**Final Report**

# Trace Metals and Hydrocarbons in Sediments of the Beaufort Lagoon, Northeast Arctic Alaska, Exposed to Long-term Natural Oil Seepage, Recent Anthropogenic Activities and Pristine Conditions

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# ABSTRACT

There is a concern that anthropogenic contaminants discharged during petroleum-related activities can accumulate in the Beaufort Lagoon sediments. In response to this concern, concentrations of 12 metals were analyzed [copper (Cu), chromium (Cr), cadmium (Cd), nickel (Ni), vanadium (V), lead (Pb), tin (Sn), zinc (Zn), arsenic (As), barium (Ba), iron (Fe), and manganese (Mn)] in the mud fraction and total mercury (THg) and hydrocarbons [saturated compounds such as normal and isoprenoid alkanes, triterpanes, steranes and polycyclic aromatic hydrocarbons (PAHs)] determined in gross sediments collected at 22 locations at the lagoon and in one natural oil seep.

The concentrations of the metals and hydrocarbons are generally lower than those reported for polluted marine sediments. Comparison of time-interval metal data on sandy mud (>75% mud) and mud collected in 1977 and 2003, respectively, shows a significant decrease in vanadium but an increase in manganese and copper from 1977 to 2003. Presumably, the differences are ascribed to disparities in the granulometry of the two sediment sets. Correlation coefficient analysis suggests that most metals are co-precipitated with iron oxy-hydroxide or occur as metal-organic complexes. There was a net increasing southeast to northwest trend in the metal concentrations, which did not relate to a possible gradient from point source such as the natural oil seep or the Distant Early Warning (DEW, now defunct) line station.

The hydrocarbon components in the sediments are essentially of terrestrial and biogenic sources with undetectable petroleum inputs, which is supported by the Organic Carbon to Nitrogen ratio (OC/N), isotope ratios of organic carbon ($\delta^{13}$C) and nitrogen ($\delta^{15}$N) of organic matter. There is no evidence of the contribution of petroleum hydrocarbons to the lagoon sediments from the onshore oil seeps. The overall composition of the hydrocarbon profiles is very similar to those found in our previous studies in the sediments from Elson Lagoon and near-shore regions of the Colville Delta–Prudhoe Bay–Canning Delta. We saw no impression of the natural oil seep and anthropogenic activities on the sediment trace metals and the hydrocarbon profile. The metal and hydrocarbon data will serve as a baseline, which will be critical for ecological risk management of the North Slope in the context of contaminant inputs, and in the better understanding of the inorganic and organic geochemistry of Arctic sediments.

**Plate 1:** Dr. Naidu pointing at the oil seep discovered south of Nuvagapak Point, Beaufort Lagoon.



**Plate 2:** Dr. Kowalik in front of the ice-infested coast bluff with peat deposit eroding.

# BACKGROUND/RELEVANCE TO FRAMEWORK ISSUES

The North Slope of Arctic Alaska, consisting of the Coastal and Foothill Provinces north of the Brooks Range, and the contiguous nearshore zone are oil- and gas-bearing regions, which have a high potential for commercial reserves. During the past 30 years, gas has been extracted from the western sector of the North Slope (NPRA) to supply the energy needs of Barrow. The Prudhoe Bay field has been the focus of petroleum production in the North Slope region. More recently, a number of subsidiary onshore and offshore oil prospects on the central North Slope adjacent to Prudhoe Bay have either been opened for operation (Alpine, Kuparuk, Milne, Northstar, Endecott) or are at various stages of consideration for development (Liberty Prospect). As part of the forthcoming oil and gas development, the U.S. Department of Interior's Minerals Management Service (MMS) has proposed lease sale 186 scheduled for 2003, sale 195 scheduled for 2005, and sale 202 scheduled for 2007. At this point, all the sales would cover the same general area, and the latter two would re-offer unleased blocks. Further, all three blocks extend beyond three miles offshore (within the Federal jurisdiction north of the barrier island), extending approximately four to twenty miles seaward of the OCS boundary that begins three miles from the coast.

The Arctic National Wildlife Refuge (ANWR), particularly the 1.5 million acre coastal plain, which has potential petroleum reserves (titled the 1002 area), is one of the most contentious areas for oil drilling, because of the presence of a variety of wildlife habitats (Douglas et al., 2002).

The petroleum-related developmental and production activities (drilling, marine and onshore coastal traffic, and housing) and associated enhanced urbanization of the native villages close to the 186, 195 and 202 lease sale areas are bound to impact the nearshore environment of the North Slope, as suggested by the consequences of similar activities elsewhere in the adjacent coastal region. A likely result is the discharge of industrial and municipal effluents (mud, fluids and formation cuttings associated with drilling, dredging operations, sewage and garbage disposal and traffic emissions) laced with toxic trace metals and hydrocarbons into adjacent waters and/or on ice. Although all of the above cited lease sales are in the offshore region, it is probable that any anthropogenic contaminants discharged will be entrained in the littoral (alongshore) currents and transported inshore into the lagoons. There is also the possibility of accidental spilling of crude into the lagoons. Plans are to transport offshore crude by submarine pipeline to the shore via the lagoons. In the lagoons the particle-reactive contaminants can be subsequently concentrated in sediments by adsorption, ion exchange and organic complex formation, and/or physical co-deposition of the fine-sized effluent particulates with mud in the relatively low-energy lagoon environment.

That concentrations of trace metals in sediments of the Alaskan Arctic can occur as a result of the discharge of drill cuttings and mud is documented in field experiments conducted in Prudhoe Bay (Northern Technical Services, 1981), in the Canadian Beaufort Sea shelf (Macdonald, 1982) and by the investigations of Snyder-Conn et al. (1990) following drilling operations at three sites around Stefansson Sound, north Arctic Alaska. These studies demonstrated that the persistence of Ba, Cr, Pb and Zn, and elevated levels of Al (elements typically associated with drilling effluents) occurred in sediments around the discharge sites. Elsewhere, for example in Campbell, Australia, the impact of exploratory offshore drilling on benthic communities has been demonstrated (Currie and Isaacs, 2005). More recently, Naidu et al. (2001, 2003a), based on 30 years of time-series monitoring of contaminants, showed a significant increase in Ba and V in sediments of the Beaufort Sea nearshore from 1977 baseline values to values reported in 1997 following oil development activities. Thus, the lagoon sediments of the North Slope, if they were to be the ultimate sink for both organic and inorganic anthropogenic chemicals, could be a major source of contaminants for benthic animals, as well as organisms which have a close link with

sediments and which serve as transfer pathways of contaminants to higher trophic levels (Long et al., 1995, 1998; Thompson et al., 1999; Valette-Silver, 1999; Krantzberg et al., 2000; Lee et al., 2002; Mucha et al., 2005). The role of contaminated marine sediments as a source of toxic metals and hydrocarbons to benthos has been documented in many case studies (refer to an excellent summary in Weis et al., 2004). Environmental contamination is of particular concern in the Arctic where marine organisms being lipid rich, having a relatively simple and short food chain and low biodiversity, are vulnerable to bioaccumulation of toxic metals.

In response to the continued concerns for the fragile environment of the north Alaskan Arctic, especially in the context of the pending lease sales scheduled by MMS in 2003–2007 (tracts 186, 195 and 202), we have extended our investigations (Naidu et al., 2001; 2003a) to establish baselines on trace metals and hydrocarbons in the sediments of the Beaufort Lagoon (Fig. 1; a map showing the study area within ANWR is illustrated in Fig. 2). Other investigations of a similar nature in the North Slope nearshore are those of Sweeney (1984), Sweeney and Naidu (1989), Trefry et al. (2003) and Naidu et al. (2003b) on trace metals and those of Steinhauer et al. (1992) on hydrocarbons. We contend that the chemical baseline data established on nearshore sediments from elsewhere in the North Slope (Colville Delta–Prudhoe Bay–Barter Island and Elson Lagoon; Naidu, 1982, Naidu et al., 2001, 2003a and references therein) cannot be extrapolated to the Beaufort Lagoon and the adjacent nearshore region east of Barter Island. The Beaufort Lagoon, which is located at the remote eastern margin of the north Alaskan Arctic coast and far from intense industrial activities (Fig.2), has an environmental setting that sets it apart from lagoons located in the eastern and central North Slope. For example, the Beaufort Lagoon (unlike the latter lagoons) is backed by the lower slopes of mountains extending close to the water margin. Consequently, the rivers opening into the Beaufort Lagoon are of relatively higher competency and presumably have coarser sediment bedload. As the dispersal of the sediments is contained within a relatively closed basin with limited marine access, the lagoon can be an effective trap for the accumulation of sediment-borne contaminants. A unique feature of the Beaufort Lagoon region is the frequent piling up of sea ice against the seaward barrier beach, even in summer, with ice fragments set floating in the lagoon. Additionally, the Beaufort Lagoon consists of three contrasting environments: two of them, Angun Point in the northwest and Nuvagapak Point around a landing strip (Fig.1) have been subjected locally to long-term natural oil seeps (Plate 1) and recent military activities, respectively. The latter activities were related to a defunct Distant Early Warning (DEW) line station, and an airstrip, which is still active (Fig.1). The activities involved land vehicular, marine boat and aircraft operations. Presumably, these and related operations exposed the lagoon region adjacent to the station with refined petroleum products and metal contaminants, which are possibly lingering in sediments. The rest of the lagoon presumably has remained pristine. It is anticipated that the chemistries of the sediments from these diverse environments will be significantly different and will be in contrast to sediments that are known to be exposed to more recent and fresh petroleum input. For example, the sediments exposed to hydrocarbons from natural oil seeps will likely consist of weathered crude oil enriched with tar and other heavy hydrocarbons, those from Nuvagapak Point of refined oil products, and those from the pristine lagoon of hydrocarbons derived from natural biogenous (terrigenous and marine) sources with little or no petroleum input. In the case of sediments that are exposed to recent petroleum contamination, there will invariably be a predominance of unweathered crude, relatively enriched with lighter hydrocarbons. Thus, a difference in composition and concentration of trace metals in sediments, reflecting influence by the different sources, can be anticipated.

This report presents the highlights of a two-year study (2003–2005), which has as its major objective the measurement of the concentrations of a suite of 12 trace metals [copper (Cu), chromium (Cr), cadmium (Cd), nickel (Ni), vanadium (V), lead (Pb), tin (Sn), zinc (Zn),

arsenic (As), barium (Ba), iron (Fe), and manganese (Mn)] in the mud fraction (<63 μm size), and total mercury (THg), sediment grain size, organic carbon (OC) and hydrocarbons (normal and isoprenoid alkanes, triterpenoids and steranes and polycyclic aromatic hydrocarbons) in the gross sediments of the Beaufort Lagoon (Figs.1 and 2). The choice of the above metals and hydrocarbons is based on the fact that these chemicals are often present in drilling effluents, crude and petroleum development and production activities (Macdonald, 1982; Snyder-Conn et al., 1990; Neff, 2002). The purpose of this study was to close a gap in baselines for sediment metals and hydrocarbons for a remote region of the North Slope coast.

## HYPOTHESIS AND OBJECTIVES

We hypothesize that the compositions and concentrations of trace metals and hydrocarbons in the sediments of Beaufort Lagoon vary between the sectors that have been exposed to long-term (prehistoric) natural oil seep (enriched in weathered crude), recent military activities of a former DEW line station (with the input of anthropogenic metals and refined petroleum products), and the pristine environment (no inputs from oil seep, crude or refined petroleum or anthropogenic metal contaminants).

The primary objective of this study is to distinguish the concentrations of 12 metals (V, Cr, Cu, Ni, Zn, As, Cd, Pb, Sn, Ba, Fe and Mn) in the mud fraction (<63 μm size), and THg and hydrocarbons (polycyclic aromatics and saturated hydrocarbons such as normal and isoprenoid alkanes, triterpenoids and steranes) in gross sediments between regions of the Beaufort Lagoon that are presumed to be exposed to long-term natural oil seep, anthropogenic input of refined petroleum products and pristine conditions. The objective is also to establish current baselines on the above trace metals and hydrocarbons in sediments of the Beaufort Lagoon for the purpose of monitoring contaminants.

## MATERIAL AND METHODS

### *Samples*

In August 2003, sediment samples from the Beaufort Lagoon were collected at 22 selected stations (Fig.1; Table 1) spread over three sectors. The samples were collected from a Boston Whaler, using a Van Veen grab sampler. A suite of four sediment samples (BLO3-12, BLO3-13, BLO3-14 and BLO3-15) was collected east of Angun Point adjacent to a known onshore natural oil seep site (Lat. 69.918° N and Long. 142.395° W, personal communication, Jim Clough, July 31, 2003; refer also to USGS, 1983), and another suite (BLO3-20 and BLO3-4B) off an oil seep site (OS) discovered by us at the bank of a small stream located south of Nuvagapak Point (Fig. 1, Plate 1). We had intended to get closer to the shoreline at Angun Point to collect samples from that area, but it was not possible to navigate to the Point because of the presence of extensive shoals in the region. A third suite of samples (BLO3-4, BLO3-4B, BLO3-18, BLO-19 and BLO3-20) was collected around Nuvagapak Point, a region that was impacted by military activities connected with a DEW line station (now defunct) and an active aircraft landing strip. A fourth suite of samples (BLO3-1, BLO3-3, BLO3-5B, BLO3-6B, BLO3-9, BLO3-9B, BLO3-10, BLO3-11A, BLO3-16 and BLO3-17) was obtained from east of the lagoon and up current of Nuvagapak Point, a lagoon sector that is presumed pristine. Table 1 shows the coordinates for the sample locations, fixed by a GPS.

The film of surficial sediment in contact with the metal sampler was discarded to minimize metal contamination. The remaining surface oxidized 2 to 4 cm portion of each of the

grab samples was taken and split, using a Teflon spatula, into three sets of sub samples. Each of the splits was transferred into three separate I-CAM glass jars, two of which were prerinsed with acid- and deionized distilled water (for trace metal, grain size and organic carbon analyses) and the third jar pre-baked and the cap lined with aluminum foil (for hydrocarbon analysis). One set was sent to Dr. M. I. Venkatesan, subcontractor at the University of California, Los Angeles for hydrocarbon analysis. A second set was sent to the subcontractor Frontier Geosciences, Seattle for trace metal analysis. The third set was retained by the PIs for analyses of the grain size, organic carbon and nitrogen and their stable isotopes at the University of Alaska Fairbanks. All these sediment samples were stored frozen until analyses.

### *Laboratory Analysis*

The methods for the analyses of trace metals and hydrocarbons on sediments were essentially the same as those adopted in previously funded CMI/MMS studies elsewhere along the North Slope nearshore (Crecelius et al., 1991; Steinhauer and Boehm, 1992; Naidu et al., 2001, 2003a). Therefore, we believe that the chemical data obtained in this study will be valid for comparison with the previous database established for the North Slope region.

A brief description of the methods follows. Twelve metals (V, Cu, Cr, Ni, Zn, As, Cd, Pb, Sn, Ba, Fe and Mn) were analyzed in the mud fraction ($<63\mu m$ size) of the sediment samples and THg in gross sediment. The rationale for choosing the mud fraction for the above 12 metals and THg on the gross sediments has been discussed in our two previous CMI/MMS-funded studies on North Slope lagoon sediments (Naidu et al., 2001, 2003a). A 5-gram split of each sediment sample was suspended in deionized distilled water and the resulting slurry was sieved through a 230-mesh nylon screen to obtain the mud fraction. The mud was freeze-dried and pulverized using an agate mortar and pestle. A 0.5 gram aliquot of the dry powder was taken into a 140-ml Teflon bomb and digested in 25 ml of a high-purity concentrated acid mixture consisting of 7ml-HF +15ml-HNO3 + 3ml-HCl

in an oven at 130°C for 12 hours. After cooling to room temperature, the digest was diluted to 100 ml with water processed by a Milli-Q Ultrapur Water Purification System, and the diluted sample returned to its original bomb. The resulting solution was dried and then again dissolved in 10% HNO3 and made up to 29 ml by adding deionized distilled water. From the final solution the 12 metals listed above were analyzed using either a direct injection Zeeman graphite furnace atomic absorption spectrometer (GF-AAS), a Perkin-Elmer Elan 6100 quadrupole inductively coupled plasma mass spectrometer (ICP/MS) or a PSA Excalibur automated hydride generation atomic fluorescence spectrometer (for As, EPA method 1632). Total Hg (THg) was analyzed on a 0.01–1.0 ml aliquot of the solution retained in the bomb, following SnCl2 reduction and dual gold amalgamation pre-concentration, and using cold-vapor atomic absorption spectrometry (CVAAS) as outlined in Bloom (1992, 1999).

The QA/QC (quality assurance/quality control) protocol prescribed by the U. S. Environmental Protection Agency (EPA) and National Oceanic and Atmospheric Administration (NOAA) for metal analysis was followed. It consisted of determining analytical precision through replicate runs, checking analytical accuracy via analyses of two Certified Reference Materials (CRM), namely NIST 2709 and IAEA 405, analyzing spiked sample and reagent blanks, and using ultrapure reagents for all analysis. As in our previous CMI-funded investigations, the trace metal analysis was subcontracted to Frontier Geosciences Inc., Seattle, which in 1997 participated successfully in the NOAA/NIST (National Institute of Standards and Testing) round robin interlaboratory exercise NOAA/11 for certification of QA/QC. The National Research Council of Canada (NRCC) conducted this exercise. The rating for the Frontier Geosciences was good to excellent. The results of the QA/QC relating to trace metals on this study are presented and discussed elsewhere in the report.

The hydrocarbon analysis for n-alkanes, PAHs, triterpenoids and steroids was done on gross sediments and according to well-established methods (Venkatesan et al., 1980,

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1982, 1987; Venkatesan, 1994). After thawing the frozen sample the wet sediment was spiked with the following surrogates: deuterated n-alkanes (for n-alkanes) and hexamethylbenzene, dodecylbenzene and deuterated terphenyl (for PAHs). After solvent extraction and separation into individual compounds by GC the alkanes were quantified using a flame ionization detector. Tricyclic, di- and pentacyclic triterpenoids and PAHs were measured by GC/mass spectrometry. As in our last two CMI/MMS-funded investigations (Naidu et al., 2001, 2003a) 24 PAHs were analyzed, as well as six additional PAHs, which are routinely analyzed by NOAA/NS&T (NOAA/National Status and Trends Program) for QA. Dr. M. I. Venkatesan, UCLA, to whom the hydrocarbon analysis was subcontracted, successfully participated first in 1992 and then in 1999 in interlaboratory round robin exercises conducted by NOAA-NS&T/NIST. The QA/QC results on hydrocarbons pertaining to this study are enumerated elsewhere in this report.

At the Institute of Marine Science, University of Alaska Fairbanks (IMS/UAF) laboratory, the sediment grain size distributions were analyzed by the sieve-pipette method (Folk, 1968). The purpose of this analysis was to gain understanding of the influence of granulometry on the concentrations of trace metals and hydrocarbons. The contents of organic carbon (OC) and total nitrogen (N) and their stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) were determined at UAF, on carbonate-free mud, following the methods outlined in Naidu et al.

(2000) and using a Thermo Finnigan Model Delta Plus XP isotope ratio mass spectrometer (IRMS). The values of $\delta^{13}C$ ($^o/_{oo}$) are referenced to the V-PDB standard and those of $\delta^{15}N$ ($^o/_{oo}$) to air standard. The standard error of the isotope analysis is $\pm 0.2\%$.

*Statistical Analysis*

Statistical Analysis consisted of the determination of the correlation coefficients between trace metals, OC, N, and the silt and clay percents in the mud fraction, to deduce the geochemical partitioning of the metals in the mud analyzed. The comparison between two time intervals was obtained for the concentrations of selected trace metals in sandy muds (>75% silt and clay, after Naidu, 1981) collected in 1977, and mud of this study, using the student 't' test. Cluster analysis (Euclidean distances, Ward's linkage) was undertaken to identify grouping, if any, of stations based on the trace metal compositions surrounding the above two point sources and the pristine lagoon. This was followed by a principal component analysis of the trace metal data to correlate station group separation by cluster analysis with sediment variables. Surface trend analysis was conducted using trace metal data, granulometry and OC content to elucidate if there are any geographical gradient(s) in the individual sediment parameters and the metals from presumptive point sources; for example, the oil seeps and the abandoned DEW line station around Angun and Nuvagapak Points, respectively.

# RESULTS

The percents of solids, gravel, sand, silt, clay and mud in gross sediments and organic carbon (OC) and nitrogen (N), OC/N ratios (weight to weight basis of OC and N) and stable isotopes of OC and N ($\delta^{13}$C and $\delta^{15}$N) in the mud fraction of the individual samples are included in Table 1. In Table 2 are shown the concentrations (on a dry weight basis) of 12 metals (V, Cr, Mn, Ni, Cu, Zn, As, Cd, Sn, Ba, Pb and Fe) in the mud fraction and of total Hg in the gross sediments. Table 2 also provides the arithmetic and geometric means of the concentrations of the metals analyzed on the 21 samples and also the standard deviations and coefficient of variations (CV) of the analysis relative to each of the metals in the 21 samples analyzed.

The results of the QA/QC procedure for the trace metal analyses in reference to calibration verification, calibration blanks, spikes, replicate analyses (for precision determination), and assessment of the analytical accuracy based on Certified Reference Materials NIST 2709 and IAEA 405 are presented in Tables 3, 4, 5, 6, and 7, respectively. The correlation coefficients (r values) determined between the concentrations of silt, clay, OC, N and the 12 metals in the mud fraction are shown in Table 8. These correlations were determined by assuming the total percentage of silt and clay in the mud fraction to be 100%, and by prorating (recalculating) the silt and clay percents based on the relative percents of silt and clay in the gross samples. In Table 9 is shown the time-interval comparison for Beaufort Lagoon in the concentrations of selected trace metals on suites of muddy sediments collected in 1977 (Naidu, 1981) and mud sampled in 2003 (this study, Table 2). The concentrations of the *n*-alkanes, polyaromatic hydrocarbons, triterpanes and steranes in sediments are shown in Tables 10, 11, 12, and 13.

# DISCUSSION

## *Sediment Grain Size, Organic Carbon (OC) and Nitrogen (N)) and Their Isotope Compositions*

The Beaufort Lagoon has a mosaic of sediment types, consisting of sandy muds to muddy sands, with occasional gravel (Table 1). Sediments from stations BL03-4B, BL03-19 and BL03-20, have significant or predominant amounts of gravel (Table 1). The mud fractions of sediments, which were taken for trace metal, OC, N and isotope analysis, generally contain relatively higher contents of silt than clay particles. In the gross sediments, which were taken for Hg analysis, there are wide differences in the contents of sand relative to mud. We discuss later the possible control of granulometry on the concentrations of 12 metals in the mud fraction and Hg in the gross sediments.

Concentrations of organic carbon (OC) and total nitrogen (N) in the mud fraction of the Beaufort Lagoon sediments in this study (Table 1) are generally higher by a factor of 1.7 compared to the gross sediments from the Simpson Lagoon–Prudhoe Bay region and by a factor of 2.9 compared to gross sediments from the Beaufort Lagoon (Naidu, 1985). The higher content of OC in mud than in gross sediments is not surprising, because OC (tied with organic and clay mineral grains) is invariably co-deposited with hydraulically similar finer silt and clay (mud) particles and also that clay minerals concentrated in mud have the greater ability to adsorb organics. Coarser particles such as sand in gross sediments are generally not associated with organic particles of similar size and, therefore, their presence in gross sediments tend to dilute the OC contents.

The OC/N ratios, and compositions of stable isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) in the Beaufort Lagoon sediments (Table 1) indicate that all the samples consist predominantly of OC/organic matter derived from terrestrial $C_3$ plant sources, with minor input, if any, from marine or macrophyte sources. This interpretation is based on the conclusions of very exhaustive investigations relating to the isotopic and OC/N signatures of the end-member sources of OC/organic matter (terrestrial, marine phytoplankton, sea ice algae and marine macrophytes) in the coastal region of the Alaskan and Canadian Beaufort Sea (Naidu et al., 2000; Macdonald et al., 2004). Results of our studies on the sources of OC/organic matter in the Beaufort Lagoon sediments are consistent with those reported for the above areas and, as discussed later, with the conclusions on the sources of organics in the lagoon sediments based on the hydrocarbon composition. It is suggested that the high input of terrestrial OC/organic matter into the Beaufort Lagoon, as well as lagoons of the contiguous coastal region, is due to the large supply of sediments derived from the peat-rich shoreline, which has among the world's highest coastal erosion rates, 2–10 m/y, (Naidu et al., 2000, Macdonald et al., 2004 and references therein).

***Trace Metal Studies***

Quality Assurance/Quality Control (QA/QC): The results of the calibration verification procedure (Table 3), consisting of, for each metal, the known initial calibration verification-true value (ICV-TV) and the ICV-Observed value (ICV-OBS) showed that the percentage ICV recovery (ICV-Rec) for all metals except Fe was at acceptable levels (close to 100%). Likewise the blank analysis (Table 4), based on initial calibration blank (ICB) and the continuation calibration blank (CCB) on several runs, indicate very low contamination from the chemicals used throughout the analysis. Further, with reference to the use of spikes (Table 5) run in duplicates, and based on the values of the mean concentration of an individual metal via replicate analyses of a sample (Mean), Spike true value (Spike-TV) and observed spike value, we show that the spike percent recovery is close to 100% for all metals except Fe and Ba. The

reason for the consistent poor showings for Fe and Ba is unknown, but perhaps reflects the inherent limitation of the use of the ICP/MS technique. The analytical precision (Table 6), as suggested by the relative percent difference (RPD) on duplicate analytical runs of two sediment samples, would seem to be excellent for all metals except Hg, in which case it is very good and at acceptable levels (< 25%). Likewise, the analytical accuracy (Table 7), determined via certified values (Cert. value), analyzed or Observed values (Obs.Value) of two Certified Reference Materials (NIST 2709 and IAEA 405) are again at accepted levels for all metals with reference to both the standards, except for Cr and Cd for CRM NIST 2709 and Fe and Sn for CRM. The above discussion indicates that the QA/QC for the trace metal analysis is generally very good to excellent and our data are of high quality.

Trace Metal Distribution Pattern: In the following we discuss the results of the statistical analysis on the trace metal concentrations and their distributions in the mud fraction. The high coefficient of variations (%CV) about the mean for all the 13 metals (Table 2) obviously indicate that there are wide inter-sample variations in the concentrations of all the metals, with relatively low variability (<15% CV) for V, Cr and Fe. The reason for the high inter-sample variability in the THg contents may be ascribed to the differences in the sand content in the gross sediments, and for the rest of the metals in the silt and clay contents within the mud fraction. The other possible reason could be the differences in the contents of organic carbon (a measure of organic matter) between sediments. Yet another reason could be the differences in the Mn and Fe contents between the sediments analyzed. It is to be expected that the greater the amount of clay size particles, Mn and Fe contents, and/or larger content of organic carbon (and by implication organic matter) in the mud fraction or gross sediments, the relatively greater the concentrations of metals. This concentration could result from several likely processes, such as adsorption of metals on clays, formation of organic-metal complexes by ligand bonding, and/or co-precipitation of metals with Fe and Mn oxy-hydroxides. That such a granulometric

control on metal content is affected in the case of the Beaufort Lagoon mud is demonstrated by the significant (p< .05) positive correlations between all trace metals, except Cr and Ba, and the clay content. The positive significant correlations observed between all the trace metals and Fe, suggests that Fe as oxy-hydroxide has an important role in scavenging and accumulating the metals in the mud of Beaufort Lagoon. In this context, it is to be noted that all the 2–5 cm surficial sediments (portions analyzed for trace metals) showed, at the time of collection, a brownish ochre coloration distinct from the underlying gray layers, an indication that Fe in the mud analyzed is most likely present in an oxidized state. Additional detailed investigations on metal partitioning on sediments from Simpson Lagoon and Beaufort Lagoon (located east of the Colville Delta), based on sequential extraction techniques, further substantiate the role of Fe oxy-hydroxides in sequestering metals in the north Alaskan Arctic sediments (Sweeney, 1984; Sweeney and Naidu, 1989). Likewise, organic carbon and Mn in the mud (Table 8) to some extent bond selected few metals (Zn, Cd, As and Sn by OC, and Ni, Sn and Pb by Mn) by forming organic-metal or Mn oxide/hydroxide-metal complexation. This interpretation is consistent with our earlier conclusions on the partitioning of trace metals on lagoon sediments from a wide region off the North Slope coast, namely from the Colville Delta–Prudhoe Bay–Canning Delta area (Naidu et al., 2001 and references therein) and from an earlier study in the Beaufort Lagoon (Naidu et al., 1981; 2003b).

Further statistical treatment of the distributions of the trace metal concentrations in the Beaufort Lagoon mud are enumerated in the following:

*Univariate distributions and tests for normality*
Histograms, box-and-whisker plots and normal probability plots suggested that most metal concentrations were near-normally distributed, but there are a number of outliers for several of the metals (Figs.3 and 4). These are of concern in statistical modeling or hypothesis testing when normality is assumed. Outliers will have a strong influence on Pearson's correlations, cluster analyses and ordinations.

Observed outliers include:

Cd: 2 large values at stations BL03-19, and BL03-20

Cr: One low value at station BL03-4

Mn: One relatively large value at station BL03-4 and one large value at station BL03-17

Ni: Low value at station BL03-4, high value at station BL03-17 (and BL03-20?)

Pb: Large value at station BL03-17

Sn: Large values at stations BL03-17, BL03-19, and BL03-20

V: Low value at station BL03-4.

Based on outliers alone, several stations clearly stand out as unusual (Fig. 4). These are BL03-4, which has low concentrations of Cr, Cu, Fe, Ni, Pb, V, and Zn, and BL03-17, which is characterized by high concentrations of Cu, Mn, Ni, Pb, and Sn. Stations BL03-19 and/or BL03-20 have similarly high concentrations of some, but not all, of these metals (e.g. Sn, Ni). These two stations are easily identified as outliers in the multivariate analysis (cluster analysis, ordination, as follows).

*Cluster analysis based on metal concentrations*
A cluster analysis based on Euclidean distances clearly indicated the different metal concentrations at stations BL03-4 and BL03-17, which did not cluster with any of the other stations (Fig.5). These two stations had a very different sediment composition from most other stations with a very low percentage of silt in the mud fraction (< 3%). The remaining stations clustered into three groups. Only one of these groups (Group C, consisting of stations BL03-4B, BL03-19, and BL03-20) formed a geographically coherent cluster (Fig.6). Stations in group C were characterized by a relatively low percentage of silt in the mud fraction and a high percentage of organic matter. These stations contained relatively high concentrations of a number of metals such as Mn, Ni, Pb, Sn and Cd. Cluster A included the four westernmost stations near Angun Point, as well as a number of stations in the southeastern part of the lagoon. Cluster B consisted of the remaining stations in the southeastern part of the lagoon and also

included station 3, which was located immediately adjacent to the three cluster C stations. Cluster A and B were distinguished by differences in sediment composition with a higher percentage of clay in the mud fraction. Stations in cluster B had generally higher concentrations of all metals, although the differences in means were small for Mn, Ni, Cd and Cr. Figure 7 summarizes the clustering of stations based on metal concentrations.

*Principal components analysis based on metal concentrations*

Results from Principal Components Analysis (PCA) suggest that much of the variability in the metal concentrations (78%) can be accounted for by only two Principal Components (Fig. 8). The station clusters, identified in the cluster analysis, map well onto the PC ordination (Fig. 9) with a clear separation between clusters. Stations BL03-4 and BL03-17 are again identified as clear outliers in the biplot (Fig. 9).

The loadings for the first two PCs (Table 14) suggest that the PC 1 reflects the average concentration of all metals, with high concentrations corresponding to high values of PC 1. That is, metal concentrations tend to increase along the x-axis in Figure 9. The PC 2 contrasts Mn, Cd, and Sn with Ba. Large values of the second PC (above zero line in Fig. 9) correspond to high concentrations of Ba, while small values of PC 2 correspond to high concentrations of Mn, Cd, and Sn.

*Correlations between PC 1/PC 2 and latitude / longitude / sediment composition*

Table 15 presents correlations between PC 1 and PC 2 with latitude, longitude, silt (%) and OC (%). PC 1 is negatively correlated with latitude, implying that most of the metals (positive loadings on PC 1) decrease with latitude from southeast to northwest. PC 1 is also positively correlated with organic carbon content, reflecting a tendency for metal content to be higher at stations with high organic carbon content. This is also evident in the generally positive correlation between metal concentrations and organic carbon.

PC 2 is strongly correlated with the percentage of silt in the mud fraction, implying that Mn, Cd, Sn and Pb (metals that are negatively correlated with PC 2, see above) decrease with silt content, while Zn and Ba increase with mud content (this is also obvious in direct correlations between metal concentrations).

The above correlations are strongly influenced by the outlying stations (BL03-4 and BL03-17). Therefore, the correlations excluding those 2 stations were computed (Table 16).

After exclusion of the 2 "outliers", PC 1 was most strongly correlated with the proportion of silt in the mud fraction and the percentage of organic carbon. This implies a strong decrease in the silt fraction and an increase in the organic carbon along the x-axis in Fig. 9 (Group C > Group B > Group A). In contrast, the PC 2 is positively correlated with the silt fraction. Thus, the silt fraction increases along the y-axis in Fig. 9 (Group B > Group A > Group C).

*Multiple regressions of PC 1 and PC 2 with latitude, longitude and sediment characteristics*

PC 1: The model that best explained variability in metal concentrations (as reflected in PC 1) was a regression of PC 1 on the silt fraction and latitude (best model chosen based on Akaike Information Criterion (AIC)). The regression (Fig. 10, Table 17) captured 72% of the variability in PC 1 and also captured the strong decrease in PC 1 with the silt fraction and with latitude. While the silt fraction explained most of the overall variability, a significant effect of latitude on PC 1 remained after accounting for the effects of silt. This effect reflected a southeast-northwest gradient in metal concentrations that primarily separates stations BL03-10, BL03-12, BL03-13, and BL03-14 in the northwestern part of the lagoon (4 points on the lower right in Fig. 11) from the remaining stations.

The geographic gradient was confirmed by simple linear regressions of individual metal concentrations on latitude/longitude (rotated axis to reflect SE–NW direction), which showed significant increases ($p < 0.05$) from NW to SE in Cu ($t = 2.72$, $p = 0.016$), Zn ($t = 2.23$, $p = 0.041$), and Ba ($t = 2.90$, $p = 0.011$).

PC 2: The best model explaining variability in PC 2 was a simple linear regression on mud content, which explained 77% of the variability in PC2. After accounting for the effects of mud, there was no significant effect of latitude, longitude or other sediment variables. A "threshold" model that fits separate means at low and high mud concentrations fit slightly better (in terms of AIC) than the linear model (Fig. 12). Stations with low mud concentrations in the lower left of Fig. 12 were characterized by low values of PC 2, reflecting high concentrations of Mn and Sn and low concentrations of Ba. These included most of the stations in the northwestern part of the lagoon.

In summary, a PCA based on metal concentrations primarily separates stations with relatively high metal concentrations from stations with relatively low concentrations along PC 1 (56% of overall variability). PC 2 (23% of overall variability) contrasts stations that tend to be high in Mn, Cd, and Sn and low in Ba (Group C and stations BL03-4 and BL03-17) with stations that tend to show the opposite pattern (e.g. Group A). These differences in metal concentrations reflect both geographical differences and differences in sediment characteristics. In general, there was a tendency for total metal concentrations (PC 1) to decrease with the silt fraction and with latitude from S to N and to increase with organic matter content.

While much of the variability in metal concentrations was explained by sediment characteristics, a significant geographical gradient remained even after accounting for the effects of sediment composition on PC 1. This gradient reflects differences in metal concentration between the "pristine" southeastern lagoon (higher concentrations of most metals) and the northwestern part of the lagoon that is not explained by differences in sediment composition.

The trends of metal concentrations decrease from southeast to northwest across the study area. It seems clear, therefore, that there are no definite distributional patterns in the concentrations of trace metals in the mud of Beaufort Lagoon, especially in the context of the hypothesis that we had mooted at the start of the

project. We had predicted that there would be significant differences in the metal concentrations between the regions exposed to natural oil seep, anthropogenic activities such as those related to the defunct DEW line station and the pristine environment portions of the lagoon. The above gradient is opposite to what one would expect, considering the presumed contaminant sources. It is suggested that any of the 13 metals investigated that might have been input into the lagoon from the oil seeps and/or past military activities are dispersed so widely and are so diluted that the effect of the point sources of the natural and anthropogenic contaminants are not decipherable in the lagoon mud. In summary, there is no significant difference between mud collected from possible "impacted areas" and the pristine portion of the lagoon, suggesting that the lagoon has remained uncontaminated as far as the trace metals analyzed in this study.

It is noted that the mean concentrations of all trace metals in the mud fraction of Beaufort Lagoon are generally close to the levels reported by us on mud samples from the Colville Delta–Prudhoe Bay–Canning Delta region (Naidu et al., 2001). Further, the mean concentration of THg in the gross sediments of Beaufort Lagoon is significantly higher (mean: 57 ng/g) than in gross sediments of the above deltaic region (mean: 19 ng/g). This difference in Hg is probably due to differences in the natural input of Hg from the hinterland sources, a proposition that remains to be further investigated.

*Time-interval comparison of the mean concentrations of metals*

A comparison is shown in Table 9 of the mean concentrations of a selected six metals between 5 sandy mud (>75% silt + clay) and 21 mud samples, which were collected in 1977 and this study (2003) respectively from Beaufort Lagoon. A significant (p< .05) decrease in V and an increase in Mn and Cu are noted from 1977 to 2003, whereas no differences in the time interval mean concentrations in Cr, Ni and Zn are identified. The differences may be artifacts of the differences in the granulometry and organic carbon contents between the two sets of samples rather than metal pollution, as alluded to previously. It is to be noted that we have

minimized the effect of granulometry by restricting the comparison to mean metal values on sandy mud samples of 1977 and mud samples in this study. The fact that there is no wholesale increase in the mean concentrations of all or most of the metals concerned is consistent with our earlier inference that the Beaufort Lagoon has remained generally a clean environment over the 26-year period (1977–2003), despite the fact that the lagoon had been subjected to past anthropogenic activities from the operation of a Distant Early Warning (DEW) Line station.

*Predicting toxicity in sediments with numeral trace metal quality guidelines*

The mean concentrations of selected trace metals in Beaufort Lagoon mud were used to determine their potential for adverse effects on resident marine benthic organisms, following the guidelines proposed by Long et al. (1995, 1998). Long et al., based upon empirical analysis of a broad database consisting of equilibrium-partitioning modeling, laboratory bioassays and field studies on total sediments have developed two sediment quality guideline (SQG) values [an effects range-low (ERL), and an effects range-medium (ERM)]. The database specifically consisted of concentrations of selected trace metals and hydrocarbons and biological effects on numerous benthic taxa in gross sediments. Further, "The two values defined concentration ranges that were: (1) rarely, (2) occasionally or (3) frequently associated with adverse effects." Comparison of the mean concentrations of heavy metals in mud from the study area with the above ERL and ERM and the three ranges for selected metals listed in Long et al., 1995 (Table 18), indicates that the mean concentrations of As, Cu and Ni in Beaufort Lagoon mud fall into ERL category and Cd, Cr, Pb, Hg and Zn are below ERL. This implies that the concentrations of As, Cu and Ni in the mud of Beaufort Lagoon are above the threshold level where incidences of adverse effects on biota would occasionally occur. However, whether the extrapolation of the guideline suggested by Long et al. (1995) is relevant and applicable to our study in the Beaufort Lagoon is a question that needs to be further investigated.  At the outset, to some it would seem that the above comparisons are incompatible, because our

metal data is on the mud fraction (<63 μm size) of gross sediments whereas Long et al's guideline is based upon trace metals concentrations in gross sediments which may not be composed entirely of mud. Any infiltration of coarser materials such as gravel or sand size particles can dilute the trace metals in gross sediment. It could be argued that the comparison is invalid because trace metals are almost invariably enriched in the mud fraction compared to gross sediments admixed with the coarses, because of the presence (partitioning) in the mud of chemically more reactive components (e.g., clay minerals and organics). The latter components have high ability to concentrate metals by adsorption and/or formation of organic-clay-metal ligands or complexes. So, in such gross sediments with little mud content the concentrations of metals will likely be low. Although we concede that the above comparison is not totally compatible we, nonetheless, contend that the comparison has some implication on predicting sediment toxicity in the study area. Our contention is based on the general premise that most benthic organisms selectively ingest fine particles (Lee et al., 2000). Therefore, by implication, any high concentration of metal(s) bound to the fine particles would expose the animals to possible adverse effects. It is suggested that any conclusions based on the Long et al.'s guidelines must be substantiated by detailed site-specific cause-effect investigations in Beaufort Lagoon on individual resident organisms. Further, it is to be noted that a lack of consensus exists as to which aspects of the sediment trace metal chemistry are responsible for the adverse effect (Grant and Briggs, 2002). It is suggested that an assessment must be made of the fractions of various metals in the gross sediment that will be potentially available for bio-accumulation. Investigations on the amounts of metals partitioned in various sediment phases [interstitial fluids, extractable phase following acid or acid-reducing agent treatment, acid volatile sulfides (Mucha et al. 2005, and references therein)] will provide more meaningful information on the bioavailability of metals from sediments. The unique problems relating to polar marine toxicology and the

future special research needs for the region has been discussed by Chapman and Riddle (2005).

### Hydrocarbon Studies

Discussions on the hydrocarbon studies are focused on two aspects; one to elucidate the sources of the hydrocarbons, and the second to assess whether the types and concentrations of hydrocarbons in the Beaufort Lagoon sediments are in any way different than from nearshore sediments elsewhere in the North Slope region.

*Criteria to infer hydrocarbon sources*

We assessed the relative abundance of the various sources of hydrocarbons (natural oil seep, refined petroleum, fresh crude and natural terrestrial and marine biogenous origin) in each of the sediments analyzed by using, for example, the following guidelines.

Natural crude seepage: Weathered petroleum; Alkane gas chromatogram with a hump (unresolved complex mixture of branched and cyclic components) (Farrington and Tripp, 1977; Simoneit and Kaplan, 1980; Venkatesan et al., 1980).

Fresh petroleum: Unweathered petroleum; characterized by *n*-alkanes distribution with no odd/even carbon preference throughout the carbon number envelope (Philip, 1985); alkylcyclohexanes and alkylbenzenes are found at significant levels, pristine and phytane are usually more dominant than $C_{17}$ and $C_{18}$ *n*-alkanes (Zafiriou et al., 1972), triterpenoids are of high thermal maturity characterized by the presence of predominantly 17α-hopanes and moretanes (17βα-hopanes) (Dastillung and Albrecht, 1976). Alkylated PAHs are more dominant than the parent PAHs (Youngblood and Blumer, 1975).

Biogenic hydrocarbons: Alkane gas chromatogram normally has baseline resolved peaks and does not have a bump (unresolved complex mixture of branched and cyclic components) (Venkatesan and Kaplan, 1982). $C_{15}$, $C_{17}$ indicates dominant *n*-alkanes from marine plankton, whereas dominance of C-25 to C-31 *n*-alkanes indicates terrestrial plant wax, with $C_{25}$, 27, 29, 31 and 33 more dominant than the even carbon *n*-alkanes (resulting in a high odd/even ratio) and with the maximum at $C_{29}$ or

$C_{31}$ *n*-alkane (Simoneit and Kaplan, 1980; Venkatesan et al., 1980). There was a presence of significant levels of alkanes from marine biota (Blumer et al., 1971). Triterpenoids are of low thermal maturity, characterized by the presence of predominantly 17β-hopanes and hopanes (Dastillung and Albrecht, 1976). There were not many alkylated PAHs.

*General characteristics of hydrocarbons as related to their sources*

In the following, we enumerate the major criteria that were used to identify the possible sources of hydrocarbons in Beaufort Lagoon sediments.

Alkanes: The alkane gas chromatogram exhibits baseline separation of the components and is generally bimodal with the major maximum at n-$C_{27}$ in 14 of the 20 samples analyzed and at n-$C_{29}$ or n-$C_{31}$ in the remaining sediments (Table 10). Normal alkanes >$C_{25}$ predominate in all the sediment samples with odd/even carbon alkanes ratio in the range from 3.5 to 8.1. These alkanes are derived from higher plants. The secondary maximum at n-$C_{17}$ is characteristic of aquatic algae. The $C_{20}$ and $C_{21}$ olefins found are derived from plankton and bacteria. Although the total *n*-alkane level varies from 0.1 to 34μg/g similar to the Elson Lagoon sediments, Beaufort Lagoon sediments, in general, seem to exhibit relatively greater vascular inputs than the Elson Lagoon sediments.

In contrast, the O.S. (Oil Seep) sample contains a 100 to 1000-fold concentration of *n*-alkanes compared to the sediments (i.e., μg/g level vs. ng/g level as found in sediments, Table 10). Very high amounts of n-$C_{10}$ through n-$C_{15}$ and significant levels of alkanes from n-$C_{20}$ to n-$C_{32}$ over a pronounced unresolved hump (UCM = unresolved complex mixture spanning n-$C_{21}$ to n-$C_{34}$) are found in this sample. The most dominant alkane is n-$C_{11}$. There is practically no single dominant *n*-alkane at the high molecular weight end where the odd/even ratio is at 1.3, typical of petroleum input. From the overall profile of the *n*-alkanes, it appears that the O.S. may be degraded petroleum.

In addition, the L/H ratio ($\sum C_{12}$-$C_{19}$/$\sum C_{20}$-$C_{33}$ alkanes) of the O.S. is 0.6, which is much

higher than in the lagoon sediments (0.05–0.13) as computed from Table 10. Only one sample (BL03-14) has measurable pristane and phytane and the O.S. has neither of the two. The $C_{20}$ and $C_{21}$ planktonic olefins, which are found in all the sediments, are absent in the O.S. sample. Therefore, the *n*-alkanes distribution in the sediment samples is markedly different from that in the O.S. sample, implying that the lagoon sediment is relatively pristine with no measurable petroleum contribution.

*Distribution and sources of hydrocarbons in Beaufort Lagoon sediments*

Polyaromatic Hydrocarbons (PAHs): The levels of total PAH in the Beaufort Lagoon sediments range from 30 to 710 ng/g (Table 11) and are comparable to sediments from Colville Delta–Prudhoe Bay–Canning Delta (2001), Elson Lagoon (Naidu et al., 2003a) and other nearshore regions of the Beaufort Sea. The PAH composition is dominated by the homologous series of phenanthrenes. The sum of parent PAH and their methyl homologs distribution follows generally in the order: phenanthrenes> naphthalenes≥chrysenes/triphenylenes >fluoranthenes/pyrenes. $C_2$- naphthalene and $C_1$-phenanthrene in all the samples and $C_1$-chrysene in four samples are the most dominant PAH homologs. The general dominance of parent and monomethylated PAHs over higher methylated homologs in the lagoon sediment samples suggests the absence of significant petroleum input in the sediments. Compared to the lower molecular weight PAHs, four and five-ring PAHs are relatively less and perylene is the most dominant parent PAH in all the samples except in BL03-17, which has the least PAH content and contains no perylene. The dominance of perylene in the sediments is consistent with its origin in the Alaskan peats, similar to that found in coastal and other lagoon sediments of north Arctic Alaska (Naidu et al., 2000, 2003a; Macdonald et al., 2004, and references therein). This interpretation is consistent with the relatively light (negative) values of carbon isotope ratios ($\delta^{13}C^o/_{oo}$, Table 1) of all sediments, which point to a predominantly terrestrial ($C_3$) plant source of OC/organic matter in Beaufort Lagoon (see also Naidu et al., 2000), from peat from coastal erosion (Plate 2).

The O.S. (oil seep) sample contains 208µg/g of total PAHs, about 1000-fold greater than the lagoon sediments, also consistent with the trend in *n*-alkanes content. Unlike in the lagoon sediments, naphthalenes are the most dominant PAHs in the O.S., and, similar to the dominance of low molecular weight $C_{10}$-$C_{15}$ *n*-alkanes over high molecular weight analogs. Further, the anomalously high value of the naphthalenes/phenanthrenes ratio in the O.S. is observed (7.62) in contrast to the very low range in the sediments (0.03–0.91). $C_2$-naphthalenes, $C_2$-phenanthrenes and $C_3$-chrysenes/triphenylenes are the most dominant methyl homologs, characteristic of petroleum. Neither any PAH beyond $C_4$-chrysenes/triphenylenes nor perylene are detected in the O.S. The sum of parent PAH and methyl homologs follow the order: naphthalenes>phenanthrenes~ chrysenes/triphenylenes>fluoranthenes/pyrenes.

The overall molecular composition of PAHs in the Beaufort lagoon sediments and a comparison to that of the O.S. sample imply an absence of petroleum in the Beaufort Lagoon sediments, which is consistent with that noted above from the alkanes profiles. The hydrocarbon composition of the sediments from the Beaufort Lagoon is comparable to those from Elson Lagoon and most of the Beaufort Sea sediments investigated by us in previous CMI/MMS studies.

Triterpanoids: Triterpanes are mostly biogenic in the sediments as reflected by the presence of five major components, i.e., 27(17β)-, 29ββ-, 29βα-, 30ββ- hopanes and diploptene (Table 12). The most dominant hopanoid is diploptene and 29ββ-hopane is the second most dominant. Thermally mature 29αβ- and 30αβ-hopanes are present in much smaller/trace amounts relative to biogenic hopanes. Extended hopanes with ≥$C_{31}$ are either not detected or present only in trace quantities and only the R isomer is detected.

Similar to *n*-alkanes, total triterpanes are at the µg/g level and are about 1000-fold greater in the O.S. sample than in the lagoon sediment samples, where they occur at the level of ng/g. Further, the O.S. contains a whole suite of thermally mature αβ-hopanes and none of the

biogenic ββ- and βα-hopanes or the hopenes. Both S and R diastereomers of the extended hopanes (i.e., $\geq C_{31}$ hopanes) are present. This hopane's distribution in the O.S. is typical of petroleum/thermally mature sediments.

The trace amounts of isolated, thermally mature (αβ and/or βα-hopanes) biomarkers detected in the sediments most probably derive from peat and/or coal. The overall fingerprint of the triterpanes in sediments of the Beaufort Lagoon does not support any contribution from the O.S.

Steranes: Steranes are generally absent in the Beaufort Lagoon sediment samples. If present, they are only in small/trace amounts, usually about 10 times lower than triterpanes (Table 13). Sediment samples, BL03-12, -13 and -14 contain almost a whole suite of target steranes and at relatively higher levels than the other sediments. This probably implies minimal petroleum input. However, this observation is not supported by triterpane or *n*-alkane profiles. Also, considering the extremely low levels of steranes in these samples, the input from petroleum may not be warranted. The other samples, which contain smaller amounts of a few steranes, are 6B, 18 and 19.

All of the target steranes usually associated with natural weathered oil are present in the O.S. sample and it is about 1000-fold greater than in the lagoon sediments. The steranes profile of O.S. clearly indicates petroleum characteristics.

In summary, normal and cyclic alkanes distribution is characteristic of biogenic origin in all the sediment samples and is different from that of the O.S. sample, thus indicating very little or no petroleum input to the Beaufort Lagoon sediments. The overall profile of alkanes in the Beaufort Lagoon sediments is similar to those of near-shore sediments from the Beaufort Sea that were analyzed by us in previous CMI/MMS projects (Naidu et al., 2001; 2003a). The alkane's distribution of O.S. sample, in contrast, clearly reflects that of petroleum. The overall profiles of the hydrocarbons indicate a significant derivation of them from terrestrial plants, which is corroborated by the OC/N and stable carbon isotope ratios. That the terrestrial organic matter pervades (50%) the organic

matter of sediments throughout the Alaskan–Canadian near-shore is substantiated by more extensive investigations on OC/N, $\delta^{13}C$, $\delta^{15}N$ and *n*-alkanes of sediments of the region (Naidu et al., 2000; Macdonald et al., 2004).

*Predicting toxicity in sediments with PAH quality guidelines*

As in the case of the trace metals, we have examined the mean concentrations of a group of PAHs in the context of Long et al.'s (1995, 1998) guidelines for identifying hydrocarbon pollution in terms of Effects Range-Low (ERL) and Effects Range-Medium (ERM) (refer to the related discussion above on trace metals). Our study indicates that the mean concentrations of all the PAHs in gross sediments of the Beaufort Lagoon are below the threshold ERL level where incidences of adverse effects would be expected on biota (Table 19).

**Conclusions**

Interpretations of the trace metal and hydrocarbon data provide the following conclusions. There are no significant disparities in the metal concentrations between the regions exposed to long-term natural oil seep, past anthropogenic activities related to the DEW line military station and the pristine environment of the lagoon. It is suggested that any of the 13 metals investigated that might have been input into the lagoon, from the oil seeps and/or past military activities, are dispersed so widely and diluted that the affect of the point sources on the metal contents are not discernable. Two time-interval comparisons of the mean concentrations of metals in muddy sediments taken at 26-year intervals (1977 to 2003) show a significant decrease in V, an increase in Mn and Cu, and similar values in Cr, Ni and Zn. Data on the rest of the metals were unavailable for 1977. The differences mentioned above likely reflect the differences in granulometry and organic carbon contents between 1977 and 2003 samples. It is to be noted that the 1977 samples were comprised of sandy mud and not entirely of mud as in the case of the 2003 samples. The mean concentrations of all trace metals, except THg, in the mud of Beaufort Lagoon are generally at the same level as those reported by us from the Colville Delta–Prudhoe Bay–Canning Delta region. The significantly higher THg values in

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Beaufort Lagoon mud (mean: 57 ng/g) than in the above region (mean: 19 ng/g) is probably due to differences in the natural input of the metal from the hinterland, a proposition that remains to be further investigated. Correlation coefficient analysis between metals, OC and granulometry, suggests that clays and Fe presumably play an important role in metal scavenging and their deposition in Beaufort Lagoon, a conclusion consistent with our results on metal partitioning in the Beaufort Sea near-shore. Based on principal component analysis, it is evident that a southeast-northwest high to low gradient is present in the study area in the concentrations of the trace metals. We attribute this trend to likely net regional variations in granulometry, organic carbon contents and/or possible changes in the natural input of metals contents along the above gradient, rather than a reflection of a gradient resulting from decreasing inputs from potential point sources of contaminants, such as from existing natural oil seeps and/or from the past activities of the Distant Early Warning (DEW) line station located south of Nuvagapak Point.

The hydrocarbon components in gross sediments from the Beaufort Lagoon are biogenic and terrestrial with little petroleum input. Their general composition is very similar to those found in the sediments from Elson Lagoon, Colville Delta–Prudhoe Bay–Canning Delta and the adjacent Canadian deltaic and inner shelf region and the inner shelf of the Beaufort Sea. The data provide no evidence to document the contribution of petroleum hydrocarbons to the Beaufort Lagoon sediments analyzed from the oil seeps located in the vicinity and anthropogenic activities. Petroleum contribution, if there is any to the sediments, is only minimal, below detection levels. The trace metal and hydrocarbon levels are either similar to or below those reported for unpolluted near-shore regions of the world. In summary, the Beaufort Lagoon sediments have remained uncontaminated as far as the analyzed trace metals and hydrocarbons are concerned.

The mean concentrations of As, Cu and Ni in the mud of the Beaufort Lagoon are above the threshold level of Effects Range-Low (ERL) that can cause adverse effects on benthic and demersal organisms. This is a tentative conclusion which must be clarified by further detailed investigations on the metal partitioning patterns and determination of the portions of metals that will likely be made available for possible bioaccumulation.The mean concentrations of all the selected 14 hydrocarbons in the gross sediments of Beaufort Lagoon are below the ERL, which implies that no adverse effects can be expected from hydrocarbons on benthic and demersal organisms.

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# EXECUTIVE SUMMARY

This project addressed the concern that concentrations of trace metals and hydrocarbons in the sediments of the Alaskan Arctic can occur as a result of petroleum exploration and production activities. Lagoon sediments of the North Slope, if they were to be the ultimate sink for both organic and inorganic anthropogenic chemicals, could be a major source of contaminants for benthic animals as well as organisms which have a close link with sediments and which serve as transfer pathways of contaminants to higher trophic levels. Recognizing the pending lease sales scheduled by MMS in 2003–2007 we have extended our investigations to establish baselines on trace metals and hydrocarbons in the sediments of the Beaufort Lagoon located at the remote eastern margin of the north Alaskan Arctic coast and far from intense industrial activities.

This report presents the highlights of a two-year study (2003–2005) which has as its major objective the measurement of the concentrations of a suite of 12 trace metals (copper (Cu), chromium (Cr), cadmium (Cd), nickel (Ni), vanadium (V), lead (Pb), tin (Sn), zinc (Zn), arsenis (As), barium (Ba), iron (Fe) and manganese (Mn) in the mud fraction (<63 um size), and total mercury (THg), sediment grain size, organic carbon (OC) and hydrocarbons (normal and isoprenoid alkanes, triterpenoids and steranes and polycyclic aromatic hydrocarbons) in the gross sediments of the Beaufort Lagoon. The choice of the above metals and hydrocarbons is based on the fact that these chemicals are often present in drilling effluents, crude, and petroleum development and production activities.  The purpose of this study was to close a gap in the baselines for sediment metals and hydrocarbons for a remote region of the North Slope Coast.

Sediment samples (Van Veen grab) from the Beaufort Lagoon were collected at 22 selected stations spread over three sectors. Six of the samples were in close proximity to natural oil seeps, another six samples from an area that was impacted by military activities connected with a DEW line station (now defunct), and a third suite of 10 samples from east lagoon which is

presumed pristine. The methods for the analyses of the trace metals and hydrocarbons on the sediments was essentially the same as those adopted in previously supported CMI/MMS studies elsewhere along the North Slope nearshore region. The QA/QC (quality assurance/quality control) protocol prescribed by the U.S. Environmental Protection Agency (EPA) for metal analysis was followed. QA/QC for the organic analyses included successful participation in the (NOAA/National Status and Trends Program).

Statistical analysis consisted of the determination of the correlation coefficients between trace metals, OC, N, and the silt and clay percents in the mud fraction to deduce the geochemical partitioning of the metals in the mud analyzed. Cluster analysis was conducted to determine if there were groupings of samples based on trace metal concentrations. In addition, principal component analysis was conducted to deduce the cause of the regional variations in metal concentrations.

Interpretations of the trace metal and hydrocarbon data provide the following conclusions. There are no significant disparities in the metal concentrations between the regions exposed to long-term natural oil seep, past anthropogenic activities related to the DEW line military station and the pristine environment of the lagoon. Any of the trace metals investigated in this study that might have originated from oil seeps or human activity are widely dispersed and diluted. The effect of any point sources on the metal content in the sediment is not discernable.

Two time interval comparisons of the mean concentrations of metals in muddy sediments taken at 26-year intervals (1977–2003) show a significant decrease in V, an increase in Mn and Cu, and similar values in Cr, Ni and Zn. These differences likely reflect the differences in granulometry and organic carbon contents between the 1977 and 2003 samples.

The mean concentration of all trace metals in the mud of Beaufort Lagoon are generally at the same level as those reported by us from the

Colville Delta, Prudhoe Bay-Canning Delta region.

The significantly higher Hg values in Beaufort Lagoon gross sediments (mean: 57ng/g) than in the Colville Delta-Prudhoe Bay-Canning Delta region (mean: 19 ng/g) are probably due to differences in the natural input of the metal from the hinterland, a proposition that remains to be further investigated.

Correlation coefficient analysis between metals, OC, and granulometry, suggests that clays and Fe oxy-hydroxide presumably play an important role in metal scavenging and their deposition in the Beaufort Lagoon. This conclusion is consistent with our results on metal partitioning in the adjacent nearshore regions of Beaufort Sea.

Based on principal component analysis, it is evident that a southeast-northwest high to low gradient is present in the study area in the concentrations of the trace metals. This trend may be attributed to net regional variations in granulometry, organic carbon contents and/or possible changes in the natural input of metals contents along the above gradients, rather than a reflection of a gradient resulting from decreasing inputs from potential point sources of contaminants, such as from natural oil seeps and/or from past activities of the Distant Early

Warning (DEW) line station located south of Nuvagapak Point.

The hydrocarbon components in gross sediments from the Beaufort Lagoon are biogenic and terrestrial. Their general composition is very similar to those found in the sediments from Elson Lagoon, Colville Delta, Prudhoe Bay, Canning Delta and adjacent Canadian deltaic and inner shelf region and the inner shelf of the Beaufort Sea. The data provide no evidence to document the contribution of petroleum hydrocarbons to the Beaufort Lagoon sediments analyzed from the oil seeps located in the vicinity and anthropogenic activities. The trace metal and hydrocarbon levels are either similar to or below those reported for unpolluted near-shore regions of the world. The Beaufort Lagoon sediments have remained uncontaminated as far as the analyzed trace metals and hydrocarbons are concerned.

The mean concentrations of As, Cu and Ni in the mud of the Beaufort Lagoon are above the threshold level of the Effects Range-low (ERL), as stated in Long et al., (1995, 1998), that can cause adverse effects on benthic and demersal organisms. However, the mean concentrations of all the selected 14 hydrocarbons in the gross sediments of Beaufort Lagoon are below the ERL, which implies that no adverse effects can be expected from current levels of hydrocarbons on the above organisms.
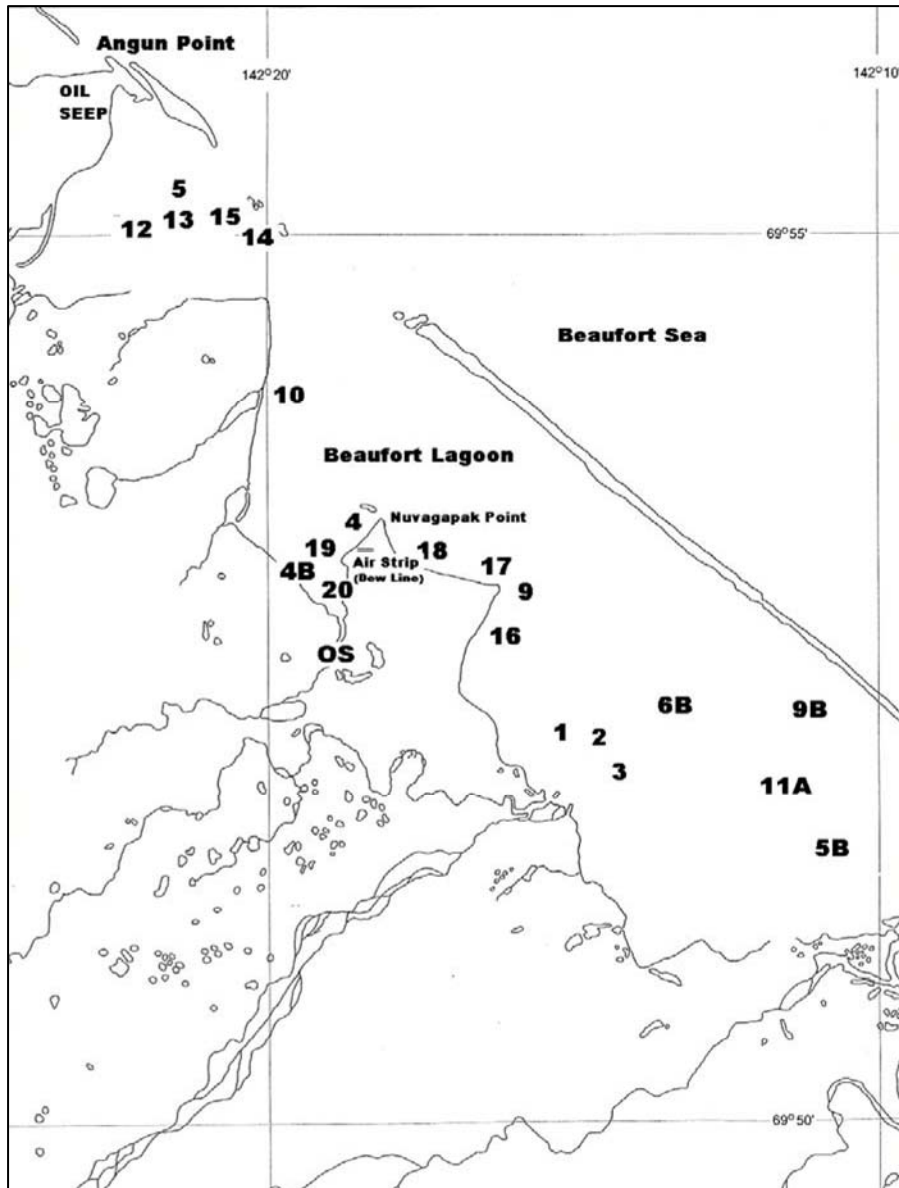
**Figure 1:** Study area showing locations of sediment samples in the Beaufort Lagoon.
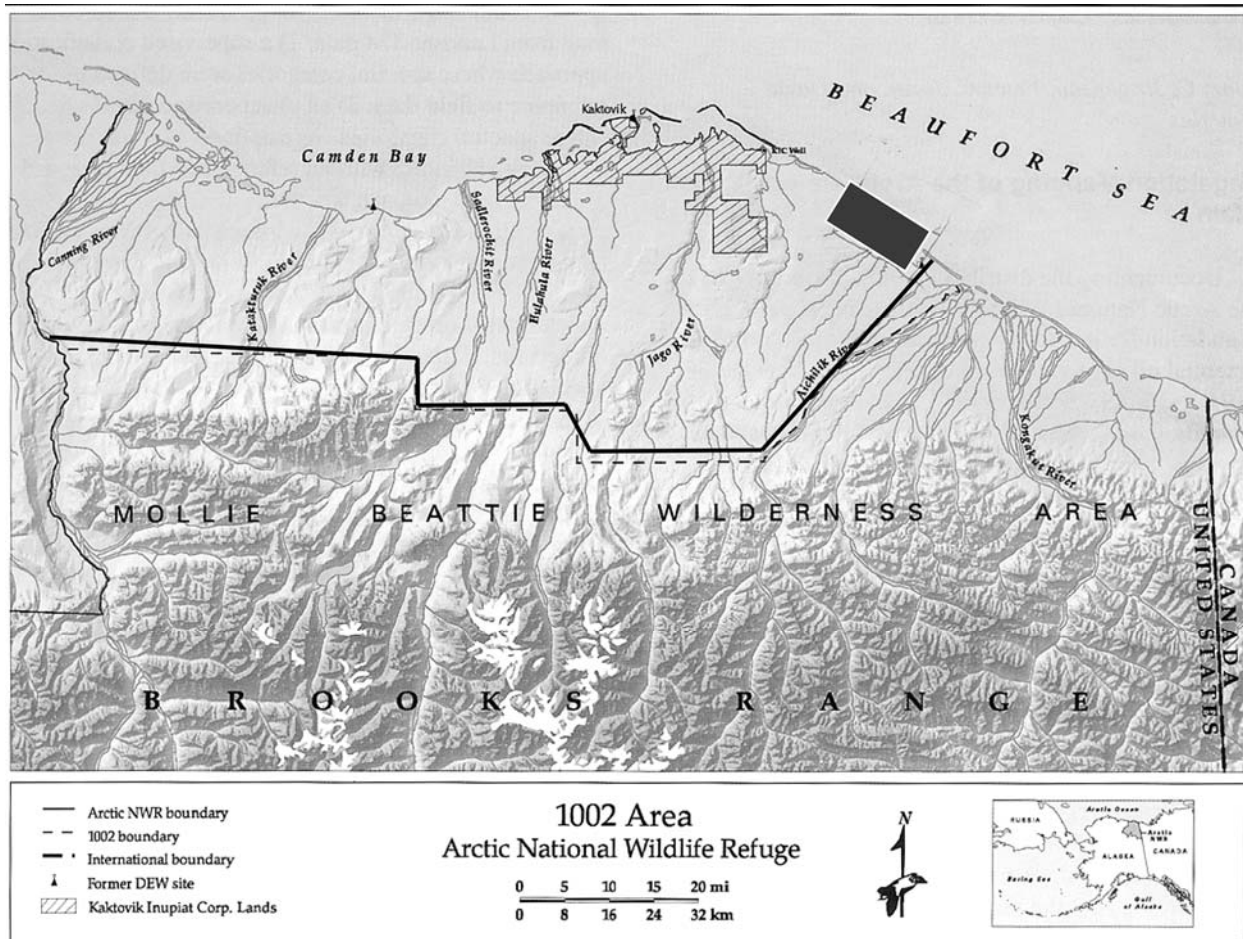
**Figure 2:** Map showing the study area (in filled rectangle) relative to the Arctic National Wildlife Refuge (ANWR) including the coastal plain unit.
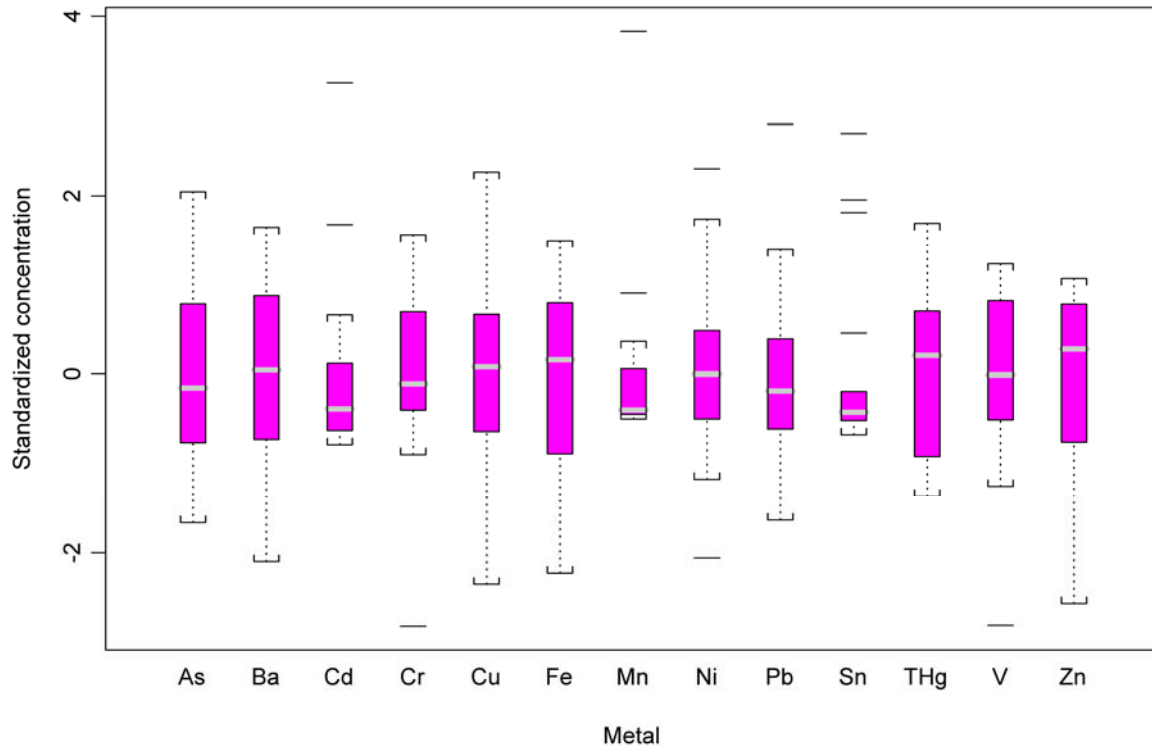
**Figure 3:** Boxplots of standardized concentrations of 12 metals in Beaufort Lagoon sediments.
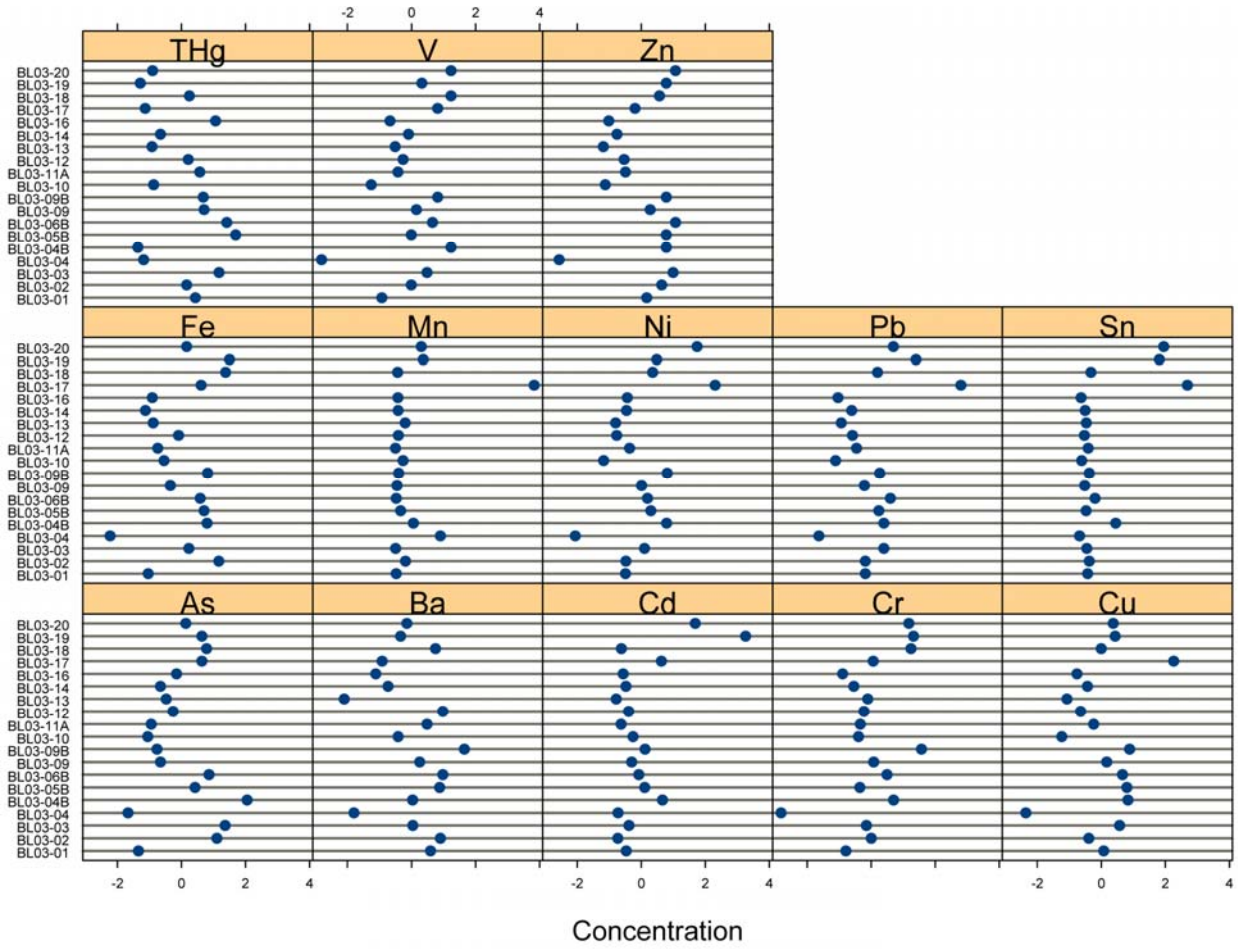
**Figure 4:** Dotplots of metal concentrations for 12 metals by station in Beaufort Lagoon.
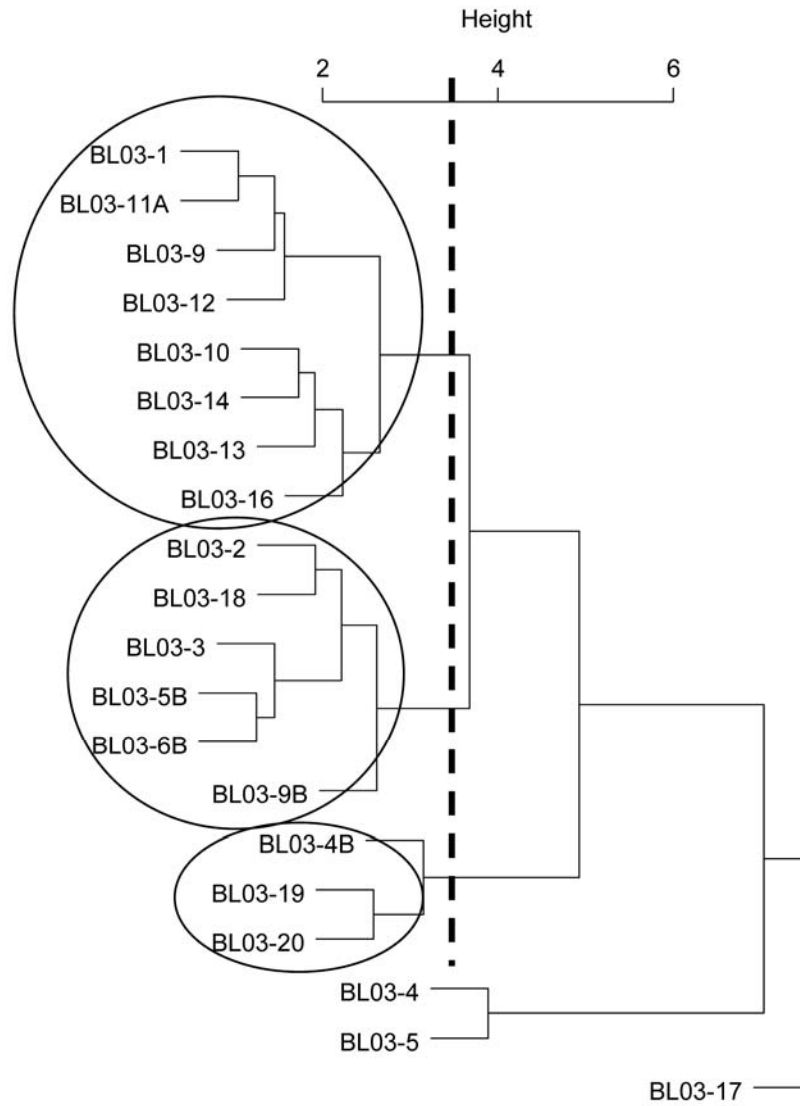
**Figure 5:** Dendrogram showing Ward's linkage clustering (Euclidean distances) based on concentrations of 12 metals measured at each station.
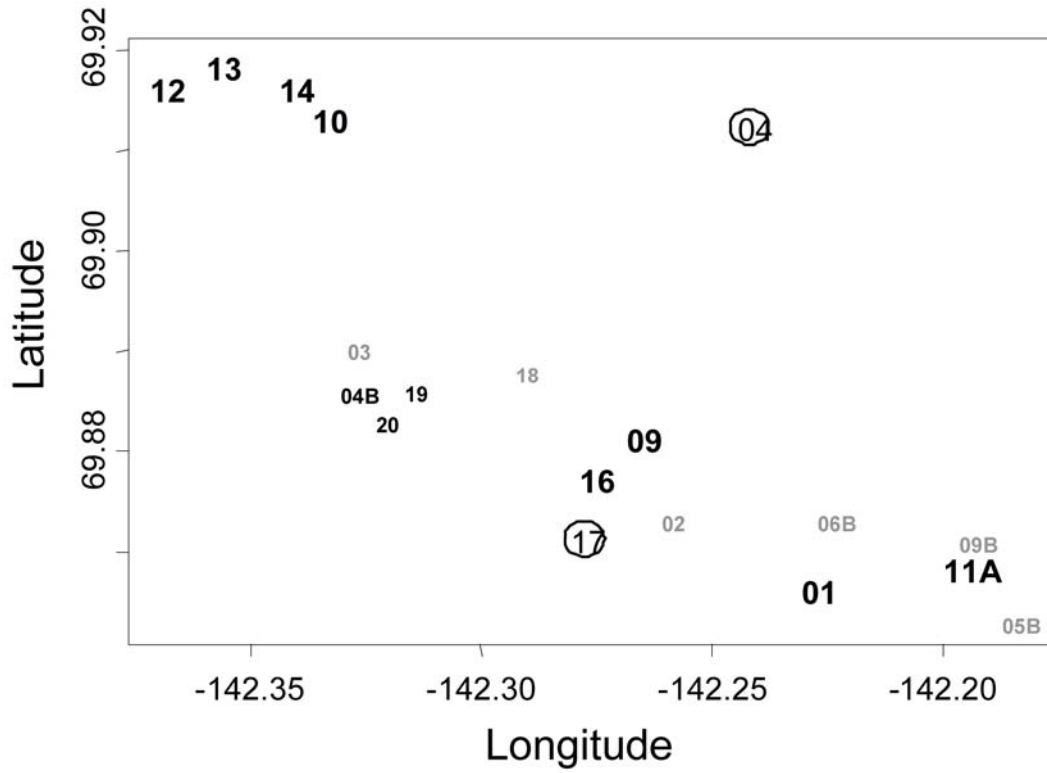
**Figure 6:** Map showing relative locations of stations (coastline not shown) and group membership corresponding to clusters as shown in Figure 5. Stations BL03-4 and BL03-17 (circled) did not cluster with any other stations.
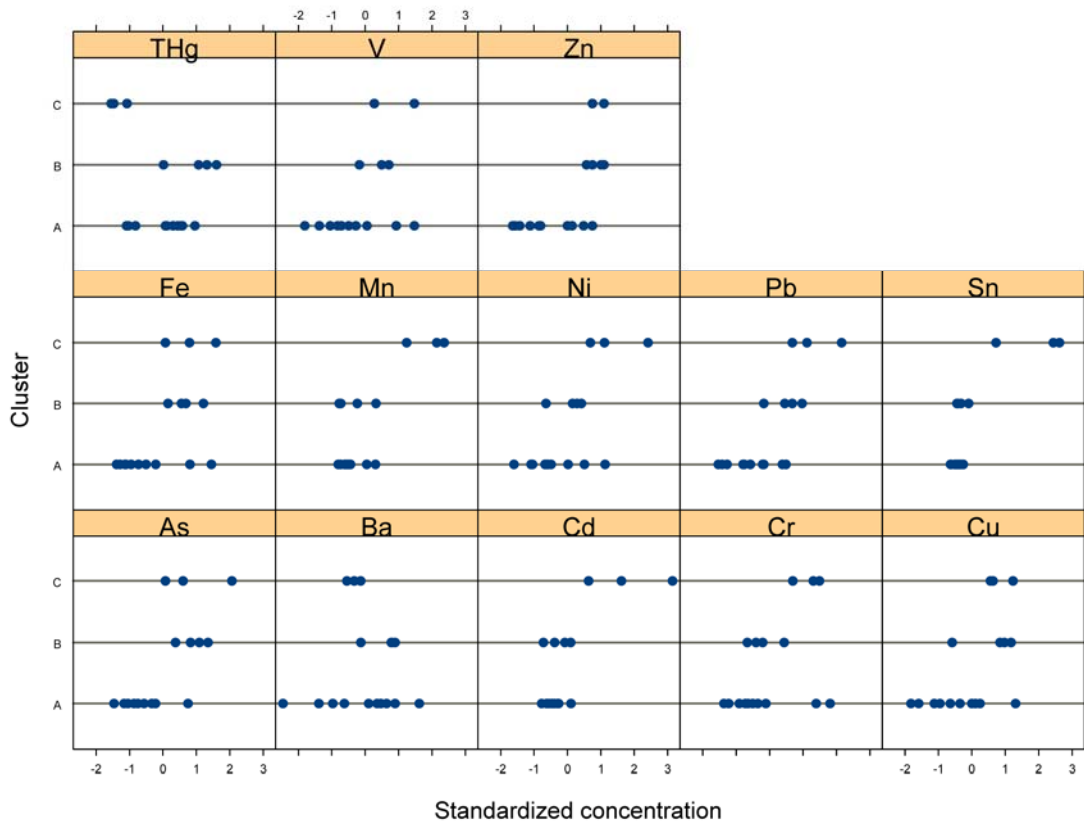
**Figure 7:** Dotplots of metal concentrations for 12 metals by cluster (see Fig. 5 for clusters).
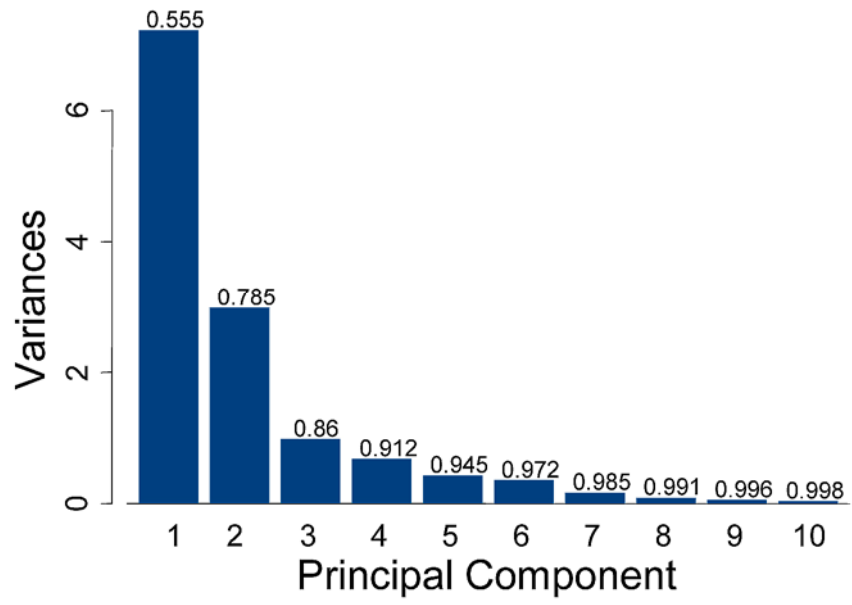
**Figure 8:** Cumulative amount of variance explained by the first ten Principal Components.
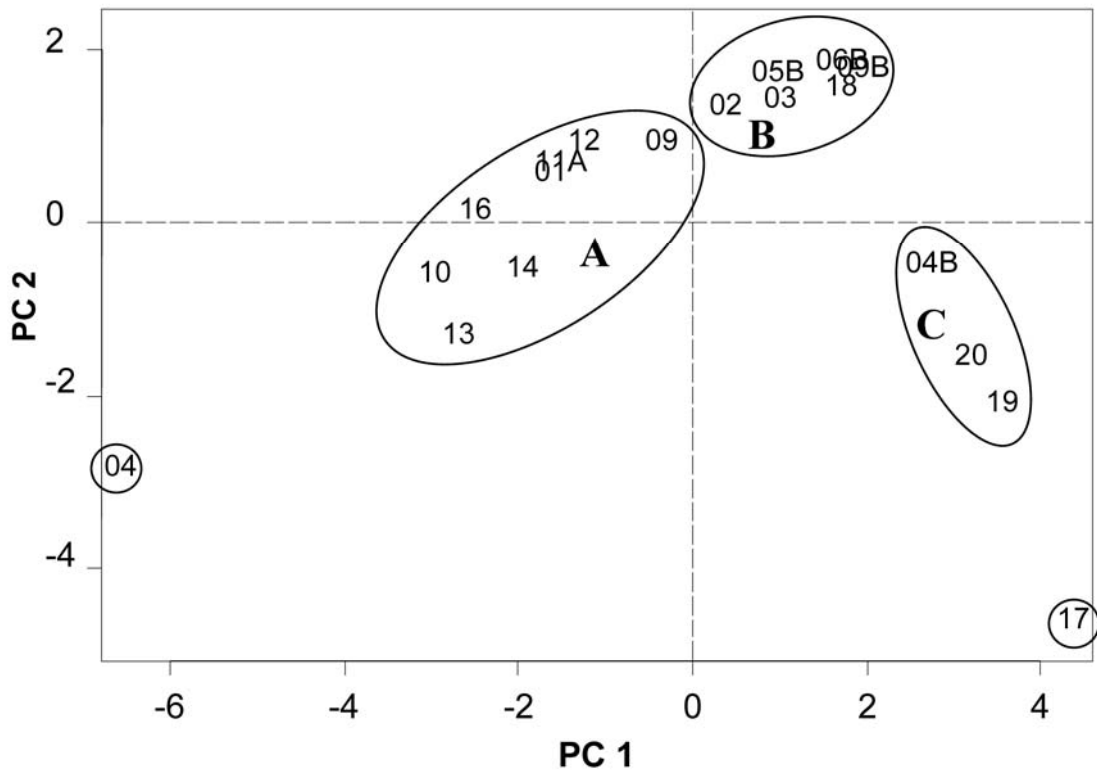
**Figure 9:** Beaufort Lagoon stations in the space of the first two principal components. Groups identified by a cluster analysis (see Fig. 5) are indicated.
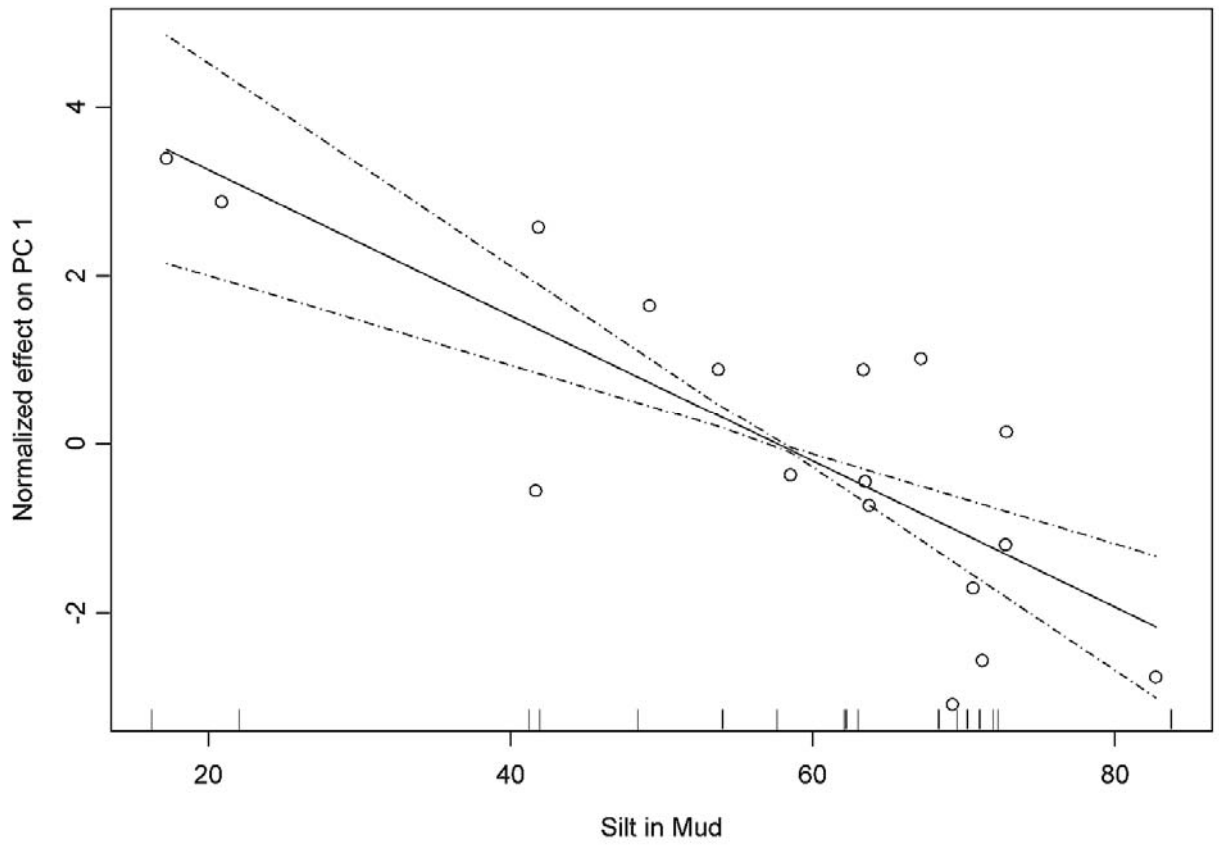
**Figure 10:** Partial fit of PC 1 on silt in mud fraction after accounting for effects of latitude (stations BL03-4 and BL03-17 were excluded from regression).
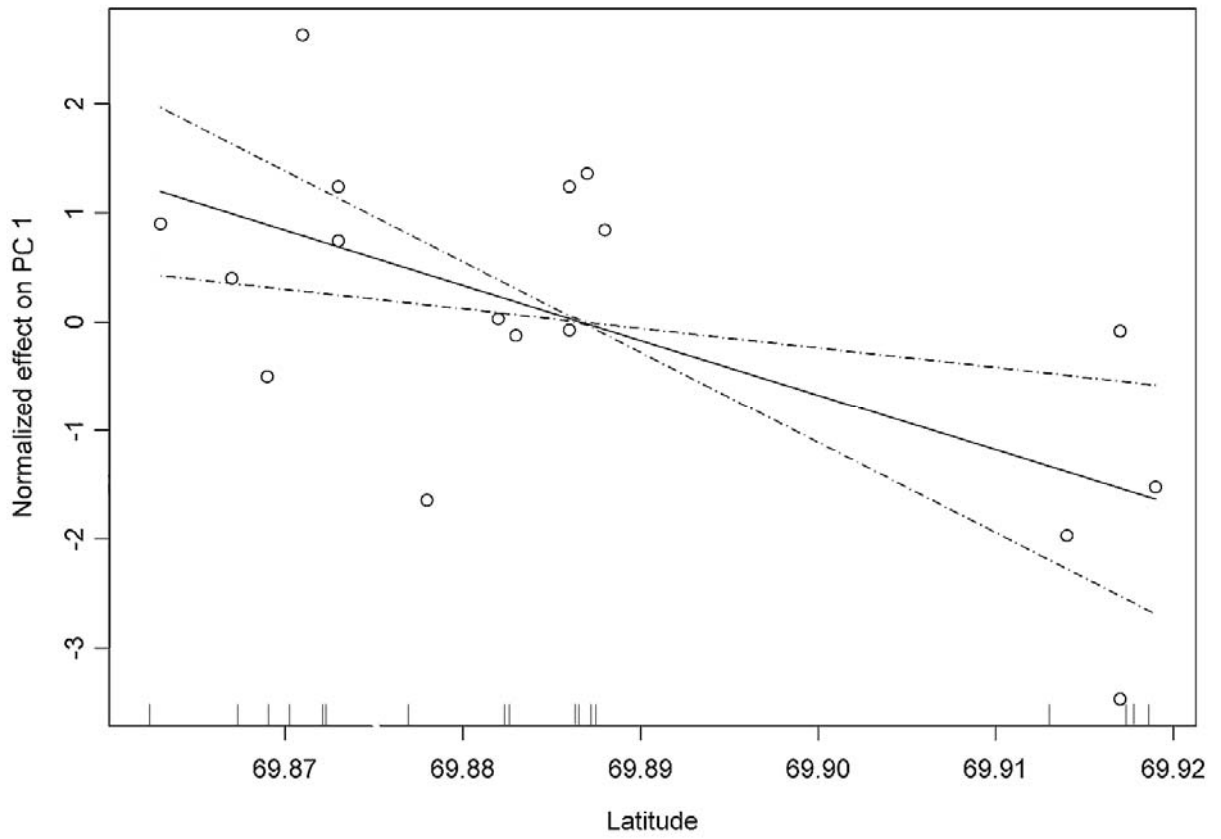
**Figure 11:** Partial fit of PC 1 on latitude after accounting for effects of silt in mud fraction (stations BL03-4 and BL03-17 were excluded from regression).
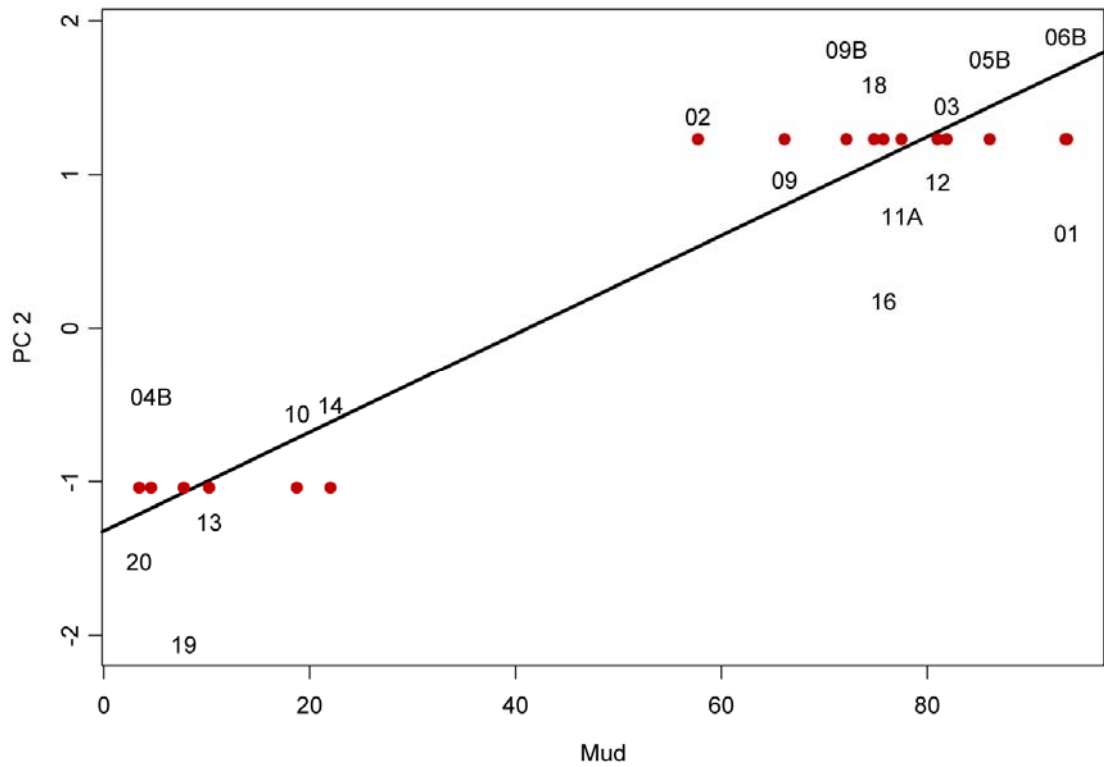
**Figure 12:** Linear regression of PC 2 on percentage of mud in sediment (stations BL03-4 and BL03-17 were excluded from regression). Red points show mean values of PC 2 corresponding to mud concentrations below and above 50%.

**Table 1:** Sample locations, grain sizes, organic carbon (OC), nitrogen (N), OC/N, and stable isotopes of OC ($\delta^{13}$C ‰) and N ($\delta^{15}$N) of Beaufort Lagoon sediments.

| Sample | Lat °N | Long °W | Solids % | Gravel % | Sand % | Silt % | Clay % | Mud % | OC % | N % | OC/N | $\delta^{13}$C | $\delta^{15}$N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BL03-1 | 69.87 | 142.23 | 53.4 | 0.00 | 6.43 | 77.39 | 16.18 | 93.57 | 2.39 | 0.22 | 10.86 | −26.94 | 1.88 |
| BL03-2 | 69.87 | 142.26 | 67.9 | 0.00 | 42.28 | 36.63 | 21.09 | 57.72 | 2.33 | 0.20 | 11.60 | −26.89 | 2.02 |
| BL03-3 | 69.89 | 142.33 | 51.9 | 0.00 | 18.11 | 51.87 | 30.02 | 81.89 | 2.17 | 0.20 | 10.85 | −26.36 | 0.83 |
| BL03-4 | 69.91 | 142.24 | 79.5 | 0.00 | 95.55 | 0.09 | 4.36 | 4.45 | 1.72 | 0.17 | 10.11 | −24.98 | 2.90 |
| BL03-4B | 69.89 | 142.33 | 91.5 | 92.87 | 2.54 | 1.92 | 2.66 | 4.59 | 3.29 | 0.32 | 10.28 | −26.99 | 3.09 |
| BL03-5 | 69.93 | 142.36 | 99.10 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| BL03-5B | 69.86 | 142.18 | 52.9 | 0.00 | 13.94 | 50.36 | 35.70 | 86.06 | 2.00 | 0.18 | 11.11 | −26.24 | 1.60 |
| BL03-6B | 69.87 | 142.22 | 56.8 | 0.00 | 6.56 | 50.22 | 43.22 | 93.44 | 2.02 | 0.19 | 10.63 | −26.49 | 2.05 |
| BL03-9 | 69.88 | 142.27 | 61.2 | 0.28 | 33.60 | 42.13 | 23.98 | 66.12 | 3.96 | 0.36 | 11.00 | −27.35 | 1.95 |
| BL03-9B | 69.87 | 142.19 | 65.0 | 0.00 | 27.86 | 48.44 | 23.69 | 72.14 | 2.27 | 0.19 | 11.94 | −26.24 | 1.79 |
| BL03-10 | 69.91 | 142.33 | 74.9 | 0.00 | 81.25 | 13.24 | 5.50 | 18.75 | 2.38 | 0.20 | 11.90 | −27.14 | 3.41 |
| BL03-11A | 69.87 | 142.20 | 61.9 | 0.00 | 22.51 | 55.19 | 22.30 | 77.49 | 1.55 | 0.13 | 11.92 | −27.26 | 1.07 |
| BL03-12 | 69.92 | 142.37 | 61.4 | 0.00 | 19.01 | 58.97 | 22.02 | 80.99 | 2.04 | 0.17 | 12.00 | −26.85 | 2.21 |
| BL03-13 | 69.92 | 142.36 | 76.6 | 0.00 | 89.76 | 7.45 | 2.79 | 10.24 | 1.43 | 0.12 | 11.91 | −26.85 | 2.07 |
| BL03-14 | 69.92 | 142.34 | 67.0 | 0.00 | 77.97 | 9.18 | 12.85 | 22.03 | 1.66 | 0.15 | 11.07 | −26.96 | 1.75 |
| BL03-15 | 69.92 | 142.34 | NA | 0.00 | 83.42 | 3.15 | 13.42 | 16.58 | 1.76 | 0.17 | 10.35 | −26.49 | 1.76 |
| BL03-16 | 69.88 | 142.28 | 43.8 | 0.00 | 24.24 | 52.46 | 23.30 | 75.76 | 3.20 | 0.26 | 12.30 | −27.53 | 1.80 |
| BL03-17 | 69.87 | 142.28 | 79.6 | 0.12 | 97.88 | 0.05 | 1.95 | 1.99 | 2.57 | 0.30 | 8.56 | −25.84 | 3.12 |
| BL03-18 | 69.89 | 142.29 | 56.4 | 0.00 | 25.17 | 36.81 | 38.02 | 74.83 | 2.60 | 0.23 | 11.30 | −26.85 | 2.83 |
| BL03-19 | 69.89 | 142.31 | 89.8 | 28.60 | 63.62 | 1.34 | 6.45 | 7.78 | 4.05 | 0.38 | 10.66 | −26.76 | 1.80 |
| BL03-20 | 69.88 | 142.32 | 79.3 | 37.75 | 58.80 | 0.72 | 2.73 | 3.45 | 3.75 | 0.37 | 10.13 | −27.21 | 2.23 |
| OS | 69.88 | 142.31 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |

**Table 2:** Concentrations of metals in Beaufort Lagoon sediments. All are µg/g, except Hg (ng/g) and Fe (%).

| Sample | V µg/g | Cr | Mn | Ni | Cu | Zn | As | Cd | Sn | Ba | Pb µg/g | THg ng/g | Fe % |
|--------|------|------|------|------|------|------|------|-------|------|------|------|------|------|
| BL03-1 | 110 | 68.6 | 318 | 36.9 | 38.5 | 98.4 | 10.9 | 0.224 | 1.78 | 559 | 16.8 | 68.5 | 2.64 |
| BL03-2 | 121 | 73.7 | 506 | 37.0 | 34.9 | 105 | 17.7 | 0.195 | 1.83 | 585 | 16.8 | 58.8 | 3.44 |
| BL03-3 | 127 | 72.7 | 311 | 40.6 | 42.3 | 110 | 18.4 | 0.233 | 1.76 | 512 | 19.1 | 94.6 | 3.10 |
| BL03-4 | 87.3 | 55.5 | 1222 | 27.2 | 19.9 | 60.2 | 10.0 | 0.196 | 1.53 | 355 | 11.0 | 11.7 | 2.21 |
| BL03-4B | 136 | 78.2 | 668 | 44.9 | 44.3 | 107 | 20.3 | 0.345 | 2.65 | 511 | 19.1 | 5.2 | 3.31 |
| BL03-5 | 94.7 | 59.9 | 182 | 25.7 | 16.2 | 48.2 | 6.9 | 0.085 | 1.32 | 436 | 12.0 | 118 | 2.17 |
| BL03-5B | 121 | 71.4 | 407 | 41.8 | 44.0 | 107 | 15.8 | 0.286 | 1.73 | 583 | 18.5 | 113 | 3.27 |
| BL03-6B | 129 | 76.9 | 319 | 41.2 | 43.0 | 111 | 17.0 | 0.266 | 2.01 | 592 | 19.9 | 103 | 3.23 |
| BL03-9 | 123 | 74.2 | 339 | 40.0 | 39.2 | 100 | 12.8 | 0.242 | 1.69 | 530 | 16.7 | 78.1 | 2.89 |
| BL03-9B | 131 | 83.8 | 370 | 45.0 | 44.7 | 107 | 12.5 | 0.287 | 1.83 | 649 | 18.6 | 77.1 | 3.31 |
| BL03-10 | 106 | 71.1 | 457 | 32.7 | 28.5 | 80.4 | 11.7 | 0.246 | 1.60 | 473 | 13.1 | 22.8 | 2.82 |
| BL03-11A | 116 | 71.5 | 305 | 37.7 | 36.1 | 89.1 | 12.0 | 0.206 | 1.80 | 550 | 15.7 | 73.4 | 2.75 |
| BL03-12 | 118 | 72.2 | 364 | 35.2 | 33.0 | 88.5 | 13.9 | 0.232 | 1.68 | 592 | 15.2 | 60.6 | 2.98 |
| BL03-13 | 115 | 73.0 | 503 | 35.0 | 29.7 | 79.5 | 13.3 | 0.190 | 1.74 | 329 | 13.8 | 20.9 | 2.69 |
| BL03-14 | 120 | 70.2 | 359 | 37.1 | 34.6 | 85.5 | 12.8 | 0.223 | 1.71 | 446 | 15.1 | 30.1 | 2.61 |
| BL03-16 | 113 | 67.9 | 351 | 37.3 | 32.1 | 81.9 | 14.2 | 0.214 | 1.58 | 413 | 13.4 | 90.7 | 2.69 |
| BL03-17 | 131 | 74.1 | 3132 | 54.3 | 55.2 | 93.3 | 16.4 | 0.341 | 4.86 | 430 | 28.7 | 13.4 | 3.24 |
| BL03-18 | 136 | 81.7 | 346 | 42.2 | 37.9 | 104 | 16.8 | 0.207 | 1.88 | 572 | 18.3 | 62.0 | 3.52 |
| BL03-19 | 125 | 82.2 | 868 | 43.0 | 41.2 | 107 | 16.4 | 0.623 | 3.99 | 479 | 23.1 | 7.89 | 3.56 |
| BL03-20 | 136 | 81.3 | 829 | 50.8 | 40.8 | 111 | 15.0 | 0.454 | 4.13 | 496 | 20.3 | 21.5 | 3.07 |
| | | | | | | | | | | | | | |
| A-Mean | 120 | 73.0 | 608 | 39.0 | 37.0 | 94 | 14.0 | 0.265 | 2.00 | 505 | 17.0 | 57.0 | 2.98 |
| Std AM | 13 | 7.0 | 643 | 6.8 | 8.9 | 17 | 3.2 | 0.110 | 0.98 | 85 | 4.1 | 37.3 | 0.4004 |
| G-Mean | 119 | 73.0 | 472 | 39.0 | 36.0 | 92 | 14.0 | 0.246 | 2.00 | 497 | 17.0 | 41.0 | 2.95 |
| Std GM | 13 | 7.0 | 658 | 6.9 | 9.0 | 17 | 3.2 | 0.110 | 0.99 | 85 | 4.1 | 40.7 | 0.4014 |
| % CV | 11 | 9.7 | 139 | 17.7 | 25.2 | 19 | 23.2 | 46.400 | 49.40 | 17 | 24.3 | 99.9 | 14 |

A-Mean:  Arithmetic mean
Std AM:  Standard deviation of arithmetic mean
G-Mean:  Geometric mean
Std GM:  Standard deviation of geometric mean
% CV:  Percent coefficient of variation

**Table 3:** Results of the QA/QC analysis concerning calibration verification.

| Analyte (unit) | Batch ID | ICV-TV | ICV-Obs | ICV-Rec | CCV1-TV | CCV1-Obs | CCV1-Rec | CCV2-TV | CCV2-Obs | CCV2-Rec |
|---|---|---|---|---|---|---|---|---|---|---|
| V    (µg/L) | A | 50 | 45.3523091 | 90.7046182 | 10 | 10.10702359 | 101.0702359 | 10 | 9.869872351 | 98.69872351 |
| Cr | A | 50 | 46.96249819 | 93.92499637 | 10 | 10.42038436 | 104.2038436 | 10 | 10.31545133 | 103.1545133 |
| Mn | A | 50 | 45.61942801 | 91.23885601 | 10 | 10.47879367 | 104.7879367 | 10 | 10.2695745 | 102.695745 |
| Fe | A | 100 | 73.05313706 | 73.05313706 | 50.00000381 | 39.06361265 | 78.12721935 | 50.00000381 | 38.63918732 | 77.27836875 |
| Ni | A | 50 | 50.8867821 | 101.7735642 | 10 | 10.68007653 | 106.8007653 | 10 | 10.66856767 | 106.6856767 |
| Cu | A | 50 | 50.30532361 | 100.6106472 | 10 | 10.60041579 | 106.0041579 | 10 | 10.43874602 | 104.3874602 |
| Zn | A | 50 | 51.36481686 | 102.7296337 | 20 | 20.94026515 | 104.7013258 | 20 | 20.49771425 | 102.4885713 |
| As | A | 50 | 45.45553065 | 90.91106131 | 10 | 10.38048842 | 103.8048842 | 10 | 10.02663014 | 100.2663014 |
| Cd | A | 5 | 4.649514064 | 92.99028129 | 1 | 1.029401306 | 102.9401306 | 1 | 1.003388809 | 100.3388809 |
| Sn | A | 50 | 53.76962124 | 107.5392425 | | 2.003951832 | | | 1.91100463 | |
| Ba | A | 100 | 97.20926536 | 97.20926536 | 10 | 9.892735523 | 98.92735523 | 10 | 9.796689174 | 97.96689174 |
| Pb  (µg/L) | A | 5 | 5.148574426 | 102.9714885 | 2 | 2.219005835 | 110.9502917 | 2 | 2.193373488 | 109.6686744 |
| THg  (ng/L) | B | 15 | 15.14149028 | 100.9432685 | 20 | 19.85846544 | 99.29232721 | 20 | 20.06355132 | 100.3177566 |

| Analyte (unit) | Batch ID | CCV3-TV | CCV3-Obs | CCV3-Rec | CCV4-TV | CCV4-Obs | CCV4-Rec | CCV5-TV | CCV5-Obs | CCV5-Rec |
|---|---|---|---|---|---|---|---|---|---|---|
| V    (µ/L) | A | 10 | 9.991375273 | 99.91375273 | 10 | 10.17824322 | 101.7824322 | 10 | 9.986948267 | 99.86948267 |
| Cr | A | 10 | 10.23747284 | 102.3747284 | 10 | 10.43125707 | 104.3125707 | 10 | 10.25176255 | 102.5176255 |
| Mn | A | 10 | 10.15512333 | 101.5512333 | 10 | 10.37120146 | 103.7120146 | 10 | 10.31078947 | 103.1078947 |
| Fe | A | 50.00000381 | 36.14374571 | 72.28748591 | 50.00000381 | 38.91393305 | 77.82786016 | 50.00000381 | 37.1038113 | 74.20761693 |
| Ni | A | 10 | 10.50028633 | 105.0028633 | 10 | 10.74240442 | 107.4240442 | 10 | 10.50248384 | 105.0248384 |
| Cu | A | 10 | 10.44103275 | 104.4103275 | 10 | 10.48291771 | 104.8291771 | 10 | 10.47122489 | 104.7122489 |
| Zn | A | 20 | 20.84492497 | 104.2246249 | 20 | 20.58320021 | 102.9160011 | 20 | 20.72900602 | 103.6450301 |
| As | A | 10 | 10.07112922 | 100.7112922 | 10 | 10.24800377 | 102.4800377 | 10 | 9.968211442 | 99.68211442 |
| Cd | A | 1 | 1.025773372 | 102.5773372 | 1 | 1.021258889 | 102.1258889 | 1 | 1.018553729 | 101.8553729 |
| Sn | A | | 1.928422781 | | | 1.926497615 | | | 1.897775196 | |
| Ba | A | 10 | 9.859105991 | 98.59105991 | 10 | 9.892031641 | 98.92031641 | 10 | 9.648629084 | 96.48629084 |
| Pb  (µg/L) | A | 2 | 2.169817453 | 108.4908727 | 2 | 2.173315751 | 108.6657876 | 2 | 2.166242576 | 108.3121288 |
| THg  (ng/L) | B | 20 | 20.16609426 | 100.8304713 | 20 | 20.2686372 | 101.343186 | | | |

| Analyte (unit) | Batch ID | CCV6-TV | CCV6-Obs | CCV6-Rec | CCV7-TV | CCV7-Obs | CCV7-Rec | CCV8-TV | CCV8-Obs | CCV8-Rec |
|---|---|---|---|---|---|---|---|---|---|---|
| V    (µg/L) | A | 10 | 9.849617357 | 98.49617357 | 10 | 9.783745819 | 97.83745819 | 10 | 9.586111375 | 95.86111375 |
| Cr | A | 10 | 10.1783771 | 101.783771 | 10 | 10.02781438 | 100.2781438 | 10 | 9.836530337 | 98.36530337 |
| Mn | A | 10 | 10.09998875 | 100.9998875 | 10 | 10.10092558 | 101.0092558 | 10 | 9.867526868 | 98.67526868 |
| Fe | A | 50.00000381 | 38.19419485 | 76.38838388 | 50.00000381 | 36.77596348 | 73.55192136 | 50.00000381 | 37.05366884 | 74.10733202 |
| Ni | A | 10 | 10.36700825 | 103.6700825 | 10 | 10.13588373 | 101.3588373 | 10 | 9.880873234 | 98.80873234 |
| Cu | A | 10 | 10.31545979 | 103.1545979 | 10 | 10.4797927 | 104.797927 | 10 | 10.41173962 | 104.1173962 |
| Zn | A | 20 | 20.23273385 | 101.1636692 | 20 | 21.04050314 | 105.2025157 | 20 | 20.66332202 | 103.3166101 |
| As | A | 10 | 9.847302208 | 98.47302208 | 10 | 9.983570755 | 99.83570755 | 10 | 9.73225454 | 97.3225454 |
| Cd | A | 1 | 1.002141532 | 100.2141532 | 1 | 1.031852437 | 103.1852437 | 1 | 0.985930772 | 98.59307716 |
| Sn | A | | 1.887518769 | | | 1.858317909 | | | 1.881666636 | |
| Ba | A | 10 | 9.763108636 | 97.63108636 | 10 | 9.730458986 | 97.30458986 | 10 | 9.69027078 | 96.9027078 |
| Pb  (µg/L) | A | 2 | 2.09613605 | 104.8068025 | 2 | 2.12493247 | 106.2466235 | 2 | 2.112768494 | 105.6384247 |
| THg  (ng/L) | B | | | | | | | | | |

Table 3. (cont.)

| Analyte (unit) | Batch ID | CCV9-TV | CCV9-Obs | CCV9-Rec | CCV10-TV | CCV10-Obs | CCV10-Rec | CCV11-TV | CCV11-Obs | CCV11-Rec |
|---|---|---|---|---|---|---|---|---|---|---|
| V (µg/L) | A | 10 | 9.650594968 | 96.50594968 | 10 | 9.30736503 | 93.0736503 | 10 | 9.423536979 | 94.23536979 |
| Cr | A | 10 | 9.76573373 | 97.6573373 | 10 | 9.544484373 | 95.44484373 | 10 | 9.628965848 | 96.28965848 |
| Mn | A | 10 | 9.827188222 | 98.27188222 | 10 | 9.458645312 | 94.58645312 | 10 | 9.694133285 | 96.94133285 |
| Fe | A | 50.00000381 | 39.53449401 | 79.06898199 | 50.00000381 | 42.37362985 | 84.74725323 | 50.00000381 | 47.00665316 | 94.01329915 |
| Ni | A | 10 | 9.932683621 | 99.32683621 | 10 | 9.576026001 | 95.76026001 | 10 | 9.668495115 | 96.68495115 |
| Cu | A | 10 | 10.2025627 | 102.025627 | 10 | 9.890386321 | 98.90386321 | 10 | 10.0324925 | 100.324925 |
| Zn | A | 20 | 20.3137235 | 101.5686175 | 20 | 19.52618759 | 97.63093797 | 20 | 19.51674111 | 97.58370555 |
| As | A | 10 | 9.585721832 | 95.85721832 | 10 | 9.299644052 | 92.99644052 | 10 | 9.489074512 | 94.89074512 |
| Cd | A | 1 | 0.989542451 | 98.9542451 | 1 | 0.947602132 | 94.76021317 | 1 | 0.971535371 | 97.15353708 |
| Sn | A | | 1.918633807 | | | 1.824633062 | | | 1.902547083 | |
| Ba | A | 10 | 9.838818362 | 98.38818362 | 10 | 9.148799712 | 91.48799712 | 10 | 9.62317503 | 96.2317503 |
| Pb (µg/L) | A | 2 | 2.12562117 | 106.2810585 | 2 | 2.025839268 | 101.2919634 | 2 | 2.117560977 | 105.8780489 |
| THg (ng/L) | B | | | | | | | | | |

| Analyte (unit) | Batch ID | CCV12-TV | CCV12-Obs | CCV12-Rec | CCV13-TV | CCV13-Obs | CCV13-Rec | CCV14-TV | CCV14-Obs | CCV14-Rec |
|---|---|---|---|---|---|---|---|---|---|---|
| V (µg/L) | A | 10 | 9.438779146 | 94.38779146 | 10 | 10.11357487 | 101.1357487 | 10 | 10.02901924 | 100.2901924 |
| Cr | A | 10 | 9.5126383 | 95.126383 | 10 | 10.31263132 | 103.1263132 | 10 | 10.23583896 | 102.3583896 |
| Mn | A | 10 | 9.651176105 | 96.51176105 | 10 | 10.29423463 | 102.9423463 | 10 | 10.19991661 | 101.9991661 |
| Fe | A | 50.00000381 | 53.94851826 | 107.8970283 | 50.00000381 | 43.16024445 | 86.32048232 | 50.00000381 | 38.81284795 | 77.62568998 |
| Ni | A | 10 | 9.577118118 | 95.77118118 | 10 | 10.4172239 | 104.172239 | 10 | 10.22561713 | 102.2561713 |
| Cu | A | 10 | 9.803673602 | 98.03673602 | 10 | 10.22385582 | 102.2385582 | 10 | 10.20193347 | 102.0193347 |
| Zn | A | 20 | 19.1865418 | 95.93270898 | 20 | 20.44292065 | 102.2146032 | 20 | 20.36064296 | 101.8032148 |
| As | A | 10 | 9.149850875 | 91.49850875 | 10 | 9.69797573 | 96.9797573 | 10 | 9.683501646 | 96.83501646 |
| Cd | A | 1 | 0.947509367 | 94.75093668 | 1 | 1.017795471 | 101.7795471 | 1 | 0.993801395 | 99.38013952 |
| Sn | A | | 1.87476249 | | | 1.934516221 | | | 1.935159194 | |
| Ba | A | 10 | 9.423369849 | 94.23369849 | 10 | 9.725311342 | 97.25311342 | 10 | 9.599800774 | 95.99800774 |
| Pb (µg/L) | A | 2 | 2.101084924 | 105.0542462 | 2 | 2.142351295 | 107.1175648 | 2 | 2.113897098 | 105.6948549 |
| THg (ng/L) | B | | | | | | | | | |

**Table 4:** Results of the QA/QC analysis concerning calibration blanks.

| Analyte (unit) | Batch ID | ICB | CCB1 | CCB2 | CCB3 | CCB4 | CCB5 | CCB6 | CCB7 |
|---|---|---|---|---|---|---|---|---|---|
| V  (µg/L) | A | −0.019412662 | −0.022915678 | 0.003640651 | 0.017759003 | 0.048708424 | 0.023439894 | 0.02438426 | 0.002141815 |
| Cr | A | −0.002122966 | 0.003766614 | 0.010165725 | −0.002818597 | −0.009003925 | −0.023367497 | −0.030559529 | −0.051678352 |
| Mn | A | 0.001514224 | −0.000366763 | 0.001696906 | 0.000215278 | 0.001268211 | −0.000454617 | 0.00102575 | 0.000273924 |
| Fe | A | −1.281956901 | 2.199543674 | 2.977579904 | 2.51391155 | 1.110781557 | 0.8398272 | 0.879905186 | −1.557955314 |
| Ni | A | 0.006692471 | 0.001049361 | 0.003343839 | 0.001642198 | 0.001944399 | 0.002645204 | 0.001884406 | 0.003968292 |
| Cu | A | −0.002534501 | −0.01197791 | −0.016823747 | −0.010802005 | −0.007336244 | −0.004534008 | −0.005354424 | −0.010948432 |
| Zn | A | 0.009717066 | −0.007442436 | 0.000322795 | 0.006762036 | −0.006444729 | 0.008655965 | 0.006723209 | −0.002946931 |
| As | A | 0.03487219 | 0.023736137 | 0.056976428 | 0.045339725 | 0.040974748 | 0.03895845 | 0.078805291 | 0.045033425 |
| Cd | A | 0.001390389 | 0.00066378 | *8.54564E−05* | 0.000269234 | −0.000194387 | 0.000389272 | −0.000239253 | *−9.69004E−05* |
| Sn | A | 0.247473511 | 0.019964263 | 0.023887361 | 0.026699068 | 0.02564591 | 0.020272009 | 0.02815594 | 0.027853262 |
| Ba | A | 0.010189992 | 0.001502795 | 0.000655891 | 0.000560007 | 0.001351205 | 0.001324258 | 0.002003348 | 0.00180285 |
| Pb (µg/L) | A | 0.000486244 | 0.000574009 | 0.000689952 | 0.000983047 | 0.000643604 | 0.000557415 | 0.000284386 | *−9.19744E−05* |
| THg (ng/L) | B | 0.005127147 | 0.010254294 | 0.020508588 | 0.076907204 | 0.061525765 | | | |

| Analyte (unit) | Batch ID | | CCB8 | CCB9 | CCB10 | CCB11 | CCB12 | CCB13 | CCB14 |
|---|---|---|---|---|---|---|---|---|---|
| V  (µg/L) | A | | −0.010947072 | −0.016725359 | 0.011709312 | 0.027295459 | 0.010289739 | −0.013957262 | −0.006775751 |
| Cr | A | | −0.056714697 | −0.075768997 | −0.066915037 | −0.094584515 | −0.116960163 | −0.131259752 | −0.112840693 |
| Mn | A | | −0.001074566 | 0.002161963 | 0.03136897 | 0.054314014 | 0.051490255 | 0.01542742 | 0.016643044 |
| Fe | A | | 2.653762053 | 2.800329156 | 9.014763907 | 14.93157478 | 8.144938152 | 1.341967988 | 1.754123921 |
| Ni | A | | 0.012223274 | 0.01125807 | 0.033918849 | 0.047015877 | 0.046362983 | 0.063122249 | 0.068449487 |
| Cu | A | | −0.008492945 | −0.000696379 | 0.013466952 | 0.027762757 | 0.027535099 | 0.006185382 | 0.006529685 |
| Zn | A | | 0.033953836 | 0.038064624 | 0.099442749 | 0.102272735 | 0.1616685 | 1.112588417 | 1.239113157 |
| As | A | | 0.061924645 | 0.084226575 | 0.115874334 | 0.115621475 | 0.148838907 | 0.073167584 | 0.093352707 |
| Cd | A | | *−1.18679E−05* | 0.000420587 | 0.002093238 | 0.003724701 | 0.004472952 | 0.000266891 | 0.001259444 |
| Sn | A | | 0.020168967 | 0.01414789 | 0.033233545 | 0.026029557 | 0.025150975 | 0.013041776 | 0.013497487 |
| Ba | A | | 0.000679496 | 0.001074303 | 0.025160283 | 0.044806803 | 0.045522298 | 0.011303463 | 0.011303808 |
| Pb (µg/L) | A | | −0.000259981 | −0.000394815 | 0.004911209 | 0.009329379 | 0.009550545 | 0.005268769 | 0.005122446 |
| THg (ng/L) | B | | | | | | | | |

**Table 5:** Results of the QA/QC analysis concerning spikes.

| Analyte (unit) | Batch ID | Sample ID | Mean | Spike TV | Dup Spike TV | Obs Spike Value | Dup Obs Spike Value | Spike % Rec | Dup Spike % Rec | RPD |
|---|---|---|---|---|---|---|---|---|---|---|
| V (mg/kg) | A | BL03-4 | 87.22 | 98.81 | 98.81 | 190.0 | 190.8 | 104.0 | 104.8 | 0.7 |
| V | A | BL03-3 | 126.6 | 79.37 | 79.68 | 205.3 | 207.9 | 99.1 | 102.0 | 2.9 |
| Cr | A | BL03-4 | 55.07 | 98.81 | 98.81 | 157.7 | 158.3 | 103.8 | 104.4 | 0.6 |
| Cr | A | BL03-3 | 72.52 | 79.37 | 79.68 | 145.8 | 142.0 | 92.3 | 87.2 | 5.7 |
| Mn | A | BL03-4 | 1215 | 98.81 | 98.81 | 1324 | 1324 | 110.4 | 109.6 | 0.8 |
| Mn | A | BL03-3 | 312.4 | 79.37 | 79.68 | 385.4 | 394.4 | 92.1 | 102.9 | 11.1 |
| Fe | A | BL03-3 | 30902 | 79.37 | 79.68 | 32448 | 30620 | 1949 | −353.9 | 288.8 |
| Fe | A | BL03-4 | 21899 | 494.1 | 494.1 | 22701 | 22647 | 162.3 | 151.4 | 6.9 |
| Ni | A | BL03-3 | 40.88 | 79.37 | 79.68 | 124.0 | 126.3 | 104.8 | 107.2 | 2.3 |
| Ni | A | BL03-4 | 27.48 | 123.5 | 123.5 | 154.7 | 156.6 | 103.0 | 104.5 | 1.4 |
| Cu | A | BL03-4 | 20.40 | 123.5 | 123.5 | 148.1 | 146.4 | 103.4 | 102.0 | 1.4 |
| Cu | A | BL03-3 | 42.67 | 79.37 | 79.68 | 127.3 | 128.1 | 106.7 | 107.2 | 0.5 |
| Zn | A | BL03-3 | 111.6 | 79.37 | 79.68 | 187.8 | 188.3 | 96.1 | 96.3 | 0.2 |
| Zn | A | BL03-4 | 60.59 | 247.0 | 247.0 | 311.7 | 313.3 | 101.6 | 102.3 | 0.6 |
| As | A | BL03-3 | 18.48 | 79.37 | 79.68 | 91.56 | 92.81 | 92.1 | 93.3 | 1.3 |
| As | A | BL03-4 | 9.84 | 98.81 | 98.81 | 113.1 | 111.9 | 104.5 | 103.3 | 1.1 |
| Cd | A | BL03-3 | 0.229 | 79.37 | 79.68 | 76.35 | 76.99 | 95.9 | 96.3 | 0.4 |
| Cd | A | BL03-4 | 0.196 | 9.881 | 9.881 | 10.47 | 10.27 | 103.9 | 101.9 | 2.0 |
| Sn | A | BL03-3 | 1.774 | 79.37 | 79.68 | 80.55 | 79.81 | 99.3 | 97.9 | 1.3 |
| Sn | A | BL03-4 | 1.523 | 24.70 | 24.70 | 27.54 | 26.69 | 105.3 | 101.9 | 3.3 |
| Ba | A | BL03-3 | 497.2 | 79.37 | 79.68 | 596.7 | 521.8 | 125.4 | 30.9 | 120.9 |
| Ba | A | BL03-4 | 357.1 | 197.6 | 197.6 | 578.6 | 576.8 | 112.1 | 111.2 | 0.8 |
| Pb | A | BL03-3 | 19.08 | 79.37 | 79.68 | 98.77 | 98.35 | 100.4 | 99.5 | 0.9 |
| Pb (mg/kg) | A | BL03-4 | 11.04 | 24.70 | 24.70 | 35.68 | 35.48 | 99.7 | 99.0 | 0.8 |
| THg (ng/g) | B | BL03-4 | 12.62 | 48.75 | 50.20 | 59.84 | 61.63 | 96.9 | 97.6 | 0.8 |

**Table 6:** Results of the QA/QC analysis concerning replicates (precision determination).

| Analyte (unit) | Batch ID | Sample ID | Sample | Duplicate | Mean | RPD |
|---|---|---|---|---|---|---|
| V  (mg/kg) | A | BL03-4 | 87.28 | 87.17 | 87.22 | 0.1 |
| V | A | BL03-3 | 127.0 | 126.2 | 126.6 | 0.6 |
| Cr | A | BL03-4 | 55.46 | 54.68 | 55.07 | 1.4 |
| Cr | A | BL03-3 | 72.70 | 72.35 | 72.52 | 0.5 |
| Mn | A | BL03-4 | 1222 | 1209 | 1215 | 1.1 |
| Mn | A | BL03-3 | 310.5 | 314.3 | 312.4 | 1.2 |
| Fe | A | BL03-3 | 30998 | 30805 | 30902 | 0.6 |
| Fe | A | BL03-4 | 22087 | 21711 | 21899 | 1.7 |
| Ni | A | BL03-3 | 40.63 | 41.13 | 40.88 | 1.2 |
| Ni | A | BL03-4 | 27.23 | 27.74 | 27.48 | 1.8 |
| Cu | A | BL03-4 | 19.87 | 20.94 | 20.40 | 5.3 |
| Cu | A | BL03-3 | 42.27 | 43.07 | 42.67 | 1.9 |
| Zn | A | BL03-3 | 110.4 | 112.8 | 111.6 | 2.1 |
| Zn | A | BL03-4 | 60.21 | 60.96 | 60.59 | 1.2 |
| As | A | BL03-3 | 18.36 | 18.60 | 18.48 | 1.3 |
| As | A | BL03-4 | 9.97 | 9.71 | 9.84 | 2.6 |
| Cd | A | BL03-3 | 0.233 | 0.225 | 0.229 | 3.4 |
| Cd | A | BL03-4 | 0.196 | 0.196 | 0.196 | 0.2 |
| Sn | A | BL03-3 | 1.76 | 1.79 | 1.77 | 1.6 |
| Sn | A | BL03-4 | 1.53 | 1.51 | 1.52 | 1.1 |
| Ba | A | BL03-3 | 511.6 | 482.8 | 497.2 | 5.8 |
| Ba | A | BL03-4 | 355.0 | 359.2 | 357.1 | 1.2 |
| Pb | A | BL03-3 | 19.10 | 19.05 | 19.08 | 0.2 |
| Pb (mg/kg) | A | BL03-4 | 11.03 | 11.05 | 11.04 | 0.2 |
| THg (ng/g) | B | BL03-4 | 11.68 | 13.56 | 12.62 | 14.9 |
| % Total Solids | C | BL03-4 | 79.5 | 78.9 | 79.2 | 0.8 |
| % Total Solids | C | BL03-17 | 79.6 | 79.5 | 79.6 | 0.1 |

**Table 7:** Results of the QA/QC analysis concerning analytical accuracy using certified reference materials, NIST 2709 and IAEA 405.

| Analyte (unit) | Batch ID | CRM Identity | Cert Value | Obs Value | % Rec |
|---|---|---|---|---|---|
| V (mg/kg) | A | NIST 2709 | 112.00 | 97.12 | 86.7 |
| V | A | BlankSpike | 80.00 | 85.78 | 107.2 |
| V | A | IAEA 405 | 95.00 | 90.21 | 95.0 |
| Cr | A | IAEA 405 | 84.00 | 67.42 | 80.3 |
| Cr | A | BlankSpike | 80.00 | 86.14 | 107.7 |
| Cr | A | NIST 2709 | 130.00 | 93.28 | 71.8 |
| Mn | A | NIST 2709 | 538.00 | 420.18 | 78.1 |
| Mn | A | IAEA 405 | 495.00 | 384.99 | 77.8 |
| Mn | A | BlankSpike | 80.00 | 87.95 | 109.9 |
| Fe | A | BlankSpike | 80.00 | 58.29 | 72.9 |
| Fe | A | NIST 2709 | 35000.00 | 28463.83 | 81.3 |
| Fe | A | IAEA 405 | 37400.00 | 29885.25 | 79.9 |
| Ni | A | IAEA 405 | 32.50 | 32.42 | 99.8 |
| Ni | A | BlankSpike | 80.00 | 93.66 | 117.1 |
| Ni | A | NIST 2709 | 88.00 | 76.19 | 86.6 |
| Cu | A | BlankSpike | 80.00 | 89.09 | 111.4 |
| Cu | A | NIST 2709 | 34.60 | 37.34 | 107.9 |
| Cu | A | IAEA 405 | 47.70 | 54.28 | 113.8 |
| Zn | A | IAEA 405 | 279.00 | 281.40 | 100.9 |
| Zn | A | NIST 2709 | 106.00 | 106.90 | 100.8 |
| Zn | A | BlankSpike | 80.00 | 83.51 | 104.4 |
| As | A | NIST 2709 | 17.70 | 16.84 | 95.1 |
| As | A | IAEA 405 | 23.60 | 23.47 | 99.5 |
| As | A | BlankSpike | 80.00 | 75.32 | 94.2 |
| Cd | A | BlankSpike | 80.00 | 78.38 | 98.0 |
| Cd | A | NIST 2709 | 0.38 | 0.65 | 172.1 |
| Cd | A | IAEA 405 | 0.73 | 0.74 | 101.8 |
| Sn | A | IAEA 405 | 7.60 | 9.54 | 125.5 |
| Sn | A | BlankSpike | 80.00 | 79.93 | 99.9 |
| Ba | A | NIST 2709 | 968.00 | 845.36 | 87.3 |
| Ba | A | BlankSpike | 80.00 | 97.11 | 121.4 |
| Pb | A | NIST 2709 | 18.90 | 19.29 | 102.1 |
| Pb | A | IAEA 405 | 74.80 | 77.83 | 104.0 |
| Pb (mg/kg) | A | BlankSpike | 80.00 | 78.63 | 98.3 |
| THg (ng/g) | B | IAEA 405 | 810.00 | 765.78 | 94.5 |

**Table 8:** Correlation coefficients for chemical and physical parameters of muds from Beaufort Lagoon (N = 19; significant correlations [p <0.05] are shown in bold and insignificant correlations are in gray).

| | V | Cr | Mn | Ni | Cu | Zn | As | Cd | Sn | Ba | Pb | Fe | OC % | Silt % | Clay % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| V | 1.00 | | | | | | | | | | | | | | |
| Cr | 0.89 | 1.00 | | | | | | | | | | | | | |
| Mn | 0.07 | −0.07 | 1.00 | | | | | | | | | | | | |
| Ni | 0.85 | 0.71 | 0.48 | 1.00 | | | | | | | | | | | |
| Cu | 0.80 | 0.64 | 0.39 | 0.91 | 1.00 | | | | | | | | | | |
| Zn | 0.84 | 0.78 | −0.16 | 0.69 | 0.76 | 1.00 | | | | | | | | | |
| As | 0.72 | 0.52 | 0.12 | 0.55 | 0.58 | 0.68 | 1.00 | | | | | | | | |
| Cd | 0.41 | 0.54 | 0.30 | 0.57 | 0.45 | 0.45 | 0.31 | 1.00 | | | | | | | |
| Sn | 0.48 | 0.43 | 0.74 | 0.78 | 0.61 | 0.35 | 0.40 | 0.78 | 1.00 | | | | | | |
| Ba | 0.53 | 0.57 | −0.38 | 0.31 | 0.47 | 0.70 | 0.26 | 0.08 | −0.12 | 1.00 | | | | | |
| Pb | 0.70 | 0.50 | 0.80 | 0.89 | 0.92 | 0.58 | 0.68 | 0.63 | 0.86 | 0.10 | 1.00 | | | | |
| Fe | 0.73 | 0.85 | 0.28 | 0.58 | 0.62 | 0.77 | 0.71 | 0.59 | 0.50 | 0.48 | 0.70 | 1.00 | | | |
| OC % | 0.37 | 0.40 | 0.12 | 0.42 | 0.31 | 0.62 | 0.44 | 0.66 | 0.46 | 0.07 | 0.38 | 0.44 | 1.00 | | |
| Silt % | −0.63 | −0.40 | −0.75 | −0.81 | −0.73 | −0.51 | −0.72 | −0.73 | −0.93 | 0.19 | −0.88 | −0.52 | −0.44 | 1.00 | |
| Clay % | 0.64 | 0.40 | 0.74 | 0.82 | 0.75 | 0.55 | 0.72 | 0.72 | 0.93 | −0.17 | 0.88 | 0.52 | 0.58 | −1.00 | 1.00 |

**Table 9:** Time-interval changes in the mean concentrations (µg/g dry wt) of trace metals in sediments of Beaufort Lagoon.[a]

| Year | V | Cr | Mn | Ni | Cu | Zi |
|---|---|---|---|---|---|---|
| 1977[b] | | | | | | |
| N=5 | | | | | | |
| $\overline{X}$ | **139** | 69 | **359** | 48 | **22** | 81 |
| SD | 17 | 12 | 69 | 6 | 4 | 11 |
| CV% | 12 | 17 | 19 | 13 | 18 | 14 |
| | | | | | | |
| 2003[c] | | | | | | |
| N=21 | | | | | | |
| $\overline{X}$ | **119** | 73 | **472** | 39 | **36** | 92 |
| SD | 13 | 7 | 659 | 7 | 9 | 17 |
| CV% | 11 | 10 | 139 | 18 | 25 | 19 |

[a]Significant differences (p<0.05) in bold
[b]Naidu [1981]
[c]This study (Table 2)

**Table 10:** Distribution (ng/g dry wt) of *n*-alkanes in gross sediments of Beaufort Lagoon. All sample numbers have the prefix BL03.

| Sample ID – UCLA No. | 1 | 2 | 3 | 3D* | 4 | 4R* | 5B | 6B | 9 | 9B | 9BD* | 10 | 11A | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Surrogate Recovery (%)** | | | | | | | | | | | | | | |
| Deu C14 | nd$ | 52 | 52 | 53 | 56 | 57 | 53 | 55 | 52 | 62 | 62 | 52 | 55 | 53 |
| Deu C24 | nd$ | 66 | 67 | 69 | 69 | 64 | 70 | 63 | 65 | 76 | 76 | 76 | 66 | 67 |
| Deu C36 | nd$ | 67 | 78 | 75 | 61 | 66 | 72 | 65 | 66 | 66 | 79 | 66 | 65 | 67 |
| | | | | | | | | | | | | | | |
| ***n*-alkane (ng/g dry wt)** | | | | | | | | | | | | | | |
| *n*-C10 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| *n*-C11 | nd | nd | nd | nd | nd | nd | 62.9 | 217.6 | nd | nd | nd | nd | nd | nd |
| *n*-C12 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| *n*-C13 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 38.9 |
| *n*-C14 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 46.9 |
| *n*-C15 | 67.1 | 34.4 | 60.7 | 52.6 | nd | nd | 38.7 | 72.3 | 45.5 | 41.1 | 30.7 | 0.0 | 55.1 | 70.9 |
| *n*-C16 | 96.2 | 26.0 | 56.6 | 41.9 | nd | nd | 32.8 | 62.5 | 56.9 | 50.9 | 40.5 | 0.0 | 58.9 | 77.4 |
| *n*-C17 | 184.3 | 70.9 | 192.5 | 172.5 | 3.2 | 3.8 | 117.0 | 198.8 | 192.8 | 98.5 | 76.0 | 51.6 | 137.6 | 163.6 |
| pr | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 51.6 |
| *n*-C18 | 89.6 | 38.2 | 108.7 | 98.0 | 1.8 | 2.2 | 63.5 | 110.4 | 102.0 | 54.3 | 46.2 | 29.4 | 76.8 | 95.0 |
| ph | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| *n*-C19 | 280.1 | 99.8 | 317.3 | 287.4 | 3.8 | 4.6 | 181.5 | 307.2 | 321.8 | 162.1 | 140.2 | 73.9 | 215.4 | 231.6 |
| *n*-C20 | 166.5 | 65.2 | 198.8 | 180.4 | 2.8 | 3.4 | 116.9 | 202.4 | 191.1 | 110.5 | 96.5 | 52.3 | 148.5 | 167.6 |
| *n*-C21 | 579.0 | 204.2 | 630.6 | 584.7 | 7.3 | 7.5 | 382.1 | 627.9 | 623.2 | 360.7 | 316.3 | 162.5 | 496.3 | 501.2 |
| *n*-C22 | 312.8 | 116.1 | 323.6 | 311.7 | 5.1 | 5.7 | 196.5 | 332.7 | 330.7 | 196.8 | 180.1 | 91.0 | 285.4 | 292.6 |
| *n*-C23 | 990.9 | 354.0 | 1056.6 | 974.1 | 13.2 | 14.9 | 672.8 | 1068.7 | 995.0 | 676.7 | 605.0 | 302.1 | 943.3 | 948.8 |
| *n*-C24 | 268.7 | 105.7 | 287.0 | 294.6 | 5.6 | 6.0 | 186.8 | 318.7 | 305.5 | 188.1 | 184.1 | 86.3 | 277.8 | 279.1 |
| *n*-C25 | 826.3 | 341.2 | 839.9 | 814.5 | 14.9 | 14.6 | 573.5 | 951.2 | 819.1 | 735.8 | 661.7 | 318.9 | 1403.9 | 1126.0 |
| *n*-C26 | 126.6 | 58.2 | 153.8 | 146.9 | 3.9 | 3.6 | 103.0 | 178.8 | 146.2 | 112.4 | 109.5 | 48.8 | 155.5 | 162.3 |
| *n*-C27 | 1015.9 | 472.0 | 1483.4 | 1450.0 | 18.1 | 18.5 | 867.3 | 1239.8 | 1738.7 | 1496.4 | 1370.4 | 460.7 | 1817.5 | 1985.2 |
| *n*-C28 | 73.3 | 34.5 | 94.5 | 176.6 | 3.5 | 3.4 | 70.0 | 120.0 | 80.1 | 81.0 | 144.5 | 33.3 | 110.7 | 108.0 |
| *n*-C29 | 886.5 | 376.5 | 1217.9 | 1346.5 | 17.9 | 18.6 | 933.4 | 1323.9 | 1054.3 | 1160.3 | 1450.2 | 414.2 | 1342.7 | 1413.3 |
| *n*-C30 | 83.2 | 29.9 | 128.9 | 141.1 | 3.6 | 2.8 | 79.0 | 129.8 | 35.0 | 100.8 | 116.7 | 38.8 | 126.0 | 128.2 |
| *n*-C31 | 749.0 | 308.8 | 1190.4 | 1330.8 | 18.4 | 18.4 | 889.2 | 1312.5 | 938.5 | 988.7 | 1152.2 | 378.4 | 1201.3 | 1269.8 |
| *n*-C32 | 146.2 | 46.7 | 82.0 | 39.4 | 1.8 | 2.0 | 49.0 | 86.0 | 41.5 | 68.5 | 39.2 | 39.9 | 85.4 | 41.5 |
| *n*-C33 | 210.3 | 90.1 | 378.7 | 444.7 | 7.1 | 7.1 | 274.4 | 424.7 | 264.6 | 300.5 | 375.4 | 119.7 | 377.4 | 407.1 |
| *n*-C34 | nd | 26.7 | 58.2 | 63.3 | 2.4 | 2.0 | nd | 67.6 | 80.1 | nd | 47.9 | nd | nd | 71.0 |
| *n*-C35 | nd | nd | nd | 44.7 | 2.0 | 2.6 | nd | nd | nd | nd | nd | nd | nd | nd |
| *n*-C36 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| | | | | | | | | | | | | | | |
| Total n-alkanes (ng/g dry wt) | 7152.4 | 2899.1 | 8860.1 | 8996.4 | 136.5 | 142.0 | 5890.2 | 9353.3 | 8362.6 | 6984.2 | 7183.3 | 2701.9 | 9315.4 | 9625.9 |
| Σ C12–C19 (ng/g dry wt) | 717.3 | 269.4 | 735.9 | 652.3 | 8.8 | 10.7 | 433.5 | 751.2 | 719.0 | 407.0 | 333.5 | 155.0 | 543.7 | 724.4 |
| Σ C20–C33 (ng/dry wt) | 6435.1 | 2603.0 | 8066.0 | 8236.0 | 123.2 | 126.7 | 5393.8 | 8316.9 | 7563.5 | 6577.3 | 6801.8 | 2546.9 | 8771.7 | 8830.5 |
| Pr/Ph | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Odd/Even** | 4.2 | 4.3 | 4.9 | 5.0 | 3.5 | 3.5 | 5.5 | 4.7 | 5.1 | 6.3 | 6.1 | 5.4 | 6.0 | 5.7 |

Table 10.  (cont.)

| Sample ID – UCLA No. | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | OS# | Pr. Blk | XSPIKE 1 % Recovery | XSPIKE 2 % Recovery | XSPIKE % Rec Avg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Surrogate Recovery (%)** | | | | | | | | | | | | | |
| Deu C14 | 57 | 55 | 58 | nd$ | 53 | 58 | 60 | 54 | nd$ | 51 | 52 | 52 | 52 |
| Deu C24 | 76 | 64 | 61 | nd$ | 65 | 68 | 61 | 66 | nd$ | 57 | 64 | 66 | 65 |
| Deu C36 | 80 | 65 | 58 | nd$ | 92 | 70 | 65 | 68 | nd$ | 66 | 74 | 72 | 73 |
| | | | | | | | | | µg/g dry wt | | | | |
| **_n_-alkane (ng/g dry wt)** | | | | | | | | | | | | | |
| _n_-C10 | nd | nd | nd | nd | nd | nd | 25.4 | nd | 499.6 | nd | 18 | 19 | 19 |
| _n_-C11 | nd | nd | nd | nd | nd | nd | 34.2 | nd | 3761.2 | nd | 28 | 22 | 25 |
| _n_-C12 | nd | nd | nd | nd | nd | nd | 17.3 | nd | 489.6 | nd | 33 | 35 | 34 |
| _n_-C13 | nd | 32.2 | nd | nd | nd | nd | nd | nd | 253.8 | nd | 40 | 41 | 41 |
| _n_-C14 | nd | 27.2 | nd | nd | nd | nd | nd | nd | 148.3 | nd | 50 | 50 | 50 |
| _n_-C15 | 74.2 | 66.1 | nd | nd | 2.7 | 31.7 | 14.9 | 17.0 | 65.0 | nd | 57 | 58 | 57 |
| _n_-C16 | 55.7 | 53.9 | nd | 223.8 | 2.0 | 31.4 | 15.2 | 9.6 | nd | nd | 66 | 64 | 65 |
| _n_-C17 | 170.8 | 144.6 | 75.4 | 754.9 | 5.7 | 103.6 | 66.4 | 37.1 | nd | nd | 65 | 68 | 67 |
| pr | nd | 38.7 | nd | nd | nd | 13.1 | 7.7 | nd | nd | nd | 67 | 68 | 67 |
| _n_-C18 | 94.4 | 80.1 | 41.0 | 339.8 | 3.9 | 58.9 | 37.5 | 19.1 | nd | nd | 69 | 69 | 69 |
| ph | nd | 18.4 | nd | nd | nd | nd | nd | nd | nd | nd | 69 | 69 | 69 |
| _n_-C19 | 36.0 | 208.0 | 103.7 | 1141.0 | 1.9 | 174.1 | 122.4 | 62.6 | nd | nd | 70 | 70 | 70 |
| _n_-C20 | 146.1 | 147.8 | 73.7 | 680.8 | 5.3 | 112.2 | 76.4 | 36.1 | 58.1 | 1.51 | 72 | 72 | 72 |
| _n_-C21 | 421.2 | 464.0 | 227.0 | 2275.8 | 13.9 | 364.2 | 246.9 | 109.3 | 86.9 | nd | 72 | 72 | 72 |
| _n_-C22 | 36.9 | 260.3 | 138.3 | 1238.2 | 7.5 | 199.6 | 127.8 | 61.3 | 53.2 | nd | 76 | 72 | 74 |
| _n_-C23 | 831.6 | 834.4 | 444.2 | 4079.3 | 20.6 | 630.8 | 400.8 | 167.0 | 67.6 | nd | 69 | 66 | 68 |
| _n_-C24 | 35.0 | 250.1 | 142.8 | 1116.4 | 6.9 | 186.7 | 112.7 | 51.3 | 71.8 | nd | 60 | 63 | 62 |
| _n_-C25 | 911.3 | 888.6 | 491.9 | 3918.1 | 19.4 | 556.5 | 349.5 | 136.0 | 218.4 | nd | 65 | 69 | 67 |
| _n_-C26 | 191.3 | 124.6 | 86.3 | 574.5 | 4.2 | 100.5 | 52.0 | 27.0 | 87.9 | nd | 70 | 69 | 70 |
| _n_-C27 | 1608.1 | 1718.1 | 863.0 | 5131.4 | 20.6 | 1085.1 | 369.4 | 146.4 | 179.1 | nd | 69 | 70 | 69 |
| _n_-C28 | 159.2 | 97.3 | 65.5 | 328.6 | 3.1 | 64.3 | 26.1 | 15.5 | 60.2 | nd | 66 | 70 | 68 |
| _n_-C29 | 1628.0 | 1538.0 | 682.9 | 4763.2 | 25.7 | 855.6 | 325.2 | 143.7 | 138.0 | nd | 66 | 67 | 67 |
| _n_-C30 | 149.4 | 98.4 | 60.2 | 334.1 | 2.2 | 93.1 | 41.0 | 20.4 | 230.1 | nd | 66 | 65 | 66 |
| _n_-C31 | 1621.1 | 1150.4 | 600.7 | 4488.1 | 25.2 | 861.2 | 339.9 | 156.5 | 171.2 | nd | 67 | 64 | 66 |
| _n_-C32 | 68.6 | 32.3 | 0.0 | 784.7 | 0.0 | 26.2 | 15.1 | 11.8 | 169.6 | nd | 64 | 69 | 66 |
| _n_-C33 | 564.4 | 354.9 | 195.2 | 1339.2 | 8.3 | 271.3 | 110.5 | 51.0 | nd | nd | 66 | 63 | 64 |
| _n_-C34 | 49.4 | 52.6 | nd | 330.4 | nd | 45.8 | 29.9 | 13.5 | nd | nd | 64 | 62 | 63 |
| _n_-C35 | 75.2 | 30.2 | nd | nd | nd | 24.4 | 10.9 | nd | nd | nd | 60 | 63 | 62 |
| _n_-C36 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 69 | 69 | 69 |
| Total n-alkanes (ng/g dry wt) | 8927.9 | 8654.2 | 4291.7 | 33842.3 | 179.2 | 5877.3 | 2967.7 | 1292.1 | 6819.4 | | | | |
| Σ C12–C19 (ng/g dry wt) | 431.1 | 612.2 | 220.1 | 2459.5 | 16.1 | 399.7 | 273.8 | 145.3 | 956.6 | | | | |
| Σ C20–C33 (ng/g dry wt) | 8372.3 | 7959.2 | 4071.7 | 31052.4 | 163.1 | 5407.4 | 2593.5 | 1133.3 | 1602.1 | | | | |
| Pr/Ph | nd | 2.1 | nd | nd | nd | na† | na† | nd | nd | | | | |
| Odd/Even** | 8.1 | 6.2 | 6.1 | 4.7 | 4.1 | 5.4 | 4.4 | 3.9 | 1.3 | | | | |

\* Duplicate (D) or replicate (R) analysis
\*\* Summed _n_-C15–_n_-C36
\# OS=oil spill sample; note change in units of concentration
nd$=dilution too great to measure surrogates
nd=not detected
na†=not applicable, phytane not detected

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**Table 11:** Distribution (ng/g dry wt) of PAHs in gross sediments of Beaufort Lagoon. All lagoon sample numbers have the prefix BL03.

| Sample ID – UCLA No. | 1 | 2 | 3 | 3D* | 4 | 5B | 6B |
|---|---|---|---|---|---|---|---|
| **Surrogate Recovery (%)** | | | | | | | |
| hexamethylbenzene | 62 | 53 | 50 | 50 | 38 | 41 | 44 |
| n-dodecylbenzene | 57 | 58 | 62 | 64 | 59 | 59 | 60 |
| 4-terphenyl-D14 | 64 | 60 | 75 | 68 | 68 | 65 | 57 |
| | | | | | | | |
| **PAH (ng g⁻¹ dry wt)** | | | | | | | |
| naphthalene | 7.7 | 7.4 | 13.0 | 16.7 | nd | 7.3 | 6.7 |
| C1-naphthalenes | 18.9 | 21.3 | 26.3 | 27.2 | nd | 15.4 | 21.4 |
| 2-methylnaphthalene | 10.0 | 10.7 | 14.8 | 14.9 | nd | 6.4 | 12.1 |
| 1-methylnaphthalene | 8.9 | 10.6 | 11.6 | 12.4 | nd | 9.0 | 9.4 |
| C2-naphthalenes | 27.1 | 33.3 | 41.6 | 48.2 | 0.4 | 28.9 | 50.0 |
| 2,6-dimethylnaphthalene | 8.0 | 8.5 | 6.9 | 7.5 | nd | 5.6 | 16.0 |
| C3-naphthalenes | 14.7 | 26.8 | 34.1 | 37.8 | 0.5 | 13.8 | 39.6 |
| 2,3,5-trimethylnaphthalene | nd | 4.4 | 6.1 | 7.0 | nd | 2.4 | 3.8 |
| C4-naphthalenes | 1.7 | 12.0 | 17.9 | 19.8 | nd | 7.0 | 18.9 |
| biphenyl | 5.6 | 4.3 | 9.2 | 9.9 | nd | 4.9 | 7.1 |
| acenaphthylene | nd | nd | nd | nd | nd | nd | nd |
| acenaphthene | nd | 0.6 | 0.9 | 1.1 | nd | nd | nd |
| fluorene | nd | 2.9 | 4.9 | 5.1 | nd | 2.7 | 5.4 |
| 2-methylfluorene | nd | 2.7 | 4.3 | 5.1 | nd | nd | nd |
| C1-fluorenes | 3.2 | 3.8 | 6.4 | nd | tr | 2.8 | 5.8 |
| C2-fluorenes | 4.9 | 6.7 | 13.3 | nd | tr | 6.4 | 18.6 |
| C3-fluorenes | tr | tr | nd | nd | nd | tr | tr |
| phenanthrene | 19.5 | 15.2 | 27.8 | 32.0 | 1.1 | 17.9 | 33.4 |
| 1-methylphenanthrene | 4.4 | 4.9 | 6.7 | 7.5 | nd | 3.4 | 8.8 |
| anthracene | 1.6 | nd | 1.3 | 1.3 | nd | nd | nd |
| C1-phenanthrenes/anthracenes | 47.9 | 51.3 | 72.5 | 77.1 | 20.8 | 34.6 | 123.2 |
| C2-phenanthrenes/anthracenes | 12.8 | 26.7 | 32.6 | 35.7 | 1.8 | 19.4 | 57.5 |
| 3,6-dimethylphenanthrene | nd | 1.2 | 3.7 | 4.2 | nd | nd | 1.8 |
| C3-phenanthrenes/anthracenes | 18.0 | 23.7 | 43.7 | 46.6 | 4.7 | 22.2 | 58.3 |
| C4-phenanthrenes/anthracenes | 5.2 | 10.9 | 17.0 | 17.5 | 1.0 | 9.5 | 28.0 |
| 2,3-benzofluorene | nd | 1.6 | 2.5 | 3.2 | nd | 1.3 | 2.9 |
| 1,1´-binaphthalene | nd | nd | nd | nd | nd | nd | nd |
| dibenzothiophene** | nd | 3.4 | 5.4 | 7.6 | 0.2 | 3.4 | 6.7 |
| C1-dibenzothiophenes** | 2.5 | 3.5 | 3.5 | 3.8 | 0.3 | 2.1 | 6.3 |
| C2-dibenzothiophenes** | 2.6 | 4.6 | 6.1 | 6.6 | nd | 2.9 | 12.0 |
| C3-dibenzothiophenes** | 5.9 | 23.7 | 6.5 | 6.8 | nd | 1.8 | 6.8 |
| C4-dibenzothiophenes** | nd | tr | 1.8 | 1.9 | nd | nd | nd |
| fluoranthene | 3.8 | 2.7 | 4.1 | 4.3 | nd | 2.5 | 5.6 |
| pyrene | 5.7 | 4.9 | 7.6 | 8.6 | 0.6 | 4.4 | 9.6 |
| C1-fluoranthenes/pyrenes | 3.8 | 4.2 | 6.8 | 7.1 | tr | 4.3 | 10.8 |
| C2-fluoranthenes/pyrenes | 7.5 | 7.2 | 7.9 | 8.1 | tr | 7.2 | 12.8 |

| PAH (ng g⁻¹ dry wt) (cont.) | 1 | 2 | 3 | 3D* | 4 | 5B | 6B |
|---|---|---|---|---|---|---|---|
| C3-fluoranthenes/pyrenes | 4.9 | 2.6 | 2.2 | 2.3 | nd | 1.3 | 5.2 |
| C4-fluoranthenes/pyrenes | nd | 1.7 | 3.3 | 3.6 | nd | tr | 6.3 |
| benz(a)anthracene | 4.0 | 1.4 | 2.7 | 3.7 | 0.5 | 1.3 | 3.9 |
| chrysene/triphenylene | 12.0 | 8.0 | 14.8 | 15.3 | 0.8 | 9.5 | 19.4 |
| C1-chrysenes/triphenylenes | 7.9 | 9.2 | 12.5 | 13.0 | tr | 7.6 | 18.9 |
| C2-chrysenes/triphenylenes | 2.6 | 4.3 | 6.0 | 6.4 | nd | 1.0 | 8.1 |
| C3-chrysenes/triphenylenes | tr | tr | nd | nd | nd | nd | nd |
| C4-chrysenes/triphenylenes | nd | nd | nd | nd | nd | nd | nd |
| benzo(k)fluoranthene | 3.8 | 1.0 | 1.0 | 1.1 | 0.3 | 0.5 | 1.8 |
| benzo(b)fluoranthene | 7.6 | 4.5 | 8.0 | 8.5 | 0.5 | 6.8 | 13.3 |
| benzo(e)pyrene | 9.2 | 5.6 | 8.1 | 8.8 | 0.5 | 5.4 | 12.0 |
| benzo(a)pyrene | 3.8 | 1.6 | 1.6 | 1.9 | 0.2 | 1.5 | 1.7 |
| 9,10-diphenylanthracene | nd | nd | nd | nd | nd | nd | nd |
| perylene | 30.3 | 35.9 | 42.5 | 43.1 | 2.6 | 22.1 | 53.4 |
| indeno(1,2,3-cd)pyrene | nd | nd | nd | nd | nd | nd | nd |
| dibenz(a,h)anthracene | nd | nd | nd | nd | nd | nd | nd |
| picene | nd | nd | nd | nd | nd | nd | nd |
| benzo(ghi)perylene | nd | 3.6 | 4.6 | 5.0 | nd | nd | nd |
| anthanthrene | nd | nd | nd | nd | nd | nd | nd |
| coronene | nd | nd | nd | nd | nd | nd | nd |
| 1,2,4,5-dibenzopyrene | nd | nd | nd | nd | nd | nd | nd |
| C1-C20H12 aromatics | 9.5 | 5.1 | 6.9 | 7.2 | nd | 5.5 | 15.3 |
| C2-C20H12 aromatics | tr | 1.7 | 2.6 | 2.7 | nd | 1.0 | 2.9 |
| C3-C20H12 aromatics | nd | tr | nd | nd | nd | nd | nd |
| C4-C20H12 aromatics | nd | tr | nd | nd | nd | nd | nd |
| | | | | | | | |
| sum-naphthalenes(N) | 70.1 | 100.9 | 132.9 | 149.6 | 0.9 | 72.3 | 136.7 |
| sum-fluorenes(F) | 8.1 | 13.4 | 24.6 | 5.1 | nd | 11.9 | 29.8 |
| sum-phenanthrenes/anthracenes(PA) | 105.1 | 127.9 | 194.8 | 210.2 | 29.3 | 103.6 | 300.5 |
| sum-dibenzothiophenes(D) | 11.0 | 35.2 | 23.3 | 26.7 | 0.6 | 10.2 | 31.8 |
| sum-fluoranthenes/pyrenes(FP) | 25.8 | 23.2 | 31.8 | 33.9 | 0.6 | 19.7 | 50.3 |
| sum-chrysenes(C) | 22.5 | 21.5 | 33.3 | 34.7 | 0.8 | 18.2 | 46.4 |
| sum-C20H12 aromatics(C20) | 64.2 | 55.2 | 70.6 | 73.4 | 4.1 | 42.9 | 100.3 |
| sum- 4,5 PAH (4,5 PAH) | 107.0 | 94.6 | 128.9 | 135.8 | 6.0 | 75.4 | 182.7 |
| sum-PAH(t-PAH) | 316.4 | 388.8 | 531.3 | 556.7 | 36.7 | 286.3 | 709.7 |
| N/PA | 0.67 | 0.79 | 0.68 | 0.71 | 0.03 | 0.70 | 0.46 |
| N/perylene | 2.31 | 2.81 | 3.13 | 3.47 | 0.34 | 3.26 | 2.56 |
| F/perylene | 0.27 | 0.37 | 0.58 | 0.12 | nd | 0.54 | 0.56 |
| PA/perylene | 3.47 | 3.56 | 4.59 | 4.88 | 11.16 | 4.68 | 5.62 |
| FP/perylene | 0.85 | 0.65 | 0.75 | 0.79 | 0.22 | 0.89 | 0.94 |
| t-PAH/perylene | 10.45 | 10.83 | 12.51 | 12.92 | 13.99 | 12.93 | 13.29 |

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Table 11. (cont.)

| Sample ID – UCLA No. | 9 | 9B | 10 | 11A | 12 | 13 | 14 | | 9 | 9B | 10 | 11A | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Surrogate Recovery (%)** | | | | | | | | **PAH (ng/g dry wt) (cont.)** | | | | | | | |
| hexamethylbenzene | 46 | 43 | 39 | 44 | 40 | 40 | 45 | C3-fluoranthenes/pyrenes | 1.6 | 2.9 | 1.3 | 2.0 | 3.7 | 1.0 | 3.6 |
| n-dodecylbenzene | 66 | 50 | 59 | 62 | 56 | 56 | 59 | C4-fluoranthenes/pyrenes | nd | 3.2 | 1.1 | nd | tr | nd | 1.9 |
| 4-terphenyl-D14 | 72 | 63 | 72 | 63 | 69 | 69 | 71 | benz(a)anthracene | 1.8 | 1.7 | 0.6 | 1.6 | 2.0 | 0.9 | 2.1 |
| | | | | | | | | chrysene/triphenylene | 9.3 | 8.9 | 3.3 | 12.3 | 15.6 | 3.9 | 12.8 |
| **PAH (ng/g dry wt)** | | | | | | | | C1-chrysenes/triphenylenes | 6.7 | 6.8 | 2.4 | 12.4 | 18.5 | 3.2 | 14.6 |
| naphthalene | 8.3 | 7.6 | 1.7 | 8.9 | 3.3 | 1.0 | 9.7 | C2-chrysenes/triphenylenes | 1.9 | 2.4 | 0.9 | 4.8 | 12.4 | tr | 6.0 |
| C1-naphthalenes | 19.2 | 12.4 | 4.4 | 26.4 | 18.2 | 4.6 | 25.9 | C3-chrysenes/triphenylenes | nd | nd | nd | 3.8 | tr | nd | nd |
| 2-methylnaphthalene | 9.7 | 7.0 | 2.5 | 13.8 | 9.3 | 2.7 | 14.8 | C4-chrysenes/triphenylenes | nd | nd | nd | nd | tr | nd | nd |
| 1-methylnaphthalene | 9.5 | 5.5 | 2.0 | 12.7 | 8.9 | 1.9 | 11.2 | benzo(k)fluoranthene | nd | 0.6 | 0.3 | 1.1 | 1.3 | 0.4 | 1.2 |
| C2-naphthalenes | 23.3 | 19.5 | 7.8 | 42.7 | 46.9 | 9.4 | 46.7 | benzo(b)fluoranthene | 4.7 | 5.3 | 2.1 | 7.0 | 8.5 | 2.2 | 9.6 |
| 2,6-dimethylnaphthalene | 7.3 | 6.2 | 2.0 | 14.4 | 12.9 | 2.5 | 12.1 | benzo(e)pyrene | 4.1 | 4.8 | 2.0 | 5.9 | 9.6 | 2.5 | 7.5 |
| C3-naphthalenes | 16.5 | 13.6 | 7.7 | 33.0 | 40.1 | 7.4 | 34.0 | benzo(a)pyrene | nd | nd | 0.4 | nd | nd | nd | nd |
| 2,3,5-trimethylnaphthalene | 3.0 | nd | nd | 3.1 | 4.2 | 0.9 | 4.1 | 9,10-diphenylanthracene | nd | nd | nd | nd | nd | nd | nd |
| C4-naphthalenes | 7.0 | 6.5 | 2.6 | 13.1 | 16.1 | 4.6 | 18.4 | perylene | 15.6 | 79.8 | 13.7 | 32.5 | 44.8 | 16.5 | 20.3 |
| biphenyl | 4.5 | 4.8 | 1.3 | 7.2 | 4.7 | 1.5 | 5.9 | indeno(1,2,3-cd)pyrene | nd | nd | nd | nd | nd | nd | nd |
| acenaphthylene | nd | nd | nd | nd | nd | nd | nd | dibenz(a,h)anthracene | nd | nd | nd | nd | nd | nd | nd |
| acenaphthene | nd | nd | nd | nd | nd | nd | nd | picene | nd | nd | nd | nd | nd | nd | nd |
| fluorene | 2.5 | 2.6 | nd | 4.3 | 4.0 | 1.1 | 4.0 | benzo(ghi)perylene | nd | nd | nd | 4.8 | 7.6 | nd | nd |
| 2-methylfluorene | nd | nd | nd | nd | 3.1 | 0.8 | 3.0 | anthanthrene | nd | nd | nd | nd | nd | nd | nd |
| C1-fluorenes | 3.5 | 3.1 | 1.2 | 5.3 | 5.5 | 1.2 | 6.3 | coronene | nd | nd | nd | nd | nd | nd | nd |
| C2-fluorenes | 6.0 | 5.6 | 2.6 | 15.0 | 13.1 | 1.9 | 13.1 | 1,2,4,5-dibenzopyrene | nd | nd | nd | nd | nd | nd | nd |
| C3-fluorenes | tr | tr | tr | tr | tr | tr | tr | C1-C20H12 aromatics | 2.7 | 4.4 | 3.1 | 4.6 | 2.2 | 3.1 | 4.3 |
| phenanthrene | 14.9 | 17.3 | 5.3 | 24.0 | 25.1 | 6.4 | 21.3 | C2-C20H12 aromatics | nd | 3.7 | 0.7 | tr | tr | nd | 2.2 |
| 1-methylphenanthrene | 3.1 | 5.1 | 1.6 | 6.7 | 8.0 | 1.9 | 6.5 | C3-C20H12 aromatics | nd | nd | nd | tr | nd | nd | nd |
| anthracene | nd | nd | nd | nd | nd | nd | nd | C4-C20H12 aromatics | nd | nd | nd | nd | nd | nd | nd |
| C1-phenanthrenes/anthracenes | 25.9 | 37.2 | 41.5 | 112.8 | 138.0 | 56.6 | 193.7 | | | | | | | | |
| C2-phenanthrenes/anthracenes | 15.9 | 18.1 | 10.0 | 36.0 | 52.7 | 11.9 | 47.3 | sum-naphthalenes(N) | 74.3 | 59.5 | 24.2 | 124.0 | 124.7 | 26.9 | 134.7 |
| 3,6-dimethylphenanthrene | 1.2 | 1.2 | 0.4 | 1.8 | 1.8 | 0.4 | 1.9 | sum-fluorenes(F) | 12.0 | 11.3 | 3.8 | 24.6 | 22.6 | 25.6 | 23.4 |
| C3-phenanthrenes/anthracenes | 15.0 | 14.1 | 17.2 | 63.7 | 82.7 | 21.4 | 100.4 | sum-phenanthrenes/anthracenes(PA) | 81.5 | 94.5 | 79.4 | 256.8 | 317.1 | 102.7 | 385.6 |
| C4-phenanthrenes/anthracenes | 6.3 | 7.8 | 5.4 | 20.3 | 18.6 | 6.4 | 22.9 | sum-dibenzothiophenes(D) | 16.8 | 6.3 | 4.4 | 19.9 | 23.5 | 2.9 | 17.0 |
| 2,3-benzofluorene | 1.1 | nd | 0.3 | 2.1 | 2.6 | nd | 2.1 | sum-fluoranthenes/pyrenes(FP) | 15.5 | 24.6 | 9.1 | 27.1 | 36.7 | 9.2 | 33.2 |
| 1,1´-binaphthalene | nd | nd | nd | nd | nd | nd | nd | sum-chrysenes(C) | 17.8 | 18.1 | 6.6 | 33.3 | 46.5 | 7.1 | 33.4 |
| dibenzothiophene** | 3.5 | 3.3 | 1.0 | 5.0 | nd | 1.4 | 3.7 | sum-C20H12 aromatics(C20) | 27.1 | 98.6 | 22.3 | 51.1 | 66.4 | 24.7 | 45.2 |
| C1-dibenzothiophenes** | 2.1 | 1.8 | 1.5 | 4.4 | 6.5 | 1.5 | 6.0 | sum- 4,5 PAH (4,5 PAH) | 59.6 | 134.8 | 34.8 | 108.4 | 149.4 | 38.7 | 107.3 |
| C2-dibenzothiophenes** | 3.1 | 1.2 | 1.2 | 6.3 | 8.5 | nd | 4.1 | sum-PAH(t-PAH) | 252.6 | 319.4 | 152.0 | 552.5 | 654.5 | 201.4 | 682.6 |
| C3-dibenzothiophenes** | 8.0 | nd | 0.7 | 4.2 | 8.4 | nd | 3.1 | N/PA | 0.91 | 0.63 | 0.30 | 0.48 | 0.39 | 0.26 | 0.35 |
| C4-dibenzothiophenes** | tr | nd | nd | nd | tr | nd | nd | N/perylene | 4.78 | 0.75 | 1.77 | 3.82 | 2.79 | 1.63 | 6.64 |
| fluoranthene | 3.2 | 2.4 | 0.9 | 4.1 | 5.1 | 1.2 | 3.7 | F/perylene | 0.77 | 0.14 | 0.28 | 0.76 | 0.51 | 1.55 | 1.15 |
| pyrene | 4.6 | 4.8 | 1.5 | 6.5 | 8.5 | 2.1 | 7.6 | PA/perylene | 5.24 | 1.18 | 5.80 | 7.90 | 7.09 | 6.23 | 19.00 |
| C1-fluoranthenes/pyrenes | 3.0 | 3.4 | 1.7 | 6.7 | 8.0 | 2.3 | 7.6 | FP/perylene | 1.00 | 0.31 | 0.66 | 0.83 | 0.82 | 0.56 | 1.64 |
| C2-fluoranthenes/pyrenes | 3.1 | 7.8 | 2.6 | 7.7 | 11.4 | 2.5 | 8.8 | t-PAH/perylene | 16.24 | 4.00 | 11.11 | 17.00 | 14.62 | 12.23 | 33.63 |

Table 11. (cont.)

| Sample ID – UCLA No. | 15 | 16 | 17 | 18 | 19 | 20 | OS[#] | PAH (ng/g dry wt) (cont.) | 15 | 16 | 17 | 18 | 19 | 20 | OS[#] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Surrogate Recovery (%) | | | | | | | µg/g dry wt | | | | | | | | µg/g-dry wt |
| hexamethylbenzene | 44 | 46 | 43.0 | 47 | 40 | 51 | 50 | C3-fluoranthenes/pyrenes | 1.5 | nd | tr | 2.4 | 0.6 | 0.3 | 1.1 |
| n-dodecylbenzene | 63 | 59 | 50.0 | 58 | 59 | 56 | 61 | C4-fluoranthenes/pyrenes | 2.0 | nd | nd | tr | 0.7 | 0.2 | 1.4 |
| 4-terphenyl-D14 | 70 | 68 | 69.0 | 63 | 68 | 69 | 70 | benz(a)anthracene | 0.8 | 4.8 | 0.1 | 1.6 | 0.4 | nd | 2.5 |
| | | | | | | | | chrysene/triphenylene | 6.8 | 10.2 | 0.3 | 9.9 | 3.7 | 1.3 | 2.8 |
| PAH (ng/g dry wt) | | | | | | | | C1-chrysenes/triphenylenes | 6.1 | 6.6 | 0.1 | 10.5 | 4.3 | 0.7 | 1.6 |
| naphthalene | nd | 9.1 | nd | 9.6 | 1.3 | 0.5 | 2.9 | C2-chrysenes/triphenylenes | 2.5 | nd | nd | 2.0 | 5.3 | 0.4 | 2.4 |
| C1-naphthalenes | nd | 11.9 | 0.1 | 24.2 | 2.7 | 1.0 | nd | C3-chrysenes/triphenylenes | nd | nd | nd | nd | 1.1 | nd | 2.6 |
| 2-methylnaphthalene | nd | 8.7 | 0.1 | 12.1 | 1.5 | 0.5 | nd | C4-chrysenes/triphenylenes | nd | nd | nd | nd | tr | nd | 2.1 |
| 1-methylnaphthalene | nd | 3.3 | nd | 12.0 | 1.2 | 0.5 | 4.8 | benzo(k)fluoranthene | 0.8 | nd | nd | 0.7 | 0.4 | nd | nd |
| C2-naphthalenes | nd | 20.9 | 0.3 | 34.6 | 4.5 | 1.9 | 83.0 | benzo(b)fluoranthene | 3.8 | 5.9 | 0.2 | 5.7 | 1.1 | nd | nd |
| 2,6-dimethylnaphthalene | nd | 7.5 | nd | 10.0 | 1.4 | 0.4 | 31.0 | benzo(e)pyrene | 4.5 | nd | 0.2 | 6.1 | 1.5 | nd | nd |
| C3-naphthalenes | 4.9 | 7.7 | 0.3 | 26.2 | 4.3 | 1.4 | 44.2 | benzo(a)pyrene | nd | nd | nd | nd | nd | nd | nd |
| 2,3,5-trimethylnaphthalene | nd | nd | nd | 4.5 | 0.8 | nd | 7.4 | 9,10-diphenylanthracene | nd | nd | nd | nd | nd | nd | nd |
| C4-naphthalenes | 5.9 | nd | nd | 13.2 | 2.1 | 0.6 | 15.0 | perylene | 19.2 | 29.2 | nd | 18.8 | 4.8 | 1.1 | nd |
| biphenyl | nd | 4.8 | 0.1 | 5.4 | 0.8 | 0.3 | nd | indeno(1,2,3-cd)pyrene | nd | nd | nd | nd | nd | nd | nd |
| acenaphthylene | nd | nd | nd | nd | nd | nd | nd | dibenz(a,h)anthracene | nd | nd | nd | nd | nd | nd | nd |
| acenaphthene | nd | nd | nd | nd | nd | nd | 0.5 | picene | nd | nd | nd | nd | nd | nd | nd |
| fluorene | nd | nd | nd | 3.3 | 0.7 | nd | 1.5 | benzo(ghi)perylene | nd | nd | nd | 5.3 | nd | nd | nd |
| 2-methylfluorene | nd | nd | nd | 2.7 | 0.4 | nd | 2.2 | anthanthrene | nd | nd | nd | nd | nd | nd | nd |
| C1-fluorenes | 2.7 | nd | 0.3 | 3.9 | 0.9 | 0.8 | 2.0 | coronene | nd | nd | nd | nd | nd | nd | nd |
| C2-fluorenes | 8.5 | nd | 0.4 | 10.6 | 3.7 | 1.6 | 2.1 | 1,2,4,5-dibenzopyrene | nd | nd | nd | nd | nd | nd | nd |
| C3-fluorenes | tr | nd | tr | nd | tr | tr | nd | C1-C20H12 aromatics | 4.2 | tr | 0.3 | 2.9 | 0.7 | 1.9 | 7.5 |
| phenanthrene | 10.3 | 17.1 | 1.0 | 18.3 | 3.6 | 1.9 | 2.3 | C2-C20H12 aromatics | nd | tr | nd | nd | tr | 0.8 | 4.1 |
| 1-methylphenanthrene | nd | 3.7 | nd | 4.8 | 0.9 | nd | 1.1 | C3-C20H12 aromatics | nd | nd | nd | nd | nd | nd | 1.7 |
| anthracene | nd | nd | nd | nd | nd | nd | 0.7 | C4-C20H12 aromatics | nd | nd | nd | nd | nd | nd | nd |
| C1-phenanthrenes/anthracenes | 86.7 | 25.3 | 15.0 | 124.1 | 24.2 | 109.3 | 3.8 | | | | | | | | |
| C2-phenanthrenes/anthracenes | 25.8 | 13.6 | 1.4 | 36.5 | 6.5 | 10.6 | 4.4 | sum-naphthalenes(N) | 10.9 | 49.6 | 0.7 | 107.8 | 14.8 | 5.3 | 145.0 |
| 3,6-dimethylphenanthrene | nd | nd | nd | 1.8 | 0.2 | nd | 0.3 | sum-fluorenes(F) | 11.2 | nd | 0.7 | 17.8 | 5.4 | 2.4 | 5.5 |
| C3-phenanthrenes/anthracenes | 64.0 | 6.8 | 7.2 | 61.9 | 21.9 | 57.4 | 5.7 | sum-phenanthrenes/anthracenes(PA) | 200.3 | 62.8 | 26.0 | 265.0 | 62.2 | 185.5 | 19.0 |
| C4-phenanthrenes/anthracenes | 13.5 | nd | 1.4 | 24.3 | 5.9 | 6.2 | 2.1 | sum-dibenzothiophenes(D) | 12.8 | nd | 0.6 | 11.3 | 2.8 | 2.6 | 1.7 |
| 2,3-benzofluorene | 1.4 | nd | nd | 1.3 | nd | nd | nd | sum-fluoranthenes/pyrenes(FP) | 18.5 | 8.0 | 0.9 | 21.3 | 6.9 | 3.9 | 8.9 |
| 1,1´-binaphthalene | nd | nd | nd | nd | nd | nd | nd | sum-chrysenes(C) | 15.4 | 16.8 | 0.4 | 22.3 | 14.4 | 2.3 | 11.4 |
| dibenzothiophene** | 2.2 | nd | 0.2 | 2.8 | 0.5 | 0.3 | nd | sum-C20H12 aromatics(C20) | 32.5 | 35.2 | 0.7 | 34.1 | 8.5 | 3.8 | 13.3 |
| C1-dibenzothiophenes** | 3.2 | nd | 0.3 | 3.5 | 0.7 | 0.6 | 0.4 | sum- 4,5 PAH (4,5 PAH) | 62.9 | 64.7 | 1.9 | 76.4 | 29.5 | 7.4 | 22.8 |
| C2-dibenzothiophenes** | 3.2 | nd | 0.1 | 2.8 | 0.8 | 0.4 | 0.3 | sum-PAH(t-PAH) | 303.7 | 181.9 | 30.3 | 493.2 | 116.3 | 206.1 | 207.9 |
| C3-dibenzothiophenes** | 4.3 | nd | tr | 2.1 | 0.9 | 1.4 | 0.5 | N/PA | 0.05 | 0.79 | 0.03 | 0.41 | 0.24 | 0.03 | 7.62 |
| C4-dibenzothiophenes** | nd | nd | nd | nd | tr | nd | 0.5 | N/perylene | 0.57 | 1.70 | na | 5.75 | 3.06 | 4.80 | na |
| fluoranthene | 2.4 | 2.6 | 0.2 | 3.2 | 1.8 | 0.7 | 2.5 | F/perylene | 0.58 | nd | na | 0.95 | 1.11 | 2.14 | na |
| pyrene | 4.3 | 4.5 | 0.3 | 4.9 | 2.0 | 0.8 | 2.0 | PA/perylene | 10.45 | 2.15 | na | 14.13 | 12.85 | 167.36 | na |
| C1-fluoranthenes/pyrenes | 4.5 | 0.9 | 0.1 | 5.6 | 1.0 | 0.7 | 0.9 | FP/perylene | 0.96 | 0.27 | na | 1.13 | 1.43 | 3.54 | na |
| C2-fluoranthenes/pyrenes | 3.7 | nd | 0.3 | 5.2 | 0.8 | 1.2 | 1.1 | t-PAH/perylene | 15.84 | 6.22 | na | 26.30 | 24.01 | 185.96 | na |

Table 11. (cont.)

| Sample ID – UCLA No. | Pr. Blk | X-SPIKE 1 | X-SPIKE 2 | X-SPIKE Avg | Ref Sed SRM 1941[†] | NIST Values[†] |
|---|---|---|---|---|---|---|
| **Surrogate Recovery (%)** | | | | | | |
| hexamethylbenzene | 40 | 55 | 55 | 55 | 43 | |
| n-dodecylbenzene | 65 | 71 | 61 | 66 | 64 | |
| 4-terphenyl-D14 | 75 | 83 | 93 | 88 | 67 | |
| | | | | | | |
| **PAH (ng/g dry wt)** | | | | | | |
| naphthalene | nd | 34 | 30 | 32 | 1230 | 1322±14 |
| C1-naphthalenes | nd | | | 43 | | |
| 2-methylnaphthalene | nd | 44 | 40 | 42 | 336 | 406±36 |
| 1-methylnaphthalene | nd | 43 | 45 | 44 | 214 | 229±19 |
| C2-naphthalenes | nd | | | 49 | | |
| 2,6-dimethylnaphthalene | nd | 50 | 48 | 49 | 237 | 198±23 |
| C3-naphthalenes | nd | | | 57 | | |
| 2,3,5-trimethylnaphthalene | nd | 59 | 55 | 57 | 87 | 96.3 |
| C4-naphthalenes | nd | | | 57 | | |
| biphenyl | nd | 57 | 65 | 61 | 104 | 115±15 |
| acenaphthylene | nd | 58 | 60 | 59 | 106 | 115±10 |
| acenaphthene | nd | 57 | 53 | 55 | 46 | 52±2 |
| fluorene | nd | 57 | 59 | 58 | 88 | 104±5 |
| 2-methylfluorene | nd | 80 | 76 | 78 | 61 | 73.7 |
| C1-fluorenes | nd | | | 78 | | |
| C2-fluorenes | nd | | | 75 | | |
| C3-fluorenes | nd | | | 75 | | |
| phenanthrene | nd | 81 | 79 | 77 | 551 | 577±59 |
| 1-methylphenanthrene | nd | 80 | 76 | 78 | 92 | 109±6 |
| anthracene | nd | 78 | 78 | 78 | 171 | 202±42 |
| C1-phenanthrenes/anthracenes | nd | | | 78 | | |
| C2-phenanthrenes/anthracenes | nd | | | 75 | | |
| 3,6-dimethylphenanthrene | nd | 79 | 71 | 75 | 56 | 78.0 |
| C3-phenanthrenes/anthracenes | nd | | | 75 | | |
| C4-phenanthrenes/anthracenes | nd | | | 75 | | |
| 2,3-benzofluorene | nd | 76 | 84 | 80 | 139 | 124.8 |
| 1,1´-binaphthalene | nd | 70 | 82 | 76 | 98 | 117.0 |
| dibenzothiophene** | nd | 35 | 41 | 38 | 163 | 209.8 |
| C1-dibenzothiophenes** | nd | | | 78 | | |
| C2-dibenzothiophenes** | nd | | | 75 | | |
| C3-dibenzothiophenes** | nd | | | 75 | | |
| C4-dibenzothiophenes** | nd | | | 75 | | |
| fluoranthene | nd | 80 | 88 | 84 | 1132 | 1220±240 |

| Sample ID – UCLA No. | Pr. Blk | X-SPIKE 1 | X-SPIKE 2 | X-SPIKE Avg | Ref Sed SRM 1941[†] | NIST Values[†] |
|---|---|---|---|---|---|---|
| **PAH (ng/g dry wt) (cont.)** | | | | | | |
| pyrene | nd | 78 | 86 | 82 | 976 | 1080±200 |
| C1-fluoranthenes/pyrenes | nd | | | 78 | | |
| C2-fluoranthenes/pyrenes | nd | | | 75 | | |
| C3-fluoranthenes/pyrenes | nd | | | 75 | | |
| C4-fluoranthenes/pyrenes | nd | | | 75 | | |
| benz(a)anthracene | nd | 59 | 63 | 61 | 449 | 550±79 |
| chrysene/triphenylene | nd | 88 | 84 | 86 | 622 | 641.0 |
| C1-chrysenes/triphenylenes | nd | | | 78 | | |
| C2-chrysenes/triphenylenes | nd | | | 75 | | |
| C3-chrysenes/triphenylenes | nd | | | 75 | | |
| C4-chrysenes/triphenylenes | nd | | | 75 | | |
| benzo(k)fluoranthene | nd | 61 | 67 | 64 | 386 | 444±49 |
| benzo(b)fluoranthene | nd | 74 | 74 | 74 | 712 | 780±19 |
| benzo(e)pyrene | nd | 68 | 60 | 64 | 534 | 573.0 |
| benzo(a)pyrene | nd | 56 | 62 | 59 | 561 | 670±130 |
| 9,10-diphenylanthracene | nd | 77 | 74 | 76 | | |
| perylene | nd | 68 | 62 | 65 | 397 | 422±33 |
| indeno(1,2,3-cd)pyrene | nd | 63 | 64 | 63 | 466 | 569±40 |
| dibenz(a,h)anthracene | nd | 62 | 60 | 61 | | |
| picene | nd | 69 | 71 | 70 | | |
| benzo(ghi)perylene | nd | 62 | 66 | 64 | 438 | 516±83 |
| anthanthrene | nd | 52 | 56 | 54 | | |
| coronene | nd | 70 | 70 | 70 | | |
| 1,2,4,5-dibenzopyrene | nd | 58 | 66 | 62 | | |
| C1-$C_{20}H_{12}$ aromatics | nd | | | 78 | | |
| C2-$C_{20}H_{12}$ aromatics | nd | | | 75 | | |
| C3-$C_{20}H_{12}$ aromatics | nd | | | 75 | | |
| C4-$C_{20}H_{12}$ aromatics | nd | | | 75 | | |

\* Duplicate analysis
\*\* Very low recovery due to activated copper treatment for sulfur removal
[#] OS = oil spill sample; note change in units of concentration

nd = not detected, below MDL
tr = trace amounts, not quantifiable
na = not applicable

[%] recovery of some methylated homologs assumed to be the same as that of methylated phenanthrenes

**Table 12:** Distribution (ng/g dry wt) of triterpenoids in gross sediments of Beaufort Lagoon. All sample numbers have the prefix BL03. O. is the oil spill sample.

| SAMPLE ID – UCLA No.<br>Triterpanes (ng/g dry wt)* | 1 | 2 | 3 | 4 | 5B | 6B | 9 | 9B | 10 | 11A |
|---|---|---|---|---|---|---|---|---|---|---|
| 18α(H),21β(H)-22,29,30-trisnorhopane | tr[#] | tr | tr | tr | tr | 2 | 1 | 1 | 1 | 1 |
| 17 α(H),21 β(H)-22,29,30-trisnorhopane | 9 | tr | 6 | tr | tr | 6 | 4 | 3 | 1 | 3 |
| 17 β(H),21 β(H)-22,29,30-trisnorhopane | 54 | 20 | 51 | 1 | 24 | 51 | 55 | 25 | 14 | 27 |
| 17 α(H),18α(H),21 β(H)-28,30-bisnorhopane | nd[##] | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 17 α(H),21 β(H)-30-norhopane | 16 | 10 | 20 | 1 | 11 | 22 | 18 | 11 | 2 | 13 |
| 17 β(H),21α(H)-30-norhopane | 32 | 12 | 30 | 1 | 15 | 32 | 28 | 15 | 8 | 17 |
| 17 β(H),21 β(H)-30-norhopane** | 138 | 37 | 111 | 2 | 61 | 125 | 128 | 39 | 33 | 39 |
| 18 α(H)-oleanane | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 17 α(H),21 β(H)-hopane | 8 | 5 | 11 | 1 | 5 | 13 | 7 | 5 | 3 | 7 |
| 17 β(H),21α(H)-hopane | tr | 9 | nd | tr | 16 | tr | tr | 27 | tr | nd |
| 17 β(H),21 β(H)-hopane | 14 | 6 | 14 | nd | 7 | 14 | 12 | 6 | 3 | 8 |
| 22S-17 α(H),21 β(H)-30-homohopane | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 22R-17 α(H),21 β(H)-30-homohopane | tr | tr | tr | nd | nd | 15 | tr | nd | nd | nd |
| 17 β(H),21 β(H)-30-homohopane | 10 | 3 | 13 | tr | 6 | 13 | 8 | 6 | 2 | 5 |
| 22S-17 α(H),21 β(H)-30,31-bishomohopane | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 22R-17 α(H),21 β(H)-30,31-bishomohopane | nd | nd | tr | nd | nd | nd | nd | nd | nd | nd |
| 22S-17 α(H),21 β(H)-30,31-trishomohopane | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 22R-17 α(H),21 β(H)-30,31-trishomohopane | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 22S-17 α(H),21 β(H)-30,31-tetrahomohopane | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 22R-17 α(H),21 β(H)-30,31-tetrahomohopane | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| hop-13(18)-ene | 32 | 13 | 25 | 1 | 14 | 26 | 40 | 27 | 8 | 4 |
| hop-21(22)-ene | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| diploptene | 260 | 112 | 182 | 3 | 148 | 254 | 181 | 173 | 93 | 116 |

| SAMPLE ID – UCLA No.<br>Triterpanes (ng/g dry wt)* | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | OS<br>µg/g<br>dry wt |
|---|---|---|---|---|---|---|---|---|---|---|
| 18α(H),21β(H)-22,29,30-trisnorhopane | 1 | 3 | 1 | 3 | nd | nd | 1 | 1 | nd | 56 |
| 17 α(H),21 β(H)-22,29,30-trisnorhopane | 6 | 8 | 5 | 4 | 13 | nd | 5 | 2 | 1 | 57 |
| 17 β(H),21 β(H)-22,29,30-trisnorhopane | 44 | 32 | 36 | 16 | 202 | nd | 46 | 18 | 7 | nd |
| 17 α(H),18α(H),21 β(H)-28,30-bisnorhopane | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 17 α(H),21 β(H)-30-norhopane | 24 | 23 | 23 | 15 | 57 | 1 | 19 | 8 | 2 | 315 |
| 17 β(H),21α(H)-30-norhopane | 24 | 17 | 18 | 11 | 118 | 1 | 26 | 11 | 5 | 30 |
| 17 β(H),21 β(H)-30-norhopane** | 87 | 70 | 83 | 29 | 398 | 1 | 107 | 45 | 13 | 56 |
| 18 α(H)-oleanane | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 17 α(H),21 β(H)-hopane | 11 | 16 | 9 | 9 | 18 | nd | 8 | 3 | 1 | 263 |
| 17 β(H),21α(H)-hopane | tr | nd | nd | 12 | nd | nd | nd | nd | nd | nd |
| 17 β(H),21 β(H)-hopane | 13 | 11 | 10 | 2 | 44 | nd | 13 | 4 | 2 | nd |
| 22S-17 α(H),21 β(H)-30-homohopane | nd | nd | nd | nd | nd | nd | nd | nd | nd | 103 |
| 22R-17 α(H),21 β(H)-30-homohopane | nd | 6 | nd | nd | nd | nd | nd | 1 | nd | 68 |
| 17 β(H),21 β(H)-30-homohopane | 11 | 6 | 9 | 3 | 11 | nd | 11 | 3 | 2 | nd |
| 22S-17 α(H),21 β(H)-30,31-bishomohopane | nd | nd | nd | nd | nd | nd | nd | nd | nd | 44 |
| 22R-17 α(H),21 β(H)-30,31-bishomohopane | nd | nd | nd | nd | nd | nd | nd | nd | nd | 31 |
| 22S-17 α(H),21 β(H)-30,31-trishomohopane | nd | nd | nd | nd | nd | nd | nd | nd | nd | 27 |
| 22R-17 α(H),21 β(H)-30,31-trishomohopane | nd | nd | nd | nd | nd | nd | nd | nd | nd | 7 |
| 22S-17 α(H),21 β(H)-30,31-tetrahomohopane | nd | nd | nd | nd | nd | nd | nd | nd | nd | 7 |
| 22R-17 α(H),21 β(H)-30,31-tetrahomohopane | nd | nd | nd | nd | nd | nd | nd | nd | nd | Tr |
| hop-13(18)-ene | 32 | 30 | 18 | 15 | 53 | nd | 21 | 9 | 2 | ? |
| hop-21(22)-ene | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| diploptene | 352 | 211 | 314 | 143 | 903 | 1 | 184 | 64 | 28 | nd |

 * Quantification based on m/z 191; also note change in the units for OS sample
** May be coeluting with C30 βα hopane in some samples
 [#] Trace amounts, not quantifiable      [##] Not detected, below detection limits

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**Table 13:** Distribution (ng/g dry wt) of steroids in gross sediments of Beaufort Lagoon. All sample numbers have the prefix BL03. OS is the oil spill sample.

| SAMPLE ID – UCLA No.<br>Steranes (ng/g dry wt)* | | 1 | 2 | 3 | 4 | 5B | 6B | 9 | 9B | 10 | 11A |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 5α(H)androstane | | nd## | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 5α(H)pregnane | | nd | nd | 1.4 | 0.1 | nd | nd | nd | nd | nd | nd |
| 5β(H)pregnane | | nd | 0.7 | 1.6 | 0.1 | 0.7 | 2.8 | 1.1 | nd | nd | nd |
| 20-methyl-5α(H)pregnane | | nd | nd | nd | 0.2 | 0.4 | 1.0 | nd | nd | nd | nd |
| 20S-13β(H),17α(H)-diacholestane** | S1# | nd | nd | nd | 0.3 | 0.8 | 3.7 | 1.0 | 0.9 | nd | 1.3 |
| 20R-13β(H),17α(H)-diacholestane | S2 | nd | nd | nd | 0.2 | 0.7 | 2.3 | 0.7 | 0.9 | nd | nd |
| 20S-5α(H),14α(H),17α(H)-cholestane | S3 | nd | nd | nd | 0.2 | 0.8 | 2.6 | 1.1 | 1.0 | nd | 1.2 |
| 20R-5α(H),14α(H),17α(H)-cholestane | S6 | nd | nd | nd | 0.2 | 0.8 | 2.6 | 0.8 | nd | nd | nd |
| 20R-5α(H),14β(H),17β(H)-cholestane | S4 | nd | nd | nd | 0.4 | 2.8 | 6.7 | 1.8 | nd | nd | nd |
| 20S-5α(H),14β(H),17β(H)-cholestane | S5 | nd | nd | nd | 0.2 | 1.5 | 5.2 | nd | nd | nd | 3.3 |
| 20R-24-ethyl-13β(H),17α(H)-diacholestane | S7 | nd | nd | nd | 0.2 | 1.2 | 3.2 | 1.8 | nd | nd | nd |
| 20S-5α(H),14α(H),17α(H)-ergostane | S8 | nd | nd | nd | nd | nd | nd | nd | nd | 1.3 | nd |
| 20R-5α(H),14α(H),17α(H)-ergostane | S11 | nd | nd | nd | 0.2 | nd | nd | 2.5 | nd | nd | nd |
| 20R-5α(H),14β(H),17β(H)-ergostane | S9 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20S-5α(H),14β(H),17β(H)-ergostane | S10 | nd | nd | nd | 0.2 | nd | nd | nd | nd | nd | nd |
| 20S-5α(H),14α(H),17α(H)-stigmastane | S12 | nd | nd | nd | 0.2 | nd | nd | nd | nd | nd | nd |
| 20R-5α(H),14α(H),17α(H)-stigmastane | S15 | 7.5 | 6.9 | 5.4 | 0.1 | 3.1 | 3.2 | 1.6 | 1.4 | 2.0 | 1.1 |
| 20R-5α(H),14β(H),17β(H)-stigmastane | S13 | nd | nd | nd | 0.3 | 0.8 | 2.3 | 1.5 | nd | 1.1 | nd |
| 20S-5α(H),14β(H),17β(H)-stigmastane | S14 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

| SAMPLE ID – UCLA No.<br>Steranes (ng/g dry wt)* | | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | OS<br>μg/g<br>dry wt |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 5α(H)androstane | | nd | nd | nd | nd | nd | nd | nd | nd | nd | 8 |
| 5α(H)pregnane | | nd | 1.5 | 0.8 | nd | nd | nd | nd | nd | nd | 8 |
| 5β(H)pregnane | | 1.4 | 4.2 | 1.9 | 2.1 | nd | 0.1 | nd | 0.7 | nd | 11 |
| 20-methyl-5α(H)pregnane | | 0.9 | 1.7 | 1.4 | nd | nd | 0.1 | 0.8 | nd | nd | 4 |
| 20S-13β(H),17α(H)-diacholestane** | S1# | 1.7 | 4.4 | 2.0 | 3.1 | nd | 0.1 | 1.7 | 0.9 | 0.5 | 116 |
| 20R-13β(H),17α(H)-diacholestane | S2 | 1.8 | 2.6 | 1.3 | 1.8 | nd | nd | 1.0 | 0.6 | 0.2 | 92 |
| 20S-5α(H),14α(H),17α(H)-cholestane | S3 | 1.3 | 1.9 | 2.4 | 2.3 | nd | 0.1 | 1.5 | 0.8 | nd | 64 |
| 20R-5α(H),14α(H),17α(H)-cholestane | S6 | 1.7 | 2.9 | 1.7 | nd | nd | nd | 0.9 | 0.5 | 0.2 | 55 |
| 20R-5α(H),14β(H),17β(H)-cholestane | S4 | 4.2 | 6.6 | 3.4 | nd | nd | nd | 2.1 | 1.1 | 0.6 | 215 |
| 20S-5α(H),14β(H),17β(H)-cholestane | S5 | 2.3 | 3.9 | 1.8 | nd | nd | nd | 2.3 | 1.3 | 0.3 | 125 |
| 20R-24-ethyl-13β(H),17α(H)-diacholestane | S7 | 1.0 | 5.0 | 1.5 | nd | nd | nd | 1.1 | 0.5 | 0.2 | 170 |
| 20S-5α(H),14α(H),17α(H)-ergostane | S8 | nd | 5.2 | nd | nd | nd | nd | nd | nd | nd | 37 |
| 20R-5α(H),14α(H),17α(H)-ergostane | S11 | nd | 7.5 | 1.3 | nd | nd | nd | 2.3 | nd | nd | 126 |
| 20R-5α(H),14β(H),17β(H)-ergostane | S9 | 5.5 | 4.3 | nd | nd | nd | nd | 1.9 | nd | nd | 217 |
| 20S-5α(H),14β(H),17β(H)-ergostane | S10 | nd | 7.2 | 5.5 | nd | nd | nd | nd | nd | nd | 63 |
| 20S-5α(H),14α(H),17α(H)-stigmastane | S12 | nd | 1.0 | 1.5 | nd | nd | nd | nd | nd | nd | 69 |
| 20R-5α(H),14α(H),17α(H)-stigmastane | S15 | 3.7 | 5.4 | 13.0 | 8.7 | 38.2 | 0.1 | 2.1 | 1.4 | 1.2 | 26 |
| 20R-5α(H),14β(H),17β(H)-stigmastane | S13 | 3.2 | 3.0 | 2.4 | nd | nd | nd | 2.0 | 0.7 | nd | 141 |
| 20S-5α(H),14β(H),17β(H)-stigmastane | S14 | nd | nd | nd | nd | nd | nd | nd | nd | nd | 55 |

 * Note change in the units for OS sample
** Steranes of similar configuration assumed to have the same RF as in the standard compounds mixture
 # Notation to be used in figures     ## Not detected, below detection limits

**Table 14:** Component loadings for the first two PCs.

| Metal | Comp.1 | Comp.2 |
|-------|--------|--------|
| V | 0.338 | 0.120 |
| Cr | 0.311 | 0.131 |
| Mn | 0.116 | -0.473 |
| Ni | 0.343 | -0.106 |
| Cu | 0.335 | 0.010 |
| Zn | 0.316 | 0.260 |
| As | 0.269 | 0.074 |
| Cd | 0.242 | -0.232 |
| Sn | 0.264 | -0.387 |
| Ba | 0.162 | 0.434 |
| Pb | 0.338 | -0.162 |
| Fe | 0.323 | 0.143 |

**Table 15:** Correlations between PC 1 and PC 2 with latitude, longitude, silt and organic carbon.

| Parameter | PC 1 (p-value) | PC 2 (p-value) |
|-----------|----------------|----------------|
| Latitude | -0.544 (0.0160) | -0.304 (0.2058) |
| Longitude | 0.021 (0.9324) | 0.328 (0.1709) |
| Silt | -0.274 (0.2572) | 0.758 (0.0002) |
| OC | 0.547 (0.0153) | -0.242 (0.3173) |

**Table 16:** Correlations between PC 1 and PC 2 with latitude, longitude, silt and organic carbon (excluding outliers BL03-4 and BL03-17).

| Parameter | PC 1 (p-value) | PC (p-value) |
|-----------|----------------|--------------|
| Latitude | -0.428 (0.0862) | -0.473 (0.0551) |
| Longitude | 0.147 (0.5742) | 0.604 (0.0102) |
| Silt | -0.726 (0.0010) | 0.516 (0.0339) |
| OC | 0.516 (0.0341) | -0.390 (0.1218) |

**Table 17:** Analysis of Variance for the Response of PC 1.

| | Df | Sum of Sq | Mean Sq | F Value | Pr (F) |
|-----------|------|-----------|----------|----------|---------------|
| Silt | 1 | 39.30097 | 39.30097 | 26.30329 | 0.000153386 |
| Latitude | 1 | 14.34431 | 14.34431 | 9.60034 | 0.007856686 |
| residuals | 14 | 20.91805 | 1.49415 | | |

**Table 18:** Comparison of the mean concentrations of selected trace metals in Beaufort Lagoon mud with ERL and ERM guideline values, in percent incidence of biological effects in concentration ranges defined by two values as reported by Long et al. (1995).

| | THIS STUDY | | | DATA FROM LONG ET AL. [1995] | | |
| --- | --- | --- | --- | --- | --- | --- |
| | | Guidelines | | Percent (ratios) incidence of effects* | | |
| | | ERL | ERM | | | |
| | Beaufort Lagoon | | | < ERL | ERL-ERM | >ERM |
| | ppm dry wt | ppm dry wt | | | | |
| As | 14 | 8.2 | 70 | 5.0 (2/40) | 11.1 (8/73) | 63.0 (17/27) |
| Cd | 0 | 1.2 | 9.6 | 6.6 (7/106) | 36.6 (32/87) | 65.7 (44/67) |
| Cr | 73 | 81 | 370 | 2.9 (3/102) | 21.1 (15/71) | 95.0 (19/20) |
| Cu | 36 | 34 | 270 | 9.4 (6/64) | 29.1 (32/110) | 83.7 (36/43) |
| Pb | 17 | 46.7 | 218 | 8.0 (7/87) | 35.8 (29/81) | 90.2 (37/41) |
| Ni | 39 | 20.9 | 51.6 | 1.9 (1/54) | 16.7 (8/48) | 16.9 (10/59) |
| Zn | 92 | 150 | 410 | 6.1 (6/99) | 47.0 (31/66) | 69.8 (37/53) |
| THg | 0.04 | 0.15 | 0.71 | 8.3 (4/48) | 23.5 (16/68) | 42.3 (22/52) |

* Number of data entries within each concentration range in which biological effects were observed divided by the total number of entries within each range.

**Table 19:** Comparison of the mean concentrations of selected hydrocarbons in Beaufort Lagoon gross sediments with ERL and ERM guideline values, and percent incidence of biological effects in concentration ranges defined by two values as reported by Long et al. (1995).

| | THIS STUDY | DATA FROM LONG ET AL. [1995] | | | | |
|---|---|---|---|---|---|---|
| | | Guidelines | | Percent (ratios) incidence of effects* | | |
| | Beaufort Lagoon | ERL | ERM | < ERL | ERL-ERM | >ERM |
| | ng g$^{-1}$ dry wt | ppb dry wt | | | | |
| naphthalene | 6.00 | 160 | 2100 | 16.0 (4/25) | 41.0 (16/39) | 88.9 (24/27) |
| 2-methylnaphthalene | 12.40 | 70 | 670 | 12.5 (2/16) | 73.3 (11/15) | 100 (15/15) |
| acenaphthylene | nd | 44 | 640 | 14.3 (1/7) | 17.9 (5/28) | 100 (9/9) |
| acenaphthene | nd | 16 | 500 | 20.0 (3/15) | 32.4 (11/34) | 84.2 (16/19) |
| fluorene | 2.18 | 19 | 540 | 27.3 (3/11) | 36.5 (19/52) | 86.7 (26/30) |
| phenanthrene | 15.67 | 240 | 1500 | 18.5 (5/27) | 46.2 (18/39) | 90.3 (28/31) |
| anthracene | 0.21 | 85.3 | 1100 | 25.0 (4/16) | 44.2 (19/43) | 85.2 (23/27) |
| fluoranthene | 2.73 | 600 | 5100 | 20.6 (7/34) | 63.6 (28/44) | 92.3 (36/39) |
| pyrene | 4.69 | 665 | 2600 | 17.2 (5/29) | 53.1 (17/32) | 87.5 (28/32) |
| benz(a)anthracene | 1.80 | 261 | 1600 | 21.1 (4/19) | 43.8 (14/32) | 92.6 (25/27) |
| chrysene/triphenylene# | 8.91 | 384 | 2800 | 19.0 (4/21) | 45.0 (18/40) | 88.5 (23/26) |
| benzo(a)pyrene | 0.63 | 430 | 1600 | 10.3 (3/29) | 63.0 (17/27) | 80.0 (24/30) |
| dibenz(a,h)anthracene | nd, below MDL | 63.4 | 260 | 11.5 (3/26) | 54.5 (12/22) | 66.7 (16/24) |
| Sum PAH | 314.44 | 4022 | 44792 | 14.3 (3/21) | 36.1 (13/36) | 85.0 (17/20) |

*Number of data entries within each concentration range in which biological effects were observed divided by the total number of entries within each range*
*# Reported as chrysene in the Long et al. study.*