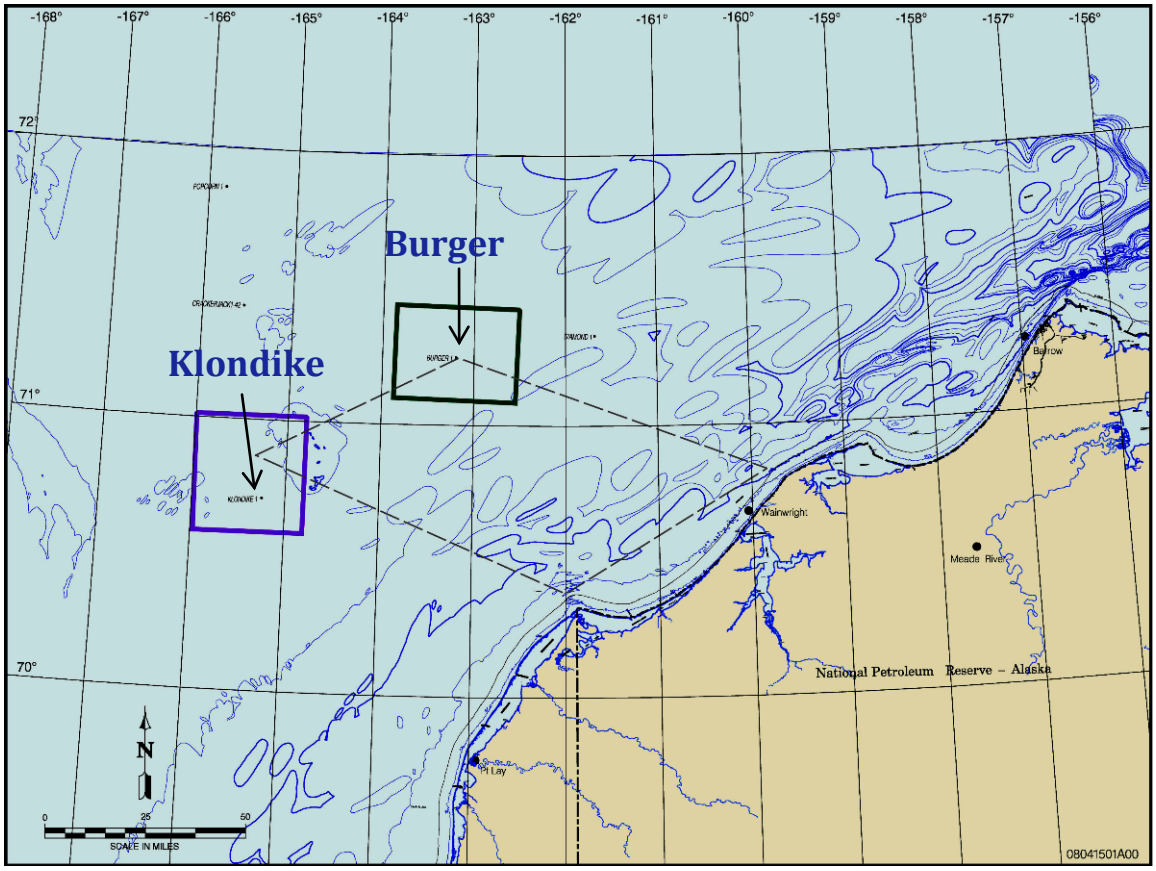

Figure 1-1. The Chukchi Sea study area showing the locations of the Burger and Klondike survey areas and the locations of two exploratory wells drilled in 1989.

The Chukchi Sea outer continental shelf where the Klondike and Burger survey areas are located is a highly productive marine ecosystem (Dunton et al., 1989; Feder et al., 1989; Grebmeier and Dunton, 2000; Moran et al., 2005; Lein et al., 2007). Much of the particulate organic carbon (POC), produced primarily by phytoplankton photosynthesis or in runoff from land, is exported

to the sediments or off the shelf. The POC also supports blooms of zooplankton communities, dominated by calanoid copepods and euphausiids, which are consumed by bowhead whales. POC in sediments supports development of a rich benthic fauna that supports benthic feeders, such as walrus and many species of demersal fish, and results in strong benthic/pelagic coupling of nutrients. Sediments in the northeast Chukchi Sea contain high concentrations of organic matter from marine and terrigenous sources (Yunker et al., 2005). This organic matter tends to sequester metals and hydrocarbons rendering them less bioavailable to benthic fauna, decreasing bioaccumulation and trophic transfer of chemicals in the Chukchi Sea food web.

1.2. Project Background

Four lease sales were held for different parts of the Chukchi Sea shelf in 1988 and 1991 (Sales 97, 109, 124, and 126). Five exploratory wells were drilled in blocks leased in sales 97 and 109 (Table 1-1). Shell Western E&P, Inc. drilled exploratory wells in the Klondike and Burger survey areas during the summer and fall of 1989. The other three wells were drilled between October 1989 and September 1991. The Burger well discovered gas and condensate resources estimate at 7.6 to 27.5 trillion ft^3 and 393 to 1,404 million barrels, respectively (Craig and Sherwood, 2004). The Klondike well discovered small oil plays at several depths. Two of the other three wells also discovered small plays of oil. The discoveries were not considered economic at the time and the wells were plugged and abandoned.

Table 1-1. Exploratory wells drilled in the Chukchi Sea Planning Area, ordered by spud date. All wells were drilled with the Canmar Explorer III drill ship. Information is from BOEMRE: http://www.mms.gov/alaska/fo/wellhistory/CK_WELLS.HTM.

Historic Well	Latitude	Longitude	Spud Date	Water Depth (m)
Klondike	70 42' 39.171"N	165 14' 59.107"W	7/15/89	43
Burger	71 15' 0.4995"N	163.11' 40.499"W	9/22/89	45
Popcorn	71 51' 16.385"N	165.48' 24.893"W	10/14/89	44
Crackerjack	71 25' 7.665"N	165.32' 29.253"W	9/23/90	42
Diamond	71 19' 48.34"N	161 40' 48.01"W	9/7/91	46

ConocoPhillips Alaska, Inc. (CPAI) and Shell Exploration and Production (Shell E&P) submitted bids for lease blocks in the Burger and Klondike Survey areas in the February 6, 2008 Chukchi Sea Lease Sale 193. CPAI is managing a scientific field survey program in these two survey areas on behalf of both CPAI and Shell E&P. The field program will provide baseline (pre-drilling) information on the physical, chemical, biological, and oceanographic environment, including assessment of zooplankton and benthic biological communities, and distribution and concentrations of chemicals associated with offshore oil and gas operations (metals and hydrocarbons) in the Klondike and Burger survey areas. An assemblage of bottom-founded acoustic recorders were also placed within the areas to capture calls from vocalizing marine mammals, as well as record sound from ambient conditions (currents, ice, etc.).

Exploratory drilling activities anticipated in the Chukchi Sea have the potential to release chemicals into the marine environment that could accumulate in sediments, from which they could pass through the local food web to valued ecosystem components, such as marine fish, mammals, and birds. The chemical classes of greatest environmental concern associated with offshore oil and gas exploration, development, and production are metals and hydrocarbons (Neff, 1987, 2010). The principle permitted (by NPDES permit from EPA Region 10) discharges associated with offshore exploratory drilling are drilling muds and drill cuttings (Neff, 2010). The only permitted discharges anticipated for exploration of Chukchi Sea fossil fuel resources are water based drilling muds (WBM) and associated drill cuttings generated during drilling of exploratory wells. The chemicals greatest environmental concern associated with discharge of WBM and cuttings are metals (particularly barium, cadmium, copper, chromium, lead, mercury, and zinc) and hydrocarbons (Neff, 2010). Hydrocarbon-based lubricants often were added to WBM in the past to lubricate the bit and drill string and to free stuck pipe. EPA (1993, 1996) banned the discharge to the ocean of drilling muds containing diesel fuel or free oil. Modern polymer WBM, such as the WBM being proposed by Shell and ConocoPhillips for exploratory drilling in the Beaufort and Chukchi Seas, have substantially higher lubricity than standard bentonite clay (gel) muds, and so lubricants usually are not required to drill difficult expandable shale formations.

Petroleum also may enter the Chukchi Sea in accidental discharges or spills during exploration. The chemical constituents of primary environmental concern in petroleum are polycyclic aromatic hydrocarbons (PAH).

1.3. Objective and Scope of the Chemical Characterization Program

The objective of the CPAI Chukchi Sea Environmental Studies Program is to develop baseline information about the marine environment in the Burger and Klondike Survey areas for submission to the Minerals Management Service (MMS). The objective of the Chemical Characterization Program component of the Chukchi Sea Environmental Studies Program is to determine baseline (pre-exploration) concentrations of metals and hydrocarbons in sediments and tissues of zooplankton, benthic invertebrates, and fish in the study area. The pre-drilling baseline information will be used as part of an analysis of potential effects of offshore oil and gas activities on the Chukchi Sea marine environment and its resources, particularly valued resource species such as bowhead whales, gray whales, walrus, ice seals, seabirds, and fishery resources. This analysis may be used in preparation of selected regulatory documents, including National Pollution Discharge Elimination System (NPDES) permits, and National Environmental Policy Act (NEPA) documents.

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2.0 METHODS

This section summarizes the methods used in the field sampling, the laboratory sample analyses, and the quality assurance/quality control (QA/QC) measures that were employed to ensure data quality. The field and laboratory work, including the technical procedures, are described in more detail in the Study Plan (Appendix D) and the Field Survey Report (Appendix E).

2.1. Field Methods

2.1.1. Sampling Design

The sampling design is described in detail in the Field Survey Report (Appendix E). The overall design of the field sampling program is based on a stratified-random strategy, in which each of the two survey areas was gridded for random sampling stations. The historic drill sites in each survey area were considered a central location for site-specific sampling stations, along with other fixed locations based on oceanographic and biological features (e.g., depositional basins, productive shoals, whale and walrus feeding areas, etc). Sampling stations were divided into three categories: fixed stations, site-specific historic drill site stations, and primary and secondary random stations (Figure 2-1 and 2-2; Table 2-1).

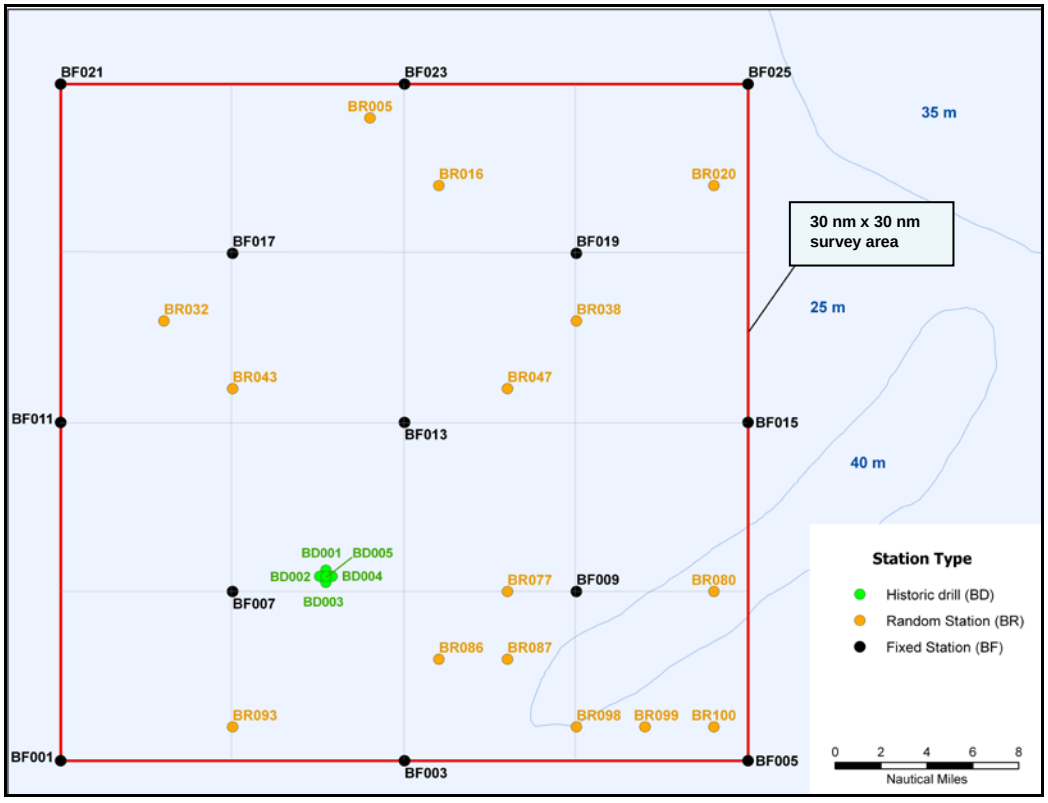


Figure 2-1. Burger Survey Area Showing Sampling Stations.

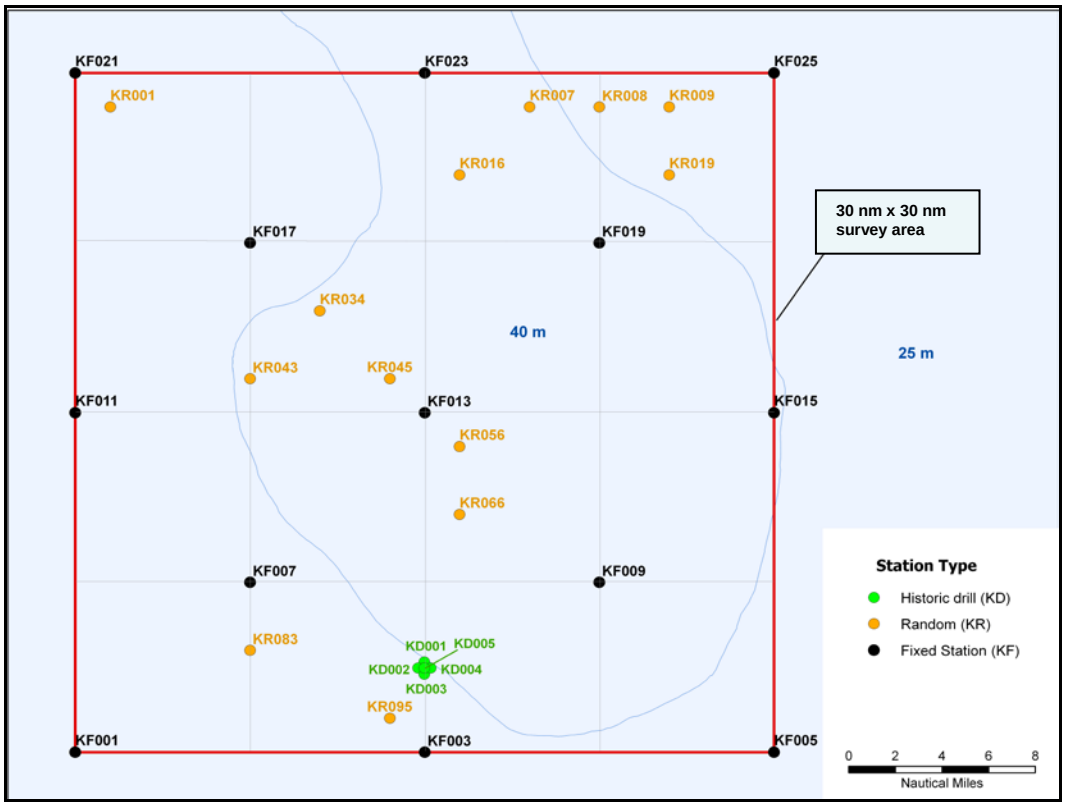


Figure 2-2. Klondike Survey Area Showing Sampling Stations.

Table 2-1. Numbers of sediment and marine invertebrate sampling stations in the Burger and Klondike survey areas. See Appendix E, Tables 1 and 5, for station names locations, water depths, sampling dates, and times.

Site	Fixed	Primary Random	Secondary Random or Other	Historic Drill Site	Total
Burger	13	13	3[a]	5	34
Klondike	13	13	0	5	31
Total	26	26	3	10	65

[a] Includes one "New Station" sample collected at station BN001.

Fixed Station Strategy (26 Stations)

- The study design included 13 fixed stations from each survey area that were selected based on a 7.5 nautical mile (nm) grid of each 30 x 30 nm survey area, with stations on the grid corners and every other grid block intersection.

Random Sampling Strategy (29 stations)

- The random station design involved establishing a 3 nm square grid throughout each of the two 30 nm square study blocks (900 square nm).

- Each block was sequentially numbered and 13 stations were selected randomly for chemical sampling from each of the two study areas.
- Alternate random stations also were established in case a selected random station did not yield acceptable depositional sediment substrate (e.g. coarse gravel, etc.) or overlapped a fixed station. Two of these secondary random stations were sampled.
- The selection of stations with depositional sediment (>20 % silt/clay) is essential for the study, as little monitoring information on chemicals will be gained from sampling coarse-grained areas sediments.

Site-Specific Sampling Strategy (10 stations)

- The site-specific stations were established on four radials around each of the historic exploratory drill sites in Klondike and Burger survey areas.
- The radials were oriented along the axis of and perpendicular to the prevailing currents in the study area (roughly North-South and East-West).
- A total of 5 historic drill site stations were sampled at the Burger well and 5 stations were sampled at the Klondike well.

All stations selected for sediment sampling for chemical analysis were candidates for sampling of marine invertebrates (bivalve mollusks, amphipods, crabs, polychaete worms, and zooplankton). However, because of the patchy distribution of marine invertebrates in the study areas, only a subset of stations yielded sufficient biota for chemical analysis.

Burger and Klondike stations from which sediment, amphipod, crab, clam, worm, and zooplankton samples were collected and analyzed are summarized in Tables 2-2 and 2-3. Additional sediment and invertebrate samples were collected at these and other stations and were archived should they be of interest at a later time. Archived samples are summarized in Appendix D, Chemical Characterization Project Study Plan. A total of 38 sediment and 118 invertebrate samples, including four sea cucumber and four snail samples, were archived. Most of the archived sediment samples were replicates of samples that were analyzed. Most of the archived invertebrate samples contained an insufficient mass of tissue for analysis. Zooplankton samples from 13 Burger stations and 12 Klondike stations were composited by region into four samples each for Burger and Klondike. No zooplankton samples were archived.

Table 2-2. Stations and number of samples in the Burger survey from which sediment and marine invertebrates were collected and analyzed.

Station	Sediment	Amphipods	Crabs	Clams		Worms	Zooplankton
	0-2 cm	Anonyx sp	Opillio sp	Macoma sp	Astarte sp	Maldanidae	Mixed Species
Fixed Stations							
BF001	1				1		1
BF003	1				1	1	1
BF005	3		1		1		1
BF007	1				1		1
BF009	1						1
BF011	1	1	1		1		
BF013	1	3	1				
BF015	1			1	1		
BF017	1				1	1[a]	
BF019	1						
BF021	1					1	
BF023	1		1				
BF025	1		1	1			
Random Stations							
BR005	1				1		
BR016	1						
BR020	1						
BR032	1						
BR038	1	1		1			
BR043	1		1				
BR047	1						
BR077	1						
BR080	1	1	1		1		
BR086	1					1	
BR087						1	
BR093	1				1	1	
BR098	1				1	1	
BR099	1	1			1	1	
BR100	1		1			1	

Table 2–2. Stations and number of samples in the Burger survey from which sediment and marine invertebrates were collected and analyzed, continued.

Station	Sediment	Amphipods	Crabs	Clams		Worms	Zooplankton
	0-2 cm	Anonyx sp	Opillio sp	Macoma sp	Astarte sp	Maldanidae	Mixed Species
Historic Drill Site Stations							
BD001	1			1	1		
BD002	1						
BD003	1						
BD004	1	1	1[a]				
BD005	6[b]	1					
Total Samples Analyzed	39	9	9	4	13	9	5

[a] Sample not analyzed for metals. [b] Includes sediment core sample.

Table 2-3. Stations and number of samples in the Klondike survey from which sediment and marine invertebrates were collected and analyzed.

Station	Sediment	Amphipods	Crabs	Clams		Worms	Zooplankton
	0-2 cm	Anonyx sp	Opillio sp	Macoma sp	Astarte sp	Maldanidae	Mixed Species
Fixed Stations							
KF001	1	1[a]					1[a]
KF003	1						1
KF005	1					1	1
KF007	1						1[a]
KF009	1						1[a]
KF011	1						
KF013	1					1	
KF015	1						
KF017	1						
KF019	1						
KF021	1		1				

Table 2–3. Stations and number of samples in the Klondike survey from which sediment and marine invertebrates were collected and analyzed.

Station	Sediment	Amphipods	Crabs	Clams		Worms	Zooplankton
	0-2 cm	Anonyx sp	Opillio sp	Macoma sp	Astarte sp	Maldanidae	Mixed Species
KF023	1		1				
KF025	1		1			1	
Random Stations							
KR001	1		1				
KR007	1				1[a]		
KR008	1		1		1		
KR009	1				1[a]	1	
KR016	1		1				
KR019	1		1		1[a]	1	
KR034	1					1[a]	
KR043	1						
KR045	3					1	
KR056	1						
KR066	1						
KR083	1						
KR095	1			1[a]			
Historic Drill Site Stations							
KD001	1						
KD002	4[b]		1			1[a]	
KD003	1						
KD004	1						
KD005	6[b]		1		1[a]	1[a]	
Total Samples Analyzed	41	1	9	1	5	9	5

[a] Sample not analyzed for metals. [b] Includes sediment core sample.

2.1.2. Field Sampling Procedures

2.1.2.1. Navigation

Each "station" was defined as a 0.2 nautical mile (nm) radius around the target station position. The actual latitude and longitude of the station were recorded from satellite transmissions from a global positioning system (GPS) when the station was successfully sampled for sediments with a Van Veen sampler. The coordinates for each sampling station are the GPS latitude and longitude

values for the location where the sample was collected. The latitude and longitude recorded for benthic grabs, used to collect benthic invertebrates for chemical analysis, are those for the position where the first of three grabs was collected.

2.1.2.2. Equipment Decontamination

Equipment decontamination procedures were followed at all times during sampling activities. The double Van Veen Grab, used to collect the sediment samples, was decontaminated between each sampling station, and always prior to the first sampling in each shift period. The Kynar™-coated 2-cm scoop used to collect the sediment samples for chemical analysis, plastic spoons used to homogenize and aliquot the sediment samples, and a Teflon™ siphon used to remove overlying water from the grab surface, were all decontaminated prior to all sampling activities and between sampling stations. The decontamination procedure included a site-water rinse and physical removal of visible sediment debris, followed by a Liquinox™-water rinse and cleaning with scrub brushes, an additional site-water rinse, a distilled water rinse, and a wipe-down with acetone wipes. Plastic spoons were rinsed with reagent-grade ethanol, rather than wiped with acetone wipes, to avoid disintegration of the spoon. After decontamination, plastic spoons, the Kynar-coated 2-cm scoop, and the Teflon syringe were stored in clean plastic bags to avoid contamination prior to use. To assess potential sample contamination, QA/QC samples were collected periodically from cleaned equipment and vessel sources, (e.g. water system, air, and lubricants). Section 2.3.2 contains a summary of the QA/QC samples collected in this study.

2.1.2.3. Sediment Sampling

Surface sediment samples were collected using a modified double Van Veen grab sampler (Figure 2-3). Extreme care was taken throughout the subsampling process to avoid contact with metals and hydrocarbon sources during the collection and handling of sediment samples from the grab sampler. Samples were taken from the center of the grab and away from the sides of the grab. No metal spatulas were used for the collection of the sediment samples for trace metal and hydrocarbon samples. Plastic or Kynar-coated scoops were used for sediment sampling. Clean gloves were worn during all sampling activities and the grab was protected during sampling and storage as much as possible from stack exhaust, grease drips from winches and wires, and other potential airborne contamination.

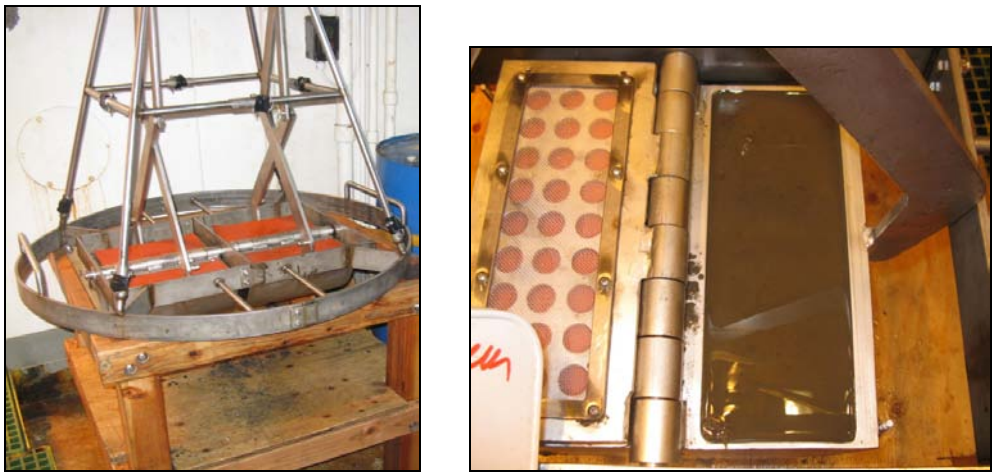


Figure 2-3. Double Van Veen Surface Sediment Sampler.

Sediment samples were collected from the top 2 cm of the grab to represent recent accumulation. Upon retrieval of the grab onto the vessel, the grabs were opened and the samples were checked for acceptability. If the grabs were over or under-filled and/or there was sign of sediment loss from the grab, and/or a thin layer of overlying water was not present, the grab was deemed unacceptable and was discarded. When this occurred, the site was resampled until an acceptable grab was obtained. In most cases, grabs were consistently acceptable, and the overlying water was gently siphoned off using a decontaminated Teflon syringe. The sediment sample was collected following removal of the overlying water. Unconsolidated sediment 2-cm deep was removed from the grab with a Kynar-coated scoop. The scoop was 2-cm deep to facilitate accurate depth collection of the sediment. The top 2 cm of sediment was collected by a series of several scoops from only those portions of the sediment grab not touching the sides of the grab. The number of scoops collected was appropriate to fill a 500-mL pre-cleaned glass sample jar with a Teflon lined plastic lid (typically 4 to 6 scoops). The sediment was then homogenized to consistent texture and color in the 500-mL sample jar, and approximately 250 mL was removed using a decontaminated plastic spoon and aliquoted into two 125-mL pre-cleaned glass sample jars with Teflon lined plastic lids. The sediment sample from each station was divided into three sample containers: one 500-mL jar containing approximately 200 to 250 mL of sediment for hydrocarbon analysis, one 125-mL jar containing approximately 100 mL of sediment for metals and total organic carbon (TOC) analysis, and one 125-mL jar containing approximately 100 mL of sediment for grain size analysis. The sediment samples were stored either frozen (i.e., samples for hydrocarbons, metals, and TOC analysis) or refrigerated (i.e., samples for grain size analysis), as indicated in the 2008 Field Survey Plan (Exponent, 2008).

Table 2-4. Numbers of sediment samples from the Burger and Klondike stations that were sampled and analyzed (in parentheses).

Site	Fixed	Primary Random	Secondary Random or Other	Historic Drill Site	Field Reps	Total
Burger	13 (13)	13 (13)	3 (1)	27 (10)	4 (2)	60[a] (39)
Klondike	13 (13)	13 (13)	0	29 (13)	4 (2)	59 (41)
Total	26 (26)	26 (26)	3 (1)	56 (23)	8 (4)	119 (80)

[a] Includes one "New Station" sample collected at station BN001.

A total of 60 sediment samples were collected at 34 stations in the Burger survey area; 59 sediment samples were collected at 31 stations in the Klondike survey area (Tables 2-2, 2-3, and 2-4). The sediment samples were surface samples, with the exception of the samples from the historic drill sites stations in the Burger and Klondike survey area; sediment "cores" with four to seven 2-cm depth intervals were collected from the sediment grab to include both the unconsolidated upper 2-cm surface layer and the >2 cm, deeper, consolidated sediment layers at these stations. Thirty nine sediment samples from Burger and 41 from Klondike were analyzed for chemical concentrations (Table 2-4). The remaining samples were archived for possible later analysis, should that be of interest (most of the chemicals of interest are stable for an extended period of time, if stored properly). The rational for collecting extra samples, and the selection of samples for analysis, is discussed in Section 3.

The goal was to collect samples with at least 20% fine sediment (e.g., silt and clay). In all cases, the grab samples consisted primarily of fine-grained sediments. All observations, notes, and details were documented in a field log book and in individual station logs for each site. Photographs of each grab from which a sediment sample was collected for chemical analysis were obtained and documented.

2.1.2.4. Marine Invertebrate Sampling

A total of 148 amphipod, clam, polychaete worm, crab, and zooplankton samples were collected from Burger and Klondike stations for chemical analysis (Table 2-5). Forty nine marine invertebrate samples from Burger stations and 30 marine invertebrate samples from Klondike stations were analyzed for chemical concentrations. The remaining invertebrate samples were archived for possible later analysis, should that be of interest. Snails and sea cucumbers also were collected at several stations, but were not analyzed.

Table 2-5. Numbers of marine invertebrate samples from the Burger and Klondike stations that were sampled and analyzed (in parentheses).

Site	Amphipods	Crabs	Clams	Worms	Zooplankton	Total
Burger	9 (9)	16 (9)	36 (17)	10 (9)	14 (5)	85 (49)
Klondike	1 (1)	16 (9)	10 (6)	24 (9)	12 (5)	63 (30)
Total	10 (10)	32 (18)	46 (13)	34 (18)	26 (10)	148 (79)

2.1.2.4.1 Amphipod Sampling. Amphipod traps were deployed at multiple stations. Amphipod collections were more successful in the Burger study area than in the Klondike study area (Table 2-5). Amphipods (*Anonyx* sp.) were collected in Nytex mesh-lined plastic minnow traps baited with sardines (Figure 2-4). The traps were deployed for different durations, from approximately 2 hours to 32 hours, depending on the schedule of the vessel and the demands for transport from the other scientific groups on board. The amphipod traps were deployed with a long line anchor and a float with a flashing beacon. The sardine bait was placed in an enclosed Nytex mesh pouch to reduce the possibility of amphipods ingesting sardine tissue and to ensure that sardine particles do not become entrained with the amphipods. Upon trap retrieval, amphipods were removed from the traps, gently rinsed with site-seawater, and placed in a clean sieve for sorting.

Figure 2-4. Amphipod Traps and Amphipods.

Representative photographs were taken of the samples. Any non-*Anonyx* sp. amphipods and/or isopods were removed with clean forceps or by hand with clean gloves prior to transfer into the appropriate sample container. Effort was made to minimize any sediment particles entering the sample container with the amphipods to avoid skewing the chemical analysis.

2.1.2.4.2 Other Benthic Invertebrate Sampling. Bivalve, worm, crab, snail, and sea cucumber samples were collected at multiple stations where they were found in large enough amounts to support chemical analysis (Figures 2-5 and 2-6). They were collected by both Van Veen grab and clam dredge in coordination with the benthic invertebrate sampling team. Sediment grabs were collected into large plastic buckets and sieved through a 2-cm stainless steel sieve with site-seawater pumped through a stainless steel pump. Biota collected in the 10-minute clam dredge deployment were placed in a large plastic bucket, cleaned with site-seawater, and sorted into sample containers. The clam dredge consisted of a four-foot wide rake with approximately 2-inch long stainless steel prongs at two inch centers. A stiff polyethylene mesh net (~1 in. diameter holes) was attached to the rake to collect the dredge materials. Clams (probably *Astarte* sp. and *Macoma* sp.) were present in limited numbers at Klondike with larger numbers at Burger. Where found, clams were collected, rinsed with site-seawater, photographed, and placed in sample jars. Polychaete worms (tentatively identified as family Maldanidae) were collected, removed by hand from any tubes and/or sediment, rinsed, photographed, and placed in sample jars. Crabs (tentatively identified as *Opillio* sp.) were collected solely from the clam dredges, photographed, rinsed, counted, and placed in sample jars.

Figure 2-5. Crabs, Clams, Worms, and Other Animals and Material Collected from the Seafloor.

Figure 2-6. Clams and Crabs in Samples Jars Being Prepared for Storage.

2.1.2.4.3 Zooplankton Sampling. Zooplankton samples for chemical analysis were collected at all odd numbered fixed station locations (except KF011, due to miscommunication at the first chemistry zooplankton site of the survey) with a bongo net for a 10-minute deployment (Figure 2-7). The Bongo net was deployed using oblique tow methods, moving down and then up vertically through the water column while being towed horizontally. Approximately 250 mL of zooplankton/seawater slurry was collected for each sample. Effort was made to remove large jellyfish from the zooplankton samples aliquoted for chemical analysis.

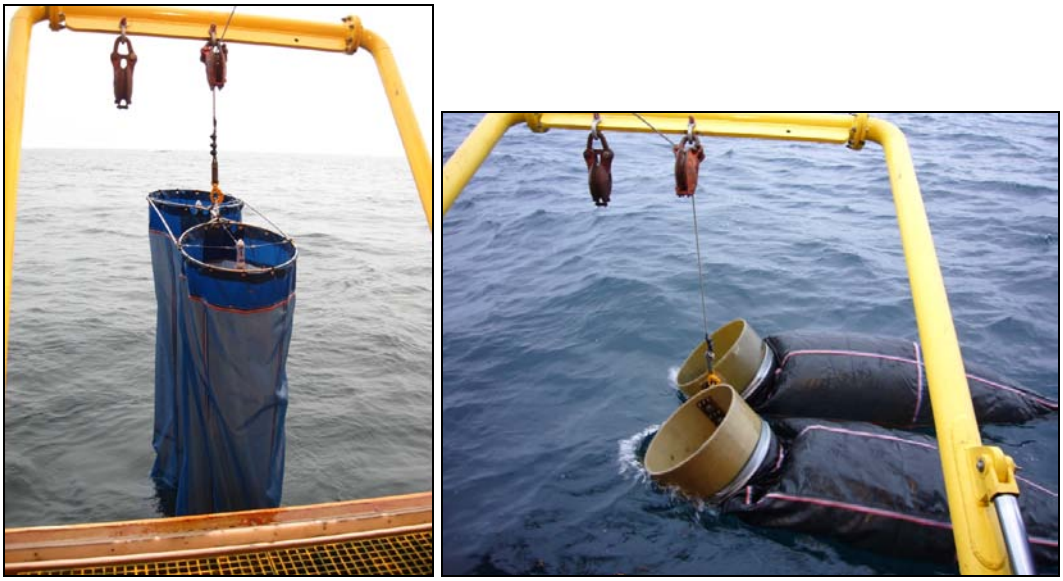


Figure 2-7. Plankton Nets Being Prepared for Sampling.

2.1.3. Field Sample Handling and Shipment

2.1.3.1. Sample Handling

All sediment, biota, and quality control samples for chemical analysis were inventoried (in a field log book maintained by the Chemical Characterization Program field personnel and on chain of custody [COC] forms) and stored in secure areas on the vessel immediately after collection. Inventory included counting all samples to ensure that all samples were collected and safely returned to the custody area on board, documenting all samples, and preparing a COC form. Sample ID's were cross-checked against the COC logs prior to packaging samples in coolers for shipment to the analytical laboratories. Sediment and biota samples for organics, metals, and TOC (sediment only) analysis were frozen immediately in on-board scientific freezers after collection to ensure their integrity and temperature. Sediment samples for grain size analysis were refrigerated in scientific incubators immediately after collection. The sediment samples remained either frozen or refrigerated (depending on the particular analysis) prior to and during transportation to the respective analytical laboratories. Sample integrity and custody was maintained at all times. Sample handling and storage requirements for the different analytical samples types are presented in the 2008 Field Survey Plan (Exponent, 2008).

Every effort was made to deliver the samples to the analytical laboratories in a timely manner to ensure that sample temperatures remained below 4 to 6° C (i.e., coolers containing samples were custody-sealed and samples were shipped on blue ice by priority overnight shipment). Sediment samples for organics analysis were shipped to Battelle (Duxbury, MA). Sediment samples for metals, TOC, and grain size analysis were shipped to Florida Institute of Technology ([FIT] Melbourne, FL). All marine invertebrate samples were shipped to Battelle for homogenizing and aliquoting. Aliquots of biota samples were sent from Battelle to FIT for metals analysis.

2.1.3.2. Sample Shipping

At the end of the sampling efforts in each study area, the Chemical Characterization Program samples were packed in coolers for priority overnight shipment to the two analytical laboratories. The samples remained on-board the M/V Bluefin until the completion of the entire field survey and until the vessel returned to port in Seward, AK. Samples were removed in the packaged coolers from the boat, palletized and shrink-wrapped, and stored in a secured freezer and refrigerator (depending on the particular chemical analysis) in Seward for approximately one month. The palletized coolers were then transported by refrigerated truck from Seward to Anchorage, AK. Samples were then shipped priority overnight from Anchorage, AK, to the respective laboratories (i.e., Battelle and FIT). All COC and custody procedures were followed and maintained throughout the collection, packaging, and shipping process. Fully executed COCs with receipt conditions reported by the laboratories are presented in Appendix D. The shipping carrier was Federal Express. Samples were shipped frozen (organics, metals, and TOC), or refrigerated (grain size) with frozen gel ice with two custody seals on the outside of each cooler and COC forms inside each cooler (as per Exponent SOP GEN-02 and -03). No hazardous materials were included in the shipments.

2.2. Analytical Methods

The sediment and marine invertebrate tissue samples were analyzed for several classes of hydrocarbons, several metals, and ancillary sediment parameters (sediment grain size and total organic carbon concentration) necessary for the complete interpretation of the data. The analytical methods employed were originally developed, refined, and validated specifically for trace-level analysis of marine sediment and biological tissue. The analyte list includes selected hydrocarbons and metals that may be present in permitted or accidental discharges during exploratory and development. Additionally, these analyses may be useful in identifying potential sources of these chemicals in sediments and marine invertebrate tissues.

Analysis of hydrocarbons in sediment and marine invertebrate tissue samples was performed at Battelle (Duxbury, MA). Samples were analyzed for polycyclic aromatic hydrocarbons (PAH), sterane/triterpane petroleum biomarkers (S/T), total petroleum hydrocarbons (TPH), and saturated hydrocarbons (SHC). Tissue samples were also analyzed for total lipid concentration. Trace metal, sediment grain size, and sediment total organic carbon and carbonate analyses were performed by Florida Institute of Technology (FIT; Melbourne, FL). Thirteen metals were analyzed in sediments and 12 metals were analyzed in marine invertebrates. Aluminum was analyzed only in sediments. These analyses are summarized in Table 2-6. Grain size, total organic carbon, and total organic matter/carbonate analysis was also performed on the sediments, and the lipid content was determined for the biological tissue samples.

Table 2-6. Summary of chemical and physical analyses for sediment analyses of sediment and marine invertebrate tissue samples.

Parameter	Sediment	Invertebrate Tissue
Hydrocarbons and Lipids		
Parent and Alkylated PAH (PAH)	X	X
Petroleum Biomarkers (S/T)	X	X
Saturated Hydrocarbons (SHC)	X	X
Total Petroleum Hydrocarbons (TPH)	X	X
Total Lipids		X
Metals and Ancillary Parameters		
Ag, Al, As, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Pb, Se, Zn	X	
Ag, As, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Pb, Se, Zn		X
Grain Size	X	
Total Organic Carbon (TOC) and Carbonate	X	

2.2.1. Analysis of Sediment Grain Size and Total Organic Carbon (TOC)

2.2.1.1. Sediment Grain Size

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

The glass bottle containing muddy water (<63 µm) was shaken for about 15 minutes and gently poured into a 1-L cylinder. The cylinder was stirred vigorously with a stirring rod and a timer was started as soon as the rod was removed. Dispersant was not needed in these samples of marine sediment because the mud fraction dispersed very well. After 20 seconds, 20 mL of sample were withdrawn from a depth of 20 cm using a Class A pipette. The pipette sample was drained into weighed beaker #3, dried at 100 to 110°C for 24 hours, and weighed for total silt + clay. After 2 hours and 3 minutes, 20 mL of samples were withdrawn from a depth of 10 cm using a Class A pipette. This pipette sample was drained into weighed beaker #4, dried at 100 to 110°C for 24 hours, and weighed for total clay. All masses were determined to the nearest 0.01 g. The total mass of sample was equal to the sum of masses in beakers #1 + #2 + #3(x50). The individual percentages were calculated as follows:

% gravel = (beaker #1 sediment/sum) x 100%
% sand = (beaker #2 sediment/sum) x 100%
% silt = {[(50 x beaker #3) – (50 x beaker #4)]/sum} x 100%
% clay = [(50 x beaker #4)/sum] x 100%

2.2.1.2. Total Organic Carbon (TOC) and Carbonate

A 0.5- to 1-g portion of freeze-dried sediment was placed in a 20-mL glass beaker. Five mL of 10% phosphoric acid (H_3PO_4) were added to remove any inorganic carbon (carbonate) present. The sediment was dried at 60ºC and re-weighed to determine the increase in weight due to the precipitation of calcium phosphate from reaction of phosphoric acid with calcium carbonate, and liberation of carbonate from the sediment. Then, approximately 400 to 800 mg of pre-treated sediment were weighed into ceramic boats and combusted at 900ºC in a Shimadzu TOC-5050A carbon system with a SSM-5000A solid sampling module following the manufacturer's instructions. The total organic carbon (TOC) content of the sediment samples was determined using a four-point calibration curve with pure sucrose as the standard. The TOC concentrations were corrected to account for the increase in sediment mass following the addition of H_3PO_4. Carbonate concentration was estimated as the difference between the mass of dry sediment and phosphoric acid added and the mass of the dried sediment/phosphoric acid mixture. The calibration curve was checked every 10 samples by analyzing certified reference material (CRM) MESS-3, a marine sediment issued by the National Research Council (NRC) of Canada.

2.2.2. Preliminary Sample Processing

Different types of marine invertebrate samples for the Chemical Characterization Project were homogenized at Battelle and split for analysis. Sample splits were shipped to FIT for metals analysis and moisture content determination. Sediment samples were split in the field and sent directly to FIT and Battelle. The procedures listed below describe sample homogenization and splitting of the biota samples.

Amphipods and Worms: Frozen amphipods and worms were completely thawed. The overlying water was poured off and the sample was homogenized in a glass jar by maceration with a Tissuemizer™ or blender equipped with Teflon™ gaskets and titanium probes.

Crabs: Crabs were partially thawed and rinsed with reagent water to remove extraneous material. The overlying water was be poured off. The whole crab body (including shell) was crushed with a mortar and pestle. The crab sample was transferred to a glass jar and homogenized with a Tissuemizer™ equipped with Teflon™ gaskets and titanium blades.

Clams: Clams were partially thawed and were shucked with a titanium knife to remove soft tissues from shell. The overlying water was poured off and the clams were homogenized in a glass jar by maceration with a Tissuemizer™ equipped with Teflon™ gaskets and titanium probes.

Zooplankton: The zooplankton samples were composited by field track lines, to obtain sufficient sample mass for analysis. Table 2-7 lists the samples that were composited. Each sample was transferred into a 250 mL glass centrifuge tube and centrifuged at 2,000 rpm for 15 minutes. The overlying water from each sample was filtered through an 8-µm glass fiber filter. The same filter was used for all samples composited. The solids isolated from the centrifugation were combined with all samples composited. The solids from the filter were added to the composite sample.

Table 2-7. Zooplankton sample compositing scheme. 26 zooplankton samples were composited into 10 composited samples, five each from Burger and Klondike.

Battelle ID	Field ID	Station Samples in Each Composite	New Battelle ID
Q5905	08-03-BF001-01-ZC	BF001, BF011, and BF021 composite	Q6098
Q6030	08-03-BF011-01-ZC		
Q6020	08-03-BF021-01-ZC		
Q5880	08-03-BF003-01-ZC	BF003, BF013, and BF023 composite	Q6099
Q5907	08-03-BF013-01-ZC		
Q5757	08-03-BF023-01-ZC		
Q5733	08-03-BF005-01-ZC	BF005, BF015, and BF025 composite	Q6100
Q5716	08-03-BF015-01-ZC		
Q5765	08-03-BF025-01-ZC		
Q5902	08-03-BF007-01-ZC	BF007 and BF017 composite	Q6101
Q6016	08-03-BF017-01-ZC		
Q5730	08-03-BF009-01-ZC	BF009 and BF019 composite	Q6102
Q5770	08-03-BF019-01-ZC		
Q5784	08-03-KF001-01-ZC	KF001 and KF021 composite	Q6103
Q5663	08-03-KF021-01-ZC		
Q5813	08-03-KF003-01-ZC	KF003, KF013 and KF0023 composite	Q6104
Q5702	08-03-KF013-01-ZC		
Q5667	08-03-KF023-01-ZC		
Q5827	08-03-KF005-01-ZC	KF005, KF015 and KF0025 composite	Q6105
Q5825	08-03-KF015-01-ZC		
Q5788	08-03-KF025-01-ZC		
Q5700	08-03-KF007-01-ZC	KF007 and KF017 composite	Q6106
Q5681	08-03-KF017-01-ZC		
Q5709	08-03-KF009-01-ZC	KF009 and KF019 composite	Q6107
Q5807	08-03-KF019-01-ZC		

All samples could not be analyzed for all target parameters. The hydrocarbon analyses were given higher priority than the metals analyses, if a measurement had to be eliminated. Therefore, the following guidelines were used for splitting samples for analysis.

A. For samples with >25-30 g total wet weight, the samples were split 5:2 (Battelle:FIT).

B. For samples with >8-10 g but <25-30 g total wet weight, the samples were split 1:1 (Battelle:FIT). Somewhat less than the optimum sample mass was used for the laboratory analyses, and FIT may eliminate the mercury analysis from the analysis plan.

C. For samples with < 8-10 g total wet weight, Battelle retained the whole sample and FIT did not perform any metals analysis. Battelle performed the moisture content on the few samples that were not split for metals analysis.

There was insufficient tissue mass for 15 samples intended for all analyses, therefore they were analyzed for hydrocarbons only. There were 1 amphipod, 5 clam, 1 crab, 5 worms, and 3 zooplankton composite samples that could not be analyzed for metals. In addition, one zooplankton sample had enough mass for all analyses except mercury. The details on which samples had limited sample mass are presented in the Study Plan (Appendix D).

2.2.3. Analysis of Hydrocarbons

The sediment and biological tissue samples were analyzed for a large suite of parent and alkylated polycyclic aromatic hydrocarbon (PAH), petroleum biomarker (steranes/triterpanes; S/T), saturated hydrocarbon compounds (SHC), and total petroleum hydrocarbons (TPH). The laboratory sample analyses are summarized below.

2.2.3.1. Sediment Sample Preparation for Analysis

Sediment samples were stored frozen at approximately -20°C until laboratory processing could begin. The 80 sediment samples selected for analysis were processed in four laboratory analytical batches. Each batch contained a set of QC samples that included a procedural blank (PB), laboratory control sample (LCS), standard reference material (SRM), matrix spike (MS), and sample duplicate (DUP). In addition, a reference crude oil was analyzed with each batch to monitor instrument performance.

Sediment samples were extracted as described in Battelle SOP 5-192, *Soil/Sediment Extraction Using an Orbital Shaker Table Method for Trace Level Semi-Volatile Organic Contaminant Analysis*. Approximately 30 grams of well mixed sediment was spiked with the appropriate amount of SHC, PAH, and biomarker surrogate internal standards (SIS) and serially extracted three times with dichloromethane (DCM) using orbital shaker table techniques. The combined extracts were dried over anhydrous sodium sulfate and concentrated by Kuderna-Danish and N_2 evaporation techniques. Activated copper was added to the sample extracts to remove residual sulfur. The extracts were then purified using a combination of alumina clean up column and silica gel column fractions, isolating the saturated hydrocarbon and petroleum biomarker fraction from the aromatic hydrocarbon fraction. The F1 fraction was collected, concentrated, and spiked with internal standards (IS) and analyzed for SHC and TPH by gas chromatography with flame ionization detection (GC/FID) and petroleum biomarkers by gas chromatography/mass spectrometry (GC/MS). The pre-injection volume (PIV) for the F1 extracts was 250 µL. The F2 fraction was collected, concentrated, and spiked with IS and analyzed for PAH by GC/MS. The PIV of the F2 extracts was 500 µL.

2.2.3.2. Tissue Sample Preparation for Analysis

Tissue samples were stored frozen at approximately -20°C until laboratory processing could begin. The 79 marine invertebrate tissue samples were processed in five batches. Each batch included a set of QC samples that included a PB, LCS, SRM, MS, and DUP. In addition, a reference crude oil was analyzed with each batch to monitor instrument performance.

Marine invertebrate tissue samples were extracted as described in Battelle SOP 5-190, *Tissue Extraction for Trace Level Semi-Volatile Organic Contaminant Analysis*. Approximately 20 g of homogenized tissue was spiked with the appropriate amount of SHC, PAH, and biomarker SIS and serially extracted three times with DCM by Tissuemizer™ and orbital shaker table techniques. Between extractions, the samples were centrifuged to facilitate solvent removal. The combined extract was dried over anhydrous sodium sulfate and concentrated by Kuderna-Danish and N2 evaporation techniques. A portion of the extract was removed prior to determine the total extractable organics (TEO), or total lipid weight, by a gravimetric analysis. The extracts were processed through alumina columns and fractionated on silica gel columns to isolate the

hydrocarbon fraction of interest. The F1 fraction was collected, concentrated, and spiked with IS and analyzed for SHC and TPH by GC/FID and petroleum biomarkers by GC/MS. The F2 fraction was collected, concentrated, and spiked with IS and analyzed for PAH by GC/MS.

2.2.3.3. Instrumental Analysis of Hydrocarbons in Sediment and Tissues

2.2.3.3.1 PAH and Petroleum Biomarkers. Sediment and marine invertebrate tissue samples were analyzed for PAH and petroleum biomarkers as described in Battelle SOP 5-157, *Identification and Quantification of Semi-Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry*. The method described in the SOP is a modification of EPA Method 8270, modified to include additional target compounds (e.g., alkyl PAHs and petroleum biomarkers), and to obtain lower detection limits and better specificity by operating the MS detector in the selected ion monitoring (SIM) mode. The target parent and alkylated PAH are summarized in Table 2-8 and target petroleum biomarkers are summarized in Table 2-9.

Table 2-8. Target parent and alkylated polycyclic aromatic hydrocarbons (PAH), surrogate compounds, and recovery internal standards.

PAH	Reporting Code	SIS/ RIS	PAH	Reporting Code	SIS/ RIS
Naphthalene	C0N	A/1	Benzo[a]anthracene	BAA	B/3
C1-Naphthalenes	C1N	A/2	Chrysene	C0C	B/3
C_2-Naphthalenes	C2N	A/2	C_1-Chrysenes	C1C	B/3
C_3-Naphthalenes	C3N	A/2	C_2-Chrysenes	C2C	B/3
C_4-Naphthalenes	C4N	A/2	C_3-Chrysenes	C3C	B/3
Acenaphthylene	ACEY	A/2	C_4-Chrysenes	C4C	B/3
Acenaphthene	ACE	A/2	Benzo[b]fluoranthene	BBF	B/4
Biphenyl	BIP	A/2	Benzo[k]fluoranthene	BKF	B/4
Dibenzofuran	DBF	A/2	Benzo[e]pyrene	BEP	B/4
Fluorene	C0F	A/2	Benzo[a]pyrene	BAP	B/4
C_1-Fluorenes	C1F	A/2	Perylene	PER	B/4
C_2-Fluorenes	C2F	A/2	Indeno[1,2,3-c,d]pyrene	IND	B/4
C_3-Fluorenes	C3F	A/2	Dibenzo[a,h]anthracene	DAH	B/4
Anthracene	C0A	A/3	Benzo[g,h,i]perylene	BGP	B/4
Phenanthrene	C0P	A/3	Total PAH	TPAH	
C_1-Phenanthrenes/Anthracenes	C1P/A	A/3			
C_2-Phenanthrenes/Anthracenes	C2P/A	A/3			
C_3-Phenanthrenes/Anthracenes	C3P/A	A/3			
C_4-Phenanthrenes/Anthracenes	C4P/A	A/3			
Dibenzothiophene	C0D	A/3	***Surrogate Compounds***		
C_1-Dibenzothiophenes	C1D	A/3	Naphthalene-d_8	D8N	A/1
C_2-Dibenzothiophenes	C2D	A/3	Acenaphthene-d_{10}	D10ACE	A/2
C_3-Dibenzothiophenes	C3D	A/3	Phenanthrene-d_{10}	D10PH	A/3
Fluoranthene	FLANT	A/3	Benzo(a)pyrene-d_{12}	D12BAP	B/4
Pyrene	PYR	A/3			
C_1-Fluoranthenes/Pyrenes	C1F/P	A/3	***Recovery Internal Standard***		
C_2-Fluoranthenes/Pyrenes	C2F/P	A/3	Fluorene-d_{10}	D10F	A
C_3-Fluoranthenes/Pyrenes	C3F/P	A/3	Chrysene-d_{12}	D12C	B

Table 2-9. Target petroleum biomarker (S/T), surrogate compound, and recovery internal standard.

Sterane/Triterpane	Reporting Code	SIS/RIS
C_{23} Diterpane	T4	A/1
13β,17α-diacholestane(20S)	S4	A/1
13β,17α-diacholestane(20R)	S5	A/1
C_{29} Tricyclictriterpane	T9	A/1
C_{29} Tricyclictriterpane	T10	A/1
5α,14α,17α-cholestane(20R) [a]	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 [a]	T23	A/1
Surrogate Compound		
5β(H)-cholane	5B	1
Recovery Internal Standard		
Chrysene-d_{12}	D12C	A

[a] Compound used in calibration, but not reported

The analysis was performed with an Agilent 6890 GC with an Agilent 5973 mass spectral detector (MSD). The GC was equipped with a 60-m DB-5 column (0.25-mm ID, 0.25-µm film thickness) and a split/splitless injector, operating in the splitless mode. A data system interfaced to the GC/MS was used to control the acquisition and to store, retrieve, and manipulate mass spectral data.

Prior to the analysis of analytical standards and samples, the mass spectrometer was tuned with perfluorotributlyamine (PFTBA) to maximize the sensitivity of the instrument. The GC/MS was calibrated with a 5-point calibration consisting of target compounds to demonstrate the linear range of the analysis. Typically, the calibration for this method ranges from 0.010 ng/µL to 10 ng/µL. The concentration of the low standard is 2 to 3 times the method detection limit (MDL). Calibration verification was performed at the beginning and end of each 24 hour period in which samples were analyzed.

Concentrations of the individual PAH and biomarkers were calculated by the internal standard method. Target PAH and S/T concentrations were quantified using average response factors (RF) generated from the five-point linear calibration. Alkyl homologue PAH series concentrations were determined using the average RF for the corresponding parent compound, steranes were assigned the RF of cholestane, and triterpanes were assigned the RF of moretane. Well established alkyl homologue pattern recognition and integration techniques were used to determine alkyl homologues. S/T were identified based on characteristic elution patterns. Final concentrations were determined versus the appropriate surrogate compound.

2.2.3.2 TPH and SHC in Sediments and Tissues. Sediment and marine invertebrate samples were also analyzed for SHC and TPH as describe in Battelle SOP 5-202, *Determination of Low Level Total Petroleum Hydrocarbon and Individual Hydrocarbon Concentrations in Environmental Samples by GC/FID*. The SOP is a modification of EPA Method 8015, modified to obtain improved sensitivity and specificity, to include a number of additional key target parameters, and to ensure that the analysis is appropriate for complex sediment and biological tissue samples. The target SHC analytes are summarized in Table 2-10.

Table 2-10. Target saturated hydrocarbons (SHC), surrogate compounds, and recovery internal standard.

Compound	Reporting Code	SIS/ RIS	Compound	Reporting Code	SIS/ RIS
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	Total SHC	ΣSHC	A/1
n-Nonadecane	C19	A/1	TPH	TPH	A/1
n-Eicosane	C20	A/1			
n-Heneicosane	C21	A/1			
n-Docosane	C22	A/1	***Surrogate Compounds***		
n-Tricosane	C23	A/1	Tetracosane-d_{50}	D50T	A/1
n-Tetracosane	C24	A/1	5a-Androstane	5AA	B/1
n-Pentacosane	C25	A/1			
n-Hexacosane	C26	A/1	***Recovery Internal Standard***		
n-Heptacosane	C27	A/1	Eicosane-d_{42}	D42E	1

The analysis was performed with an Agilent 6890 GC equipped with a 30-m DB-5 column (0.32-mm ID, 0.25-µm film thickness) and a split/splitless injector, operating in the splitless mode. The operating conditions provide for the baseline resolution of hydrocarbons in the C_8 to C_{40} range, and resolves pristane from C_{17}, and phytane from C_{18}. A data system interfaced to the GC was used to control the data acquisition, analyte quantitation, and generation of chromatograms.

Prior to sample analysis, the GC was calibrated with a 5-point calibration consisting of the target compounds to demonstrate the linear range of the analysis. The concentration of the calibration solutions ranged from 1 to 100 µg/mL. The low calibration standard was selected at a concentration near, but above the MDL. Calibration verification was performed at the beginning and end of each 24 hour period in which samples were analyzed.

Concentrations of SHC and TPH were calculated by the internal standard method. Normal alkanes were quantified using the RF generated from the initial calibration. Isoprenoid hydrocarbon concentrations were quantified using the RF of the n-alkane immediately preceding each target isoprenoid hydrocarbon. TPH concentrations were quantified using the average RF of C_8 through C_{40}. TPH was measured by integrating the resolved and unresolved peaks in a sample extract in the n-C8 through n-C40 range and subtracting out the response generated from baseline drift attributed by the GC column bleed. The baseline drift was determined by analyzing a solvent blank spiked with IS and quantifying the response generated in the same manner as the sample extracts. Final concentrations were determined versus the appropriate surrogate compound. Based on this quantification approach, total SHC ($\sum$SHC) is defined as the sum of all resolved and quantified normal and isoprenoid alkanes. TPH is defined as the sum of all resolved and unresolved peaks between n-C_8 and n-C_{40} minus the response generated from baseline drift in the F1 fraction of the sample extract. It does not include the aromatic hydrocarbons, steranes/triterpanes, and other nonpolar organic compounds in the F2 fraction, or the high molecular weight compounds (mainly resins and asphaltenes) in the F3 fraction.

2.2.4. Analysis of Metals

2.2.4.1. Sediment Sample Preparation for Analysis

Frozen sediment samples were initially brought to room temperature. Then, each wet sediment sample was homogenized in the original 75-mL plastic vial with a Teflon™ mixing rod. Approximately 20 g of sediment were transferred into pre-weighed plastic vials to determine water content. Once transferred, the wet sediment and the vial were re-weighed. In addition, about 2 to 4 grams of sample were transferred into glass centrifuge tubes to determine the Hg content of the sediments. The portion used for determining water content was frozen, freeze-dried, and re-weighed. The dried sediment samples were again homogenized using a Teflon mixing rod.

About 0.4 gram of freeze-dried, homogenized sediment and standard reference material (SRM) #2709 were totally digested in Teflon beakers with concentrated, high-purity hydrofluoric acid (HF), nitric acid (HNO_3) and perchloric acid ($HClO_4$). Complete digestion of the sediment was chosen because it accounts for the entire amount of metal in the sample. In the digestion process, 1 mL $HClO_4$, 3 mL HNO_3, and 3 mL HF were added to the sediment in the Teflon beaker, covered with a Teflon watch cover, and heated at 50°C until a moist paste formed. The mixture was heated for another 3 hours at 80°C with an additional 3 mL HNO_3 and 3 mL HF before bringing the sample to dryness. Finally, 1 mL HNO_3 and ~30 mL distilled-deionized water (DDW) were added to the sample and heated strongly to dissolve perchlorate salts and reduce the volume. The completely dissolved and clear samples were diluted to 20 mL with DDW.

Sediment samples and CRM MESS-3 were digested for Hg (element symbols are defined in Table 2-11) analysis by heating 2 to 4 grams of wet sediment in acid-washed, glass centrifuge tubes with 4 mL HNO_3 and 2 mL sulfuric acid (H_2SO_4). Sample tubes were heated for 1 hour in a 90°C water bath and allowed to cool. Each tube was centrifuged at 2,000 revolutions per minute (rpm) and the supernatant decanted into a 25-mL graduated cylinder. The sediment pellet was rinsed twice with 5 mL DDW, centrifuged, and decanted into the graduated cylinder and diluted to a final volume of 20 mL with DDW.

Labware used in the digestion process was acid-washed with hot 8 Normal (N) HNO_3 and rinsed three times with DDW. Two procedural blanks, two duplicate samples, and two portions of the SRM 2709 or CRM MESS-3 were prepared with each set of 40 samples.

2.2.4.2. Instrumental Analysis of Metals in Sediment

Sediment samples, reference materials, and procedural and reagent blanks were analyzed by flame atomic absorption spectrometry (FAAS), cold vapor atomic absorption spectrometry (CVAAS), or inductively coupled plasma/mass spectrometry (ICP/MS). The methods used for each element and the corresponding MDLs are listed in Table 2-11. All analytical techniques followed manufacturers' specifications, laboratory standard operating procedures (SOPs), and the QA/QC methods provided in Section 2.3.4 below. These methods are based on USEPA methods described for Series 7000 (FAAS), Series 7470 (CVAAS), and Series 6010A (ICP/MS) (USEPA, 1993).

Table 2-11. Methods and method detection limits (MDLs) for metals and TOC in sediment and tissues. Concentrations of metals are µg/g dry wt. (parts per million) and of TOC are %.

Metal	Method	Sediment		Tissues	
		MDL	RL	MDL	RL
Ag – silver	ICP-MS	0.01	0.05	0.004	0.02
Al – aluminum	FAAS	10	50	NA	---
As – arsenic	ICP-MS	0.2	1.0	0.03	0.15
Ba – barium	ICP-MS	1.0	5.0	0.1	0.5
Cd – cadmium	ICP-MS	0.02	0.1	0.01	0.05
Cr – chromium	FAAS (ICP-MS)[a]	1.0	5.0	0.01	0.05
Cu – copper	FAAS	0.2	1.0	0.7	3.5
Fe – iron	FAAS	10	50	2.5	12.5
Hg – mercury	CVAAS	0.001	0.005	0.001	0.005
Mn – manganese	FAAS	3.0	15	1.1	5.5
Pb – lead	ICP-MS	0.2	1.0	0.003	0.015
Se – selenium	ICP-MS	0.04	0.20	0.03	0.15
Zn – zinc	FAAS	0.2	1.0	0.4	2.0
TOC	Shimadzu Carbon System	0.1%	0.5	NA	---

[a] Chromium in sediment was analyzed by FAAS and in tissue by ICP-MS.
CVAAS = Cold Vapor Atomic Absorption Spectrometry
FAAS = Flame Atomic Absorption Spectrometry
ICP/MS = Inductively Coupled Plasma/Mass Spectrometry

2.2.4.3. Tissue Sample Preparation for Analysis

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

Concentrations of all metals (except Hg) were determined using 4 to 6 grams of wet tissue weighed into 100-mL glass digestion flasks. These subsamples were freeze-dried, reweighed for

percent water content, and then digested by the sequential addition of concentrated, high-purity HNO_3 and hydrogen peroxide (H_2O_2) with gentle refluxing. Tissue SRMs 2976 (Mussel Tissue) and 1566b (Oyster Tissue) were digested along with the experimental samples. Once the tissue samples and SRMs were completely dissolved, the clear solutions were transferred to graduated cylinders, diluted to 20 mL with DDW rinses of the digestion flasks, and then stored in labeled 30-mL polyethylene screw-cap bottles for trace metal analysis.

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

2.2.4.4. Instrumental Analysis of Metals in Tissues

Metal concentrations in the digested tissue samples, SRMs and blanks were determined by FAAS, CVAAS or ICP-MS. The method used for each element and the corresponding MDLs are given in Table 2-11. All analytical techniques followed manufacturers' specifications, SOPs on file at FIT, and the QA/QC described in Section 2.3.4 below. These methods are based on EPA methods described for Series 7000 (FAAS), Series 7470 (CVAAS), and Series 6010A (ICP-MS) (EPA 1993).

2.3. Quality Assurance/Quality Control

A quality assurance (QA) plan, which included all specific quality control (QC) measures, was employed for this program. Laboratory QA procedures were documented in the Survey Plan (Appendix D) and Field Survey Report (Appendix E), and laboratory procedures were documented in project-specific quality assurance project plans (QAPPs) and/or the laboratory's Standard Operating Procedures (SOPs). The following sections present key elements of the plan.

2.3.1. Quality Assurance

All project activities conducted by Battelle followed a Quality System described in Battelle's Quality Management Plan (QMP). Battelle's Quality Assurance Manual (QAM) details the application of the Quality System specifically to Battelle's Analytical and Environmental Chemistry Laboratory and other operations. Similar QA/QC procedures and documentation were in place at Florida Institute of Technology, where key project data also were generated.

Specific project activities were defined in a laboratory quality assurance project plan (QAPP) that was prepared by the Project's Task Leader and reviewed by the Project Manager. The Quality Assurance Unit (QAU) at Battelle monitored the analytical components of the project according to existing Battelle standard operating procedures (SOPs) to ensure the accuracy, integrity, and completeness of the data. All sample receipt, storage, preparation, analysis, and reporting procedures followed written Standard Operating Procedures (SOPs). Project staff members were responsible for following these procedures and ensuring that data quality objectives (DQOs) were achieved. In the event that a DQO was not met, the analytical staff documented all corrective actions taken related to that exceedance. The task leader reviewed and

approved corrective actions. An independent QC Chemist reviewed all sample preparation and analytical documentation for completeness and accuracy and conducted full error checking of reported project data. The task leader was responsible for ensuring that project objectives were met and that the data were traceable and defensible.

2.3.2. Field Quality Control

Quality assurance/quality control (QA/QC) samples were collected as part of the sampling program to assess data quality. All field personnel (including boat crew members) were briefed on the potential for contamination and cross-contamination of samples and were given guidance on techniques to avoid such problems (e.g., cigarette smoking). This included the use of pre-cleaned sample containers, the use of clean sampling equipment, the use of the decontamination protocol described above, and good laboratory practices in general. It also included the following specified sampling procedures and protocols in accordance with Exponent SOPs. Several types of field quality control samples were collected during the survey, including equipment blanks, field blanks, and replicate (triplicate) samples. The equipment blanks, field blank, and field source samples were not analyzed. These samples were held in frozen archive awaiting analysis in case contamination issues were suspected with the samples.

2.3.2.1. Replicate Samples

Triplicate sediment samples were collected at two sampling locations in each study area (i.e., two stations in Burger [BF005, BR032] and two stations in Klondike [KR019, KR045]) to assess the heterogeneity of the environment and sample collection reproducibility.

2.3.2.2. Field Blank and Source Samples

Equipment blank samples were collected as a distilled water rinse of a decontaminated plastic spoon, decontaminated 2-cm scoop, or decontaminated Van Veen grab during the field investigation. Field blank samples consisted of blank sample jars and site-seawater pumped through the pump hoses. Field source samples were collected using pre-baked GFB Whatman filters and were collected from two different source possibilities including a sheave used for the winch-operation of the Van Veen grab and two 55-gallon oil drums containing Chevron Rykon oil and Chevron Clarity Hydraulic Oil AW.

2.3.3. Laboratory Quality Control for Hydrocarbon Analysis

Quality control (QC) is an integral part of the laboratory activities. It demonstrates the quality of operations and analyses, provides analysts with metrics about method performance, and aids project managers in identifying and correcting systematic and random problems that can plague field and laboratory operations, and in interpreting the results. QC procedures to assure analytical integrity included the following:

- Documentation of method detection limits
- Documentation of analytical accuracy
- Documentation of analytical precision
- Documentation of potential background laboratory interference/contamination

2.3.3.1. Quality Control Samples

A routine set of QC samples accompanied every set of samples processed and analyzed for any work conducted at the laboratory. The following QC samples will be analyzed with each batch of samples:

- Procedural Blank (PB) - A procedural blank is combination of solvents, surrogates, and all reagents used during sample processing, processed concurrently with the field samples. It is intended to monitor purity of reagents and potential laboratory background contamination.
- Laboratory Control Sample (LCS) - An LCS sample is a contaminant-free matrix-specific sample [e.g., Ottawa sand or sodium sulfate (sediment) and clean Tilapia (tissue)] that is prepared with each processing batch. It is spiked with the analytes of interest and processed identically to the field samples to assess the analyte recovery and method accuracy in the absence of a field sample matrix. The LCS is prepared for organic analysis only.
- Matrix spike (MS) - A matrix spike is a field sample spiked with the analytes of interest at approximately 10 × the MDL, processed concurrently with the field samples. It is intended to monitor the analyte recovery and method accuracy in the presence of a field sample matrix.
- Sample duplicate (QADU) - A duplicate is a second aliquot of a field sample processed and analyzed to monitor analytical precision. The duplicate may be a second matrix spike sample.
- Standard reference material (SRM) – A standard reference material is a field sample with certified and naturally incurred analyte concentrations. An SRM is prepared and analyzed to assess the accuracy of the analytical procedures.
- North Slope Crude (NSC) Reference Oil - A NSC oil sample is used to evaluate the instrumental accuracy and also provides petroleum pattern information, aiding in the qualitative identification of target analytes. The NSC is only prepared for organic compound analysis.
- Surrogate Internal Standards – (1 to 3 per sample for organic analyses) SIS compounds are spiked into each field and quality control sample prior to organic compound extraction and analysis. The surrogate recoveries provides a measure of the overall sample extraction and processing efficiency. SIS compounds are only added for organic compound analysis.

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 included in the laboratory QAPPs specific for the project. The DQO for each QC parameter listed above is presented in Table 2-12.

Table 2-12. Data quality objectives for hydrocarbon analysis.

QC Sample Type	Data Quality Objective	Corrective Action
Procedural Blank	Hydrocarbons: < 5×MDL, or field sample concentration >5×MDL.	Re-extraction, re-analysis, and/or document and justify – determined by PM; all corrective actions documented
Laboratory Control Sample (LCS)	Hydrocarbons: 70 – 130% Recovery	Re-extraction, re-analysis, and/or document and justify – determined by PM; all corrective actions documented
Matrix Spike (MS)	Hydrocarbons: 70 – 130% Recovery Spike levels >5× unspiked field sample concentration for DQO to apply.	Re-extraction, re-analysis, and/or document and justify – determined by PM; all corrective actions documented
Duplicate (DUP)	Hydrocarbons: RPD < 30% Field sample concentration >5× MDL for DQO to apply.	Re-extraction, re-analysis, and/or document and justify – determined by PM; all corrective actions documented
Reference Material (SRM)	Hydrocarbons: Values must be within 30% of the certified value on average for all compounds, not to exceed 35% of the certified value for more than 30% of the compounds. Target concentration > 5× MDL for DQO to apply.	Re-extraction, re-analysis, and/or document and justify – determined by PM; all corrective actions documented
Control Oil	Hydrocarbons: < 30% Difference from control values for 90% of the analytes. Concentration > 5× MDL for DQO to apply.	Re-extraction, re-analysis, and/or document and justify – determined by PM; all corrective actions documented
SIS Recovery	Hydrocarbons: 40 – 120% recovery	Results examined by PM or task leader. Corrective action (re-extraction, re-analysis) or justification documented.
Initial Calibration	Hydrocarbons: < 25% RSD	Re-extraction, re-analysis, and/or document and justify – determined by PM; all corrective actions documented
Continuing Calibration	Hydrocarbons: < 25% PD	Re-extraction, re-analysis, and/or document and justify – determined by PM; all corrective actions documented

2.3.3.2. Method Detection Limits

The method detection limit (MDL) is defined as the minimum concentration that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. Reporting limits (RL) are defined by the sample concentration of a compound that is equivalent to the final extract concentration based on the low calibration standard concentration.

Target compounds confidently detected below the RL (typically down to a concentration using a signal-to-noise ratio criteria of approximately 3:1) will be reported and qualified appropriately, regardless of how it compares to the calculated MDL. Approximate MDLs and RLs for each matrix for hydrocarbons are presented in Table 2-13.

Table 2-13. Method detection limits (MDLs) and reporting limits (RLs) for hydrocarbons in sediments and marine invertebrate tissues. Concentrations are µg/kg dry wt (parts per billion).

Compound Class	MDL[a]	RL[b]
PAH and Alkylated PAH		
Sediment	0.02-0.1	1.0
Biological tissue	0.09-2.3	5.0
Petroleum Biomarkers		
Sediment	0.6	5.0
Biological tissue	1.9	25
Saturated Hydrocarbons		
Individual SHC Compounds		
Sediment	30-50	200
Biological tissue	60-400	100
Total SHC and TPH		
Sediment	2,400	NA
Biological tissue	52,000	NA

[a] MDL: Method detection limit (per EPA MDL protocol). Detection limits are based on a PIV of 0.50mL for sediment and 0.25 for tissue, dilution factor of 2 for sediment and 1 for tissue, and a dry weight sample mass of 20 g for sediment 2 g for tissue.

[b] RL: Reporting Limit; field sample concentration equivalent to a final extract concentration equal to that of the low calibration standard (based on a dry weight sample mass of 20 g for sediment and 2 g for tissue)

2.3.4. Laboratory Quality Control for Metals Analysis

Each sediment and tissue sample received by the Marine & Environmental Chemistry Laboratories at FIT was carefully inspected to ensure that it was intact and that the identification number on the sample container matched that found on the custody sheet. All sediment and tissue samples for metal analysis were kept frozen (-20°C) until processed for analysis. Grain size samples were kept refrigerated (~1ºC) until processed.

Electronic balances used for weighing samples and reagents were calibrated prior to each use with certified (NIST traceable) standard weights. All pipettes (electronic or manual) were calibrated prior to use. Each of the spectrometers used for metal analysis was initially standardized with a three- to five-point calibration with a linear correlation coefficient of $r \geq 0.999$ required before experimental samples could be analyzed. Analysis of complete three- to five-point calibrations and/or single standard checks alternated every 5 to 10 samples until all the analyses were complete. The relative standard deviation (RSD) between complete calibration and standard check was required to be <15% or recalibration and reanalysis of the affected samples were performed.

2.3.4.1. Quality Control Samples

For this project, QC measures included balance calibration, instrument calibration (FAAS, CVAAS, ICP-MS, TOC analyzer), matrix spike analysis for each metal, duplicate sample analysis, reference material analysis, procedural blank analysis and standard checks. With each batch of up to 40 samples, two procedural blanks, two reference materials, two duplicate samples and two matrix-spiked samples were analyzed. Analytical QC samples include:

- Procedural Blank (PB) - Two procedural blanks were prepared with each set of up to 40 samples to monitor potential contamination resulting from laboratory reagents, glassware and processing procedures. These blanks were processed using the same analytical scheme, reagents and handling techniques as used for the experimental samples.
- Matrix Spike (MS) – Matrix spikes were prepared for a minimum of 5% of the total number of samples analyzed and included each metal to be determined. Results from matrix spike analysis using the method of standard additions provided information on the extent of any signal suppression or enhancement due to the sample matrix. If necessary (i.e., spike results outside 80-120% limit), spiking frequency was increased to 20% and a correction applied to the metal concentrations of the experimental samples.
- Duplicates (DUP) – Duplicate samples from homogenized field samples (as distinct from field replicates) were prepared in the laboratory for a minimum of 5% of the total samples. These laboratory duplicates were included as part of each set of sample digestions and analyses and provide a measure of analytical precision.
- Standard Reference Materials (SRM) – A common method used to evaluate the accuracy of environmental data is to analyze CRMs and SRMs, samples for which consensus or "accepted" analyte concentrations exist. The following reference materials were used: Marine Sediments, MESS-3 (NRC); Soil (SRM 2709 with certified value for Ba), Mussel Tissue 2976 (NIST); Oyster Tissue 1566b (NIST). Metal concentrations obtained for the reference materials were required to be within ± 20% of accepted values for >85% of other certified analyses. When no certified values existed for a metal, matrix spikes were used to evaluate analytical accuracy.

Data quality objectives (DQOs) for these QC measurements are provided in Table 2-14.

2.3.4.2. Method Detection Limits

The method detection limit (MDL) is defined as the minimum concentration that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDLs for metals were determined by the method outlined in U.S. Federal Register (U.S. EPA, 1997). The RL for metals is defined as 5 times the MDL.

MDLs and RLs for metals in sediments and tissues of marine invertebrates are summarized in Table 2-11.

Table 2-14. Data quality objectives for metal analyses.

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

3.0 RESULTS

This section summarizes the results of analyses of hydrocarbons, trace metals, total organic carbon, and grain size in sediments from the Burger and Klondike survey areas, and hydrocarbons and trace metals in tissues of benthic invertebrates and zooplankton in the two survey areas. A larger number of samples were collected than were analyzed in the laboratory; 119 and 148 discrete sediment and marine invertebrate samples were collected, respectively (Tables 2-4 and 2-5). Potentially useful samples of opportunity were collected during the field effort, as it is impossible to predict the overall success of the sample collection in advance, resulting in more samples than were needed or scoped for laboratory analysis. The available samples were reviewed by the senior scientists. Considering the objectives of the project, a subset of samples was selected for laboratory analysis that would optimize the information that could be obtained with the scoped and budgeted number of samples. Considerations included sample location and biota type. The final number of sediment samples that were analyzed for hydrocarbons is summarized in Table 3-1. The number of samples of each of the target marine invertebrate taxa that were analyzed for hydrocarbons is summarized in Table 3-2. Station names where all sediment and marine invertebrate samples chosen for analysis were collected are summarized in Tables 2-2 and 2-3. Detailed information on the samples collected and analyzed can be found in the Study Plan (Appendix D).

Table 3-1. Number of sediment samples from Burger and Klondike survey areas that were analyzed for hydrocarbons and metals. Numbers in parentheses are numbers including additional replicate samples analyzed for metals.

Survey Area	Fixed	Primary Random	Secondary Random or Other	Historic Drill Site	Field Rep	Total
Burger	13	13	1	10	2 (3)	39 (40)
Klondike	13	13	0	13	2 (5)	41 (46)
Total	26	26	1	23	4	80

Table 3-2. Numbers of marine invertebrate tissue samples from Burger and Klondike survey areas that were analyzed for hydrocarbons and metals. Numbers in parentheses are those for metals if they were different from those for hydrocarbons. There was insufficient tissue mass in some samples to permit metals analysis (See Tables 2-2 and 2-3).

Survey Area	Clams	Amphipods	Crabs	Worms	Zooplankton	Total
Burger	17	9	9	9 (8)	5	49 (48)
Klondike	6 (1)	1 (0)	9	9 (5)	5 (2)	30 (17)
Total	23 (18)	10 (9)	18	18 (13)	10 (7)	79 (65)

The detailed sediment and tissue chemistry results for each site and parameter are summarized in Appendix A and B. All hydrocarbon, metal, TOC, and sediment grain size concentration data in this report are presented on a dry weight basis. The use of dry weight to report chemical concentrations reduces data variability caused by variations in the amounts of water retained by the sediment and tissues, and provides for a more reliable data comparison.

All hydrocarbon concentration data are presented as surrogate corrected data in this report. Target compounds are corrected for the recovery of a representative surrogate compound in the sample. The main purpose of the correction is to account for sample loss that may have occurred during sample processing, and more accurately represent the actual hydrocarbon concentration in the sample.

3.1. Ancillary Measurements

3.1.1. Sediment Grain Size

Sediment grain size was quite variable from station to station with the following results based on all samples: gravel ranged from 0 to 61%, sand ranged from 14 to 96%, silt ranged from 4 to 64% and clay ranged from 0 to 36% (Table 3-3). Overall, the mean value for silt + clay (mud) in surface sediments was ~50%. The Burger area surface sediments contained more mud than the Klondike area surface sediments, with a mean mud concentration of 53% for all Burger surface sediments relative to 40% for all Klondike surface sediments (Table 3-3; Figure 3-1 and 3-2).

Table 3-3. Summary data for sediment grain size and total organic carbon (TOC) concentration in surface sediments (0 – 2 cm) and sediment cores from the Burger and Klondike survey areas.

Area	Statistic	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	Silt + Clay (%)	TOC (%)
Burger Surface Sediments	Mean (n = 32)	4.4	42.7	33.2	19.7	52.9	0.95
	SD	7.7	14.1	11.2	6.8	17.2	0.26
	Max	32.0	68.9	54.7	36.2	84.9	1.54
	Min	0.0	13.7	14.2	7.7	21.9	0.47
Klondike Surface Sediments	Mean (n = 31)	7.2	52.5	27.8	12.5	40.4	0.73
	SD	15.5	17.1	12.9	5.4	17.3	0.31
	Max	61.0	92.3	64.5	21.7	86.2	1.54
	Min.	0.0	13.8	4.0	0.0	7.7	0.12
Burger Sediment Core	Mean (n = 6)	1.2	35.9	35.6	27.4	58.2	1.01
	SD	1.6	9.2	12.1	5.5	9.7	0.13
	Max	4.4	52.7	43.1	36.2	71.0	1.26
	Min	0.0	28.5	11.0	19.3	43.5	0.90
Klondike Sediment Cores	Mean (n = 10)	4.9	48.3	30.2	16.6	46.8	1.01
	SD	7.4	7.5	6.9	3.8	10.1	0.44
	Max	21.9	61.1	47.2	22.0	66.6	2.25
	Min	0.0	32.9	18.9	29.3	29.3	0.64

Subsurface sediments (2 – 12 cm) from cores collected at the historic drill site areas at Burger and Klondike contained higher mean mud concentrations (58% and 47%, respectively) than the surface sediments from throughout the two survey areas (Table 3-3). The surface sediment layer from the Burger core contained the same concentration of mud as the deeper layers (59%), but the surface layer of the two cores collected at the drill site at Klondike contained lower concentrations of mud (33% and 29%) than the deeper layers.

Surface sediments from 10 of 31 stations in the Burger area contained ≥60% mud. These 10 stations were located farthest from the coast (Figure 3-1). Offshore transport of fine-grained sediment from the strong water currents from the Bering Sea, river runoff, and coastal erosion is favored, because of the slow settling velocities of fine-grained sediments. Coarse-grained sands and gravel are more likely to be deposited in nearshore areas. In addition, offshore areas with coarse-grained sediments probably are erosional, preventing deposition of fine-grained sediments. No obvious relationship between water depth and grain size was observed in the Burger area where water depths range from 38 to 45 m. Surface sediments in the Burger area containing <40% mud occurred at 8 sites, 4 along the southern boundary nearest to the coast, and 4 near the northern boundary (Figure 3-1).

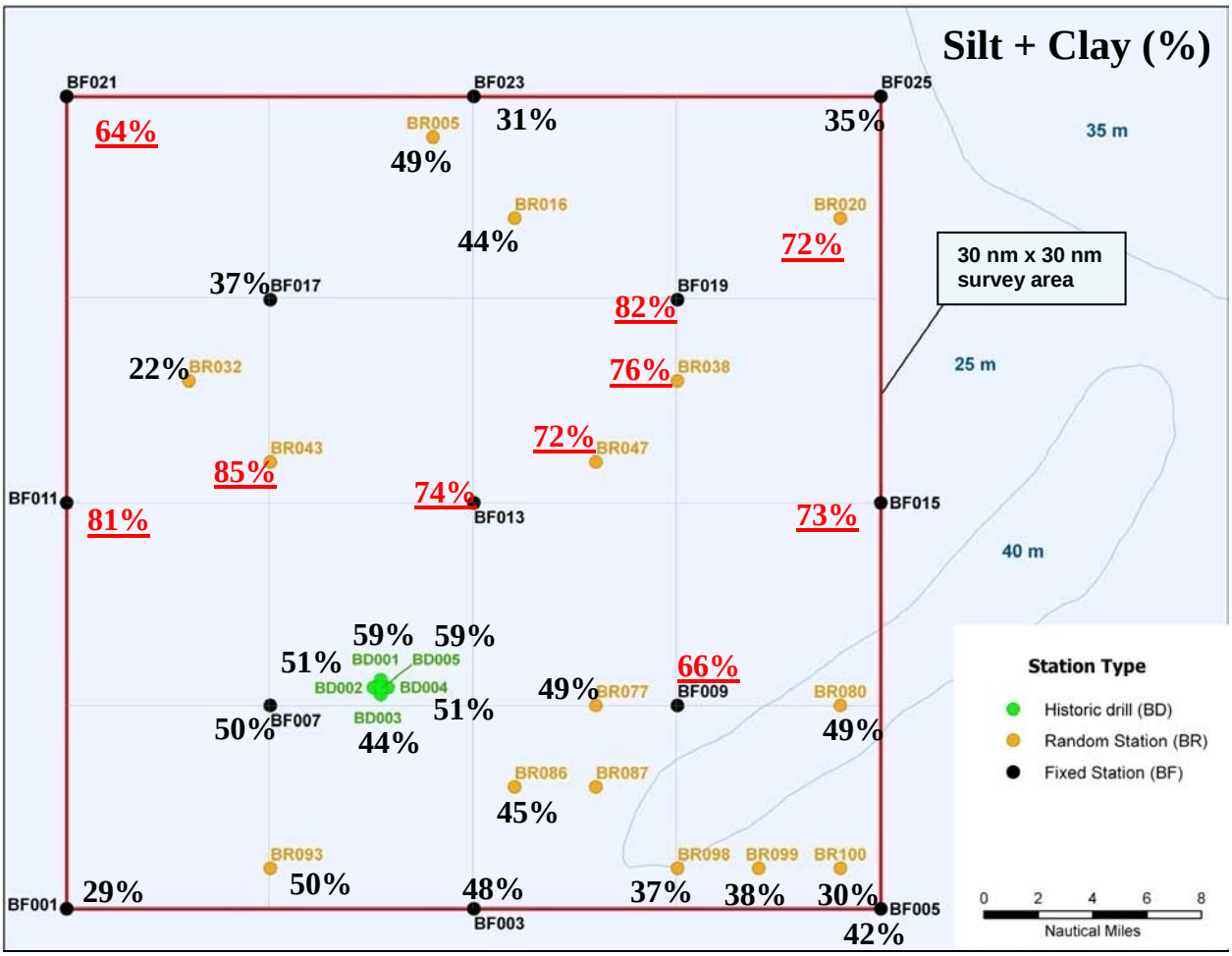


Figure 3-1. Map showing stations in the Burger survey area with concentrations of silt + clay (mud) as % dry weight. Numbers in red and underlined identify samples that contained ≥60% mud.

Only 4 of 28 surface sediment samples from the Klondike area contained ≥60% mud and all were located farthest from the coast in the upper northwestern corner of the study area (Figure 3-2). Surface sediments from 20 of 28 stations throughout the Klondike area contained <40% mud, compared to only 8 of 31 stations in the Burger area (Figures 3-1 and 3-2). Once again, no obvious relationship was found for water depth and distance from the coast, and sediment grain size distribution.

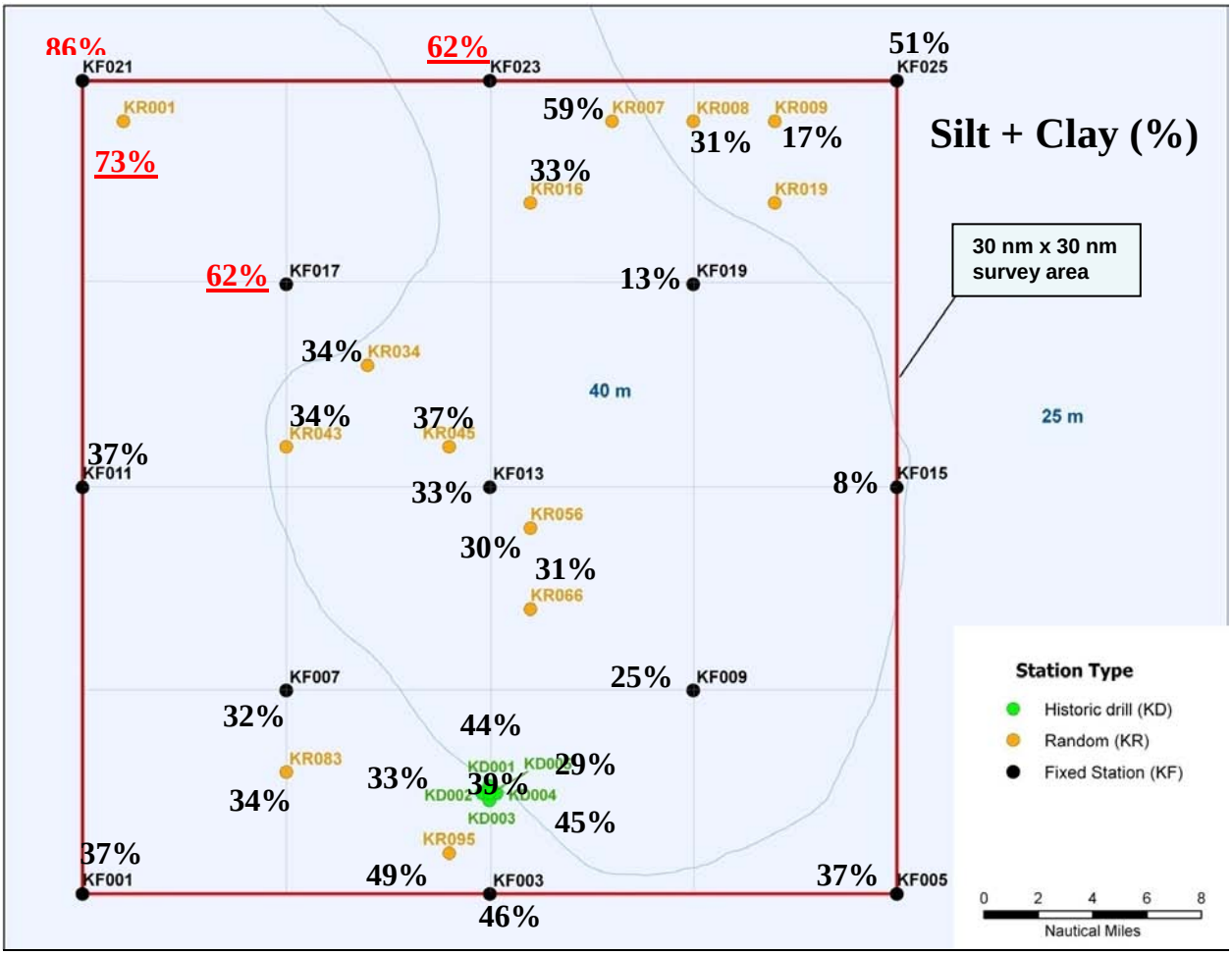


Figure 3-2. Map showing stations in Klondike area with concentrations of silt + clay (mud) as % dry weight. Numbers in red and underlined identify samples that contained ≥60% silt + clay.

3.1.2. Total Organic Carbon

The overall range of TOC concentrations in all sediments was 0.12 to 2.25% with a lower average of 0.73 % for surface sediment samples from the Klondike area compared to 0.95% for surface sediment samples from the Burger area (Table 3-3). Mean TOC concentrations in subsurface sediments was the same in cores from Burger and Klondike (1.0%). Concentrations of TOC correlated moderately well with concentrations of mud in surface sediments (r = 0.78, Figure 3-3); thus, the highest TOC concentrations were found farthest from the coast. In general, finer grained sediments containing a higher concentration of mud have a greater surface area and a larger mass of adsorbed organic matter. Figure 3-3 also shows the linear relationship between % TOC and % mud in sediments from Burger and Klondike and the tendency for sediments from Klondike to contain lower concentrations of TOC and mud than sediments from Burger. Metals and nonpolar organic chemicals, including hydrocarbons, usually are present at higher concentrations in fine-grained, organic-rich sediments than in coarse sediments, as demonstrated later in this report. Most metals and hydrocarbons are associated with the mud fraction of sediments.

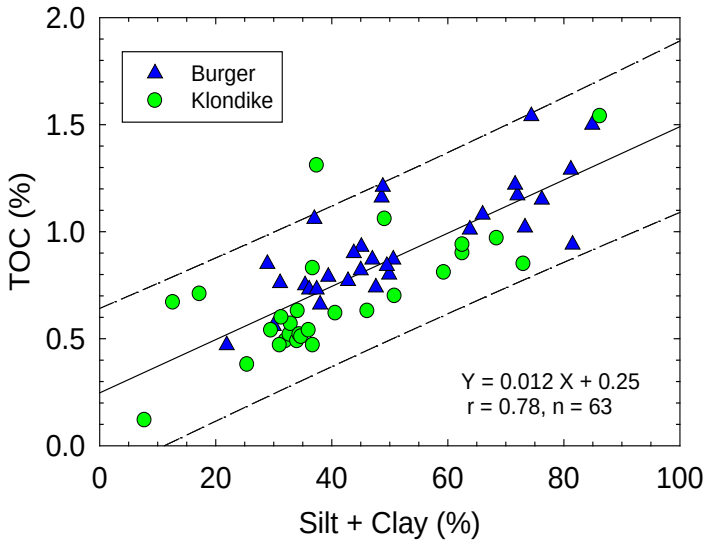


Figure 3-3. Linear regression of total organic carbon (TOC) versus silt + clay (mud) concentrations in surface sediments from Burger and Klondike areas. The regression equation, trend line, 95% prediction interval and correlation coefficient are included.

3.2. Hydrocarbons

Concentrations of individual and total polycyclic aromatic hydrocarbons (PAH,) sterane/triterpane petroleum biomarkers (S/T), saturated hydrocarbons (SHC), and total petroleum hydrocarbons (TPH) were measured in sediments and marine invertebrates collected in the Burger and Klondike survey areas. Concentrations of different hydrocarbon classes in the sediment and tissue samples are summarized in Tables 3-4 and 3-5, respectively. The summary statistics are presented for the Klondike and Burger survey areas separately, and the marine invertebrate tissue data are separated by taxon group.

Table 3-4. Summary of concentrations of hydrocarbons in sediments from fixed and random and historic drill site stations in the Burger and Klondike survey areas. All concentrations are µg/kg dry wt (parts per billion).

Hydrocarbon Type	Burger				Klondike			
	Fixed and Random Stations (n=29)				Fixed and Random Stations (n=27)			
	Mean	SD	Min	Max	Mean	SD	Min	Max
TPH	9,340	4,860	2,430	18,000	5,330	3,180	461	15,300
ΣSHC	2,300	751	963	3,920	1,660	701	371	4,010
Pristane	28.3	8.33	11.6	43.8	23.9	8.49	7.17	44.8
Phytane	11.5	3.50	3.46	18.6	7.07	2.79	1.81	14.5
Pr/Phy Ratio	2.48	0.17	2.0	2.8	3.41	0.72	2.2	5
Total PAH	300	93.1	121	482	192	89.5	47.2	451
LPAH	208	65.2	85.2	333	135	63.6	33.0	325
HPAH	91.9	28.2	36.2	149	56.2	26.1	14.2	126
Perylene	18.1	5.99	6.68	30.5	11.6	5.42	3.35	25.1
Total S/T	18.8	5.91	7.18	28.4	11.7	4.67	2.94	23.7

Table 3–4. Summary of concentrations of hydrocarbons in sediments from fixed and random and historic drill site stations in the Burger and Klondike survey areas. All concentrations are µg/kg dry wt (parts per billion), continued.

Hydrocarbon Type	Burger Historic Drill Stations (n=10)				Klondike Historic Drill Stations (n=13)			
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
TPH	13,800	7,610	1,870	22,200	12,000	6,690	4,040	22,200
ΣSHC	2,890	591	1,980	3,440	3,000	1,180	1,840	5,600
Pristane	39.7	11.7	23.8	56.8	67.3	48.6	27.4	184
Phytane	19.0	8.40	9.20	31.7	25.0	23.1	8.41	78.8
Pr/Phy ratio	2.22	0.38	1.70	2.90	3.45	2.49	2.10	11.5
Total PAH	445	144	253	650	792	799	265	3,080
LPAH	314	104	176	462	650	724	187	2,750
HPAH	131	40.2	75.9	188	142	76.5	74.7	336
Perylene	25.3	7.44	14.8	36.1	21.3	5.94	13.7	31.3
Total S/T	32.5	13.8	16.0	52.2	31.8	21.4	13.6	79.7

Table 3-5. Summary of concentrations of hydrocarbons in soft tissues of different taxa of marine invertebrates from all stations sampled in the Burger and Klondike survey areas. All concentrations are in µg/kg dry wt (parts per billion).

Hydrocarbon Type	Burger				Klondike			
	Clam (n=17)				Clam (n=6)			
	Mean	SD	Min	Max	Mean	SD	Min	Max
TPH	31,600	32,300	4,690	129,000	156,000	68,500	79,800	247,000
ΣSHC	1,900	816	1,020	3,230	5,530	3,090	1,720	8,830
Pristane	110	132	31.0	470	428	699	55.0	1,850
Phytane	10.3	5.98	3.46	24.1	25.9	16.3	7.95	50.1
Pr/Phy Ratio	10.2	9.71	2.57	38.3	14.2	17.4	4.89	49.1
Total PAH	82.5	62.1	26.7	204	202	108	70.6	355
LPAH	62.1	49.8	19.0	165	143	78.5	47.8	255
HPAH	20.4	14.7	4.47	44.5	58.8	29.2	22.8	100
Total S/T	4.66	5.05	0	15.4	3.40	3.90	0	8.76
	Amphipod (n=9)				Amphipod (n=1)			
	Mean	SD	Min	Max	Mean	SD	Min	Max
TPH	14,800	12,300	3,150	38,400	33,700			
ΣSHC	4,880	4,000	1,050	12,600	6,340			
Pristane	3,770	3,790	350	10,800	1,060			
Phytane	5.61	4.23	0	12.9	42.8			
Pr/Phy Ratio	489	701	0	2070	24.8			
Total PAH	37.6	4.29	32.2	45.8	84.8			
LPAH	34.8	3.61	31.0	40.9	65.2			
HPAH	2.79	1.29	1.11	4.86	19.6			
Total S/T	2.89	1.83	0	5.43	25.8			

Table 3–5. Summary of concentrations of hydrocarbons in soft tissues of different taxa of marine invertebrates from all stations sampled in the Burger and Klondike survey areas. All concentrations are in µg/kg dry wt (parts per billion), continued.

Hydrocarbon Type	Burger				Klondike			
	Crab (n=9)				Crab (n=9)			
	Mean	SD	Min	Max	Mean	SD	Min	Max
TPH	4,760	2,560	1,450	8,010	9,130	5,760	885	19,800
ΣSHC	1,180	1,100	500	3,980	6,120	5,010	794	14,200
Pristane	56.8	69.2	9.01	204	5,240	5,070	10.8	13,400
Phytane	5.01	4.41	2.18	16.5	3.95	2.83	2.64	5.13
Pr/Phy Ratio	13.1	17.4	1.67	55.0	1260	1100	3.19	2820
Total PAH	36.3	24.2	22.7	99.9	44.4	12.8	30.5	69.8
LPAH	28.3	16.1	18.4	70.4	37.9	12.4	25.4	62.3
HPAH	8.01	8.11	3.86	29.5	6.44	2.04	2.77	8.89
Total S/T	4.61	0.73	3.71	5.83	8.41	4.81	5.10	17.8
	Worm (n=9)				Worm (n=9)			
	Mean	SD	Min	Max	Mean	SD	Min	Max
TPH	65,400	44,100	3,400	130,000	64,000	46,600	4,720	133,000
ΣSHC	5,160	2,760	3,110	10,900	4,490	1,320	2,410	6,480
Pristane	59.0	20.4	21.1	94.0	88.5	55.7	23.7	177
Phytane	18.1	14.3	8.25	54.7	15.2	3.94	11.6	23.5
Pr/Phy Ratio	3.82	1.18	1.72	5.21	5.81	3.75	2.04	13.1
Total PAH	200	48.5	154	302	182	58.4	133	315
LPAH	126	28.8	95.3	192	120	43.4	85.5	223
HPAH	73.9	21.7	50.9	112	61.7	15.7	46.6	92.1
Total S/T	25.0	19.2	13.3	75.2	19.0	4.58	14.5	28.8
	Zooplankton (n=5)				Zooplankton (n=5)			
	Mean	SD	Min	Max	Mean	SD	Min	Max
TPH	170,000	107,000	113,000	361,000	559,000	219,000	291,000	888,000
ΣSHC	82,000	43,500	27,000	143,000	220,000	140,000	90,800	449,000
Pristane	78,100	43,200	22,600	138,000	204,000	135,000	81,900	424,000
Phytane	37.1	6.34	31.7	46.0	81.5	30.8	45.8	117
Pr/Phy Ratio	2,090	1,070	697	3,320	2,460	1,180	1,460	3,880
Total PAH	86.0	6.66	75.7	92.1	253	92.1	140	360
LPAH	68.3	6.81	61.3	78.4	195	66.8	108	274
HPAH	17.7	3.91	13.7	22.2	57.8	26.2	32.2	86.2
Total S/T	22.9	10.7	13.0	40.5	259	146	134	459

The summary results include the following hydrocarbon data:

- Total PAH (TPAH) – the sum of the 42 parent and alkylated PAH isomer groups (Table 2-8)
- Low molecular weight PAH (LPAH) – the sum of 2- and 3-ring PAH
- High molecular weight PAH (HPAH) – the sum of 4-, 5-, and 6-ring PAH
- Pristane
- Phytane

- Pristane/phytane – a useful source and weathering indicator for oil and biogenic hydrocarbon mixtures
- Sum SHC (ΣSHC) – the sum of individual resolved saturated hydrocarbons (38 n-alkanes and isoprenoids) (Table 2-10)
- Total petroleum hydrocarbons (TPH) – sum of the resolved and unresolved, primarily saturated, hydrocarbons in the n-C9 through n-C40 range
- Total sterane/triterpane biomarkers (S/T) – the sum of 17 steranes and triterpanes – a source indicator for complex hydrocarbon assemblages (Table 2-9).

LMW PAH frequently are associated with refined and unrefined petroleum products (petrogenic PAH). HMW PAH are primarily derived from the combustion of fossil fuels or as principal components of pyrogenic tars (e.g., creosote- and coal tar-type formulations) (pyrogenic PAH). Pristane and phytane often are abundant in crude oil and peat. Phytane is rare in modern living organisms, but pristane is biosynthesized in large amounts by some marine animals, particularly calanoid copepods (Avigan and Blumer, 1968), important components of the Chukchi Sea pelagic food Web. Thus, pristane/phytane ratios in environmental samples may be useful as an indicator of the source of hydrocarbon assemblages and the degree of weathering.

TPH concentration in this report is based on the analysis of the F1 laboratory fraction of a solvent extract of an environmental sample. The F1 fraction consists primarily of saturated hydrocarbons and does not fully capture all petroleum hydrocarbons in the sample (e.g., the aromatics that are in the F2 laboratory fraction). This approach makes it possible to obtain the TPH and SHC results from the same analysis, and is consistent with other petroleum baseline and impact monitoring programs (including other programs conducted in Alaska).

3.2.1. Sediment

3.2.1.1. Saturated Hydrocarbons (TPH and SHC)

Concentrations of TPH in surface sediments and sediment core samples range from 460 (surface sediments at Klondike) to 22,200 µg/kg (historic drill sites at -6-cm depth at Burger and at the -4-cm depth at Klondike), with most of the samples having TPH concentrations less than 10,000 µg/kg (Table 3-4, Figure 3-4). Mean TPH concentrations range from 5,330 ± 3,180 µg/kg in surface sediments at fixed and random stations in the Klondike area to 13,800 ± 7,610 µg/kg in sediments from the historic drill stations in the Burger area. The highest sediment TPH concentrations are at the two historic drill site stations, KD005[1] with concentrations ranging from 10,400 to 22,200 µg/kg, and BD005 with concentrations ranging from 11,600 to 22,100 µg/kg. Highest sediment TPH concentrations in sediment cores occur at a depth of -6 cm in the core from the drill site at Burger, -2 cm in the core from a station (KD002) west of the Klondike drill site, and -4 cm in the core at the Klondike drill site. Surface and subsurface sediment TPH concentrations show a high degree of variability throughout the study area (Figure 3-4).

[1] Stations KD005 and BD005 are positioned at the center locations of the historic Klondike and Burger drilling platform sites.

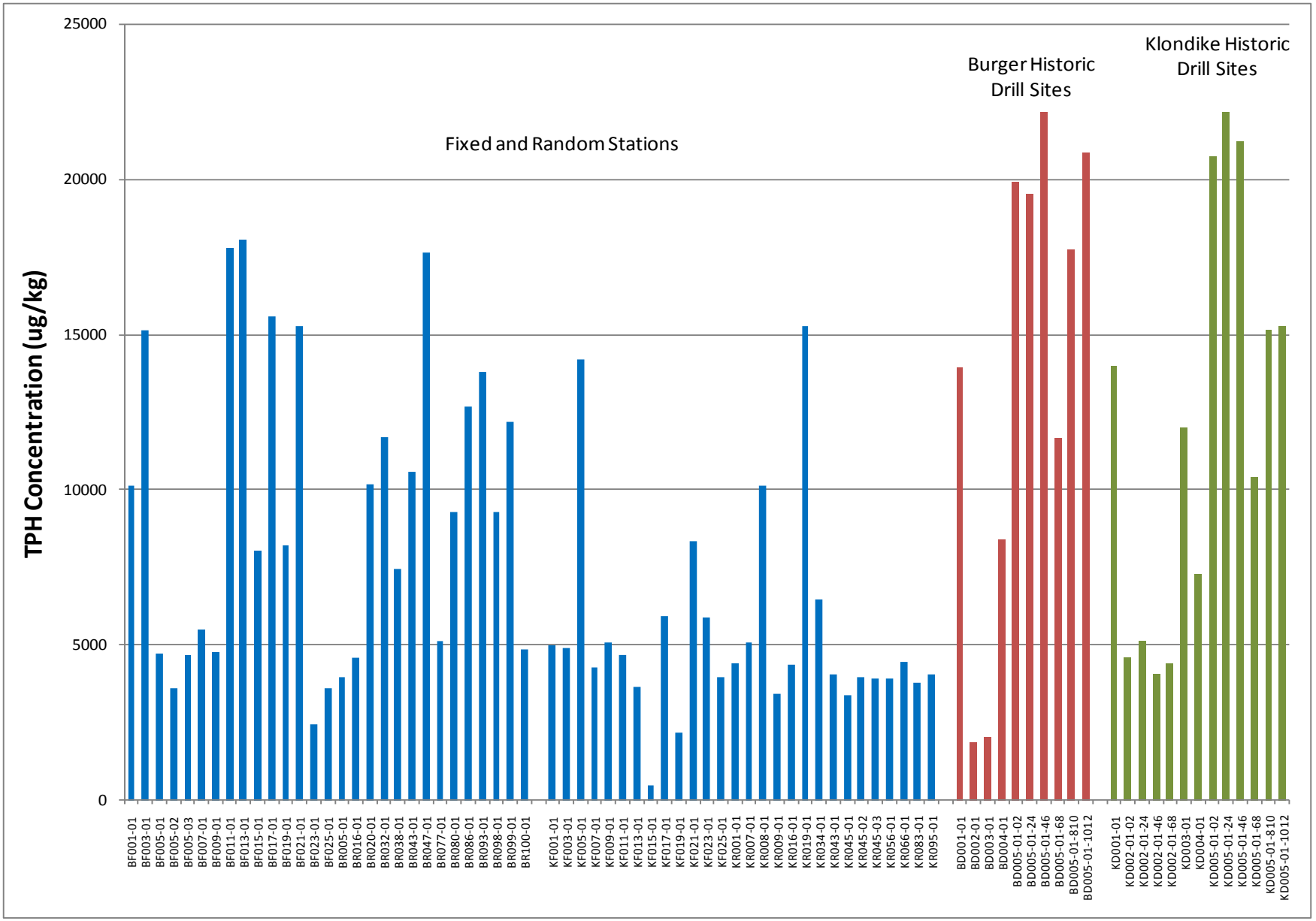


Figure 3-4. TPH concentrations in individual sediment samples from fixed, random, and historic drill sites in the Burger and Klondike survey areas.

Mean concentrations of ∑SHC in sediments are one-third to one-fourth those of TPH (Table 3-4) and concentrations in individual sediment samples are less variable than those of TPH. Sediment ∑SHC concentrations range from 371 µg/kg in surface sediments from fixed and random stations at Klondike to 5,600 µg/kg in surface sediments from the historic drill site at Klondike. ∑SHC concentrations in the -3- to -12-cm depth interval of cores range from 2,060 to 4,480 µg/kg. The most abundant resolved alkanes in all sediment samples are the higher molecular weight n-alkanes (above n-C_{20}), with the most abundant n-alkane in all sediment samples from both Burger and Klondike survey areas being n-C_{27}.

Concentrations of the isoprenoid hydrocarbons, pristane and phytane, and the pristane/phytane ratio in environmental samples can be used as a rough indicator of the sources of the hydrocarbon mixture (Wang et al., 2009). Both pristane and phytane are relatively abundant in most crude oils and coals. Pristane also is biosynthesized by marine animals, particularly planktonic calanoid copepods. Phytane usually is rare in environmental samples not containing fossil fuels. Thus, the pristane/phytane ratio can be used to help differentiate among sources of petroleum mixtures in sediments, and the sources of saturated hydrocarbons in tissues of marine animals. Pristane and phytane also biodegrade more slowly than n-alkanes of similar molecular weight, making them useful indicators of the weathering status of petroleum hydrocarbon mixtures in sediments.

Lowest concentrations of pristane and phytane were in surface sediments from Burger and Klondike survey areas, respectively (Table 3-4). Highest concentrations were in surface sediments at the historic drill site at Klondike. Mean pristane/phytane ratios in surface sediments from fixed and random stations, and in surface and subsurface sediments at historic drill sites stations at Burger are 2.48 ± 0.17 and 2.22 ± 0.38, respectively. The pristane/phytane ratios in sediments from Klondike are 3.41 ± 0.72 and 3.45 ± 2.49, respectively. These differences suggest that the sources of the hydrocarbon assemblages are different at Burger and Klondike survey areas.

3.2.1.2. Polycyclic Aromatic Hydrocarbons (PAH)

Concentrations of Total PAH (TPAH) in surface sediment and sediment core samples range from 47 to 3,100 µg/kg with the majority of the samples having TPAH concentrations less than 500 µg/kg (Table 3-4, Figure 3-5). Figure 3-5 clearly shows that KD005 drill site sediments are enriched in PAH and that BD005 drill site sediments are slightly enriched in PAH, as compared to the surface fixed and random station sediments that are representative of the regional PAH background. Sediment TPAH concentrations are highest at the locations of the two historic drill sites and range from 635 to 3,100 µg/kg at KD005 and from 470 to 650 µg/kg at BD005. The Total PAH concentrations for both the KD005 and BD005 sediments exceed the 95% confidence interval (CI) range of 35 to 458 µg/kg determined for all of the fixed and random sediment samples, indicating that these two center drill site locations have PAH concentrations that are significantly higher than the regional background.

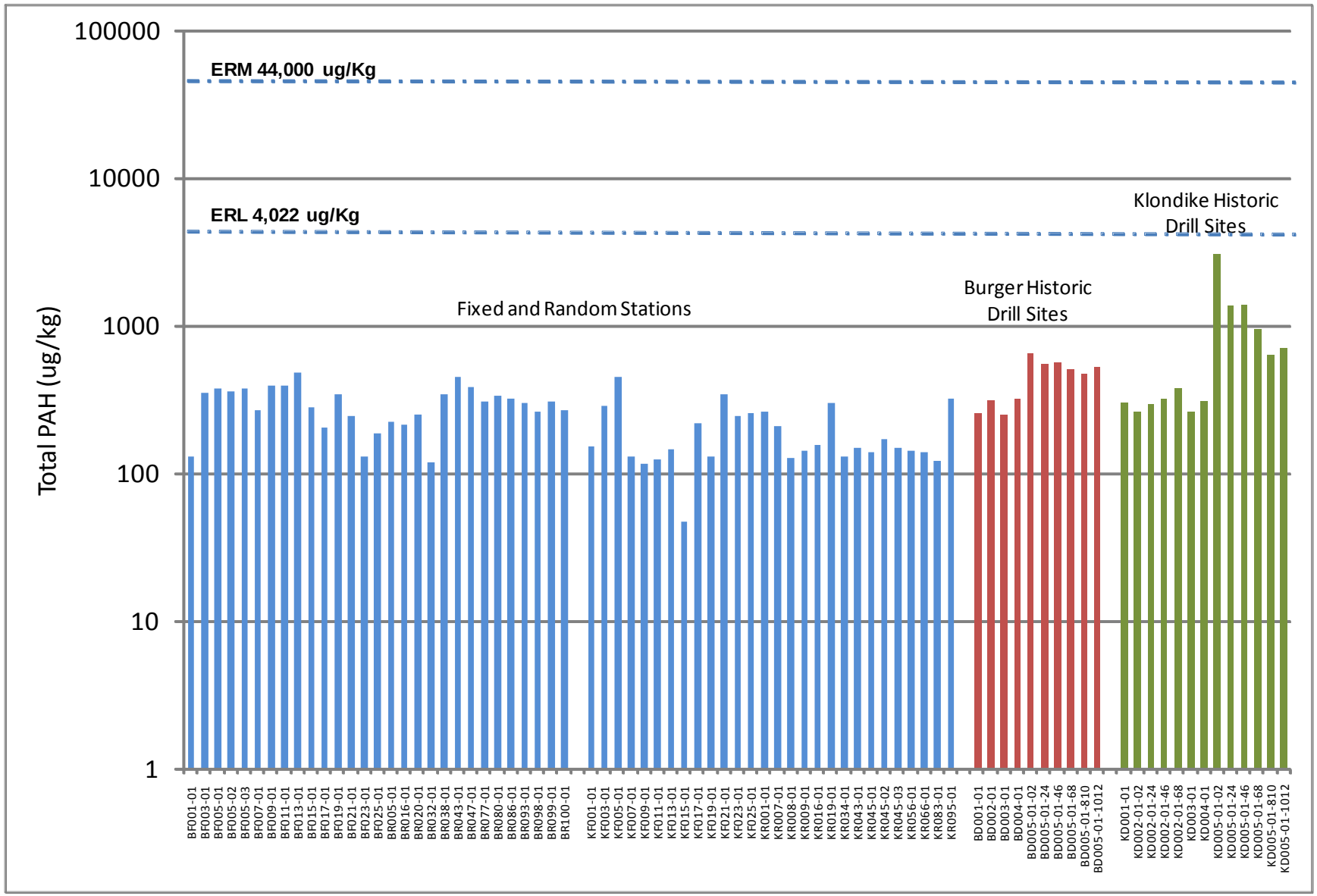


Figure 3-5. Total PAH concentrations in surface sediments from fixed and random stations and in surface and subsurface (-2 to -12 cm) sediments at the historic drill sites in the Burger and Klondike survey areas. Effects range low (ERL) and effects range median (ERM) TPAH concentrations, indicating potentially toxic concentrations to sediment-dwelling marine animals are included for reference.

The composition of the PAH assemblage in sediments in the Burger and Klondike survey areas show little among-station variability, with a few exceptions. The PAH assemblage in all sediment samples is composed of a full suite of both parent and alkyl PAH, indicative of a mixture of pyrogenic (from pyrolysis and combustion of organic matter), petrogenic (from fossil fuels or their precursors), and biogenic (e.g., perylene from recent anaerobic diagenesis of certain natural organic chemicals) hydrocarbon sources. This PAH assemblage is typical of the background for the region, which is comprised of a mixture of fossil fuel (petroleum, peat, and coal) PAH, with lesser contributions of pyrogenic PAH (Figures 3-6A and 3-6B). The PAH distributions for historic drill site KD005 sediments are different from the regional background sediments in that they are enriched in parent and alkylated naphthalenes (Figure 3-6C). However, the PAH distributions in sediments at historic drill site BD005 (Figure 3-6D) are similar those in the fixed and random background sediments.

Perylene represents 4 to 6% of the TPAH in surface and subsurface sediments at both Burger and Klondike. Although most crude oils contain some perylene, much of the perylene in sediments is derived from the anaerobic diagenesis of recent plant materials (Venkatesan, 1988). Highest concentrations were in subsurface sediments at the historic drill sites at Burger and Klondike.

3.2.1.3. Biomarkers - Steranes and Triterpanes (S/T)

Concentrations of Total S/T in surface sediments and sediment core samples range from 2.9 to 80 μg/kg with the majority of the samples having total S/T concentrations less than 30 μg/kg (Table 3-4, Figure 3-7). Figure 3-7 clearly shows that historic drill site KD005 and BD005 sediments are enriched in biomarkers compared to the fixed and random background surface sediment samples. The Total S/T concentrations in station KD005 sediments ranged from 29 to 80 μg/kg and for station BD005 sediments from 32 to 52 μg/kg, with highest concentrations at the surface and at -4 cm, respectively. The Total S/T concentrations for BD005 and KD005 sediments are outside the 95% CI range of 2.6 to 28 μg/kg calculated for the fixed and random background samples.

The majority of the sterane and triterpane extracted ion profiles (EICPs) in the Chukchi sediments throughout the study area show little variation and are similar to the biomarker distributions observed in Beaufort Sea sediments (Brown et al. 2010). The triterpane distributions in the KD005 and BD005 sediment samples are generally similar to the regional background samples but show relative increases in the triterpanes that are usually are predominant in Alaskan (North Slope) crude oil (i.e., T15, T19, T21, T22; Figure 3-8). Triterpane distributions for the station KD005 and BD005 sediment samples suggest that the hydrocarbons present in these samples are a mixture of regional background and petrogenic hydrocarbons from crude oil, including seep oil, peat, kerogens from organic-rich shales, and coal (Venkatesan and Kaplan, 1982; Anders and Magoon, 1985).

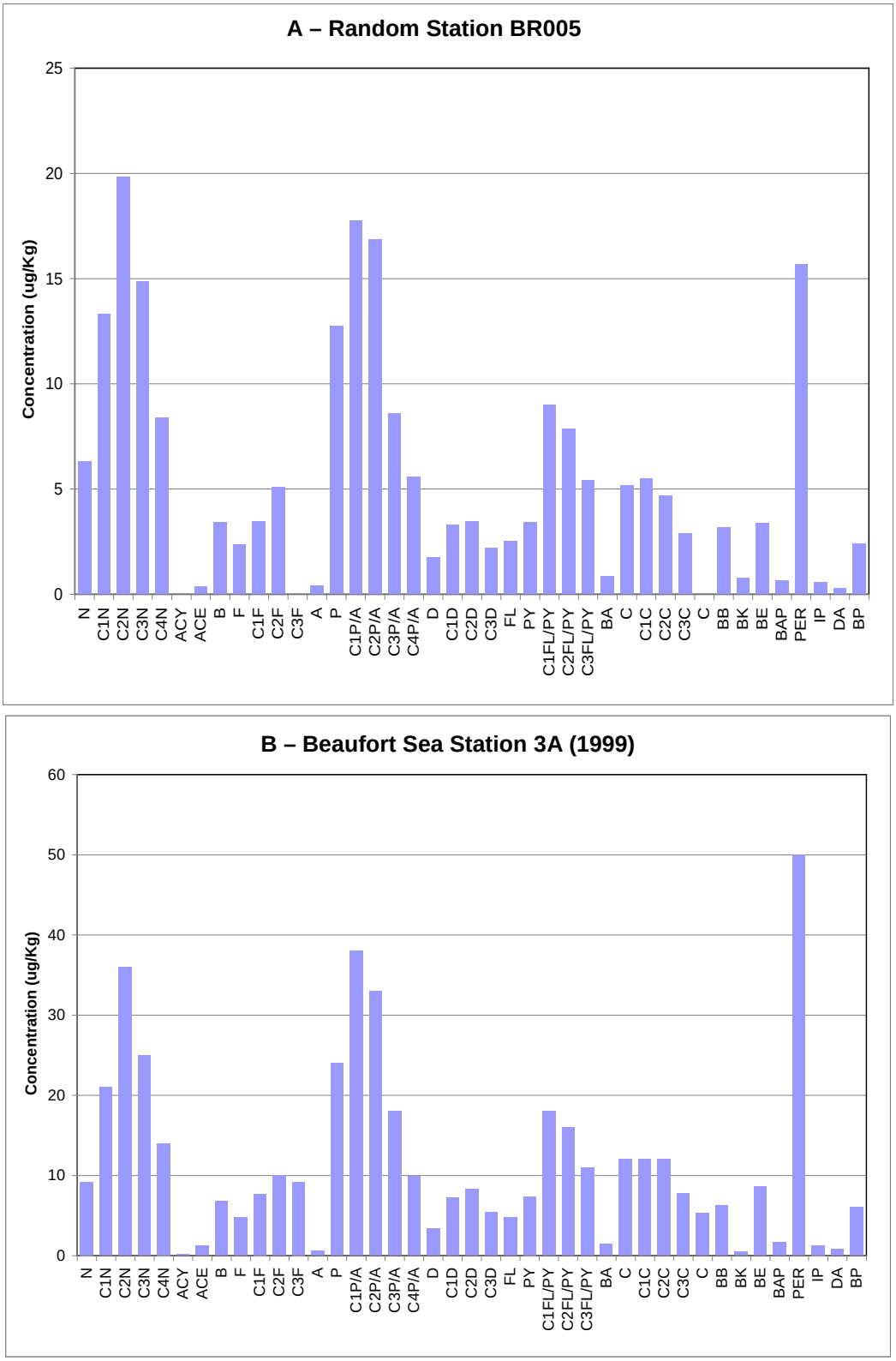
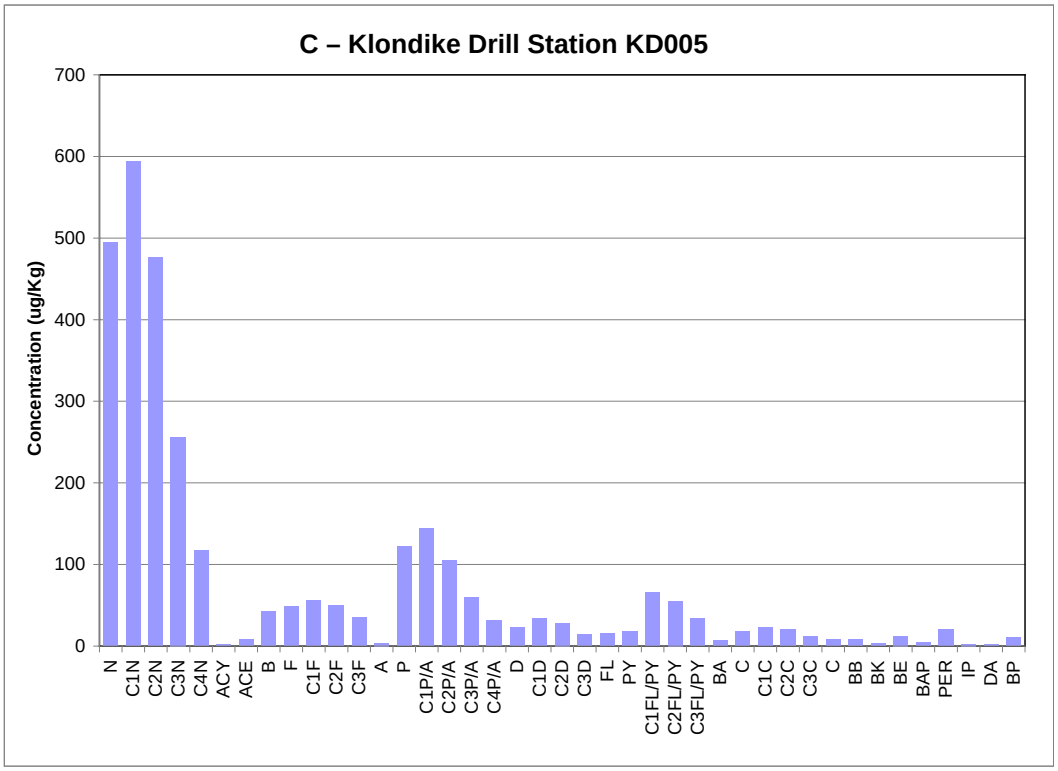


Figure 3-6. PAH profiles in surface sediments from random station BR005, Beaufort Sea sediment, and historic drill site stations BD005 and KD005.



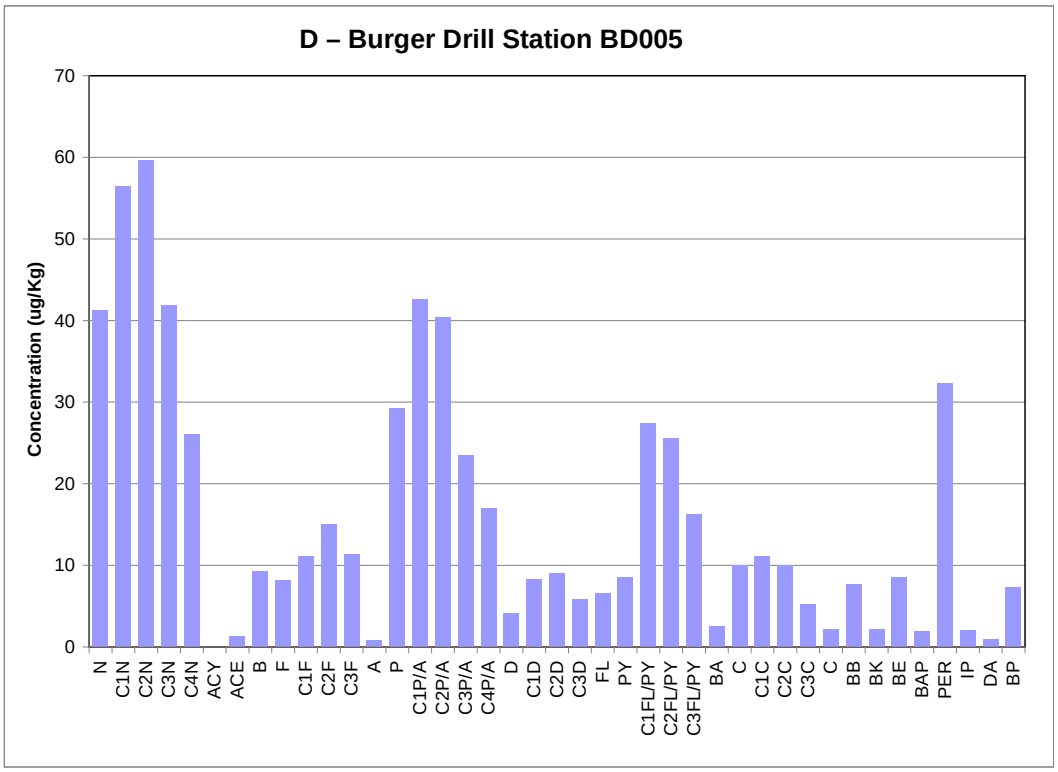


Figure 3–6. PAH profiles in surface sediments from random station BR005, Beaufort Sea sediment, and historic drill site stations BD005 and KD005, continued.

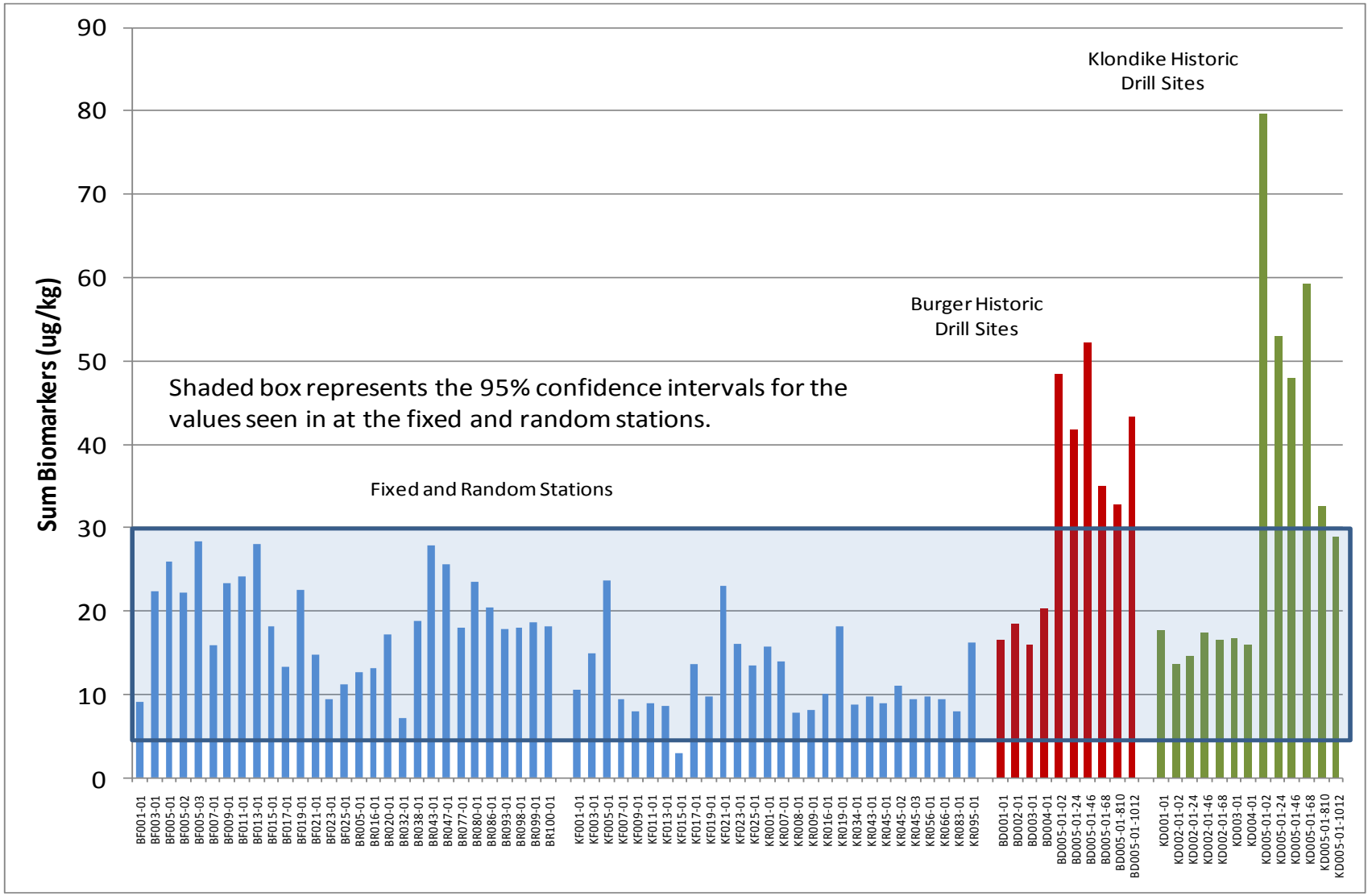
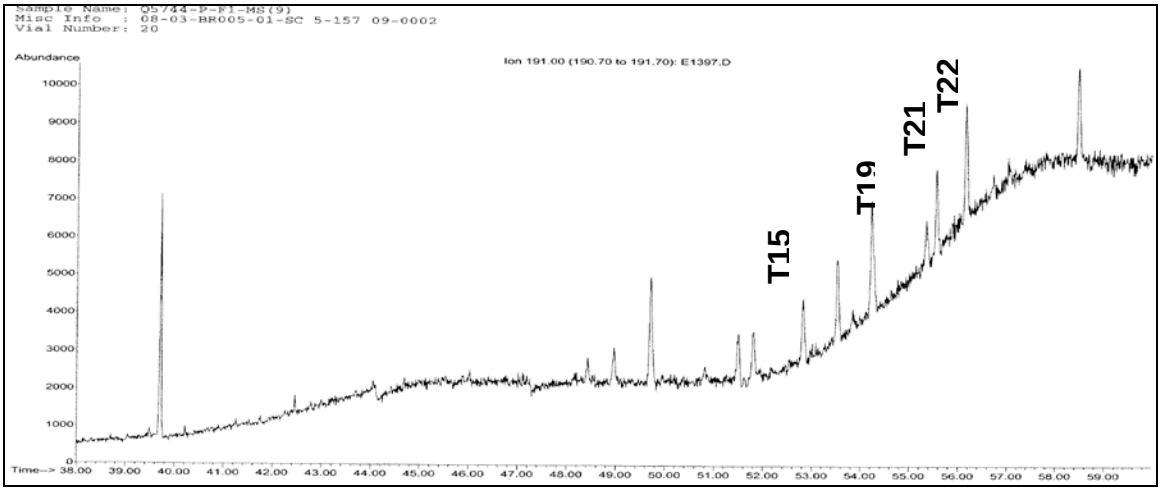
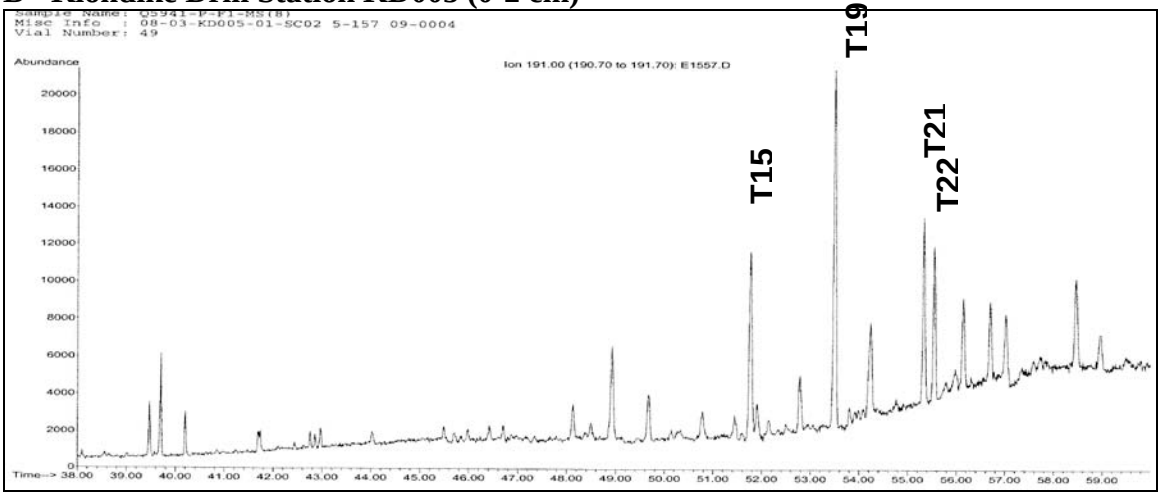


Figure 3-7. Sterane/triterpane (S/T) petroleum biomarker concentrations in Burger and Klondike survey area sediments.

A – Burger Random Station BR005 (0-2 cm)



B - Klondike Drill Station KD005 (0-2 cm)



C – Beaufort Sea Station 3A (1999)

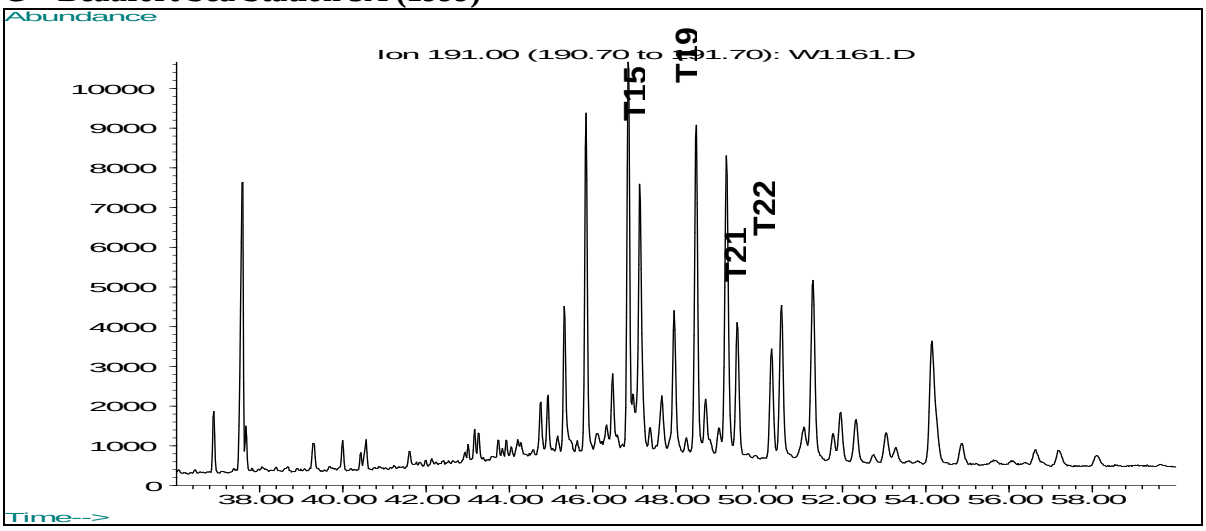


Figure 3-8. Representative Triterpane Extracted Ion Current Profiles for sediments from Burger (A), Klondike (B), the Beaufort Sea (C) and for North Slope crude oil (D).

D – North Slope Crude Oil

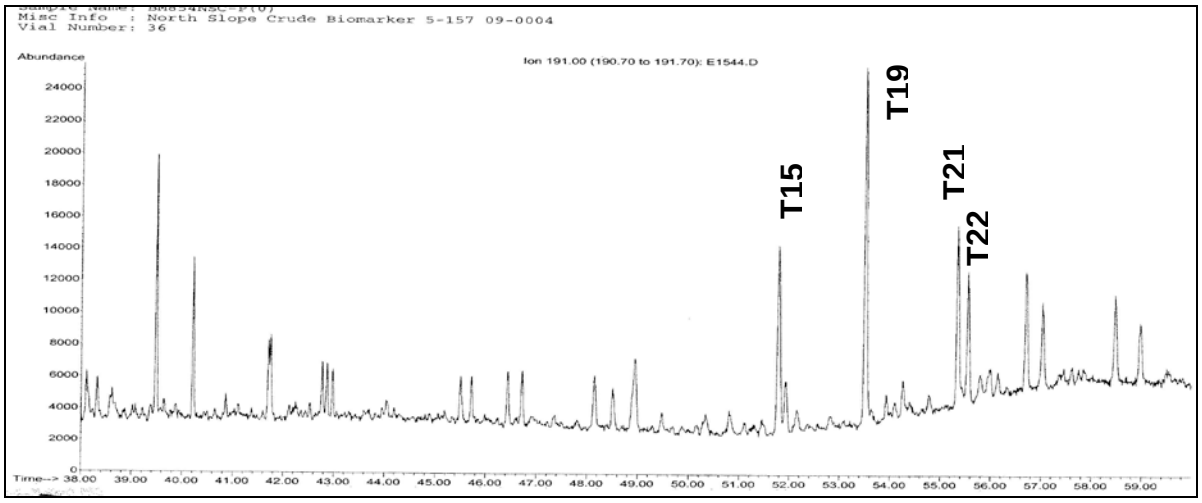


Figure 3–8. Representative Triterpane Extracted Ion Current Profiles for sediments from Burger (A), Klondike (B), the Beaufort Sea (C) and for North Slope crude oil (D). (continued)

3.2.2. Marine Invertebrate Tissues

3.2.2.1. Saturated Hydrocarbons (TPH and SHC)

TPH concentrations in marine invertebrate tissue samples are quite variable and usually more than twice the concentrations of ΣSHC and TPAH combined (Table 3-5). Tissue TPH probably is primarily biogenic (e.g., precursors of fatty acids). Crabs have the lowest TPH concentrations and zooplankton the highest. TPH concentrations usually are lower in marine invertebrates collected at Burger than in those collected at Klondike. Figure 3-9 summarizes the mean TPH concentrations in different invertebrates from the two study areas. The mean TPH concentrations range from 4,760 to 170,000 µg/kg in crabs and mixed zooplankton, respectively, from Burger and from 9,130 to 558,000 µg/kg in crabs and mixed zooplankton from Klondike (Table 3-5). Only five marine invertebrate samples (amphipods, crabs, and clams) were collected at the historic drill site in the Burger survey and three samples (crab and clams) were collected at the historic drill site in the Klondike survey area Therefore, meaningful comparisons could not be made between hydrocarbon concentrations in tissues of invertebrates from fixed, regional, and historic drill site stations.

Mean ∑SHC concentrations in marine invertebrate tissues range from 1,180 µg/kg in tissues of crabs from Burger to 6,340 µg/kg in the single amphipod sample from Klondike (Table 3-5). ∑SHC represents 4 to 67% of TPH in the invertebrate tissues, with clams and worms having the lowest mean percentages and the two crustacean species having the highest percentages. Between 39 and 48% of the TPH in mixed zooplankton is ∑SHC.

Amphipods and mixed zooplankton from both Burger and Klondike contain high relative concentrations of pristine, compared to concentrations of other saturated hydrocarbons; crabs from Klondike also contain high concentrations of pristane (Table 3-5). Pristane concentrations in amphipods, crabs and zooplankton range from 350 to 424,000 µg/kg, with zooplankton

containing the highest concentrations. Crabs and worms contain 21 to 13,400 µg/kg pristane. Pristane is the most abundant alkane in the ΣSHC fraction of amphipods, crabs, and zooplankton. Pristane represents 77% and 17% of ΣSHC in amphipods from Burger and Klondike, respectively, and 93 to 95% of ΣSHC in zooplankton from the two survey areas. Pristane also represents 5% and 86% of ΣSHC in crabs from Burger and Klondike, respectively. Between 1 and 8% of the ΣSHC in sediments, clams, and worms is pristane.

Phytane concentrations are much lower than those of pristane in all four marine invertebrates sampled. Mean phytane concentrations range from <MDL in amphipods from Burger to 117 µg/kg in zooplankton from Klondike (Table 3-5). The resulting pristane/phytane ratios range from 0 (amphipods from Burger) to 3,880 (zooplankton from Klondike). A high pristane/phytane ratio indicates that the saturated hydrocarbons in the tissues are primarily from the food or biosynthesized by the invertebrates. The large differences in pristane concentrations in tissues of the different species of marine invertebrates from the two survey areas reflect differences in the contribution of zooplankton or zooplankton detritus (POC) in their diets. Virtually all the pristane in the Chukchi Sea is biosynthesized from phytoplankton phytol by calanoid copepods (Avigan and Blumer, 1968).

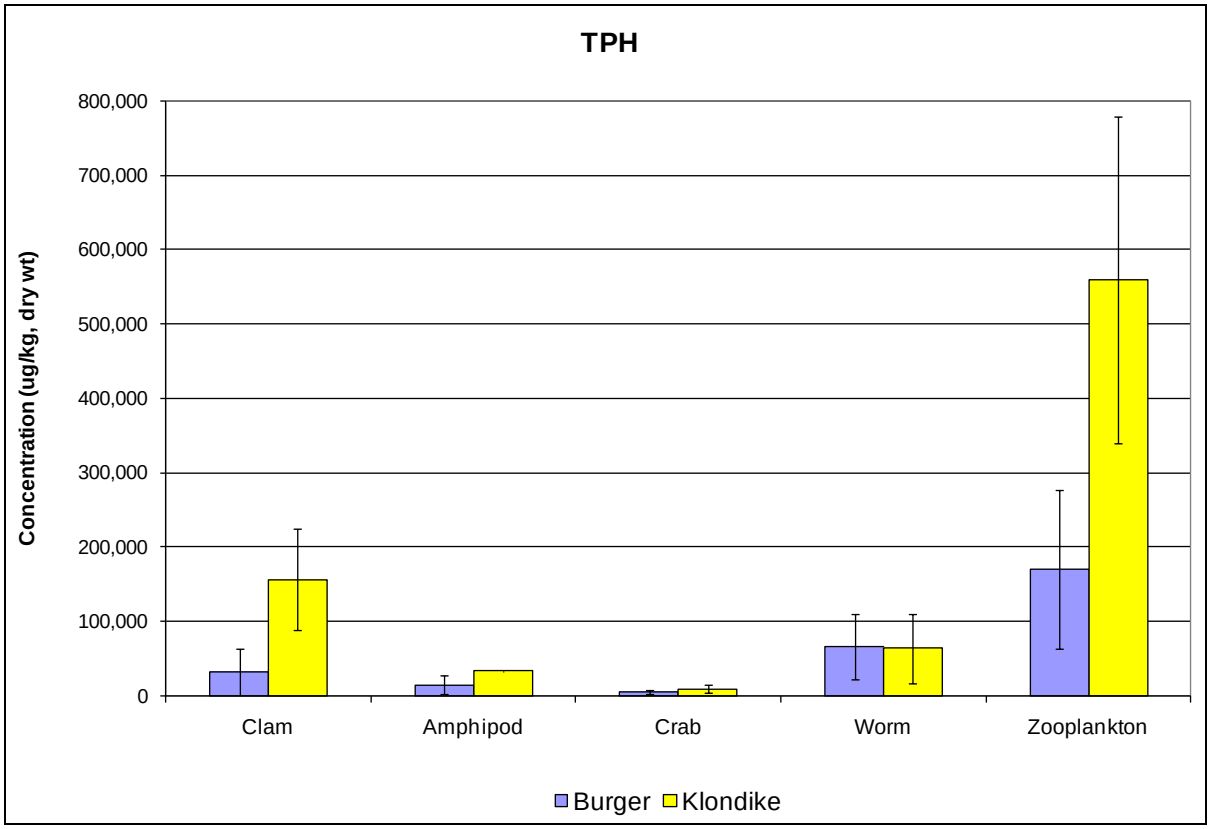


Figure 3-9. Mean TPH concentrations in field biota at Burger and Klondike.

3.2.2.2. Polycyclic Aromatic Hydrocarbons (PAH)

Figure 3-10 summarizes the means and standard deviations of TPAH marine invertebrate tissues collected from the two study areas. TPAH concentrations in the tissue samples are low and variable. Most amphipod and crab samples contain lower TPAH concentrations than the clam, worm, and zooplankton samples (Table 3-5). Mean TPAH concentrations are lower in all invertebrates, except worms, collected from Burger than in those collected from Klondike.

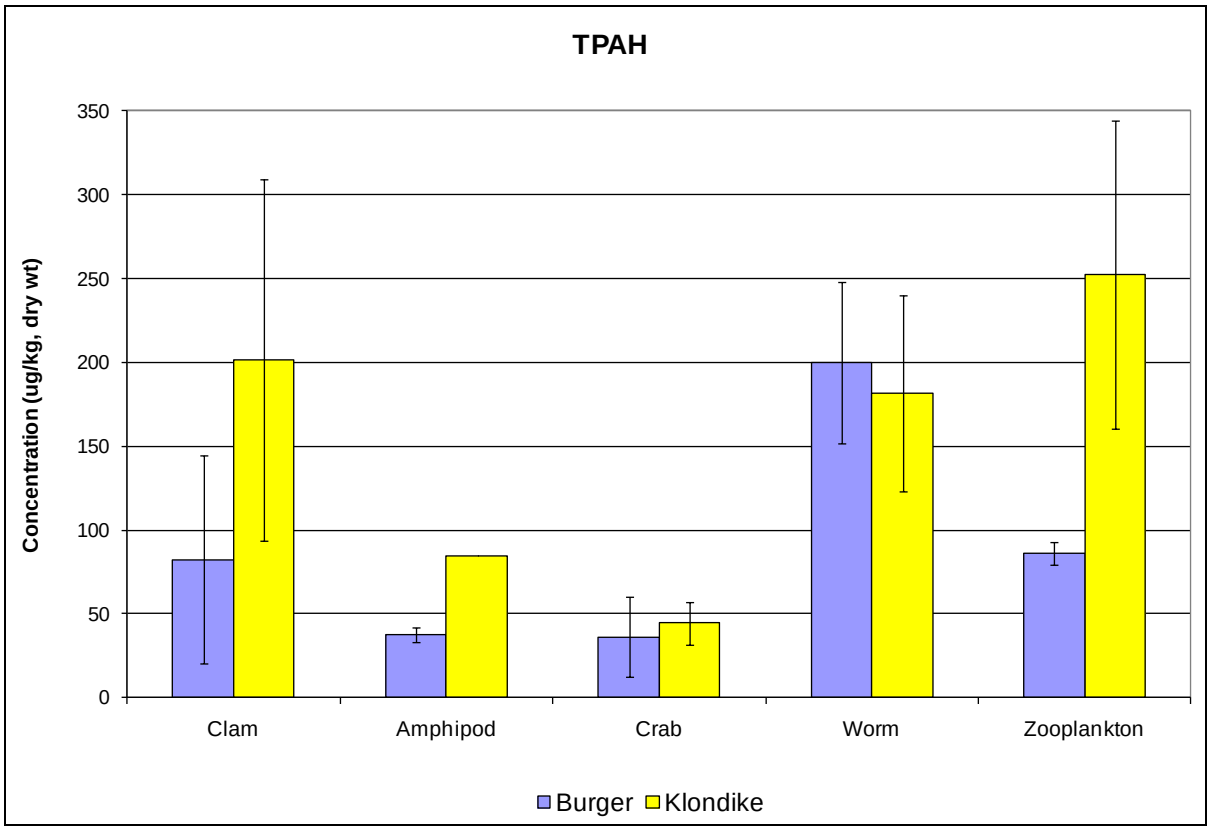


Figure 3-10. Mean TPAH concentrations in marine invertebrates collected at Burger and Klondike.

Mean TPAH concentrations range from 36.3 µg/kg in crabs from Burger to 253 µg/kg in zooplankton from Klondike (Table 3-5 and Figure 3-10). The lowest TPAH concentration in the Burger samples was measured in crabs collected from BF011 (22.7 µg/kg) and the highest TPAH concentration was measured in worms collected from BF021 (302 µg/kg) (Table 3-5). The mean concentration of TPAH ranged from 44.4 (crabs) to 253 µg/kg (zooplankton) in the tissues collected from Klondike. The lowest TPAH concentration in Klondike samples was measured in crabs collected from KR019 (30.5 µg/kg) and the highest concentration of TPAH (360 µg/kg) was measured in zooplankton composited from KF001 and KF021 on the western border of the Klondike study area. This sample also contained the highest concentrations of TPH and S/T, indicating that it may contain a tar ball.

Figure 3-11 through Figure 3-15 show the mean PAH profile in clam, amphipod, crab, worm, and zooplankton samples, respectively. The PAH composition, and relative concentrations of

individual PAH, varies somewhat among marine invertebrate taxa and sampling sites. However, a petrogenic PAH signature with significant contributions of alkylated PAH (e.g., the alkyl naphthalenes, fluorenes phenanthrene/anthracenes, and dibenzothiophenes) is evident for all species, and is particularly evident in clams, worms, and zooplankton. The higher molecular weight, primarily pyrogenic, PAH (e.g., benzo(b/k)fluoranthenes, benzo(e/a)pyrene, and benzo(g,h,i)perylene), and sometimes notable concentrations of the biogenic PAH, perylene, are also present in most samples. Perylene concentrations are highest in the benthic infaunal clams (Figure 3-11) and worms (Figure 3-14) and probably are derived from ingestion of sediments. The relatively high concentrations of fluoranthene and pyrene in all taxa also is a strong indicator of a pyrogenic (e.g., combustion soot) source for part of the PAH assemblage in the invertebrate tissues.

The most abundant PAH group in the marine invertebrates from both locations is the phenanthrenes. Naphthalenes and dibenzothiophenes are almost equally abundant. One or more alkyl isomer group usually is more abundant than the parent PAH. Sometimes, parent naphthalene is more abundant than alkyl-naphthalenes, particularly in tissues containing low concentrations of TPAH (e.g., amphipods: Figure 3-12). Naphthalene frequently is present in laboratory blanks, and the elevated tissue levels may be due in part to laboratory contamination. The low molecular weight, two- and three-ring PAH, including alkyl homologues, (LPAH) nearly always are more abundant than high molecular weight 4- through 6-ring PAH, including alkyl homologues (HPAH) (Table 3-5). The LPAH/HPAH ratio ranges from 1.7 in worms from Burger to 12.5 in amphipods from Burger. The predominance of LPAH over HPAH in all species is consistent with a petrogenic source for much of the PAH in the tissues.

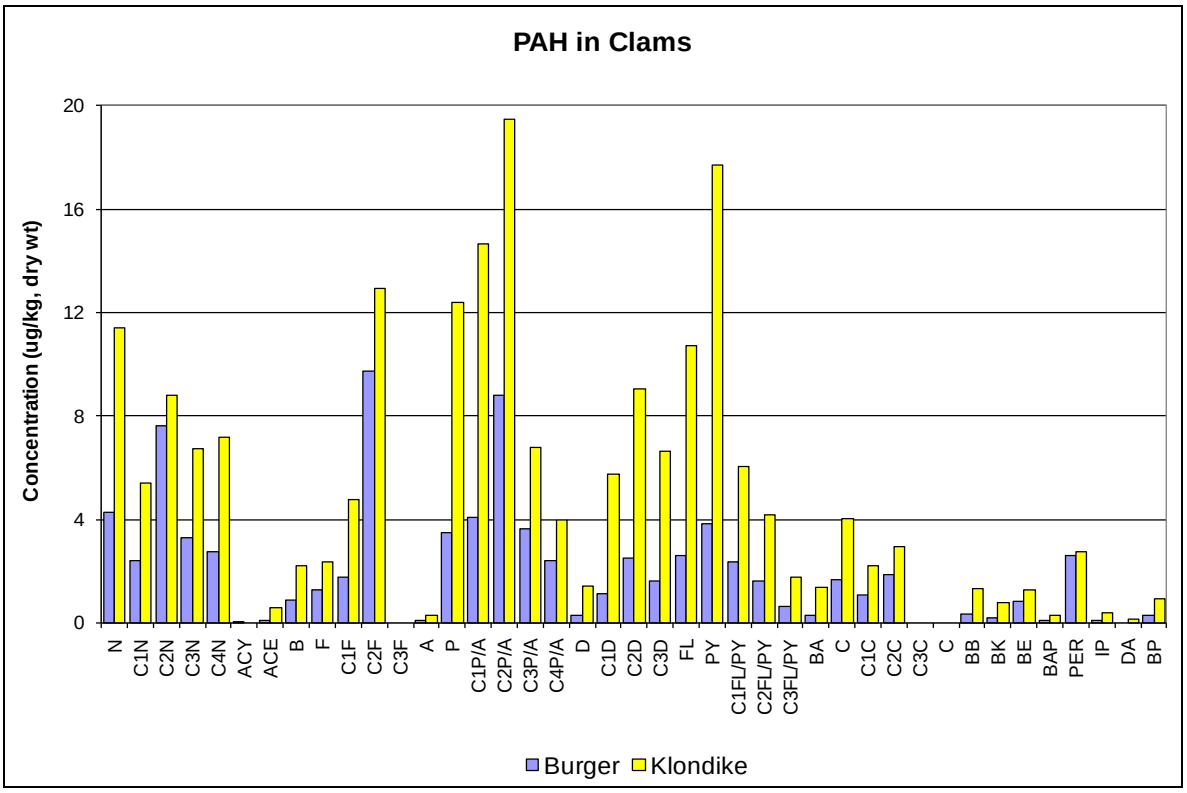


Figure 3-11. Mean PAH profiles in clams from Burger and Klondike.

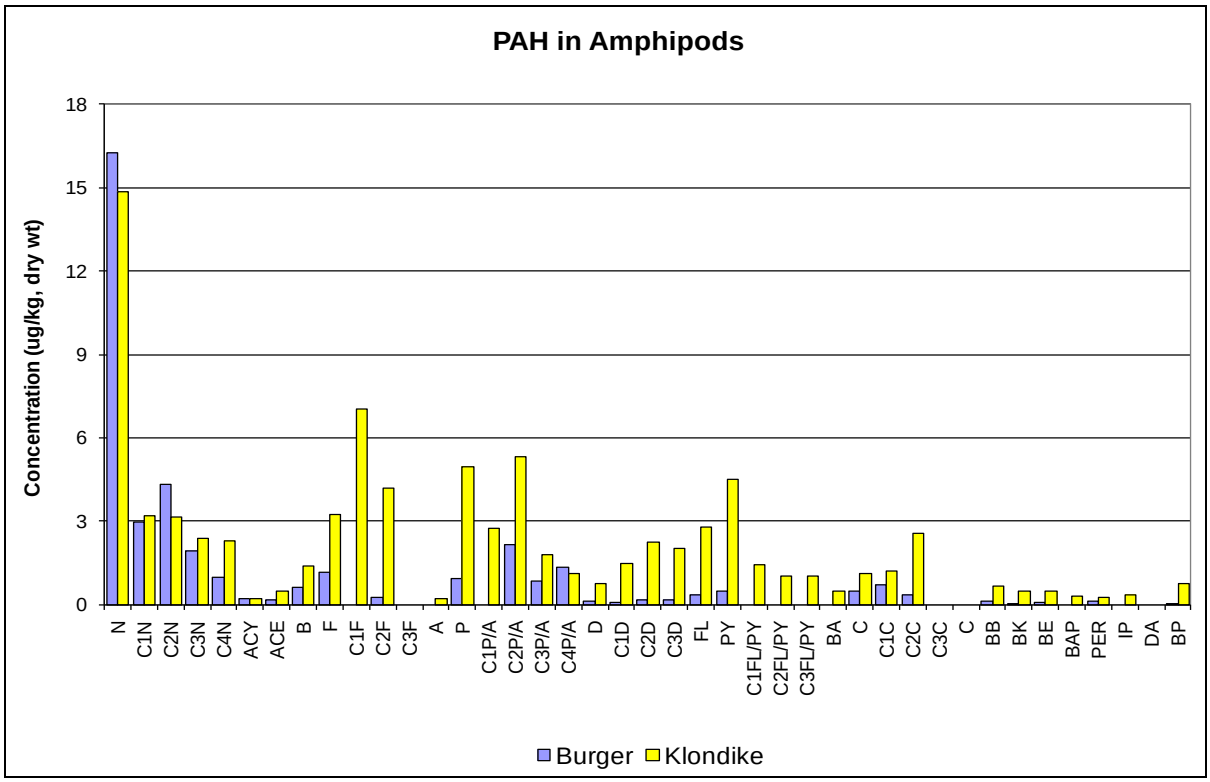


Figure 3-12. Mean PAH profiles in amphipods from Burger and Klondike.

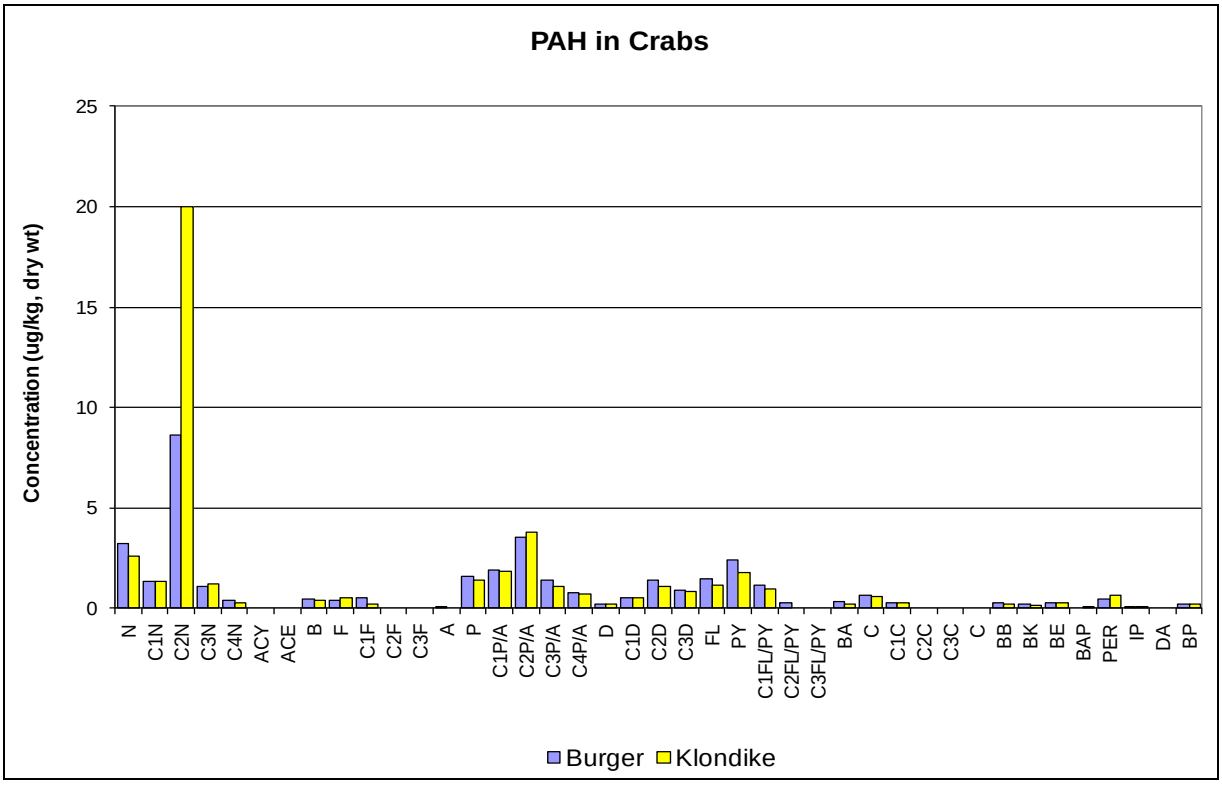


Figure 3-13. Mean PAH profiles in crabs from Burger and Klondike.

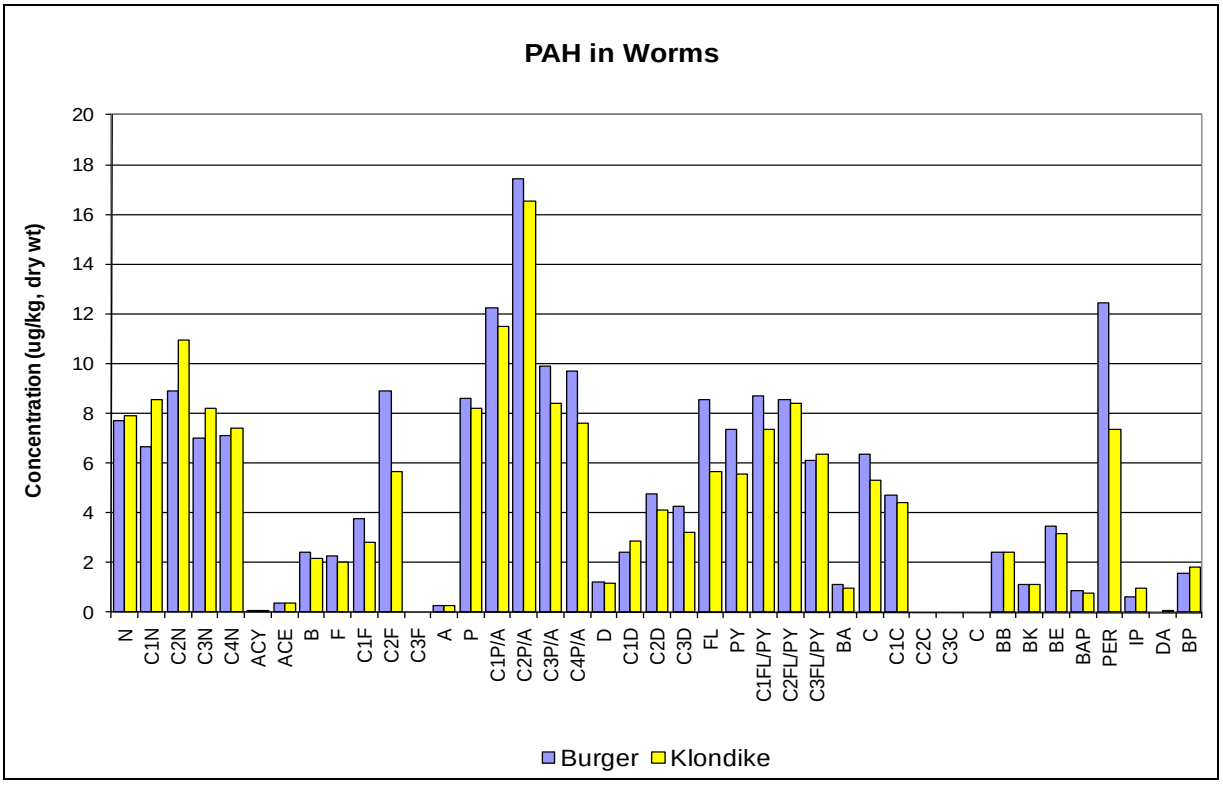


Figure 3-14. Mean PAH profiles in worms from Burger and Klondike.

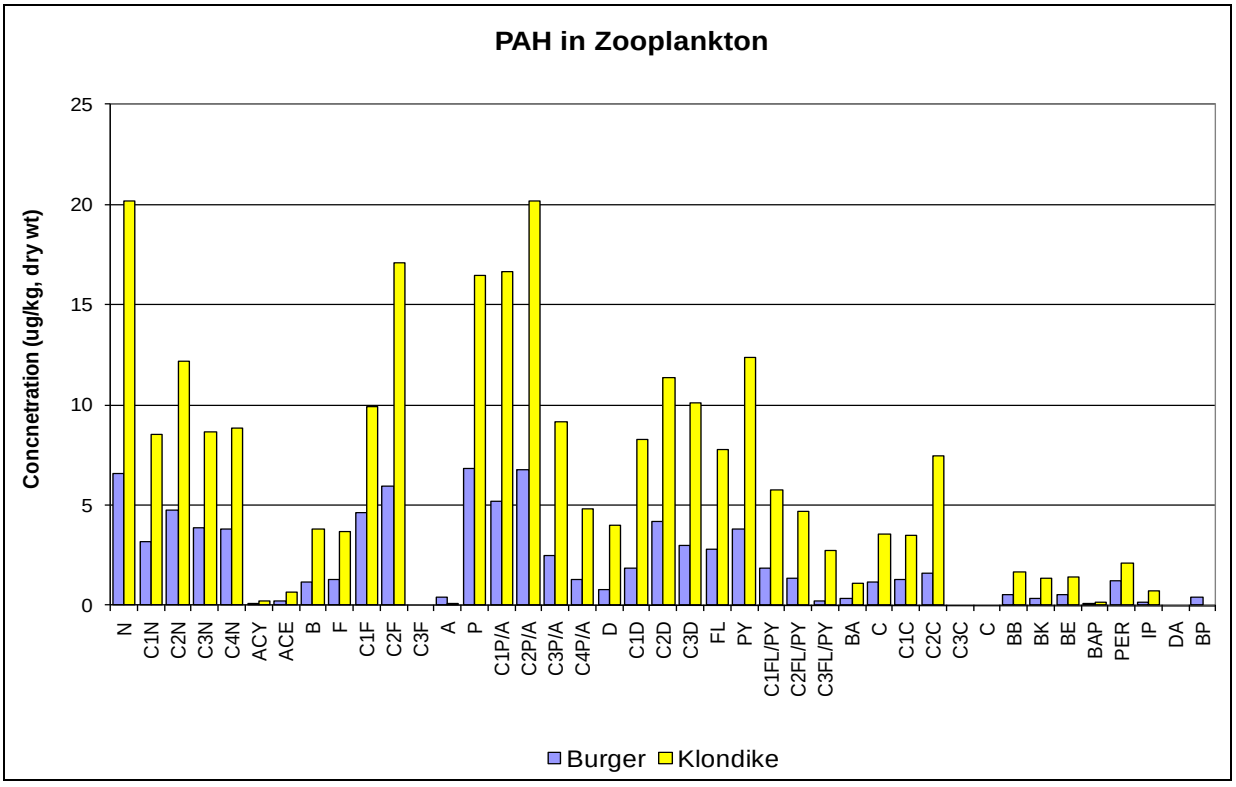


Figure 3-15. Mean PAH profiles in zooplankton composite samples from Burger and Klondike.

3.2.2.3. Petroleum Biomarkers – Steranes/Triterpanes (S/T)

Figure 3-16 shows the triterpane biomarker profile (eicp m/z 191) for the zooplankton sample from the composite of zooplankton collected at KF001 and KF021. A profile for an oil reference standard is shown in Figure 3-17, for comparison. The concentrations of total S/T are low and highly variable in marine invertebrates collected in the Burger and Klondike survey areas (Table 3-5). The mean total S/T concentrations range from 2.89 ± 1.83 µg/kg in amphipods from Burger to 259 ± 146 µg/kg in zooplankton from Klondike. The total S/T concentration in individual tissue samples collected at Burger range from non-detect in several clam and amphipod samples to 75.2 µg/kg in worms collected at station BF021 in the northwest corner of the Burger survey area (Table 3-5). The total S/T concentration in individual tissue samples collected at Klondike range from non-detect in several clam samples to 459 µg/kg measured in zooplankton composited from stations KF001 and KF021 along the western boundary of the Klondike survey area. The total biomarker concentrations are below the summed MDL value of 37.5 µg/kg for the majority of the samples.

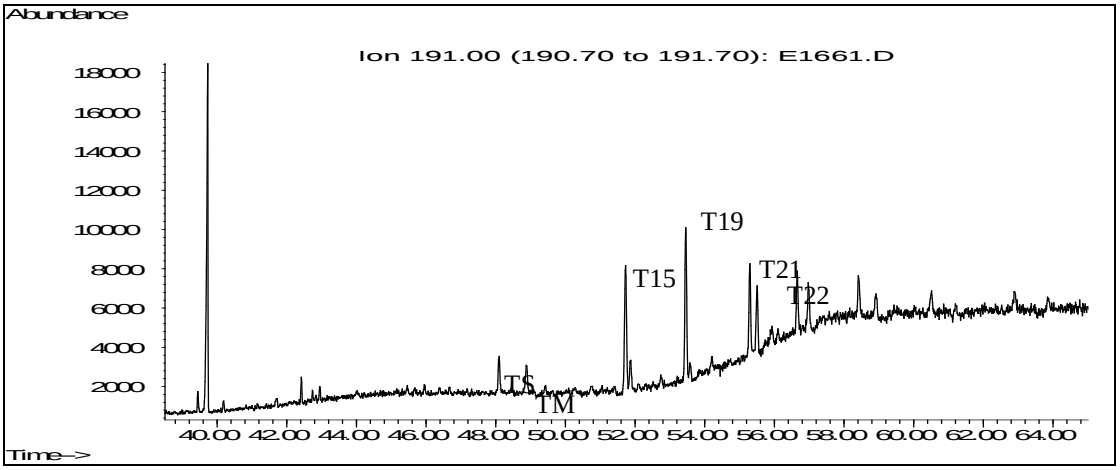


Figure 3-16. Triterpane profile (eicp m/z 191) of zooplankton composited from KF001 and KF021

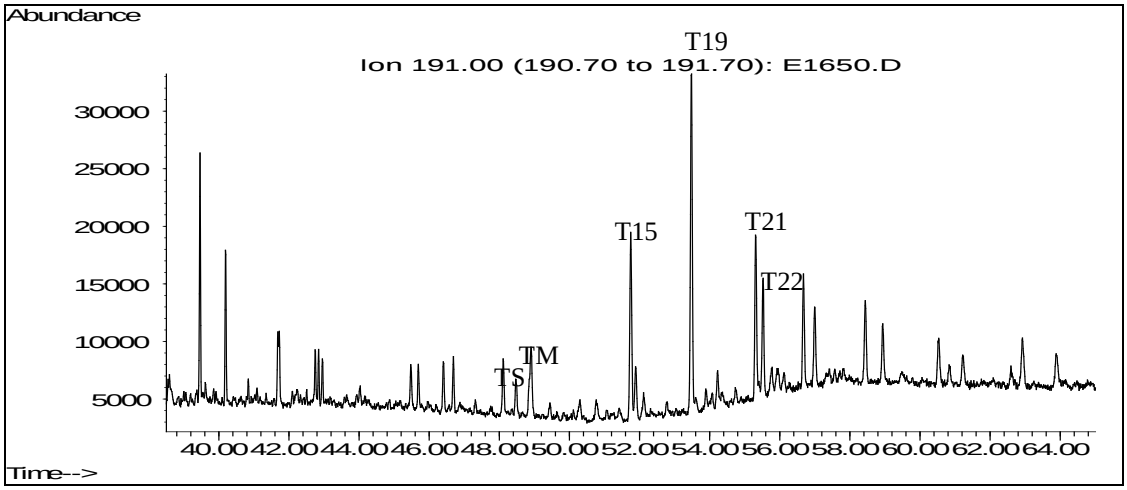


Figure 3-17. Triterpane profile (eicp m/z 191) of oil reference standard (NSC)

3.3. Metals

3.3.1. Sediment

Total concentrations of Ag, Al, As, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Pb, Se and Zn were determined for 63 surface sediments plus 13 additional, sub-surface samples from three sediment cores. Metal concentrations are quite variable as shown by the large ranges in concentrations for each metal (Table 3-6). Average concentrations of all metals, except As and Ba, are lower than those reported for average marine sediment (Table 3-6). Arsenic is a naturally abundant metal in seawater and concentrations in many nearshore marine sediments are naturally higher than the averages provided in Table 3-6. For example, Trefry et al. (2003) reported average As concentrations of 11 ± 4 µg/g for the coastal Beaufort Sea. For Ba, the average of 853 ± 489 µg/g reported for this study in Table 3-6 is skewed by higher mean Ba concentrations of 1,410 ± 681 µg/g and 1,300 ± 666 µg/g for core samples collected at the historic Burger and Klondike drill sites (Table 3-7), indicating that residues of drilling mud barite may still be present at the former drill sites. Excluding the subsurface layers of core samples, the average Ba concentrations in surface sediments in the Burger and Klondike survey areas are 639 ± 76 µg/g and 595 ± 53 µg/g, respectively (Table 3-7). These concentrations are closer to averages for marine sediment and continental crust reported in Table 3-6. Discussion of As, Ba and the other metals will be developed in more detail in Section 4.

The observed variations in concentrations of metals were directly related to variations in sediment grain size as shown for Al in surface sediments in Figure 3-18. The finer-grained material with a higher % mud was richer in Al-bearing clay minerals whereas the coarser grained sediment contained Al-poor quartz sands and carbonate shell fragments. Figure 3-18 also shows that concentrations of Al and % mud are generally higher in the Burger area than the Klondike area as previously suggested with the grain size results. Likewise, concentrations of the other metals were higher in the finer-grained sediments from the Burger area (Table 3-7).

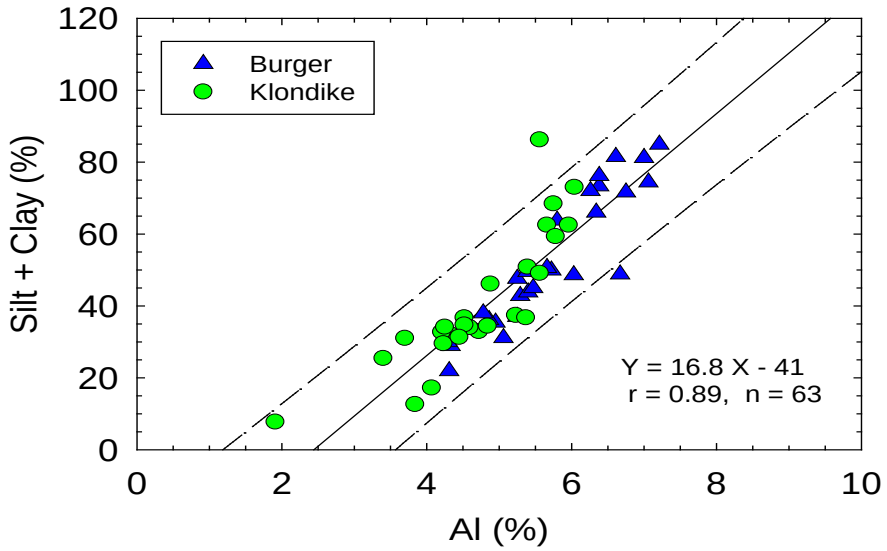


Figure 3-18. Concentrations of silt + clay (mud) versus Al for surface sediments from the Burger and Klondike areas. Equation and solid line are from a linear regression, dashed line shows 95% prediction interval and r is the correlation coefficient.

Table 3-6. Means, standard deviations (SD), maximums (Max) and minimums (Min) for concentrations of metals in all sediment samples from the 2008 survey in the Chukchi Sea. Metal values for average marine sediment and average continental crust are provided for reference. Concentrations are µg/g dry wt (parts per million) or %.

Statistic	Ag (µg/g)	Al (%)	As (µg/g)	Ba (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Hg (µg/g)	Mn (µg/g)	Pb (µg/g)	Se (µg/g)	Zn (µg/g)
This Study													
Mean (n = 76)	0.12	5.33	13.5	853	0.18	75.0	13.6	2.86	0.034	298	12.3	0.55	71.8
SD	0.01	0.89	5.0	489	0.03	11.6	3.1	0.58	0.009	45	2.3	0.24	15.1
Max	0.14	7.21	37.5	2,420	0.26	99.5	21.7	4.63	0.064	422	23.8	1.55	111
Min	0.09	1.91	7.4	436	0.08	30.3	4.3	0.99	0.010	154	8.2	0.18	19.3
Ave. Marine Sed.*	0.16	7.2	7.7	460	0.17	72	33	4.1	0.19	770	19	0.42	95
Ave. Cont. Crust**	0.07	8.0	1.7	584	0.1	126	25	4.3	0.040	716	15	0.12	65

*Salomons and Förstner (1984)
**Wedepohl (1995)

Table 3-7. Means, standard deviations (SD), minimums (Min) and maximums (Max) for concentrations of metals in all surface sediments from fixed and random stations, and historic drill site stations, including sediment cores to -12, in the Burger and Klondike survey areas. Concentrations are µg/g dry wt or %.

Summary Parameter	Burger				Klondike			
	Fixed and Random Stations (n=26)				Fixed and Random Stations (n=26)			
	Mean	SD	Min	Max	Mean	SD	Min	Max
Ag	0.12	0.01	0.10	0.14	0.11	0.01	0.09	0.14
Al*	5.77	0.85	4.31	7.21	4.66	0.89	1.91	6.04
As	16.7	6.3	10.1	37.5	11.7	2.6	8.3	18.3
Ba	639	76	519	775	595	53	436	725
Cd	0.18	0.02	0.15	0.26	0.16	0.03	0.08	0.21
Cr	79.0	11.1	64.2	100	68.2	11.8	30.3	88
Cu	14.8	3.1	9.2	21.7	11.8	2.6	4.3	15.7
Fe*	3.19	0.67	2.20	4.63	2.46	0.50	0.99	3.18
Hg	0.033	0.007	0.018	0.049	0.031	0.011	0.01	0.064
Mn	300	54	225	422	290	53	154	386
Pb	12.3	1.7	10.6	15.7	11.0	1.1	8.2	12.6
Se	0.75	0.34	0.25	1.55	0.41	0.13	0.18	0.75
Zn	77.8	15.5	49.4	111	61.2	13.5	19.3	81.5
	Historical Drill Stations (n=10)				Historical Drill Stations (n=13)			
	Mean	SD	Min	Max	Mean	SD	Min	Max
Ag	0.12	0.01	0.10	0.12	0.12	0.01	0.11	0.13
Al*	5.74	0.42	4.9	6.20	5.41	0.25	4.99	5.73
As	11.7	1.65	9.4	14.7	11.5	3.35	7.4	19.8
Ba	1410	681	604	2,420	1,300	666	618	2,130
Cd	0.20	0.03	0.16	0.23	0.20	0.02	0.17	0.22
Cr	80.0	8.14	67.2	91.1	77.0	5.24	68.7	84.5
Cu	16.2	2.82	12.3	21.1	12.9	1.95	9.8	16.0
Fe*	3.03	0.29	2.61	3.44	2.84	0.11	2.56	2.96
Hg	0.04	0.01	0.029	0.058	0.03	0.00	0.28	0.40
Mn	312	27.2	260	337	295	12.1	276	317
Pb	14.2	2.73	10.8	19.2	13.2	3.29	10.8	23.8
Se	0.56	0.13	0.31	0.75	0.54	0.11	0.4	0.73
Zn	81.9	8.38	68.6	91.4	72.5	5.36	63.3	79.2

*Results in %

Because most of the metals and TOC in sediment are associated primarily with the finer, mud fraction, the variability of sediment metal concentrations throughout the two study areas can be reduced by normalizing metal values to Al and thereby removing variations in metal concentrations from differences in grain size, TOC and/or mineralogy. For example, Figure 3-19 shows strong, positive relationships for Al versus Fe and Al versus Cr. Iron concentrations correlated very well (r = 0.95) with Al values (Figure 3-19a) because both metals are enriched in fine-grained, clay-rich sediments. A second example of a metal/Al plot is given for Cr (Figure 3-19b) to show the effectiveness of the normalization process. Even though individual metal concentrations were quite variable from station to station due to variations in grain size, TOC and/or mineralogy, they can be normalized using concentrations of Al. Concentrations of Fe, Cr

and other metals follow Al in that higher values were found in aluminosilicate clays and lower values were found in quartz and carbonate sands. Thus, plots such as those shown in Figure 3-19 show the natural trend (i.e., the natural Cr/Al ratio) for area sediments. Positive deviations from a prediction interval constructed around the regression line can often be related to anthropogenic inputs of that metal. These concepts are developed in detail in Section 4.

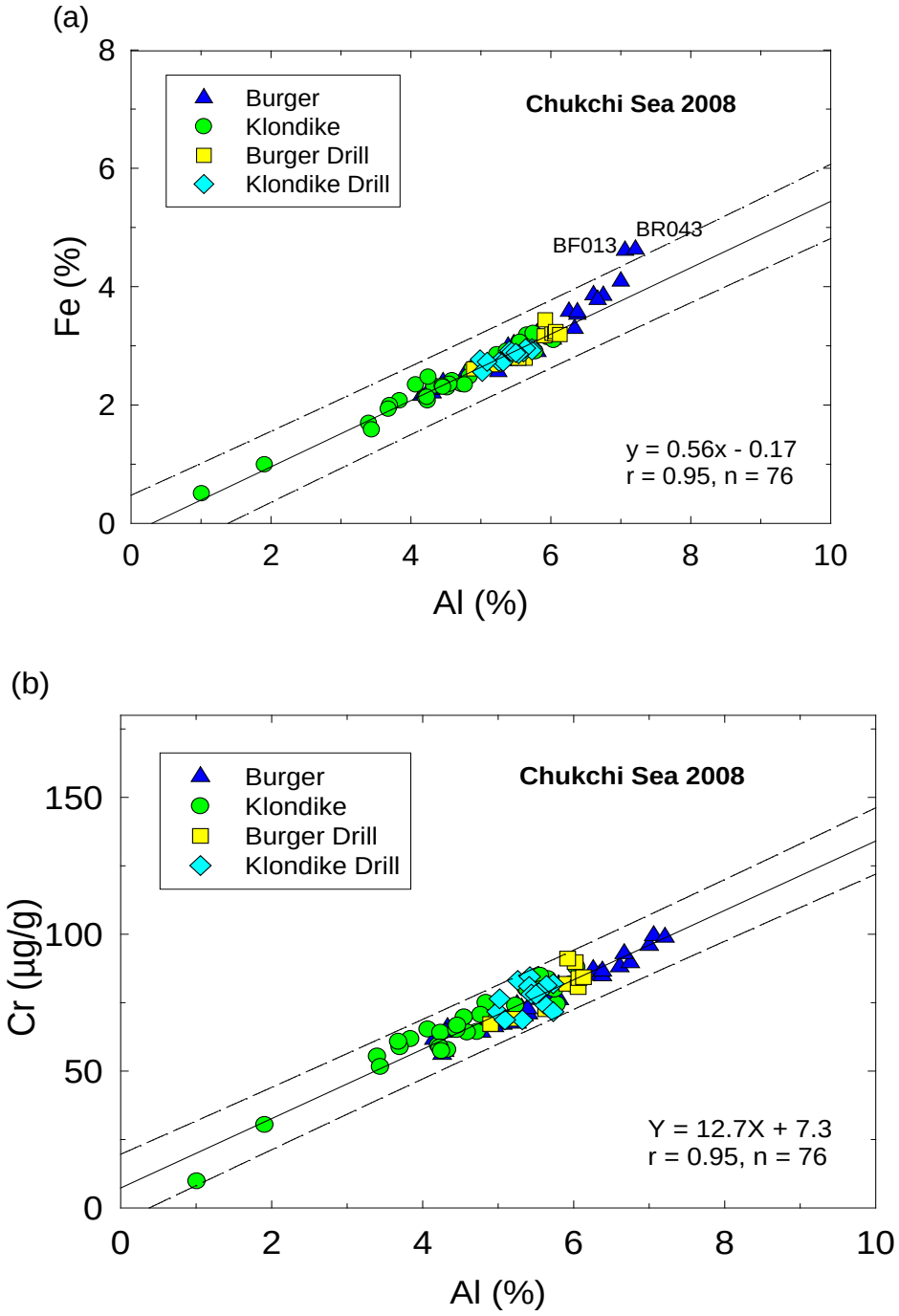


Figure 3-19. Concentrations of (a) Fe and (b) Cr versus Al for all sediments from the 2008 Chukchi Sea study. Equations and solid lines are from linear regression analyses, dashed lines show 99% prediction intervals and r is the correlation coefficient.

Concentrations of metals also were determined for sediments from three cores collected near previous drill sites, one in the Burger area and two in the Klondike area (the BD and KD stations are shown in Figures 2-1 and 2-2). Concentrations of all metals, except Ba in samples from the drill site stations, BD005 and KD005, are similar in the sediment core samples to values reported above for background surface sediments (Tables 3-6, 3-7, 3-8; Figures 3-20, 3-21 and 3-22). As mentioned previously, and to be discussed more below, sediments collected near the former drill sites have elevated Ba concentrations (1,600 to 2,400 µg/g relative to background values of 600 to 700 µg/g), most likely due to the presence of a small amount of residual barite from discharged drilling mud. The elevated Ba values can be followed throughout the 12-cm cores from both stations BD005 and KD005 in Figures 3-20 and 3-22. Barium is at background values throughout the core from station KD002 (Figure 3-21), a short distance from the former drill site.

Two other minor anomalies were observed in metal data for the sediment cores. First, the As concentration in the top 2 cm of the core from station KD002 was almost 50% higher than the average value for the study area and As concentrations in the sediments at 2 to 8 cm were lower than typical for the area (Figure 3-21). Similar enrichment of As was found in surface samples at stations BR43, BR13 and BR47. These As enrichments are most likely due to natural diagenetic remobilization of As under reducing conditions that leads to dissolution of As in subsurface sediments and re-precipitation and enrichment of upwardly diffusing, dissolved As in oxidizing surface sediments (Farmer and Lovell, 1986). The second anomaly was enrichment of Pb and TOC in the 2 to 4 cm layer of sediment in the core from station KD005 (Figure 3-22), possibly due to small anthropogenic additions, a point to be discussed in more detail in Section 4.

3.3.2. Marine Invertebrate Tissues

Metal concentrations were quite variable among different taxa of marine invertebrates in the two study areas; however, variations in metal values were much smaller within each taxon (Table 3-9). For example, average concentrations of As in marine invertebrates from the Burger area ranged from 1.29 µg/g (dry wt.) in zooplankton to 19.1 µg/g in worms (Table 3-9, Figure 3-23a). However, the relative standard deviation (RSD) for As in clams (*Macoma*) was only 7% and the highest RSD found for As was in worms at 24%. The relatively small variations in metal concentrations for the same species are demonstrated by the data for standard deviation and the (maximum/minimum) values in Table 3-9.

Iron was the most abundant metal in all species, with mean concentrations ranging from 230 ± 47 µg/g in amphipods from Burger to 4,484 µg/g in worms from Klondike (Table 3-9). Sediment was present in the guts of most of the worm samples and this partly explains the high Fe and Ba concentrations in worms (Table 3-9). The second most abundant metal in all marine invertebrate tissues was Zn (Table 3-9). Manganese or Cu were the third most abundant metal depending on the species (Table 3-9). Iron, Zn, Mn and Cu are all essential elements for all animals. Metal concentrations usually were lowest in the zooplankton samples and highest in the sediment-containing worm samples (Table 3-9, Figures 3-23 and 3-24). Concentrations of Cd were markedly higher (37.3 ± 9.2 µg/g) in the clams (*Astarte*) clams than in the other species of clams collected (*Macoma*) and in the other marine invertebrates sampled in this study (Figure 3-9c). In a similar manner, Zn concentrations were much higher in the amphipods and mercury concentrations were higher in worms than in the other marine invertebrates (Figure 3-24). These and other differences among metals and organisms will be discussed in more detail in Section 4.

Table 3-8. Means, standard deviations (SD), maximums (Max) and minimums (Min) for concentrations of metals in sediment cores from Burger station BD005 and Klondike stations KD002 and KD005.

Statistic	Ag (µg/g)	Al (%)	As (µg/g)	Ba (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Hg (µg/g)	Mn (µg/g)	Pb (µg/g)	Se (µg/g)	Zn (µg/g)
Burger Station BD005													
Mean (n = 6)	0.12	6.02	10.8	1,912	0.22	85.3	18.1	3.24	0.045	331	16.0	0.57	88.1
SD	0.00	0.09	1.2	293	0.01	4.2	1.5	0.10	0.007	6	1.9	0.15	2.2
Max	0.12	6.13	12.8	2,420	0.23	91.1	21.1	3.44	0.058	337	19.2	0.75	91.4
Min	0.12	5.91	9.4	1,590	0.20	80.7	16.6	3.17	0.038	322	14.7	0.31	85.4
Klondike Station KD002													
Mean (n = 4)	0.12	5.41	11.8	641	0.19	74.2	11.6	2.84	0.035	290	11.7	0.54	71.8
SD	0.01	0.33	5.5	20	0.01	5.7	1.2	0.11	0.005	10	0.7	0.12	5.8
Max	0.12	5.73	19.8	661	0.20	81.9	13.0	2.96	0.040	303	12.4	0.72	76.7
Min	0.11	4.99	7.4	618	0.17	68.7	10.4	2.73	0.028	280	10.8	0.46	64.1
Klondike Station KD005													
Mean (n = 6)	0.12	5.53	11.3	1,974	0.21	79.1	14.6	2.91	0.036	296	15.4	0.62	76.0
SD	0.00	0.13	2.4	171	0.01	4.3	0.8	0.03	0.002	9	4.2	0.07	1.9
Max	0.13	5.73	15.5	2,130	0.22	84.5	16.0	2.96	0.039	312	23.8	0.73	79.2
Min	0.12	5.41	8.5	1,645	0.20	71.7	13.7	2.87	0.034	288	13.1	0.52	73.7

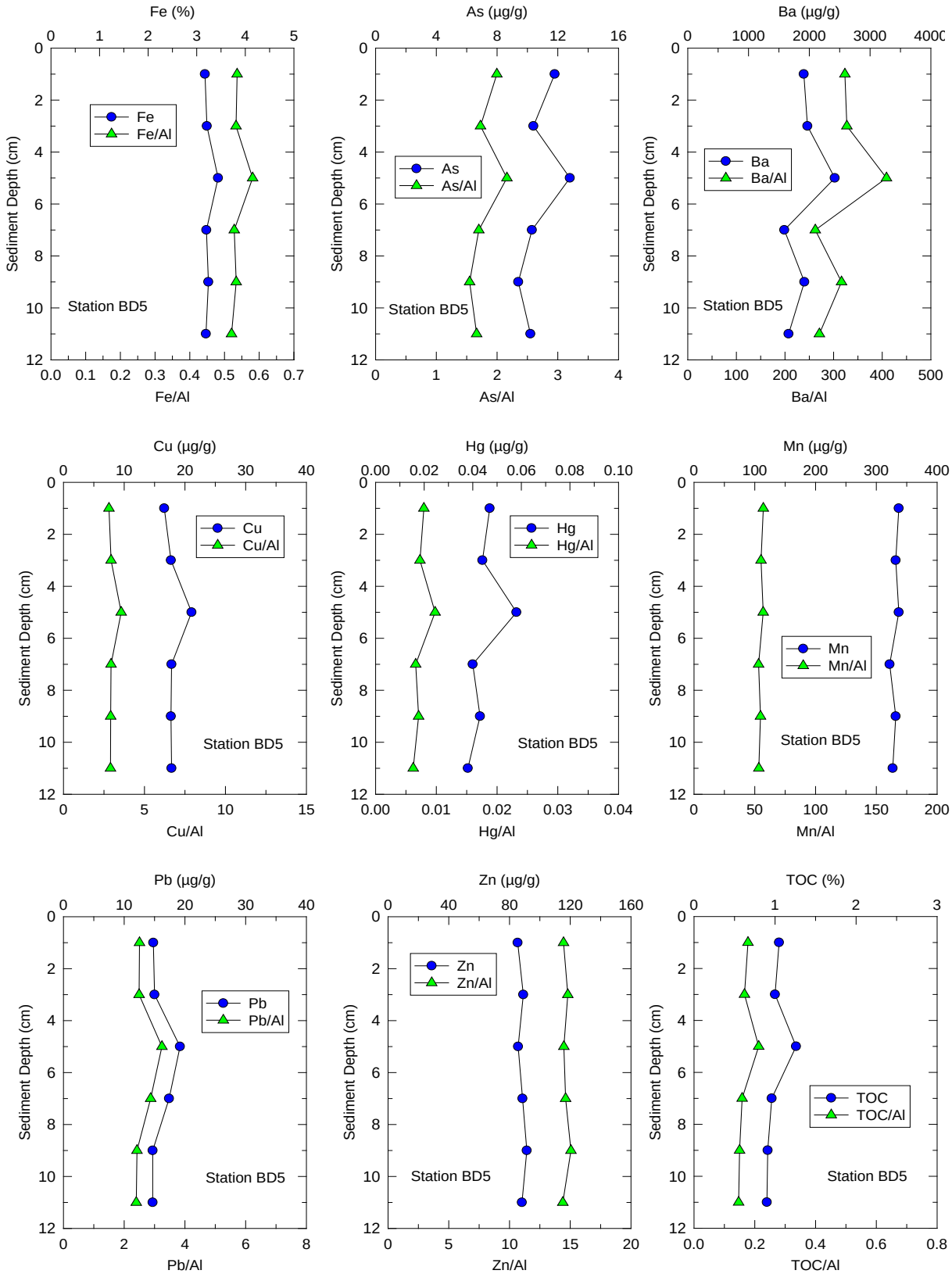


Figure 3-20. Vertical profiles for metals in sediment core from Burger station BD005.

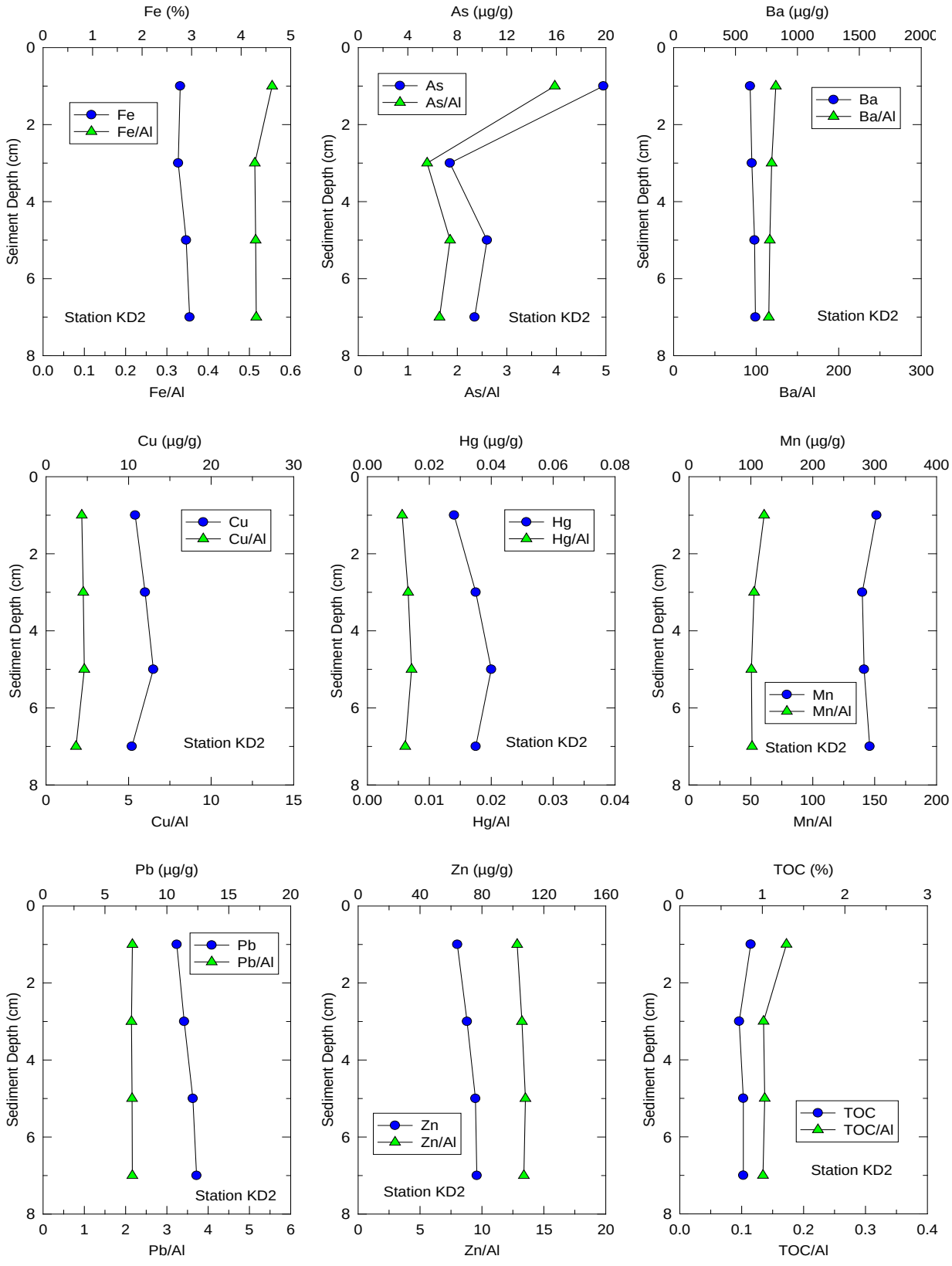


Figure 3-21. Vertical profiles for metals in sediment core from Klondike station KD002.

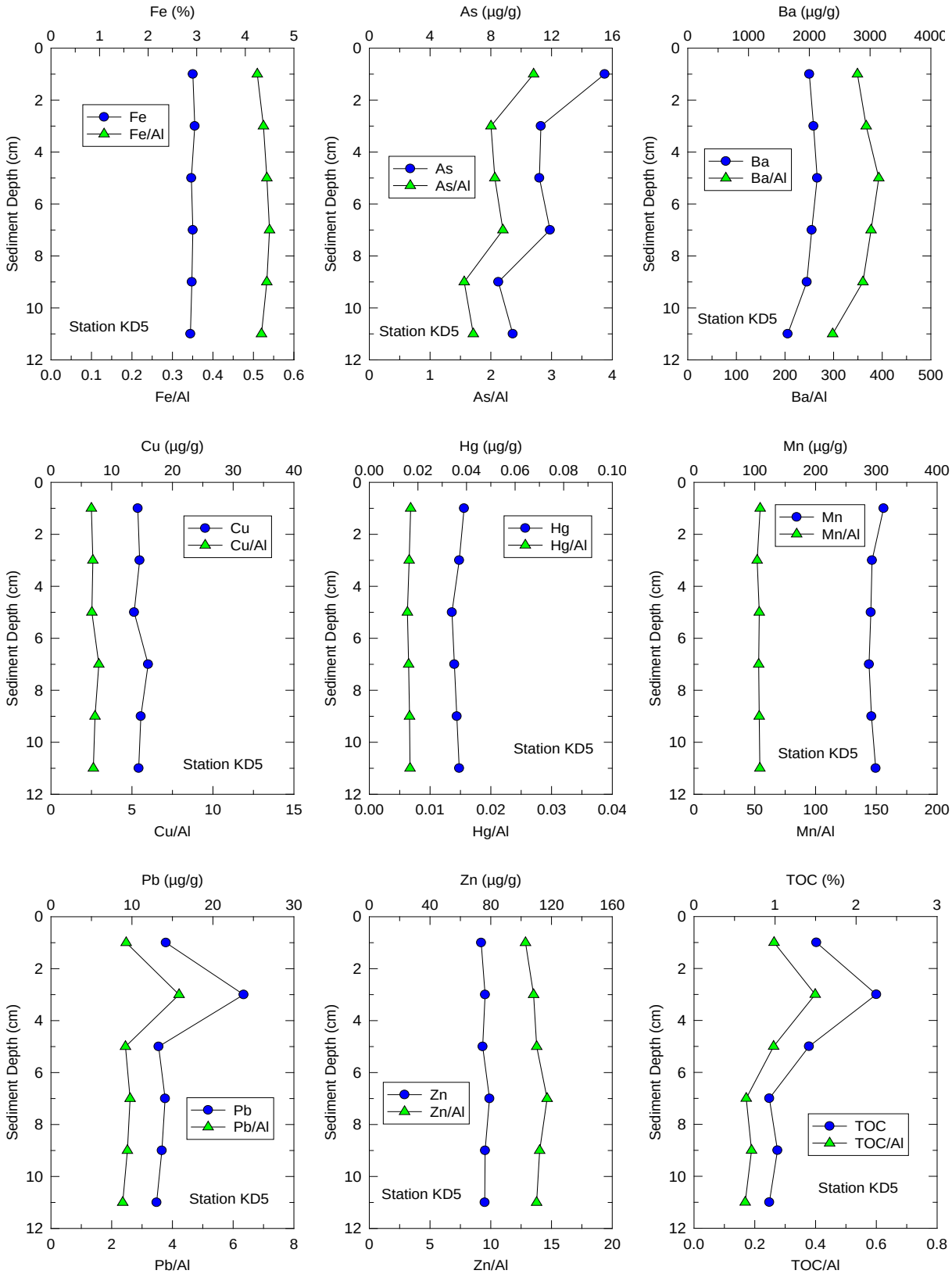


Figure 3-22. Vertical profiles for metals in sediment core from Klondike station KD005.

Comparison of metal concentrations in the biota from the Burger versus Klondike areas is difficult because no amphipods, no *Macoma* clams, only two samples of *Astarte* clams, and two samples of zooplankton were collected from the Klondike area (Table 3-9). Furthermore, the sediment content in the worms was variable and made direct comparisons among samples difficult. Eight or nine crab samples were collected from the two study areas. Concentrations of As, Cd and Hg averaged a rather uniform 2.7 ± 0.2 times higher in the crabs from the Klondike area than the Burger area. Concentrations of the other 9 metals in crabs averaged only about 28% higher in the samples from the Klondike area relative to the Burger area. The enrichment of As, Cd and Hg in the crabs may be due to higher concentrations of these three metals in water and lower trophic level foods in the two areas; however, sufficient data are not available at this time to support that conclusion.

Table 3-9. Mean, standard deviation, minimum (min), and maximum (max) concentrations of metals in soft tissues of five taxa of marine invertebrates collected in the Burger and Klondike survey areas. Concentrations are µg/g dry wt (parts per million).

Summary Parameter	Burger				Klondike			
	Clam (n=17)				Clam (n=1)			
	Mean	SD	Min	Max	Mean	SD	Min	Max
Ag	0.27	0.16	0.026	0.61	0.14			
As	11.5	1.49	9.3	14.7	10.7			
Ba	16.1	8.38	6.59	26.3	37.3			
Cd	28.7	17.9	0.31	61.6	14.0			
Cr	1.44	0.33	0.88	1.83	1.24			
Cu	12.0	5.15	7.7	13.3	10.6			
Fe	1,520	761	833	4,110	949			
Hg	0.06	0.02	0.033	0.107	0.059			
Mn	22.5	9.89	8	46.9	23.2			
Pb	0.79	0.16	0.565	0.858	0.670			
Se	7.51	2.63	2.62	9.64	7.52			
Zn	83.2	8.75	61.6	94.1	73.6			
	Amphipod (n=7)				Amphipod (n=0)			
	Mean	SD	Min	Max	Mean	SD	Min	Max
Ag	0.83	0.21	0.54	1.05				
As	12.8	2.79	8.21	17.1				
Ba	8.25	1.08	7.22	10				
Cd	3.88	0.66	3.25	5.17				
Cr	0.47	0.15	0.31	0.74				
Cu	40.4	5.58	33.5	48.9				
Fe	230	47.0	181	304				
Hg	0.10	0.02	0.063	0.115				
Mn	10.3	1.54	8.65	12.3				
Pb	0.14	0.03	0.096	0.19				
Se	3.65	0.92	2.26	5.35				
Zn	163	28.3	114	197				

Table 3–9. Mean, standard deviation, minimum (min), and maximum (max) concentrations of metals in soft tissues of five taxa of marine invertebrates collected in the Burger and Klondike survey areas. Concentrations are µg/g dry wt (parts per million), continued.

Summary Parameter	Burger				Klondike			
	Crab (n=8)				Crab (n=9)			
	Mean	SD	Min	Max	Mean	SD	Min	Max
Ag	0.714	0.35	0.38	1.41	0.95	0.54	0.19	1.71
As	9.33	1.36	7.95	12.5	24.9	3.4	17.7	29.6
Ba	11.8	1.3	10.6	14.7	12.7	1.8	10.1	15.1
Cd	1.13	0.31	0.74	1.56	3.01	0.66	1.74	3.83
Cr	0.624	0.10	0.48	0.77	0.92	0.36	0.70	1.83
Cu	45.9	15.8	22.6	68.6	51.3	9.8	36.6	68.4
Fe	362	97.5	248	490	443	118	295	638
Hg	0.026	0.007	0.020	0.039	0.066	0.020	0.039	0.090
Mn	25.1	8.1	18.8	42.9	38.5	16.0	18.4	64.5
Pb	0.164	0.046	0.105	0.217	0.194	0.041	0.144	0.272
Se	2.94	0.66	2.12	3.83	3.81	0.72	2.75	4.67
Zn	63.1	4.2	55.5	69.1	68.2	6.9	55.9	78.6
	Worm (n=8)				Worm (n=5)			
	Mean	SD	Min	Max	Mean	SD	Min	Max
Ag	1.81	0.75	0.91	3.29	1.36	0.49	0.75	1.91
As	19.1	3.3	16.1	23.9	23.9	6.0	19.2	32.5
Ba	34.2	5.1	27.3	41.0	42.7	4.4	38.0	48.0
Cd	7.65	2.26	5.17	12.0	7.50	2.53	4.81	11.4
Cr	2.01	0.23	1.67	2.34	3.32	0.44	2.75	3.97
Cu	18.2	2.9	14.4	22.2	17.7	1.4	15.4	19.2
Fe	3,990	698	3,210	5,330	4,484	682	3,780	5,460
Hg	0.211	0.061	0.145	0.340	0.232	0.049	0.175	0.301
Mn	55.8	8.5	38.8	66.8	64.6	7.8	58.9	76.2
Pb	1.90	0.38	1.37	2.48	2.15	0.16	1.91	2.35
Se	4.72	1.00	2.86	6.28	4.39	0.36	3.91	4.78
Zn	72.4	5.3	62.6	78.9	78.2	3.5	72.7	81.3
	Zooplankton (n=5)				Zooplankton (n=2)			
	Mean	SD	Min	Max	Mean	SD	Min	Max
Ag	0.019	0.003	0.016	0.022	0.057	0.004	0.054	0.060
As	1.29	0.18	1.05	1.49	2.22	0.11	2.14	2.30
Ba	7.39	1.53	5.79	9.27	14.6	2.4	12.9	16.3
Cd	0.58	0.10	0.48	0.71	1.01	0.40	0.72	1.29
Cr	0.73	0.11	0.60	0.88	3.19	1.01	2.47	3.90
Cu	3.2	2.0	2.0	6.8	7.8	5.1	4.2	11.4
Fe	850	121	669	979	1,875	587	1,460	2,290
Hg	0.008	0.002	0.005	0.009	-	-	-	-
Mn	16.6	3.1	14.0	22.1	68.8	24.3	51.6	86.0
Pb	0.809	0.157	0.547	0.935	2.67	0.07	2.62	2.72
Se	0.80	0.16	0.52	0.90	1.40	0.27	1.21	1.59
Zn	21.9	5.9	15.7	31.7	86.8	20.1	72.6	101

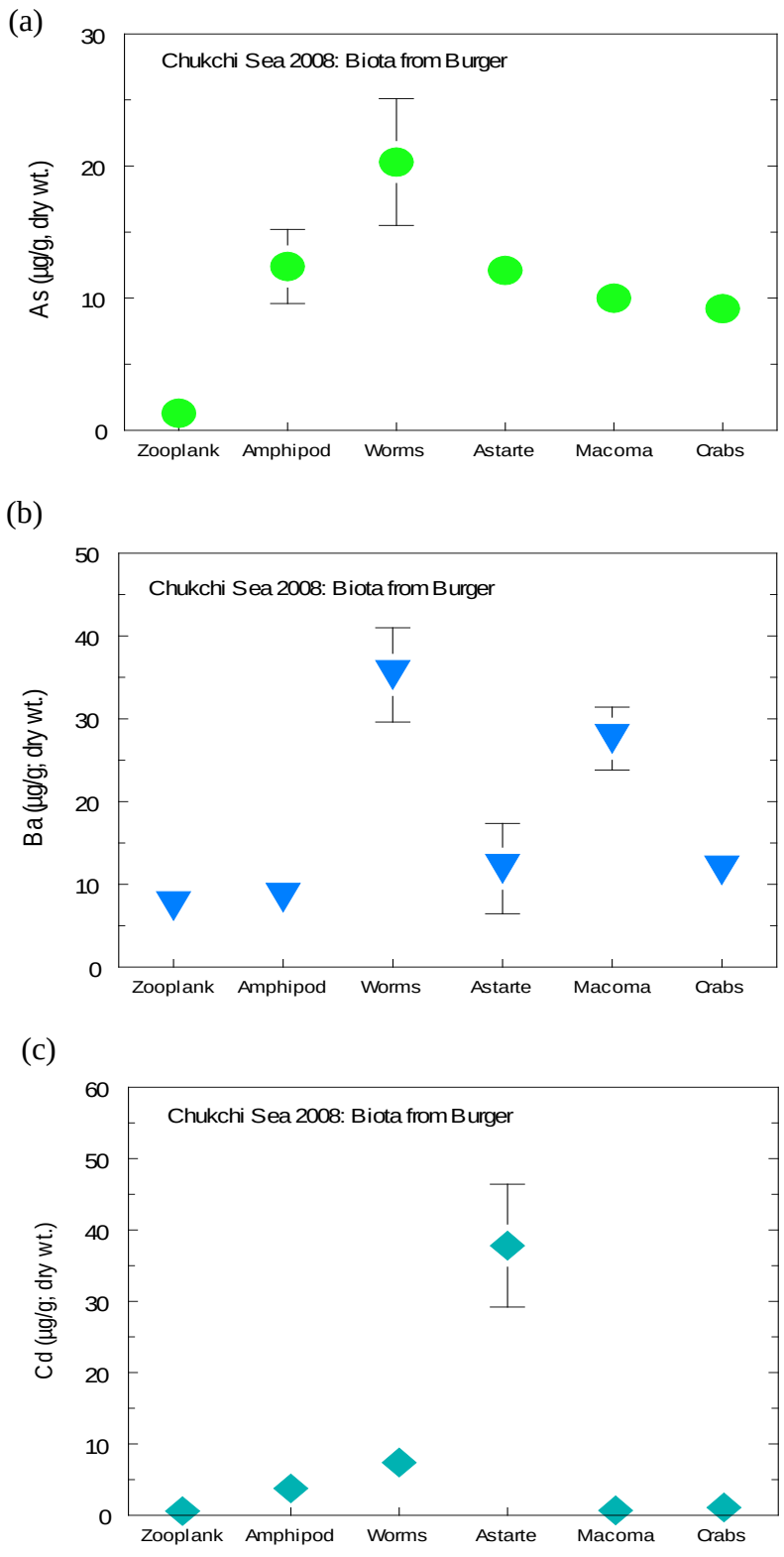


Figure 3-23. Concentrations of (a) As, (b) Ba and (c) Cd in marine invertebrates from the Burger survey area.

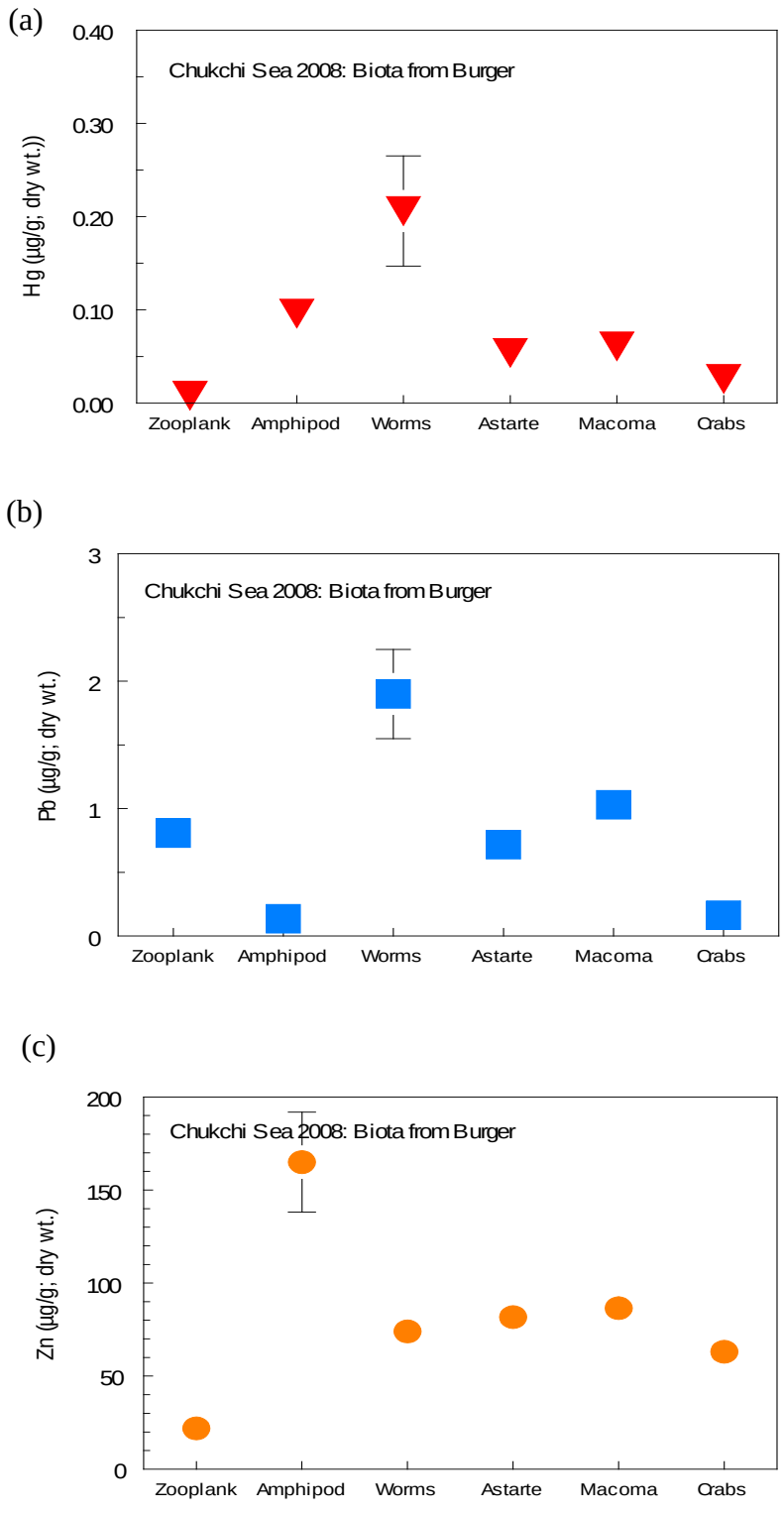


Figure 3-24. Concentrations of (a) Hg, (b) Pb and (c) Zn in marine invertebrates from the Burger survey area.

3.4. Quality Control

This section provides an evaluation of the quality and usability of the environmental data, based on the results for the field and laboratory QC samples collected and analyzed as described in section 2.3.3 and 2.3.4. The results for the hydrocarbon and metals QC samples and measures are presented in Appendix C. Detailed QC narratives describing QC matters have been delivered with the analytical data.

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

3.4.1. Field Quality Control

3.4.1.1. Field Blanks

Field blanks were collected during the survey, but were not analyzed to assess potential sample contamination introduced from surficial sediment sample collection and handling procedures. Field blanks are often a poor surrogate for potential field contamination, and are therefore often only analyzed if contamination is evident in the field data; this was not the case.

3.4.1.2. Replicate Samples

Field replicate samples were collected to assess overall precision and representativeness of the sampling and analytical efforts.

Four sets of field replicate samples were generated during the collection of the sediment samples in the form of triplicate samples collected at sampling stations BF005, BF032, KR019, and KR045. Only the triplicate samples collected from stations BF005 and KR045 were analyzed for chemical parameters. The field replicate results were evaluated to assess analytical precision relative to sample collection procedures and sample matrix.

For the triplicate samples collected at sampling stations BF005 and KR045, the precision criterion of less than 50 percent RSD for sediments was met for all metals, PAH, SHC, and S/T results detected at concentrations greater than the reporting limit. Overall, the field replicate

3.4.2. Hydrocarbon Quality Control Results

The hydrocarbon laboratory quality control measures included recovery of surrogate compounds, evaluation of procedural blanks, laboratory control sample recoveries (matrix spikes), laboratory duplicates and standard reference material analyses (sediment certified for organic target analytes).

The majority of the quality control samples prepared and analyzed along with the hydrocarbon analysis samples met the DQOs and acceptance limits. Minor quality control exceedances included trace level blank contamination, blank and matrix spike recovery exceedances, laboratory duplicate precision exceedances for some analytes, and SRM recovery exceedances. Tables 3-10 and 3-11 summarize the hydrocarbon laboratory QC results for sediments and marine tissue invertebrates, respectively. In addition, the surrogate compound recovery data, a useful measure of overall method performance, are summarized in Table 3-12. No serious data

quality issues were observed that would adversely affect the quality or use of the hydrocarbon data. The analytical data that were generated are of high quality, and can be used with confidence. Discussion and interpretation of the results are provided in the following sections.

Table 3-10. Hydrocarbon QC Result Summary for Sediments.

QC Sample or Measurement Type	Data Quality Objective	Quality Control Result Summary	Impact to Data Quality and Usability
Initial Calibration	%RSD <25% for all compounds (up to 10% of compounds can be >25%, but <35%)	All objectives were met	None
Continuing Calibration	%D <25% for all compounds (up to 10% of compounds can be >25%, but <35%)	Objectives were met for all CCVs with one exception. Indeno(1,2,3-cd)pyrene was under-recovered with a PD of 26.2%	Minor. Results indicate this slight under-recovery has little impact, if any, on the data
Surrogate Recoveries	40 to 120% recovery	Objectives were met for all samples with a few exceptions. Field samples, 08-03-BF007-01SC, 08-03-BD005-01SC24, and 08-03-KD005-01SC810 and 3 QC samples had one low PAH surrogate recovery for each sample.	Minor. The low recovery of d12-benzo(a)pyrene may have little impact on the data.
Procedural Blank	No compound to exceed 5 times the MDL unless sample amount is >10 times blank amount	All objectives were met.	Results for a few samples and few analytes that were within 5 times the blank result were qualified "B" and may be biased high or false positives.
Laboratory Control Sample Recoveries	70 to 130% recovery for spiked compounds	For the SHC analyses, the recovery of n-C9 was low for 2 LCSs. The DQOs were met for the PAH analyses..	Minor. The n-C9 concentrations may be biased low.
Laboratory Duplicate	RPD <30% for all compounds >10 times the MDL	All objectives were met.	None

Table 3–10. Hydrocarbon QC Result Summary for Sediments, continued.

QC Sample or Measurement Type	Data Quality Objective	Quality Control Result Summary	Impact to Data Quality and Usability
Matrix Spike Recoveries	70 to 130% recovery for spiked compounds	PAH: recoveries met the DQO with a couple exceptions. The recovery of benzo(b)fluoranthene, benzo(e)pyrene, and dibenzo(a,h)anthracene in one MS slightly exceeded the recovery DQO. SHC: recovery of n-C9 was low in all MS samples	Minor. The n-C9 concentration may be biased low.
Sediment SRM (1944)	Measured values must be within 30% of the true value on average for all compounds, not to exceed 35% for more than 30% of the compounds	All objectives were met.	None
Oil Reference Standard (North Slope Crude)	RPD< 30% from control values for 90% of the analytes.	All objectives were met.	None

Table 3-11. Hydrocarbon Quality Control Result Summary for Tissues.

QC Sample or Measurement Type	Data Quality Objective	Quality Control Result Summary	Impact to Data Quality and Usability
Initial Calibration	%RSD <25% for all compounds (up to 10% of compounds can be >25%, but <35%)	All objectives were met	None
Continuing Calibration	%D <25% for all compounds (up to 10% of compounds can be >25%, but <35%)	All objectives were met	None
Surrogate Recoveries	40 to 120% recovery	Objectives were met for all samples except one. Low recoveries were measured for sample 08-03-BR098-01-BC5.	The results for sample 08-03-BR098-01-BC5 may be less reliable due to low recoveries; surrogate correction of the data compensates.
Procedural Blank	No compound to exceed 5 times the MDL unless sample amount is >10 times blank amount	The PB for two batches had PAH detected and at slightly above the DQO. Where there was enough remaining material, the samples were re-extracted and reanalyzed for PAH.	Minor. Results for a few samples and analytes and within 5 times the blank result were qualified “B” and may be biased high or false positives

Table 3–11. Hydrocarbon Quality Control Result Summary for Tissues, continued.

QC Sample or Measurement Type	Data Quality Objective	Quality Control Result Summary	Impact to Data Quality and Usability
Laboratory Control Sample Recoveries	70 to 130% recovery for spiked compounds	For the SHC analyses, the recovery of n-C9 was low in all LCSs, and the recovery of n-C10 was low in two LCS	Minor. The n-C9 and n-C10 concentrations may be biased low.
Laboratory Duplicate	RPD <30% for all compounds >10 times the MDL	All objectives were met.	None
Matrix Spike Recoveries	70 to 130% recovery for spiked compounds	PAH: recoveries met the DQO with a couple exceptions. The recovery of anthracene, benzo(a)anthracene, and indeno(1,2,3-cd)pyrene in one MS slightly exceeded the upper recovery DQO. SHC: recovery of n-C9 was low in MS/MSD samples, ranging from 19 to 58%, and the recovery of n-C10 was low in several MS/MSD samples ranging from 53 % to 69%.	Minor. The n-C9 and n-C10 concentrations may be biased low.
Tissue SRM (2977)	Measured values must be within 30% of the true value on average for all compounds, not to exceed 35% of true value for more than 30% of the compounds	All objectives were met.	None
Oil Reference Standard (North Slope Crude)	RPD< 30% from control values for 90% of the analytes.	All objectives were met.	None

Table 3-12. Summary of Surrogate Recovery Results from the Organic Compound Analyses.

Matrix	Total SIS data points (including QC samples)	# Exceedances
Sediment		
PAH	428	6
Biomarker	107	0
SHC	206	0
Clam/Amphipod/Crab/Worm/Zooplankton		
PAH	552	4
Biomarker	119	1
SHC	228	2

3.4.2.1. Surrogate Results

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

The surrogate recovery results were excellent; more than 99% of the surrogate recovery data points for both sediment and tissue samples met the data quality objectives (Table 3-12), demonstrating that the analyses were widely under control and of high quality. For the SHC analyses, all of the environmental and QC sample surrogate recoveries for both sediments and tissue samples were within the recovery acceptance limits, with one exception. Tissue sample 08-03-BR098-01-BC5 had low recoveries for both SHC surrogates. During the first extraction of sample processing, the extract spilled. The results for this sample are considered to be estimated values.

For the PAH analyses all of the QC sample surrogate recoveries were within acceptable limits, with a few exceptions. Three sediment SRM samples had low d12-benzo(a)pyrene recoveries. Sediment samples 08-03-BF007-01SC, 08-03-BD005-01SC24, and 08-03-KD005-01SC810 had one low surrogate recovery for each sample. Tissue sample 08-03-BR098-01-BC5 had low recoveries for three of the four PAH surrogates, ranging from 0 to 23%. The results for this sample are considered to be estimated values.

For the biomarker analyses, all of the environmental and QC sample surrogate recoveries for both sediment and tissue were within acceptable limits, with one exception. Tissue sample 08-03-BR098-01-BC5 had low recovery for 5b(H)cholane. The results for this sample are considered to be estimated values.

3.4.2.2. Procedural Blanks

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

Although no individual SHC target compounds were detected in the PBs, TPH was detectable in one tissue PB at trace levels. Trace concentrations of select PAH were detected in the sediment and tissue PBs. Generally the concentrations were less than the MDL. The PB for two tissue batches had more target PAH compounds detected and at slightly higher concentrations. Where there was enough remaining material, the samples were re-extracted and reanalyzed for PAH only. Naphthalene was identified at trace levels in all the blanks and is a common contaminant associated with sample preparation. No biomarker compounds were detected in the PBs. Environmental sample results that were within 5 times the associated PB concentration were qualified with a “B” to indicate that the compound was also present in the blank. Overall, the PB results met the DQOs and do not indicate concentrations of laboratory contamination would adversely affect the quality or usability of the associated sample data.

3.4.2.3. Laboratory Control Sample Recoveries

A laboratory control sample (LCS) was prepared with each sample preparation batch by spiking a blank sample matrix (sodium sulfate for sediments and Tilapia for tissues) with known concentrations of a subset of the target compounds. Laboratory control samples are used to assess the accuracy of the sample preparation and analysis procedures independent of sample matrix effects. The LCS was spiked with PAH and SHC matrix spike compounds. The LCS was not spiked with biomarker compounds.

For the SHC analyses, the recovery of n-C9 was low in all LCSs, ranging from 45 to 65%. The n-C9 concentrations may be biased low but, overall, this minor data quality issue does not adversely affect the quality or usability of the associated sample data since these individual alkanes contribute only a small amount to the petroleum hydrocarbon concentration.

For the PAH analyses, the LCS recoveries were within the acceptance objectives, with one exception where the PAH recoveries ranged from 114 to 165%. The exceedances appear to be isolated to the LCS, since accuracy was demonstrated in the MS/MSD and SRM samples. These LCS exceedances do not adversely affect the quality or usability of the associated sample data.

3.4.2.4. Matrix Spike Sample Recoveries

A matrix spike and spike duplicate sample (MS/MSD) was prepared with each batch of samples by spiking a separate sample with known concentrations of a subset of the target compounds. MS/MSD samples are used to assess the accuracy and precision of the sample preparation and analysis procedures. The MS/MSD was spiked with PAH and SHC matrix spike compounds. The MS/MSD was not spiked with biomarker compounds.

For the SHC analyses, the recovery of n-C9 was low in all MS/MSD samples ranging from 19 to 69%. The n-C9 concentration may be biased low, but overall, this data quality issue does not adversely affect the quality or usability of the associated sample data since these individual alkanes contribute only a small amount to the petroleum hydrocarbon concentration.

For the PAH analyses, two MS samples (one sediment and one tissue) had recoveries exceeding the upper recovery criterion. The MS recovery exceedance does not adversely affect the quality or usability of the associated sample data, since the accuracy was demonstrated in the LCS and SRM. The duplicate precision was less than 30 percent relative percent difference (RPD), thus meeting the DQO.

3.4.2.5. Laboratory Duplicates

Laboratory duplicates were prepared with each batch by extracting a second aliquot of an environmental sample. Laboratory duplicates were evaluated to assess analytical precision related to laboratory performance.

For PAH, SHC, and biomarker analyses, good laboratory duplicate precision was noted, with relative percent difference (RPD) in the results was less than 30 percent for most compounds detected at concentration above the MDL and for the majority of the compounds detected at concentrations below the MDL. Only one sample, 08-03-KF015-01-SC had RPDs greater than

30 percent for a few compounds (C1-Fluoranthenes/Pyrenes, C2-Fluoranthenes/Pyrenes, and 30-Homohopane -22R). The variability noted for this laboratory duplicate pair may be related to sample heterogeneity.

The mean RPDs for each laboratory duplicate pair were less than 30 percent. The laboratory duplicate precision criterion does not apply to compounds detected below the MDL (or less than 10 times the MDL) due to increased variability at low concentrations.

3.4.2.6. Standard Reference Materials

A standard reference material (SRM) was prepared and analyzed with each sample preparation batch to assess the accuracy of the analytical method based on measured concentrations compared to certified concentrations. Each SRM was analyzed for PAH only. SHC and biomarker analyses were not performed on the SRMs since there are no certified values for these compounds. The SRMs analyzed met all the DQOs.

The percent difference (PD) of the measured values versus the certified values for the PAH compounds were within the acceptance criteria of 30 percent on average per SRM and 35 percent for the individual compounds.

3.4.3. Metals Quality Control Results

3.4.3.1. Sediments

All Data Quality Objectives for metals in sediments (as listed in Table 2-14) were met for results from this study. Quality assurance results for certified reference standards, percent spike recovery and precision are listed in Table 3-13. All metal and TOC values for the reference materials were within the intervals specified by U.S. NIST or the NRC of Canada. Percent spike recoveries averaged between 91 and 102% for all metals except Hg (85%) and Se (82%). The lower values are within the DQOs; however, the final calculated values for Hg and Se were corrected to 100% recovery. Analytical precision (as % relative standard deviation = [(standard deviation)/(mean)] x 100%) averaged between 0.4% for Al to 4.1% for Hg. The method detection limits (MDLs) were 5 to >1000 times lower than the value for the lowest sample analyzed (Table 3-6). Overall, the checks on data quality support a high quality data set for metals and TOC in these sediments from the 2008 survey of the Chukchi Sea.

3.4.3.2. Marine Invertebrate Tissues

All Data Quality Objectives for metals in marine invertebrate tissues (as listed in Table 2-14) were met for results from this study with the exception of the spike recovery for Hg as discussed below. Quality assurance results for certified reference standards, percent spike recovery and precision are listed in Table 3-14. All metal values for the SRMs were within the intervals specified by U.S. NIST. Percent spike recoveries averaged between 91 and 107% for all metals except Hg (64%) due to inhibition of the reduction of Hg^{2+} to Hg^{0} (gas) during analysis, most likely due to organic matter in the sediment solutions. Therefore, each sample was individually spiked and the Hg concentration was corrected based on the spike recovery. This correction is common and Hg values for the SRM were within the range of certified values (Table 3-14).

Analytical precision (as % relative standard deviation = [(standard deviation)/(mean)] x 100%) averaged between 1.3% for Zn to and 3.8% for Se. The MDLs were 3 to >300 times lower than the value for the lowest marine invertebrate sample analyzed (Table 3-9). Overall, the checks on data quality support a high quality data set for metals in these biota samples from the 2008 survey of the Chukchi Sea.

Table 3-13. Results for quality control for metals and total organic carbon (TOC) in sediments. Standard Reference Material 2709 from the U.S. National Institute for Standards and Technology was used for all metals except Hg. Certified Reference Material MESS-3 from the National Research Council of Canada was used for Hg and TOC.

Metal (units)	Results for Reference Materials (n = 6)	Certified Values for Reference Materials		MDL	Lowest Sample Value	% Spike Recovery (n = 6)	Precision (% RSD) (n = 4 sets)
	(This study)			(This study)			
Ag (µg/g)	0.41 ± 0.02	0.41 ± 0.03		0.003	0.09	93	1.4
Al (%)	7.50 ± 0.04	7.50 ± 0.06		0.01	1.01	100	0.4
As (µg/g)	17.2 ± 0.02	17.7 ± 0.8		0.02	7.9	100	2.2
Ba (µg/g)	968 ± 4	968 ± 40		0.01	436	99	1.5
Cd (µg/g)	0.37 ± 0.004	0.38 ± 0.01		0.001	0.05	91	2.2
Cr (µg/g)	132 ± 2	130 ± 4		1.6	9.7	102	1.5
Cu (µg/g)	34.6 ± 0.4	34.6 ± 0.7		0.5	2.5	96	1.8
Fe (%)	3.51 ± 0.06	3.50 ± 0.11		0.01	0.50	101	0.8
Hg (µg/g)	0.092 ± 0.004	0.091 ± 0.009		0.001	0.006	85	4.1
Mn (µg/g)	539 ± 4	538 ± 17		2	78	97	0.8
Pb (µg/g)	19.0 ± 0.2	18.9 ± 0.5		0.002	6.4	97	3.1
Se (µg/g)	1.51 ± 0.02	1.57 ± 0.08		0.02	0.18	82	3.5
Zn (µg/g)	105 ± 1	106 ± 3		0.5	10.7	98	1.2
TOC (%)	2.03 ± 0.02	2*		0.03	0.07	-	2.4

*Not a certified value.

MDL = Method Detection Limits and RSD = relative standard deviation = [(standard deviation)/(mean)] x 100%.

For spike recoveries that were <90% (Hg and Se), the final value was corrected to 100% spike recovery.

Table 3-14. Results for quality assurance for metals in biota. Standard Reference Material 2976 (Mussel Tissue) from the U.S. National Institute for Standards and Technology (NIST) was used for all metals except Ag and Ba. SRM 1566b (Oyster Tissue) the NIST was used for Ag and Ba.

Metal (units)	Results for Reference Material (n = 3)	Certified Values for Reference Material		MDL	Lowest Sample Value	% Spike Recovery (n = 6)	Precision (% RSD) (n = 5 sets)
	(This study)			(This study)			
Ag (µg/g)	0.669 ± 0.001	0.666 ± 0.009		0.001	0.026	99	2.2
As (µg/g)	13.9 ± 0.2	13.3 ± 1.8		0.012	1.0	107	1.8
Ba (µg/g)	8.5 ± 0.1	8.6 ± 0.3		0.006	5.8	100	2.4
Cd (µg/g)	0.79 ± 0.02	0.82 ± 0.16		0.001	0.31	103	1.2
Cr (µg/g)	0.50 ± 0.08	0.50 ± 0.16		0.003	0.31	91	3.4
Cu (µg/g)	4.0 ± 0.1	4.0 ± 0.3		0.7	2.0	96	2.9
Fe (µg/g)	171 ± 3	171 ± 5		2.5	181	104	1.9
Hg (µg/g)	0.063 ± 0.001	0.061 ± 0.004		0.001	0.005	64	2.5
Mn (µg/g)	33.5 ± 0.7	33 ± 2		1.1	8.0	94	2.3
Pb (µg/g)	1.12 ± 0.06	1.19 ± 0.18		0.001	0.096	96	1.4
Se (µg/g)	1.85 ± 0.10	1.80 ± 0.15		0.02	0.52	106	3.8
Zn (µg/g)	143 ± 5	137 ± 13		0.4	15.7	102	1.3

MDL = Method Detection Limits and RSD = relative standard deviation = [(standard deviation)/(mean)] x 100%.
For spike recoveries that were <90% (Hg and Se), the final value was corrected to 100% spike recovery.

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4.0 DISCUSSION

4.1. Sediment Grain Size and Total Organic Carbon (TOC)

Overall, the surface and subsurface sediments from the 2008 Chukchi Sea study averaged ~50% sand and ~50% mud (Table 4-1). Surface sediments in the Burger area were slightly finer grained with an average of ~53% mud relative to ~40% mud in sediments from the Klondike area (Table 3-3). Naidu et al. (1997) reported an average of 52% mud, 34% sand and 14% gravel from a nearby area of the Chukchi Sea with more stations located closer to the coast (Table 4-1). Sediments 10 to 20 km offshore between Icy Cape and Point Barrow contain 50 to 100% sand, with small admixtures of gravel (Luepke and Escowitz, 1989). Considerable variability in grain size was observed in both the present study and the earlier study by Naidu et al. (1997) as shown in both the ranges and standard deviations in Table 4-1. For example, gravel content ranged from 0% to ~60% and mud content ranged from <10% to >80% in both studies.

Gravel content was >10% at 4 of 32 stations in the Burger area and 5 of 31 stations in the Klondike area (Figure 4-1). A few of the sites with higher gravel content in both areas were grouped in one portion of each block (Figure 4-1). A typical mode of introducing gravel to offshore areas in the Arctic is by ice rafting (Eicken et al., 2005).

Table 4-1. Means, standard deviations (SD), maximums (Max) and minimums (Min) for grain size and total organic carbon in all samples from this 2008 survey in the Chukchi Sea and from a previous study in the same area by Naidu et al. (1997).

Statistic	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	Silt + Clay (%)	TOC (%)
This Study						
Mean (n = 76)	6	46	31	17	48	0.88
SD	11	15	12	7	18	0.33
Max	61	92	64	36	86	2.25
Min	0	14	4	0	8	0.12
Naidu et al. (1997)						
Mean (n = 31)	14	34	33	19	52	0.72
SD	20	27	23	15	34	0.38
Max	62	90	91	54	100	1.57
Min	0	0	3	0	4	0.12

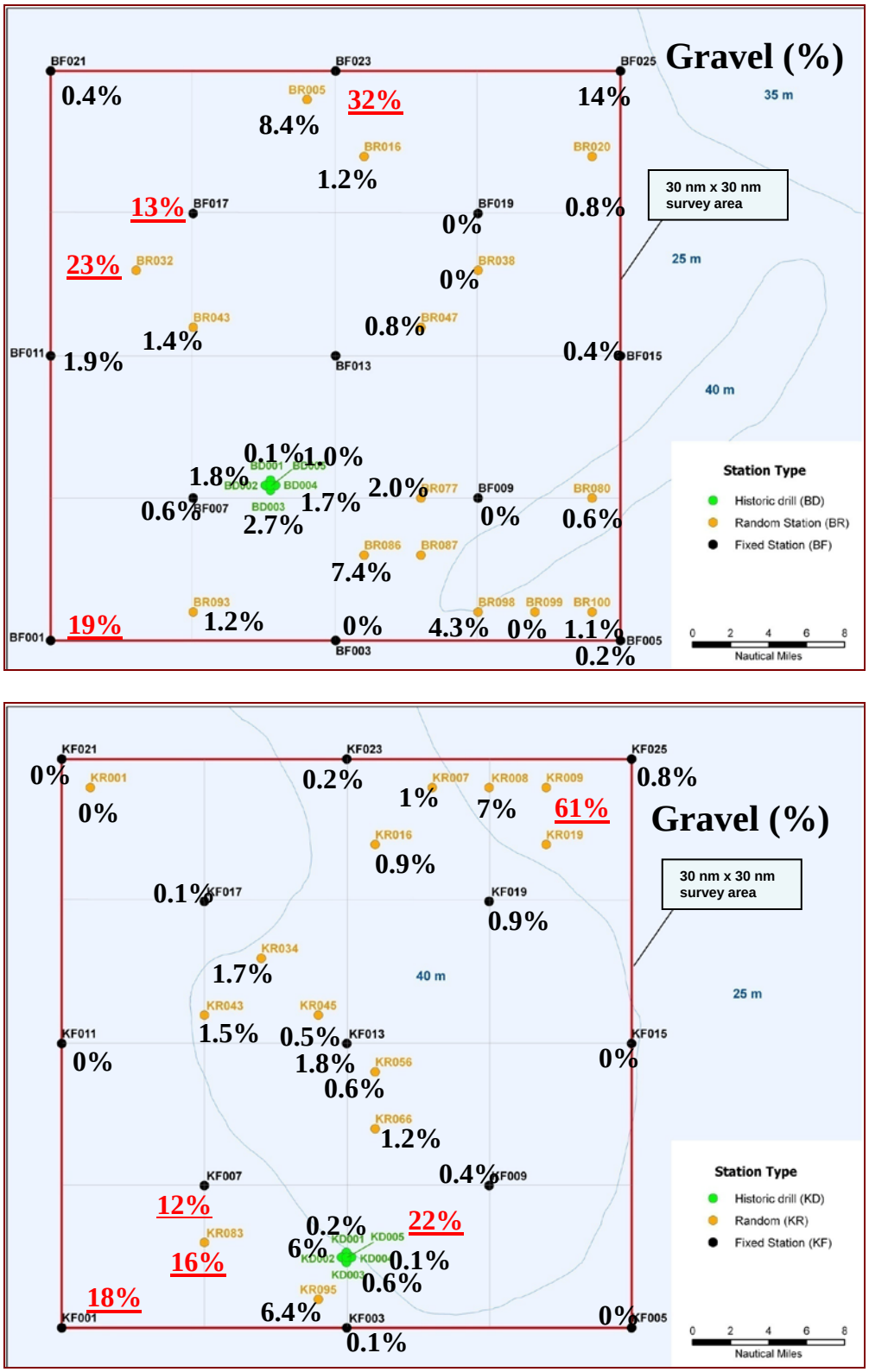


Figure 4-1. Maps showing stations in Burger (top) and Klondike (bottom) areas with concentrations of gravel as % dry weight.

(Numbers in red and underlined identify samples that contained≥10% gravel.)

A sand content ≥60% was found at only 2 of 36 stations in the Burger area, but at 15 of 33 stations in the Klondike area (Figure 4-2). The two stations with ≥60% sand in the Burger area were located in the southeastern corner of the study area. In contrast, sand content ≥60% was found in stations throughout the Klondike study area. Areas with such abundant sand can be created by a lack of recent deposition of terrestrial clays, transport of finer-grained material away from an area by bottom currents or ice rafting.

The overall range of TOC values for all sediments from the Burger and Klondike survey areas was 0.12 to 2.25% (Table 4-1), with a lower average of 0.73 % in surface sediments from the Klondike area versus 0.95% for surface sediments from the Burger area. These trends for TOC in the present study are similar to those reported by Naidu et al. (1997). Trefry et al. (2003) reported average TOC values of 0.86% for the coastal Beaufort Sea and Rember and Trefry (2005) reported average TOC values of 0.48% and 0.94% for the northern and southern portions of the Shelikof Strait, Alaska.

The main sources of sediments in the eastern Chukchi Sea include water currents from the North Pacific/Bering Sea that carry suspended sediments and nutrients, mainly from the Yukon River outflow through the Bering Strait into the Chukchi Sea (Chen et al., 2006; Ortiz et al., 2009), Anadyr water from the Russian Chukchi Sea carrying high suspended sediment loads from river runoff and coastal erosion (Stein, 2008; Levitan and Lavrushin, 2009), and the Beaufort Sea gyre that carries suspended sediments from river runoff, particularly from the Mackenzie and Colville Rivers, and coastal erosion along the Canadian and Alaskan Beaufort Sea coast (Chen et al., 2006; Trefry et al., 2009).

4.2. Hydrocarbons

4.2.1. Concentrations, Spatial Distribution, and Comparison with Other Investigations

4.2.1.1. Sediments

There is little variability in the hydrocarbon concentrations and distributions throughout the Burger and Klondike survey areas, with the exception of the historic Klondike and Burger drill sites (Figures 3-4, 3-5, and 3-7). The drill site surface and subsurface sediments contain higher concentrations of all hydrocarbon types, particularly TPAH and total S/T, than the fixed site and random site sediments (Table 3-4, Figure 4-3). The center stations at the historic drill sites (KD005 and BD005) have the highest hydrocarbon concentrations compared to the other samples, and provide evidence of the former drilling activities (i.e., traces of petrogenic hydrocarbons, probably from organic-rich geologic strata penetrated by the drill or from oil from the source rock in the drill cuttings).

TPAH and total S/T concentrations and petro/pyro PAH concentration ratios in the sediment core from the historic drill site at Klondike (KD005), but not from the historic drill site at Buger (BD005) are significantly higher at the surface and decrease with depth in the sediments (Figure 4-4), suggesting that the hydrocarbons were deposited relatively recently or that they are in refractory forms, resistant to dissolution or biodegradation Total PAH concentrations in core samples from BD005 and KD005 range from 470 to 650 µg/kg and 636 to 3,082 µg/kg,

respectively, with the highest concentration in the surface (0 to -2 cm) samples. The petro:pyro PAH ratio is elevated only in near-surface sediments in the core from KD005 (Figure 4-4), indicating that the excess PAH in surface sediments are primarily from a petrogenic source (i.e., petroleum, peat, oil-rich shale (kerogen)).

The same pattern is evident for Ba, which, as insoluble barite, is the most abundant solid in most drilling muds and may accumulate to high concentrations in sediments at a drill site (Neff, 2005, 2010). Highest concentrations of Ba in the sediment core from KD005 are in the upper 6 cm (~ 2,000 µg/g), and concentrations decreased slightly with depth to 1,650 µg/g at -12 cm. Barium concentrations at all levels in the core are four- to five-fold higher than concentrations in surface sediments from fixed and random stations in the Burger and Klondike survey areas (Table 3-7). The higher concentrations of TPAH and total S/T, and higher petro:pyro PAH ratio in sediments from KD005 than from BD005, may be related to the fact that drilling in 1989 discovered crude oil at Klondike and gas and condensate at Burger. PAH from low molecular weight condensate would be expected to be less persistent than those from higher molecular weight crude oil, resulting in a more rapid decline in PAH concentration.

The TPAH concentration in the core from KD002, a short distance from the drill site, does not vary much with depth and increases from 265 µg/kg at the surface to only 377 µg/kg at -8 cm (the bottom of the core). Thus, any hydrocarbons persisting in sediments after drilling are restricted to a small area near the drill sites.

TPH and ∑SHC concentrations in surface sediments from fixed and random background stations show a high degree of variability, whereas, the PAH and S/T concentrations and distributions for the fixed and random background sediments are similar (Table 3-4). As noted earlier, with the exception of a few historic drill site sediments, the overall concentrations of all the hydrocarbon parameters measured in this study are well within the range of the background concentrations reported by other studies in Alaskan coastal and shelf sediments (Table 4-2).

The hydrocarbon concentrations detected in sediments in the Chukchi Sea study area were compared to those in Alaskan coastal shelf waters in the Beaufort Sea, Cook Inlet, Prince William Sound, and the Shelikof Strait. Overall, the levels of hydrocarbons measured in Chukchi Sea study area sediments are within the range of values reported from previous studies of other Alaskan areas (Table 4-2). For example, the average TPAH concentrations for the Chukchi Sea study area sediments was 360 µg/kg, on a par with the TPAH concentrations in sediments from the ANIMIDA and cANIMIDA studies in the Beaufort Sea (390 to 540 µg/kg). Total PHC and Total S/T concentrations among the available studies are also comparable, with the Chukchi Sea study area sediment concentrations falling between the low and high values (although it should be noted that the total PHC concentrations for the Prince William Sound, Cook Inlet and Shelikof Strait Sediment studies included aromatic hydrocarbons in addition to the saturated hydrocarbons).

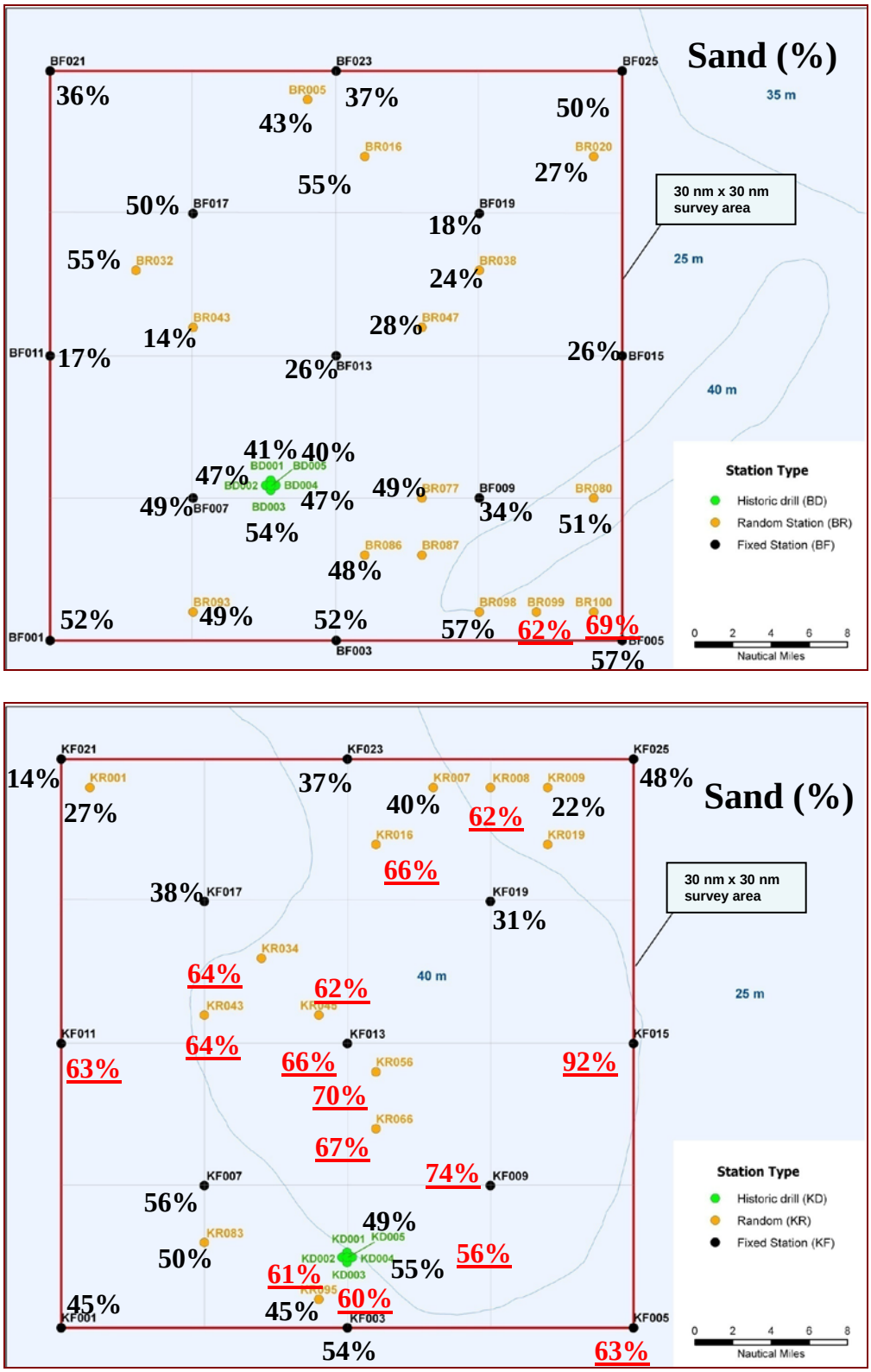
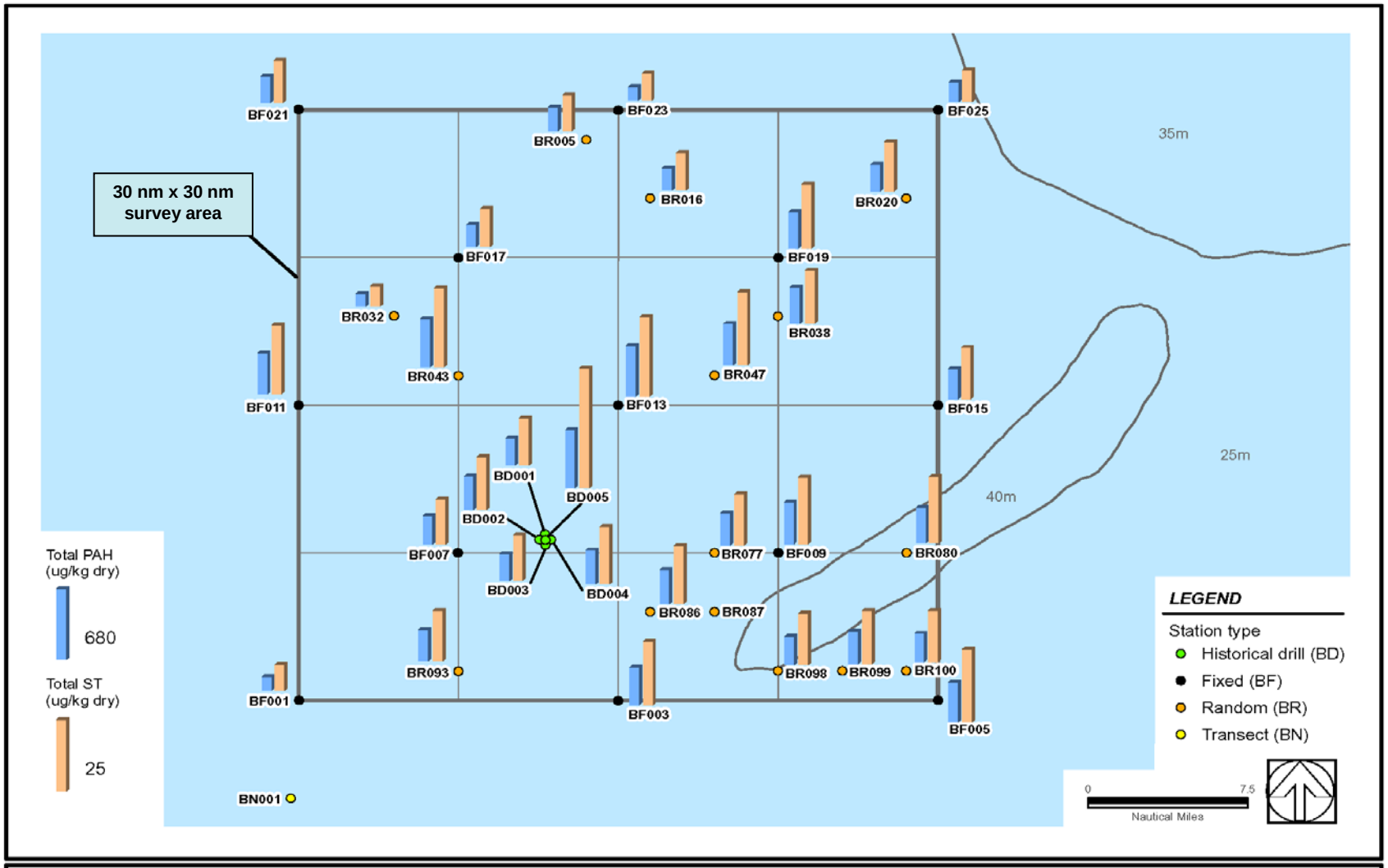


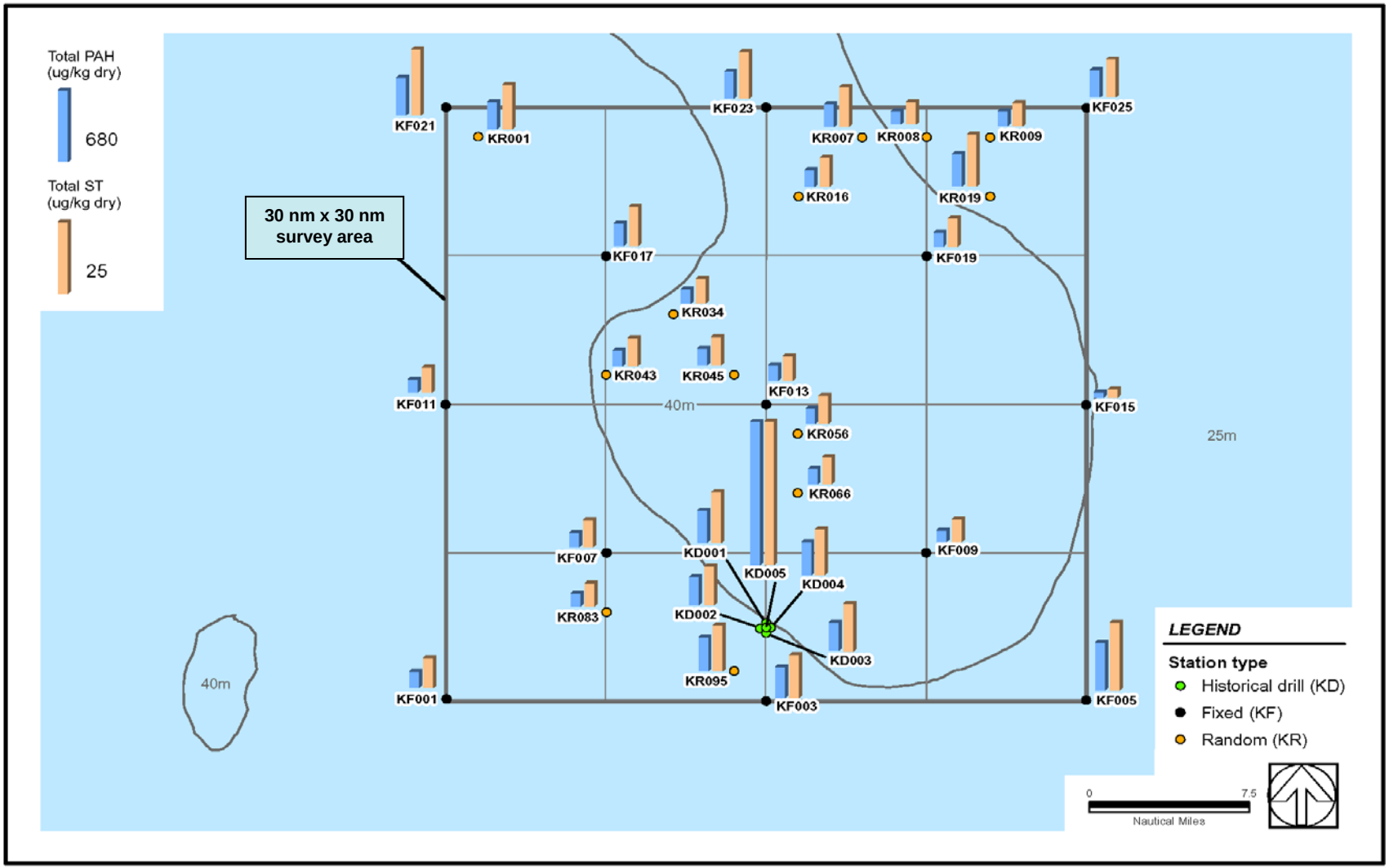
Figure 4-2. Map showing stations in Burger and Klondike areas with concentrations of sand as % dry weight. Numbers in red and underlined identify samples that contained ≥60% sand.



Total PAH and Total S/T concentrtions in Burger area sediments.

0802671 | December 29, 2008 | W:\0802673_Chukchi\GIS\projects\burger stations - no seep - w TPAH ST.mxd

Figure 4-3. Map of the Burger and Klondike areas showing station locations and concentrations of TPAH and total S/T in surface and subsurface sediments. Sediment cores were only collected at historic drill site stations, BD005, KD002, and KD005.

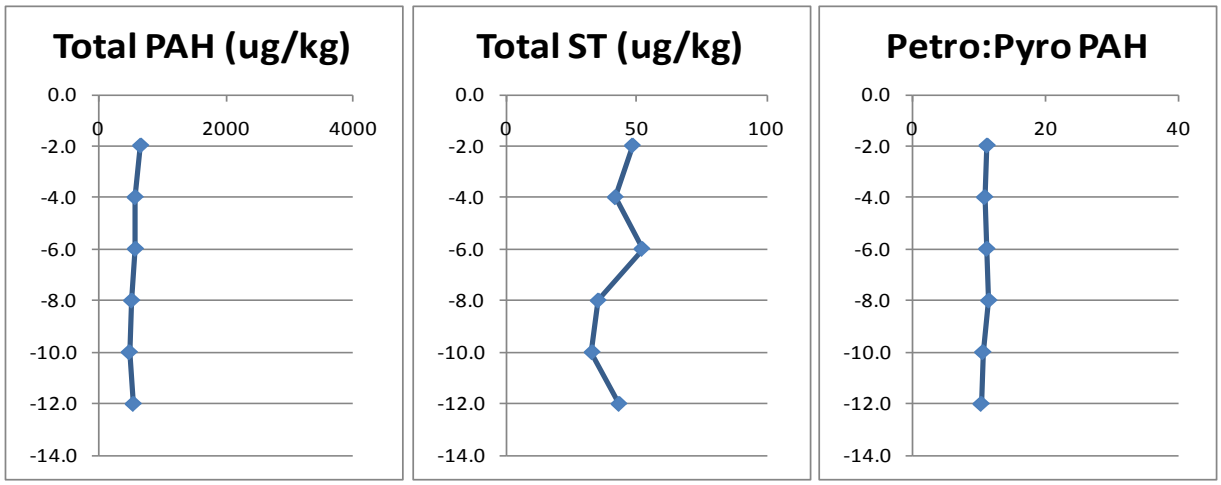


Total PAH and Total S/T concentrations in Klondike area sediments.

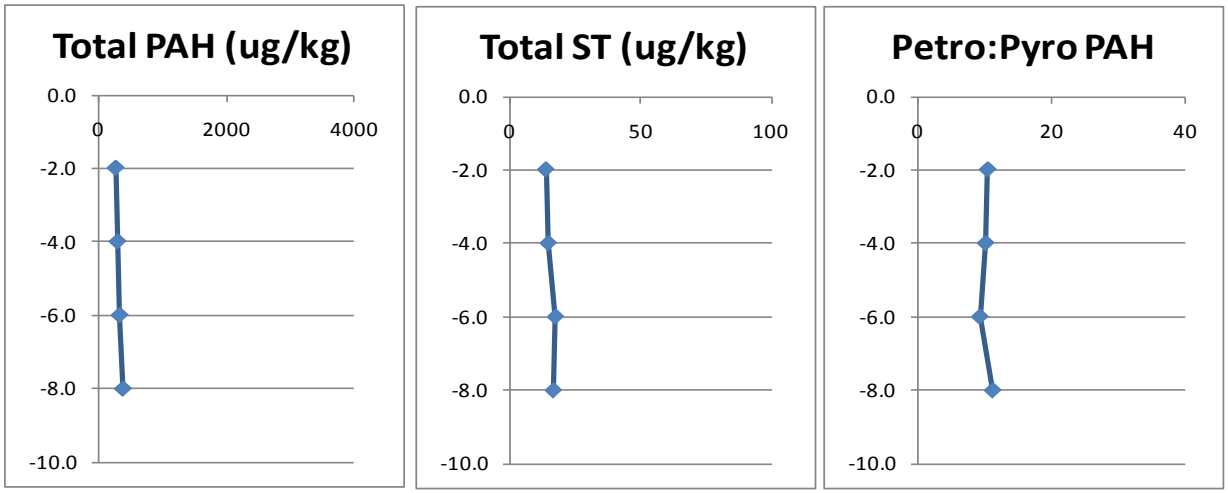
0802671 | December 29, 2008 | W:\0802673_Chukchi\GIS\projects\klondike stations - no seep - w TPAH ST.mxd

Figure 4–3. Map of the Burger and Klondike areas showing station locations and concentrations of TPAH and total S/T in surface and subsurface sediments. Sediment cores were only collected at historic drill site stations, BD005, KD002, and KD005, continued.

BD005 Sediment Core



KD002 Sediment Core



KD005 Sediment Core

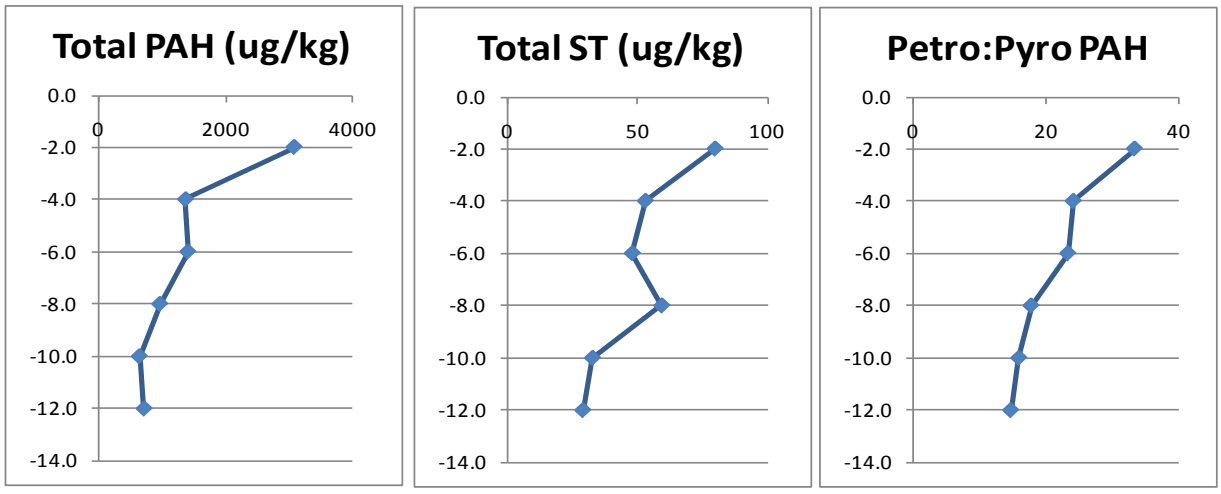


Figure 4-4. Vertical profiles of TPAH, total S/T, and petro:pyro PAH ratios in sediment cores from historic drill sites, BD005 and KD005, and from nearby KD002.

Table 4-2. Average TPAH, total PHC (similar to TPH) and total S/T in Sediments from Chukchi Study Area, ANIMIDA Study Area (Beaufort Sea), Prince William Sound, Cook Inlet, and Shelikof Strait Sediments

	Total PAH (µg/kg)	Total PHC[h] (µg/kg)	Total S/T (µg/kg)
Concentrations in Alaska Marine Sediments[a]	160 – 2,400	470 – 38,000	NA
Concentrations in Cook Inlet and Shelikof Strait Sediments[b]	1 – 1,080	900 – 69,000	9 – 87
Average (Range) Concentrations for ANIMIDA Study Area Sediment Cores[c]	540 (280 – 1,990)	9,000 (3,200 – 31,000)	59 (21 – 225)
Average (Range) Concentrations for Phase I ANIMIDA Study Area Surficial Sediments[d]	390 (7 – 2,700)	6,600 (210 – 50,000)	25 (1 – 82)
Average (Range) Concentrations for Phase II ANIMIDA Study Area Surficial Sediments[e]	490 (12 – 2,000)	9,500 (440 – 27,000)	49 (2 – 176)
Average (Range) Concentrations for cANIMIDA Study Area Surficial Sediments[f]	440 (13 – 1,100)	14,000 (1,000 – 85,000)	48 (2 – 110)
Average (Range) Concentration for Chukchi Study Area Sediments[g]	360 (47 – 3,100)	8,900 (460 – 22,000)	20 (3 – 80)

[a] Prince William Sound subtidal (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., 2004.
[f] Brown et al., 2010.
[g] Results from this study.
[h] Total PHC concentrations for the ANIMIDA, cANIMIDA, and Chukchi studies included saturated hydrocarbons only, while Total PHC for the other studies included saturated and aromatic hydrocarbons (total organic extract weight).
NA – not applicable.

Overall, the concentrations of TPAH measured in sediments the Burger and Klondike study area are within the range of values reported from previous studies of other Arctic marine areas (Table 4-3). High TPAH concentrations (>2,000 µg/kg) in surface sediments occur at historic drill sites in the Chukchi and Beaufort Seas and in the Mackenzie River delta. The composition of PAH assemblage in the Burger and Klondike surface sediments is similar to the PAH compositions observed in Beaufort Sea surface sediments (Brown et al. 2010; Figure 3-6). However, the PAH in surface sediments from the two drill sites are quite different; the PAH assemblage from KD005 sediment is dominated by alkyl naphthalenes and contains only a trace of perylene. The PAH assemblage from BD005 sediment contains similar concentrations of alkyl naphthalenes, phenanthrenes, and fluoranthenes/pyrenes, as well as a high concentration of perylene. The PAH assemblage in surface sediment from the Hammerhead drill site in Camden Bay, Beaufort Sea resembles that in BD005 sediments with an abundance of alkyl naphthalenes, phenanthrenes, and fluoranthenes/pyrenes and abundant perylene (22% of TPAH) (Trefry and Trocine, 2009).

Table 4-3. Concentrations of TPAH in marine sediments from the Beaufort Sea, Chukchi Sea, and other Arctic areas.

Location	Total PAH (mg/kg: ppm)	Reference
Chukchi Sea, Except Historic Drill Sites	47 - 482	This study
Chukchi Sea, Historic Drill Sites	253 – 3,080	This study
Beaufort Sea Surface Sediments	30 – 1,800	Brown et al., 2010
Beaufort Sea Sediment Cores (2 - 12 cm)	300 – 2,950	Brown et al., 2010
Camden Bay, Beaufort Sea, Except Hammerhead	490 – 1,300	Trefry and Trocine, 2009
Camden Bay, Beaufort Sea, Hammerhead Area	840 – 3,500	Trefry and Trocine, 2009
Beaufort Lagoon, E. Beaufort Sea	30 - 710	Naidu et al., 2006
Elson Lagoon, W Beaufort Sea	8 – 3,200	Naidu et al., 2003
Beaufort Sea	Offshore: 170 – 1,030 River mouths, 50 - 700 Coastal peat, 40 - 620	Steinhauer and Boehm, 1992
Mackenzie River Delta, Canadian Beaufort Sea	Means[a], 1,900 – 4,600	Yunker et al., 1995
Mackenzie River	Mean, 450	Elmquist et al., 2008
Barents Sea	N. Barents mean, 560 S. Barents mean, 340	Yunker et al., 1995
E Barents Sea	Means, 80 - 540	Dahle et al., 2003
SW Barents Sea	20 - 360	Boitsov et al., 2009
Russian Barents Sea	Mean 1,500	Savinov et al., 2003

[a] Mean TPAH for sediments from the main channels (highest concentrations), nearshore, and offshore (lowest concentrations) locations of the Mackenzie River delta area, Canada.

A useful technique for examining the spatial trends (variability between stations) in sediment hydrocarbons and metals, involves examining the relationship between the hydrocarbon or metal parameter of interest and the percent silt + clay in the sediment matrix (% mud or fines). The natural background concentrations of hydrocarbons and metals often vary as a function of concentration of fine-grained sediment (mud). Thus, sediments enriched in hydrocarbons or metals from anthropogenic sources can be identified by normalizing the target hydrocarbon or metal parameter to the covariate (silt + clay) and evaluating outliers. This analysis technique was used effectively for the Beaufort Sea investigation and other studies to identify sediments enriched in hydrocarbons (Brown et al. 2010) and Metals (Trefry et al., 2009). Figure 4-5 shows the relationship between TPAH concentrations and percent fines. The regression line and 95% prediction intervals were calculated for the background samples (fixed and random stations) with an R^2 of 0.49. Two sediments from station BD005 and five from station KD005 fell outside of the background predication intervals indicating TPAH enrichment in these sediments, probably from anthropogenic sources.

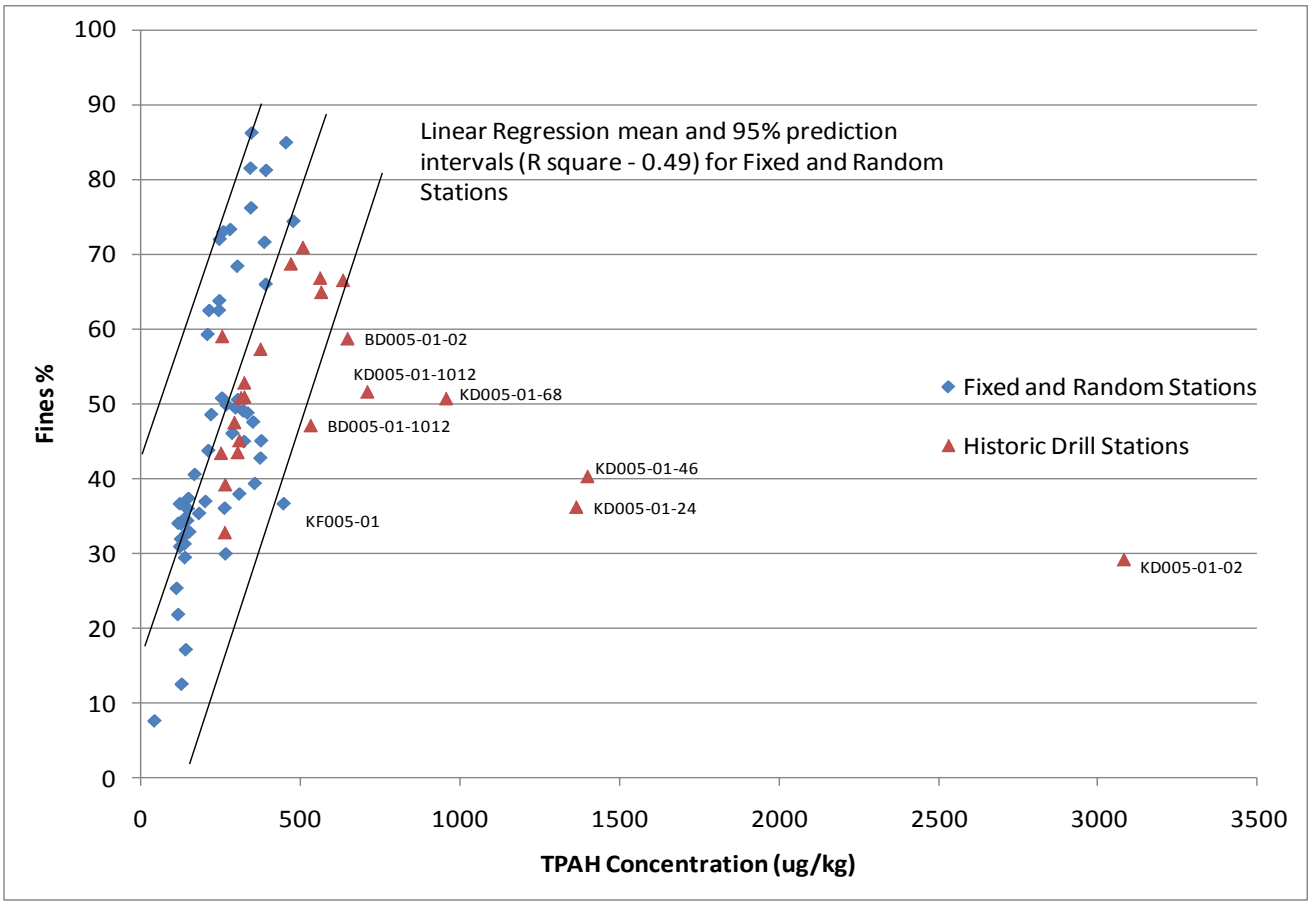


Figure 4-5. The relationship between TPAH concentration and percent fines (silt + clay) in all sediment samples collected from the Burger and Klondike survey areas.

As noted in previous investigations in the Alaskan Beaufort Sea, perylene is a better predictor of biogenic (naturally) derived PAHs than %fines or TOC (Brown et al. 2010). Perylene is not an expected contaminant from exploration or production activities and is present at low concentrations in the most Alaskan North Slope crude oils. It is found at concentrations of 2 to 80 µg/kg in many heavy crude oils and residual fuels (Uhler et al., 2007). Most perylene in sediment and tissues is associated with biogenic sources of hydrocarbons in Alaskan coastal shelf areas such as the Chukchi and Beaufort Sea. Perylene is a naturally occurring PAH formed during early diagenesis in sediments from biological source precursors (Wakeham and Farrington, 1980; Wakeham, et al., 1980; Venkatesan, 1988). It often is abundant in peat and soft coals (lignites) (Steinhauer and Boehm, 1992; Stout and Emsbo-Mattingly, 2008). Figure 4-6 shows the relationship between TPAH minus perylene concentrations and perylene concentrations in sediments from the Burger and Klondike survey areas. The mean linear regression line and 95% prediction intervals were calculated for the background samples with an R^2 of 0.91. Two sediments from station BD005 and six from station KD005 fell outside of the background predication intervals on the right indicating TPAH enrichment in these samples from sources other than the regional surface sediments. The most likely source of the excess PAH in historic drill site sediments in the Chukchi and Beaufort Seas is from discharges of drilling muds and cuttings, containing peat, kerogens, and source-rock petroleum, during exploratory drilling more than 20 years ago.

The ratio of perylene to TPAH less perylene in the Chukchi sediments averaged 0.065 for the fixed and random stations as compared to the nearshore Beaufort Sea sediments with an average value of 0.120 (Brown et al., 2010). The difference noted between these two Alaskan shelf areas probably is related to distance from shore and impact of river run-off. The nearshore Beaufort Sea is heavily influenced by spring run-off and suspended sediment and particulate organic transport from large rivers (Colville, Sagavanirktok, Kuparuk and Mackenzie Rivers – Yunker et al., 1995; Trefry et al., 2003, 2009; Brown et al., 2010). The impact of river run-off, and thus the relative abundance of perylene, is diminished in the Chukchi Sea study area since it is much farther offshore than the corresponding nearshore Beaufort Sea study area.

The ratio of petrogenic to pyrogenic (petro:pyro) PAH is another parameter useful to evaluate the spatial distribution and sources of PAH in sediments. The Chukchi Sea background sediments have petro:pyro ratios ranging from 8.2 to 11.4 (Figure 4-7; 95% CI ranged from 8.5 to 11.2). The petrogenic PAH account for approximately 90 percent of the TPAH (less perylene) mass in the background sediments and the petro:pyro ratios are comparable to those measured in the nearshore Beaufort Sea sediments (Brown et al. 2010)[2]. All historic drill site sediments have petro:pyro ratios within the 95% CI range for background samples with the exception of one station BD005 sediment and all of the station KD005 sediments. The petro:pyro ratios for station KD005 sediments ranged from 14.7-33.4, indicating a significant enrichment in petrogenic PAH from historic drilling activities at this site. The significantly higher levels of petroleum hydrocarbons at the historical Klondike drill site (KD005) and to a lesser degree at the historical Burger drill site (BD005) are clearly seen in Figure 4-3, which shows the TPAH and total S/T concentrations on maps of the Burger and Klondike areas, and also Figure 4-4.

In addition, the overall distribution of hydrocarbons in the Chukchi Sea sediments was compared to samples recently collected from the Beaufort Sea (1999 through 2006). The hydrocarbon profiles for background samples from the Chukchi and Beaufort Seas were very similar (Figure 3-6). PAH distributions were dominated by a relative abundance of petrogenic PAHs, including both parent and respective alkylated homologues of naphthalenes, fluorenes, phenanthrenes/anthracenes, fluoranthenes/pyrenes, and chrysenes.

Notable differences between the Chukchi Sea and nearshore Beaufort Sea sediments are the relatively higher concentrations of the biogenic PAH, perylene, and triterpanes in the Beaufort Sea sediments. As noted earlier, these differences are likely related to the greater influence of North Slope river run-off to the Beaufort Sea that transports suspended sediments enriched in background hydrocarbons (peat and oil-rock kerogens) and organic material to the sediments in the nearshore Beaufort Sea (Trefry et al., 2009).

[2] The average petro:pyro value in the Chukchi sediments was 9.85 and not statistically different from the average value nearshore Beaufort Sea value of 9.53.

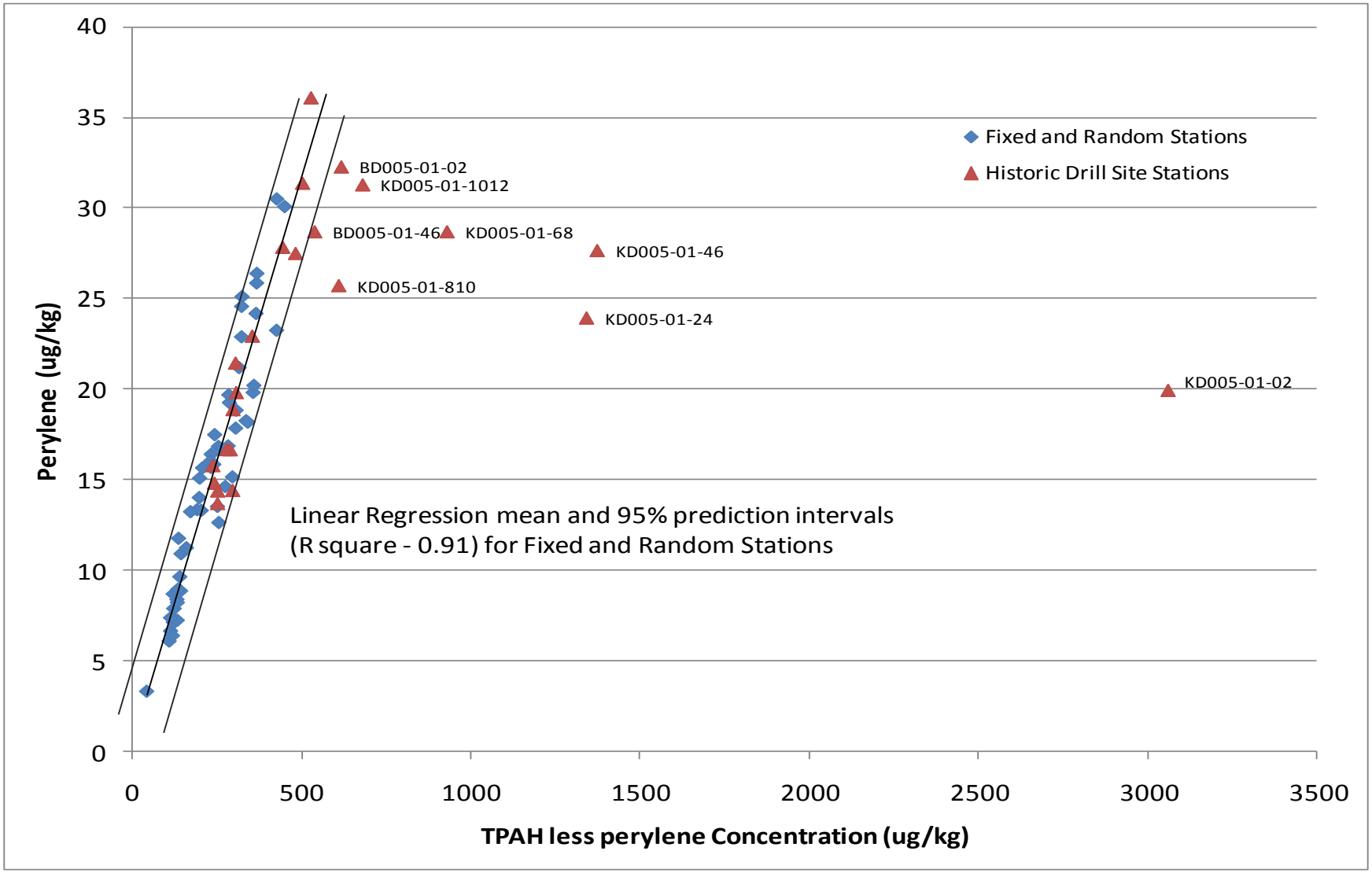


Figure 4-6. The relationship between TPAH minus perylene concentration and perylene concentration in all sediment samples collected from the Burger and Klondike survey areas.

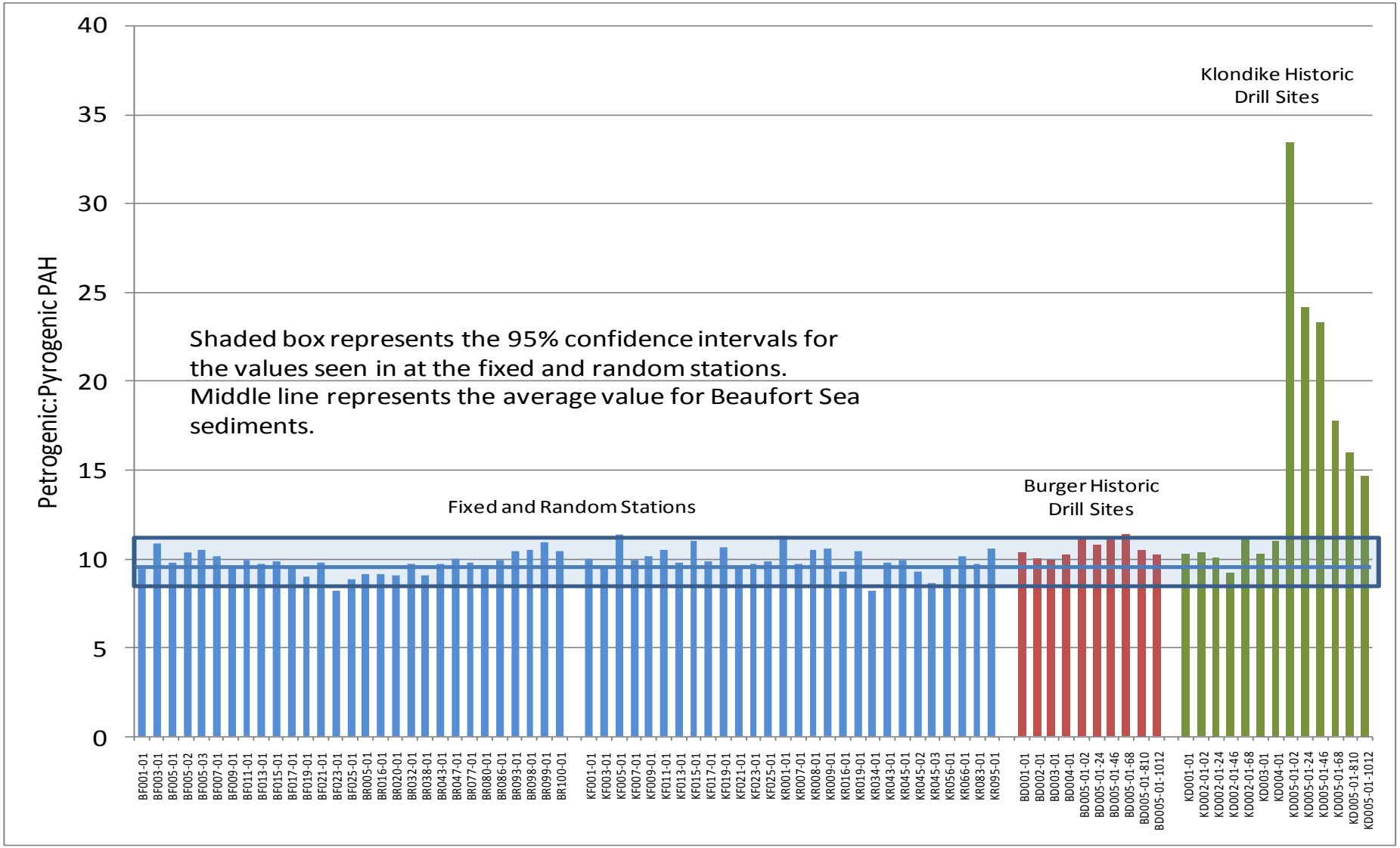


Figure 4-7. The petrogenic:pyrogenic ratio in all sediment samples from the Burger and Klondike survey areas. The 95% confidence interval for the petro:pyro ration in surface sediments from fixed and random stations is shown as a horizontal shaded area on the bar chart.

The excess TPH, PAH, and barium in sediment cores from the Berger, Klondike, and Hammerhead exploratory well sites undoubtedly were from the drilling muds and cuttings discharged at the drill sites 21 to 24 years ago. The drill-site PAH must have been sequestered or tightly bound to sediment particles, or they would have been biodegraded by sediment hydrocarbon-degrading bacteria, abundant in Beaufort and Chukchi Sea sediments (Braddock et al., 2004), in the 21 to 24 years since drilling occurred. Much of the PAH probably are bound to oil-rich shales (kerogen) or peat deposits in different geologic strata penetrated by the drill. Craig and Sherwood (2004) report that the Klondike but not Berger well penetrated shale layers [often rich in organic matter (kerogen) in Alaska (Anders and Magoon, 1985)]. These hydrocarbon rich solids were in the cuttings discharged from the wells. The Klondike well encountered several oil-bearing sandstone strata at intermediate depths, whereas the Burger well encountered an extensive gas/condensate reservoir near the bottom of the well. If cuttings generated during drilling of these hydrocarbon-bearing strata were discharged, hydrocarbon-rich cuttings would have been deposited on the sea floor near the wells. Some of the PAH also could be from lignite and gilsonite additives used frequently in WBM in the 1980s (Neff, 2010). Lignite and gilsonite are natural hydrocarbon materials (soft coal and asphaltic material). They contain traces of PAH (Stout and Emsbo-Mattingly, 2008) that are tightly bound to the organic matrix of these fossil materials and, so, are very persistent but not bioavailable or toxic to marine organisms (Rust et al., 2004).

Steinhauer and Boehm (1992) Yunker et al., (1991, 1995), and Naidu et al. (2003, 2006) and Elmquist et al. (2008) have concluded, based on the abundance of perylene in sediments from sites with and without a past history of exploratory drilling, that most of the PAH in Beaufort Sea, Barents Sea, and other Arctic sediments, including those from drill sites, comes from erosion of peat, coal, and black carbon (all of which closely resemble the lignite and gilsonite WBM additives) deposits eroding from the coast or discharged from rivers emptying into the Arctic Ocean. PAH in sediments from the Norwegian and Russian regions of the Barents Sea also have been derived in part from eroding natural deposits of kerogens, oil shales, and coals (Dahle et al., 2003; Elmquist et al., 2008; Boitsov et al., 2009). These tightly bound PAH have a low bioavailability and, therefore, are not toxic to marine plants and animals (Rust et al., 2004; Neff et al., 2005).

4.2.1.2. Marine Invertebrate Tissues

Concentrations of different hydrocarbon types are highly variable in tissues of marine invertebrates collected at the Burger and Klondike survey areas. (Table 3-5). Concentrations of most hydrocarbon types are higher in all marine invertebrate taxa from the Klondike area than in those from the Burger area. Because hydrocarbons tend to bind more strongly to organic coatings on clay particles and surface sediments from Burger contain higher mud (52.9 ± 17.2%) and TOC (0.95 ± 0.26%) concentrations than surface sediments from Klondike (40.4 ±17.3% mud and 0/73 ± 0.31% TOC), it is likely that the hydrocarbons in Burger sediments are less bioavailable than those in Klondike sediments.

Hydrocarbons usually are bioaccumulated by benthic invertebrates (the clams, worms, amphipods, and crabs) primarily from hydrocarbons desorbing from the hydrocarbon reservoir in the fine-grained sediment fraction and from ingestion of food items. Thus, there should be a relationship between concentrations of hydrocarbons in benthic marine invertebrates and in the

sediments on or in which they reside (Table 4-4). Table 4-4 summarizes hydrocarbon concentrations in two species of clams, in maldanid worms, and in the surface sediments at the stations where they were collected. There is little relationship between the concentrations of TPAH and total S/T in tissues and sediments. Only one clam (*Macoma*) and three worm samples (10% of tissue samples) contain higher TPAH concentrations than the sediments where they were collected. All but one of these samples is from the Klondike area. One *Astarte* and one worm sample were collected at the historic drill site at Klondike (KD005). These tissue samples contained 5% and 10%, respectively, of the TPAH concentration of surface sediments at KD005 (3,080 µg/kg). These results indicate that TPAH in surface sediments at Burger and Klondike, including surface sediment from the historic drill site at Klondike, have a very low bioavailability to benthic bivalve mollusks and polychaete worms residing in the sediments. Neff et al. (2003) founded that PAH in offshore sediments containing PAH from natural oil seeps, oil from the *Exxon Valdez* spill, and pyrogenic sources had a low bioavailability to polychaete worms. PAH bound to sediment organic matter have a low bioavailability and toxicity to marine animals (Neff et al., 2005).

Table 4-4. TPAH and total S/T in clams, worms, and associated sediments from Burger (BD) and Klondike (K) stations where both types of samples were collected. Concentrations are µg/kg.

Station	TPAH (µg/kg)		Total S/T (µg/kg)	
	Tissues	Sediment	Tissues	Sediment
Clams (*Macoma* sp.)				
BD001	138	257	8.8	16.6
BF015	152	284	15.4	18.1
BF025	204	187	12.3	11.2
BR038	190	349	14.3	18.8
KR095	355	325	8.8	16.2
Range	138 – 355	187 – 340	8.8 – 15.4	11.2 – 18.8
Clams (*Astarte* sp.)				
BD001	67.6	257	<1.9	16.6
BF001	26.7	132	2.59	9.07
BF003	43.4	356	0.39	22.3
BF005	27.1	381	1.34	25.9
BF007	44.6	273	4.14	15.8
BF011	36.4	396	4.45	24.2
BF017	29.2	207	3.57	13.4
BR005	27.2	225	0.72	12.6
BR038	76.0	349	1.76	18.8
BR080	113	338	4.17	23.5
BR093	27.4	302	5.25	17.9
BR098	151	267	ND	18.1
KD005	160	3,080	ND	79.7
KR007	262	213	ND	13.9
KR008	70.6	127	ND	7.84
KR009	106	145	5.09	8.17
KR019	256	306	6.53	18.2
Range	27.2 – 262	127 – 3,080	ND – 6.53	8.17 – 78.7

Table 4–4. TPAH and total S/T in clams, worms, and associated sediments from Burger (BD) and Klondike (K) stations where both types of samples were collected. Concentrations are µg/kg, continued

Station	TPAH (µg/kg)		Total S/T (µg/kg)	
	Tissues	Sediment	Tissues	Sediment
Polychaete Worms (Maldanidae)				
BF003	179	356	20.1	22.3
BF017	183	207	25.5	13.4
BF021	302	250	75.2	14.7
BR086	154	327	14.4	20.4
BR093	207	302	21.9	17.9
BR098	190	267	16.7	18.1
BR099	179	313	17.0	18.7
BR100	253	270	21.0	18.1
KD002	168	377	18.6	13.6
KD005	315	3,080	28.8	79.7
KF005	217	451	21.2	23.7
KF013	138	146	17.2	8.63
KF025	135	258	14.7	13.4
KR009	163	145	18.4	8.17
KR019	133	306	14.5	18.2
KR034	209	132	22.2	8.73
KR045	157	173	15.3	8.91
Range	133 – 315	132 – 3,080	14.4 – 75.2	8.17 – 79.7

The TPAH concentrations and the tissue/sediment TPAH ratios are higher in *Macoma* clams and maldanid worms than in *Astarte* (Table 4-4). Both *Macoma* and maldanid worms ingest large amounts of sediments, whereas *Astarte* is primarily a filter-feeder. Much of the PAH in clams and worms probably is in unassimilated form in the gut, as observed for metals in the worms.

Total S/T concentrations are higher in tissues of 26% of the clam and worm than in the associated sediments (Table 4-4). More than half the worms had bioaccumulated total S/T to concentrations higher than those in sediments. Polychaetes can metabolize and excrete PAH, but not S/T, explaining the differences in apparent bioavailability of PAH and S/T in worms. Bivalves have only a limited ability to metabolize and excrete PAH (Neff, 2002).

Concentrations of hydrocarbons, for which there are comparative data, are similar in marine invertebrates from the Burger and Klondike survey areas in the Chukchi Sea and from other marine habitats in the world (Table 4-5). Clams from hydrocarbon-contaminated environments sometimes contain elevated concentrations of TPAH. By 2002 most intertidal clams and worms in Prince William Sound, the site of the 1989 *Exxon Valdez* oils spill contained background concentrations of TPAH (Neff et al., 2006), in the range of 10 to 50 µg/kg. The most heavily contaminated clams and worms were from the shores of former industrial sites (mostly herring processing plants).

Table 4-5. Concentrations of TPAH, ∑SHC, and total S/T in tissues of marine bivalves, crustaceans, and polychaete worms from throughout the world. Concentrations are µg/kg.

Location	Taxon	TPAH	∑SHC	Total S/T
Chukchi Sea (this study)	Clams	26.7 – 355	1,020 – 8,830	0 – 15.4
Beaufort Sea[a]		37 – 195	0 – 39,700	0 – 17.1
Prince William Sound, AK[b]		10.2 – 5,775	No Data	No Data
World range[c]		3 – 17,000	No Data	No Data
Chukchi Sea (this study)	Crustaceans	22.7 – 99.9	500 – 14,200	0 – 17.8
Beaufort Sea[a]		19.7 – 175	0 – 260,000	4.5 - 55
Prince William Sound, AK[b]		1.9 – 178	No Data	No Data
World range[c]		4 – 13,400	No Data	No Data
Chukchi Sea (this study)	Worms	133 – 315	2,410 – 10,900	13.3 – 75.2
Prince William Sound, AK[b]		5.9 – 1,860	No Data	No Data
World range[c]		7.3 – 1,120	No Data	No Data

[a] Neff et al., 2009
[b] Neff et al., 2006
[c]Neff, 2002.

Concentration ranges of TPAH, ∑SHC, and total S/T overlap in clams, crustaceans, and worms, though some Beaufort Sea clams and amphipods contain high concentrations of ∑SHC. Total SHC concentrations were very high in tissues of some amphipods, crabs, and clams in both the Beaufort and Chukchi Seas (Table 4-5). Most of the SHC in amphipods and crabs, but not in clams, was a single isoprenoid hydrocarbon, pristane. Pristane is present in petroleum, but its main source in the marine environment is from zooplankton, particularly copepods of several genera, including *Neocalanus* and *Pseudocalanus*, the dominant zooplankton in Beaufort and Chukchi Sea waters in most seasons (Horner and Murphy, 1985). Crustaceans may bioaccumulate pristane and other SHC from ingestion of copepods and organic detritus that accumulates at the sediment/water interface. Pristane is present at low concentrations in peat, which is eroding into coastal waters from shoreline sediments and upland soils (Steinhauer and Boehm, 1992), and may be a source of pristane for filter-feeding clams, such as *Astarte*.

4.2.2. Potential Sources of Hydrocarbons in Sediments and Marine Invertebrate Tissues

The high variability in the concentrations of PAH, SHC, and S/T in sediments and invertebrate tissues in the Burger and Klondike areas of the Chukchi Sea can be attributed to the wide variety of sources contributing to the background hydrocarbons concentrations (e.g., shoreline/coastal erosion, terrestrial plant material, aquatic plant material, natural hydrocarbon sources (seeps, kerogen containing source rock and possibly peat and coal), and long-range atmospheric transport and deposition) (Valette-Silver et al. 1999). Overall, the levels of TPH measured in the Chukchi Sea study area are within the range of values reported from previous studies of other Alaskan coastal continental shelf areas (Tables 4-2 and 4-5).

The TPH chromatograms for the Chukchi sediments throughout the study area are generally very similar showing a series of resolved peaks in the 10 to 50 minute retention time range with little or no unresolved complex mixture. The alkane distribution shows a predominance of alkanes with an odd number of carbons indicative of a regional background dominated by terrestrial plant origin hydrocarbons (Wakeham and Carpenter, 1976; Wakeham and Farrington, 1980). The majority of the Chukchi sediments have TPH compositions similar to those observed in Beaufort Sea sediments (Brown et al. 2010). Notable differences are seen in the chromatograms for station KD005, sediments that show a bimodal distribution of alkanes with a greater abundance of light alkanes present in the 10 to 35 minute retention time range. The increase in light range alkanes and the bimodal distribution of alkanes at station KD005 indicates a mixture of natural background hydrocarbon and petroleum hydrocarbon sources.

The background hydrocarbons present throughout the Chukchi Sea study area can be attributed to a variety of sources including shoreline/coastal erosion, terrestrial plant material, aquatic plant material, natural hydrocarbon seeps, and long-range atmospheric transport and deposition (Valette-Silver et al. 1999). The results of this study identify all of these sources as the primary contributors the sediment hydrocarbon background in the Burger and Klondike areas of the Chukchi Sea. An additional significant hydrocarbon source was identified at historic drill site Stations KD005 and BD005. The source of the hydrocarbons at these two stations, dominated by increased concentrations of TPAH, petrogenic PAHs, and total S/T (Figures 3-5-3-7, 4-3, 4-7), is likely crude oil contribution from source rock cuttings associated with historic drilling activities.

The predominant crude oil PAHs present in the historic drill location samples include the alkylated homologues of naphthalenes (C_1-C4), phenanthrenes/anthracenes (C1-C4), and fluoranthenes/pyrenes ($C_1 - C_3$). The higher concentrations present at the former drill locations are focused in the center drill samples (i.e., KD005, BD005), and are not as apparent in the radii drilling locations that surround the actual drill site (i.e., KD001 – KD004). The PAH concentrations at the surface (0-2 cm), center drill site locations in the Klondike study area (KD005) and the Burger survey area (BD005) are approximately double the PAH concentrations found at depth, and at the surrounding drill sample sites (i.e., KD001 – KD004). The elevated alkyl naphthalene concentrations at the KD005 station are approximately an order of magnitude higher (depending on the specific analyte) than the same analyte series in the surrounding radius drill site locations. The fixed and random sampling locations were also dominated by petrogenic PAHs, rather than pyrogenic PAHs. This indicates a limited contribution to sediments from anthropogenic sources.

Biomarker results provide another line of evidence supporting a crude oil influence at the drill site center locations. Total biomarker concentrations for each drill site center location (BD005 and KD005) are higher than background concentrations and are enriched in the triterpanes that are predominant in Alaskan North Slope crude oil (i.e., T15, T19, T21, T22 – Figures 3-7 and 3-8) indicative of crude oil contribution from historic drilling sources.

Although concentrations of PAH, SHC, and S/T are lower in most benthic invertebrates than in the sediments in which they reside (Table 4-3), these hydrocarbons probably are bioaccumulated from hydrocarbons desorbing from the sediments, or from ingestion of organisms and organic detritus in sediments. Zooplankton probably bioaccumulate hydrocarbons from ingestion of

organic particles, including other zooplankton and organic detritus. Since PAH, and other hydrocarbons do not biomagnify in marine food chains (Neff, 2002), trophic transfer is inefficient and hydrocarbon concentrations are unlikely to reach high concentrations in upper trophic level animals, such as fish, bowhead and beluga whales, seals, and polar bears.

4.3. Metals

4.3.1. Concentrations, Spatial Distribution and Comparison with Other Investigations

4.3.1.1. Sediments

As previously introduced, concentrations of each metal were variable throughout both study areas with an overall average of ~18% higher metal concentrations in the somewhat finer-grained sediments in the Burger area than in the Klondike area (Table 4-6). Concentrations of Al in surface sediments from the 2008 study ranged from 4.3 to 7.2% in the Burger area and from 1.9 to 6.0% in the Klondike area (Figures 4-8 and 4-9). The spatial distribution of Al was strongly related to grain size as shown by the positive correlation between Al and clay content (Figure 4-10) and the negative correlation between Al and sand content (Figure 4-11). Clay is rich in Al-bearing aluminosilicates and sand contains Al-poor quartz and carbonate. More clay and less sand were found in the Burger area in support of the higher Al values (Tables 3-3, 4-6 and Figures 4-8 and 4-9). The highest Al values were found in the northern part of the Burger area and the northwestern quadrant of the Klondike area.

As previously introduced, concentrations of Al and other metals generally correlate well with each other because metals are more abundant in fine-grained clay minerals (aluminosilicates). Plots for Al versus Fe and Cr (Figure 3-19) for the 2008 data for sediments from the Chukchi Sea showed strong positive correlations ($r = 0.95$). These plots have been redrawn for this discussion section with a template that includes the linear regression lines and 99% prediction interval that were constructed using data from the coastal Beaufort Sea (Figure 4-12). The Chukchi Sea data for Fe and Cr fit within the prediction intervals on the metal versus Al plots from the Beaufort Sea data very well (Figure 4-12). Likewise, the slopes from the Chukchi Sea and Beaufort Sea data sets for Fe/Al (0.56 versus 0.49) and Cr/Al (12.7 and 12.4) agree within 14% and 2%, respectively. These results suggest that Al, Fe and Cr in sediments from the coastal Chukchi and Beaufort seas may have very similar source minerals that were derived from the Brooks Range and the north slope of Alaska. The data for Cr also suggest that all samples collected during the 2008 study of the Chukchi Sea contained background Cr values with no anthropogenic inputs of Cr. This conclusion is based on the assumption that data points for sediments with an anthropogenic Cr component will plot above the upper prediction interval on the Cr versus Al plot. Aluminum is present at percent levels in the sediment, relative to concentrations in parts per million (µg/g) for trace metals; and, Al is not commonly introduced to marine sediments in sizeable amounts by anthropogenic processes. Therefore, any fractional changes in Al values are expected to be small relative to possible shifts in concentrations of trace metals due to anthropogenic or diagenetic influences (e.g., Bruland et al., 1974; Trefry et al., 1976; Schropp et al., 1990; Trefry et al., 2003).

Table 4-6. Means, standard deviations (SD), maximums (Max), minimums (Min), % relative deviation (RSD) and Max/Min for concentrations of metals in all surface sediments from the Burger and Klondike.

Statistic	Ag (µg/g)	Al (%)	As (µg/g)	Ba (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Hg (µg/g)	Mn (µg/g)	Pb (µg/g)	Se (µg/g)	Zn (µg/g)
Burger area													
Mean (n = 32)	0.12	5.68	16.0	721	0.19	77.7	14.5	3.11	0.035	296	12.4	0.67	76.8
SD	0.01	0.82	6.1	229	0.03	11.0	2.9	0.62	0.007	47	1.6	0.30	15.1
Max	0.14	7.21	37.5	1910	0.26	99.5	21.7	4.63	0.049	422	15.7	1.55	111
Min	0.09	4.27	10.1	577	0.13	56.6	9.2	2.20	0.018	216	9.8	0.25	49.4
% RSD	8	14	38	32	16	14	20	20	21	16	13	45	20
Max/Min	1.6	1.7	3.7	3.3	2.0	1.8	2.4	2.1	2.7	2.0	1.6	6.2	2.2
Klondike area													
Mean (n = 31)	0.11	4.80	12.3	657	0.17	69.5	12.0	2.54	0.032	296	11.1	0.42	62.9
SD	0.01	0.88	3.0	261	0.03	11.8	2.5	0.48	0.011	52	1.2	0.14	13.2
Max	0.14	6.04	19.8	2000	0.21	87.9	15.7	3.21	0.064	386	14.2	0.75	81.5
Min	0.09	1.91	8.3	436	0.08	30.3	4.3	0.99	0.010	154	8.2	0.18	19.3
% RSD	9	18	24	40	18	17	21	19	34	18	9.2	33	21
Max/Min	1.6	3.2	2.4	4.6	2.6	2.9	3.6	3.2	6.4	2.5	1.7	4.2	4.2

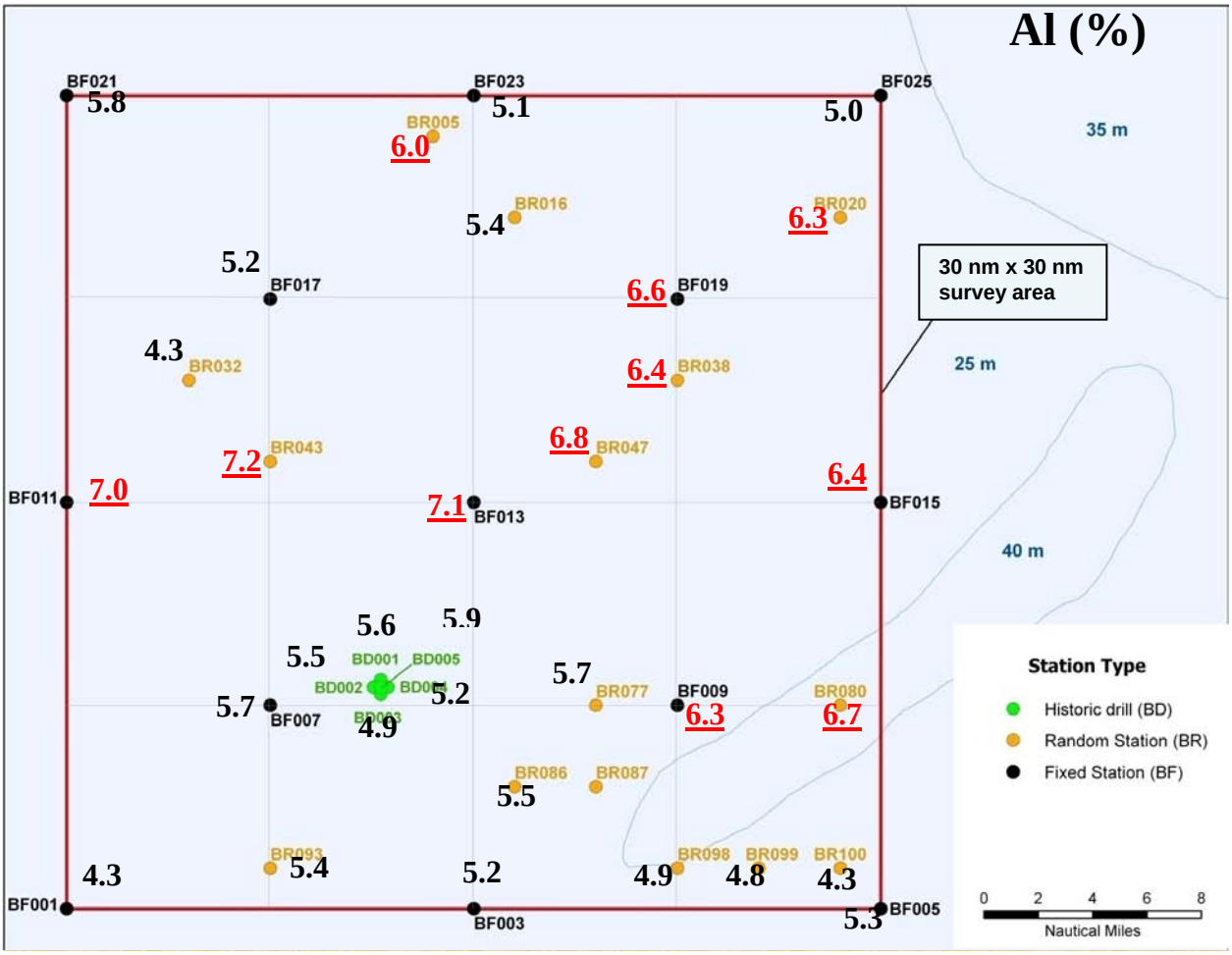


Figure 4-8. Map showing stations in Burger area with concentrations of Al in % (dry weight). Numbers in red and underlined identify samples that contained ≥6% Al.

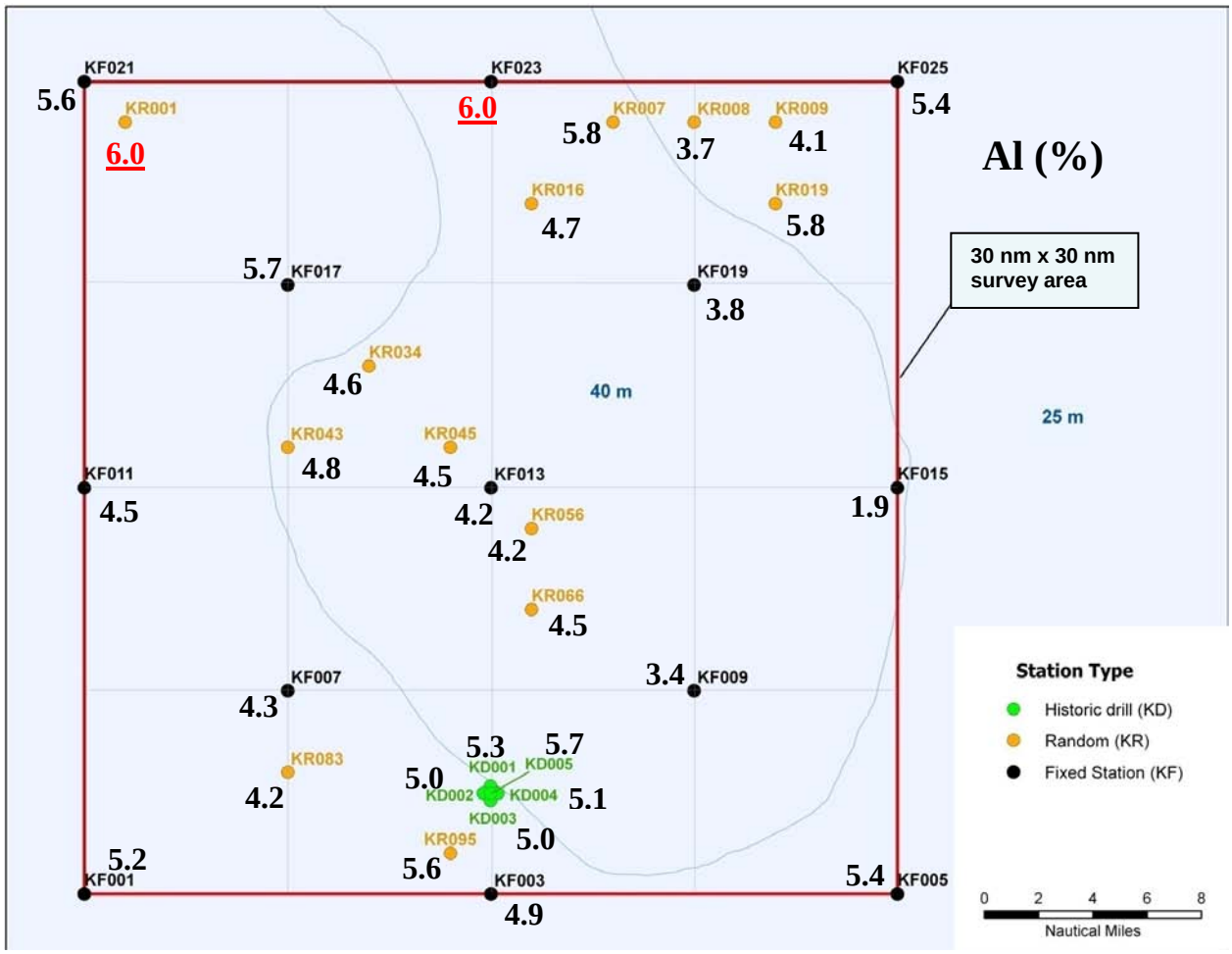


Figure 4-9. Map showing stations in Klondike area with concentrations of Al. Numbers in red and underlined identify samples that contained ≥6% Al.

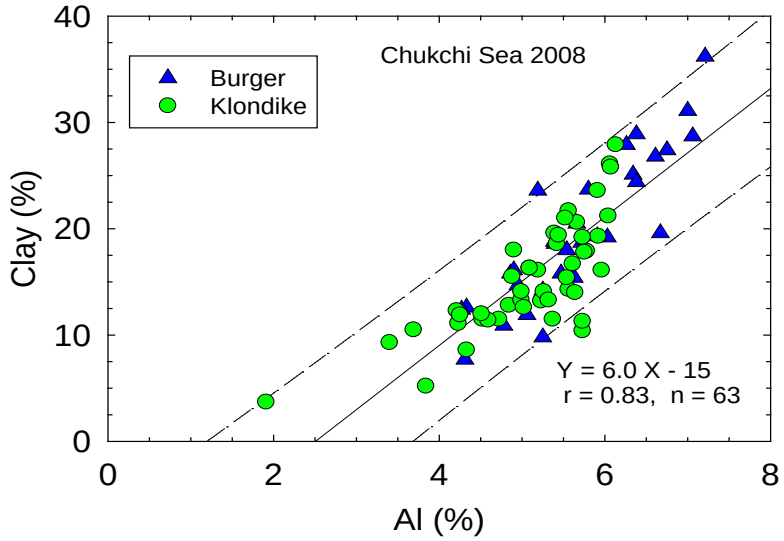


Figure 4-10. Clay content versus concentrations of Al for Burger and Klondike areas. Equation and solid line are from a linear regression, dashed lines show 95% prediction interval and r is the correlation coefficient.

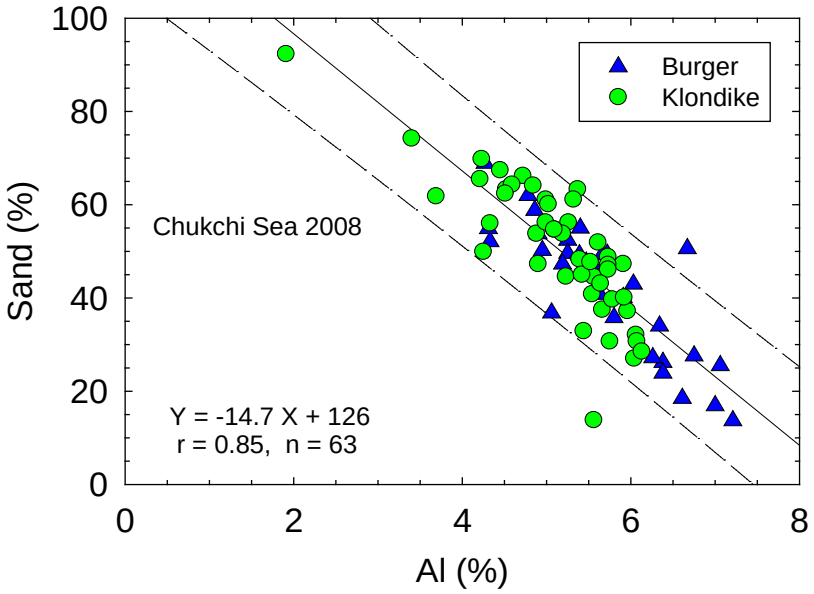


Figure 4-11. Sand content versus concentrations of Al for surface sediments from the Burger and Klondike areas. Equation and solid line are from a linear regression, dashed lines show 95% prediction interval and r is the correlation coefficient.

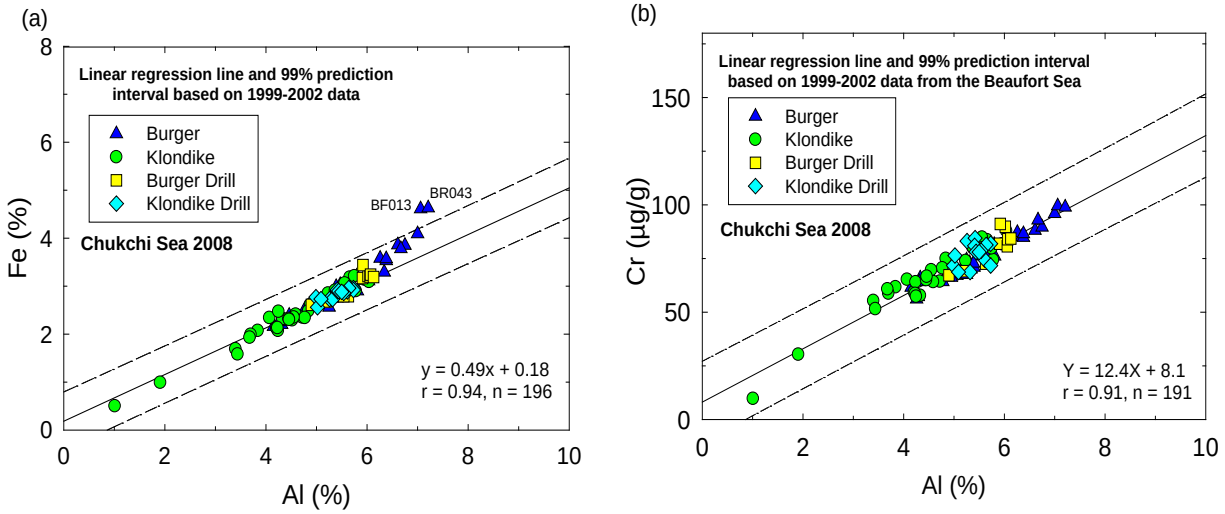


Figure 4-12. Concentrations of (a) Fe and (b) Cr versus Al for all sediments from the 2008 Chukchi Sea study. Equations and solid lines are from linear regressions using sediment data from the coastal Beaufort Sea from Trefry et al. (2003), dashed lines show 95% prediction intervals and r is the correlation coefficient.

Future monitoring of trends in concentrations of Cr (and other metals) will use graphs such as Figure 3-12b and others to be introduced below where the linear regression line and prediction interval were calculated using Chukchi Sea data. The comparison of results from the Chukchi Sea with those from the Beaufort Sea was carried out here to provide a frame of reference for Chukchi Sea data relative to other results for metals in Arctic sediments.

As appropriate, concentrations of each additional metal will be reviewed below based on metal/Al trends for the Beaufort Sea (after Trefry et al., 2003) and based on the 2008 data from the Chukchi Sea. These comparisons will help identify similarities between Beaufort and Chukchi sea sediments and define metal/Al relationships for the Chukchi Sea. When Cd concentrations in sediments from the 2008 Chukchi Sea study were plotted on the template from the Beaufort Sea, the points all plotted below the linear regression line (Figure 4-13a). Thus, sediments from the Chukchi Sea seem to contain lower Cd concentrations, relative to Al, than sediments from the coastal Beaufort Sea. When a Cd versus Al plot was developed using the 2008 Chukchi Sea data (Figure 4-13b), the correlation coefficient was higher than previously found for the Beaufort Sea data and the slope for Cd/Al was 0.029 (Chukchi) versus 0.052 (Beaufort, Figure 4-13). All data points from the 2008 Chukchi Sea study plotted within the 99% prediction interval on Figure 4-13b and no indication of any anthropogenic inputs of Cd were observed.

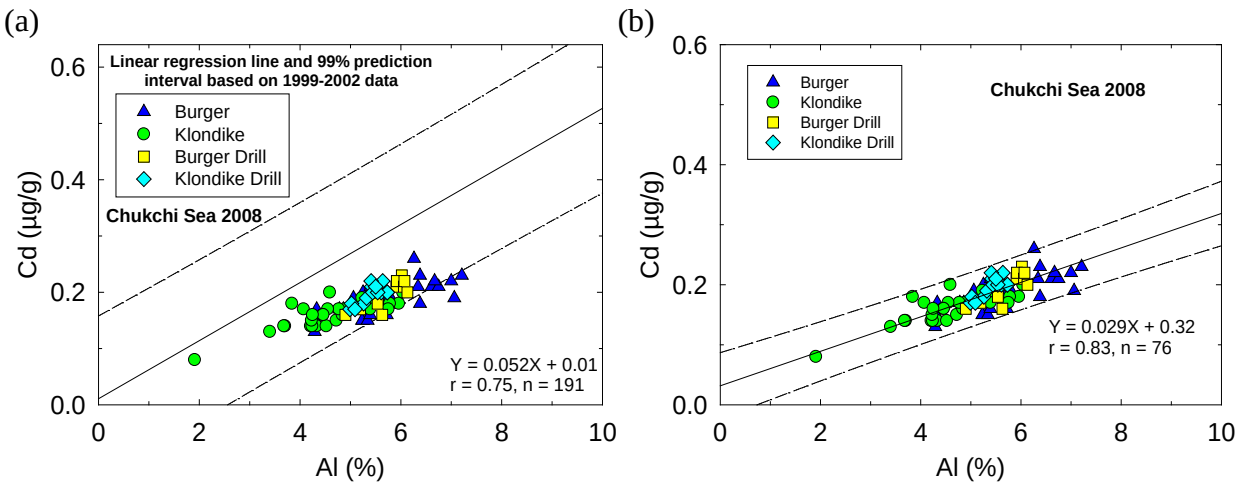


Figure 4-13. Concentrations of Cd versus Al for all sediments from the 2008 Chukchi Sea study. Equations and solid lines are from linear regressions using data for (a) the coastal Beaufort Sea from Trefry et al. (2003) and (b) the 2008 Chukchi Sea. Dashed lines show 99% prediction intervals and r is the correlation coefficient.

Similar to the trend observed for Cd versus Al, the Zn versus Al plot shows lower Zn concentrations, relative to Al, for the Chukchi Sea than for the Beaufort Sea sediments, based on the template in Figure 4-14a. When a linear regression analysis was carried out for the 2008 Chukchi Sea data, the slope was 10% lower and the correlation coefficient was higher (Figure 4-14). No indication of any anthropogenic inputs of Zn to the Chukchi Sea study area was observed and a good template for future monitoring of any anthropogenic metal inputs was established (Figure 4-14b). The trends for Cu were similar to those for Cd and Zn (Figure 4-15) with a 57% lower slope for Cu/Al for the Chukchi Sea samples than previously found for the Beaufort Sea. One minor difference in the Cu versus Al plot was that one data point plotted above the upper prediction interval. This sample from 4 to 6 cm in the core from station BD005 also had the highest Ba concentration in the overall data set and may represent a minor anthropogenic contribution as discussed below.

When concentrations of Ba were plotted versus Al on a graph with a template (linear regression line plus prediction interval) from the Beaufort Sea data, many points plotted above the upper prediction interval (Figure 4-16). The greatest positive deviations were for points from sediment cores at the historic Burger and Klondike Drill sites (BD005 and KD005) where elevated Ba values ranged from ~1,500 to 2,400 µg/g (Figure 4-16). Vertical profiles for Ba in cores from stations BD005 and KD005 (Figures 3-20 and 3-22) also show the high Ba concentrations that are most likely from a small barite residue from drilling mud that was discharged. The highest Ba concentration of ~2400 µg/g (at 4-6 cm in the core from station BD005) was about ~1700 µg/g greater than predicted by the upper prediction interval at an Al concentration of 6%.

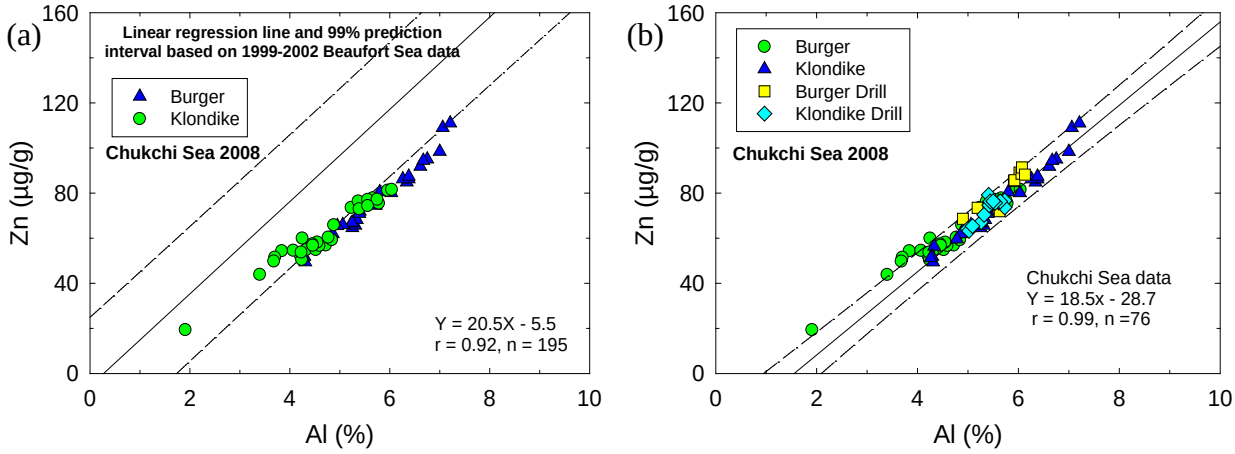


Figure 4-14. Concentrations of Zn versus Al for sediments from the 2008 Chukchi Sea study. Equations and solid lines are from linear regressions using data for (a) the coastal Beaufort Sea from Trefry et al. (2003) and (b) the 2008 Chukchi Sea. Dashed lines show 99% prediction intervals and r is the correlation coefficient.

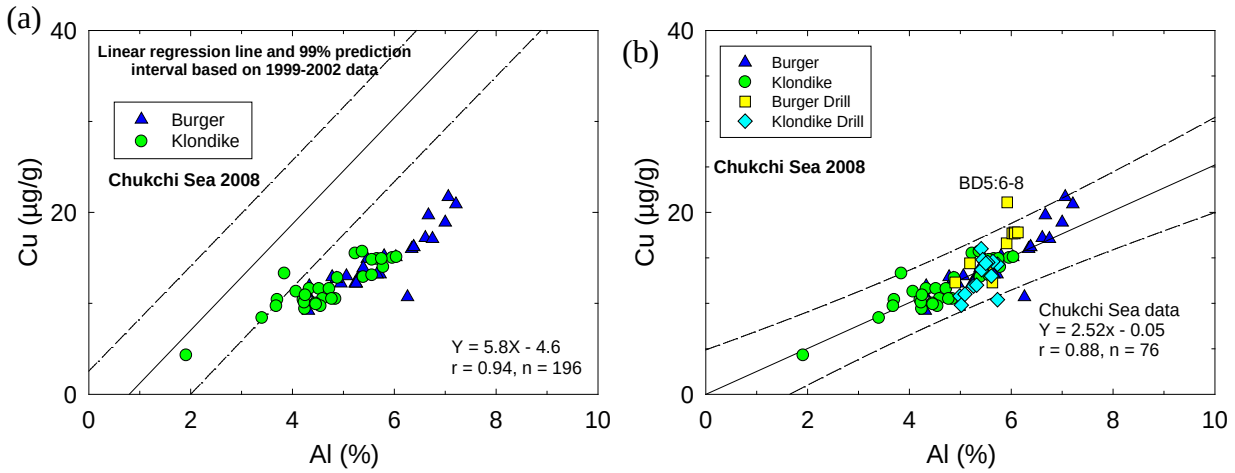


Figure 4-15. Concentrations of Cu versus Al for sediments from the 2008 Chukchi Sea study. Equations and solid lines are from linear regressions using data for (a) the coastal Beaufort Sea from Trefry et al. (2003) and (b) the 2008 Chukchi Sea. Dashed lines show 99% prediction intervals and r is the correlation coefficient.

Industrial barite contains about 53% Ba (or Ba at 530,000 µg/g; Trefry et al., 2007). Thus, the Ba anomalies in the drill site cores at stations BD005 and KD005 can be explained by a residue of 0.3% barite or less [(1,700 µg/g)/(530,000 µg/g)]. Data points from BD stations 001- 004 and KD stations 001- 003 did not contain excess Ba. Sediment from station KD004 (0-2 cm) contained Ba at 919 µg/g.

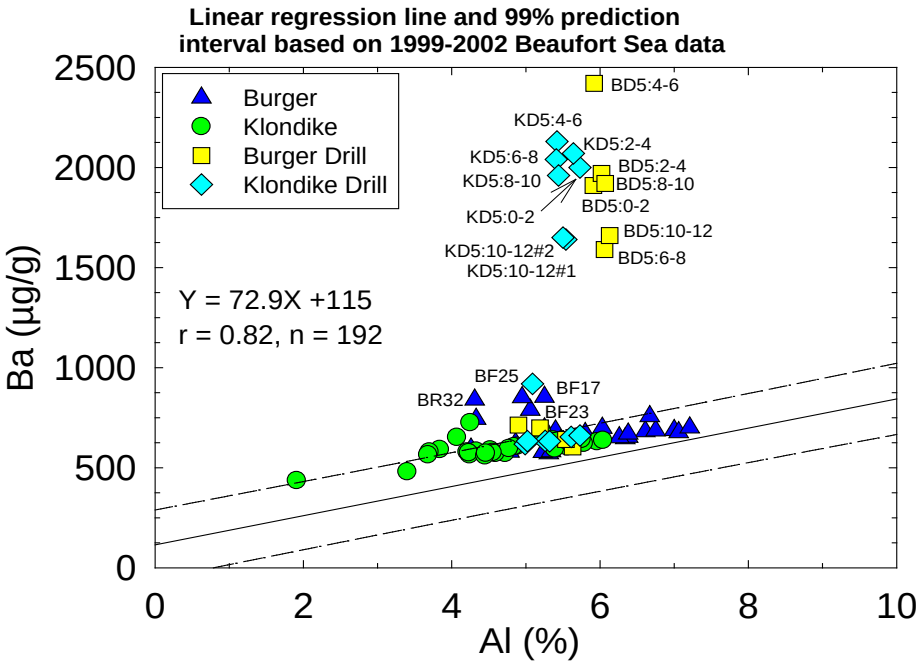


Figure 4-16. Concentrations of Ba versus Al for all sediments from the 2008 Chukchi Sea study. Equations and solid lines are from linear regressions using data for the coastal Beaufort Sea from Trefry et al. (2003). Dashed lines show 99% prediction interval and r is the correlation coefficient.

Barium concentrations in surface sediments from the Burger and Klondike stations are plotted on maps in Figures 4-17 and 4-18. The higher Ba values at the one Burger and two Klondike drill sites are shown in solid rectangles. In addition to the drill sites, concentrations of Ba also were elevated at four stations in the northern reaches of the Burger area (Figures 4-17 and 4-18). These secondary enrichments in sediment Ba are most likely due to natural diagenetic remobilization and surface sediment enrichment of Ba as previously described for continental sediments by McManum et al. (1994) and Torres et al. (1995). Some of the excess Ba may also have been derived from the non-magnetic heavy mineral fraction of coarse-grained sediments in the northeast Chukchi Sea. The mean Ba concentration in this heavy mineral fraction is 11,443 ± 6,600 µg/g (Luepke and Escowitz, 1989). The Ba versus Al graph in Figure 4-16 will be modified as additional data become available to develop a linear regression line and prediction interval that is specific to the Chukchi Sea.

Most of the data points for Pb from the 2008 Chukchi Sea survey fit the 99% prediction interval developed for the coastal Beaufort Sea (Figure 4-19). One point from the KD005 core (2-4 cm) and one point from the BD005 core (4-6 cm) contained Pb concentrations higher than the upper prediction interval (Figure 4-19). Both of these samples contained elevated Ba concentrations and the slight excess Pb may be related to drilling discharges.

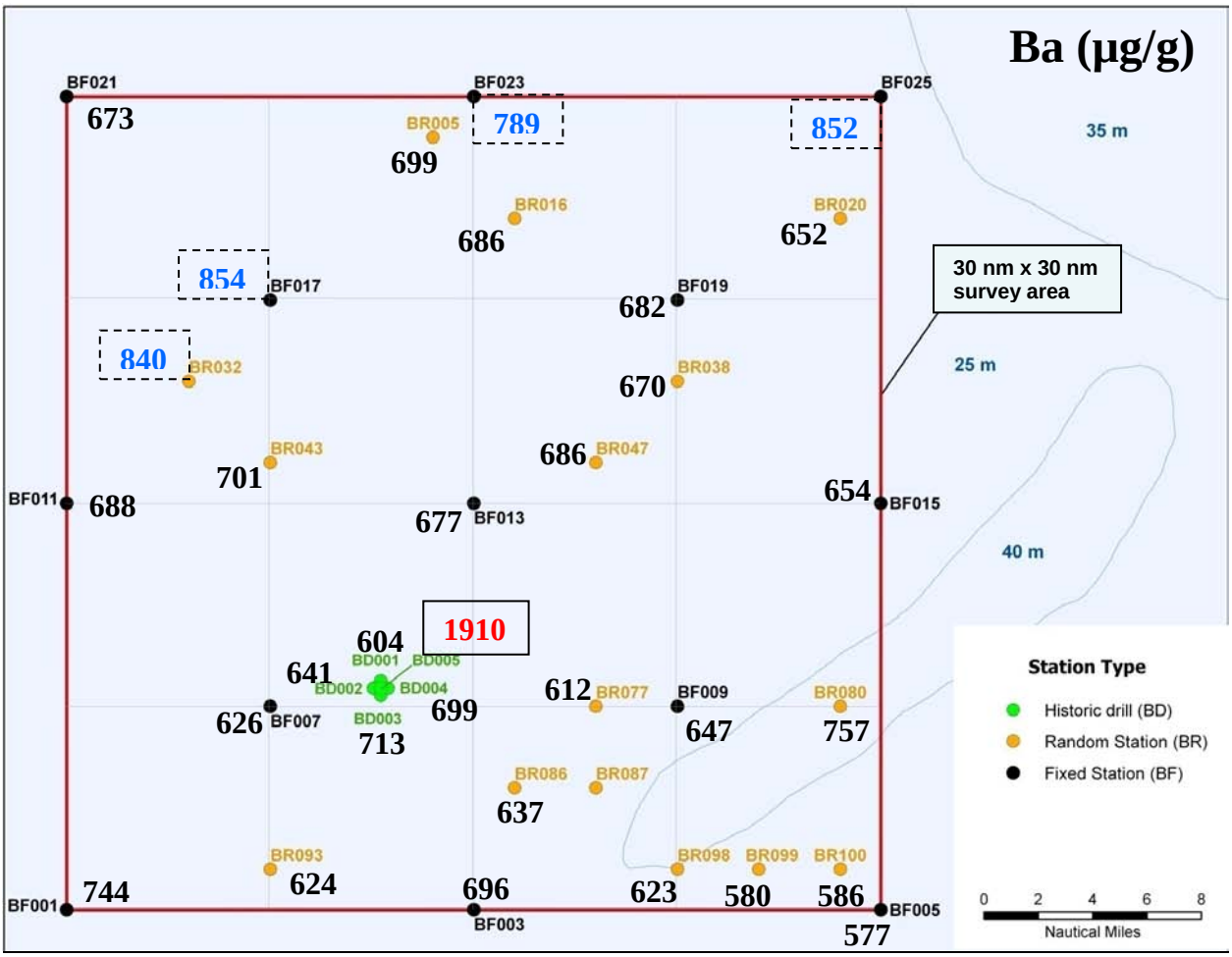


Figure 4-17. Map showing stations in Burger area with concentrations of Ba in µg/g (dry weight). Red number in rectangle with solid line is for sample that is believed to have residual Ba from previous drilling operations as discussed in the text. Blue numbers in rectangles with dashed lines identify samples that contain Ba at greater than background values, most likely due to diagenetic processes as discussed in text.

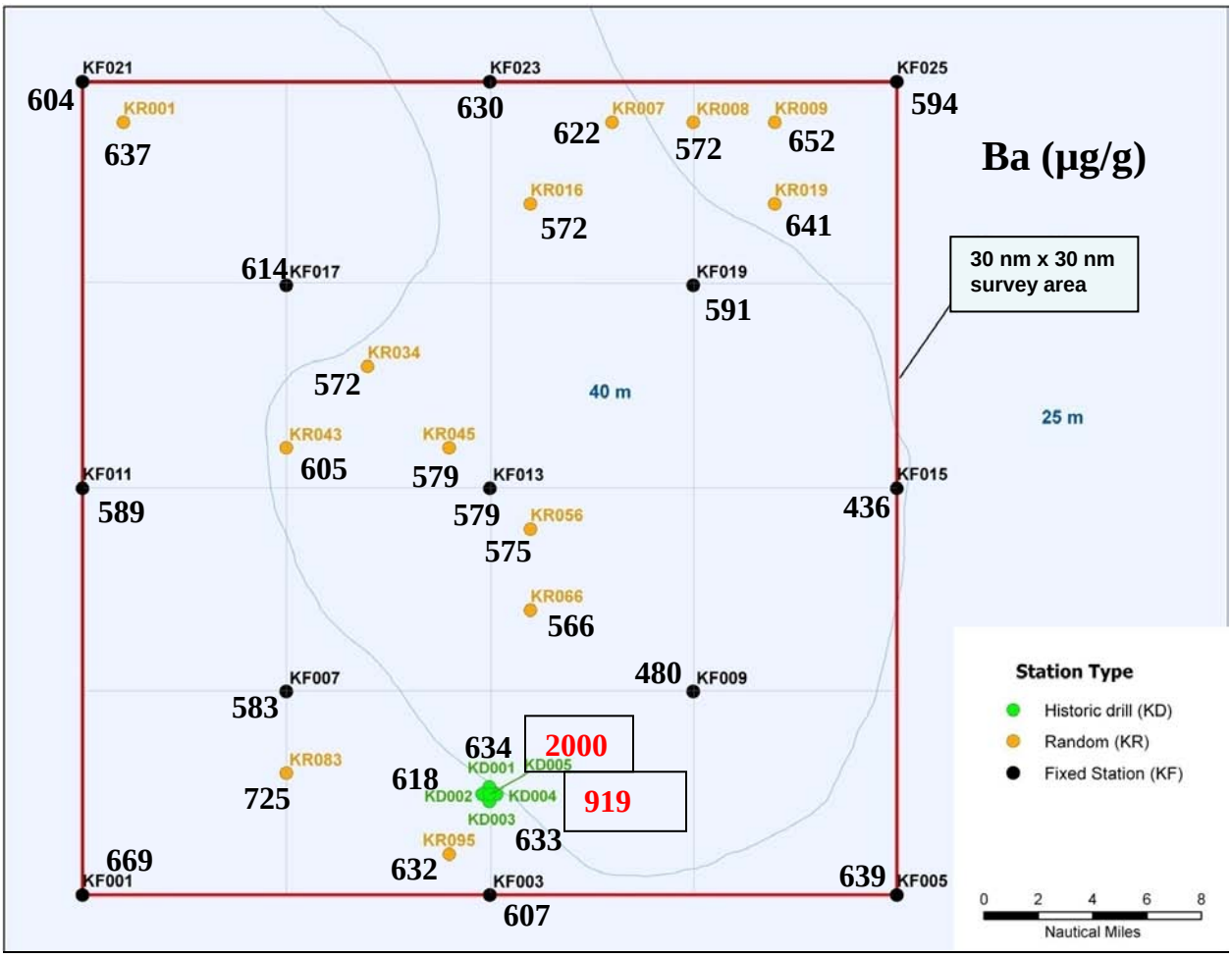


Figure 4-18. Map showing stations in Klondike area with concentrations of Ba in µg/g (dry weight). Numbers in rectangles are for samples that are believed to have residual Ba from previous drilling operations as discussed in the text.

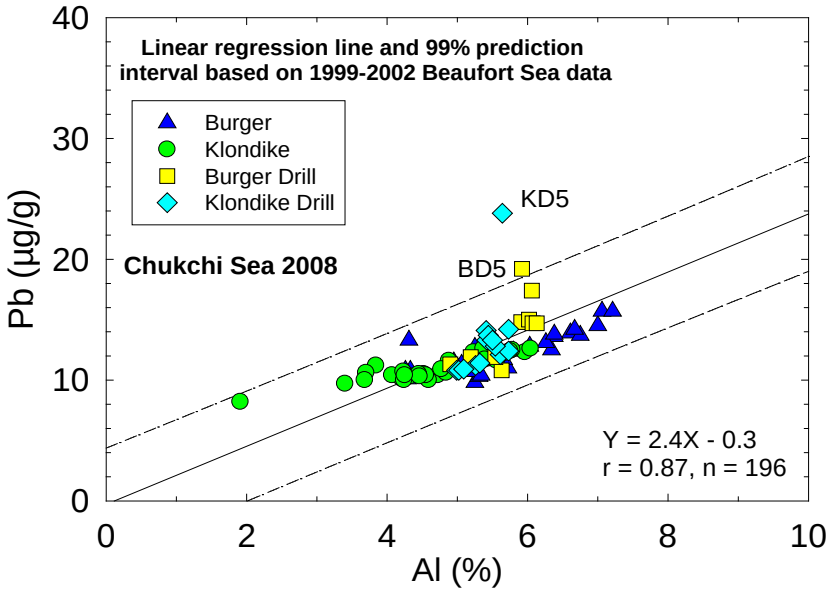


Figure 4-19. Concentrations of Pb versus Al for all sediments from the 2008 Chukchi Sea study. Equations and solid lines are from linear regressions using data for the coastal Beaufort Sea from Trefry et al. (2003), dashed lines show 99% prediction interval and r is the correlation coefficient.

Most Hg concentrations from the Burger areas plotted below the lower prediction interval on the Hg/Al graph that was prepared with a template from the Beaufort Sea (Figure 4-20). The other points plotted at or below the linear regression line. Thus, sediment Hg concentrations in Chukchi Sea sediments are lower, relative to Al, than previously found for the Beaufort Sea. When a linear regression was plotted for the 2008 Chukchi Sea data, three points plotted above the upper prediction interval. Two of the points were from the northern boundary of the Klondike area and no explanations for those anomalies are currently available. The third data point was sediment from the BD005 core. No relationship between Hg and Ba was observed in this study and the barite used in the drilling mud has not left an identifiable Hg signal in the sediments.

All Ag concentrations were <0.15 µg/g with a relatively small range in concentrations at 0.09 to 0.14 µg/g (Table 4-5 and Figure 4-21a). The Ag values from the 2008 Chukchi Sea survey fit within the prediction interval established on the Ag/Al plot based on data from the Beaufort Sea. No evidence of anthropogenic inputs of Ag were observed. The weak r value for Ag versus Al for the Beaufort Sea data (r = 0.57) also was obtained for the 2008 Chukchi Sea data (r = 0.47) because Ag concentrations were low and relatively uniform. Any significant anomalies in sediment Ag concentrations in the future will most likely be detectable due to the low natural Ag values.

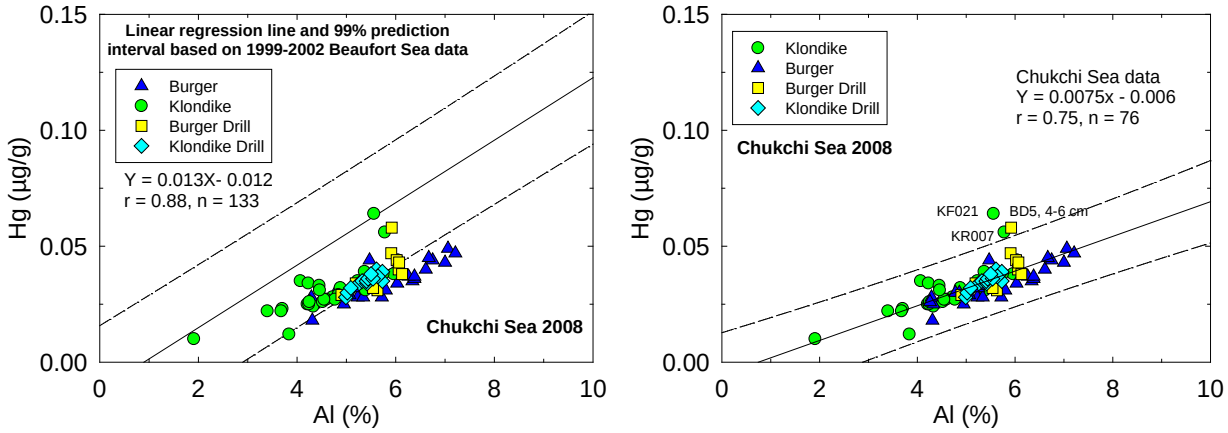


Figure 4-20. Concentrations of Hg versus Al for all sediments from the 2008 Chukchi Sea study. Equations and solid lines are from linear regressions using data for (a) the coastal Beaufort Sea from Trefry et al. (2003) and (b) the 2008 Chukchi Sea. Dashed lines show 99% prediction intervals and r is the correlation coefficient.

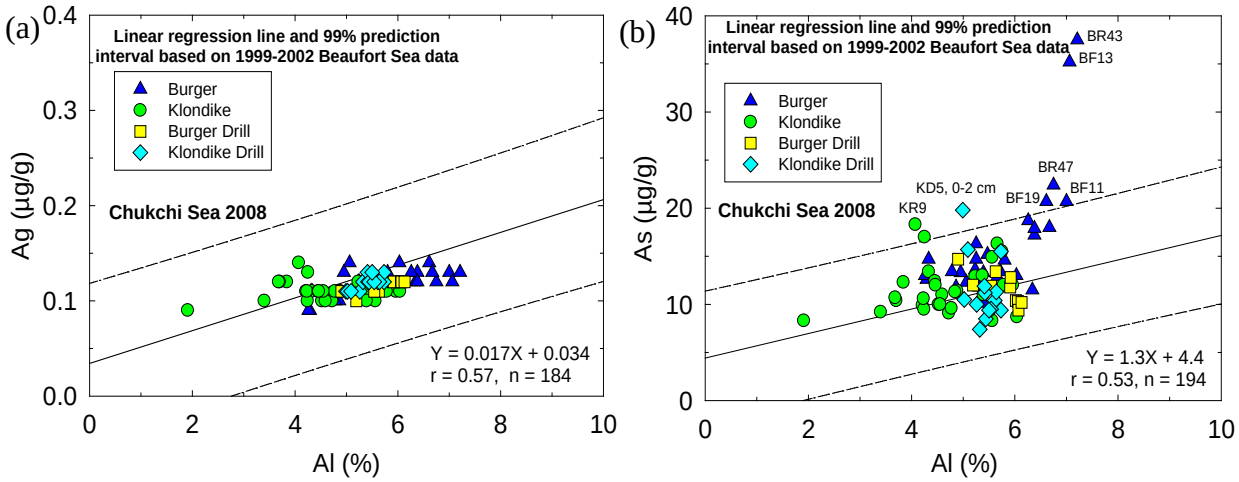


Figure 4-21. Concentrations of (a) Ag and (b) As versus Al for all sediments from the 2008 Chukchi Sea study. Equations and solid lines are from linear regressions using sediment data from the coastal Beaufort Sea from Trefry et al. (2003), dashed lines show 99% prediction intervals and r is the correlation coefficient.

Seven data points for As plotted above the upper prediction interval based on metal data for Beaufort Sea sediments (Figure 4-21b). Arsenic enrichment in the top 2 cm of the core from station KD002 was previously discussed as a likely diagenetic effect whereby As was remobilized in subsurface sediments and re-precipitated in surface, oxic sediments (Figure 3-21). As a result of this natural process, As concentrations in the core from station KD002 were depleted at sediment depths >2 cm relative to typical area sediments. The same process most likely explains the observed As enrichment in the other samples with elevated As concentrations.

Five of the seven As-rich samples from the Burger area track across the area from stations BF011 to BR043 to BF013 to BR047 and on to BF019 (see map, Figure 4-17). Furthermore, the surface sediments with the two highest As values (35 µg/g at BF011 and 38 µg/g at BR043) were enriched with Fe (Figure 4-12a) and contained TOC values of ~1.5% relative to an overall average of 0.88% TOC for the study area. Decomposition of organic matter is needed to create reducing conditions. Iron commonly follows a similar behavior to As and thus the observed Fe enrichment at stations BF11 and BR43 is consistent with the natural diagenetic process.

Concentrations of Se correlate relatively well (r = 0.85) with Al, excluding the four data points marked with inverse triangles (Figure 4-22). Selenium was not included in the Trefry et al. (2003) study of Beaufort Sea sediments. Sediments with the four anomalous points on Figure 4-22 also contained elevated concentrations of As. These enrichments were most likely due to a similar natural diagenetic process as described for As.

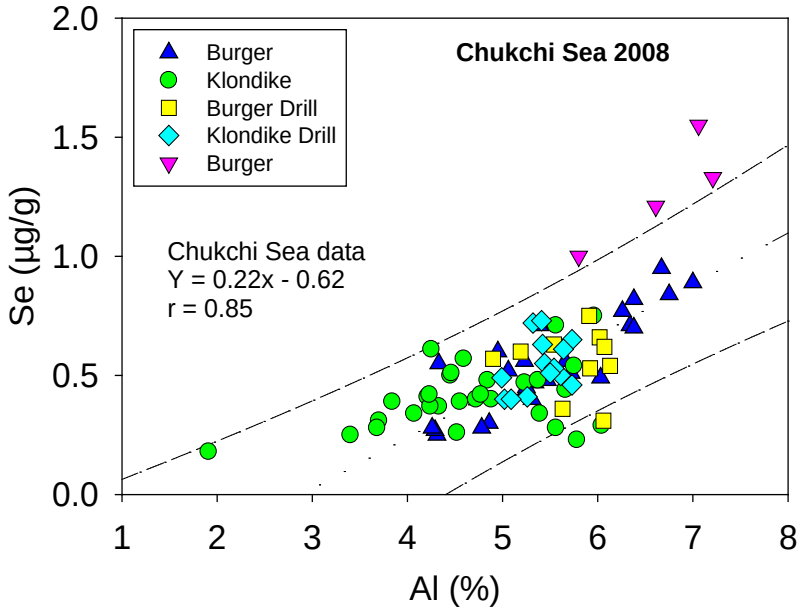


Figure 4-22. Concentrations of Se versus Al for all sediments from the 2008 Chukchi Sea study. Equation and solid line are from linear regressions, dashed lines show 99% prediction intervals and r is the correlation coefficient.

Concentrations of Al, Cr, Cu, Fe, Mn and Zn in sediments from this 2008 survey of the Chukchi Sea were very similar to concentrations of these metals reported by Naidu et al. (Naidu et al. (1997) for an overlapping area in the Chukchi Sea and for sediments in the coastal Beaufort Sea (Table 4-7). Most of the data for Fe and Al from Naidu et al. (1997) fit the prediction interval established using the 2008 data for the Chukchi Sea (Figure 4-23a). The four data points from the Naidu et al. (1997) data set that plotted above the upper prediction interval in Figure 4-23a may indicate that some variations in sediment minerals and the Fe/Al ratio exist in the Chukchi Sea. For example, two data points from the 2008 study plotted above the upper prediction interval (Figure 3-19a).

Table 4-7. Means, standard deviations (SD), maximums (max) and minimums (min) for concentrations of metals in all sediment samples from the 2008 survey in the Chukchi Sea.

Statistic	Silt + Clay (%)	TOC (%)	Al (%)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Mn (µg/g)	Zn (µg/g)
Chukchi Sea (this study)								
Mean (n = 82)	48	0.85	5.2	73.6	13.3	2.8	292	70.3
SD	17	0.34	1.0	13.6	3.3	0.6	52	16.6
Max	86	2.25	7.2	99.5	21.7	4.6	422	111
Min	8	0.07	1.0	9.7	2.5	0.5	78	10.7
Chukchi Sea (Naidu et al. , 1997)								
Mean (n = 31)	52	0.72	4.7	85.5	16.9	3.0	252	61
SD	34	0.38	1.9	26.5	6.1	1.3	97	22
Max	100	1.57	8.3	141	31	8.1	610	106
Beaufort Sea (Trefry et al., 2003)								
Mean (n = 88)	47	0.86	3.9	56.9	18.9	2.2	317	70
SD	30	0.70	1.6	23.4	10.5	0.9	144	31
Max	99	7.4	7.3	104	40	3.9	700	131
Min	1	0.1	1.1	13	4	0.7	72	15
Ave. Marine Sed.*	-	-	7.2	72	33	4.1	770	95
Ave. Cont. Crust**	-	-	8.0	126	25	4.3	716	65

*Salomons and Förstner (1984)
**Wedepohl (1995)

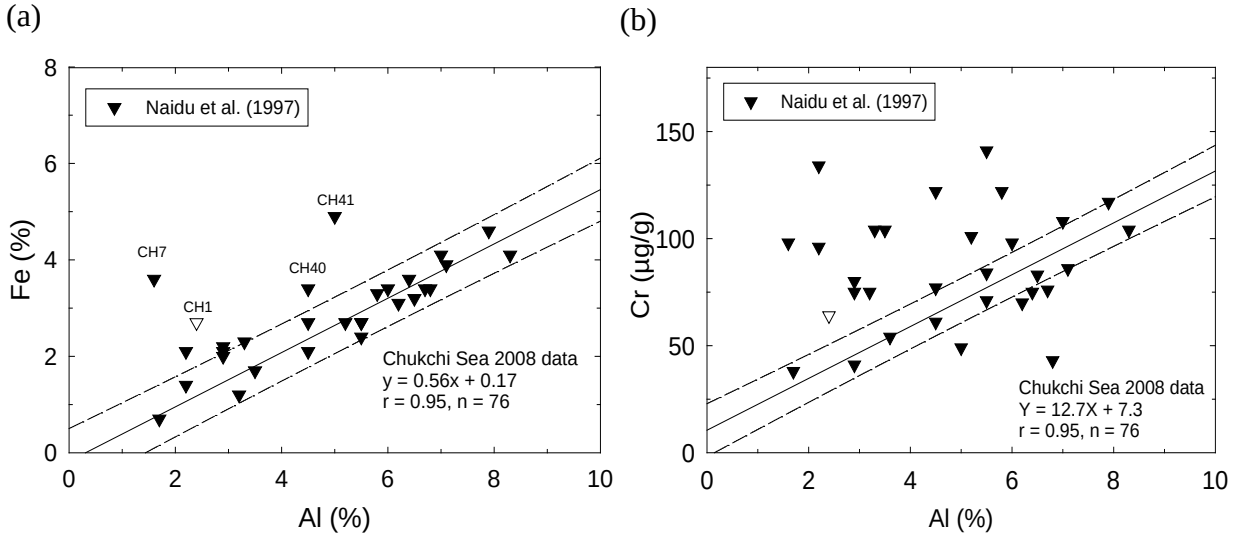


Figure 4-23. Concentrations of (a) Fe and (b) Cr versus Al for sediments from the 1997 study in Chukchi Sea by Naidu et al. (1997). Equations and solid lines are from a linear regression using data from the 2008 survey of the Chukchi Sea, dashed lines show 99% prediction interval and r is the correlation coefficient.

Data from Naidu et al. (1997) were a bit scattered on the Cr versus Al graph (Figure 4-23b) and no explanation for this scatter currently is available. Overall, previous sediment metal data from the Chukchi Sea (Lepke and Escowitz, 1989; Naidu et al., 1997) and the Beaufort Sea (Trefry et al., 2003) are in reasonably close agreement with the 2008 sediment data for the Chukchi Sea (Table 4-7) and represent in almost all cases, background concentrations in sediments.

4.3.1.2. Marine Invertebrate Tissues

Comparison of metal concentrations in marine invertebrates from the Burger and Klondike areas is limited to crabs with 9 data points for each area and worms with 9 data points from Burger and 6 data points from Klondike. No *Macoma* clams were collected from the Klondike area and only two samples of *Astarte* clams and zooplankton were collected from the Klondike area. The low abundance of bivalve mollusks in the Klondike area is associated with the lower benthic production in the Klondike than in the Burger area (Blanchard et al., 2010), due in part to different oceanographic regimes and nutrient inputs (Walsh et al., 2005; Chen et al., 2006).

Concentrations of As, Cd, Hg and Mn were significantly higher in crabs in the Klondike area than in the Burger area (t-test, 2-tailed, $\alpha = 0.05$, Table 4-8). These differences may be due to differences in metal concentrations in the water column or in other biota, or more likely to redox processes in sediments, leading to mobilization of these metals; however, no data are presently available to support such considerations. Concentrations of Ba and Cr were statistically higher in worms from the Klondike area than the Burger area (Table 4-8); these two metals would be most impacted by sediment incorporation in the worms because the sediment concentrations of these metals are high relative to typical values for marine invertebrates.

A geographic comparison can be made for the clam *Astarte* from the 2008 survey in the Chukchi Sea because a sizeable data set is available for the Beaufort Sea for several years between 1986 and 2006. The results show that concentrations of As, Ba, Cr, Cu, Fe, Hg, Pb and Zn in *Astarte* from the Chukchi Sea are not significantly different from values determined for the Beaufort Sea (Figures 4-24 and 4-25). In contrast, clams from the Chukchi Sea contain higher concentrations of Cd and lower concentrations of Mn than clams from the Beaufort Sea (Figures 4-24 and 4-25).

In addition to the comments presented in Section 3 about metals in the biota, several additional points are provided below for the samples from the Burger area where all species of marine invertebrates were collected. The highest average concentrations of all metals except Cd, Cu, Se and Zn were found in worms (Tables 3-9 and 4-8; Figures 3-23, 3-24, 4-26 and 4-27). Concentrations of Cd and Se were highest in *Astarte* with highest Cu in crabs, and the highest Zn in amphipods. The results for the worms do not provide a reliable measure of tissue residues because of abundant sediment in their guts. The lowest concentrations of all metals except Cr, Fe, Mn and Pb were in the zooplankton that bioaccumulate metals from the ambient water and phytoplankton (Tables 3-9 and 4-8; Figures 3-23, 3-24, 4-26 and 4-27). However, as expected, there is no evidence of trophic transfer of any metals from zooplankton to benthic fauna (Tables 3-9 and 4-8, Figures 3-23, 3-24, 4-26 and 4-27). The higher concentrations of As, Cd, Hg, and Mn in crabs from Klondike than from Burger may be related to dissolution of iron and manganese oxides at low sediment redox values, releasing adsorbed metals.

Table 4-8. Means, standard deviations (SD), maximum (max) and minimum (min) concentrations of metals in biota from the Klondike area. Numbers in bold, underlined and shaded are significantly greater than the corresponding value for the same metal and organism from the other study area (t-test, 2-tailed, α = 0.05). No t-tests were carried out for the clams and zooplankton because only 2 data points were available from the Klondike area for each metal.

Statistic	H_2O (%)	Ag (µg/g)	As (µg/g)	Ba (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Hg (µg/g)	Mn (µg/g)	Pb (µg/g)	Se (µg/g)	Zn (µg/g)
Crabs from Burger													
Mean (n = 9)	71.2	0.73	9.2	11.7	1.09	0.63	43.4	350	0.026	24.4	0.16	2.9	63.1
SD	1.5	0.33	1.3	1.2	0.31	0.10	16.5	99	0.006	7.8	0.04	0.6	4.0
Crabs from Klondike													
Mean (n = 9)	74.4	1.0	24.9	12.7	3.0	0.90	51.3	443	0.066	38.5	0.19	3.8	68.2
SD	2.7	0.5	3.4	1.8	0.66	0.36	9.8	118	0.020	16.0	0.04	0.7	6.0
Worms from Burger													
Mean (n = 9)	80.5	1.7	20.3	35.3	7.4	2.1	18.6	4,080	0.206	55.7	1.9	4.6	74.0
SD	2.6	0.8	4.8	5.7	2.3	0.4	3.0	705	0.059	8.0	0.4	1.0	6.9
Worms from Klondike													
Mean (n = 6)	78.7	1.4	23.2	42.2	7.3	3.2	17.5	4,480	0.256	63.0	2.2	4.4	75.1
SD	2.0	0.4	5.6	4.2	2.3	0.5	1.3	610	0.073	8.0	0.1	0.3	8.2
Clams (Astarte) from Burger													
Mean (n = 16)	82.3	0.22	12.1	11.9	37.8	1.3	9.3	1,416	0.054	21.6	0.72	9.0	81.7
SD	1.4	0.16	1.4	5.4	8.6	0.3	1.4	754	0.020	12.1	0.09	0.5	8.7

Table 4-8. Means, standard deviations (SD), maximum (max) and minimum (min) concentrations of metals in biota from the Klondike area. Numbers in bold, underlined and shaded are significantly greater than the corresponding value for the same metal and organism from the other study area (t-test, 2-tailed, α = 0.05). No t-tests were carried out for the clams and zooplankton because only 2 data points were available from the Klondike area for each metal, continued.

Statistic	H_2O (%)	Ag (µg/g)	As (µg/g)	Ba (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Hg (µg/g)	Mn (µg/g)	Pb (µg/g)	Se (µg/g)	Zn (µg/g)
Clams (Astarte) from Klondike													
Mean (n = 2)	83.1	0.13	10.7	37.5	14.5	1.1	9.9	738	0.057	67	0.59	7.5	81.2
SD	1.1	0.02	0	0.3	0.6	0.1	1.1	298	0.003	62	0.11	0.05	10.7
Zooplankton from Burger													
Mean (n = 5)	94.7	0.019	1.3	7.4	0.58	0.73	3.2	850	0.008	16.6	0.81	0.80	21.9
SD	0.4	0.003	0.2	1.5	0.10	0.11	2.0	120	0.002	3.1	0.16	0.16	5.9
Zooplankton from Klondike													
Mean (n = 2)	94.6	0.057	2.2	14.6	1.0	3.2	7.8	1,875	-	68.8	2.7	1.4	878
SD	0.8	0.004	0.1	2.4	0.4	1.0	5.1	587	-	24.3	0.1	0.3	20

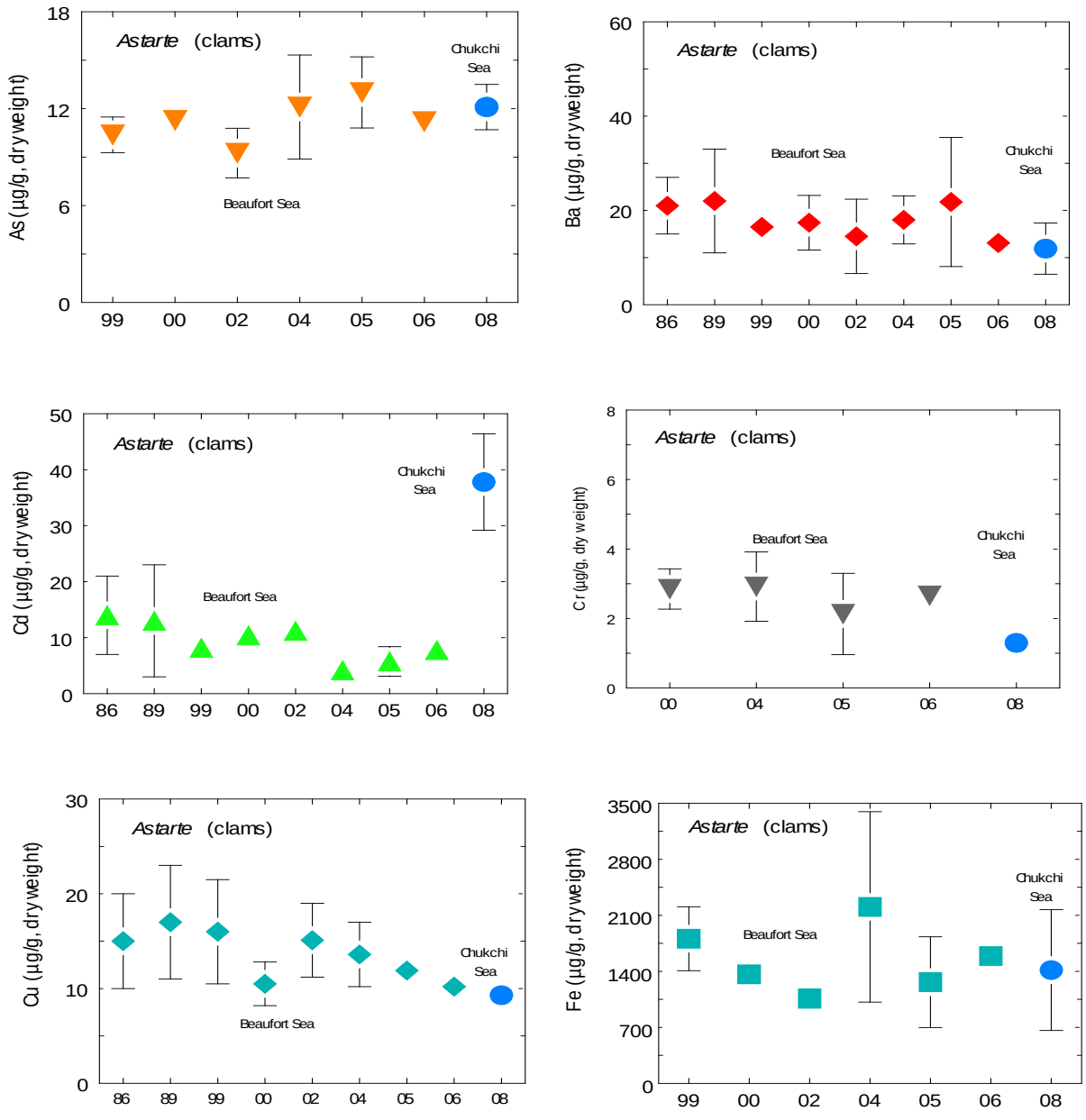


Figure 4-24. Concentrations of As, Ba, Cd, Cr, Cu and Fe in clams (*Astarte*) from the Beaufort Sea for selected years between 1986 and 2006 and from the Chukchi Sea for 2008. Markers show mean values and bars show standard deviations.

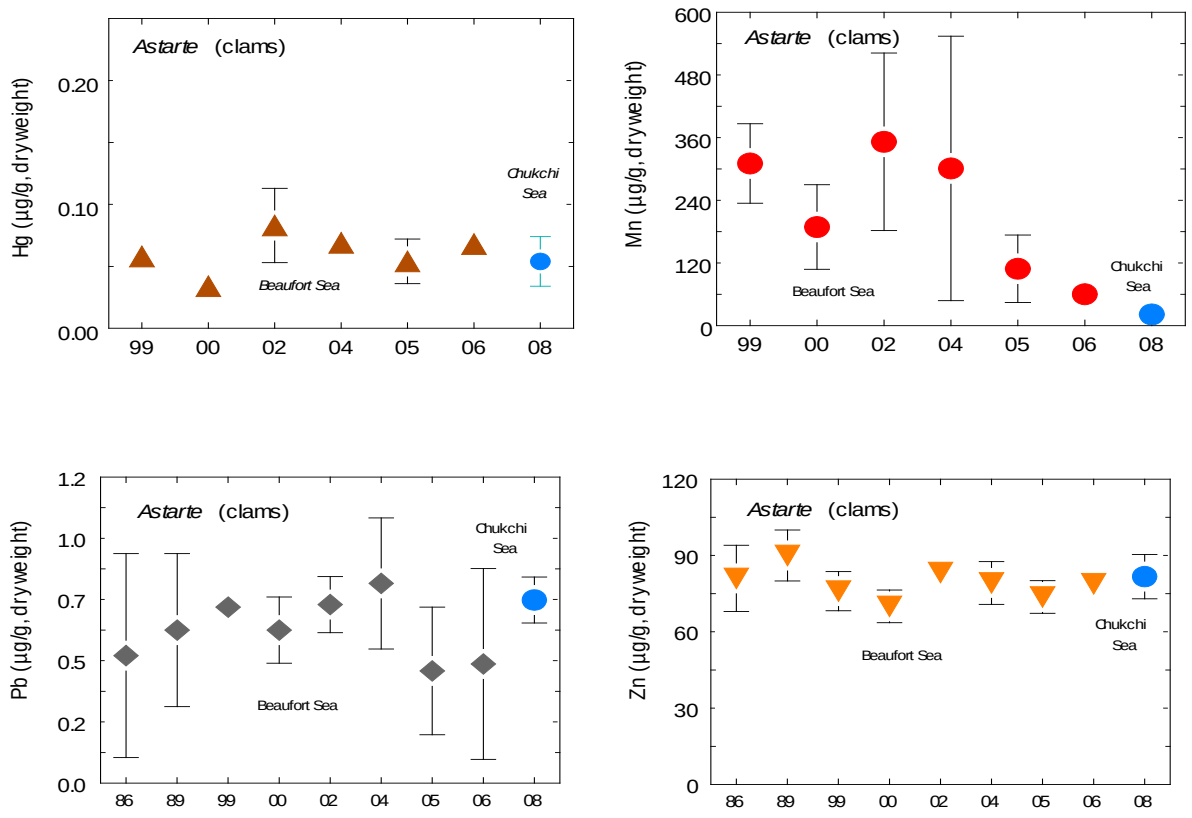


Figure 4-25. Concentrations of Hg, Mn, Pb and Zn in clams (*Astarte*) from the Beaufort Sea for selected years between 1986 and 2006 and from the Chukchi Sea for 2008. Markers show mean values and bars show standard deviations.

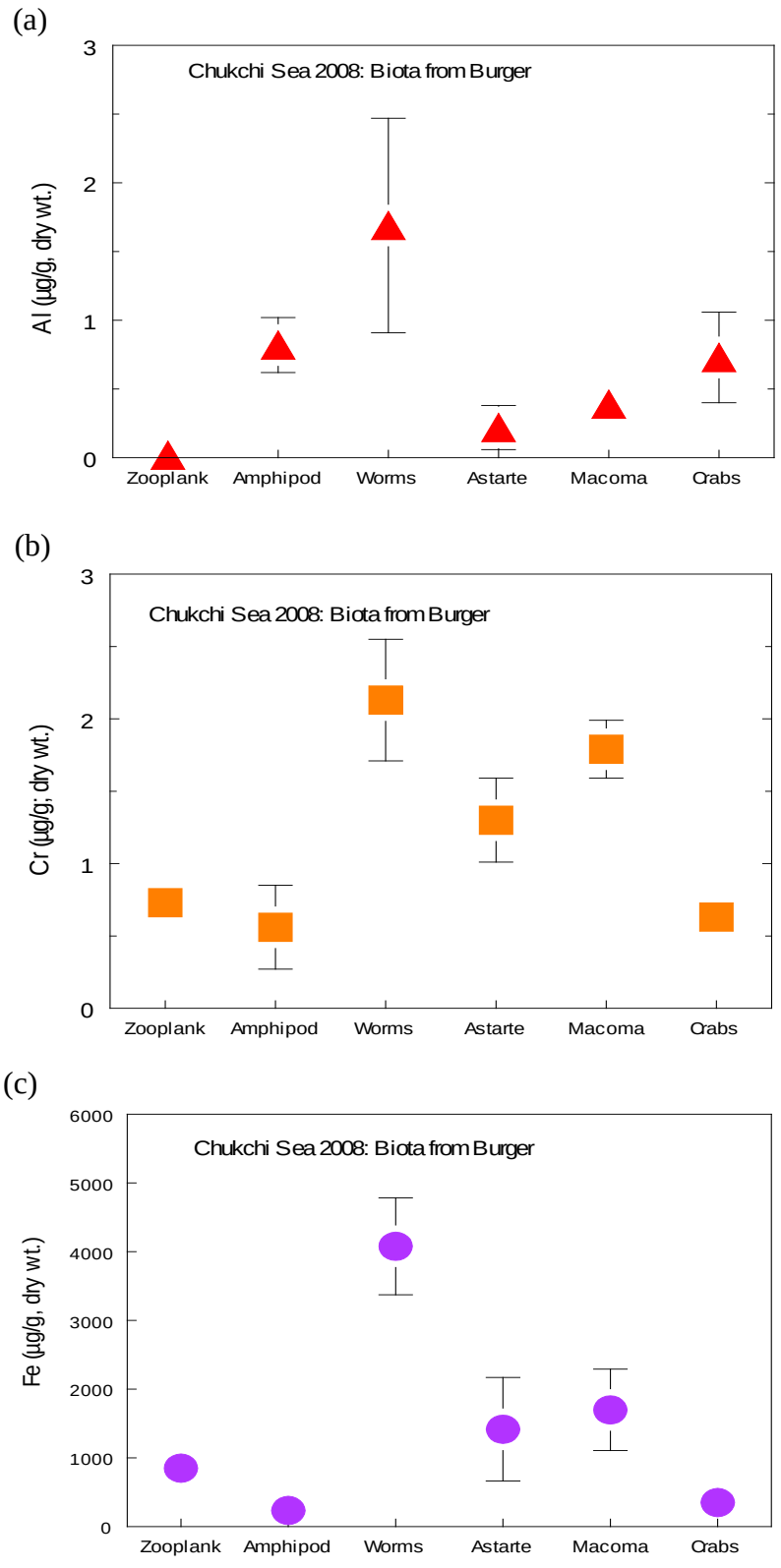


Figure 4-26. Concentrations of (a) Al, (b) Cr and (c) Fe in biota from the Burger area.

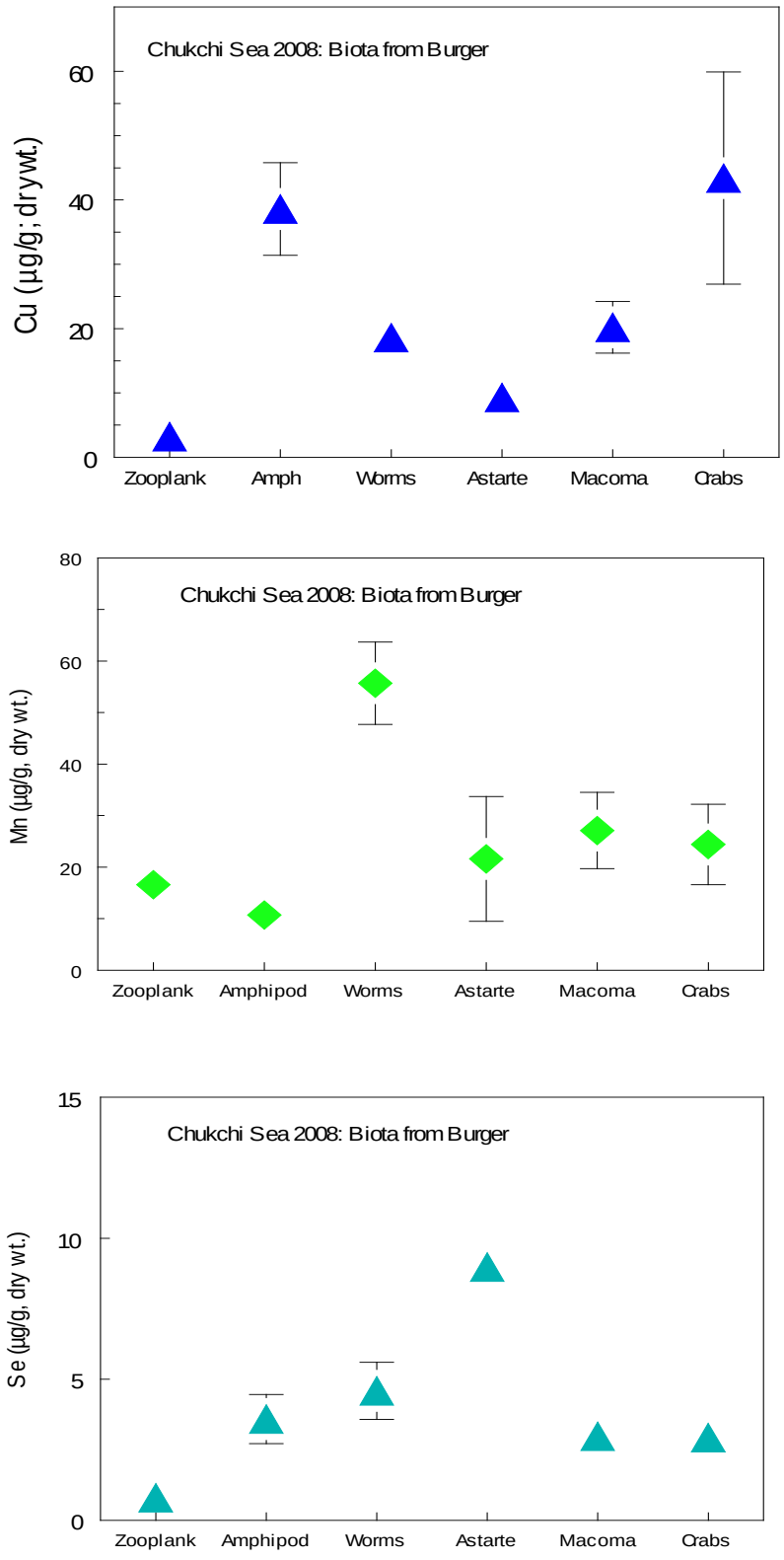


Figure 4-27. Concentrations of (a) Cu, (b) Mn and (c) Se in biota from the Burger area.

4.4. Ecological Significance of Hydrocarbon and Metals Concentrations in Sediments and Marine Invertebrate Tissues in the Chukchi Sea

4.4.1. Hydrocarbons

A technique of evaluating the significance of the measured sediment hydrocarbons to overall ecological risk of the region involves comparisons to sediment quality guidelines. Sediment quality guidelines have been developed to assess possible adverse biological effects from metals, polychlorinated biphenyls (PCBs), pesticides, and PAH. The commonly utilized criteria are the Effects Range-Low (ERL) and Effects Range-Median (ERM) from Long et al. (1995). The guidelines can be interpreted to indicate that adverse biological effects are "rarely" (<10% of the time) observed when individual metal or TPAH concentrations in sediments are lower than the ERL, "occasionally" observed when metals or TPAH is present at concentrations between the ERL and ERM, and "frequently" observed when concentrations exceed the ERM. However, O'Connor (2004) demonstrates that the ERL is a poor predictor of the maximum non-toxic concentration of a chemical in marine sediments. Concentrations of metals and PAH usually are higher in fine-grained than coarse sediments, and toxicity of these chemicals also is higher (lower concentrations are associated with toxicity) in fine than coarse sediments. In relatively pristine environments, such as the Beaufort and Chukchi Seas, the toxicity of metals and PAH in sediments is dependent on the chemical form of the metal and PAH in the sediments. Chemicals that are tightly bound to sediment particles and POC have a low bioavailability and toxicity compared to the same chemicals in solution or associated with an oil phase in sediment pore water (Neff, 2002).

A comparison of TPAH concentrations in all Chukchi Sea sediments to the ERL and ERM guidelines shows that none of the TPAH concentrations determined in this study exceed the ERL (Figure 4-28). Station KD005 had the highest measured TPAH concentration at 3,082 μg/kg, which was well below the ERL value of 4,022 μg/kg. Similarly, the individual PAH concentrations did not exceed the ERL for the individual 13 PAH with a couple of exceptions. Naphthalene at Station KD005 at 0-2 cm was detected at 495 μg/kg above the ERL value of 240 μg/kg. The C1-naphthalene parameter in this study is reported as the sum of the two individual naphthalene isomers – 1-methylnaphthalene and 2-methylnaphthalene. The C1-naphthalenes values for the six Station KD005 sediments ranged from 77 to 593 μg/kg and were higher than the ERL value listed for the single 2-methylnaphthalene isomer (70 μg/kg). Given that most of the PAH appear to be tightly bound to sediment organic matter, as discussed above, it is highly likely that the concentrations of individual and total PAH are well below concentrations that might be toxic to benthic marine invertebrates inhabiting the sediments.

Olsen et al. (2007) used benthic microcosms to study the effects of oily sediment on benthic infaunal communities from the Barents Sea (Arctic) and Oslofjord (temperate). There was a significant decrease in a few species of infauna in the high oil treatment in both the Barents Sea and Oslofjord sediments. TPAH concentrations in the Barents Sea microcosms were 6634 μg/kg in surface sediments and 1765 ng/L in the water at the start of the experiment, well above the highest concentrations observed in Chukchi Sea sediments. Although the effects observed may have been caused by oxygen depletion on the oily sediments, the authors attributed the loss of a few benthic species from the sediments to the PAH and suggested that Arctic benthos is more

sensitive than temperate benthos. Nevertheless, these results confirm that the concentrations of TPAH in Chukchi Sea sediments are well below concentrations that might pose a hazard to sensitive Arctic benthic fauna.

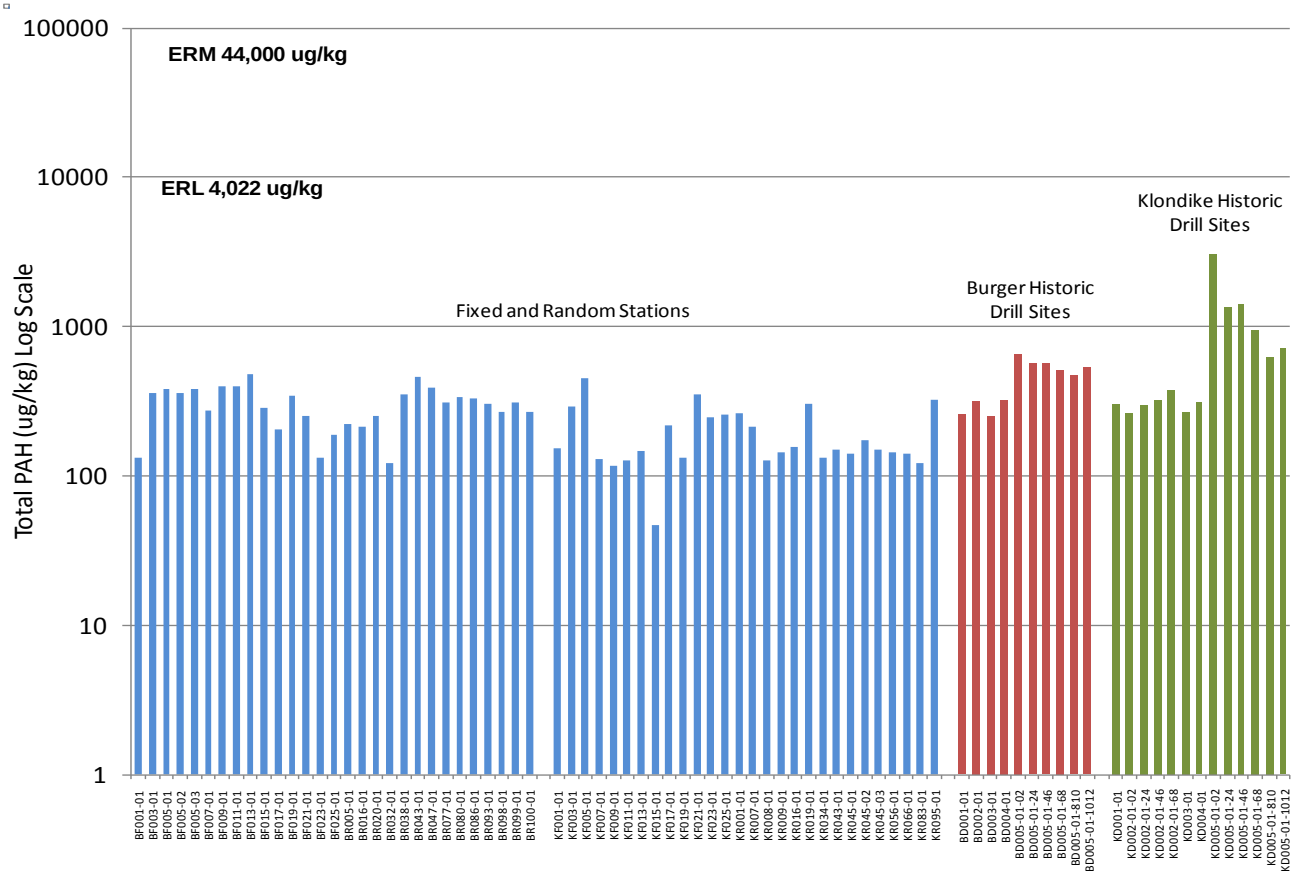


Figure 4-28. Comparison of TPAH concentrations in sediments from Burger and Klondike with sediment quality screening concentrations (Long et al., 1995)

Potential toxicity of the PAHs present in Chukchi sediments was further evaluated using EPA's Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures (USEPA 2003). Based on this approach, if the sum of Equilibrium Partitioning Sediment Benchmark Toxic Units ($\Sigma ESBTU_{FCV}$) 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. $\Sigma ESBTU_{FCV}$ values were calculated for each sediment sample with values ranging from 0.02 to 0.36, with the majority of values less than 0.10. The highest $\Sigma ESBTU_{FCV}$ values were associated with the Station KD005 sediments. The ESB approach provides evidence the concentrations of PAH present in the Chukchi sediments throughout the study area are not toxic to benthic organisms.

4.4.2. Metals

Concentrations of Ag, Al, Cd, Cr, Fe, Mn and Zn in sediments clearly were at background values and, therefore, the sources of these metals to the sediments of the Chukchi Sea are natural and most likely include natural levels of metals in clays and heavy minerals in local sediments (Mull, 1989) and runoff of soils/sediments via rivers and coastal erosion Trefry et al. (2009). Based on the metal versus Al regressions presented above, concentrations of As, Ba, Cu, Hg, Pb and Se one or more sediment samples are above the upper prediction interval on metal versus Al plots for Chukchi Sea sediments; this does not mean that the sediments are necessarily contaminated with these metals (Tables 4-6 and 4-7).

For example, enrichment of As in sediment at 7 locations and Se at 4 locations is most likely due to a natural diagenetic process that leads to surface enrichment of these metals in sediments where there is a sharp gradient of decreasing redox potential with depth in sediments.

Concentrations of Ba in sediments were elevated above background values by greater than a factor of 3 at three of the 63 stations sampled. These three stations were in the vicinity of previous drill sites where drilling mud and cuttings were discharged to the sea. The likely source of this Ba is barite (barium sulfate), an insoluble weighting agent present at high concentrations in most drilling muds (Neff, 2010). Concentrations of Pb were enriched in two of the Ba-rich samples and values for Cu and Hg were slightly enriched in sediments at one of the stations with elevated Ba concentrations (Table 4-6). These Pb, Cu and Hg enrichments are small, and concentrations are in the range expected for fine-grained marine sediments from other locations; thus it is difficult to identify metal sources; however, it may be due to minor enrichment in the drilling mud or cuttings.

Many attempts have been made to develop sediment quality guidelines to help identify sediment metals concentration that could harm benthic communities (e.g., Long et al., 1995; MacDonald et al., 1996; Field et al., 1999; USEPA, 2005). As described above, Effects Range Low (ERL) and Effects Range Median (ERM) guidelines have been developed for several metals (Long et al., 1995). The ERL/ERM sediment guidelines and other guidelines for metals have similar or even greater limitations than guidelines for PAH, discussed above (O'Connor, 2004; Simpson and Batley, 2007). The marine toxicity of metals depends strongly on metal species and physical form. For example, arsenite (As III) is more toxic than arsenate (As V) but is stable only under suboxic conditions (Neff, 1997); chromate salts (Cr VI) are much more toxic than chromic salts (Cr III) of the low solubility of the latter (Neff, 2002). The metals in drilling mud barite are present primarily as insoluble sulfides that are not bioavailable or toxic (Neff, 2008). Thus, sediment quality guidelines for metals in marine sediments should be used only to identify sediments that warrant further evaluation.

Five metals (Ag, Cd, Hg, Pb and Zn) of the 11 trace metals investigated during this study have been assigned realistic ERL and ERM concentrations by Long et al. (1995). These guidelines are continually 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 and Cu as the values for the ERL (Long et al., 1995) are lower than typical continental crust (Wedepohl, 1995). For example, the ERL for Cr is 82 µg/g when average continental crust contains Cr at 126 µg/g and average marine sediments have Cr values that average 72 µg/g (Table 3-6). The choices of

ERL values for Cr and Cu were most likely taken from a database compiled by Long et al. (1995) that used metal concentrations from an acid leach of the sediment rather than a total digestion. For example, only a minor fraction (<25%) of the total Cr is removed by a strong acid leach (Trefry and Presley, 1976; Sinex et al., 1980). Thus, a leachable Cr value equal to the ERL level of 82 µg/g is more likely comparable with a total Cr level of >200 µg/g, a value considerably higher than Cr values for continental crust or any samples from this study. Similar trends can be shown for Cu and the ERL values for these two metals need to be revised in future iterations of the sediment quality criteria.

Overall, the sediment quality data should be used primarily as a guideline at this time. No concentrations of any of the five metals (Ag, Cd, Hg, Pb and Zn) in all sediments from the 2008 survey of the Chukchi Sea exceeded their respective values for the ERL or ERM (Table 4-9). Therefore, adverse biological effects, attributed to metals concentrations, are extremely unlikely. No sediment quality criteria are available for Ba however, Starczak et al. (1992) found no significant differences in growth rates for the polychaete (worm) *Mediomastus ambiseta* between natural sediments and sediments containing 10% barite (Ba at ~50,000 µg/g).

Table 4-9. Values for the effects range low (ERL) and effects range median (ERM) from Long et al. (1995) along with highest metal concentrations in sediments from this study and summary of number of stations with data points that exceeded the upper prediction interval (UPI) on metal versus Al graphs or exceeded the ERL or ERM.

Metal	Highest Concentration (this study) (µg/g)	ERL	ERM		No. of stations with values >UPI in surface sediments	No. data points >ERM	No. data points >ERL
Ag	0.14	1.0	3.7		0	0	0
As	37.5	-	-		7*	-	-
Ba	2,420	-	-		4* and 3**	-	-
Cd	0.26	1.2	9.6		0	0	0
Cr	99.5	-	-		0	0	-
Cu	21.7	34	270		1	-	-
Hg	0.064	0.15	0.71		3	0	0
Pb	23.8	46.7	218		2	0	0
Se	1.55	-	-		4*	-	-
Zn	111	150	410		0	0	0

*Enrichments believed to be due to natural diagenetic processes.
**Enrichments believed to be due to anthropogenic inputs.

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5.0 CONCLUSIONS

5.1. Sediments

- Sediments in the Burger survey area contain slightly higher concentrations of fine-grained, silt/clay sediments and total organic carbon (TOC) than sediments from the Klondike survey area. Hydrocarbons and most metals are associated primarily with the organic fraction of fine-grained sediments, and their concentrations tend to be higher in Burger than Klondike sediments.

- Hydrocarbon concentrations and distributions are variable in surface sediments throughout the Burger and Klondike survey areas, with higher concentrations in some surface and subsurface sediments at the historic drill sites at Klondike and Burger. The concentrations of all the hydrocarbon types in sediments are well within the range of the background concentrations reported by other studies in Alaskan coastal and shelf sediments, with the exception of surface and subsurface sediments at the two historic drill sites.

- Surface and subsurface sediments from the two historic drill sites contain higher concentrations of all hydrocarbon types than sediments from the rest of the survey areas, particularly TPAH and total S/T, than the surface sediments from the other stations. There were higher concentrations of TPAH and total S/T in the sediments from the Klondike drill site than the Burger drill site, which may be related to the fact that drilling in 1989 discovered crude oil at Klondike and gas and condensate at Burger.

- The same pattern of elevated concentrations at the former drill site is evident for barium, which is a well-known indicator of drilling mud and cuttings accumulation on the sea floor. Highest concentrations of Ba are in the upper 6 cm of a sediment core from the Klondike drill site, in reasonable agreement with the expected sediment deposition rate at the drill sites. Barium concentrations throughout the core are four- to five-fold higher than concentrations in surface sediments from fixed and random stations in the Burger and Klondike survey areas.

- All concentrations of Ag, Al, Cd, Cr, Fe, Mn and Zn in sediments were at background values. Therefore, the sources of these metals in the sediments of the Chukchi Sea are natural and comparable to metals concentrations in suspended sediments in Arctic rivers, soils eroding from coastal cliffs, and natural accumulations of heavy minerals in coarse-grained Chukchi Sea sediments. Concentrations of Cu, Hg, and Pb were enriched in a few of the drill site sediment samples containing elevated concentrations of Ba. These metals may have been associated with drilling mud barite or drill cuttings discharged during exploratory drilling in 1989.

5.2. Marine invertebrates

- Concentrations of different hydrocarbon types are variable in tissues of marine invertebrates collected at the Burger and Klondike survey areas, with higher concentrations, in most cases, in invertebrates from Klondike. Hydrocarbons may be more tightly bound to Burger sediments, which contain higher concentrations of fine sediments and TOC, than Klondike sediments, and, therefore may be less bioavailable.

- Concentrations of TPAH vary by a factor of about 10 in surface sediments and clam tissues collected in the two survey areas. TPAH concentrations in the other invertebrate taxa are less variable (2.3 to 4.7-fold), reflecting their ability to rapidly excrete accumulated PAH.

- There is little relationship between the concentrations of ∑SHC, total S/T, and total PAH in tissues of benthic invertebrates and the sediments where they reside. In most cases, concentrations are lower in tissues than in sediment, indicating that the sediment-bound hydrocarbons have a low bioavailability.

- PAH, SHC, TPH, and S/T in sediments and invertebrate tissues in the Burger and Klondike survey areas of the Chukchi Sea are derived from a variety of sources contributing to the background hydrocarbon concentrations. Hydrocarbons throughout the two survey areas are from a combination of biogenic, petrogenic, and pyrogenic sources. Most of the PAH in sediments and marine invertebrate tissues, particularly those from the two historic drill site, appear to be primarily from petrogenic sources, including peat, kerogens, and petroleum products. The TPH and SHC are primarily from natural biogenic sources.

- Concentrations of PAH in sediments and tissues of marine invertebrates from throughout the Burger and Klondike survey areas are below concentrations that might pose an ecological risk to marine animals of the Chukchi Sea.

- Concentrations of all measured metals in tissues of marine invertebrates from the Burger and Klondike survey areas were in the range found in the same or related species from the Beaufort Sea and other marine areas. Therefore, there is a very low risk of adverse biological effects from metals in Chukchi Sea sediments.

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