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Historical changes in trace metals and hydrocarbons  
in the inner shelf sediments, Beaufort Sea: Prior and  
subsequent to petroleum-related industrial developments

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**Final Report**

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Final Report

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by

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## Abstract

This was a two-year study (1997–99) of historical changes in concentrations of selected trace metals in sediments of the Beaufort Sea nearshore, arctic Alaska—from Harrison Bay to the Canning River delta. The research involved the metals V, Cr, Cu, Ni, Zn, As, Cd, Pb, Ba, Fe and Mn in sediment mud fractions (<62 µm), and concentrations in gross sediments of total Hg (THg) and methyl Hg (MeHg), saturated hydrocarbons (normal and isoprenoid alkanes, triterpenoids and steranes) and polycyclic aromatic hydrocarbons (PAH). The primary purpose of the study was to ascertain if there were any significant increases in concentrations of the trace metals and hydrocarbons subsequent to the recent development of petroleum-related industrial activities. An additional purpose was to gain an understanding of the sources of hydrocarbons accumulated in the sediments in view of ongoing, as well as proposed, oil and gas development in the region.

Time-series comparisons of mean concentrations of trace elements in muddy sediments of the Beaufort Sea nearshore, at approximately 10-year intervals (1977, 1986 and 1997), show significantly increased concentrations in V in 1986 and 1997 from the initial concentration measured in 1977, and in Ba from 1986 to 1997 accompanied by no changes in other elements. However, these findings are not reflected in the stratigraphic variations of the elements in two cores examined. The stratigraphy demonstrates a net significant decrease up core in MeHg, Zn, Cd, and Pb accompanied by no significant change in concentrations of the other elements. The reasons for the increased concentrations in V and Ba are unknown. Despite increased concentrations in V and Ba detected during the past 30 years, the levels of these and other elements are below or comparable to those in unpolluted marine sediments.

Correlation coefficient analysis suggests that V, Cu, Ni, Zn, As and Mn are primarily chelated (with ligand formation) with organic matter, whereas some of the V is also adsorbed on the clays. Cluster analysis of the elemental data indicates the presence of two major station groups that are discriminated by differences in MeHg contents. These differences could have evolved from several factors, such as regional variations in natural terrestrial or industrial inputs of Hg, the methylation process, sediment granulometry, or all three.

The molecular markers investigated in the sediments are of mixed marine and terrigenous origin. Generally, the resolved *n*-alkanes are less and the total PAHS more than those found by others in the same region a decade ago. The PAH assemblage in the surface sediments is different from that found in Prudhoe Bay crude oil but is very similar to that observed in coastal peat and North Slope fluvial sediments. The triterpenoid and sterane profiles reinforce the biogenic rather than the petrogenic origin of major portions of the hydrocarbons. Only in isolated cases is a petroleum signature documented by the presence of thermally mature hopanes and steranes in small amounts. The fingerprint of triterpanes/steranes rather than some internal ratio parameters in the current samples helps to clearly distinguish biogenic inputs from petrogenic sources. The composition of triterpenoids/steranes should serve as an important diagnostic tool in future monitoring studies that follow subtle changes in hydrocarbon inputs to the study region, especially from oil-related activities.

In summary, the environment of the study area has remained clean as far as trace metals and hydrocarbons are concerned in spite of recent oil-related industrial activities. Results of our investigations should serve as a baseline for future monitoring of trace metal and hydrocarbon contamination within the study area.

## **Introduction**

### **Background and relevance to Framework Issues**

In recent years considerable attention has been given to assessing the state of the arctic environment, especially in relation to the presence and biological effects of anthropogenic contaminants [e.g., AMAP 1997; Johansen et al. 2000]. The arctic region, most of which lies far away from major industries, is no longer pristine, as attested to by the levels of industrial contaminants found there [Chernyak et al. 1996; AMAP 1997; Naidu et al. 1997 and references therein]. Anthropogenic discharge of chemicals and radioactive nuclides into high arctic coastal and shelf regions of Russia [Yablokov et al. 1993; Molnia and Taylor 1994] has raised the possibility of transport of these contaminants by ocean currents into adjacent marine regions of Alaska [Barrie et al. 1992]. Atmospheric transport of contaminants to the Alaskan and Canadian Arctic could also contribute pollutants [LaFlamme and Hites 1978; Atlas and Giam 1981; Snyder-Conn et al. 1997; Macdonald et al. 2000]. In order to understand the sources and processes of trace metal and hydrocarbon bioaccumulation in Alaskan arctic seas, it is pertinent to first document the regional concentrations and historical changes in trace metals and hydrocarbons in sediments. Such information will be critical in any effort relating to ecological risk assessment in marine areas with a high input of anthropogenic inorganic and organic contaminants. Anomalously high contents of trace metals, radionuclides, and organochlorines of unknown source have been reported in several species of arctic biota which are either directly consumed by the indigenous people or constitute food chain(s) related to animals harvested for subsistence use [Hansen 1986; Hansen et al. 1990; Bidelman et al. 1989; Taylor et al. 1989; Asmund 1992; Varanasi et al. 1993; Zhu et al. 1995; Becker et al. 1995; Loring and Asmund 1987; Duffy et al. 1998; Hamilton and Nriagu 2000 and articles therein]. Arctic marine organisms which are lipid rich and which have relatively simple food web structure and biodiversity are particularly vulnerable to bioaccumulation of toxic metals. Marine sediments, which serve as an initial sink for particle-reactive trace metals and hydrocarbons, could be a major source of contaminants for benthic animals as well as other organisms which have a close link with sediments and serve as transfer pathways of contaminants to higher trophic levels [Long et al. 1998; Thompson et al. 1999; Valette-Silver 1999; Krantzberg et al. 2000]. For the Alaskan high arctic seas, little information is available on bioaccumulation of contaminants and the geochemical pathways of contaminants involving sediments. However, several papers have been published on the concentrations of trace metals in sediments of the above region [Sweeney and Naidu 1989; Crecelius et al. 1991; Naidu et al. 1997; Valette-Silver et al. 1999].

Possible anthropogenic sources in the Alaskan Beaufort Sea, for example, could be industrial activities such as the Endicott and Prudhoe Bay petroleum projects; the ongoing, projected or potential oil prospects such as North Star, Liberty, Point Thomson, Badami, and Alpine; Outer Continental Shelf (OCS) oil and gas development; or offshore dredging for gravel. Potential trace metal contaminants concerned with the above projects are V, Ni, and a variety of hydrocarbons as constituents of crude oil; Cr, Cu, Zn, Ni, and Ba (in barites) associated with drilling fluids; and Pb, Cd, Hg, and As as products of municipal and industrial effluents. Further, several trace metals associated with subsurface sediment interstitial fluids can be mobilized subsequent to dredging operations and eventually reaccumulate on surface sediments. It is also possible that there have been incidental or chronic anthropogenic discharges of crude or industrial petroleum products during the past three decades resulting from the various oil exploration, developmental and exploitation activities. Prior to this study one could only speculate whether three decades of ongoing activities would lead to significant trace metal and hydrocarbon contamination of sediments in the Beaufort Sea nearshore.

Considering the potential hazards of the above metal contaminants on the health of marine organisms in the Beaufort Sea, a study was initiated to determine the current concentrations and temporal changes in V, Cr, Cu, Ni, Zn, As, Cd, Pb, Ba, total and methyl Hg (THg and MeHg) and a selected group of hydrocarbons in sediment samples from the nearshore Alaskan Beaufort Sea. The study's primary

purpose was to identify any recent occurrence of site-specific large scale contamination of trace metals and hydrocarbons, and to determine whether the metal levels in the sediments are above the thresholds [Long et al. 1995] known to cause potential adverse effects on the health of benthic or demersal organisms. This report describes the results of the trace element and hydrocarbon investigations that were conducted from 1997 through 1999.

## **Report organization**

The report is organized into two major sections—one relating to the trace metals and the other to hydrocarbons in the sediments of the study area. This approach is justified, as each section can be read independently of the other without losing a sense of continuity. However, the descriptions of sample collection and statistical analysis of data are reported jointly, as these were common to both of the tasks. The report also includes published data on sediment  $\delta^{13}\text{C}$  and OC/N [Naidu et al. 2000] on splits of samples collected in this study. The data collection was not a task of this contract, but is included here to support conclusions on sources of organic matter that were deduced based on the hydrocarbon study.

## **Hypothesis/Objectives**

Petroleum-related developmental activities on the North Slope during the last three decades have led to a significant increase in the levels of trace metals and hydrocarbons in the marine sediments of the nearshore Alaskan Beaufort Sea.

The specific objectives of the study were to determine historical changes in the concentrations of V, Cr, Cu, Ni, Zn, As, Cd, Pb and Ba in the sediment mud fractions, and concentrations of total and methyl Hg, saturated hydrocarbons (normal and isoprenoid alkanes, triterpenoids and steranes) and polycyclic aromatic hydrocarbons in gross (or bulk) sediments of the nearshore Alaskan Beaufort Sea, and to assess if any of the changes are related to recent industrial development within the study area.

## **Sampling Methods**

Triplicate surficial sediment samples from 21 stations and sediment core samples from two stations in the nearshore Beaufort Sea area located within the Colville–Canning Delta region (Figure 1, Table 1) were collected in September 1997, using a Kynar-coated van Veen grab sampler and a gravity/Haps corer, respectively. Of the 21 stations, 20 were at the same locations as those occupied during the Beaufort Sea Monitoring Program (BSMP) by Battelle in 1984–1989 [Crecelius et al. 1991]. Such coverage has provided representative sediment samples for contaminant monitoring of all major oil prospect areas in the North Slope region of Alaska (e.g., Liberty, Alpine, Badami, Point Thomson and North Star) that have been slated for oil development in the next four years. The purpose of collecting the triplicate samples at each station was to check station sampling precision.

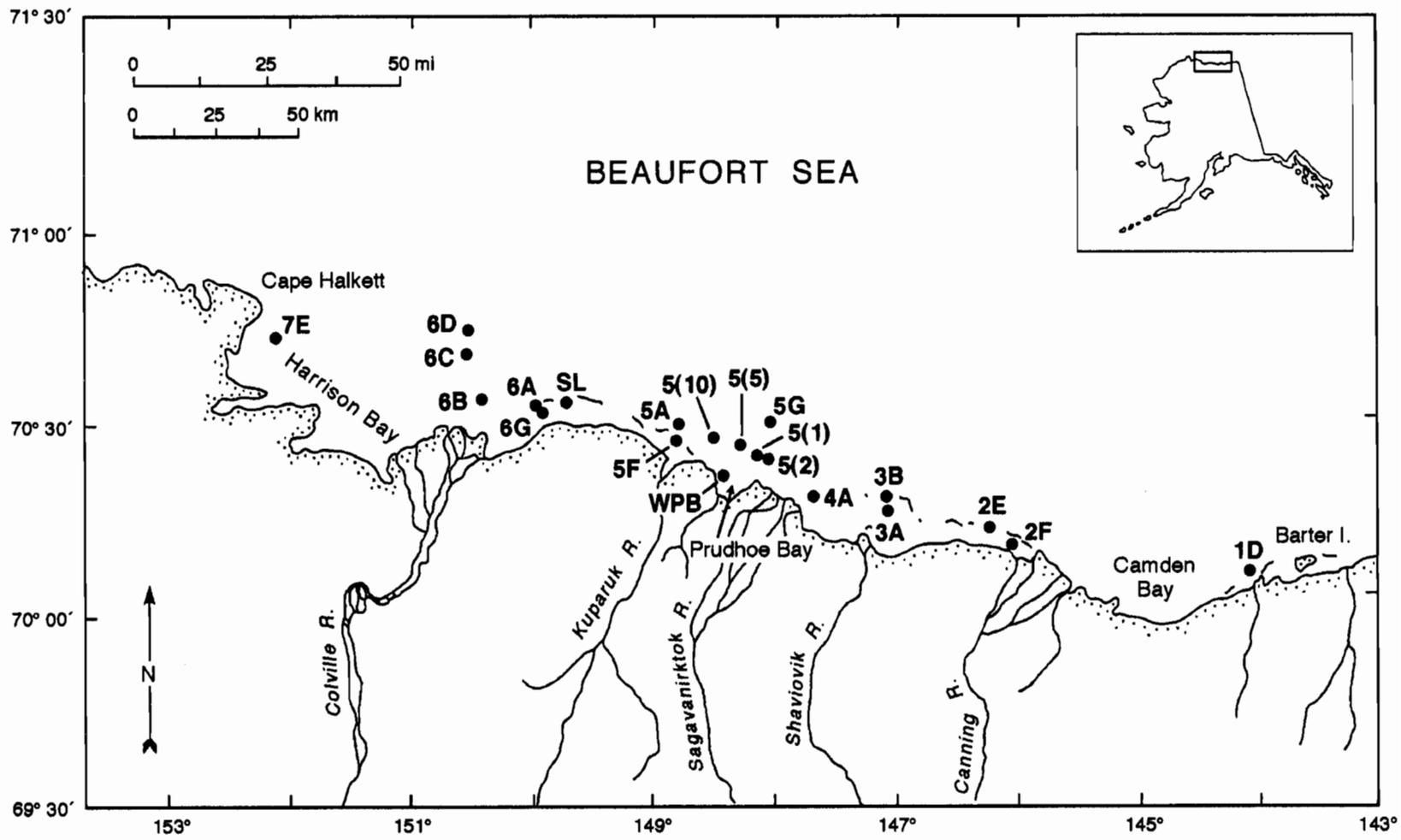


Figure 1. Study area showing locations of sediment samples for trace metal analysis.

Each of the samples was processed immediately after collection. For the surficial sediment sample, the upper 2-cm oxidized layer was sectioned from the top of the grab and core top using Teflon-coated (for trace metals) and stainless steel (for hydrocarbons) knives. The core samples were further sectioned at 1-cm intervals and divided into two splits. One of the splits was stored for trace element stratigraphic analysis and the other for establishing geochronology. Each of the samples thus collected was transferred into duplicate Environmental Protection Agency (EPA)-approved I-CAM glass jars and kept frozen until analyzed for the various chemicals. An additional split from each of the grab samples was collected and stored in polyethylene bags for sediment grain size analysis. Splits of the sediment samples from selected stations and all benthic bivalve samples collected were provided to Jawed Hameedi (National Oceanic and Atmospheric Administration/Office of Ocean Resources Conservation and Assessment [NOAA/ORCA]) for analyses by him (independent of this project) for persistent organic pollutants and trace metals.

Samples from the above suite were shipped frozen to Frontier Geosciences Inc., Seattle for analyses of trace metals and to Indira Venkatesan (University of California, Los Angeles) for analysis of hydrocarbons. Sediment core sections were shipped to Mark Baskaran (Texas A&M, Galveston) for analyses of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  relating to geochronology. Sediments for analyses of Fe and Mn were processed at the University of Alaska Fairbanks (UAF) Institute of Marine Science (IMS), and then analyzed at Northern Testing Laboratories, Inc., Fairbanks. The sediment organic matter, ratios of stable isotopes of carbon ( $\delta^{13}\text{C}$ ), carbonate and granulometry were analyzed at IMS.

### **Statistical analysis**

Statistical analyses were conducted to determine:

- 1) within station variability of chemical and physical data to check within station sampling precision;
- 2) historical changes of the contaminants in sediments by investigating stratigraphic variations in trace metal data available for the past two hundred years from the  $^{210}\text{Pb}$ -based dated sediment cores, and from comparison of time-series decadal data including those from the present study (1997) and those collected in 1977 and 1986 [Feder et al. 1976; Naidu 1982; Sweeney and Naidu 1983; Sweeney 1984; Boehm et al. 1987; Sweeney and Naidu 1989; Crecelius et al. 1991], and by comparing hydrocarbon data collected during the past 25 years [Peake et al. 1972; Wong et al. 1976; Shaw et al. 1979; Venkatesan and Kaplan 1982; Steinhauer and Boehm 1992] with those of the present study;
- 3) partial and multiple correlation coefficients [after Shine et al. 1995] to understand interanalyte relationships;
- 4) if there is a "downstream" concentration gradient in the contaminants from potential sources;
- 5) cluster analysis to identify grouping of stations based on analyte levels on a regional or geographic basis;
- 6) stepwise multiple discriminant analysis of the chemical data to correlate station group separation by cluster analysis with sediment variables. These analyses were conducted to gain an understanding of geochemical partitioning, sources of contaminants and extent of contamination within the study area since industrial development began; and
- 7) level of significance of the time-series differences in V and Ba using Student's t-test.

## TRACE METAL STUDIES

### Analytical Methods

Traditionally, in most inorganic contaminant studies trace metals are analyzed on gross sediments. However, data obtained on gross sediments are generally of limited use, especially if the suite of sediments analyzed consists of individuals with significantly different granulometry. In such cases, the trace metal concentrations become difficult to compare between samples within a suite or with other suites unless the data are first normalized to the sediment granulometry [for further discussion see Loring 1991; Daskalakis and O'Connor 1995; Naidu et al. 1997]. Therefore, it was decided to analyze the concentrations of V, Cr, Cu, Ni, Zn, As, Cd, Pb and Ba in the mud fraction (<63  $\mu\text{m}$  size class including silt plus clay) of the sediment samples. By restricting the elemental analysis to the mud fraction it was possible to overcome the problem discussed above. There are additional justifications for considering the mud fraction for analysis. This fraction, which is enriched in clay minerals and organics, is invariably the predominant host for concentrating particle-reactive elements by clay-metal adsorption and/or complexation. Consequently, mud size is a more desirable component for monitoring metal pollution. The other justification is that earlier trace metal data for the study area are on the mud fraction or muddy sediments [Naidu 1982; Sweeney 1984; Boehm et al. 1987; Crecelius et al. 1991]. Thus, it would seem relevant to continue analysis on the same sediment fraction to make results compatible for comparison with past time-series benchmark data, especially for detecting pollution.

Analyses of trace metals from the mud fraction were accomplished following the methods outlined in the BSMP-Battelle study [Boehm et al. 1987; Crecelius et al. 1991] and as described below. A 5-g split of each of the grab and core section sediment samples was suspended in deionized distilled water (DDW) and homogenized. This suspension was sieved through a 230-mesh (pore opening 63  $\mu\text{m}$ ) nylon screen to separate the fine (<63  $\mu\text{m}$ , consisting of silt and clay or mud) and the coarse (>63  $\mu\text{m}$ , consisting of sand and gravel) fractions. After centrifuging the suspension and siphoning out the supernatant water, the fine fraction was dried at 60°C, and then powdered using an agate mortar and pestle. It is possible that during the process of separating the mud fraction by wet sieving the gross sediment may have hydrolyzed some metals, or desorbed them from the sediment (or both). If this occurred then some metal portions were thus lost to the water that was subsequently siphoned and discarded. It is assumed that the fraction of the metals thus lost, and excluded from the analysis, was negligible. This is based on earlier results, within the study area, of elemental analysis on sequential extracts of sediments by various chemicals [Sweeney 1984]. At the Frontier Geosciences laboratory a 0.5-g portion of the mud powder was dissolved in a Teflon bomb by digesting it in a microwave oven in high-purity, concentrated HF-HNO<sub>3</sub> acid. Subsequently, the dried residue of the digest was dissolved in warm 10% HNO<sub>3</sub> and made up to 20 ml with DDW. From this solution, the concentrations of V, Cr, Cu, Ni, Zn, Cd, Pb and Ba were analyzed. A separate 0.1-g powder sample was dissolved at the IMS laboratory by the LiBO<sub>2</sub> fusion-HNO<sub>3</sub> acid technique [Medlin et al. 1969] and the solution was analyzed for Fe and Mn at Northern Testing Laboratories. The purpose of the Fe and Mn analyses was to gain insight into the possible geochemical role of the oxyhydroxides of these two elements in scavenging trace metals. The above ten elements were analyzed using either a direct injection Zeeman graphite furnace atomic absorption spectrometer (GF-AAS, Hitachi model Z-4110 or Z-5000) or an inductively coupled plasma/mass spectrometer (ICP/MS, Perkin-Elmer model Elan-6000). In a separate split of the mud fraction As was analyzed by Excaliber automated hydride generation atomic fluorescence spectrometry, using EPA method 1632.

The analyses of total Hg and the relatively more toxic methyl Hg [Bloom 1992; ATSDR 1993; Phillips et al. 1997] were on gross sediments rather than on the mud fraction as was done for the rest of the metals. The reason for this is that significant portions of the volatile Hg could be lost during the wet sieving process. The analysis of THg was by cold vapor atomic absorption spectrometry (CV-AAS). The

analysis of MeHg in sediment was performed on alkaline leachates of the sediment, using a cold vapor atomic fluorescence detector following cryogenic GC separation [Bloom 1989].

The method detection limits (MDL) for MeHg and THg are expressed in ng/g on a wet weight basis of sample, whereas the MDL for the rest of the elements are expressed in µg/g on a dry weight basis with 3 SD of the blanks. The MDL of the trace element analysis are estimated as follows: V = 1.29, Cr = 3.91, Cu = 0.15, Ni = 1.25, Zn = 0.66, As = 1.37, Cd = 0.066, Pb = 0.12, Ba = 1.80, THg = 0.15 and MeHg = 0.004. The QA/QC protocol prescribed by the EPA for trace metal analysis was followed, which included analysis of spiked reagent blanks, establishment of analytic precision through replicate runs and checking analytic accuracy via analyses of U.S. Geological Survey (MAG-1) and/or National Research Council of Canada (BCSS-1 and MESS-2) sediment reference standards. Throughout the analytic process, ultrapure chemical reagents were used and care was taken to minimize contamination of the laboratory ware and sample-holding containers. Additionally, analytical accuracy and precision was checked by interlaboratory comparison performance evaluation, which consisted of successful participation of our subcontractor, Frontier Geosciences, in the 1997 NOAA/NIST (National Institute of Standards and Testing) round robin interlaboratory exercise NOAA/11 that was conducted by the National Research Council of Canada (NRC). The Frontier Geosciences rating was good to excellent.

## Other Analyses

To establish geochronology on two representative core samples from the study area (stations 3B and SL) excess  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{ex}}$ ) and  $^{137}\text{Cs}$  activities were analyzed in stratigraphic samples separated from selected core depths. These analyses were accomplished by following the methods outlined in Weiss and Naidu [1986] and Baskaran and Naidu [1995 and references therein] and by using high resolution alpha and gamma mass spectrometers.

Because sediment grain size, total organic matter (OM), and carbonate generally control the trace metal concentrations of sediment [Loring 1991; Daskalakis and O'Connor 1995; Naidu et al. 1997], these three variables were also analyzed. The analyses were conducted at the Institute of Marine Science in portions of the same sediment mud fraction and gross sediment that were taken for analyses of trace metals, Hg and hydrocarbons, respectively. The OM and carbonate contents were estimated using the stepwise loss in powder weight subsequent to ignition at 550°C/hr and 1000°C/hr, respectively [Dean 1974]. The analyses for gravel, sand, silt, and clay contents in gross sediments and the percentages of silt and clay in the mud fraction were by the conventional sieve-pipette method [Folk 1968].

## Results

The results of the analysis for QA/QC on the reference sediments (MESS-2, NIST-2709) and selected representative mud samples from the study area for trace metals, with special reference to analytical accuracy and precision as applicable, are shown in Table 2.

Table 3 shows the concentrations of V, Cr, Cu, Ni, Zn, As, Cd, Pb, Ba, silt, clay, carbonate and total organic matter on a dry weight basis for the mud fraction, and MeHg on a wet weight basis of gross sediments for the replicate samples at each of the 21 stations of the study area. The table also illustrates the mean (geometric) concentrations and the coefficient of variations (CV) of the variables for each of the stations. Additionally, the concentrations of THg (wet weight), and Fe and Mn (dry weight) are provided for a representative sample of gross sediment and mud, respectively, for each station. The grand mean

(geometric) concentrations and CV for each of the variables based on integrating data on all of the sediments analyzed for the study areas listed are at the end of the table.

Table 4 shows the stratigraphic variations in the concentrations of ten elements of the two cores analyzed (3B and SL). The variations are graphically represented in Figure 2. Figure 3 shows the expanded view of the down-core variations in MeHg in the individual cores. Results of the initial correlation coefficient analysis and subsequent multiple and partial correlation coefficient analysis run on the means of all the chemical and physical parameters analyzed (refer to Table 3) are shown in Tables 5 and 6, respectively. Likewise, Table 7 reports the inter-element correlation coefficients for the elemental abundance within the 3B and SL cores and the elemental variations with core depth.

The dendrogram displaying results of the cluster analysis, based on all the data analyzed from the 21 stations, is presented in Figure 4a, which demonstrates the presence of two predominant station cluster groups. Group I includes stations generally clustered around Prudhoe Bay, whereas Group II includes stations that are located in the lagoon region adjacent to the bay on the east and west (Figure 4b). In attempting to gain an understanding of the sediment factors which led to the above clustering of the two groups of stations, stepwise multiple discriminant analysis (SMDA) was run. All of the sediment analytes in the study were included in this analysis. The statistical highlights are included in Table 8 and graphically displayed in Figure 5. Briefly, the two stations are discriminated based on the relative differences in the contents of MeHg, CO<sub>3</sub>, Mn and Cd in the sediments. Further details on the SMDA analysis can be found on p. 14. No linear geographic gradient is identified in any of the metal concentrations. Table 9 shows the time-series variations (at approximately 10-year intervals for the past 30 years) of the mean concentrations of selected metals in the study area, as well as, for comparison with trace metal data [Yang et al. 1997], samples analyzed from the Barrow nearshore region, northwest of the study area. In this comparison, trace element data pertaining to sediments with similar granulometry were considered (data on mud fraction of sediments for 1986 and 1997 and data on muddy sediments [ $>75\%$  mud for 1977]). By comparing elemental data on a specific size class, it is assumed that the elemental concentrations are normalized to the sediment granulometry [Loring 1991].

Table 10 includes the specific activities of total <sup>210</sup>Pb in gross sediments separated at 1-cm intervals from the core tops of cores 3B and SL, and the activities of <sup>226</sup>Ra and <sup>137</sup>Cs at selected core intervals. A comparison of the mean concentrations of a suite of trace metals in muds of the study area with the mean concentrations of elements in muddy sediments of selected circum-arctic shelves is shown in Table 11.

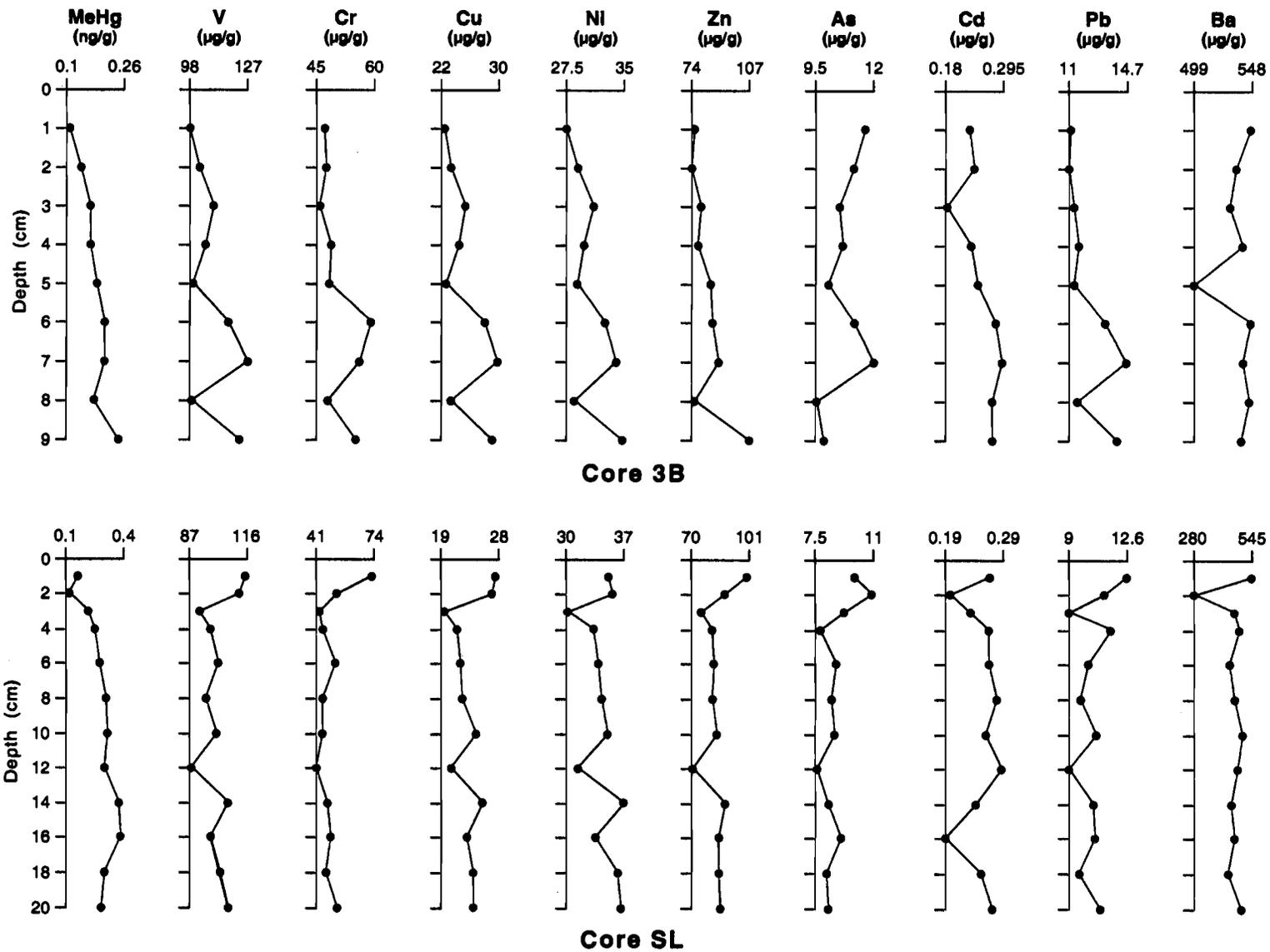


Figure 2. Stratigraphic variations in trace metal content in cores 3B and SL. Concentrations of all metals except MeHg are in  $\mu\text{g/g}$  dry weight in mud; MeHg is expressed in ng/g wet weight in gross sediments.

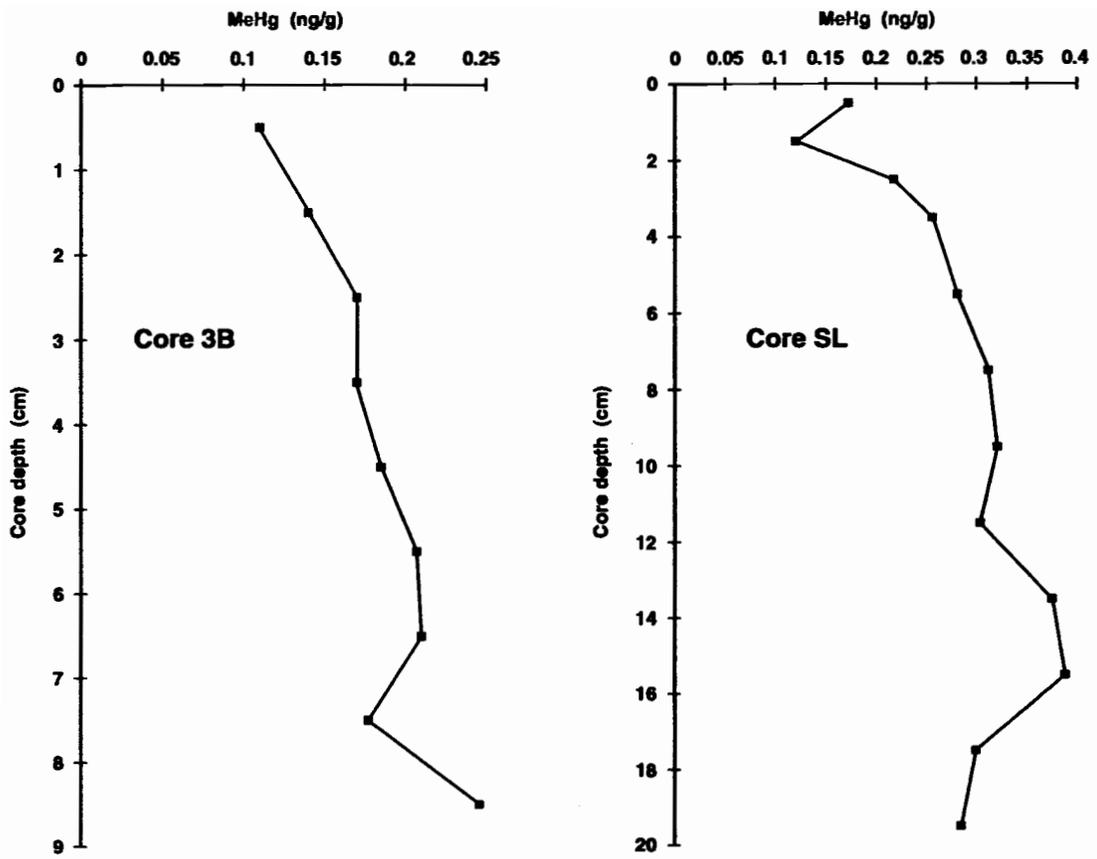


Figure 3. Stratigraphic variations in the concentration of MeHg in cores 3B and SL. (ng/g wet weight in gross sediments)

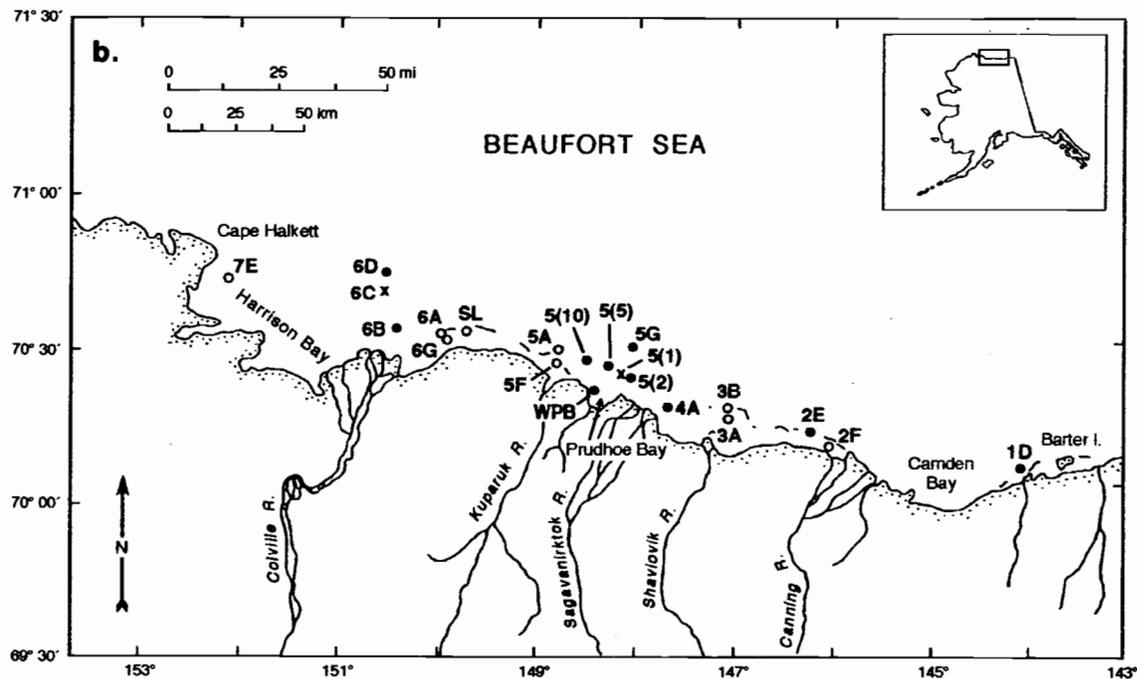
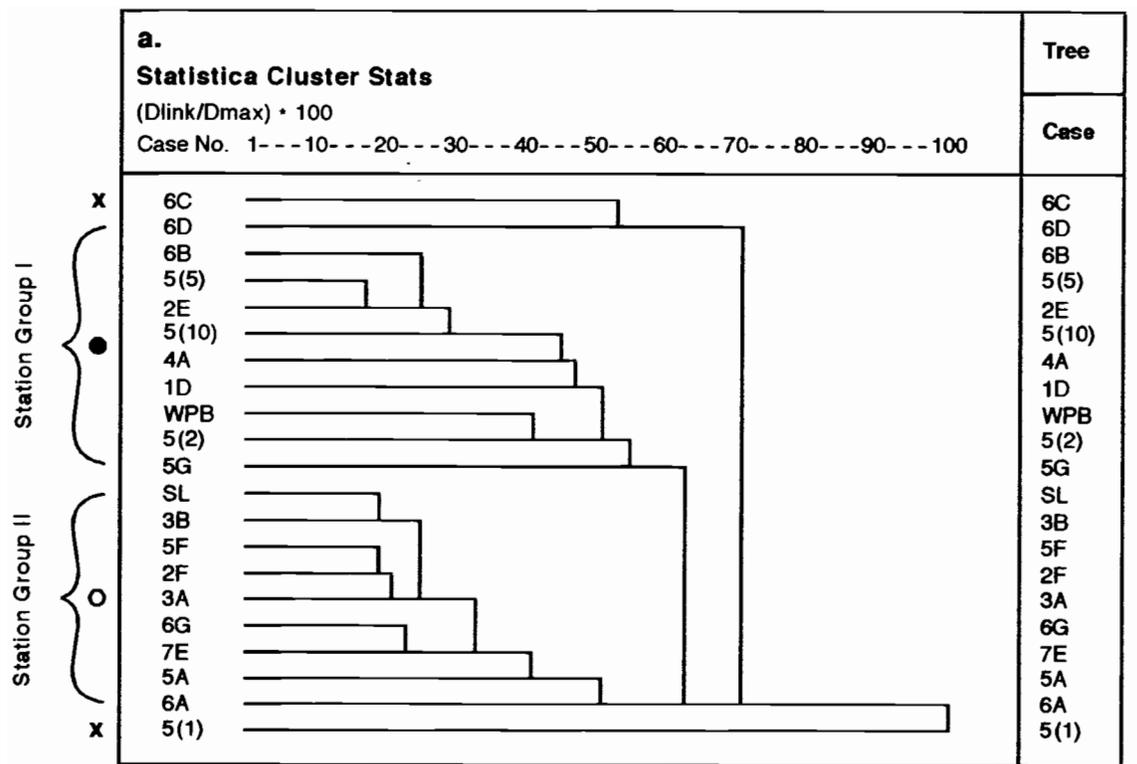


Figure 4. Dendrogram showing station groups formed by group averaging cluster analysis of sediment trace metal concentrations (4a) and location of group members on study area map (4b).

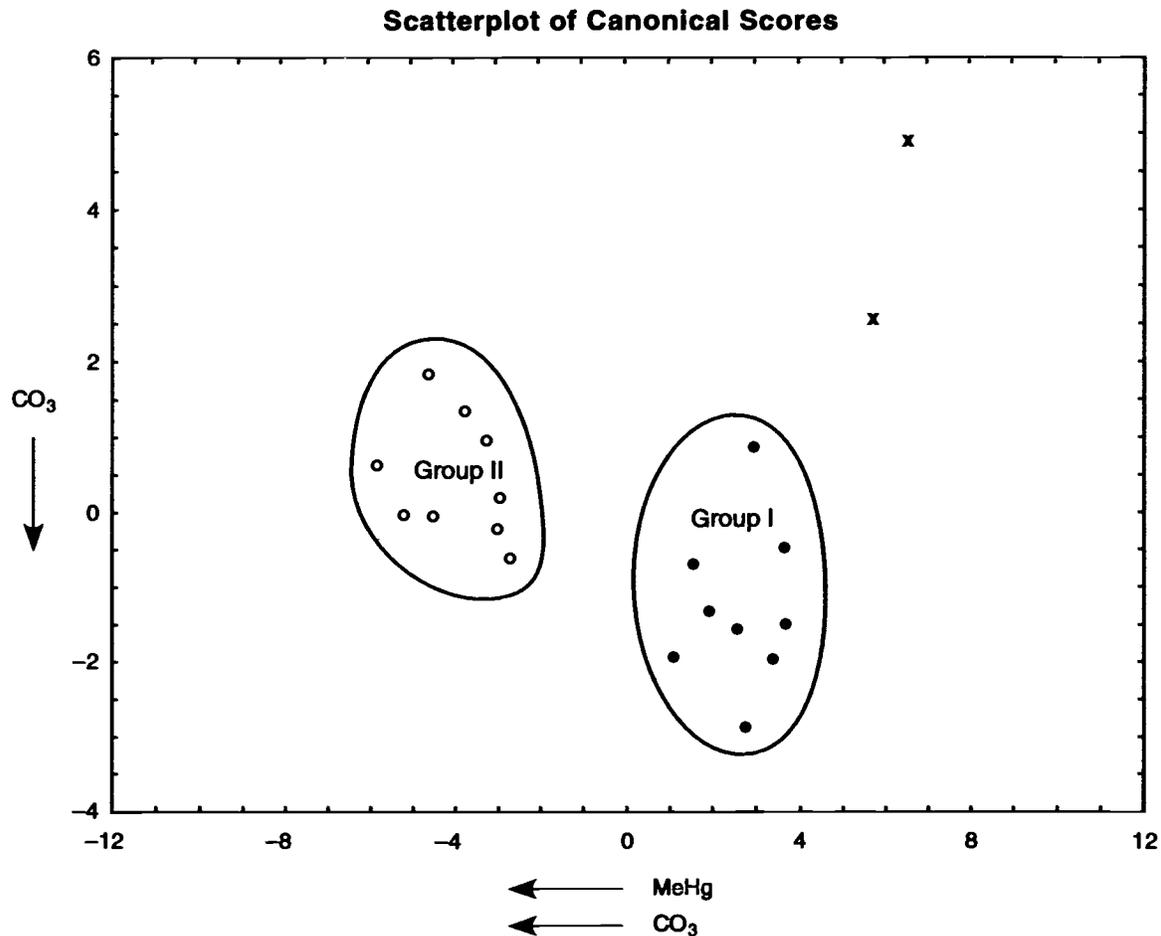


Figure 5. Station plots of the results from stepwise multiple discriminant analysis. Groupings are determined by cluster analysis.

## Discussion

### Trace element QA/QC

As mentioned earlier, Frontier Geosciences was the subcontractor for the trace element analysis on sediments. Frontier Geosciences participated in the interlaboratory exercise conducted in 1997 by NRC for NOAA/11 to ensure that the QA/QC requirements for the analysis were met (Scott Willie, National Research Council of Canada, personal communication; see also Table 2). The analytical precision relating to the individual elements included in this study was excellent. Consequently, trace element data presented in this report can be considered to be of high quality.

### Precision and accuracy of sampling and analyses

Results of the analyses of various parameters in replicate samples from a specific station (Table 3) provide the within station variability for individual analytes in the study area. The results show that for some stations there are significant variabilities (relatively high % CV) in a few analytes (especially MeHg). The cases with high variability at any one station and a specific analyte are probably due to large differences in the contents of silt, clay and/or OM between the replicate samples and, therefore, are

an artifact of sediment sampling. Although during sampling it is assumed that the replicates are being collected at one specific site, such sampling may not always be precise. Poor precision may result when the research vessel swings around a site (even though it is anchored) where the substrate is highly variable within a few meters. The problem relating to “within station” variability in sediment trace metals for the Simpson Lagoon study area was addressed in great detail by Sweeney [1984].

### **Historical changes in trace elements of the Beaufort Sea nearshore**

In this study, two approaches were adopted to assess historical changes in the concentrations of trace elements in sediments of the Beaufort Sea nearshore. The first compares the mean concentrations of individual elements that have been reported on sample suites at approximately 10-year intervals for the study area since 1977 (1977 and 1986) with those analyzed in this study (i.e., samples collected in 1997). The second includes assessment of elemental changes as demonstrated in stratigraphic samples of sediment cores with known geochronology, an approach similar to those followed elsewhere [e.g., Finney and Huh 1989]. The time-series data in Table 9 clearly illustrate significant increases (at the 99% confidence level) in the mean concentrations of V in 1986 and 1997 from 1977 and an increase (at the 99% confidence level) in the mean concentrations of Ba from 1986 to 1997. No significant changes were noted in the concentrations of other elements.

The stratigraphic data on cores 3B and SL demonstrate trends that are partly consistent with the above decadal time-series changes. For example, core 3B exhibits increases only in As and Ba toward the core top from about midway down the core (Figure 3). In core SL the trend is an apparent increase in concentrations of most elements toward younger layers within the upper 2-cm core top. However, statistical analyses of trace element data extended to the entire length of the individual cores 3B and SL (Table 7, Figures 2 and 3) indicate a net significant decrease (at the 99% confidence level) up core in Zn, Cd, MeHg and Pb in 3B and only in MeHg in SL, accompanied by no significant changes in the remaining elements, including V and Ba.

Some difficulty was encountered in attempting to match stratigraphic trends in trace elements with the elemental trends suggested on the decadal basis (Table 9). The difficulty stems from an inability to establish a firm geochronology for the two cores examined. Attempts to date the cores based on the  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  methods have failed because the activities of the two radionuclides were extremely low throughout the cores. For example, the activity of total  $^{210}\text{Pb}$  was typically between 1–2 dpm/g, which is close to the activity of the radionuclide's parent,  $^{226}\text{Ra}$ , with yields of excess  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{ex}}$ ) generally less than 1 dpm (Table 10). Additionally, no significant down-core exponential decreases in the  $^{210}\text{Pb}_{\text{ex}}$  were noted in either of the cores. The activity of  $^{137}\text{Cs}$  was generally below 200 dpm/kg in core 3B and below detection levels in core SL. The  $^{137}\text{Cs}$  dating method is based primarily on detection of a well-defined spike, with highest activity generally noted in a subsurface section of a core and corresponding to the years 1961–1964, which marked the maximum injection of the radionuclide into the atmosphere from nuclear weapon testing. However, this spike was not identified in core 3B. Because of these constraining factors, attempts to define the geochronology of the two cores failed. Despite the relatively very low activity (<2 dpm/g) in  $^{210}\text{Pb}$  that is generally reported in sediments of the continental shelf region of the Alaskan Arctic [Weiss and Naidu 1986; Baskaran and Naidu 1995; Naidu et al. 1999], it has nonetheless been possible to use the radionuclide to estimate the sediment accumulation rates for selected sites within the study area (e.g., Simpson Lagoon, located at the western end of the area [Weiss and Naidu 1986]). The mean linear and mass accumulation rates (LAR and MAR respectively) for three sites within Simpson Lagoon are 0.61 cm/yr and 0.77 g/cm<sup>2</sup>/yr, respectively [Weiss and Naidu 1986]. The three sites are located adjacent to where core SL was collected. Assuming that the above mean LAR is applicable generally to the entire area of our investigation (as the sediment depositional setting is comparable throughout) and that there has been a constant rate of sedimentation, the times of elemental changes in

the cores can be deduced. Based on these assumptions the maximum ages of cores 3B (10 cm long) and SL (20 cm long) are estimated to be about 15 and 33 years respectively. Thus, the basal sections of the cores, where an up-core progressive increase in concentrations of some elements (Ba and As) is observed, presumably correspond to dates ca. 1993 and ca. 1990, respectively, considering that the cores were collected in 1997. However, these dates do not mesh well with the older dates, when increases in V and Ba are based on comparison of data on a decadal interval basis (Table 9).

There can be several reasons for the above mismatch: 1) our basic assumptions are faulty, including that the cores represent undisturbed samples; 2) the estimated linear accumulation rates by Weiss and Naidu [1986] are questionable as they were based on trace activities of  $^{210}\text{Pb}$ , and the net exponential decrease down-core in  $^{210}\text{Pb}$  is tenuous at best [Naidu et al. 1999]; 3) elemental concentrations in the mud fractions of the two cores (Table 3) have not been normalized to the relative differences in the silt and clay contents in the muds. It is possible that higher fluxes of elements such as V and Ba were indeed introduced in the study area earlier than 1990–93 but are not demonstrated in the core stratigraphy because the associated sediments have more silt. If this were true, then the elemental concentrations would be diluted in the silty sections. (The influence of silt and clay in mud on elemental abundance in the study area is well demonstrated in Table 5.) The possible influence of granulometry on elemental concentrations in the core samples could be further verified by grain size analysis on the cores.

The reasons for the decadal time-series changes in the concentrations of V and Ba (Table 9) are unknown; however, it is tempting to speculate that the increasing contents of the two elements in post-1977 samples may be associated with petroleum-related industrial activities within the study area. For example, V is a common trace constituent of crude oil and Ba is associated with barites ( $\text{BaSO}_4$ ) used in drilling fluids. Any barites discharged from the drilling fluids into the Beaufort Sea nearshore will not likely be dispersed widely and, thus, could lead to enrichment of Ba in sediments close to the points of discharge [Northern Technical Services 1981; Macdonald 1982]. It is difficult to conceive that the excess V since 1977 has resulted from any large-scale spill of Prudhoe Bay crude oil into the environment (i.e., in the order of several millions of barrels), because such a large-scale discharge has not occurred. The exact source, mode and mechanics of transport and deposition of the two recent contaminants into the sediments of the nearshore Beaufort Sea are yet to be resolved. In spite of the trends exhibited in the increasing concentrations of V and Ba in the muds since the start of intensified industrial activities in the North Slope, the levels of these two elements throughout the study area are in ranges reported for unpolluted marine nearshore sediments, especially within the circum-arctic shelf regions (Table 11). The study area has remained a relatively clean environment as far as the elements analyzed are concerned despite the industrialization during the past 25 years.

### **Regional differences in trace element abundance**

As mentioned earlier, the cluster analysis dendrogram shows the presence of two predominant cluster station groups in the study area, I and II, based on statistical analysis of all physical and inorganic chemical data gathered (Figure 4). Most of the Group I stations are clustered in Prudhoe Bay and its vicinity, whereas the Group II stations are located in the lagoonal regions east and west of Prudhoe Bay. Also as shown in Figure 5 and Table 8, the stepwise multiple discriminant analysis (SMDA) indicates that station grouping is defined by significantly lower concentrations of MeHg in gross sediments of Group I (mean: 0.058 ng/g wet wt) than in Group II (mean: 0.164 ng/g wet wt). Although the THg and Mn abundance were not included in the SMDA because of the limited number of samples analyzed (i.e., one analysis from each of the nine stations from each of the two groups), it is apparent that differences in the mean concentrations in Mn and THg also exist between the two station groups. In Group I, the mean concentrations of THg and Mn are 18.22 ng/g and 678  $\mu\text{g/g}$ , respectively, whereas in Group II the mean

concentrations of THg and Mn are 24.42 ng/g and 368 µg/g, respectively. The differences between the two groups relative to the levels of the two Hg species and Mn could conceivably be related to a number of factors, such as differences in the inputs of the elements from natural terrigenous sources via the various fluvial systems and coastal erosion, the extent of supply of the elements from the different industrial sources based along the North Slope coast, the differences in sediment granulometry, or all three. For example, the higher concentrations of the particle-reactive (affinity of an element to be adsorbed by particle) Hg in Group II could likely be accounted for in the significantly higher concentrations of mud in gross sediments in Group II (mean: 71.34%) than those found in gross sediments in Group I (mean: 21.60%). This can be verified by further detailed investigations of Hg speciation on a site-specific basis and on sediments from potential sources. Snyder-Conn et al. [1997], investigating the regional differences in trace element concentrations in snow samples of the North Slope coast, reported that a snow sample in the Prudhoe Bay area close to the central gas facility was relatively enriched in Hg and several other elements. These authors alluded to possible higher air emission and subsequent deposition of anthropogenic Hg and other elements in the specific Prudhoe Bay facility area, resulting from local oil-related activities such as flaring of gas or natural gas liquid (NGL) from the gas handling facility located there (the largest in the world). However, a second snow sample collected within the Prudhoe Bay region, but away from the gas facility, had the lowest concentration of Hg. The sediment study results do not run parallel to the first snow samples, inasmuch as there were relatively lower concentrations of THg and MeHg in the sediments of Prudhoe Bay and its vicinity compared to sediments from other regions in the North Slope nearshore. This finding was contrary to the assumption that melting snow near the Prudhoe Bay gas facility, with its higher burden of Hg and other elements, would be an effective source of elemental contamination for the adjacent bay. Apparently this does not seem to be the case.

### **Geochemical partitioning of elements**

The single and multiple correlation coefficient analyses (Tables 5 and 6) provide insight into the geochemical partitioning of the elements analyzed in this study. As suggested by the high levels of positive correlations (Table 5), total organic matter and the clay size particles (<4 µm size) in our samples have major roles in the partitioning of most elements. Table 5 also demonstrates that all the elements except Cd, Fe, Mn, MeHg and THg are, at least to an extent, partitioned in the clay size, presumably in the adsorbed phase. Likewise, OM content also seems to be a factor (as a possible chelating agent forming ligands) on the abundance of all trace metals except Cd, Ba, MeHg and THg. Results of subsequent multiple correlation coefficient analysis (Table 6) helped clarify that the amount of OM is the more dominant factor than the amount of clay in partitioning of Cu, Ni, Zn, As and Mn, whereas Cd and Ba appear to be partitioned in a phase(s) other than OM and clay. The lack of significant covariance between OM and THg and MeHg (Table 5) was surprising, as organic matter in sediments generally serves as an important scavenger of Hg [Gagnon et al. 1997]. It is suggested that further investigations similar to those conducted in Simpson Lagoon by Sweeney [1984] and Sweeney and Naidu [1989], using sequential chemical extraction of sediments, will assist in better understanding the geochemical partitioning of the elements.

The study demonstrates a net increase in concentrations of MeHg in gross sediments down the two cores investigated (Figure 3, Tables 4 and 7). It would seem that the stratigraphic trends in THg or MeHg in marine regions vary widely in the world. For example, in the nearshore deep water sediments in the Greenland fjords a net up-core increase in THg is reported [Asmund and Nielsen 2000]. The MeHg profiles shown in our core samples generally run parallel to those reported by Gagnon et al. [1997] for the Saguenay Fjord, Quebec and for THg in Lavaca Bay, Texas [Bloom et al. 1999]. However, trends for MeHg in the cores in our study do not completely match those shown in Lavaca Bay cores. In the latter,

the highest concentrations of MeHg were in the upper 0–3 cm of the cores, decreasing rapidly with depth. Consistent to some extent with the above, a significant increase in MeHg within the upper 1-cm layer in one of our cores (SL) was also noted (Figure 3, Table 4), but further down the core, as mentioned earlier, there was a net increase in MeHg. We discuss below the possible reasons for the MeHg profile recorded in our study.

Several biogeochemical factors may control the stratigraphic variations in the concentrations of MeHg and THg in marine sediments [Gagnon et al. 1997; Bloom et al. 1999; Asmund and Nielsen 2000]. For example, Asmund and Nielsen [2000] conclude that the up-core increase in THg in the Greenland fjords during the past 100 years is due to a steady increase in anthropogenic inputs. The highest level of MeHg in the Lavaca Bay surficial sediment is due to a narrowly constrained redox cycle [Bloom et al. 1999]. The up-core decreases in THg concentrations from a subsurface maximum in Lavaca Bay and the Saguenay Fjord are attributed to a progressive decrease in the discharge of Hg contaminants from old chlor-alkali plants [Gagnon et al. 1997; Bloom et al. 1999]. In our study area, where there have been no chlor-alkali plants, no such Hg contamination could have occurred. That the up-core decrease in MeHg (Figure 3) is due to a net historical decrease in the atmospheric flux of anthropogenic Hg does not seem possible. During the last century anthropogenic emissions probably have led to a significant increase in Hg concentrations in ocean waters and arctic ice sheets [Weiss et al. 1971; Mason et al. 1994; Boutron et al. 1998].

An alternative explanation for the MeHg stratigraphic trends (Figure 3) is that there is a progressive increase down the core in the methylation of Hg<sup>++</sup>. Conceivably this process may include several steps. We suggest an initial complexation of Hg by sulfides (FeS) in successively anaerobic sediments [Gagnon et al. 1997; Bloom et al. 1999; Jay et al. 2000], followed by oxidation of the sulfide [Schippers and Jorgensen 2001], release of the Hg, and finally its biological methylation [Jernelov 1974]. Such an explanation will, of course, have to be clarified by further detailed laboratory and field studies.

The finding of increased levels of the relatively more toxic MeHg in subsurface deeper sediments of cores in the study area could have potential environmental implications, especially if the MeHg concentrations were to increase significantly in the future because of elevated anthropogenic discharge. It is possible that some of the subsurface MeHg could be mobilized into overlying water subsequent to resuspension of bottom sediments by any of the several natural or anthropogenic sediment reworking processes (i.e., ice gouging, storm-induced wave-current action, dredging). Any particle-held MeHg thus mobilized during the early freeze-up period could be encapsulated in sea ice. Several possible mechanisms have been suggested for sediment entrainment in waters of the Beaufort Sea inner shelf [Barnes et al. 1982; Naidu et al. 1984]. If a large flux of MeHg concentrated in sea ice were to be released suddenly into the water during spring break up, some of it could be sequestered by primary producers and passed ultimately into the food chain with possible deleterious effects to higher trophic levels.

## Conclusions

The major conclusions of the trace element study are as follows:

1. Comparison of the mean concentrations of V, Cr, Cu, Ni, Zn, As, Cd, Pb, Ba, Fe and Mn in the mud fraction (<62  $\mu\text{m}$  size class) of sediments from this study with those reported for the past 30 years (at approximately 10-year intervals) for the Alaskan Beaufort Sea nearshore indicates no significant temporal change in the metals with the exception of V and Ba. There are significant increases in V from 1977 to 1986 and 1997, and in Ba from at least 1986 to 1997. The reason for the increases in V and Ba in the surface sediment samples is unknown.
2. Attempts to define the  $^{210}\text{Pb}$ - and  $^{137}\text{Cs}$ -based geochronologies for the two cores included in this study were thwarted because of the very low specific activities of the two radionuclides. Nonetheless, based on extrapolation of the mean sediment accumulation rate from other sites within the study area to the two cores, it was possible to determine the dates for major shifts in the concentrations of selected metals. However, the time-series changes in the sediment trace metals as identified on a decadal basis are not matched in the stratigraphic record of the metals within the cores. The stratigraphy demonstrates net significant decreases up core in MeHg, Zn, Cd and Pb accompanied by no change in the concentrations of other metals, including V and Ba. The above disparity could be due to comparison of samples with different granulometry or to faulty deduction of geochronology based on the aforementioned extrapolation.
3. It can be concluded that the increase in MeHg down the core is most likely related to increased methylation of Hg, or due to increased scavenging of Hg by acid volatile sulfides in progressively more intense anoxic and sulfide-forming subsurface layers. This MeHg buildup could be recycled physically to the overlying waters with possible deleterious affects to the food chain.
4. Cluster analysis of all data has identified two major station cluster groups. Group I stations are located within Prudhoe Bay and its vicinity and Group II stations are east and west of this area. The delineation of the two groups is determined by relatively higher concentrations of MeHg in Group II. These differences are either due to regional differences in the natural terrigenous inputs and methylation process of Hg, or to significantly higher concentrations of mud in Group II stations.
5. Single and multiple correlation coefficient analyses of all data suggest that most of the V, Cu, Ni, Zn, As, Pb and Mn in mud are chelated (ligand formation) with organic matter, whereas some of the V is also adsorbed on clays.
6. Although increasing concentrations in V and Ba in mud have been detected with time during the past 30 years, the levels of these elements are below or comparable to the values reported for unpolluted nearshore marine sediments.

In summary, the environment of the study area has remained clean as far as trace metals are concerned despite the recent oil-related industrial activities. Results of these investigations should serve as a baseline for future monitoring of trace metal contamination within the study area.

Table 1. Sample date, station location, water depth, water content (wt %) and grain sizes of gross sediments for samples in the nearshore Beaufort Sea, and samples selected for analysis in 1997–98 (Phase I) and 1998–99 (Phase II). TM=trace metal, HC=hydrocarbon, \*=sediment core station

	Sample	Gravel %	Sand %	Silt %	Clay %	Mud %	
<b>Station</b>	<b>1D</b>						
Date	6 Sep 97	1	0.00	95.99	1.80	2.21	2.01
Latitude (N)	70° 05.7'	2	0.00	94.87	2.72	2.41	5.13
Longitude (W)	144° 05.4'	3	0.00	96.42	1.33	2.25	3.58
Depth (m)	6.0	Mean	0.00	95.76	1.95	2.29	3.57
Water (%)	23.4	SD	0.00	0.65	0.58	0.09	1.27
Phase I/II	/TM+HC						
<b>Station</b>	<b>2E</b>						
Date	5 Sep 97	1	0.00	93.03	4.48	2.49	6.97
Latitude (N)	70° 12.8'	2	0.00	94.79	2.33	2.88	5.21
Longitude (W)	146° 11.6'	3	0.00	93.97	3.25	2.79	6.04
Depth (m)	7.4	Mean	0.00	93.93	3.35	2.72	6.07
Water (%)	20.5	SD	0.00	0.88	1.08	0.20	0.88
Phase I/II	TM/HC						
<b>Station</b>	<b>2F</b>						
Date	5 Sep 97	1	0.00	64.97	24.67	10.36	35.03
Latitude (N)	70° 10.3'	2	0.00	74.14	19.31	6.55	25.86
Longitude (W)	146° 02.0'	3	0.00	62.67	28.99	8.34	37.33
Depth (m)	1.9	Mean	0.00	67.26	24.32	8.42	32.74
Water (%)	21.4	SD	0.00	6.07	4.85	1.91	6.07
Phase I/II	TM+HC/						
<b>Station</b>	<b>3A</b>						
Date	5 Sep 97	1	0.76	20.13	59.31	19.79	79.10
Latitude (N)	70° 17.9'	2	0.61	15.70	61.38	22.31	83.69
Longitude (W)	147° 05.5'	3	0.86	16.56	62.53	20.06	82.59
Depth (m)	6.2	Mean	0.74	17.46	61.07	20.72	81.79
Water (%)	36.0	SD	0.13	2.35	1.63	1.38	2.40
Phase I/II	TM+HC/						
<b>Station</b>	<b>3B*</b>						
Date	5 Sep 97	1	0.00	20.61	53.06	26.43	79.49
Latitude (N)	70° 17.9'	2	0.00	23.58	57.07	19.13	76.20
Longitude (W)	147° 02.3'	3	0.00	24.22	51.31	24.47	75.78
Depth (m)	4.2	Mean	0.00	22.80	53.81	23.34	77.16
Water (%)	36.4	SD	0.00	1.93	2.95	3.78	2.03
Phase I/II	TM/HC						
<b>Station</b>	<b>4A</b>						
Date	5 Sep 97	1	80.67	3.59	6.04	9.70	15.74
Latitude (N)	70° 18.5'	2					
Longitude (W)	147° 40.2'	3	30.82	16.68	21.21	31.29	52.50
Depth (m)	4.5	Mean	55.75	10.14	13.63	20.50	34.12
Water (%)	19.5	SD	35.25	9.26	10.73	15.27	25.99
Phase I/II	TM+HC/						
<b>Station</b>	<b>WPB</b>						
Date	7 Sep 97	1	0.00	82.22	12.58	5.20	17.78
Latitude (N)	70° 20.6'	2	0.00	84.26	11.21	4.53	15.74
Longitude (W)	148° 23.2'	3	0.00	83.84	12.22	3.94	16.16
Depth (m)	2.5	Mean	0.00	83.44	12.00	4.56	16.56
Water (%)	23.2	SD	0.00	1.08	0.71	0.63	1.08
Phase I/II	TM+HC/						

		Sample	Gravel %	Sand %	Silt %	Clay %	Mud %
<b>Station</b>	<b>5(1)</b>						
Date	4 Sep 97	1	0.34	96.56	0.58	2.53	3.11
Latitude (N)	70° 25.0'	2	0.15	97.37	0.10	2.38	2.49
Longitude (W)	148° 03.5'	3	0.00	98.13		1.87	1.87
Depth (m)	5.8	Mean	0.16	97.35	0.34	2.26	2.49
Water (%)	na	SD	0.17	0.79	0.34	0.35	0.62
Phase I/II	TM/HC						
<b>Station</b>	<b>5(2)</b>						
Date	4 Sep 97	1	0.00	96.84	1.08	2.09	3.17
Latitude (N)	70° 25.4'	2	0.00	97.91	0.96	1.13	2.09
Longitude (W)	148° 03.5'	3	0.00	94.69	3.00	2.21	5.21
Depth (m)	5.8	Mean	0.00	96.48	1.68	1.81	3.49
Water (%)	19.7	SD	0.00	1.34	0.93	0.48	1.29
Phase I/II	/TM						
<b>Station</b>	<b>5(5)</b>						
Date	4 Sep 97	1	7.25	70.90	15.33	6.52	21.85
Latitude (N)	70° 26.1'	2	20.69	61.77	12.16	5.38	17.54
Longitude (W)	148° 18.1'	3	3.04	71.21	16.40	9.34	25.74
Depth (m)	6.7	Mean	10.33	67.96	14.63	7.08	21.71
Water (%)	16.9	SD	9.22	5.36	2.20	2.04	4.10
Phase I/II	TM/HC						
<b>Station</b>	<b>5(10)</b>						
Date	4 Sep 97	1	0.00	92.91	2.32	4.76	7.08
Latitude (N)	70° 27.3'	2	0.00	92.16	2.98	4.85	7.83
Longitude (W)	148° 30.1'	3	0.00	90.85	4.95	4.19	9.14
Depth (m)	8.2	Mean	0.00	91.97	3.42	4.60	8.02
Water (%)	19.8	SD	0.00	1.04	1.37	0.36	1.04
Phase I/II	TM/HC						
<b>Station</b>	<b>5A</b>						
Date	4 Sep 97	1	0.00	0.79	49.46	49.75	99.21
Latitude (N)	70° 29.7'	2	0.00	5.06	58.57	36.37	94.94
Longitude (W)	148° 46.0'	3	0.00	2.99	49.18	47.82	97.00
Depth (m)	11.4	Mean	0.00	2.95	52.40	44.65	97.05
Water (%)	56.4	SD	0.00	2.14	5.34	7.23	2.14
Phase I/II	/TM						
<b>Station</b>	<b>5F</b>						
Date	4 Sep 97	1	0.00	50.79	38.22	10.98	49.20
Latitude (N)	70° 26.5'	2	0.00	50.62	39.93	9.45	49.38
Longitude (W)	148° 49.6'	3	0.00	63.40	29.66	6.94	36.60
Depth (m)	1.5	Mean	0.00	54.94	35.94	9.12	45.06
Water (%)	25.1	SD	0.00	7.33	5.50	2.04	7.33
Phase I/II	TM+HC/						
<b>Station</b>	<b>5G</b>						
Date	4 Sep 97	1	0.00	81.47	14.72	3.81	18.53
Latitude (N)	70° 29.3'	2	0.00	83.04	20.83	1.85	22.68
Longitude (W)	148° 02.6'	3	0.00	73.17	20.35	6.48	26.83
Depth (m)	9.3	Mean	0.00	79.23	18.63	4.05	22.68
Water (%)	19.2	SD	0.00	4.33	2.77	1.90	3.39
Phase I/II	/TM						

		Sample	Gravel %	Sand %	Silt %	Clay %	Mud %
<b>Station</b>	<b>SL*</b>						
Date	2 Sep 97	1	0.00	29.23	51.42	19.35	70.77
Latitude (N)	70° 32.6'	2	2.79	34.55	50.14	12.52	62.66
Longitude (W)	149° 38.9'	3	0.00	24.53	13.24	62.23	75.47
Depth (m)	2.4	Mean	0.93	29.44	38.27	31.37	69.63
Water (%)	28.5	SD	1.61	5.01	21.68	26.95	6.48
Phase I/II	TM+HC/						
<b>Station</b>	<b>6A</b>						
Date	2 Sep 97	1	0.00	6.62	10.98	82.40	93.38
Latitude (N)	70° 32.1'	2	0.00	3.37	11.08	85.55	96.63
Longitude (W)	149° 57.6'	3	0.00	2.26	27.83	69.91	97.74
Depth (m)	3.6	Mean	0.00	4.08	16.63	79.29	95.92
Water (%)	37.5	SD	0.00	2.27	9.70	8.27	2.27
Phase I/II	/TM+HC						
<b>Station</b>	<b>6B</b>						
Date	4 Sep 97	1	0.00	83.74	8.03	8.22	16.25
Latitude (N)	70° 33.4'	2	0.00	87.51	12.49	0.00	12.49
Longitude (W)	150° 24.6'	3	0.00	91.24	5.70	3.06	8.76
Depth (m)	5.5	Mean	0.00	87.50	8.74	3.76	12.50
Water (%)	18.3	SD	0.00	3.75	3.45	4.15	3.75
Phase I/II	TM+HC/						
<b>Station</b>	<b>6C</b>						
Date	3 Sep 97	1	0.00	64.27	2.03	33.71	35.74
Latitude (N)	70° 40.3'	2	0.00	86.36	1.65	11.99	13.64
Longitude (W)	150° 32.1'	3	0.00	41.70	3.57	54.74	58.31
Depth (m)	16.1	Mean	0.00	64.11	2.42	33.48	35.90
Water (%)	22.9	SD	0.00	22.33	1.02	21.38	22.34
Phase I/II	TM/HC						
<b>Station</b>	<b>6D</b>						
Date	3 Sep 97	1	0.00	77.57	10.89	0.00	0.00
Latitude (N)	70° 44.9'	2					
Longitude (W)	150° 28.5'	3					
Depth (m)	18.4	Mean					
Water (%)	32.5	SD					
Phase I/II	/TM						
<b>Station</b>	<b>6G</b>						
Date	2 Sep 97	1	0.00	16.88	67.36	15.76	83.12
Latitude (N)	70° 31.3'	2	0.00	50.72	40.32	8.95	49.27
Longitude (W)	149° 53.9'	3	0.00	18.01	63.22	18.77	81.99
Depth (m)	2.1	Mean	0.00	28.54	56.97	14.49	71.46
Water (%)	37.1	SD	0.00	15.69	11.89	4.11	15.70
Phase I/II	/TM						
<b>Station</b>	<b>7E</b>						
Date	3 Sep 97	1	0.00	5.25	72.25	22.50	94.75
Latitude (N)	70° 43.6'	2	0.00	5.03	73.00	21.97	94.97
Longitude (W)	152° 04.4'	3	0.00	8.18	72.87	18.96	91.83
Depth (m)	3.3	Mean	0.00	6.15	72.71	21.14	93.85
Water (%)	48.0	SD	0.00	1.44	0.33	1.56	1.43
Phase I/II	/TM						

Table 2. Results of analysis for QA/QC on sediments for trace metals, with special reference to analytical accuracy and precision. MESS-2, NIST-2709 and IAEA-356 refer to certified reference materials (standards), whereas other samples are representative sediment samples from the study area.

Sample	MeHg ng/g (Wet)	Trace Metals, µg/g (ppm) Dry Weight (Mud) Basis								
		V	Cr	Cu	Ni	Zn	As	Cd	Pb	Ba
Blank-1	0.020	0.61	1.27	0.06	0.37	-0.41	0.10	-0.030	0.05	0.69
Blank-2	0.018	0.36	1.06	0.16	0.14	-0.51	-0.04	0.014	0.12	1.01
Blank-3	0.020	0.29	0.89	0.10	0.03	-0.06	-0.14	-0.034	0.05	1.43
Blank-4	0.017	-0.05	-1.14	0.42*	-0.36	-0.29	1.25*	0.49*	0.398*	2.00
Blank-5	0.019	-0.44	-1.41	0.09	-0.62	-0.45	0.83	0.009	0.12	2.20
Blank-6	0.019	-0.40	-1.33	0.03	-0.61	-0.71	0.76	-0.015	0.04	1.90
Mean	0.019	0.06	-0.11	0.09	-0.18	-0.41	0.30	-0.011	0.08	1.54
SD	0.001	0.43	1.30	0.05	0.42	0.22	0.46	0.022	0.04	0.60
Estimated MDL	0.004	1.29	3.91	0.15	1.25	0.66	1.37	0.066	0.12	1.80
MESS-2 Rep 1		222.7	94.9	50.4	54.4	147.2	22.1	0.291	21.4	918.9
MESS-2 Rep 2		196.2	84.0	43.0	45.6	137.3	19.3	0.352	20.6	903.2
MESS-2 Rep 3		234.3	87.4	43.0	49.1	127.7	20.3	0.271	19.5	1029.1
Mean		217.7	88.8	45.5	49.7	137.4	20.6	0.305	20.5	950.4
SD		19.5	5.6	4.3	4.4	9.8	1.4	0.042	1.0	68.6
Certified		252	106	39.3	49.3	172	20.7	0.24	21.9	
Range		10	8	2.0	1.8	16	0.8	0.01	1.2	
NIST-2709		106.3	97.8	37.0	79.2	95.8	19.5	0.445	17.3	861.9
Certified		112.0	130.0	34.6	88.0	106.0	17.7	0.380	18.9	968.0
Range		5.0	4.0	0.7	5.0	3.0	0.8	0.010	0.5	40.0
IAEA-356 Rep 1	5.880									
IAEA-356 Rep 2	5.093									
Mean	5.487									
SD	0.556									
Certified	5.49									
Range	0.71									
3B/2-2 + 1.047 ng/g	1.218									
% Recovery	99.4									
3B/2-2 + 1.084 ng/g	1.323									
% Recovery	105.7									
RPD (%)	6.1									
5(10)/3 + 1000 µg/g										1475.6
% Recovery										94.1
5(10)/3 + 1000 µg/g										1465.2
% Recovery										93.0
RPD (%)										0.7
SL/1 + 0.970 ng/g	1.057									
% Recovery	91.3									
SL/1 + 0.944 ng/g	0.982									
% Recovery	85.9									
RPD (%)	6.1									

Sample	MeHg ng/g (Wet)	Trace Metals, µg/g (ppm) Dry Weight (Mud) Basis								
		V	Cr	Cu	Ni	Zn	As	Cd	Pb	Ba
4A/1 Rep 1		141.7	65.7	40.8	48.6	124.7	16.0	0.427	17.2	
4A/1 Rep 2		137.4	70.7	39.6	46.8	121.8	16.1	0.387	16.0	
Mean		139.5	68.2	40.2	47.7	123.2	16.1	0.407	16.6	
RPD (%)		3.1	7.4	3.2	3.7	2.4	0.7	9.8	7.2	
WPB/1 Rep 1		118.8	94.1	28.3	41.3	109.4	14.2	0.349	13.1	
WPB/1 Rep 2		124.4	89.2	29.5	43.1	112.8	13.4	0.326	12.0	
Mean		121.6	91.7	28.9	42.2	111.1	13.8	0.337	12.6	
RPD (%)		9.3	10.8	8.3	8.4	6.1	11.7	13.9	16.5	
6C/1 Rep 1		166.3	89.4	41.9	52.0	111.9	17.7	0.209	17.8	657.1
6C/1 Rep 2		169.7	91.9	42.7	52.1	119.5	18.1	0.187	18.2	775.8
Mean		168.0	90.6	42.3	52.1	115.7	17.9	0.198	18.0	716.5
RPD (%)		2.1	2.7	1.9	0.1	6.5	2.3	11.5	2.3	16.6
SL/1 Rep 1		113.9	72.9	27.6	35.1	99.6	9.9	0.238	12.7	
SL/1 Rep 2		116.8	74.4	27.7	35.2	100.8	9.8	0.186	12.5	
Mean		115.4	73.6	27.7	35.1	100.2	9.8	0.2	12.6	
RPD (%)		2.5	1.9	0.5	0.4	1.2	1.3	24.5	2.1	
Spike Level		200.0	200.0	200.0	200.0	200.0	200.0	200.0	200.0	
3B/2-2 MS		286.7	235.4	211.0	216.3	270.9	195.8	189.7	205.5	
% Recovery		93.9	93.6	93.7	93.9	97.3	93.1	94.7	96.9	
Spike Level		200.0	200.0	200.0	200.0	200.0	200.0	200.0	200.0	
3B/2-2 MS		291.9	242.9	221.6	225.6	277.2	205.2	197.7	216.4	
% Recovery		98.5	97.3	99.0	98.5	100.5	97.8	98.7	102.4	
RPD (%)		2.7	3.9	5.5	4.8	3.2	4.9	4.1	5.5	
Spike Level		200.0	200.0	200.0	200.0	200.0	200.0	200.0	200.0	
3B/10-10 MS		279.2	229.3	205.8	207.7	252.9	191.5	177.8	194.5	
% Recovery		93.9	92.6	92.7	91.7	92.6	89.3	88.8	91.9	
Spike Level		200.0	200.0	200.0	200.0	200.0	200.0	200.0	200.0	
3B/10-10 MS		297.0	240.8	214.8	218.9	274.3	205.7	194.4	213.4	
% Recovery		102.8	98.4	97.2	97.3	103.3	96.4	97.1	101.4	
RPD (%)		9.0	6.1	4.7	5.9	10.9	7.7	8.9	9.7	
Spike Level		193.4	193.4	193.4	193.4	193.4	193.4	193.4	193.4	
WPB/1 MS		312.4	285.9	253.6	255.3	313.0	216.6	192.7	207.8	
% Recovery		98.7	100.4	116.2	110.2	104.4	104.9	99.5	100.9	
Spike Level		201.3	201.3	201.3	201.3	201.3	201.3	201.3	201.3	
WPB/1 MSD		319.0	295.5	250.9	253.3	320.9	222.6	199.0	218.7	
% Recovery		98.1	101.3	110.3	104.9	104.2	103.7	98.7	102.4	
RPD (%)		0.6	0.8	5.2	5.0	0.2	1.1	0.8	1.5	
MSA		0.972	0.987	0.936	0.951	0.997	0.951	1.023	0.973	0.981

\*Anomalous data RPD (%) = relative percent difference (between the sample and a duplicate); a measure of precision

Table 3. Chemical and granulometric composition of sediments from the study area. The mean (geometric) and CV% at the end of the table are calculated based on all samples analyzed. Concentrations of MeHg and THg are based on gross sediment wet weights whereas others are per dry weight on mud samples. Phase I: analyzed in 1997–98, Phase II: analyzed in 1998–99.

Station/ Sample	OM (%)	CO <sub>3</sub> (%)	Silt (%)	Clay (%)	MeHg (ng/g)	THg (ng/g)	V (µg/g)	Cr (µg/g)	Cu (µg/g)	Ni (µg/g)	Zn (µg/g)	As (µg/g)	Cd (µg/g)	Pb (µg/g)	Ba (µg/g)	Fe (%)	Mn (µg/g)
<b>Phase I</b>																	
2E/1	7.0	8.8	64.3	35.7	0.020	13.1	126	81	30	33	101	17	0.277	15	663	2.42	421
2E/2	9.1	9.0	44.7	55.3	0.028		109	50	24	31	77	14	0.219	11	593		
2E/3	7.9	8.7	53.8	46.2	0.026		87	57	24	26	76	12	0.215	10	519		
Mean	8.0	8.9	54.3	45.7	0.025	13.1	107	63	26	30	85	14	0.237	12	592	2.42	421
CV%	13.34	1.63	18.04	21.40	16.88		17.90	25.45	13.78	12.24	16.58	18.23	14.64	24.40	12.11		
2F/1			70.4	29.6	0.121		104	46	31	33	94	12	0.345	11	487		
2F/2			74.7	25.3	0.143	20.6	115	67	30	32	103	14	0.294	14	508	1.98	335
2F/3			77.7	22.3	0.184		81	48	20	23	74	9	0.278	9	439		
Mean			74.2	25.8	0.149	20.6	100	54	27	29	90	12	0.306	11	478	1.98	335
CV%			4.92	14.18	21.41		17.29	21.84	22.65	18.19	16.41	20.60	11.45	19.97	7.44		
3A/1	6.1	8.0	75.0	25.0	0.115	19.6	117	53	26	31	83	12	0.200	12	852	3.65	331
3A/2	4.8	8.6	73.3	26.7	0.099		114	55	26	30	82	15	0.231	13	602		
3A/3	6.0	7.8	75.7	24.3	0.137		108	52	25	29	76	14	0.234	12	568		
Mean	5.6	8.1	74.7	25.3	0.117	19.6	113	53	26	30	80	14	0.222	13	674	3.65	331
CV%	13.07	5.50	1.63	4.79	16.31		4.39	2.53	2.55	3.99	4.67	9.16	8.49	3.49	23.00		
3B/1	6.2	7.2	66.8	33.3	0.246	25.0	122	55	29	35	107	10	0.277	14	539	3.44	360
3B/2	6.7	6.9	74.9	25.1	0.177		99	48	24	29	76	10	0.278	12	546		
3B/3	7.5	6.5	67.7	32.3	0.210		127	57	30	34	89	12	0.298	15	540		
Mean	6.8	6.8	69.8	30.2	0.211	25.0	116	53	27	32	91	11	0.284	13	542	3.44	360
CV%	9.44	5.63	6.38	14.74	16.36		12.98	8.23	12.44	10.20	16.69	12.45	4.17	11.85	0.63		
4A/1	8.9	7.3	38.4	61.6	0.033		140	68	40	48	123	16	0.407	17	677	4.17	493
4A/2	6.6	8.7	40.4	59.6	0.044	30.9	100	42	26	34	77	10	0.520	10	702		
Mean	7.7	8.0	39.4	60.6	0.039	30.9	120	55	33	41	100	13	0.484	13	689	4.17	493
CV%	21.30	12.66	3.64	2.37	20.20		23.05	33.78	30.86	23.11	33.07	33.72	17.24	37.78	2.65		
WPB/1	8.8	10.2	70.8	29.3	0.057	8.4	122	92	29	42	111	14	0.337	13	663	4.89	1089
WPB/2	6.5	11.4	71.2	28.8	0.044	14.8	119	83	30	38	113	13	0.369	13	684		
WPB/3	8.8	8.3	75.6	24.4	0.092		132	88	32	40	117	14	0.290	15	544		
Mean	8.0	10.0	72.5	27.5	0.064	10.9	124	87	30	40	114	14	0.332	13	630	4.89	1089
CV%	16.44	15.68	3.70	9.78	38.59	35.82	5.77	4.92	5.46	4.71	2.44	7.16	11.97	9.48	12.02		
5(1)/1	8.5	12.0	18.7	81.4	0.001		168	77	39	38	147	45	0.378	41	585		
5(1)/2	8.2	12.4	4.0	96.0	0.001		137	61	30	34	104	26	0.253	22	536		
5(1)/3			0.0	100.0	0.012		120	60	30	29	102	26	0.287	22	550		
Mean	8.3	12.2	7.6	92.4	0.005		142	66	33	34	118	32	0.306	28	557		
CV%	2.46	2.03	129.89	10.62	136.09		17.22	14.37	15.96	12.84	21.61	34.18	21.12	38.36	4.48		

Station/ Sample	OM (%)	CO <sub>3</sub> (%)	Silt (%)	Clay (%)	MeHg (ng/g)	THg (ng/g)	V (µg/g)	Cr (µg/g)	Cu (µg/g)	Ni (µg/g)	Zn (µg/g)	As (µg/g)	Cd (µg/g)	Pb (µg/g)	Ba (µg/g)	Fe (%)	Mn (µg/g)
5(5)/1	5.3	10.0	70.2	29.8	0.008	15.4	107	48	24	30	78	13	0.206	12	393	3.07	432
5(5)/2	5.2	11.1	69.3	30.7	0.041		110	53	24	30	83	14	0.222	12	546		
5(5)/3	5.6	9.0	63.7	36.3	0.043		119	69	29	33	98	15	0.239	14	600		
Mean	5.4	10.0	67.7	32.3	0.031	15.4	112	57	26	31	86	14	0.222	13	513	3.07	432
CV%	3.24	10.52	5.18	10.87	64.09		5.66	19.49	12.18	5.79	12.02	7.78	7.42	10.54	20.87		
5(10)/1	6.4	13.1	32.8	67.2	0.013	6.1	111	59	24	29	85	16	0.260	12	526	2.38	597
5(10)/2	7.9	11.2	38.1	61.9	0.023		90	49	20	24	79	13	0.286	9	489		
5(10)/3	6.7	11.9	54.2	45.8	0.024		103	61	23	25	87	17	0.240	13	535		
Mean	7.0	12.1	41.7	58.3	0.020	6.1	101	57	22	26	84	15	0.262	12	517	2.38	597
CV%	11.36	7.96	26.74	19.10	30.41		10.07	11.32	11.21	10.46	4.92	13.36	8.80	18.27	4.70		
5F/1	5.0	9.0	77.7	22.3	0.115	14.7	101	62	25	33	97	10	0.259	10	422	3.04	323
5F/2	5.2	9.1	80.9	19.1	0.095		97	49	22	31	82	10	0.249	9	482		
5F/3	5.7	9.5	81.0	19.0	0.101		109	68	27	34	99	11	0.344	12	528		
Mean	5.3	9.2	79.9	20.1	0.104	14.7	102	60	24	32	93	10	0.284	10	477	3.04	323
CV%	7.23	3.21	2.37	9.38	9.90		5.70	16.39	10.46	4.54	9.73	6.98	18.38	13.48	11.21		
SL/1	5.4	7.1	17.5	82.5	0.172	23.8	115	74	28	35	100	10	0.212	13	545	3.06	294
SL/2	5.8	8.1	80.0	20.0	0.121		113	54	27	36	89	11	0.282	11	280		
SL/3	3.6	10.1	72.7	27.3	0.218		93	43	20	30	75	9	0.246	9	466		
Mean	4.9	8.5	56.7	43.3	0.170	23.8	107	57	25	34	88	10	0.247	11	431	3.06	294
CV%	24.09	18.09	60.18	78.93	28.54		11.67	26.98	18.12	8.96	14.09	8.19	14.19	16.80	31.62		
6B/1	5.7	10.0	49.4	50.6	0.024	8.0	96	63	20	32	75	11	0.180	9	613	3.48	513
6B/2	6.4	8.8	100.0	0.0	0.013		92	70	19	28	81	11	0.213	9	610		
6B/3	7.7	8.5	65.1	34.9	0.020		95	63	21	29	88	12	0.195	10	662		
Mean	6.6	9.1	71.5	28.5	0.019	8.0	95	66	20	30	81	11	0.196	9	628	3.48	513
CV%	15.12	8.45	36.22	90.85	29.30		2.44	6.39	6.18	6.21	8.22	5.58	8.43	4.09	4.65		
6C/1	7.4	2.4	5.7	94.3	0.074	22.3	168	91	42	52	116	18	0.198	18	717	3.68	576
6C/2	8.6	4.6	12.1	87.9	0.015		140	78	34	40	105	26	0.191	17	629		
6C/3	7.4	2.8	6.1	93.9	0.063		166	87	40	50	116	15	0.175	18	696		
Mean	7.8	3.3	8.0	92.0	0.051	22.3	158	85	39	47	112	19	0.188	17	680	3.68	576
CV%	8.94	36.82	45.02	3.90	61.92		9.78	7.63	11.31	13.78	5.75	30.12	6.27	3.15	6.70		
<b>Phase II</b>																	
1D/1	6.0	4.3	44.9	55.1	0.032	10.7	122	73	25	36	104	23	0.105	22	624		
1D/2	6.2	3.9	53.0	47.0	0.020		105	63	19	32	87	20	0.056	20	554	3.57	404
1D/3	5.9	4.2	37.2	62.8	0.023		113	67	22	33	96	22	0.075	21	598		
Mean	6.0	4.1	45.0	55.0	0.025	10.7	113	68	22	34	96	22	0.079	21	592	3.57	404
CV%	2.66	4.99	17.63	14.43	24.99		7.50	7.27	12.78	6.49	8.95	5.86	31.40	6.47	5.98		
5(2)/1	9.4	11.1	34.1	65.9	0.021	24.0	134	56	29	38	107	28	0.292	27	456	3.64	1796
5(2)/2	8.8	9.4	45.9	54.1	0.076		145	60	32	39	118	32	0.281	31	496		
5(2)/3	9.2	8.3	56.5	43.5	0.028		126	57	29	35	107	27	0.264	22	454		
Mean	9.1	9.6	45.5	54.5	0.036	24.0	135	58	30	37	111	29	0.279	26	469	3.64	1796
CV%	3.46	14.79	24.66	20.59	83.16		7.07	2.86	4.99	6.00	5.74	9.55	5.06	17.09	5.06		



Table 4. Stratigraphic variations in the concentrations of trace metals in mud fractions of cores 3B and SL.

Depth cm	MeHg ng/g (Wet gross)	Trace Metals, µg/g Dry Weight (Mud) Basis								
		V	Cr	Cu	Ni	Zn	As	Cd	Pb	Ba
<b>Core 3B</b>										
0-1	0.110	98.7	47.3	22.6	27.7	75.6	11.7	0.231	11.2	547.4
1-2	0.140	103.2	47.6	23.3	29.1	74.1	11.2	0.242	11.1	535.3
2-3	0.170	110.4	45.9	25.3	31.2	79.6	10.6	0.186	11.4	529.5
3-4	0.170	106.6	49.0	24.6	29.8	77.9	10.7	0.236	11.7	540.9
4-5	0.185	100.0	48.6	22.7	29.0	85.1	10.1	0.249	11.4	499.0
5-6	0.207	117.5	59.2	28.1	32.7	85.8	11.2	0.286	13.3	546.8
6-7	0.210	126.9	56.5	29.8	34.0	89.4	12.0	0.298	14.6	540.3
7-8	0.177	98.8	48.3	23.5	28.6	76.3	9.6	0.278	11.6	545.7
8-9	0.246	122.2	55.1	28.9	34.6	106.5	9.9	0.277	14.0	539.4
<b>Core SL</b>										
0-1	0.172	115.4	73.6	27.7	35.1	100.2	9.8	0.212	12.6	545.2
1-2	0.121	112.5	53.7	27.0	35.7	88.5	10.9	0.282	11.2	280.1
2-3	0.218	92.5	43.4	19.6	30.2	75.4	9.3	0.246	9.0	466.2
3-4	0.256	97.8	44.7	21.7	33.3	81.7	7.8	0.213	11.6	487.9
5-6	0.281	102.1	52.5	22.1	33.9	82.4	8.8	0.213	10.2	443.5
7-8	0.312	95.2	44.9	22.4	34.3	81.5	8.5	0.200	9.7	464.6
9-10	0.321	101.3	45.1	24.6	35.1	84.2	8.7	0.220	10.7	502.5
11-12	0.304	88.1	41.6	20.6	31.4	71.4	7.6	0.191	9.0	482.1
13-14	0.375	106.9	47.8	25.6	37.0	88.2	8.3	0.235	10.5	451.4
15-16	0.388	98.0	49.7	23.0	33.6	84.9	9.1	0.289	10.6	470.8
17-18	0.300	103.0	47.1	24.1	36.3	84.6	8.2	0.228	9.6	435.9
19-20	0.285	107.0	52.9	24.1	36.6	85.8	8.3	0.209	10.9	494.8

Table 5. Correlation coefficients for chemical and physical parameters of muds from the Beaufort Sea nearshore, north arctic Alaska (N=62 except where noted; only significant correlations [p<.05] are shown).

	OM%	CO <sub>3</sub> %	Silt%	Clay%	MeHg	THg	V	Cr	Cu	Ni	Zn	As	Cd	Pb	Ba	Fe	Mn
OM%	1.00 <sup>a</sup>																
CO <sub>3</sub> %		1.00 <sup>a</sup>															
Silt%	-0.38 <sup>a</sup>		1.00														
Clay%	0.38 <sup>a</sup>		-1.00	1.00													
MeHg	-0.41 <sup>a</sup>				1.00												
THg					0.86 <sup>c</sup>	1.00 <sup>c</sup>											
V	0.57 <sup>a</sup>	-0.48 <sup>a</sup>	-0.52	0.52			1.00										
Cr	0.45 <sup>a</sup>	-0.44 <sup>a</sup>	-0.34	0.34			0.75	1.00									
Cu	0.57 <sup>a</sup>	-0.34 <sup>a</sup>	-0.42	0.42			0.88	0.69	1.00								
Ni	0.47 <sup>a</sup>	-0.54 <sup>a</sup>	-0.39	0.39			0.87	0.77	0.86	1.00							
Zn	0.49 <sup>a</sup>	-0.36 <sup>a</sup>	-0.39	0.39			0.88	0.78	0.84	0.84	1.00						
As	0.55 <sup>a</sup>		-0.50	0.50			0.71	0.42	0.53	0.43	0.68	1.00					
Cd		0.41 <sup>a</sup>						-0.28					1.00				
Pb	0.46		-0.45	0.45			0.72	0.41	0.53	0.46	0.70	0.94		1.00			
Ba		-0.32 <sup>a</sup>	-0.41	0.41			0.30	0.39	0.26	0.34	0.27				1.00		
Fe	0.61 <sup>c</sup>	-0.50 <sup>c</sup>					0.56 <sup>b</sup>			0.53 <sup>b</sup>				0.48 <sup>b</sup>		1.00 <sup>b</sup>	
Mn	0.73 <sup>c</sup>											0.71 <sup>b</sup>		0.65 <sup>b</sup>		0.44 <sup>b</sup>	1.00 <sup>b</sup>

<sup>a</sup>N=58    <sup>b</sup>N=22    <sup>c</sup>N=21 (see Table 3 for individual values)

Table 6. Multiple and partial correlation coefficients for regression of sediment metal contents against organic matter, clay and iron contents.

Metal	Partial Correlation Coefficients			Multiple Correlation Coefficient (R <sup>2</sup> )
	r <sub>xOM/ClayFe</sub>	r <sub>xClay/OMFe</sub>	r <sub>xFe/OMClay</sub>	
MeHg	ns	ns	ns	0.1407
THg	ns	ns	ns	0.0933
V	0.5137	0.4937	ns	0.6892
Cr	ns	ns	ns	0.4379
Cu	0.4796	ns	ns	0.5229
Ni	0.4900	ns	ns	0.5947
Zn	0.5020	ns	ns	0.4837
As	0.5369	ns	ns	0.4766
Cd	ns	ns	ns	0.0686
Pb	ns	ns	ns	0.4894
Ba	ns	ns	ns	0.2876
Mn	0.6529	ns	ns	0.5411

ns – not significant (p>0.05)

Table 7. Correlation coefficients for metal concentrations in muds in core samples 3B and SL. Only significant correlations ( $p < .05$ ) are shown. The number of samples analyzed for cores 3B and SL were 9 and 12, respectively.

7a. Core 3B	Core Depth (cm)	MeHg	V	Cr	Cu	Ni	Zn	As	Cd	Pb	Ba
Core Depth (cm)	1										
MeHg	0.88	1									
V		0.77	1								
Cr		0.73	0.81	1							
Cu		0.80	0.99	0.86	1						
Ni		0.86	0.98	0.80	0.97	1					
Zn	0.71	0.87	0.74		0.74	0.83	1				
As								1			
Cd	0.74			0.79					1		
Pb	0.71	0.81	0.94	0.90	0.96	0.92	0.79		0.73	1	
Ba											1

7b. Core SL	Core Depth (cm)	MeHg	V	Cr	Cu	Ni	Zn	As	Cd	Pb	Ba
Core Depth (cm)	1										
MeHg	0.73	1									
V			1								
Cr			0.80	1							
Cu			0.93	0.72	1						
Ni			0.76		0.80	1					
Zn			0.92	0.87	0.90	0.69	1				
As		-0.67	0.58					1			
Cd								0.65	1		
Pb			0.77	0.76	0.72		0.84			1	
Ba									-0.58		1

Table 8. Summary of the stepwise multiple discriminant analysis among the two station groups formed by cluster analysis of all the data included in Table 3.

Statistica Discriminant Stats	Discriminant Function Analysis Results		
Stepwise analysis – Step 4 (final step)			
Number of variables in model: 4			
Last variable entered: Cd			
Wilks' Lambda: .0160729		F(2, 14) = 2.817974	p <.0937
		approx. F(8, 28) = 24.10715	p <0.0000

Statistica Discriminant Stats	Discriminant Function Analysis Summary					
Step 4 Number of variables in model: 4 Grouping: Group (3 grps)						
Wilks' Lambda: .01607 approx. F(8, 28) = 24.107 p <0.0000						
N = 20	Wilks' Lambda	Partial Lambda	F-remove (2, 14)	p-level	Tolerance	1-Tolerance (R-Square)
MeHg	.1662909	.0966550	65.42252	.0000001	.3883676	.6116324
CO <sub>3</sub>	.0865345	.1857392	30.68725	.0000076	.3499699	.6500301
Mn	.0357755	.4492697	8.58084	.0036945	.5918576	.4081424
Cd	.0258359	.6221135	4.25197	.0360651	.4119508	.5880492

Statistica Discriminant Stats	Classification Matrix			
Rows: Observed classifications				
Columns: Predicted classifications				
Group	Percent Correct	g_1:1 p = .33333	g_2:2 p = .33333	g_3:3 p = .33333
g_1:1	100.0000	2	0	0
g_2:2	100.0000	0	9	0
g_3:3	100.0000	0	0	9
Total	100.000	2	9	9

Statistica Discriminant Stats	Standardized Coefficients for Canonical Variables	
Variable	Root 1	Root 2
MeHg	-1.54958	.294932
CO <sub>3</sub>	-1.33190	-.953473
Mn	.99230	-.057311
Cd	.96229	.248501
Eigenvalue	16.42408	2.570731
Cumulative Properties	.86466	1.000000

Table 9. Time-series changes in the mean concentrations of trace elements in mud of the nearshore region of the Beaufort Sea. The differences in V concentrations between 1977 and 1985–86 or between 1977 and 1997, and the difference in Ba concentrations between 1985–86 and 1997 at are the 95% confidence level.

Year	MeHg	THg	V	Cr	Cu	Ni	Zn	As	Cd	Pb	Ba	Fe	Mn
<b>1977<sup>a</sup></b>													
N=12													
X			87	60	21	30	94					2.58	368
SD			3	5	4	2	10					0.22	96
CV%			3	8	19	7	11					9	26
<b>1985–86<sup>b</sup></b>													
N=13													
X			115	78	24		93		0.19	15	347		
SD			17	10	4		13		0.06	4	77		
CV%			15	13	17		14		32	27	22		
<b>1997<sup>c</sup></b>													
N=62													
X	0.123	29	117	63	27	34	96	16	0.264	15	569	3.4	540
SD	0.121	17	23	13	7	7	18	7	0.115	6	114	0.88	337
CV%	99	57	20	21	25	20	19	43	43	39	20	26	62
<b>1997<sup>d</sup> (Vicinity of Barrow)</b>													
Barrow North Salt Lagoon													
X				112	26	39	77				11		
AB46 Elson Lagoon													
X				50	10	13	32		0.9	9			
AB68 Elson Lagoon													
X				77	19	24	61		0.5	14			

<sup>a</sup>Sweeney [1984], Sweeney and Naidu [1989]

<sup>b</sup>Creclius et al. [1991] and Boehm et al. [1987]

<sup>c</sup>Naidu et al. [1999]

<sup>d</sup>after Yang et al. [1997]

Table 10. Activities of  $^{210}\text{Pb}$  (total),  $^{226}\text{Ra}$  and  $^{137}\text{Cs}$  with core depth (cm) in cores 3B and SL.

Sample	Total $^{210}\text{Pb}$ (dpm/g)	$^{226}\text{Ra}$ (dpm/g)	$^{137}\text{Cs}$ (dpm/kg)
<b>3B</b>			
0	2.59±0.11	1.73±0.11	195.3±45.2
1			
2	3.06±0.13	1.86±0.11	232.6±46.3
3	2.02±0.10		
4	2.74±0.10		
5	3.22±0.17		
6	2.09±0.17	1.61±0.10	210.6±38.4
7	1.84±0.15		
8	1.92±0.18		
9	2.05±0.20	1.45±0.07	110.6±26.1
10	1.98±0.11	1.53±0.09	70.0±36.6
<b>SL</b>			
1	1.58±0.07 (1.59±0.09)		
2	1.51±0.05		
3	1.75±0.07		
4	1.63±0.06	1.63±0.09	bd
5	1.69±0.10		
6	1.43±0.06	1.70±0.12	bd
7	1.31±0.06		
8	1.24±0.06	1.62±0.12	bd
9	1.56±0.11		

bd – below detection

Table 11. Mean concentrations of trace metals ( $\mu\text{g/g}$ ), Fe (wt %) and organic carbon (OC, wt %) in muddy sediments of the study area compared with those in muds from selected circum-arctic shelf regions [after Naidu et al. 2000].

Shelf	n	OC	V	Cr	Cu	Ni	Zn	As	Cd	Pb	Ba	Fe	Mn	Co	Hg
Chukchi Sea <sup>a</sup>	12	0.75	116	82	22	27	79					3.46	295	26	
	SD	0.44	30	21	6	6	18					0.64	37	5	
Beaufort Sea <sup>b</sup>	12	0.83	87	60	21	30	94					2.58	368	89	
	SD	0.20	3	5	4	2	10					0.22	96	14	
Beaufort Sea <sup>c</sup>	13		115	78	24		93		0.19	15					
	SD		17	10	4		13		0.06	4					
Beaufort Sea <sup>d</sup> (this study)	62		117	63	27	34	96	16	0.27	15	569	3.36	540		0.017
	SD		24	13	7	7	18	7	0.11	6	116	0.89	337		0.007
Pechora Sea <sup>e</sup>	40		175	110	21	43	84	33	0.11						
	SD		46	15	2	9	9	55	0.05						
Kara Sea <sup>e</sup>	36		147	110	20	42			0.11						
	SD		27	25	6	10			0.07						
Kara Sea <sup>f</sup>	16			97	27	44	80		0.09	14		4.39			0.028
	SD			12	14	17	22		0.03	3		1.41			0.009
Svalbard <sup>e</sup>	15		248	153		50	107		0.22						
	SD		11	5		1	3		0.03						
E. Greenland <sup>g</sup>	10		162	118	46	59	89		0.11	19					
	SD		65	45	32	29	20		0.05	7					
W. Greenland <sup>g</sup>	22		129	163	49	82	77		0.15	18					
	SD		70	154	40	96	19		0.16	8					
W. Baffin Bay <sup>h</sup>	12		91	63	29	22	61								
	SD		32	19	8	9	14								
E. Siberian Sea <sup>f</sup>	24			68	16	26	85	18	0.14	18	644	3.49			0.037
	SD			14	6	8	25	6	0.08	5	69	0.95			0.019
Laptev Sea <sup>f</sup>	11			78	19	30	92	15	0.11	20	611	3.97			0.037
	SD			12	7	7	15	6	0.06	5	71	0.92			0.016
Laptev Sea <sup>i</sup>	10				15	28	98		0.06	18		4.06	206		
	SD				4	7	22		0.02	3		1.00	175		

<sup>a</sup>Naidu et al. [1997]

<sup>b</sup>Sweeney [1984], Naidu [1982]

<sup>c</sup>Creelius et al. [1991]

<sup>d</sup>this study

<sup>e</sup>Loring et al. [1995]

<sup>f</sup>Esnough [1996]

<sup>g</sup>Loring and Asmund [1996]

<sup>h</sup>Loring [1984]

<sup>i</sup>Nolting et al. [1996]

# HYDROCARBON STUDIES

## Introduction

The hydrocarbon data from the surface sediments from the nearshore and continental shelf regions of the Beaufort Sea were initially acquired about three decades ago [Peake et al. 1972; Shaw et al. 1979; Wong et al. 1976; Venkatesan and Kaplan 1982]. A more recent Minerals Management Service (MMS) sponsored project on hydrocarbons in the surface sediments of the region was carried out by Boehm et al. 1987 and Steinhauer and Boehm 1992. In an extensive study, Wong et al. [1976] also reported hydrocarbons in water, organisms and fish from the Beaufort Sea. Additionally, Varanasi et al. [1993] measured polycyclic aromatic hydrocarbons, chlorinated hydrocarbons, PCBs and trace elements in tissues of marine mammals such as whales and seals from Alaskan seas. The latter study implies that sediments and water in the same region could be contaminated with similar anthropogenic compounds. Further, a large terrigenous influx of organic matter occurs in the Beaufort Sea nearshore, as suggested by stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) of the total organic carbon of sediments [Naidu et al. 2000]. The Meade, Sagavanirktok, Ikpikpuk and Colville rivers contribute to the sedimentary regime of northern arctic Alaska. Hydrocarbon profiles of sediments from the continental shelf of the Beaufort Sea analyzed earlier in the Outer Continental Shelf Environmental Assessment Program (OCSEAP) by Venkatesan and Kaplan [1982] documented a mixed input from terrigenous and marine sources. Yunker et al. [1993, 1995, 1996] demonstrated that the Mackenzie River is the major source of hydrocarbons in the adjacent Mackenzie shelf in the eastern Beaufort Sea. Valette-Silver et al. [1999] more recently conducted a comprehensive study of radionuclides and inorganic and organic compounds to assess the current level of contamination in the western Beaufort Sea. With increasing anthropogenic activities around the region, influx of industry-based contaminants is likely. Further, long-range atmospheric transport of contaminants into remote areas via particulates generated by combustion could also contribute PAHs and PCBs [LaFlamme and Hites 1978; Atlas and Giam 1981, among others] to the study region included in this report. Therefore, the current study in the Beaufort Sea nearshore was undertaken in order to understand the sources and processes of hydrocarbon accumulation in sediments in view of ongoing and proposed oil and gas development in the region.

## Analytical Methods

Surficial sediments from 20 stations (Figure 6) of the Beaufort Sea nearshore were sampled in 1997 for hydrocarbon analyses. Organically clean I-CHEM jars were used for the samples. The sediments were frozen, stored and shipped to the University of California at Los Angeles (UCLA) and kept frozen until analyzed. During the first year (1997–98) of the project, 21 sediment samples were extracted with organic solvents and processed; the samples consisted of triplicates from seven stations. In the second year (1998–99), 18 sediment samples from 13 stations including one duplicate and two triplicates were analyzed. Samples from both years were analyzed, adopting the same methodology as described below. The wet sediments were spiked with the following surrogates: deuterated *n*-alkanes (for *n*-alkanes) and hexamethylbenzene, dodecylbenzene and deuterated terphenyl (for PAHs) before extraction with methanol and then with methylene chloride using a homogenizer. The extracts were concentrated in a rotary evaporator to 2 ml and, after elemental sulfur removal, were divided into two parts. One half was run through a silica column for isolating the saturated fraction and the other half through a silica/alumina column to recover the aromatic fraction. The details of extraction and silica and silica/alumina column chromatography are discussed in Venkatesan et al. [1987] and Venkatesan [1994]. Following fractionation, the samples were analyzed using GC/FID and GC/MS.

Each batch of field samples was accompanied by procedure blank analysis and NIST reference sediment and matrix spike samples. Only reagent grade chemicals were used and necessary pre-cleaning of all reagents was performed as described below.

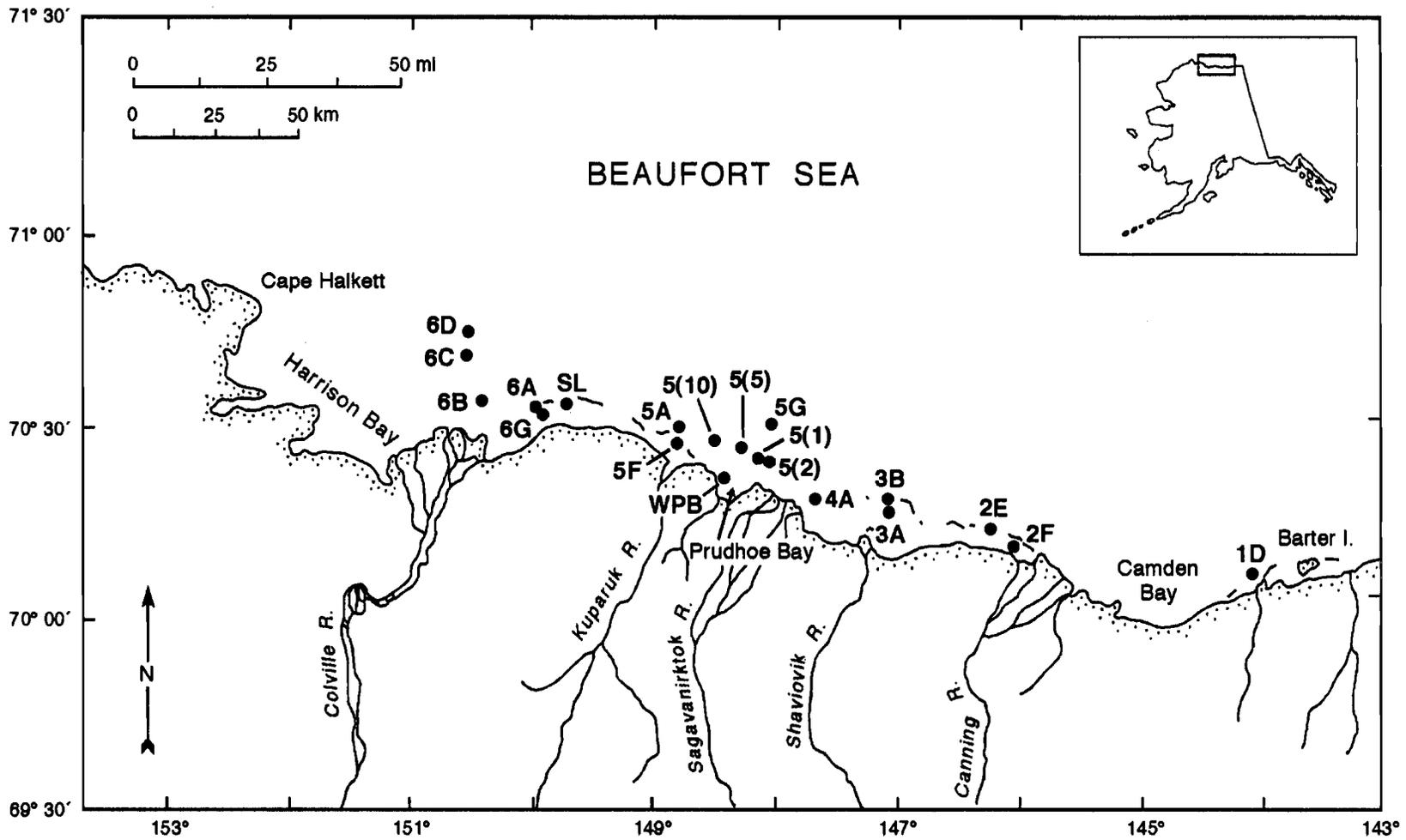


Figure 6. Study area showing locations of sediment samples for hydrocarbon analysis.

**Glassware:** Glassware was cleaned with soap and water, soaked in Chromerge for at least one hour, then rinsed successively with tap water, deionized water, Milli-Q+ water and finally with methanol before being dried in the oven. Individual pieces were capped with aluminum foil and stored. Immediately prior to use, the glassware was rinsed with methanol and methylene chloride. Glass vials of 2-ml capacity for storing fractions were purchased pre-cleaned with Teflon-lined septum caps. These vials were rinsed with methylene chloride before use.

**Reagents:** Milli-Q+ water contained no analytes above the method detection limit. However, it was extracted with methylene chloride three times before use. Hexane, methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) and methanol (MeOH) were Fisher Optima grade. Silica gel (40–140 mesh, Baker Analyzed) was cleaned ultrasonically with 1:1  $\text{CH}_2\text{Cl}_2$ :MeOH and dehydrated in the drying oven, activated at  $235^\circ\text{C}$  for 16 hours and used within five days after activation. Sodium sulfate and sodium chloride (analytical reagent grade) were also cleaned ultrasonically and dehydrated in the drying oven. Sodium sulfate was further baked at  $450^\circ\text{C}$  overnight and stored at  $120^\circ\text{C}$  until cooled in a desiccator just before use. Fine copper granules (Mallinckrodt) were soaked in 6N HCl for about 15 minutes and then the acid was decanted. The excess acid was washed six times each with methanol and then methylene chloride and stored in  $\text{CH}_2\text{Cl}_2$ , sealed and used the same day.

All standards and surrogate spiking solutions were made from analytical reagent grade chemicals purchased from Ultra Scientific, AccuStandards or the NIST Standard Reference Materials Program.

**Apparatus:** A Virtis homogenizer with stainless steel shaft and blade was used to extract sediments with organic solvents. A Varian 3400 gas chromatograph equipped with a septum-equipped programmable injector (SPI) and flame ionization detector (FID) was used to analyze alkanes. A Finnigan 4000 GC/mass spectrometer with an INCOS data system and a 9600 Varian chromatograph were used for PAH determination.

**Precautions:** To prevent inter-contamination of samples, the same glassware and syringe stayed with a given sample throughout the processing. Separate, clearly labeled micro-syringes were dedicated exclusively for designated surrogate or standard solutions.

**Quality assurance/Quality control measures:** For QA/QC measures, control samples were processed along with field samples following an identical protocol. A procedure blank was run with every sample set. Acceptable blank levels were below  $2 \times \text{MDL}$ . If the level of any interfering target compound exceeded this limit, samples in that batch were re-extracted and reprocessed. A matrix spike was run with target analytes spiked at the level of  $10 \times \text{MDL}$ . Surrogate spikes (deuterated alkanes for the saturated fraction and hexamethylbenzene, dodecylbenzene and terphenyl for PAH fractions) at the level of  $10 \times \text{MDL}$  were used in every sample.

The sediment reference material (NIST SRM #1941) with certified aromatic concentrations was analyzed to establish control reference data for the working protocol.

UCLA produced acceptable PAH data conforming to the consensus values generated by the above-described methodology in the inter-laboratory exercises conducted by NIST in 1992 and in 1999. The relatively low values reported for acenaphthylene and 1,6,7-trimethylnaphthalene in the 1999 inter-laboratory exercise data set were due to the very low and unpredictable recovery of these compounds from the SPI which was newly-installed in the GC/MS just before the 1999 inter-laboratory exercise. However, all of the sediment from this project and the 1992 inter-laboratory exercise samples had been analyzed previously with a Varian Grob injector which did not have this problem. In summary, the

analytical precision and accuracy of all polycyclic aromatic hydrocarbons reported in this study are excellent and the reported data are of high quality.

**Instrumental analysis:** The saturated fraction was analyzed for alkane profiles by an SPI-equipped Varian 3400 gas chromatograph. A 30-m DB-5 fused silica capillary column (0.25-mm I.D., 0.25 micron film, J&W Scientific) was used. Normal and isoprenoid alkanes were quantitated by the GC/FID internal standard method using dodecylbenzene. (This compound elutes completely in the aromatic fraction from both silica and silica/alumina columns and its use as a surrogate in the PAH fraction does not interfere with its use as an internal standard in the saturated hydrocarbon fraction). The fractions were then analyzed by GC/MS for fingerprinting alkanes, isoprenoids, triterpanes and steranes.

Polycyclic aromatic hydrocarbons were quantitated by GC/MS in the selective ion-monitoring (SIM) mode using deuterated internal standard mixtures. The matrix recovery spike and external standards solution contained the same components and was made to order by Supelco. Analyses of PAHs were performed in a splitless mode in the Varian 9600 gas chromatograph interfaced with a mass spectrometer. A DB-5 column with specifications as described in the previous paragraph was used. An electron energy of 70 eV was used and the unit was tuned according to the manufacturer's specifications to maximize the sensitivity of the instrument. An INCOS 4000 data system allowed continuous acquisition, storage and retrieval of all data during and after the GC/MS analyses. The mass spectrometer was operated on SIM mode using appropriate optimum windows to include the quantitation and confirmation of masses for the analytes.

A five-point response factor calibration curve was established which demonstrated the linear range of the detector. Standard concentrations used to construct the calibration curve were: 1, 5, 10, 20 and 50 ng/ $\mu$ l. The identification of compounds detected at concentrations above the MDL was double checked by the confirmation ions. If the concentration of the target analyte exceeded the linear range of the calibration standards, the fraction was either concentrated or diluted and reanalyzed. After every 6–8 samples, a calibration standard (10 ng/ $\mu$ l) was run to verify the response for PAHs relative to internal standards. The daily response factor for each analyte was compared to the initial calibration curve. Analyses would proceed only if the average daily response factor for the analyte fell within 10–15% of the calibration curve. If it exceeded 20% of the calibration curve, a five-point calibration was repeated for the analyte in question prior to sample analysis.

The target compounds were identified quantitatively based on relative retention time (RRT) falling within an acceptable window. The characteristic masses of each analyte should maximize in the same or within one scan of each other. The retention time should fall within  $\pm 12$  s (peak width at half height  $\times 3.5$ ) of the retention time of the authentic standard. The mass spectrometer was tuned to perfluorotributylamine (PFTBA) criteria established by the manufacturer. The relative peak heights of the primary ion and secondary ion masses were examined for confirming the identity of the compound.

## Results

Results of the QA/QC analysis on *n*-alkanes are listed in Table 12 and QA/QC results for PAHs are in Table 13. The distributions of the *n*-alkanes, PAHs, triterpenoids and steroids in the gross sediments are presented in Tables 14, 15, 16 and 17, respectively. In these tables of quantitative data, analytical values below the MDL are not included in the summation. Total alkanes comprise from C<sub>10</sub> to C<sub>36</sub>. All parent PAHs, including dibenzothiophene and perylene and all alkylated PAHs listed in the table were summed. The alkanes and PAH values have been corrected for recovery based on the values obtained from the average matrix spike data. Representative gas chromatograms of the saturated hydrocarbon fraction in sediments, without and with petroleum characteristics are shown in Figures 7 and 8, respectively.

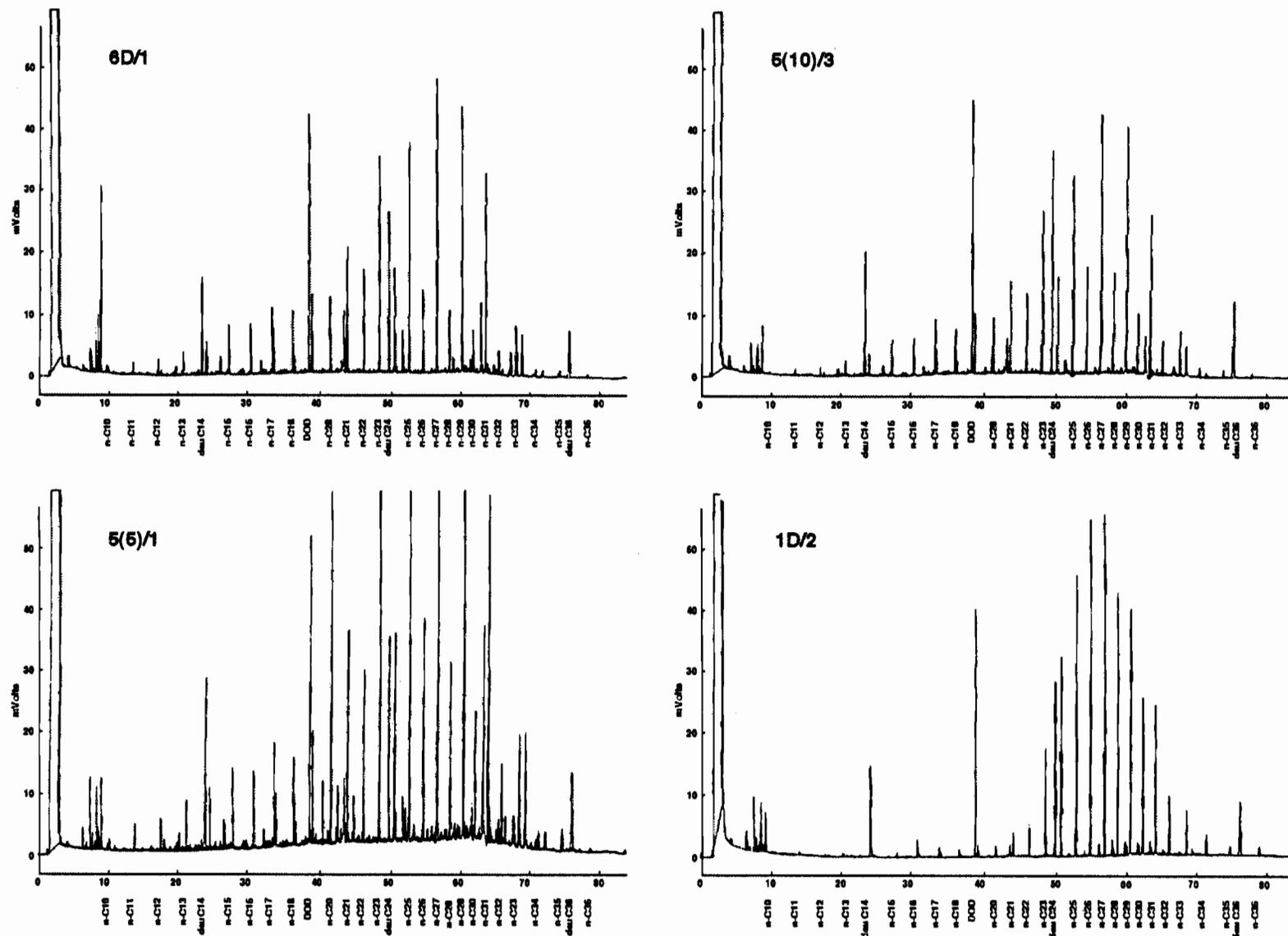


Figure 7. Representative gas chromatograms of the saturated hydrocarbon fraction from sediments not exhibiting petroleum characteristics.

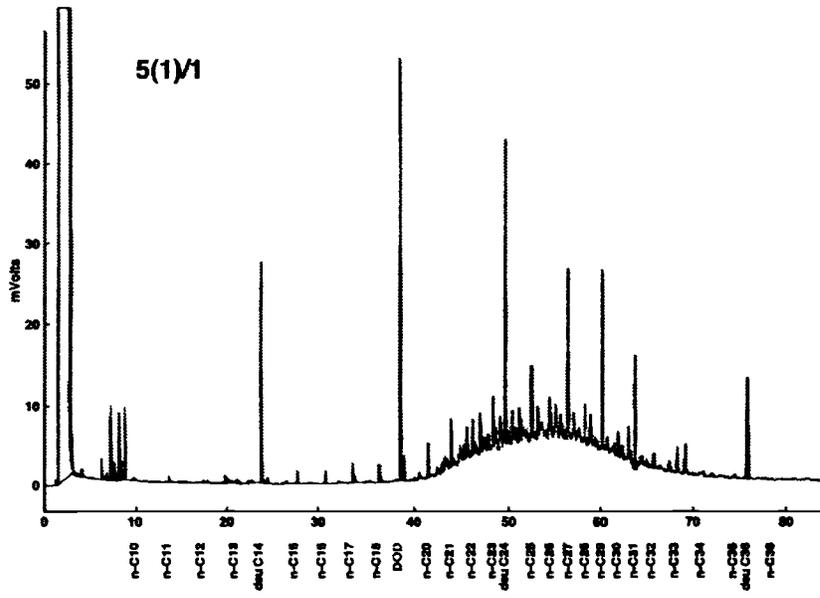
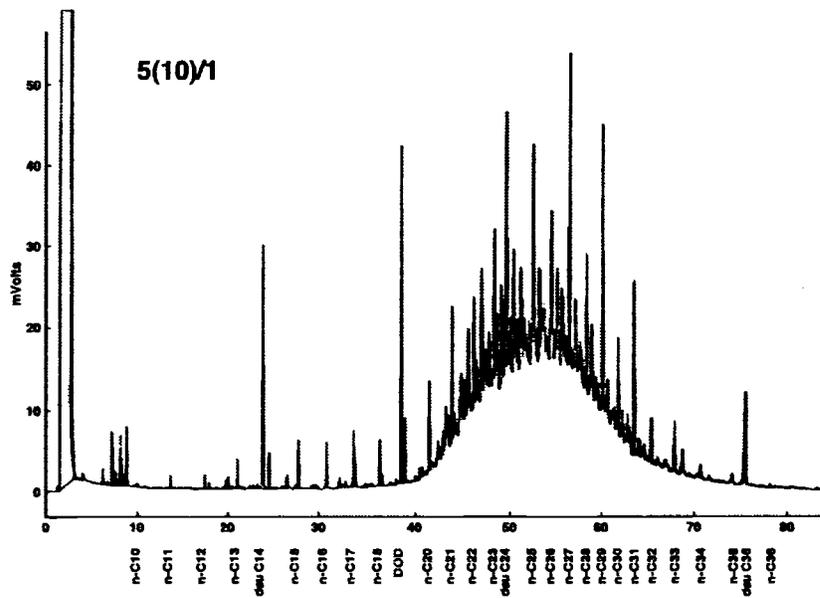


Figure 8. Representative gas chromatograms of the saturated hydrocarbon fraction from sediments exhibiting petroleum characteristics.

Figures 9 and 10 illustrate examples of mass chromatograms from the gas chromatography/mass spectrometric analyses of representative sediments for triterpenoid distribution without and with petroleum signatures. Likewise, representative sterane distribution from corresponding sediments is shown in Figures 11 and 12. Tables 18 and 19 list triterpenoids and steranes identified in Figures 9 & 10 and 11 & 12, respectively. The relative abundance of naphthalene and phenanthrene/anthracene homologs in the Beaufort Sea sediments is shown in Figure 13. The mean concentrations (geometric means) of *n*-alkanes, ratios of pristane/phytane and odd/even *n*-alkanes, granulometry and total organic matter (OM) of gross sediments of the Beaufort Sea are shown in Table 20. The correlation coefficients between selected parameters of the hydrocarbons, granulometry and OM are presented in Table 21. Results of the cluster analysis displaying three major station groups are shown in a dendrogram (Figure 14a), stable organic carbon and OC/N in Table 22, and the results of the stepwise multiple discriminant analysis defining the station grouping are shown in Figure 15 and Table 23. A comparison of the concentrations and ratios of selected hydrocarbon parameters including data gathered in this study and by Boehm et al. [1987] are in Table 24.

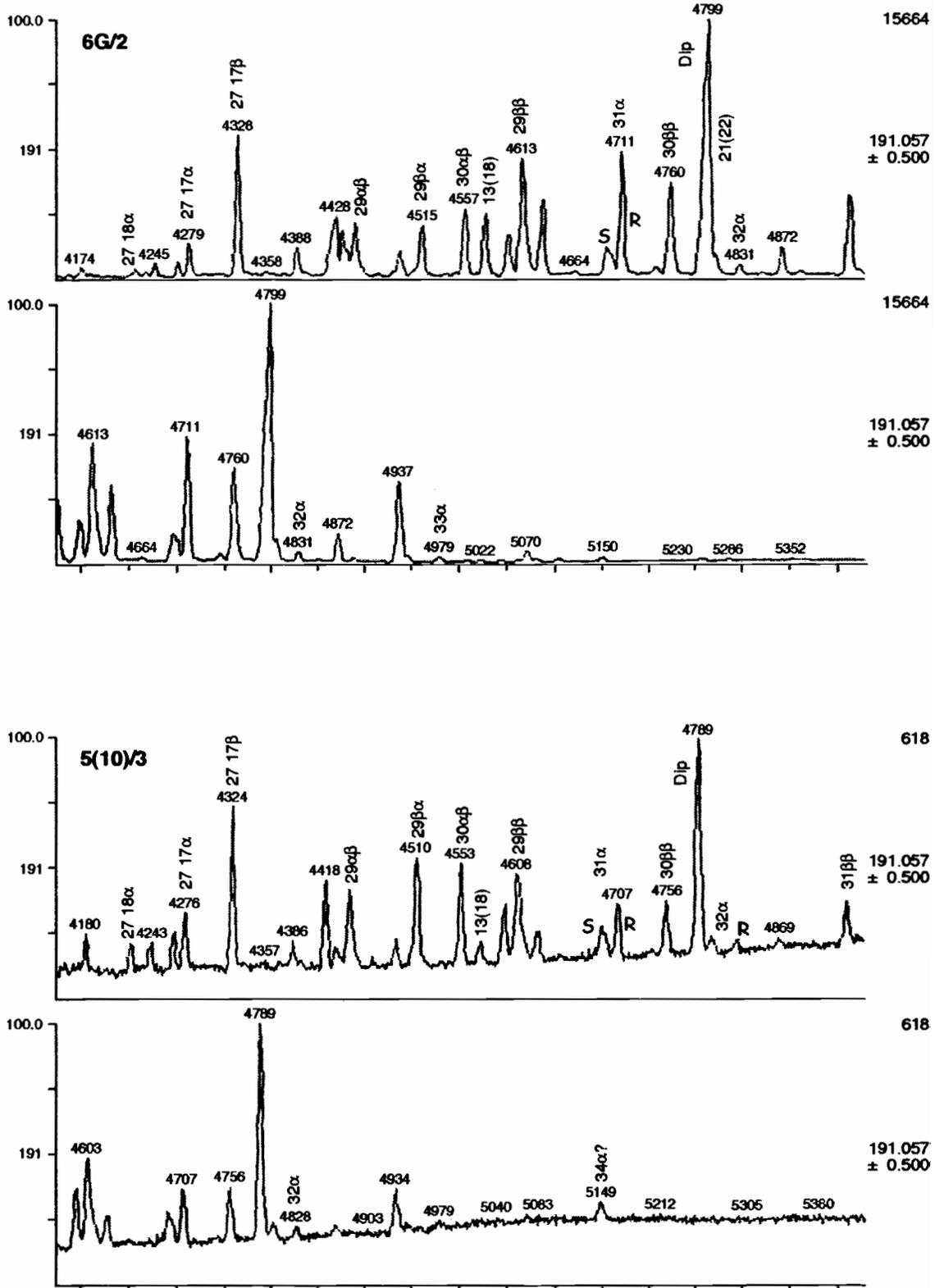


Figure 9. Representative triterpenoid distribution from sediments not exhibiting petroleum characteristics.

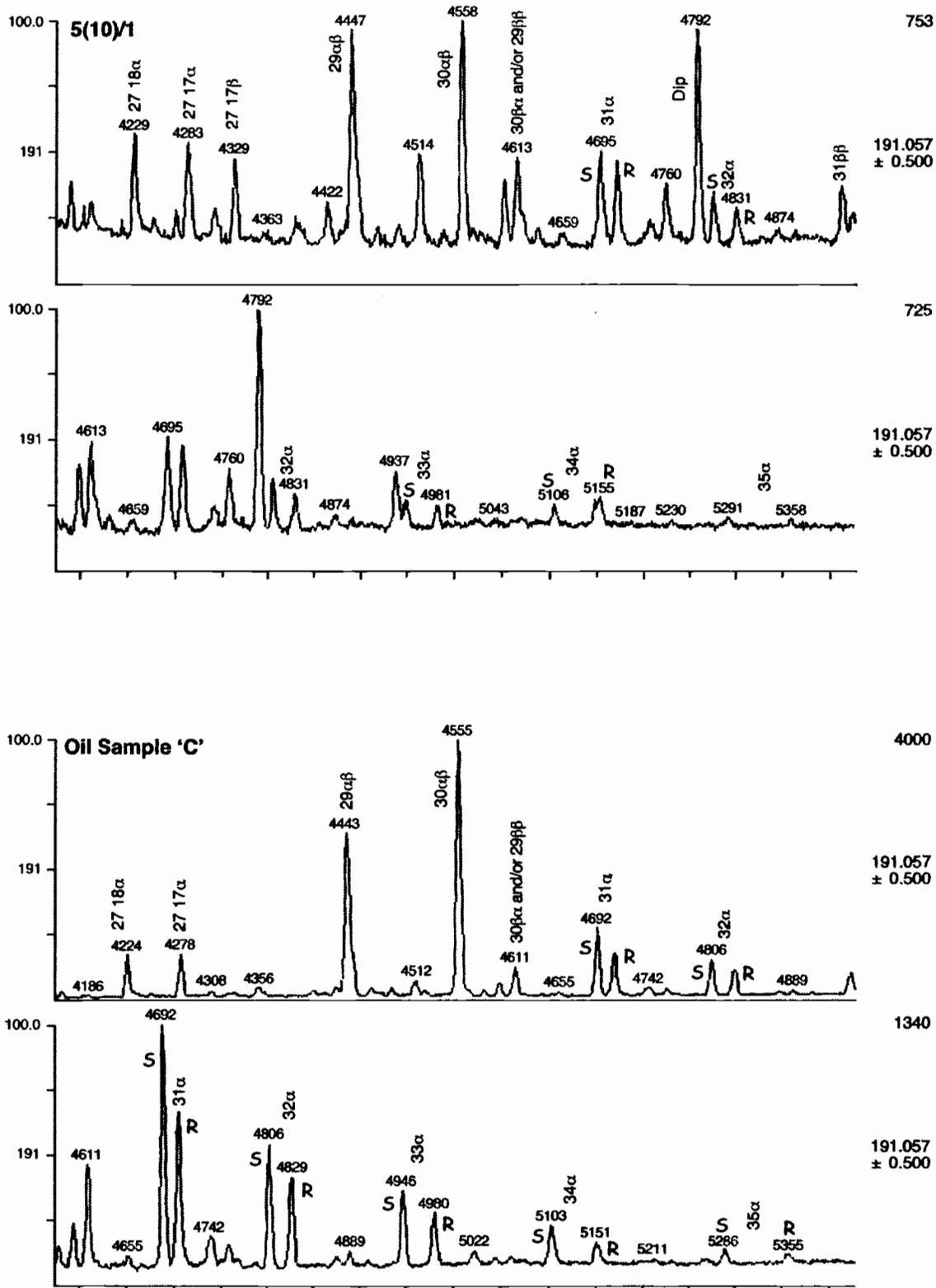


Figure 10. Triterpenoid distribution from sediments exhibiting a petroleum signature and an oil.

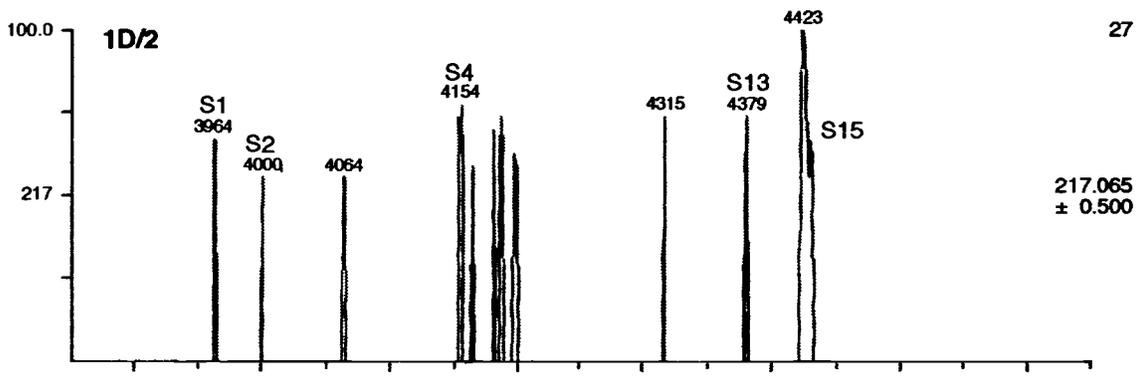
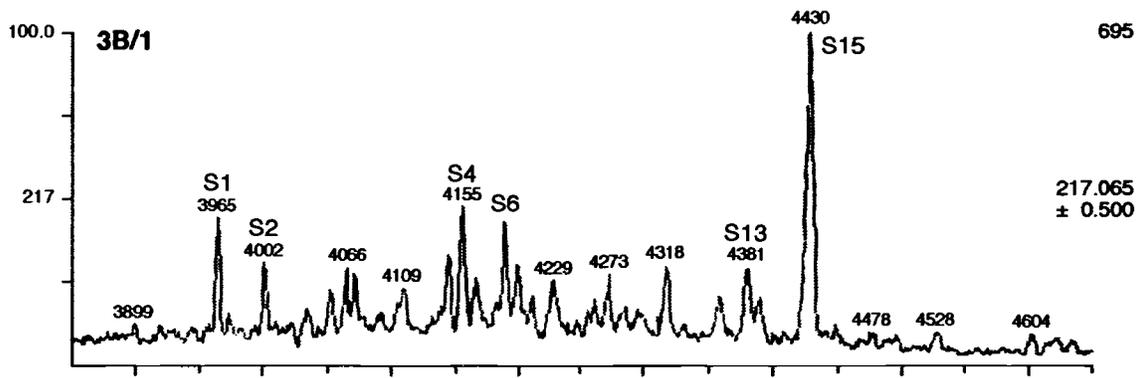
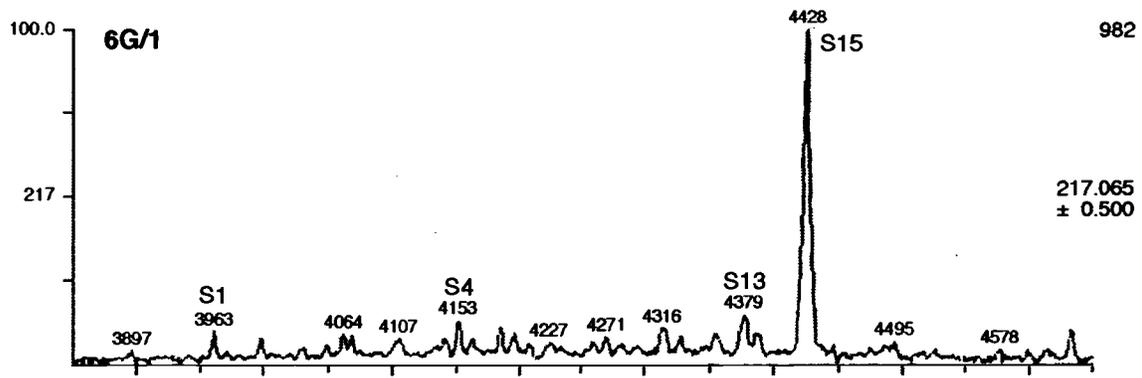


Figure 11. Representative sterane distribution from sediments not exhibiting petroleum characteristics.

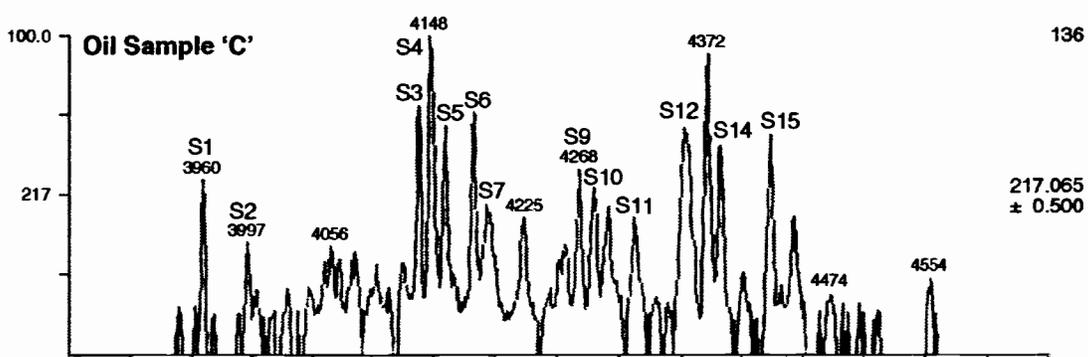
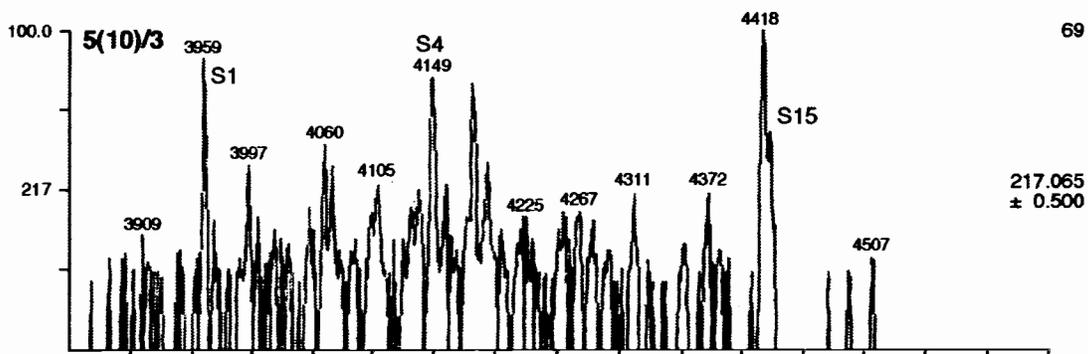
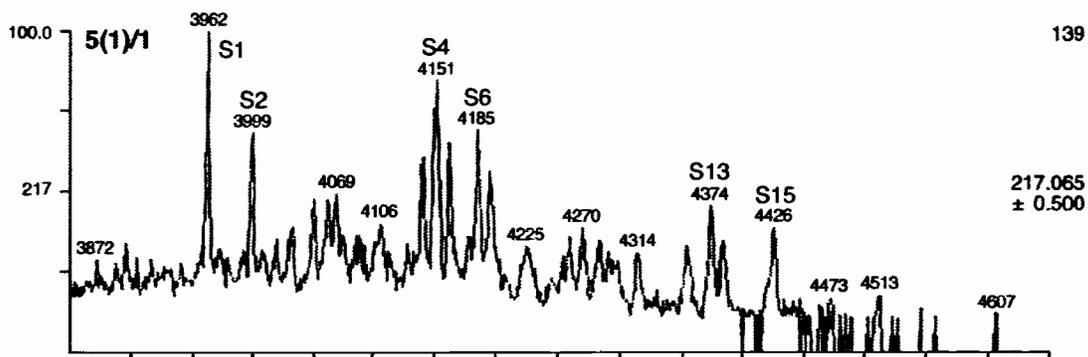
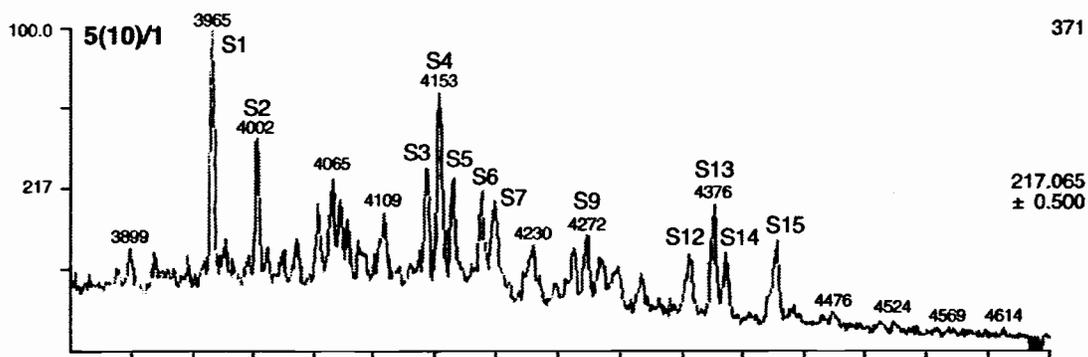


Figure 12. Sterane distribution from sediments exhibiting a petroleum signature, a pristine sediment and an oil.

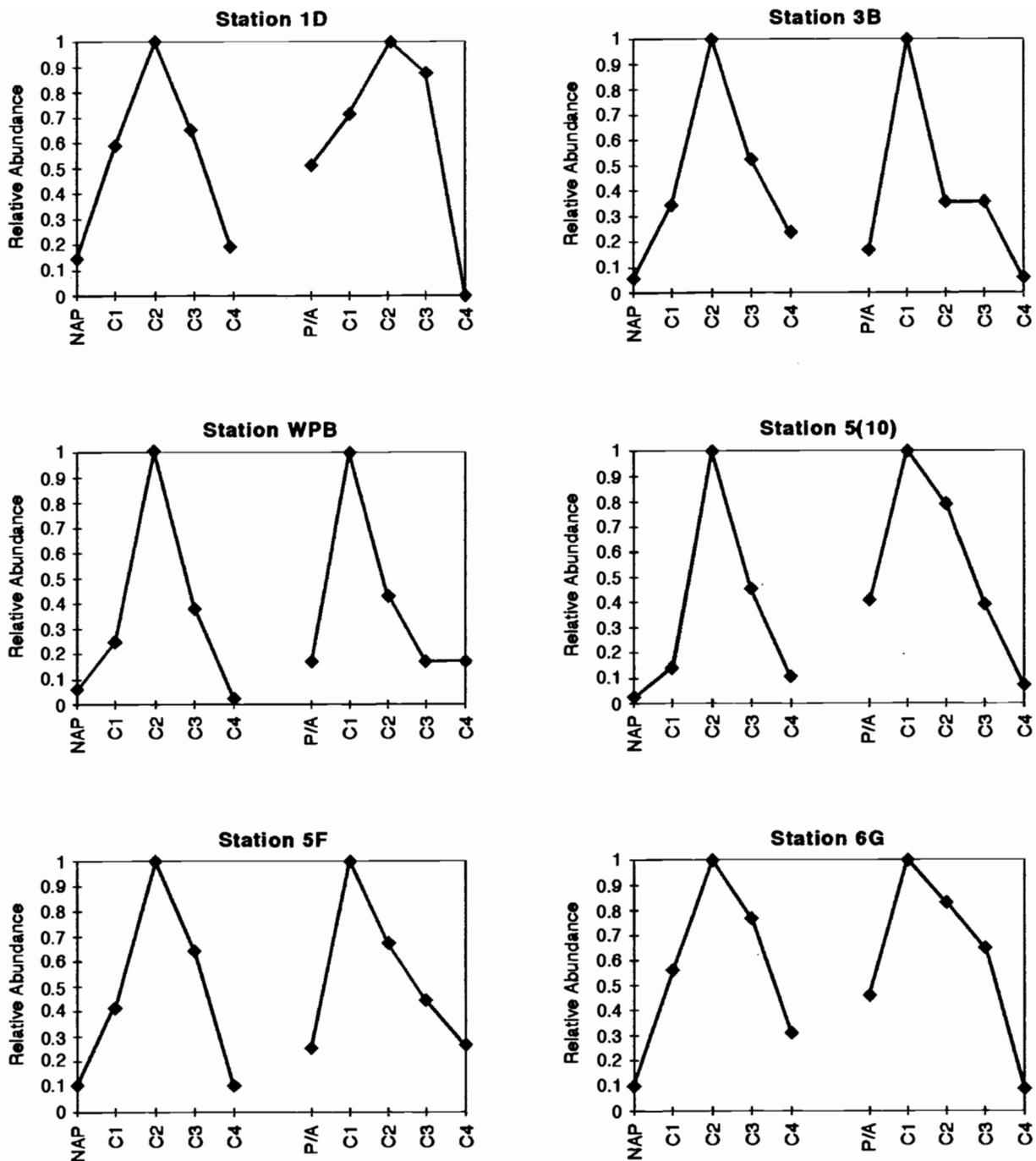


Figure 13. Relative abundance of naphthalene and phenanthrene/anthracene homologs in Beaufort Sea sediments.

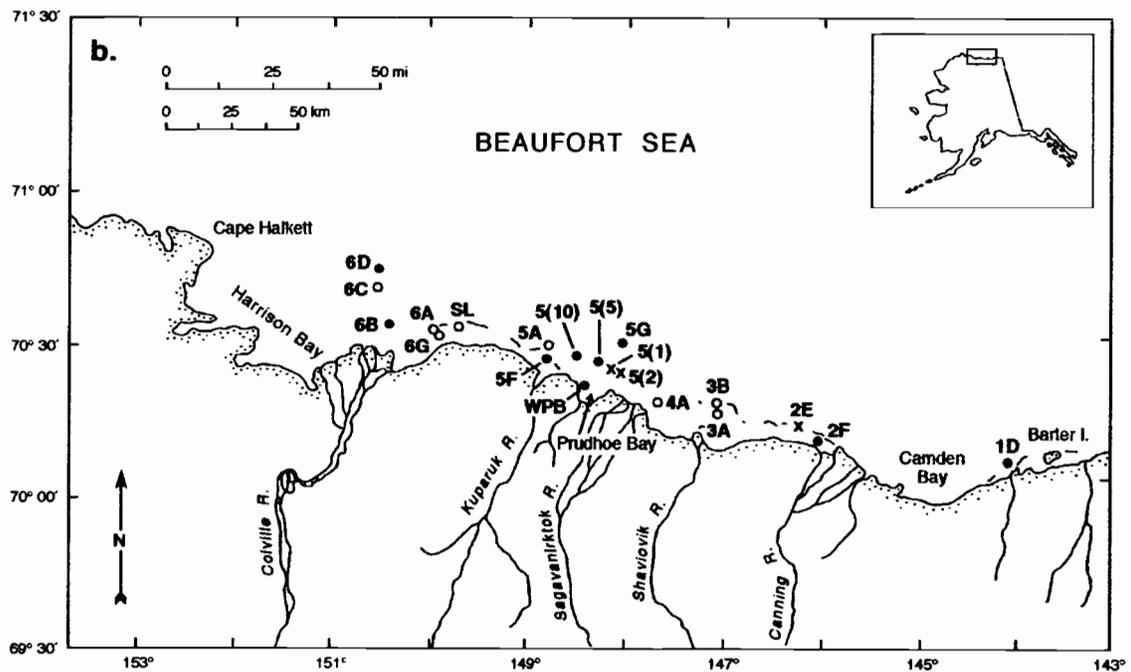
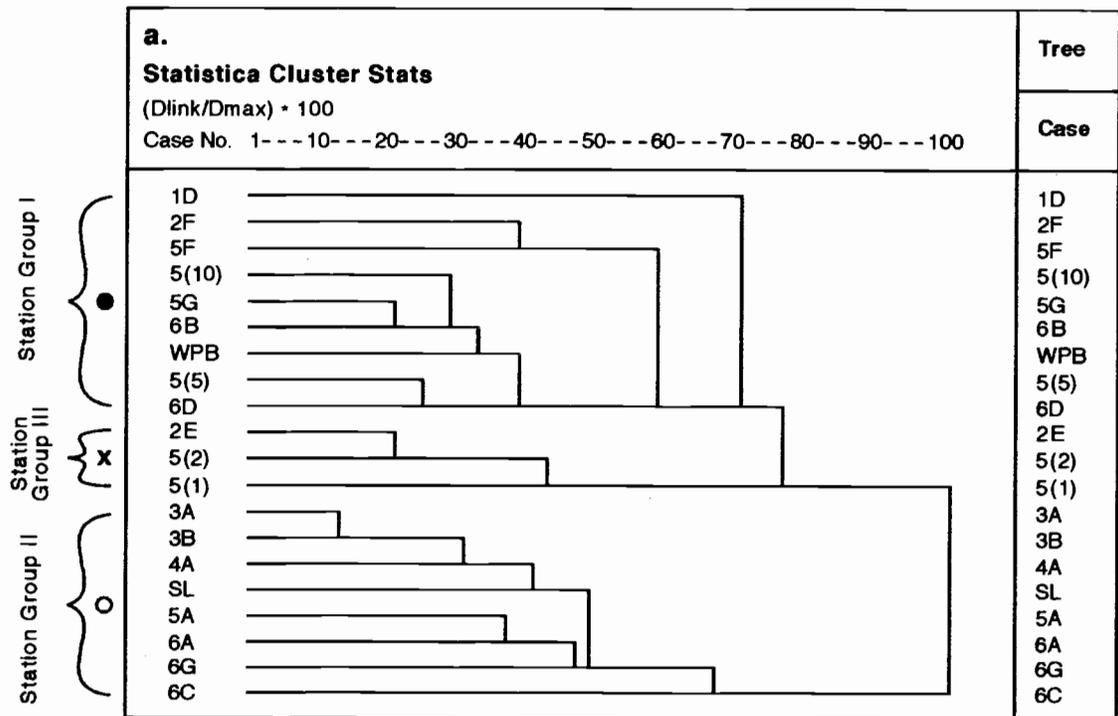


Figure 14. Dendrogram showing station groups formed by group averaging cluster analysis of sediment hydrocarbon concentrations (14a) and location of group members on study area map (14b).

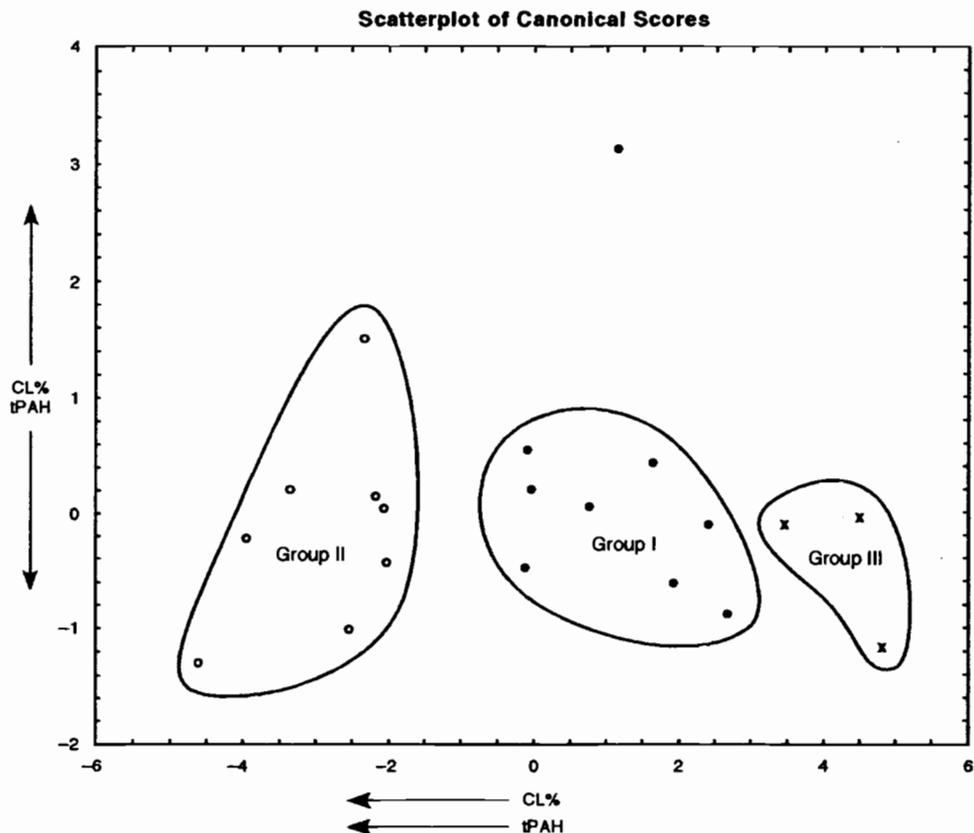


Figure 15. Station plots of the results from stepwise multiple discriminant analysis. Groupings are determined by cluster analysis.

## Discussion

Triplicate analyses of the sediments in the first year provided generally concordant data for alkanes and PAHs within the replicates from a given site. For example, triplicates from three sites (3A, 5F and 6B) yielded internally consistent results. The maximum variation in the data among triplicates at three other sites (2F, 4A and WPB) was a factor of only 1.5 to 2. This suggests that the sediments are reasonably homogenous within the general area of sampling. Therefore, in the second year, the number of analyses on duplicate and triplicate samples was reduced to enable greater area coverage by single samples.

Results of procedure blanks (Table 12) indicated that they represented less than 5% of the total alkanes found in the samples. Procedure blank data were normalized to 80 g dry weight of sediments (average of the sediment weight of all the samples) for direct comparison. Matrix spike recoveries of *n*-alkanes from C<sub>14</sub> to C<sub>36</sub> ranged from 48 to 84%. The recovery of deuterated alkanes ranged from 47 to 87% in the matrix spikes and from 32 to 104% in the samples. Matrix spike recoveries of PAHs ranged from 22 to 99 except for dibenzothiophene which had a very low recovery due to treatment of the extract with copper to remove elemental sulfur. The PAH surrogate spikes were recovered at the level of 30 to 126%. The *n*-alkane and PAH data were corrected for recovery.

Values for selected samples that were analyzed in duplicate to check for the reproducibility of the extraction, sample processing and instrumental analysis agreed within acceptable analytical errors.

**Resolved *n*-alkanes:** The resolved *n*-alkanes had concentrations generally comparable to values previously reported from the general region and relatively higher than other Alaskan coastal regions [Venkatesan and Kaplan 1982; Boehm et al. 1987; Steinhauer and Boehm 1992]. The stations studied contained total *n*-alkanes roughly in the following order:

5A ~ 6G > 6A > SL > 4A ~ 3A > 1D ~ 6C > 2F ± 5F > 5(5) ~ 6D > WPB ~ 6B > 5G ~ 3B > 2E ~ 5(10) > 5(2) > 5(1).

In general, the highest total *n*-alkane contents (TALK) were found in the east Harrison Bay, Kuparuk and Foggy Island samples, while those from Endicott and Camden Bay had lower values (Table 24). This trend is consistent with the findings of Boehm et al. [1987] and Steinhauer and Boehm [1992], although the range of total alkanes found in the current study is uniformly lower in all of the areas (Table 14).

The *n*-alkanes in the sediments have a bimodal distribution typical of a mixture of marine autochthonous and terrestrial allochthonous inputs (Figure 7). The ratio, LALK/TALK (low molecular weight alkanes/total *n*-alkanes), varies over a narrow range of 0.1 to 0.28 (Table 24), comparable to the findings of Boehm et al. [1987] and Steinhauer and Boehm [1992]. The maximum at C<sub>17</sub> reflects algal input. Among the LALK only *n*-C<sub>12</sub> is slightly relatively more abundant than *n*-C<sub>11</sub> in all the samples from the 1997–98 study. It is roughly equal to *n*-C<sub>11</sub> in a few samples in the 1998–99 study (i.e., 5(5)/1). In seven of the 18 samples from 1998–99 *n*-C<sub>14</sub> is greater than *n*-C<sub>13</sub> (i.e., 5G/2, 6G). However, the overall distribution reflects an odd/even preference in the LALK composition. This is in contrast to the smooth distribution with no odd or even predominance of the alkanes in the range C<sub>10</sub> to C<sub>20</sub> reported for sediments from the same stations [Steinhauer and Boehm 1992].

The high molecular weight *n*-alkanes ≥C<sub>21</sub> are the major components in the alkane fraction for all of the samples. The dominant maximum at C<sub>27</sub> and occasionally at C<sub>29</sub> and the odd/even ratios ranging from 2.0 to 4.8 are clearly due to inputs from terrigenous detritus (plant wax components). This was to be expected from the geographical location of the stations. For example, the Colville and other rivers contribute significant amounts of particulate organic matter to the nearshore sedimentary regime in the Alaskan Beaufort Sea [Naidu et al. 2000]. Coastal peats could be a major contributor to the *n*-alkane budget in the sediments as reported previously by Yunker et al. [1991] from their study of sediments from the Mackenzie shelf in the Canadian Beaufort Sea. Only one sample, 1D/2, did not show an odd/even preference of *n*-alkanes and the gas chromatogram resembles one from fresh petroleum input (cf. triterpanes and steranes below).

**Unresolved complex mixture:** The unresolved complex mixture (UCM) or chromatographic “hump” was insignificant in all of the samples. Only two samples, 5(1)/1 and 5(10)/1, as illustrated in Figure 8, exhibited this hump. This is discussed later under triterpenoids and under steranes. Note that replicate samples 5(10)/2 and 5(10)/3 have a baseline resolution similar to all other samples in the current study as illustrated by the latter sample (Figure 8). This is in contrast to the general trend in all the samples collected and analyzed a decade ago which were reported to exhibit significant amounts of UCM [cf. Table 4 in Boehm et al. 1987].

**Isoprenoid alkanes:** The isoprenoid alkanes, pristane and phytane, are present in all of the samples (0.01 to 0.1 μg/g, Table 14). Although the absolute concentrations vary over a range, the overall pristane/phytane ratio is relatively constant around 2.0 for all the samples from the different regions studied over the two years (Tables 14 and 20). This is consistent with the findings of Venkatesan and Kaplan [1982] and Steinhauer and Boehm [1992]. These isoprenoids are most likely of biogenic origin

from bacteria [Maxwell et al. 1971]. Some pristane could also have originated in the shoreline peats [Steinhauer and Boehm 1992].

**Triterpenoids:** The triterpenoids consist predominantly of  $17\beta$ (H),  $21\beta$ (H)-hopanes ( $C_{27}$ ,  $C_{29}$  and  $C_{30}$ ), their extended homologs ( $C_{31}$ - $C_{32}$ ) and olefinic triterpenoids (Figure 9).  $17\beta$ (H)-22,29,30-trisnorhopane and  $17\beta$ (H)-hop-22(29)-ene (diploptene) are usually the dominant components, with the latter being the most prevalent. Diploptene probably originates from marine productivity [Venkatesan 1988a]. Relatively smaller amounts of the thermally mature  $17\alpha$ (H) analogs of  $C_{29}$  and  $C_{30}$  hopanes compared to the thermally immature  $\beta\beta$  and  $\beta\alpha$  homologs were detected in all the samples (Table 16). Possible trace amounts of the mature hopanes of composition  $\geq C_{31}$  were detected in a few samples with only one of the S and R isomers. Occasionally, if both isomers were present, their ratio was not characteristic of mature petroleum and their fingerprint was very different from those of the shales and oils from the region [Seifert et al. 1979]. The overall distribution of dominantly immature triterpenoids reflects biogenic origin, mainly from bacteria or algae, similar to that reported by Venkatesan and Kaplan [1982] for the Beaufort Sea samples, with some contribution from the peats in the region. In summary, most of these sediments including 1D/2 (cf. above discussion on *n*-alkanes) do not contain a significant amount of triterpenoids characteristic of petroleum origin although the detection of the two hopanes,  $C_{29}$  and  $C_{30}$  of  $17\alpha$ ,  $21\beta$  configuration, would indicate the presence of thermally mature carbon, possibly derived from peat and/or coal.

Only two samples clearly show the presence of mature petroleum in the triterpane profile as evident from Figure 9 where  $17\alpha\beta$  hopanes predominate over  $17\beta\beta$  and  $17\beta\alpha$  hopanes. The triterpenoid profile of an oil sample "C" (source of this oil is proprietary information from the company which provided the sample to us) is included for comparison. The presence of petroleum hopanes of carbon number  $\geq C_{31}$  with both the S and R isomers is also clearly evident in contrast to all other samples. It is noteworthy that petroleum was present in only one of the triplicate samples from station 5(10). The only sample analyzed from station 5(1) also exhibited petroleum characteristics. This is consistent with the significant UCM associated with the alkane chromatogram of these two samples as noted above. Unfortunately, the potential source components such as indigenous peat, coal, shale or oil were not analyzed concurrently in the present study to compare their fingerprints with the surface sediment samples to infer the origin of biomarkers precisely.

The various study regions exhibited differences in the total content of alkanes; however, the distribution of the compounds was compositionally homogeneous, pointing towards a mixed marine and terrestrial source of organic carbon in the entire Beaufort Sea study area.

**Steranes:** The sterane data are presented in representative mass fragmentograms of *m/z* 217 from GC/MS analysis in Figure 11. Most of the samples are biogenic and have very little sterane content; their fingerprints are different from that of an oil sample as shown in Figure 11 and literature data of indigenous shales and oils from the region [Seifert et al. 1979]. Again, the only two samples showing sterane fingerprint characteristics of oil are 5(10)/1 and 5(10)/1, consistent with the alkane chromatogram and triterpane profile confirming the presence of small amounts of petroleum in the sediment samples (Figure 11). The replicate sample, 5(10)/3, and also 1D/2, are almost entirely biogenic as found from their triterpane profiles. In the future, sterane fingerprints of source materials would allow for better comparison with the surface sediments and identification of their source.

**Polycyclic aromatic hydrocarbons:** Total PAHs (sum of all parent and methylated PAHs from two to seven rings—naphthalene to coronene) range from 0.06 to 2.0  $\mu\text{g/g}$  of dry sediment (Table 15). We did not find PAHs above five rings in significant concentrations in any of the samples. Total PAHs in the gross sediments of the study area varied in the stations in the following order:

6G > 5A > 6A > SL > 4A > 3A > 1D ~ 6C > 2F > 5F > 5(5) ~ 6D > WPB ~ 6B > 3B > 2E > 5G ~ 5(10) > 5(2) > 5(1).

This order is similar to that listed above for *n*-alkane concentrations, with the samples from east Harrison and Kuparuk bays relatively enriched in PAHs, those from Endicott and Camden bay areas containing the least, and the Foggy Island samples falling between the two ranges. This trend suggests a probable similar source for both suites of compounds. Further, the PAH levels in the current study are uniformly much higher than those found by previous researchers. This difference could be partly attributed to the fact that two to seven ring compounds and their methyl homologs were summed in the current study, whereas Steinhauer and Boehm 1992 summed only two to five ring compounds (see footnote in their Table 1). However, we did not find PAHs above five rings in concentrations in any of the samples sufficient to account for this large difference. Sample 6B was an exception; it contained the maximum PAHs (0.64  $\mu\text{g/g}$ ) for all east Harrison Bay stations found by Steinhauer and Boehm [1992] in contrast to 0.1  $\mu\text{g/g}$  measured in the current study. It is likely that our sample is not exactly from the same location sampled by the other study or that PAH level has declined over the decade after their sampling of this station.

Despite the large spread of total PAH content in the sediments, the general PAH composition is dominated by the homologous series of naphthalenes and phenanthrenes. Among the four and five-ring parent compounds, perylene is always the dominant PAH and is present at anomalously high levels in some samples; chrysene/triphenylene is the next most abundant PAH. This pattern is more akin to that of sediments from the Canning and Colville river mouths as well as peat samples from representative stations in the entire area rather than the surface sediments investigated by Steinhauer and Boehm [1992, cf. Figures 8 and 9]. Trimethyl naphthalene and dimethylphenanthrene were found to be the most dominant homologs in the surface sediments from the entire study region as shown by station 6A in their Figure 6. Based on the ratio of naphthalenes to phenanthrenes (N/P) and the dominance of alkyl homologs of naphthalenes and phenanthrenes and "fossil-derived LALK" in their samples, Steinhauer and Boehm [1992] emphasized the importance of fossil fuel contribution rather than pyrolytic and other sources in the surface samples. In the current study, while dimethylnaphthalenes are the most dominant of the naphthalene homologs analogous to their findings, monomethylphenanthrenes always dominate among the phenanthrenes in all of the samples. Monomethylfluorenes are the major homologs of fluorenes in most of the samples. Phenanthrene homologs with chain lengths  $>C_3$  are either absent or present only in trace amounts (Table 15, Figure 12). This pattern is also different from that of Prudhoe Bay crude oil where dimethyl phenanthrene is the major homolog and all of the fluorene homologs are almost equally abundant [Figure 6 in Steinhauer and Boehm 1992]. Further, parent PAHs and/or monomethyl homologs are present in higher concentrations than the higher methylated homologs of the PAHs with chain length  $\geq 3$  in most of the sediment samples. The PAH distribution thus indicates the possible origin from peat, coal, other diagenetic sources and long-range atmospheric transport of combustion activities rather than from source rocks or crude oil from the region [LaFlamme and Hites 1978; Wakeham et al. 1980; Shaw et al. 1979; Venkatesan and Kaplan 1982; Venkatesan 1988b; Sporstol et al. 1983].

The results from our PAH data are consistent with the *n*-alkane (LALK and TALK) as well as triterpenoid/sterane distribution in the current study. It is relevant to point out that previous studies did not analyze the sediments or the peats for triterpenoids/steranes, which would have confirmed the presence or absence of petroleum input in their samples. When the triterpenoid data are integrated with that of PAHs, it can be concluded that some of the methyl homologs of PAHs could have been derived from peat samples as well as coal outcrops in the area and that there is no clear evidence for a significant overall contribution from a more thermally mature source rock or fossil fuel, such as crude oil, to the organic carbon of most of the sediments investigated here. These results are also consistent with the recent findings of Valette-Silver et al. [1999] from their study of western Beaufort Sea sediments (i.e., especially the diagnostic ratios of selected PAHs). In addition, as evident from Table 24, there appears to be no direct correlation between the higher abundance of LALK over TALK and naphthalenes over phenanthrenes (N/P) and the detection of petroleum triterpanes in representative stations in the current

study. In summary, samples with relatively high ratios of LALK /TALK and/or N/P are not necessarily associated with a clear indication of the presence of petroleum triterpanes/steranes.

### **Hydrocarbon–granulometry correlations**

The correlation coefficient matrix (Table 21) based on the Table 14 data for all the stations investigated in this study suggests that the distributions in the gross sediments of the total *n*-alkanes, pristane/phytane, odd/even and PAHs are strongly controlled by the relative amounts of the silt, clay and mud content (or the finer size class) of the sediments. The significant positive correlation between some of the above hydrocarbons and the presence of lower  $\delta^{13}\text{C}$  values (mean  $-25\%$ ) in the nearshore sediment TOC, Table 22 [after Naidu et al. 2000], suggests a large proportion of terrestrial as compared to marine origin for hydrocarbons in the study area.

### **Regional distribution pattern of hydrocarbons**

Cluster analysis of selected hydrocarbons and sediment parameters (Figure 14a) indicates the presence of two major and one minor cluster of station groups in the study area; however, there is no definite regional clustering of the stations. The stepwise multiple discriminant analysis suggests that the clustering of the station groups is defined by differences in total PAH (tPAH) and clay content (Cl%) in the groups (Table 23). Considering the absence of a definite regional pattern, especially with no clustering of stations close to areas of intense industrialization (e.g., Prudhoe Bay, Oliktok Point), it is suggested that the location of the various stations corresponding to a group is presumably attributed to the relative differences in the amount of PAH input from natural sources and the mud content in sediments.

### **Conclusion and Recommendations**

The surface sediments contain *n*-alkanes that are largely characteristic of biogenic sources. The low molecular *n*-alkanes, present in relatively small amounts, are largely from marine productivity. The high molecular weight *n*-alkanes, which are the major components of the hydrocarbon fraction, derive from plant waxes in the coastal peats and also possibly from some coal residues.

The overall triterpenoid/sterane distribution in all of the samples comprises thermally immature components with almost none to trace amounts of petroleum, except in isolated cases where the petroleum signature is clearly evident as reflected by characteristic hopanes and steranes in small amounts. The triterpenoid and sterane profiles thus reinforce the biogenic origin of the major proportion of the carbon in the entire study area.

The PAH assemblage in the surface sediments is different from that found in Prudhoe Bay crude oil but is very similar to that observed in coastal peats and river sediments. This and the sediment  $\delta^{13}\text{C}$  values of the TOC of gross sediments are consistent with the major origin of PAHs from terrestrial inputs such as peat, coal, river sediments and, to a smaller extent, from atmospheric inputs.

In summary, the molecular markers investigated in the sediments are of mixed marine and terrestrial origin. It is also likely that the petroleum inputs detected in the surface sediments by others a decade ago have currently decreased to such a low level that their signature is not discernible in recent samples collected in 1997.

The composition/fingerprint of triterpanes/steranes, rather than some internal ratio parameters in the current samples, helps clearly distinguish the biogenic input from petrogenic sources. Composition of triterpenoids/steranes should serve as an important diagnostic tool in future monitoring studies to follow subtle changes in the hydrocarbon inputs to the region, especially from oil-related activities. This information is particularly vital in Beaufort Sea sediments where the *n*-alkane and PAH content are relatively higher than and the composition different from many other regions on the Alaskan continental shelf.

In order to exploit the triterpenoid/sterane data to the fullest in future monitoring programs, it is recommended that such information be gathered concurrently from peat and coal outcrops, oils and oil shales, as well as from river mouth sediments in the region along with the surface sediments for direct comparison of fingerprints.

Other anthropogenic contaminants such as polychlorinated biphenyls and chlorinated hydrocarbon pesticides, as well as sewage tracers such as fecal sterols (i.e., coprostanol), should also be analyzed in the surface sediments to assess recent pollution from increased human activities in the coastal region of the study area in addition to hydrocarbons.

Table 12. Results of the QA/QC analysis of *n*-alkanes. nd—not detected

Blanks & Spikes	Pr blk	Pr blk	Pr Blk	Pr Blk	X Spike	X Spike	X Spike	X Spike	X Spike	X Spike
	I	II	I	II	I	II	Avg	I	II	Avg
	ng				%Recovery					
	Phase I		Phase II		Phase I			Phase II		
<b>Surrogate Recovery %</b>										
Deu C14	61	58	50	53	49	47	48	50	47	49
Deu C24	103	99	60	67	79	76	78	56	51	54
Deu C36	104	103	72	72	87	83	85	78	68	73
<b><i>n</i>-alkane (ng/g dry)</b>										
n-C10	nd	nd	0.15	0.55	15.65	14.79	15.22	8.65	17.60	13.12
n-C11	2.44	nd	nd	nd	23.82	22.48	23.15	18.23	24.95	21.59
n-C12	nd	nd	nd	nd	32.00	30.16	31.08	27.81	32.29	30.05
n-C13	nd	nd	nd	0.24	41.47	39.31	40.39	40.58	40.28	40.43
n-C14	nd	nd	nd	nd	52.07	49.53	50.80	51.41	48.26	49.83
n-C15	nd	nd	nd	nd	61.88	58.94	60.41	58.17	54.98	56.58
n-C16	nd	nd	0.71	nd	69.00	65.84	67.42	65.27	60.68	62.97
n-C17	0.24	nd	nd	nd	74.04	70.66	72.35	70.13	62.66	66.39
pr	nd	nd	nd	nd	75.52	72.16	73.84	71.59	63.43	67.51
n-C18	0.30	nd	nd	nd	77.00	73.66	75.33	73.04	64.19	68.61
ph	nd	nd	nd	nd	77.36	74.09	75.73	73.76	64.67	69.22
n-C19	0.32	nd	nd	nd	77.90	74.75	76.32	74.48	65.15	69.82
n-C20	0.52	0.17	nd	nd	78.43	75.41	76.92	75.91	66.11	71.01
n-C21	0.81	0.27	nd	nd	79.55	76.46	78.01	76.03	66.52	71.28
n-C22	1.18	0.48	0.22	0.14	80.68	77.52	79.10	76.14	66.93	71.53
n-C23	2.29	0.94	0.27	0.17	80.68	77.41	79.04	70.33	61.70	66.02
n-C24	1.31	0.58	0.27	0.20	80.68	77.29	78.99	64.51	56.46	60.48
n-C25	2.13	0.91	0.36	0.28	81.03	76.84	78.93	69.27	60.45	64.86
n-C26	1.01	0.43	0.33	0.36	81.38	76.39	78.88	74.02	64.44	69.23
n-C27	2.40	1.07	0.65	0.58	82.72	76.42	79.57	73.60	63.46	68.53
n-C28	0.81	0.35	0.28	0.57	84.07	76.45	80.26	73.17	62.47	67.82
n-C29	1.60	0.98	0.66	0.75	82.82	75.70	79.26	71.93	60.90	66.42
n-C30	0.63	0.21	0.42	0.95	81.57	74.94	78.26	70.68	59.32	65.00
n-C31	1.21	0.48	0.49	0.83	81.49	74.67	78.08	70.02	58.60	64.31
n-C32	0.57	0.20	0.44	1.03	81.40	74.40	77.90	69.36	57.87	63.61
n-C33	0.52	0.15	0.21	0.31	79.46	74.18	76.82	68.45	57.43	62.94
n-C34	0.30	nd	0.26	0.64	77.51	73.96	75.73	67.53	56.99	62.26
n-C35	nd	nd	nd	nd	76.80	74.20	75.50	64.99	55.43	60.21
n-C36	nd	nd	0.14	0.39	76.08	74.45	75.27	62.44	53.87	58.16

Table 13. Results of QA/QC analysis of PAHs.

Spikes and Standards	X Spike I	X Spike II	SRM 1941 (1)	SRM 1941 (2)	NIST Certified Values
<b>Surrogate Recovery (%)</b>					
hexamethylbenzene	59	44	72	69	
n-dodecylbenzene	55	68	78	82	
4-terphenyl-D14	72	78	67	105	
<b>PAH (ng/g dry)</b>					
	<b>% Recovery<sup>†</sup></b>				
naphthalene	30	22	1362.2	1202.7	1322±14
C1-naphthalenes	36	36			
2-methylnaphthalene	35	35	340.2	356.9	406±36
1-methylnaphthalene	38	36	286.5	294.2	229±19
C2-naphthalenes	56	42			
2,6-dimethylnaphthalene <sup>◊</sup>	56	42	256.8	177.0	198±23
C3-naphthalenes	76	59			
2,3,5-trimethylnaphthalene	76	59			
C4-naphthalenes	76	59			
biphenyl	51	42	127.1	153.2	115±15
acenaphthylene	51	35	95.4	127.1	115±10
acenaphthene	67	54	58.5	55.9	52±2
fluorene	85	63	110.3	134.2	104±5
2-methylfluorene	90	65			
C1-fluorenes	90	65			
C2-fluorenes	99	74			
C3-fluorenes	99	74			
phenanthrene	82	62	603.4	842.5	577±59
1-methylphenanthrene	88	68	122.4	101.9	109±6
anthracene	80	61	243.8	277.1	202±42
C1-phenanthrenes/anthracenes	88	68			
C2-phenanthrenes/anthracenes	99	74			
3,6-dimethylphenanthrene	99	74			
C3-phenanthrenes/anthracenes	99	74			
C4-phenanthrenes/anthracenes	99	74			
2,3-benzofluorene	97	80			
1,1'-binaphthalene	99	77			
dibenzothiophene <sup>#</sup>	13	14			
C1-dibenzothiophenes <sup>#</sup>	88	68			
C2-dibenzothiophenes <sup>#</sup>	99	74			
C3-dibenzothiophenes <sup>#</sup>	99	74			
C4-dibenzothiophenes <sup>#</sup>	99	74			
fluoranthene	93	72	1014.1	1034.6	1220±240
pyrene	93	73	783.5	892.2	1080±200
C1-fluoranthenes/pyrenes	88	68			
C2-fluoranthenes/pyrenes	99	74			

Spikes and Standards	X Spike I	X Spike II	SRM 1941 (1)	SRM 1941 (2)	NIST Certified Values
<b>PAH (ng/g dry) (cont.)</b>					
	<b>% Recovery<sup>‡</sup></b>				
C3-fluoranthenes/pyrenes	99	74			
C4-fluoranthenes/pyrenes	99	74			
benz(a)anthracene	89	68	538.4	499.3	550±79
chrysene/triphenylene	85	65	754.3	670.8	641
C1-chrysenes/triphenylenes	88	68			
C2-chrysenes/triphenylenes	99	74			
C3-chrysenes/triphenylenes	99	74			
C4-chrysenes/triphenylenes	99	74			
benzo(k)fluoranthene	92	76	709.2	537.9	444±49
benzo(b)fluoranthene	95	76	821.3	971.3	780±19
benzo(e)pyrene	88	70	525.6	549.6	573
benzo(a)pyrene	80	61	679.0	711.0	670±130
9,10-diphenylanthracene	85	64			
perylene	82	66	389.9	368.8	422±33
indeno(1,2,3-cd)pyrene	96	63	814.8	483.3	569±40
dibenz(a,h)anthracene	78	52			
picene	83	75			
benzo(ghi)perylene	78	53	472.8	457.8	516±83
anthanthrene	49	48			
coronene	59	71			
1,2,4,5-dibenzopyrene	60	68			
C1-C20H12 aromatics	88	68			
C2-C20H12 aromatics	99	74			
C3-C20H12 aromatics	99	74			
C4-C20H12 aromatics	99	74			
Sum naphthalenes (N)					
Sum fluorenes (F)					
Sum phenanthrenes/anthracenes (PA)					
Sum dibenzothiophenes (D)					
Sum fluoranthenes/pyrenes (FP)					
Sum chrysenes (C)					
Sum C20H12 aromatics (C20)					
Sum 4,5 PAH (4,5 PAH)					
Sum PAH (t-PAH)					
N/PA					
N/perylene					
F/perylene					
PA/perylene					
FP/perylene					
t-PAH/perylene					

† - PAH fraction partially lost    ◊ - coelutes with another isomer    # - very low recovery due to activated Cu treatment for S removal    \* - duplicate analysis  
 § - % recovery of some methylated homologs assumed to be the same as that of methylated phenanthrenes    nd - not detected, below MDL

Table 14. Distribution (ng/g dry weight) of *n*-alkanes in gross sediments. Phase I: analyzed in 1997–98, Phase II: analyzed in 1998–99.

Sample	Phase I	2F/1	2F/2	2F/3	3A/1	3A/2*	4A/1	4A/2	4A/3	WPB/1	WPB/2	WPB/3	5F/1
<b>Surrogate Recovery %</b>													
Deu C14		47.19	48.38	53.18	52.79	43.57	64.43	57.77	50.45	40.64	42.98	45.22	48.40
Deu C24		59.95	64.14	65.91	60.10	43.53	83.36	73.83	67.12	51.85	57.53	54.74	52.21
Deu C36		59.95	60.37	60.62	55.47	41.81	83.89	77.08	55.20	53.51	63.61	56.11	55.92
<b><i>n</i>-alkane (ng/g dry)</b>													
n-C10		18.80	19.50	33.08	32.22	13.19	86.19	27.26	76.94	10.07	8.96	14.39	17.70
n-C11		30.19	31.17	52.45	48.38	29.16	105.53	42.40	107.66	15.94	15.66	22.42	26.19
n-C12		29.92	34.17	65.64	56.30	45.59	124.23	47.80	119.86	17.31	16.68	25.51	28.34
n-C13		38.69	56.32	84.19	73.82	68.43	168.67	64.65	152.21	23.49	22.78	35.06	32.24
n-C14		36.34	38.69	64.96	67.03	46.17	140.83	57.36	118.21	20.62	21.48	28.29	31.53
n-C15		43.13	46.05	70.58	83.03	61.17	158.40	69.90	137.22	25.34	23.42	34.80	34.82
n-C16		35.46	34.92	54.54	57.20	43.19	116.45	52.14	95.99	18.89	19.20	25.34	26.57
n-C17		44.83	45.63	75.04	87.32	66.38	139.37	111.04	112.76	22.81	23.22	34.14	41.90
pr		28.87	28.45	48.59	51.90	39.51	79.65	40.43	69.80	10.42	10.45	14.41	20.04
n-C18		32.61	32.20	53.36	55.98	42.50	103.60	47.50	86.83	16.32	16.97	22.85	29.31
ph		12.86	13.25	22.49	24.62	19.85	34.54	17.85	29.76	6.62	7.98	8.16	9.65
n-C19		41.74	41.37	73.05	79.08	60.84	122.95	58.77	104.42	20.02	19.51	32.77	50.47
n-C20		37.37	36.40	63.70	70.32	53.05	109.02	51.96	94.40	16.59	16.88	26.45	40.38
n-C21		64.43	62.79	127.86	146.05	109.90	172.96	87.13	150.31	26.85	27.13	55.90	110.66
n-C22		51.51	49.43	80.02	110.67	82.86	143.30	70.80	124.91	21.88	22.23	42.57	81.79
n-C23		112.35	107.58	243.68	264.01	196.11	269.55	139.88	226.36	43.34	43.35	104.53	14.33
n-C24		49.56	46.98	95.80	105.54	78.00	129.88	65.04	113.82	20.50	20.97	40.91	80.96
n-C25		136.97	129.29	336.42	346.79	261.40	283.08	153.59	243.47	46.59	45.83	108.60	267.88
n-C26		38.05	37.50	78.23	81.97	60.74	93.60	51.28	90.39	15.78	16.51	31.51	60.38
n-C27		230.47	212.77	553.20	559.22	418.12	162.63	234.33	380.31	72.68	72.01	164.44	419.23
n-C28		35.27	26.78	58.14	60.84	45.56	87.49	36.27	68.54	10.91	11.41	20.24	39.95
n-C29		202.39	181.58	191.66	510.17	376.81	53.24	241.94	453.89	58.99	60.89	133.70	327.36
n-C30		22.64	21.29	45.59	47.96	34.68	52.60	26.88	48.04	8.27	8.02	16.16	31.50
n-C31		160.24	150.57	165.81	427.85	311.98	67.43	211.39	429.66	47.03	47.83	53.94	275.13
n-C32		13.28	12.55	26.18	32.33	23.66	27.50	15.69	25.22	1.33	1.85	3.62	14.89
n-C33		46.91	43.97	91.95	133.98	90.04	49.02	68.95	142.41	15.23	17.00	34.29	99.71
n-C34		4.54	3.65	6.88	7.59	5.63	10.05	5.92	9.05	2.75	1.39	3.55	5.14
n-C35		9.29	1.22	14.48	21.65	14.85	23.78	16.53	25.31	4.44	1.50	7.74	20.49
n-C36		3.03	nd	0.92	3.02	2.71	6.55	2.81	nd	1.59	1.50	1.77	2.12
Total <i>n</i> -alkanes		1570.00	1504.38	2807.40	3570.32	2642.73	3007.91	2059.24	3738.19	605.57	604.18	1125.47	2210.94
Σ C12–C19		302.71	329.36	541.35	559.76	434.28	1074.50	509.18	927.51	184.80	163.27	238.75	275.13
Σ C20–C33		1201.44	1119.48	2158.25	2897.70	2142.91	1701.30	1455.14	2591.73	405.98	411.90	836.85	1864.17
pr/ph		2.25	2.15	2.16	2.11	1.99	2.31	2.26	2.35	1.57	1.31	1.77	2.08
odd/even**		3.38	3.39	4.43	4.18	4.16	1.69	3.25	3.14	2.84	2.81	3.25	3.99
LALK/TALK		0.19	0.22	0.19	0.16	0.16	0.36	0.25	0.25	0.27	0.27	0.21	0.12

Sample	Phase I	5F/2	5F/3	SL/1	SL/2	SL/3	6B/1	6B/2	6B/3
<b>Surrogate Recovery %</b>									
Deu C14		42.84	49.98	54.39	51.90	62.05	36.32	31.93	
Deu C24		53.28	59.60	50.38	51.14	61.48	50.80	48.47	
Deu C36		50.77	60.57	51.63	53.54	61.91	53.64	49.03	
<b><i>n</i>-alkane (ng/g dry)</b>									
n-C10		17.08	18.36	34.56	33.45	26.07	4.55	5.13	4.64
n-C11		25.33	29.79	55.74	57.32	50.74	8.97	8.82	7.95
n-C12		25.87	31.43	66.53	63.09	71.68	8.99	7.95	5.88
n-C13		30.28	39.01	83.84	70.80	88.72	11.02	9.55	7.18
n-C14		30.03	38.60	59.20	57.52	72.12	11.05	8.63	6.50
n-C15		34.04	41.33	68.28	71.32	85.68	12.49	10.39	7.85
n-C16		25.66	31.25	52.13	51.01	66.58	10.67	9.31	7.14
n-C17		40.23	45.40	71.08	79.27	97.73	13.43	11.95	8.68
pr		20.19	24.27	37.92	38.91	53.38	7.84	7.20	5.16
n-C18		27.82	32.85	52.53	52.49	65.78	10.74	9.47	6.90
ph		9.63	11.30	19.46	20.06	26.54	4.28	3.56	2.50
n-C19		45.61	50.19	81.37	84.62	88.30	13.80	12.78	8.76
n-C20		35.66	39.95	60.19	64.36	76.59	11.80	10.75	7.57
n-C21		99.61	102.80	167.50	178.29	201.66	22.19	21.81	14.35
n-C22		82.54	77.20	126.38	131.36	152.86	18.01	17.82	11.77
n-C23		218.17	217.97	5.30	4.86	416.82	45.55	45.00	27.79
n-C24		90.59	78.23	121.66	123.94	150.85	17.69	17.94	11.34
n-C25		266.90	266.39	456.93	473.54	569.13	45.87	49.78	28.05
n-C26		75.81	58.74	94.59	93.82	108.41	13.86	14.25	8.86
n-C27		363.43	354.29	559.12	656.91	765.88	67.44	66.34	41.01
n-C28		65.29	47.04	80.21	88.77	100.06	11.25	11.87	6.32
n-C29		285.56	280.51	445.69	530.11	617.03	57.01	57.00	33.83
n-C30		42.72	28.72	46.45	53.74	60.50	6.70	6.77	4.09
n-C31		243.63	234.65	382.57	473.21	520.83	46.37	45.78	26.49
n-C32		21.73	13.28	21.70	28.57	31.79	1.17	1.81	1.23
n-C33		89.10	88.47	139.88	205.88	176.88	16.00	15.42	8.86
n-C34		8.41	5.28	7.50	9.80	9.04	1.70	2.10	1.17
n-C35		20.73	23.00	46.10	26.90	40.87	4.91	3.41	1.80
n-C36		2.86	nd	nd	0.68	0.55	0.79	1.07	nd
Total <i>n</i> -alkanes		2314.65	2274.53	3386.86	3765.64	4712.96	494.02	482.91	305.81
Σ C12-C19		259.52	309.85	534.99	530.12	363.59	92.20	80.04	58.69
Σ C20-C33		1960.72	1888.24	2707.98	3107.37	3949.10	380.91	382.34	231.56
pr/ph		2.10	2.15	1.95	1.94	2.01	1.83	2.02	2.06
odd/even**		3.54	4.08	3.58	3.95	4.30	3.28	3.29	3.10
LALK/TALK		0.11	0.14	0.16	0.14	0.08	0.19	0.17	0.19

Sample	Phase II	1D/2	2E/1	2E/2	3B/1	5(1)/1	5(2)/1	5(5)/1	5(5)/1***	5(10)/1	5(10)/2	5(10)/3	5(10)/3***
<b>Surrogate Recovery %</b>													
Deu C14		57	75	48	77	59	51	65	70	69	47	53	69
Deu C24		64	68	54	59	59	50	53	58	60	57	64	72
Deu C36		69	78	64	58	71	57	71	76	65	73	78	66
<b><i>n</i>-alkane (ng/g dry)</b>													
n-C10		nd	4.91	3.95	44.01	2.36	nd	11.93	13.18	2.96	5.49	nd	5.03
n-C11		3.72	10.14	3.89	73.79	3.97	5.79	18.35	21.40	7.19	2.88	5.24	7.86
n-C12		nd	7.11	3.29	63.33	1.51	4.25	18.30	20.34	6.62	3.72	5.35	8.15
n-C13		nd	7.07	3.48	89.04	1.30	1.42	19.41	7.97	1.56	0.92	2.05	0.82
n-C14		0.81	8.27	4.61	64.97	2.01	4.82	25.46	26.10	12.42	6.78	9.38	13.80
n-C15		1.75	11.42	6.29	82.33	2.70	6.24	22.95	27.72	11.92	9.17	12.44	17.49
n-C16		0.94	8.26	4.98	51.52	2.12	4.93	19.65	20.77	10.06	7.97	11.34	13.28
n-C17		4.20	10.66	6.36	78.07	3.45	7.01	27.25	29.26	12.17	10.32	15.53	18.20
pr		1.26	7.32	4.39	40.24	1.41	3.26	15.28	16.39	5.68	5.15	7.90	9.18
n-C18		1.93	8.48	5.37	56.95	2.92	5.14	19.63	20.72	9.83	8.14	11.76	13.39
ph		0.68	3.79	2.25	22.40	1.07	1.70	7.03	7.63	4.24	2.80	4.32	4.70
n-C19		3.28	9.77	6.34	68.10	4.20	6.77	28.40	29.56	13.80	9.60	15.12	17.28
n-C20		2.83	8.88	5.92	71.73	6.44	5.85	16.25	3.90	20.30	11.09	3.72	25.32
n-C21		6.29	12.32	7.97	124.96	7.86	10.50	49.02	53.65	29.04	12.23	23.28	26.54
n-C22		9.24	10.83	7.39	89.80	7.30	8.85	38.76	41.27	23.82	10.55	20.46	21.70
n-C23		31.08	18.76	12.54	214.57	8.45	19.18	102.89	108.11	33.49	21.07	43.07	47.93
n-C24		59.50	11.75	8.78	86.41	6.27	9.76	55.38	53.86	24.11	12.19	29.47	23.92
n-C25		97.06	24.21	11.54	276.69	16.54	24.30	140.42	134.62	49.39	26.65	59.73	64.84
n-C26		114.13	11.23	8.75	66.93	1.17	6.83	53.51	31.32	25.21	8.68	30.07	18.68
n-C27		120.32	33.44	22.79	401.91	34.12	33.40	208.68	199.25	62.22	37.25	86.65	103.82
n-C28		88.15	9.60	7.18	60.63	5.87	5.64	47.91	22.43	23.01	7.91	26.25	16.08
n-C29		87.00	33.18	23.03	375.63	35.60	36.54	167.76	157.40	56.86	44.38	78.09	85.85
n-C30		50.75	8.48	4.45	48.46	4.00	3.96	33.03	15.97	17.40	5.16	21.20	11.89
n-C31		59.11	31.43	19.40	330.84	26.09	30.19	140.82	130.65	45.32	41.82	65.44	69.06
n-C32		30.82	7.85	3.96	56.51	6.86	4.05	42.24	25.33	13.51	4.76	14.27	11.00
n-C33		25.14	11.54	6.12	90.21	8.56	9.86	50.69	44.68	16.66	13.02	23.97	19.76
n-C34		14.53	5.21	1.51	5.77	0.77	0.96	10.60	4.38	3.59	1.68	5.41	2.46
n-C35		7.02	2.61	0.70	12.32	1.70	1.87	14.33	12.24	4.88	2.19	5.43	0.55
n-C36		6.82	3.59	1.10	nd	0.57	nd	1.68	1.10	nd	0.64	2.81	0.69
<b>Total <i>n</i>-alkanes</b>		<b>826.21</b>	<b>331.00</b>	<b>201.70</b>	<b>2985.51</b>	<b>204.69</b>	<b>258.12</b>	<b>1385.31</b>	<b>1257.18</b>	<b>537.34</b>	<b>326.24</b>	<b>627.54</b>	<b>665.39</b>
<b>Σ C12-C19</b>		<b>12.90</b>	<b>71.04</b>	<b>40.72</b>	<b>554.31</b>	<b>20.19</b>	<b>40.57</b>	<b>181.06</b>	<b>182.45</b>	<b>78.39</b>	<b>56.62</b>	<b>82.98</b>	<b>102.42</b>
<b>Σ C20-C33</b>		<b>781.23</b>	<b>233.51</b>	<b>149.83</b>	<b>2295.30</b>	<b>175.12</b>	<b>208.91</b>	<b>1147.36</b>	<b>1022.44</b>	<b>440.34</b>	<b>256.75</b>	<b>525.67</b>	<b>546.40</b>
pr/ph		1.85	1.93	1.95	1.80	1.32	1.92	2.17	2.15	1.34	1.84	1.83	1.95
odd/even**		1.17	2.17	2.10	3.44	3.38	3.29	2.79	3.81	1.94	2.89	2.43	2.98
LALK/TALK		0.02	0.21	0.20	0.19	0.10	0.16	0.13	0.15	0.15	0.17	0.13	0.15

Sample	Phase II	5A/1	5G/2	6A/1	6C/1	6D/1	6G/1	6G/2	6G/3
<b>Surrogate Recovery %</b>									
Deu C14		78	53	78	70	43	85	50	68
Deu C24		59	50	62	62	55	92	63	79
Deu C36		74	62	77	68	63	106	59	72
<b><i>n</i>-alkane (ng/g dry)</b>									
n-C10		96.00	5.05	64.90	17.43	6.22	86.57	55.99	56.44
n-C11		143.05	9.66	85.99	34.21	9.27	136.95	106.93	84.93
n-C12		129.99	5.88	85.70	38.05	10.04	128.98	114.69	100.13
n-C13		141.52	1.21	126.53	55.01	2.51	175.04	157.14	119.21
n-C14		31.84	7.09	110.85	52.88	15.87	3.26	161.86	132.09
n-C15		165.78	8.84	136.36	54.40	16.78	169.21	166.50	143.77
n-C16		100.23	7.52	84.48	42.54	15.31	127.40	130.36	109.75
n-C17		148.12	10.05	116.60	50.46	18.51	218.05	205.71	186.77
pr		91.18	5.92	67.52	33.07	15.05	101.88	107.37	88.62
n-C18		102.47	7.83	87.44	43.80	16.14	145.17	144.35	125.40
ph		39.89	3.37	30.73	15.19	6.50	46.23	48.05	38.89
n-C19		160.95	10.40	134.38	57.82	20.64	260.43	241.65	222.75
n-C20		171.27	13.47	161.99	71.88	22.73	83.66	52.86	249.95
n-C21		327.48	15.80	275.62	99.99	32.19	628.95	549.50	543.23
n-C22		263.52	14.30	205.22	80.65	27.44	454.92	416.50	394.20
n-C23		621.98	29.80	5.70	209.37	58.91	1253.27	1163.83	1118.54
n-C24		265.78	22.87	187.99	77.00	26.77	413.88	410.79	361.47
n-C25		727.96	34.90	673.40	215.39	73.14	1302.69	1216.42	1143.18
n-C26		247.12	23.28	137.83	59.82	21.43	310.57	317.40	273.37
n-C27		1165.50	62.96	938.67	297.69	99.78	2225.26	1946.24	1988.27
n-C28		221.92	18.73	122.36	50.48	19.76	208.68	207.57	199.66
n-C29		1051.22	70.61	663.52	242.76	91.64	1660.10	1389.09	1536.57
n-C30		136.85	11.89	73.88	27.85	12.47	174.18	158.09	192.77
n-C31		283.39	58.70	636.40	223.99	79.88	1551.00	1254.81	1444.66
n-C32		67.01	12.45	92.42	45.68	17.33	209.15	209.37	189.58
n-C33		293.17	20.89	147.62	69.63	27.73	487.10	427.20	458.11
n-C34		33.26	3.23	14.06	7.72	4.37	4.20	30.73	67.96
n-C35		30.26	3.30	25.99	18.12	5.34	72.76	79.90	64.23
n-C36		2.57	0.89	4.35	nd	2.42	6.67	6.11	7.28
Total <i>n</i> -alkanes		7130.21	491.58	5400.24	2244.43	754.64	12498.08	11321.38	11514.26
Σ C12-C19		980.91	58.81	882.34	394.76	115.80	1227.53	1322.06	1139.86
Σ C20-C33		5844.17	410.65	4322.62	1772.20	611.22	10963.40	9719.67	10093.56
pr/ph		2.30	1.76	2.20	2.18	2.32	2.20	2.23	2.28
odd/even**		3.07	2.38	3.19	3.00	2.83	4.58	4.12	4.06
LALK/TALK		0.14	0.12	0.16	0.18	0.15	0.10	0.12	0.10

\*sample 3A/3 lost

\*\*summed from n-C15-n-C34

\*\*\*duplicate analysis

nd-not detected

Table 15. Distribution (ng/g) of PAHs in gross sediments. Phase I: analyzed in 1997-98, Phase II: analyzed in 1998-99.

Sample	Phase I	2F/1	2F/2	2F/3	3A/1	3A/2	Sample	Phase I	2F/1	2F/2	2F/3	3A/1	3A/2
<b>Surrogate Recovery (%)</b>						<b>PAH (ng/g dry) (cont.)</b>							
hexamethylbenzene		31	31	53	61	82	C3-fluoranthenes/pyrenes		1.53	1.52	4.97	9.56	8.00
n-dodecylbenzene		48	48	60	84	143	C4-fluoranthenes/pyrenes		nd	nd	0.06	1.36	nd
4-terphenyl-D14		48	48	56	60	72	benz(a)anthracene		1.42	1.28	1.85	1.53	2.27
<b>PAH (ng/g dry)</b>						<b>chrysene/triphenylene</b>							
naphthalene		3.14	7.80	13.58	16.17	16.08	C1-chrysenes/triphenylenes		9.36	12.27	18.47	26.53	31.51
C1-naphthalenes		13.45	26.56	46.09	54.23	67.78	C2-chrysenes/triphenylenes		4.26	5.55	9.73	16.47	19.79
2-methylnaphthalene		7.57	15.21	25.91	30.01	37.72	C3-chrysenes/triphenylenes		nd	nd	nd	nd	nd
1-methylnaphthalene		5.98	11.55	20.51	24.80	30.54	C4-chrysenes/triphenylenes		nd	nd	nd	nd	nd
C2-naphthalenes		35.71	56.26	91.57	111.02	145.75	benzo(k)fluoranthene		0.99	0.45	nd	0.65	0.58
2,6-dimethylnaphthalene <sup>o</sup>		3.46	7.30	10.93	14.13	18.91	benzo(b)fluoranthene		2.78	3.14	4.19	7.56	8.54
C3-naphthalenes		25.24	33.98	56.37	70.29	87.87	benzo(e)pyrene		3.78	4.14	5.81	9.39	11.00
2,3,5-trimethylnaphthalene		4.71	3.68	7.97	5.73	12.04	benzo(a)pyrene		1.71	0.85	1.02	1.72	2.11
C4-naphthalenes		3.81	4.40	10.30	14.99	20.15	9,10-diphenylanthracene		nd	nd	nd	nd	nd
biphenyl		2.90	5.28	7.55	10.88	13.55	perylene		20.61	23.80	43.02	57.60	71.57
acenaphthylene		nd	nd	nd	nd	nd	indeno(1,2,3-cd)pyrene		0.81	nd	nd	nd	nd
acenaphthene		0.20	0.41	0.73	0.99	1.21	dibenz(a,h)anthracene		0.52	nd	nd	nd	nd
fluorene		2.55	2.80	4.42	6.03	7.17	picene		nd	nd	nd	nd	nd
2-methylfluorene		2.03	2.50	4.29	5.29	6.00	benzo(ghi)perylene		1.51	0.80	1.01	5.36	9.11
C1-fluorenes		0.46	0.57	1.48	1.18	1.23	anthanthrene		nd	nd	nd	nd	nd
C2-fluorenes		0.97	0.82	2.71	4.64	5.81	coronene		nd	nd	nd	nd	nd
C3-fluorenes		nd	nd	nd	nd	nd	1,2,4,5-dibenzopyrene		nd	nd	nd	nd	nd
phenanthrene		12.93	15.96	24.70	31.18	39.84	C1-C20H12 aromatics		1.75	0.93	2.03	10.22	13.31
1-methylphenanthrene		11.52	14.17	21.31	27.32	32.71	C2-C20H12 aromatics		nd	nd	nd	nd	nd
anthracene		0.52	0.38	0.71	1.18	0.31	C3-C20H12 aromatics		nd	nd	nd	nd	nd
C1-phenanthrenes/anthracenes		61.07	61.69	103.38	154.51	183.93	C4-C20H12 aromatics		nd	nd	nd	nd	nd
C2-phenanthrenes/anthracenes		34.14	44.75	61.71	78.55	105.49	Sum naphthalenes (N)		81.35	129.00	217.90	266.71	337.63
3,6-dimethylphenanthrene		1.39	2.01	2.32	3.22	4.33	Sum fluorenes (F)		3.98	4.20	8.61	11.85	14.21
C3-phenanthrenes/anthracenes		19.35	21.78	40.16	57.88	78.99	Sum phenanthrenes/anthracenes (PA)		140.03	157.25	252.63	349.43	408.55
C4-phenanthrenes/anthracenes		12.01	12.68	21.96	26.12	nd	Sum dibenzothiophenes (D)		5.53	4.00	10.84	22.72	31.61
2,3-benzofluorene		1.39	1.38	2.84	3.43	4.05	Sum fluoranthenes/pyrenes (FP)		15.92	17.02	33.70	50.63	58.03
1,1'-binaphthalene		nd	nd	nd	nd	nd	Sum chrysenes (C)		21.59	26.99	40.76	58.99	69.97
dibenzothiophene*		4.48	3.34	7.97	14.18	18.87	Sum C20H12 aromatics (C20)		31.62	33.33	56.07	87.14	107.10
C1-dibenzothiophenes*		nd	nd	nd	0.45	1.16	Sum 4,5 PAH (4,5 PAH)		68.79	77.67	130.34	188.07	224.07
C2-dibenzothiophenes*		0.86	0.65	1.94	2.81	3.56	Sum PAH (t-PAH)		308.75	380.91	634.48	869.66	1057.30
C3-dibenzothiophenes*		0.19	nd	0.93	3.16	5.47	N/PA		0.58	0.82	0.86	0.76	0.83
C4-dibenzothiophenes*		nd	nd	nd	2.11	2.55	N/perylene		3.95	5.42	5.07	4.63	4.72
fluoranthene		2.07	1.91	3.75	4.75	5.69	F/perylene		0.19	0.18	0.20	0.21	0.20
pyrene		3.19	3.07	5.14	7.14	9.99	PA/perylene		6.79	6.61	5.87	6.07	5.71
C1-fluoranthenes/pyrenes		4.70	5.49	9.66	13.01	16.56	FP/perylene		0.77	0.71	0.78	0.88	0.81
C2-fluoranthenes/pyrenes		4.42	5.02	10.12	14.81	17.80	t-PAH/perylene		14.98	16.00	14.75	15.10	14.77

† - PAH fraction partially lost    o - coelutes with another isomer    # - very low recovery due to activated Cu treatment for S removal    \* - duplicate analysis  
 § - % recovery of some methylated homologs assumed to be the same as that of methylated phenanthrenes    nd - not detected, below MDL

Sample Phase I	3A/3	4A/1	4A/2	4A/3	WPB/1†
<b>Surrogate Recovery (%)</b>					
hexamethylbenzene	68	59	64	50	21
n-dodecylbenzene	87	86	80	60	33
4-terphenyl-D14	73	67	70	49	27
<b>PAH (ng/g dry)</b>					
naphthalene	16.33	11.26	10.31	24.12	0.30
C1-naphthalenes	63.73	52.73	40.14	86.51	1.69
2-methylnaphthalene	35.27	30.93	22.99	49.86	0.99
1-methylnaphthalene	28.91	22.22	17.45	37.31	0.71
C2-naphthalenes	135.22	118.82	81.23	172.14	9.35
2,6-dimethylnaphthalene <sup>o</sup>	15.27	15.18	10.69	23.07	0.56
C3-naphthalenes	88.12	77.85	49.83	98.81	2.17
2,3,5-trimethylnaphthalene	17.08	13.78	9.26	17.55	0.22
C4-naphthalenes	19.98	15.87	9.76	19.83	nd
biphenyl	12.69	19.02	10.23	26.14	0.63
acenaphthylene	nd	nd	nd	nd	nd
acenaphthene	1.20	0.55	0.49	0.70	nd
fluorene	7.80	3.23	3.93	4.70	0.17
2-methylfluorene	4.92	2.62	3.30	4.18	nd
C1-fluorenes	2.06	1.58	0.46	0.25	nd
C2-fluorenes	5.96	7.18	3.92	5.38	nd
C3-fluorenes	nd	nd	nd	nd	nd
phenanthrene	40.52	61.00	28.95	67.20	3.00
1-methylphenanthrene	32.20	32.64	20.70	32.03	2.01
anthracene	1.06	0.49	nd	1.03	nd
C1-phenanthrenes/anthracenes	165.50	185.06	99.85	166.76	9.98
C2-phenanthrenes/anthracenes	101.30	113.01	57.84	119.05	6.27
3,6-dimethylphenanthrene	4.14	4.90	2.48	4.62	nd
C3-phenanthrenes/anthracenes	76.40	61.08	35.81	68.51	1.11
C4-phenanthrenes/anthracenes	37.66	nd	nd	nd	3.09
2,3-benzofluorene	4.51	1.13	2.98	2.24	nd
1,1'-binaphthalene	nd	nd	nd	nd	nd
dibenzothiophene <sup>#</sup>	19.92	18.40	11.14	22.83	nd
C1-dibenzothiophenes <sup>#</sup>	1.21	1.74	0.03	0.58	nd
C2-dibenzothiophenes <sup>#</sup>	3.98	3.76	2.18	4.38	nd
C3-dibenzothiophenes <sup>#</sup>	6.47	3.16	4.42	3.08	nd
C4-dibenzothiophenes <sup>#</sup>	nd	nd	nd	nd	nd
fluoranthene	6.98	6.70	4.56	7.28	0.36
pyrene	11.14	10.76	5.41	12.36	0.61
C1-fluoranthenes/pyrenes	16.98	14.33	8.60	17.21	0.11
C2-fluoranthenes/pyrenes	18.52	17.33	9.85	22.70	nd

Sample Phase I	3A/3	4A/1	4A/2	4A/3	WPB/1†
<b>PAH (ng/g dry) (cont.)</b>					
C3-fluoranthenes/pyrenes	10.21	8.40	5.36	9.76	nd
C4-fluoranthenes/pyrenes	nd	nd	nd	nd	nd
benz(a)anthracene	2.45	1.89	1.31	2.25	nd
chrysene/triphenylene	19.49	26.68	12.82	28.47	1.72
C1-chrysenes/triphenylenes	34.45	41.32	19.71	48.24	0.61
C2-chrysenes/triphenylenes	20.98	29.73	10.30	30.95	nd
C3-chrysenes/triphenylenes	nd	3.09	nd	nd	nd
C4-chrysenes/triphenylenes	nd	nd	nd	nd	nd
benzo(k)fluoranthene	0.77	0.71	nd	0.64	nd
benzo(b)fluoranthene	9.30	8.88	5.11	12.91	0.19
benzo(e)pyrene	12.07	10.62	6.51	15.78	0.33
benzo(a)pyrene	2.28	1.39	nd	1.57	nd
9,10-diphenylanthracene	nd	nd	nd	nd	nd
perylene	72.59	12.94	20.44	22.12	5.75
indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd
dibenz(a,h)anthracene	nd	nd	nd	nd	nd
picene	nd	nd	nd	nd	nd
benzo(ghi)perylene	6.94	4.53	1.83	7.03	nd
anthanthrene	nd	nd	nd	nd	nd
coronene	nd	0.44	nd	nd	nd
1,2,4,5-dibenzopyrene	nd	nd	nd	nd	nd
C1-C20H12 aromatics	16.01	22.65	5.22	25.88	0.86
C2-C20H12 aromatics	nd	nd	nd	nd	nd
C3-C20H12 aromatics	nd	nd	nd	nd	nd
C4-C20H12 aromatics	nd	nd	nd	nd	nd
Sum naphthalenes (N)	323.38	276.53	191.28	401.42	13.51
Sum fluorenes (F)	15.82	11.99	8.32	10.33	0.17
Sum phenanthrenes/anthracenes (PA)	422.45	420.64	222.45	422.56	23.45
Sum dibenzothiophenes (D)	31.58	27.06	17.77	30.86	nd
Sum fluoranthenes/pyrenes (FP)	63.83	57.52	33.78	69.31	1.09
Sum chrysenes (C)	74.93	100.83	42.82	107.65	2.32
Sum C20H12 aromatics (C20)	113.02	57.18	37.29	78.91	7.13
Sum 4,5 PAH (4,5 PAH)	238.21	194.77	109.98	232.23	9.68
Sum PAH (t-PAH)	1072.79	979.31	570.55	1159.39	48.30
N/PA	0.77	0.66	0.86	0.95	0.58
N/perylene	4.46	21.37	9.36	18.15	2.35
F/perylene	0.22	0.93	0.41	0.47	0.03
PA/perylene	5.82	32.50	10.88	19.11	4.08
FP/perylene	0.88	4.44	1.65	3.13	0.19
t-PAH/perylene	14.78	75.67	27.91	52.42	8.40

† – PAH fraction partially lost    o – coelutes with another isomer    # – very low recovery due to activated Cu treatment for S removal    \* – duplicate analysis  
 § – % recovery of some methylated homologs assumed to be the same as that of methylated phenanthrenes    nd – not detected, below MDL

Sample Phase I	WPB/2	WPB/3	5F/1	5F/1*	5F/2
<b>Surrogate Recovery (%)</b>					
hexamethylbenzene	50	65	50	54	64
n-dodecylbenzene	98	80	69	65	84
4-terphenyl-D14	59	54	52	58	69
<b>PAH (ng/g dry)</b>					
naphthalene	1.18	2.54	3.42	3.46	4.25
C1-naphthalenes	5.02	10.01	15.21	16.62	17.43
2-methylnaphthalene	2.99	5.74	8.30	9.10	9.57
1-methylnaphthalene	2.07	4.35	7.02	7.64	7.97
C2-naphthalenes	18.43	32.86	37.86	40.71	42.62
2,6-dimethylnaphthalene <sup>o</sup>	1.86	3.48	3.95	4.68	5.11
C3-naphthalenes	7.14	17.12	23.73	25.42	26.78
2,3,5-trimethylnaphthalene	1.73	3.04	4.44	4.80	4.92
C4-naphthalenes	nd	1.61	2.83	3.64	3.80
biphenyl	1.90	3.09	3.24	3.31	3.76
acenaphthylene	nd	nd	nd	nd	nd
acenaphthene	nd	0.13	0.26	0.32	0.24
fluorene	0.76	1.41	1.77	1.96	1.89
2-methylfluorene	0.52	1.16	1.57	1.63	1.67
C1-fluorenes	0.21	0.37	0.42	0.50	0.23
C2-fluorenes	nd	0.96	0.62	0.92	0.79
C3-fluorenes	nd	nd	nd	nd	nd
phenanthrene	8.03	10.09	12.34	12.36	13.36
1-methylphenanthrene	8.37	9.92	8.70	7.89	12.81
anthracene	nd	0.20	0.18	0.28	0.26
C1-phenanthrenes/anthracenes	71.32	101.62	46.32	42.06	62.35
C2-phenanthrenes/anthracenes	25.95	30.95	34.19	33.24	36.08
3,6-dimethylphenanthrene	0.83	0.95	1.35	1.34	1.52
C3-phenanthrenes/anthracenes	14.05	20.81	20.00	18.51	26.62
C4-phenanthrenes/anthracenes	7.12	9.03	nd	16.89	20.68
2,3-benzofluorene	0.13	0.45	1.20	1.23	1.33
1,1'-binaphthalene	nd	nd	nd	nd	nd
dibenzothiophene <sup>#</sup>	4.16	5.89	4.67	4.79	5.63
C1-dibenzothiophenes <sup>#</sup>	nd	nd	nd	nd	nd
C2-dibenzothiophenes <sup>#</sup>	1.97	2.36	1.61	1.61	2.00
C3-dibenzothiophenes <sup>#</sup>	0.78	1.97	0.53	0.61	1.16
C4-dibenzothiophenes <sup>#</sup>	nd	1.74	1.47	nd	nd
fluoranthene	1.13	1.64	2.76	2.94	2.92
pyrene	1.68	2.17	3.77	4.04	3.73
C1-fluoranthenes/pyrenes	1.68	3.04	5.96	4.91	5.84
C2-fluoranthenes/pyrenes	1.01	2.11	5.16	3.88	4.49

Sample Phase I	WPB/2	WPB/3	5F/1	5F/1*	5F/2
<b>PAH (ng/g dry) (cont.)</b>					
C3-fluoranthenes/pyrenes	0.05	0.24	1.55	0.68	0.83
C4-fluoranthenes/pyrenes	nd	nd	nd	nd	nd
benz(a)anthracene	0.13	0.36	1.10	0.74	1.00
chrysene/triphenylene	4.73	5.67	7.77	6.56	7.95
C1-chrysenes/triphenylenes	5.30	6.76	10.47	6.57	8.54
C2-chrysenes/triphenylenes	1.28	2.05	4.05	1.29	2.05
C3-chrysenes/triphenylenes	nd	nd	nd	nd	nd
C4-chrysenes/triphenylenes	nd	nd	nd	nd	nd
benzo(k)fluoranthene	nd	nd	nd	nd	nd
benzo(b)fluoranthene	1.58	2.07	4.11	3.18	3.31
benzo(e)pyrene	1.75	2.26	3.66	2.74	3.16
benzo(a)pyrene	nd	nd	0.45	nd	nd
9,10-diphenylanthracene	nd	nd	nd	nd	nd
perylene	13.91	17.89	35.72	33.31	36.05
indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd
dibenz(a,h)anthracene	nd	nd	nd	nd	nd
picene	nd	nd	nd	nd	nd
benzo(ghi)perylene	nd	nd	nd	nd	nd
anthanthrene	nd	nd	nd	nd	nd
coronene	nd	nd	nd	nd	nd
1,2,4,5-dibenzopyrene	nd	nd	nd	nd	nd
C1-C20H12 aromatics	1.17	1.16	1.87	0.85	0.58
C2-C20H12 aromatics	nd	nd	nd	nd	nd
C3-C20H12 aromatics	nd	nd	nd	nd	nd
C4-C20H12 aromatics	nd	nd	nd	nd	nd
Sum naphthalenes (N)	31.77	64.14	83.05	89.86	94.88
Sum fluorenes (F)	0.98	2.74	2.80	3.38	2.91
Sum phenanthrenes/anthracenes (PA)	126.48	172.69	113.03	123.35	159.35
Sum dibenzothiophenes (D)	6.91	11.97	8.28	7.01	8.79
Sum fluoranthenes/pyrenes (FP)	5.55	9.20	19.20	16.45	17.81
Sum chrysenes (C)	11.31	14.49	22.30	14.42	18.54
Sum C20H12 aromatics (C20)	18.40	23.38	45.80	40.09	43.09
Sum 4,5 PAH (4,5 PAH)	34.22	46.28	86.53	70.84	79.87
Sum PAH (t-PAH)	203.56	302.64	300.25	300.16	351.71
N/PA	0.25	0.37	0.73	0.73	0.60
N/perylene	2.28	3.58	2.33	2.70	2.63
F/perylene	0.07	0.15	0.08	0.10	0.08
PA/perylene	9.09	9.65	3.16	3.70	4.42
FP/perylene	0.40	0.51	0.54	0.49	0.49
t-PAH/perylene	14.64	16.91	8.41	9.01	9.76

† – PAH fraction partially lost    o – coelutes with another isomer    # – very low recovery due to activated Cu treatment for S removal    \* – duplicate analysis  
 § – % recovery of some methylated homologs assumed to be the same as that of methylated phenanthrenes    nd – not detected, below MDL

Sample Phase I	5F/3	SL/1	SL/1*	SL/2	SL/3
<b>Surrogate Recovery (%)</b>					
hexamethylbenzene	75	76	79	72	58
n-dodecylbenzene	97	83	86	81	85
4-terphenyl-D14	83	65	75	69	52
<b>PAH (ng/g dry)</b>					
naphthalene	5.86	21.55	21.45	15.63	14.90
C1-naphthalenes	22.76	81.52	82.81	65.35	56.64
2-methylnaphthalene	12.47	44.84	45.41	36.15	30.91
1-methylnaphthalene	10.45	37.24	37.96	29.65	26.12
C2-naphthalenes	53.10	159.85	163.30	132.38	118.33
2,6-dimethylnaphthalene <sup>o</sup>	6.04	18.14	22.29	16.34	13.83
C3-naphthalenes	35.42	98.80	102.03	83.56	77.12
2,3,5-trimethylnaphthalene	5.94	16.36	17.50	14.64	13.84
C4-naphthalenes	7.08	22.03	22.20	19.32	17.80
biphenyl	4.99	13.31	13.97	12.07	10.39
acenaphthylene	nd	nd	nd	nd	nd
acenaphthene	0.42	1.19	1.27	1.04	1.02
fluorene	2.73	7.48	7.49	6.81	5.80
2-methylfluorene	2.63	6.64	7.05	5.83	6.23
C1-fluorenes	0.41	1.18	0.61	0.81	0.52
C2-fluorenes	2.53	10.99	12.11	7.23	9.19
C3-fluorenes	nd	nd	nd	9.81	nd
phenanthrene	18.76	37.95	40.72	35.90	31.76
1-methylphenanthrene	17.85	31.61	28.12	27.15	17.66
anthracene	0.67	nd	nd	0.92	0.99
C1-phenanthrenes/anthracenes	100.29	212.06	220.29	115.15	148.68
C2-phenanthrenes/anthracenes	56.62	100.14	106.76	85.54	88.11
3,6-dimethylphenanthrene	1.95	3.61	3.50	3.72	2.25
C3-phenanthrenes/anthracenes	44.32	108.24	106.22	69.73	138.11
C4-phenanthrenes/anthracenes	31.35	73.78	75.95	53.78	82.03
2,3-benzofluorene	1.95	4.88	4.61	5.11	4.17
1,1'-binaphthalene	nd	nd	nd	nd	nd
dibenzothiophene <sup>#</sup>	6.90	20.15	22.99	15.96	16.43
C1-dibenzothiophenes <sup>#</sup>	nd	1.78	2.12	0.99	1.40
C2-dibenzothiophenes <sup>#</sup>	2.46	6.58	6.85	5.39	5.76
C3-dibenzothiophenes <sup>#</sup>	1.51	12.05	12.91	7.65	12.03
C4-dibenzothiophenes <sup>#</sup>	nd	2.31	nd	2.45	2.18
fluoranthene	4.23	7.34	8.84	6.42	6.50
pyrene	5.49	8.87	10.77	9.31	7.00
C1-fluoranthenes/pyrenes	8.71	19.85	20.00	18.53	24.23
C2-fluoranthenes/pyrenes	9.35	21.22	20.41	18.24	20.71

Sample Phase I	5F/3	SL/1	SL/1*	SL/2	SL/3
<b>PAH (ng/g dry) (cont.)</b>					
C3-fluoranthenes/pyrenes	4.03	7.01	5.77	6.64	5.95
C4-fluoranthenes/pyrenes	0.22	nd	nd	2.49	nd
benz(a)anthracene	1.54	2.11	2.74	2.71	2.04
chrysene/triphenylene	10.41	16.77	18.99	17.20	14.76
C1-chrysenes/triphenylenes	14.59	30.88	33.68	32.29	30.82
C2-chrysenes/triphenylenes	6.54	21.89	22.16	23.41	25.99
C3-chrysenes/triphenylenes	nd	0.62	0.21	0.22	1.77
C4-chrysenes/triphenylenes	nd	nd	nd	nd	nd
benzo(k)fluoranthene	0.39	0.89	1.02	0.93	1.10
benzo(b)fluoranthene	4.97	9.57	10.60	9.07	8.49
benzo(e)pyrene	4.44	9.22	10.35	8.96	8.55
benzo(a)pyrene	nd	3.00	3.19	2.41	2.94
9,10-diphenylanthracene	nd	nd	nd	nd	nd
perylene	48.99	79.57	89.08	82.42	86.49
indeno(1,2,3-cd)pyrene	nd	0.40	nd	nd	0.68
dibenz(a,h)anthracene	nd	nd	nd	nd	nd
picene	nd	nd	nd	nd	nd
benzo(ghi)perylene	nd	6.80	5.65	3.96	6.87
anthanthrene	nd	nd	nd	nd	nd
coronene	nd	nd	nd	nd	nd
1,2,4,5-dibenzopyrene	nd	nd	nd	nd	nd
C1-C20H12 aromatics	3.53	20.32	18.53	14.63	24.29
C2-C20H12 aromatics	nd	nd	nd	nd	nd
C3-C20H12 aromatics	nd	nd	nd	nd	nd
C4-C20H12 aromatics	nd	nd	nd	nd	nd
Sum naphthalenes (N)	124.23	383.75	391.79	316.23	284.80
Sum fluorenes (F)	5.67	19.65	20.21	24.65	15.50
Sum phenanthrenes/anthracenes (PA)	252.02	532.17	549.93	361.02	489.66
Sum dibenzothiophenes (D)	10.88	42.88	44.87	32.44	37.80
Sum fluoranthenes/pyrenes (FP)	32.02	64.30	65.78	61.63	64.39
Sum chrysenes (C)	31.54	70.16	75.04	73.12	73.35
Sum C20H12 aromatics (C20)	62.31	122.57	132.77	118.42	131.85
Sum 4,5 PAH (4,5 PAH)	123.89	238.82	257.80	241.25	247.34
Sum PAH (t-PAH)	527.57	1264.17	1308.63	1012.40	1122.52
N/PA	0.49	0.72	0.71	0.88	0.58
N/perylene	2.54	4.82	4.40	3.84	3.29
F/perylene	0.12	0.25	0.23	0.30	0.18
PA/perylene	5.14	6.69	6.17	4.38	5.66
FP/perylene	0.65	0.81	0.74	0.75	0.74
t-PAH/perylene	10.77	15.89	14.69	12.28	12.98

† - PAH fraction partially lost    o - coelutes with another isomer    # - very low recovery due to activated Cu treatment for S removal    \* - duplicate analysis  
 § - % recovery of some methylated homologs assumed to be the same as that of methylated phenanthrenes    nd - not detected, below MDL

Sample Phase I	6B/1	6B/2	6B/3	6C/1	P-blk/1&2
<b>Surrogate Recovery (%)</b>					
hexamethylbenzene	52	50	76	44	65 58
n-dodecylbenzene	84	85	116	77	81 75
4-terphenyl-D14	71	66	109	94	71 52
<b>PAH (ng/g dry)</b>					
naphthalene	1.67	1.25	0.80	6.82	nd
C1-naphthalenes	6.64	4.95	2.57	38.60	nd
2-methylnaphthalene	3.69	2.74	1.48	20.46	nd
1-methylnaphthalene	2.99	2.24	1.11	18.18	nd
C2-naphthalenes	20.40	16.02	10.12	82.29	nd
2,6-dimethylnaphthalene <sup>o</sup>	1.87	1.35	0.62	10.93	nd
C3-naphthalenes	9.68	6.46	2.59	61.88	nd
2,3,5-trimethylnaphthalene	1.94	1.26	0.38	11.07	nd
C4-naphthalenes	nd	nd	nd	29.62	nd
biphenyl	1.47	1.16	0.63	7.35	nd
acenaphthylene	nd	nd	nd	0.05	nd
acenaphthene	nd	nd	nd	0.55	nd
fluorene	0.92	0.61	0.29	4.80	nd
2-methylfluorene	0.72	0.22	nd	4.04	nd
C1-fluorenes	0.01	nd	nd	11.08	nd
C2-fluorenes	nd	nd	nd	17.66	nd
C3-fluorenes	nd	nd	nd	20.77	nd
phenanthrene	7.00	5.58	3.13	26.04	nd
1-methylphenanthrene	4.34	3.76	1.97	12.82	nd
anthracene	nd	nd	nd	0.41	nd
C1-phenanthrenes/anthracenes	22.65	20.88	13.46	69.36	nd
C2-phenanthrenes/anthracenes	15.41	11.86	5.47	49.23	nd
3,6-dimethylphenanthrene	0.45	0.28	nd	2.54	nd
C3-phenanthrenes/anthracenes	5.93	4.54	1.72	30.62	nd
C4-phenanthrenes/anthracenes	nd	nd	5.50	1.26	nd
2,3-benzofluorene	0.54	0.26	nd	4.02	nd
1,1'-binaphthalene	nd	nd	nd	nd	nd
dibenzothiophenes <sup>#</sup>	2.44	1.57	nd	0.76	nd
C1-dibenzothiophenes <sup>#</sup>	nd	nd	nd	0.69	nd
C2-dibenzothiophenes <sup>#</sup>	0.59	0.25	nd	nd	nd
C3-dibenzothiophenes <sup>#</sup>	nd	nd	nd	nd	nd
C4-dibenzothiophenes <sup>#</sup>	nd	nd	nd	nd	nd
fluoranthene	1.51	1.14	0.76	6.02	nd
pyrene	2.01	1.57	1.19	8.02	nd
C1-fluoranthenes/pyrenes	2.40	1.50	0.58	18.36	nd
C2-fluoranthenes/pyrenes	1.03	0.87	0.42	16.52	nd

Sample Phase I	6B/1	6B/2	6B/3	6C/1	P-blk/1&2
<b>PAH (ng/g dry) (cont.)</b>					
C3-fluoranthenes/pyrenes	nd	nd	nd	5.60	nd
C4-fluoranthenes/pyrenes	nd	nd	nd	4.99	nd
benz(a)anthracene	0.36	0.20	nd	1.93	nd
chrysene/triphenylene	4.48	3.62	2.35	15.83	nd
C1-chrysenes/triphenylenes	3.71	2.13	0.63	21.68	nd
C2-chrysenes/triphenylenes	nd	0.16	nd	14.22	nd
C3-chrysenes/triphenylenes	nd	nd	nd	4.56	nd
C4-chrysenes/triphenylenes	nd	nd	nd	nd	nd
benzo(k)fluoranthene	nd	nd	nd	1.50	nd
benzo(b)fluoranthene	2.09	1.45	0.62	12.93	nd
benzo(e)pyrene	2.07	1.48	0.50	13.80	nd
benzo(a)pyrene	nd	nd	nd	1.08	nd
9,10-diphenylanthracene	nd	nd	nd	nd	nd
perylene	21.56	17.87	10.75	52.24	nd
indeno(1,2,3-cd)pyrene	nd	nd	nd	3.98	nd
dibenz(a,h)anthracene	nd	nd	nd	2.22	nd
picene	nd	nd	nd	2.99	nd
benzo(ghi)perylene	nd	nd	nd	12.40	nd
anthanthrene	nd	nd	nd	nd	nd
coronene	nd	nd	nd	3.08	nd
1,2,4,5-dibenzopyrene	nd	nd	nd	nd	nd
C1-C20H12 aromatics	0.44	0.85	0.48	29.15	nd
C2-C20H12 aromatics	nd	nd	nd	3.61	nd
C3-C20H12 aromatics	nd	nd	nd	nd	nd
C4-C20H12 aromatics	nd	nd	nd	nd	nd
Sum naphthalenes (N)	38.39	28.68	16.08	230.14	
Sum fluorenes (F)	0.94	0.61	0.29	54.32	
Sum phenanthrenes/anthracenes (PA)	50.98	42.87	29.27	176.93	
Sum dibenzothiophenes (D)	3.03	1.82	nd	1.44	
Sum fluoranthenes/pyrenes (FP)	6.94	5.08	2.95	59.52	
Sum chrysenes (C)	8.19	5.92	2.98	56.29	
Sum C20H12 aromatics (C20)	26.16	21.65	12.35	114.32	
Sum 4,5 PAH (4,5 PAH)	41.21	31.99	17.80	199.29	
Sum PAH (t-PAH)	137.00	108.23	64.56	720.59	
N/PA	0.75	0.67	0.55	1.30	
N/perylene	1.78	1.60	1.50	4.41	
F/perylene	0.04	0.03	0.03	1.04	
PA/perylene	2.37	2.40	2.72	3.39	
FP/perylene	0.32	0.28	0.27	1.14	
t-PAH/perylene	6.36	6.06	6.01	13.79	

† - PAH fraction partially lost    ◊ - coelutes with another isomer    # - very low recovery due to activated Cu treatment for S removal    \* - duplicate analysis  
 § - % recovery of some methylated homologs assumed to be the same as that of methylated phenanthrenes    nd - not detected, below MDL

Sample Phase II	1D/2	2E/1	2E/2	3B/1†	5(1)/1
<b>Surrogate Recovery (%)</b>					
hexamethylbenzene	67	43	37	14	33
n-dodecylbenzene	103	83	56	26	70
4-terphenyl-D14	120	80	57	30	77
<b>PAH (ng/g dry)</b>					
naphthalene	12.87	0.30	0.34	0.77	0.17
C1-naphthalenes	53.25	2.37	1.19	4.21	0.35
2-methylnaphthalene	30.42	1.38	0.68	2.36	0.18
1-methylnaphthalene	22.97	1.00	0.50	1.86	0.17
C2-naphthalenes	90.50	10.20	4.74	12.10	4.41
2,6-dimethylnaphthalene <sup>o</sup>	24.58	0.98	0.49	1.30	0.15
C3-naphthalenes	58.78	5.44	3.29	6.43	0.63
2,3,5-trimethylnaphthalene	11.22	0.84	0.45	0.90	0.08
C4-naphthalenes	17.31	1.34	1.02	2.92	0.14
biphenyl	12.66	0.95	0.44	1.14	0.14
acenaphthylene	nd	nd	nd	nd	nd
acenaphthene	1.08	0.05	nd	0.08	nd
fluorene	5.23	0.56	0.31	0.56	0.12
2-methylfluorene	3.68	0.39	0.15	0.32	nd
C1-fluorenes	10.13	1.57	0.96	1.21	0.41
C2-fluorenes	12.17	1.84	1.10	1.88	0.43
C3-fluorenes	nd	3.02	nd	nd	0.87
phenanthrene	25.99	3.84	2.14	3.21	0.97
1-methylphenanthrene	1.24	2.43	1.39	1.28	0.59
anthracene	nd	nd	0.07	nd	nd
C1-phenanthrenes/anthracenes	36.14	8.91	5.67	18.79	2.59
C2-phenanthrenes/anthracenes	50.88	8.32	4.66	6.81	1.92
3,6-dimethylphenanthrene	3.88	0.37	0.22	0.39	0.08
C3-phenanthrenes/anthracenes	44.19	5.43	2.95	6.75	1.13
C4-phenanthrenes/anthracenes	nd	nd	nd	1.10	nd
2,3-benzofluorene	2.35	0.35	0.13	0.36	nd
1,1'-binaphthalene	nd	nd	nd	nd	nd
dibenzothiophene <sup>#</sup>	0.91	nd	nd	0.16	nd
C1-dibenzothiophenes <sup>#</sup>	1.77	nd	nd	0.05	nd
C2-dibenzothiophenes <sup>#</sup>	1.75	nd	nd	nd	nd
C3-dibenzothiophenes <sup>#</sup>	nd	nd	nd	nd	nd
C4-dibenzothiophenes <sup>#</sup>	nd	nd	nd	nd	nd
fluoranthene	4.10	0.57	0.35	0.54	0.27
pyrene	6.09	0.95	0.87	0.79	0.29
C1-fluoranthenes/pyrenes	13.84	1.99	1.11	1.92	0.33
C2-fluoranthenes/pyrenes	13.47	2.14	1.28	2.15	0.34

Sample Phase II	1D/2	2E/1	2E/2	3B/1†	5(1)/1
<b>PAH (ng/g dry) (cont.)</b>					
C3-fluoranthenes/pyrenes	5.09	1.81	nd	1.35	nd
C4-fluoranthenes/pyrenes	3.97	0.26	nd	0.32	nd
benz(a)anthracene	0.97	0.23	0.24	nd	nd
chrysene/triphenylene	12.39	2.53	1.76	1.76	0.95
C1-chrysenes/triphenylenes	19.19	3.78	2.24	2.92	0.54
C2-chrysenes/triphenylenes	16.51	2.34	0.88	3.14	nd
C3-chrysenes/triphenylenes	11.29	nd	nd	nd	nd
C4-chrysenes/triphenylenes	6.88	nd	nd	nd	nd
benzo(k)fluoranthene	0.32	0.17	0.14	0.24	nd
benzo(b)fluoranthene	6.22	0.98	0.66	1.21	0.41
benzo(e)pyrene	9.50	1.65	0.88	1.64	0.32
benzo(a)pyrene	1.12	0.17	nd	0.37	nd
9,10-diphenylanthracene	nd	nd	nd	nd	nd
perylene	45.47	5.17	3.14	7.49	1.91
indeno(1,2,3-cd)pyrene	2.71	nd	nd	nd	nd
dibenz(a,h)anthracene	3.67	nd	nd	nd	nd
picene	11.58	nd	nd	nd	nd
benzo(ghi)perylene	9.07	0.59	nd	0.83	nd
anthanthrene	0.69	nd	nd	nd	nd
coronene	11.66	nd	nd	nd	nd
1,2,4,5-dibenzopyrene	18.69	nd	nd	nd	nd
C1-C20H12 aromatics	22.47	nd	1.76	2.86	1.14
C2-C20H12 aromatics	24.77	nd	nd	nd	nd
C3-C20H12 aromatics	5.55	nd	nd	nd	nd
C4-C20H12 aromatics	nd	nd	nd	nd	nd
Sum naphthalenes (N)	257.30	20.62	11.05	27.74	5.85
Sum fluorenes (F)	27.53	6.99	2.37	3.65	1.83
Sum phenanthrenes/anthracenes (PA)	157.20	26.50	15.49	36.66	6.61
Sum dibenzothiophenes (D)	4.43	nd	nd	0.21	nd
Sum fluoranthenes/pyrenes (FP)	46.57	7.71	3.43	7.07	1.23
Sum chrysenes (C)	66.25	8.64	4.89	7.82	1.49
Sum C20H12 aromatics (C20)	115.41	8.13	6.60	13.80	3.78
Sum 4,5 PAH (4,5 PAH)	176.41	24.71	13.39	25.84	5.35
Sum PAH (t-PAH)	725.23	79.78	44.15	98.05	20.77
N/PA	1.64	0.78	0.71	0.76	0.89
N/perylene	5.66	3.99	3.52	3.70	3.06
F/perylene	0.61	1.35	0.75	0.49	0.96
PA/perylene	3.46	5.12	4.93	4.89	3.45
FP/perylene	1.02	1.49	1.09	0.94	0.64
t-PAH/perylene	15.95	15.42	14.04	13.09	10.85

† – PAH fraction partially lost    o – coelutes with another isomer    # – very low recovery due to activated Cu treatment for S removal    \* – duplicate analysis  
 § – % recovery of some methylated homologs assumed to be the same as that of methylated phenanthrenes    nd – not detected, below MDL

Sample Phase II	5(2)/1	5(5)/1	5(5)/1*	5(10)/1	5(10)/2
<b>Surrogate Recovery (%)</b>					
hexamethylbenzene	40	44	34	30	41
n-dodecylbenzene	56	67	63	67	63
4-terphenyl-D14	55	77	77	69	65
<b>PAH (ng/g dry)</b>					
naphthalene	0.23	1.33	0.12	nd	0.10
C1-naphthalenes	1.18	11.29	4.07	0.72	0.58
2-methylnaphthalene	0.68	6.19	2.10	0.40	0.36
1-methylnaphthalene	0.50	5.12	1.97	0.33	0.23
C2-naphthalenes	5.82	29.31	18.12	6.77	5.50
2,6-dimethylnaphthalene <sup>o</sup>	0.33	3.76	2.01	0.55	0.66
C3-naphthalenes	1.29	18.70	14.61	2.54	1.61
2,3,5-trimethylnaphthalene	0.21	3.60	2.21	0.43	0.28
C4-naphthalenes	0.08	6.46	6.56	0.35	0.27
biphenyl	0.43	3.32	1.58	0.49	0.34
acenaphthylene	nd	nd	nd	nd	nd
acenaphthene	nd	0.21	0.07	nd	nd
fluorene	0.17	1.75	1.33	0.33	0.22
2-methylfluorene	nd	0.81	2.55	0.14	nd
C1-fluorenes	0.22	3.11	3.15	0.59	0.42
C2-fluorenes	0.57	3.57	5.17	0.73	nd
C3-fluorenes	nd	2.36	3.56	0.53	nd
phenanthrene	2.19	10.98	9.73	3.45	3.04
1-methylphenanthrene	1.13	5.43	4.58	1.88	1.82
anthracene	nd	0.33	0.22	0.10	nd
C1-phenanthrenes/anthracenes	8.54	24.63	26.73	7.83	7.46
C2-phenanthrenes/anthracenes	3.17	19.79	18.84	7.73	5.62
3,6-dimethylphenanthrene	0.08	0.91	0.96	0.33	0.17
C3-phenanthrenes/anthracenes	1.15	13.57	15.18	4.48	1.83
C4-phenanthrenes/anthracenes	nd	9.95	9.15	nd	nd
2,3-benzofluorene	nd	1.24	1.24	0.24	0.09
1,1'-binaphthalene	nd	nd	nd	nd	nd
dibenzothiophene <sup>#</sup>	nd	nd	nd	nd	nd
C1-dibenzothiophenes <sup>#</sup>	nd	0.08	0.08	nd	nd
C2-dibenzothiophenes <sup>#</sup>	nd	nd	nd	nd	nd
C3-dibenzothiophenes <sup>#</sup>	nd	nd	nd	nd	nd
C4-dibenzothiophenes <sup>#</sup>	nd	nd	nd	nd	nd
fluoranthene	0.33	1.90	1.90	0.75	0.55
pyrene	0.54	2.93	2.87	1.17	0.90
C1-fluoranthenes/pyrenes	0.50	6.24	5.91	1.87	1.02
C2-fluoranthenes/pyrenes	0.39	5.67	5.54	1.86	0.73

Sample Phase II	5(2)/1	5(5)/1	5(5)/1*	5(10)/1	5(10)/2
<b>PAH (ng/g dry) (cont.)</b>					
C3-fluoranthenes/pyrenes	nd	2.30	2.50	0.65	nd
C4-fluoranthenes/pyrenes	nd	0.80	0.78	nd	nd
benz(a)anthracene	0.16	0.72	0.79	0.41	0.33
chrysene/triphenylene	1.89	7.06	6.02	2.93	2.74
C1-chrysenes/triphenylenes	1.10	9.73	8.96	3.65	2.07
C2-chrysenes/triphenylenes	nd	5.55	4.60	1.14	0.37
C3-chrysenes/triphenylenes	nd	nd	nd	nd	nd
C4-chrysenes/triphenylenes	nd	nd	nd	nd	nd
benzo(k)fluoranthene	nd	0.44	0.41	0.14	nd
benzo(b)fluoranthene	0.68	3.70	3.67	1.38	0.87
benzo(e)pyrene	0.87	4.75	4.13	1.59	1.21
benzo(a)pyrene	nd	0.72	0.70	nd	nd
9,10-diphenylanthracene	nd	nd	nd	nd	nd
perylene	6.34	33.70	24.70	9.23	8.50
indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd
dibenz(a,h)anthracene	nd	nd	nd	nd	nd
picene	nd	nd	nd	nd	nd
benzo(ghi)perylene	nd	3.09	2.03	nd	nd
anthanthrene	nd	nd	nd	nd	nd
coronene	nd	nd	nd	nd	nd
1,2,4,5-dibenzopyrene	nd	nd	nd	nd	nd
C1-C20H12 aromatics	0.89	5.95	4.62	0.98	0.96
C2-C20H12 aromatics	nd	nd	nd	nd	nd
C3-C20H12 aromatics	nd	nd	nd	nd	nd
C4-C20H12 aromatics	nd	nd	nd	nd	nd
Sum naphthalenes (N)	8.93	70.85	45.50	10.92	8.72
Sum fluorenes (F)	0.96	10.79	13.21	2.18	0.65
Sum phenanthrenes/anthracenes (PA)	15.05	79.24	79.85	23.59	17.95
Sum dibenzothiophenes (D)	nd	0.08	0.08	nd	nd
Sum fluoranthenes/pyrenes (FP)	1.76	19.85	19.50	6.31	3.20
Sum chrysenes (C)	2.99	22.35	19.58	7.72	5.18
Sum C20H12 aromatics (C20)	8.79	49.26	38.23	13.32	11.54
Sum 4,5 PAH (4,5 PAH)	12.80	86.23	73.47	26.78	19.29
Sum PAH (t-PAH)	38.73	257.25	219.63	64.63	47.33
N/PA	0.59	0.89	0.57	0.46	0.49
N/perylene	1.41	2.10	1.84	1.18	1.03
F/perylene	0.15	0.32	0.53	0.24	0.08
PA/perylene	2.37	2.35	3.23	2.56	2.11
FP/perylene	0.28	0.59	0.79	0.68	0.38
t-PAH/perylene	6.11	7.63	8.89	7.00	5.57

† - PAH fraction partially lost    ◊ - coelutes with another isomer    # - very low recovery due to activated Cu treatment for S removal    \* - duplicate analysis  
 § - % recovery of some methylated homologs assumed to be the same as that of methylated phenanthrenes    nd - not detected, below MDL

Sample Phase II	5(10)/3	5(10)/3*	5A/1	5G/2	6A/1
<b>Surrogate Recovery (%)</b>					
hexamethylbenzene	43	58	54	44	48
n-dodecylbenzene	82	73	118	79	72
4-terphenyl-D14	86	79	113	89	102
<b>PAH (ng/g dry)</b>					
naphthalene	nd	0.83	17.35	0.46	19.12
C1-naphthalenes	nd	3.85	105.43	2.75	99.39
2-methylnaphthalene	nd	2.22	58.56	1.55	54.17
1-methylnaphthalene	nd	1.64	47.08	1.21	45.39
C2-naphthalenes	5.75	11.21	204.61	10.58	200.58
2,6-dimethylnaphthalene <sup>o</sup>	0.32	1.37	52.84	0.89	28.52
C3-naphthalenes	3.22	6.24	145.51	6.14	150.58
2,3,5-trimethylnaphthalene	0.56	1.24	27.81	1.26	22.37
C4-naphthalenes	0.77	1.58	64.18	3.32	69.81
biphenyl	0.14	1.21	26.57	0.96	18.88
acenaphthylene	nd	nd	1.78	nd	nd
acenaphthene	nd	nd	2.11	0.09	1.86
fluorene	0.38	0.69	13.11	0.74	12.13
2-methylfluorene	0.24	1.19	9.49	0.40	9.73
C1-fluorenes	0.85	1.48	29.77	1.66	24.32
C2-fluorenes	1.93	2.56	nd	1.80	31.94
C3-fluorenes	nd	1.92	nd	2.29	31.02
phenanthrene	4.90	5.79	70.44	4.86	55.90
1-methylphenanthrene	2.62	2.78	37.26	1.91	26.20
anthracene	nd	0.15	1.09	0.06	0.97
C1-phenanthrenes/anthracenes	13.54	18.63	114.23	10.19	126.84
C2-phenanthrenes/anthracenes	10.27	12.38	120.50	9.25	96.42
3,6-dimethylphenanthrene	0.46	0.52	7.13	0.45	4.96
C3-phenanthrenes/anthracenes	4.93	6.90	84.94	6.21	61.31
C4-phenanthrenes/anthracenes	1.65	2.62	nd	1.44	16.30
2,3-benzofluorene	0.38	0.46	7.99	0.49	10.27
1,1'-binaphthalene	nd	nd	nd	nd	nd
dibenzothiophene*	nd	nd	1.00	nd	1.01
C1-dibenzothiophenes*	nd	nd	2.84	0.06	1.84
C2-dibenzothiophenes*	nd	nd	4.70	nd	nd
C3-dibenzothiophenes*	nd	nd	nd	nd	nd
C4-dibenzothiophenes*	nd	nd	nd	nd	nd
fluoranthene	0.99	1.13	14.50	1.13	13.71
pyrene	1.46	1.57	22.45	1.50	17.64
C1-fluoranthenes/pyrenes	2.39	3.05	36.36	2.82	35.17
C2-fluoranthenes/pyrenes	1.78	2.83	33.93	2.74	29.24

Sample Phase II	5(10)/3	5(10)/3*	5A/1	5G/2	6A/1
<b>PAH (ng/g dry) (cont.)</b>					
C3-fluoranthenes/pyrenes	nd	nd	10.80	1.77	10.08
C4-fluoranthenes/pyrenes	nd	nd	10.79	0.03	9.96
benz(a)anthracene	0.32	0.59	3.52	0.48	4.21
chrysene/triphenylene	3.85	4.31	42.78	3.13	31.98
C1-chrysenes/triphenylenes	3.72	5.21	60.81	3.97	48.66
C2-chrysenes/triphenylenes	0.88	2.02	50.27	1.18	33.83
C3-chrysenes/triphenylenes	nd	nd	27.20	nd	22.01
C4-chrysenes/triphenylenes	nd	nd	11.51	nd	1.08
benzo(k)fluoranthene	nd	0.27	3.47	0.24	1.78
benzo(b)fluoranthene	1.47	2.56	27.43	2.12	21.69
benzo(e)pyrene	2.04	2.87	32.90	2.51	24.76
benzo(a)pyrene	nd	0.32	6.00	nd	6.02
9,10-diphenylanthracene	nd	nd	nd	nd	nd
perylene	13.27	16.64	176.60	14.44	150.07
indeno(1,2,3-cd)pyrene	nd	nd	9.95	nd	8.36
dibenz(a,h)anthracene	nd	nd	6.99	nd	5.02
picene	nd	nd	24.76	nd	16.54
benzo(ghi)perylene	nd	0.67	42.95	nd	28.99
anthanthrene	nd	nd	4.08	nd	nd
coronene	nd	nd	26.28	nd	14.31
1,2,4,5-dibenzopyrene	nd	nd	76.86	nd	25.99
C1-C20H12 aromatics	0.93	1.90	69.75	1.16	66.08
C2-C20H12 aromatics	nd	nd	76.89	nd	37.09
C3-C20H12 aromatics	nd	nd	16.22	nd	9.90
C4-C20H12 aromatics	nd	nd	14.60	nd	1.07
Sum naphthalenes (N)	10.06	25.09	589.92	24.13	568.00
Sum fluorenes (F)	3.16	6.64	42.88	6.49	99.41
Sum phenanthrenes/anthracenes (PA)	35.30	46.47	391.20	32.00	357.74
Sum dibenzothiophenes (D)	nd	nd	8.54	0.06	2.85
Sum fluoranthenes/pyrenes (FP)	6.62	8.57	128.83	10.00	115.80
Sum chrysenes (C)	8.45	11.53	192.58	8.28	137.56
Sum C20H12 aromatics (C20)	17.71	24.55	423.87	20.46	318.45
Sum 4,5 PAH (4,5 PAH)	32.18	43.34	571.33	38.07	461.89
Sum PAH (t-PAH)	81.81	124.42	1958.82	102.57	1705.72
N/PA	0.29	0.54	1.51	0.75	1.59
N/perylene	0.76	1.51	3.34	1.67	3.78
F/perylene	0.24	0.40	0.24	0.45	0.66
PA/perylene	2.66	2.79	2.22	2.22	2.38
FP/perylene	0.50	0.52	0.73	0.69	0.77
t-PAH/perylene	6.16	7.48	11.09	7.11	11.37

† – PAH fraction partially lost    ◊ – coelutes with another isomer    # – very low recovery due to activated Cu treatment for S removal    \* – duplicate analysis  
 § – % recovery of some methylated homologs assumed to be the same as that of methylated phenanthrenes    nd – not detected, below MDL

Sample Phase II	6D/1	6G/1	6G/2	6G/3
<b>Surrogate Recovery (%)</b>				
hexamethylbenzene	34	68	55	56
n-dodecylbenzene	81	82	63	68
4-terphenyl-D14	126	108	114	90
<b>PAH (ng/g dry)</b>				
naphthalene	0.46	19.77	11.17	19.22
C1-naphthalenes	6.20	106.97	78.30	98.34
2-methylnaphthalene	3.05	57.91	41.75	53.46
1-methylnaphthalene	3.14	49.22	36.64	45.04
C2-naphthalenes	27.44	183.07	151.26	172.39
2,6-dimethylnaphthalene <sup>o</sup>	2.71	19.05	13.31	22.22
C3-naphthalenes	25.23	142.69	111.40	135.02
2,3,5-trimethylnaphthalene	3.88	26.52	14.35	25.64
C4-naphthalenes	9.59	61.07	40.64	56.42
biphenyl	1.93	16.97	9.47	16.98
acenaphthylene	nd	nd	nd	nd
acenaphthene	0.20	2.20	nd	1.96
fluorene	1.86	11.17	5.63	10.31
2-methylfluorene	1.30	9.02	5.76	9.60
C1-fluorenes	4.72	32.40	26.16	32.62
C2-fluorenes	1.72	44.82	30.36	42.71
C3-fluorenes	0.47	86.31	44.25	80.21
phenanthrene	12.27	60.86	34.78	55.75
1-methylphenanthrene	6.13	27.90	17.18	28.23
anthracene	0.43	0.93	0.53	67.41
C1-phenanthrenes/anthracenes	33.57	192.46	135.04	155.03
C2-phenanthrenes/anthracenes	22.62	142.74	117.17	136.10
3,6-dimethylphenanthrene	1.14	7.63	2.76	7.29
C3-phenanthrenes/anthracenes	14.38	106.39	98.78	104.12
C4-phenanthrenes/anthracenes	3.88	6.06	26.26	5.71
2,3-benzofluorene	1.86	9.78	7.00	8.36
1,1'-binaphthalene	nd	nd	nd	nd
dibenzothiophene <sup>#</sup>	nd	nd	nd	nd
C1-dibenzothiophenes <sup>#</sup>	0.43	3.83	0.75	3.20
C2-dibenzothiophenes <sup>#</sup>	0.05	1.20	nd	0.44
C3-dibenzothiophenes <sup>#</sup>	nd	nd	nd	nd
C4-dibenzothiophenes <sup>#</sup>	nd	nd	nd	nd
fluoranthene	3.84	12.31	12.96	11.04
pyrene	5.21	15.36	14.71	14.33
C1-fluoranthenes/pyrenes	6.56	38.80	25.71	38.79
C2-fluoranthenes/pyrenes	5.58	38.89	23.54	36.10

Sample Phase II	6D/1	6G/1	6G/2	6G/3
<b>PAH (ng/g dry) (cont.)</b>				
C3-fluoranthenes/pyrenes	2.13	17.48	5.55	18.44
C4-fluoranthenes/pyrenes	1.48	14.96	nd	16.63
benz(a)anthracene	1.38	3.47	2.91	3.92
chrysene/triphenylene	7.70	32.32	19.43	29.82
C1-chrysenes/triphenylenes	9.08	65.46	47.77	60.21
C2-chrysenes/triphenylenes	4.77	76.82	49.37	68.74
C3-chrysenes/triphenylenes	0.46	58.85	40.45	50.77
C4-chrysenes/triphenylenes	0.05	nd	nd	nd
benzo(k)fluoranthene	1.47	2.77	1.27	1.78
benzo(b)fluoranthene	6.48	21.35	12.35	18.63
benzo(e)pyrene	6.90	26.27	13.52	25.56
benzo(a)pyrene	2.08	5.31	3.76	5.50
9,10-diphenylanthracene	nd	nd	nd	nd
perylene	28.94	186.68	147.16	166.37
indeno(1,2,3-cd)pyrene	nd	12.44	nd	12.17
dibenz(a,h)anthracene	nd	7.70	nd	8.71
picene	nd	28.56	18.92	23.63
benzo(ghi)perylene	6.79	34.14	20.31	31.36
anthanthrene	nd	1.77	nd	1.78
coronene	2.05	16.26	10.24	16.84
1,2,4,5-dibenzopyrene	nd	28.58	20.12	31.90
C1-C20H12 aromatics	14.90	74.38	59.09	77.34
C2-C20H12 aromatics	nd	73.15	25.34	35.86
C3-C20H12 aromatics	nd	59.40	15.10	25.89
C4-C20H12 aromatics	nd	nd	nd	nd
Sum naphthalenes (N)	71.63	532.62	406.08	503.62
Sum fluorenes (F)	8.77	174.71	106.39	165.84
Sum phenanthrenes/anthracenes (PA)	87.14	509.46	412.56	524.13
Sum dibenzothiophenes (D)	0.48	5.03	0.75	3.64
Sum fluoranthenes/pyrenes (FP)	24.81	137.82	82.47	135.32
Sum chrysenes (C)	22.06	233.45	157.57	209.54
Sum C20H12 aromatics (C20)	60.76	449.30	277.16	356.92
Sum 4,5 PAH (4,5 PAH)	94.11	617.12	420.03	566.63
Sum PAH (t-PAH)	287.15	2185.22	1518.36	2034.43
N/PA	0.82	1.05	0.99	0.96
N/perylene	2.48	2.85	2.77	3.03
F/perylene	0.30	0.94	0.72	1.00
PA/perylene	3.01	2.73	2.83	3.15
FP/perylene	0.86	0.74	0.56	0.81
t-PAH/perylene	9.92	11.71	10.32	12.23

† - PAH fraction partially lost    o - coelutes with another isomer    # - very low recovery due to activated Cu treatment for S removal    \* - duplicate analysis  
 § - % recovery of some methylated homologs assumed to be the same as that of methylated phenanthrenes    nd - not detected, below MDL

Table 16. Distribution (ng/g) of triterpenoids in gross sediments. Phase I: analyzed in 1997–98, Phase II: analyzed in 1998–99.

Triterpanes (ng/g)*	Stations & Samples															
	Phase I															
	2F/1	2F/2	3A/1	3A/2	4A/1	4A/2	WPB/1	WPB/2	5F/1	5F/2	SL/1	SL/2	6B/1	6B/2		
17 $\alpha$ (H),21 $\beta$ (H)-22,29,30-trisnorhopane	2.2	1.5	4.4	5.6	3.6	1.6	1.6	1.2	4.2	3.3	6.5	8.8	2.5	1.2		
17 $\beta$ (H),21 $\beta$ (H)-22,29,30-trisnorhopane	5.4	3.8	13.1	16.4	6.0	5.6	4.1	3.0	22.2	15.6	29.3	37.3	5.5	3.2		
17 $\alpha$ (H),21 $\beta$ (H)-30-norhopane	6.8	3.9	14.3	17.7	9.3	9.8	4.6	3.3	11.3	8.7	15.8	24.8	7.0	3.5		
17 $\beta$ (H),21 $\alpha$ (H)-30-norhopane	4.8	3.0	18.5	17.4	9.8	5.7	3.2	2.0	19.9	9.2	22.9	36.9	4.0	2.3		
17 $\beta$ (H),21 $\beta$ (H)-30-norhopane <sup>o</sup>	12.5	10.9	29.5	24.7	11.9	14.5	6.1	4.1	34.7	23.3	41.6	56.8	8.9	5.9		
18 $\alpha$ (H)-oleanane	0.5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd		
17 $\alpha$ (H),21 $\beta$ (H)-hopane	4.1	2.4	8.5	11.1	7.2	6.3	3.3	2.2	7.2	5.1	8.8	17.0	4.5	2.2		
17 $\beta$ (H),21 $\beta$ (H)-hopane	2.2	1.1	6.1	6.3	2.4	2.8	2.1	1.3	11.8	6.7	11.3	16.4	2.9	1.5		
17 $\beta$ (H),21 $\beta$ (H)-30-homohopane	1.4	0.7	4.8	5.3	1.4	1.9	1.6	1.0	10.0	5.2	9.7	15.1	2.5	1.2		
hop-13(18)-ene	2.1	1.1	4.2	5.3	nd	nd	2.9	1.2	17.8	12.2	23.1	28.8	6.8	3.6		
hop-21(22)-ene	18.3	6.0	nd	nd	5.6	5.3	4.4	3.0	13.5	10.0	17.8	42.2	4.8	3.5		
diploptene	71.6	31.5	210.4	317.5	28.1	43.7	26.5	18.0	201.8	91.5	159.4	509.9	36.2	22.1		
	Phase II															
	1D/2	2E/1	2E/2	3B/1	5(1)/1	5(2)/1	5(5)/1	5(10)/1	5(10)/3	5A/1	5G/2	6A/1	6C/1	6D/1	6G/1	6G/2
17 $\alpha$ (H),21 $\beta$ (H)-22,29,30-trisnorhopane	0.46	0.37	0.34	2.90	0.58	nd	1.58	1.38	0.53	9.27	0.33	7.68	5.75	2.68	5.55	9.45
17 $\beta$ (H),21 $\beta$ (H)-22,29,30-trisnorhopane	0.49	0.62	0.53	7.51	0.53	1.07	5.93	1.02	1.70	23.50	0.60	23.85	12.61	3.65	34.02	40.89
17 $\alpha$ (H),21 $\beta$ (H)-30-norhopane	0.61	1.43	1.13	8.12	1.95	0.68	3.86	4.77	1.81	24.66	0.76	19.22	15.24	6.18	18.71	22.84
17 $\beta$ (H),21 $\alpha$ (H)-30-norhopane	nd	1.57	2.18	5.74	1.99	1.20	3.89	1.70	1.80	16.91	1.06	15.26	10.14	5.02	19.49	22.67
17 $\beta$ (H),21 $\beta$ (H)-30-norhopane <sup>o</sup>	0.89	1.08	1.52	8.43	1.46	1.04	9.24	1.96	1.74	42.26	0.90	39.36	22.25	6.86	44.34	63.99
18 $\alpha$ (H)-oleanane	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
17 $\alpha$ (H),21 $\beta$ (H)-hopane	0.45	0.85	0.66	5.50	1.27	0.43	2.71	2.54	0.86	17.51	0.47	14.04	10.71	4.28	14.07	16.35
17 $\beta$ (H),21 $\beta$ (H)-hopane	0.20	0.29	0.30	3.51	nd	0.35	2.96	0.56	0.47	9.41	0.20	11.79	8.64	2.14	18.24	22.82
17 $\beta$ (H),21 $\beta$ (H)-30-homohopane	0.15	tr	tr	2.50	tr	0.23	2.10	0.39	0.30	6.42	0.11	11.08	6.46	1.85	16.99	19.45
hop-13(18)-ene	nd	nd	nd	2.24	nd	nd	5.21	nd	tr	7.96	tr	26.98	13.14	2.44	20.54	35.56
hop-21(22)-ene	nd	nd	nd	nd	nd	nd	nd	nd	nd	tr	nd	tr	tr	nd	tr	tr
diploptene	2.36	3.47	2.32	49.34	1.78	2.02	24.74	5.02	4.99	141.15	1.37	153.55	80.61	23.44	141.81	221.73

\* – quantitation based on m/z 191

o – may be coeluting with C<sub>30</sub> $\alpha$  $\beta$  in some samples

I.S. – D<sub>2</sub>C<sub>27</sub>-ospadoamtime

nd – not detected, tr – trace amount

Table 17. Distribution (ng/g) of steroids in gross sediments. Phase I: analyzed in 1997–98, Phase II: analyzed in 1998–99.

Steranes (ng/g)*	Stations & Samples															
	Phase I															
	2F/1	2F/2	3A/1	3A/2	4A/1	4A/2	WPB/1	WPB/2	5F/1	5F/2	SL/1	SL/2	6B/1	6B/2		
5 $\alpha$ (H)-androstane	nd	nd	nd	nd	0.25	nd	nd	nd	nd	nd	nd	1.20	nd	nd		
5 $\alpha$ (H)-pregnane	nd	nd	nd	nd	0.25	nd	nd	nd	nd	nd	nd	0.85	nd	nd		
5 $\beta$ (H)-pregnane	nd	nd	0.95	0.56	1.21	nd	nd	nd	0.72	0.85	2.00	3.32	nd	nd		
20-methyl-5 $\alpha$ (H)-pregnane	nd	nd	0.44	0.83	0.48	nd	nd	nd	0.23	nd	0.76	1.47	nd	nd		
20S-5 $\alpha$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H)-cholestane	nd	nd	2.92	3.59	1.45	0.35	nd	nd	1.84	0.89	2.56	3.66	nd	nd		
20R-5 $\alpha$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H)-cholestane	nd	nd	1.85	2.24	0.89	nd	nd	nd	0.91	0.73	1.26	2.05	nd	nd		
20R-5 $\alpha$ (H), 14 $\beta$ (H), 17 $\beta$ (H)-cholestane	nd	nd	1.44	2.25	0.87	nd	nd	nd	0.92	0.58	1.48	2.80	nd	nd		
20S-5 $\alpha$ (H), 14 $\beta$ (H), 17 $\beta$ (H)-cholestane	nd	nd	1.03	1.86	0.52	nd	nd	nd	nd	nd	1.27	1.84	nd	nd		
20S-5 $\alpha$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H)-ergostane	nd	nd	5.57	5.97	1.80	nd	nd	nd	4.56	2.27	3.19	15.81	nd	nd		
20R-5 $\alpha$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H)-ergostane	nd	nd	8.69	9.51	3.41	nd	nd	nd	4.99	3.18	7.46	9.65	nd	nd		
20R-5 $\alpha$ (H), 14 $\beta$ (H), 17 $\beta$ (H)-ergostane	nd	nd	2.78	3.93	1.39	nd	nd	nd	1.81	nd	2.97	4.23	nd	nd		
20S-5 $\alpha$ (H), 14 $\beta$ (H), 17 $\beta$ (H)-ergostane	nd	nd	2.30	3.74	1.09	nd	nd	nd	1.79	nd	2.74	4.18	nd	nd		
20S-5 $\alpha$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H)-stigmastane	nd	nd	2.21	2.15	1.71	nd	nd	nd	1.36	0.57	3.52	3.93	nd	nd		
20R-5 $\alpha$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H)-stigmastane	2.00	1.51	9.24	11.43	2.86	1.99	0.23	0.12	8.42	5.68	10.76	19.26	1.28	0.88		
20R-5 $\alpha$ (H), 14 $\beta$ (H), 17 $\beta$ (H)-stigmastane	nd	0.40	2.46	3.48	1.57	0.48	nd	nd	2.32	1.39	3.12	4.64	nd	nd		
20S-5 $\alpha$ (H), 14 $\beta$ (H), 17 $\beta$ (H)-stigmastane	nd	nd	1.66	2.32	0.92	nd	nd	nd	1.33	0.67	1.70	2.41	nd	nd		
Steranes (ng/g)*	Phase II															
	1D/2	2E/1	2E/2	3B/1	5(1)/1	5(2)/1	5(5)/1	5(10)/1	5(10)/3	5A/1	5G/2	6A/1	6C/1	6D/1	6G/1	6G/2
5 $\alpha$ (H)-androstane	nd	nd	nd	0.16	nd	nd	nd	0.23	nd	nd	nd	0.49	0.14	nd	0.86	3.43
5 $\alpha$ (H)-pregnane	nd	nd	nd	0.31	0.40	nd	0.48	0.43	0.09	1.04	nd	0.46	0.23	0.30	0.46	0.81
5 $\beta$ (H)-pregnane	nd	0.24	0.11	1.80	0.73	nd	0.58	2.42	1.27	3.33	0.12	1.00	1.15	0.39	0.77	1.04
20-methyl-5 $\alpha$ (H)-pregnane	nd	0.07	0.12	0.70	0.28	0.14	0.46	0.90	0.75	1.68	0.15	0.86	1.03	0.31	0.45	0.90
20S-5 $\alpha$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H)-cholestane	0.08	0.45	0.64	1.64	0.49	0.25	0.64	0.88	0.62	5.08	0.29	2.89	1.86	1.25	1.62	2.03
20R-5 $\alpha$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H)-cholestane	nd	0.53	0.28	1.48	0.44	0.15	0.55	1.11	1.33	3.84	0.14	2.14	1.43	0.72	nd	2.38
20R-5 $\alpha$ (H), 14 $\beta$ (H), 17 $\beta$ (H)-cholestane	nd	0.28	0.18	1.25	0.96	0.16	0.47	nd	0.25	2.39	nd	2.04	0.89	0.88	nd	1.68
20S-5 $\alpha$ (H), 14 $\beta$ (H), 17 $\beta$ (H)-cholestane	nd	0.15	0.12	0.92	0.63	0.06	0.34	nd	0.23	1.91	nd	1.58	0.88	0.54	nd	1.12
20S-5 $\alpha$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H)-ergostane	nd	0.44	0.33	2.28	nd	nd	nd	nd	0.56	4.75	nd	4.20	2.87	0.52	nd	7.29
20R-5 $\alpha$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H)-ergostane	nd	0.57	0.34	1.79	nd	nd	0.88	nd	0.57	8.05	nd	6.17	3.41	1.16	3.39	5.27
20R-5 $\alpha$ (H), 14 $\beta$ (H), 17 $\beta$ (H)-ergostane	nd	0.37	0.24	1.44	0.52	nd	1.20	1.21	1.29	4.23	nd	1.96	1.18	0.66	2.01	3.11
20S-5 $\alpha$ (H), 14 $\beta$ (H), 17 $\beta$ (H)-ergostane	nd	0.37	0.13	1.11	0.61	nd	1.19	1.18	0.99	3.30	nd	1.56	0.98	0.47	1.79	2.75
20S-5 $\alpha$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H)-stigmastane	nd	0.40	0.23	1.18	nd	nd	0.43	0.90	0.81	3.51	nd	3.25	2.04	0.69	1.26	2.77
20R-5 $\alpha$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H)-stigmastane	0.13	0.31	0.25	2.86	0.50	0.09	nd	0.39	0.41	7.68	0.07	8.97	4.25	1.80	5.79	10.84
20R-5 $\alpha$ (H), 14 $\beta$ (H), 17 $\beta$ (H)-stigmastane	0.05	0.31	0.29	1.56	0.69	nd	0.97	1.36	0.98	3.33	nd	2.88	1.71	1.04	1.41	3.51
20S-5 $\alpha$ (H), 14 $\beta$ (H), 17 $\beta$ (H)-stigmastane	nd	0.20	0.16	1.05	0.67	nd	0.53	1.03	0.96	2.09	nd	1.77	1.09	0.78	0.83	2.04

\* – quantitation based on m/z 245, 217 or 218

I.S. – 3,3-d<sub>2</sub>-cholestane nd – not detected

Table 18. Triterpenoids identified in Figures 9 and 10.

Triterpenoids in Figures 9 and 10	
27 18 $\alpha$	18 $\alpha$ (H),21 $\beta$ (H)-22,29,30-trisnorhopane
27 17 $\alpha$	17 $\alpha$ (H),21 $\beta$ (H)-22,29,30-trisnorhopane
29 $\alpha\beta$	17 $\alpha$ (H),21 $\beta$ (H)-30-norhopane
29 $\beta\alpha$	17 $\beta$ (H),21 $\alpha$ (H)-30-norhopane
29 $\beta\beta$	17 $\beta$ (H),21 $\beta$ (H)-30-norhopane
30 $\alpha\beta$	17 $\alpha$ (H),21 $\beta$ (H)-hopane
30 $\beta\beta$	17 $\beta$ (H),21 $\beta$ (H)-hopane
31 $\beta\beta$	17 $\beta$ (H),21 $\beta$ (H)-30-homohopane
31 $\alpha$	22S-17 $\alpha$ (H),21 $\beta$ (H)-30-homohopane
31 $\alpha$	22R-17 $\alpha$ (H),21 $\beta$ (H)-30-homohopane
32 $\alpha$	22S-17 $\alpha$ (H),21 $\beta$ (H)-30,31-bishomohopane
32 $\alpha$	22R-17 $\alpha$ (H),21 $\beta$ (H)-30,31-bishomohopane
33 $\alpha$	22S-17 $\alpha$ (H),21 $\beta$ (H)-31,32-trishomohopane
33 $\alpha$	22R-17 $\alpha$ (H),21 $\beta$ (H)-31,32-trishomohopane
34 $\alpha$	22S-17 $\alpha$ (H),21 $\beta$ (H)-32,33-tetrakishomohopane
34 $\alpha$	22R-17 $\alpha$ (H),21 $\beta$ (H)-32,33-tetrakishomohopane
35 $\alpha$	22S-17 $\alpha$ (H),21 $\beta$ (H)-33,34-pentakishomohopane
35 $\alpha$	22R-17 $\alpha$ (H),21 $\beta$ (H)-33,34-pentakishomohopane
13(18)	hop-13(18)-ene
21(22)	hop-21(22)-ene
Dip	Diploptene

Table 19. Steranes identified in Figures 11 and 12.

Steranes in Figures 11 and 12	
S1	20S-13 $\beta$ ,17 $\alpha$ -diacholestane
S2	20R-13 $\beta$ ,17 $\alpha$ -diacholestane
S3	20S-5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-cholestane
S4	20S-24-Ethyl-13 $\beta$ ,17 $\alpha$ -diacholestane
S4	20R-5 $\alpha$ (H),14 $\beta$ (H),17 $\beta$ (H)-cholestane
S5	20S-5 $\alpha$ (H),14 $\beta$ (H),17 $\beta$ (H)-cholestane
S6	20R-5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-cholestane
S7	20R-24-Ethyl-13 $\beta$ ,17 $\alpha$ -diacholestane
S8	20S-5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-ergostane
S9	20R-5 $\alpha$ (H),14 $\beta$ (H),17 $\beta$ (H)-ergostane
S10	20S-5 $\alpha$ (H),14 $\beta$ (H),17 $\beta$ (H)-ergostane
S11	20R-5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-ergostane
S12	20S-5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-stigmastane
S13	20R-5 $\beta$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-stigmastane
S13	20R-5 $\alpha$ (H),14 $\beta$ (H),17 $\beta$ (H)-stigmastane
S14	20S-5 $\alpha$ (H),14 $\beta$ (H),17 $\beta$ (H)-stigmastane
S15	20R-5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-stigmastane

Table 20. Mean concentrations (ng/g) of *n*-alkanes, and ratios of pristane/phytane (Pr/Ph) and odd/even *n*-alkanes, granulometry, OM and PAHs of sediments, nearshore Beaufort Sea. Phase I: analyzed in 1997–98, Phase II: analyzed in 1998–99. na – not applicable

Station	Depth (m)	Total <i>n</i> -alkanes	C12–C19	C20–C33	Pr/Ph	Odd/Even	4,5 PAH	tPAH	OM %	Gr %	Sd %	St %	Cl %	Mud %
<b>Phase I</b>														
2F	1.90	1878.68	377.91	1426.51	2.19	3.40	92.26	441.38	na	0.00	67.26	24.32	8.42	32.74
3A	6.20	3071.71	493.04	2491.89	2.05	4.17	216.78	999.61	5.60	0.74	17.46	61.07	20.72	81.79
4A	4.50	2850.22	797.63	1858.20	2.31	2.58	178.99	903.08	7.70	55.75	10.14	13.63	20.50	34.12
WPB	2.50	743.97	185.90	519.18	1.54	2.96	30.06	184.83	8.80	0.00	83.44	12.00	4.56	16.56
5F	1.50	2266.30	280.73	1910.39	2.11	3.86	90.28	369.92	5.30	0.00	54.94	35.94	9.12	45.06
SL	2.40	3917.21	565.19	321.98	1.97	3.93	246.30	1776.93	4.90	2.79	29.44	38.27	31.37	69.62
6B	5.50	417.85	75.66	323.08	1.97	3.22	30.33	103.26	6.60	0.00	87.50	8.74	5.64	12.50
<b>Phase II</b>														
1D	6.00	826.21	12.90	781.23	1.85	1.17	176.41	725.23	6.00	0.00	94.87	2.72	2.41	5.13
2E	7.40	258.39	53.78	187.05	1.94	2.13	19.05	61.96	8.00	0.00	93.93	3.35	2.72	6.07
3B	4.20	2958.51	554.31	2295.30	1.80	3.44	176.41	725.23	7.50	0.00	22.80	53.81	23.34	77.16
5(1)	5.80	204.69	20.19	175.12	1.32	3.38	5.35	20.77	8.30	0.25	97.35	0.34	2.26	2.49
5(2)	5.80	258.12	40.57	208.91	1.92	3.29	12.80	38.73	9.10	0.00	96.48	1.68	1.81	3.49
5(5)	6.70	1319.45	181.75	1083.10	2.16	3.26	79.85	237.94	5.40	10.32	67.96	14.63	7.08	21.71
5(10)	8.20	586.19	78.37	424.50	1.72	2.52	26.08	64.59	7.00	0.00	91.98	3.42	4.60	8.02
5A	11.40	7130.21	980.91	5844.17	2.30	3.07	571.33	1958.82	6.80	0.00	2.95	52.30	44.64	97.05
5G	9.30	491.58	58.81	410.65	1.76	2.38	38.07	102.57	4.60	0.00	77.33	18.63	4.04	22.67
6A	3.60	5400.24	882.34	4322.62	2.20	3.19	461.89	1705.72	4.80	0.00	10.85	16.63	79.29	95.92
6B	5.50	417.85	75.66	323.08	1.97	3.22	30.33	103.26	6.60	0.00	87.50	8.74	5.64	12.50
6C	16.10	2244.43	394.76	1772.20	2.18	3.00	199.29	720.59	7.80	0.00	64.11	2.42	33.48	35.90
6D	18.40	754.64	115.80	611.22	2.32	2.83	94.11	287.15	7.60	0.00	77.57	10.89	11.54	22.43
6G	2.10	11766.83	1227.57	10245.83	2.23	4.25	534.59	1912.67	5.60	0.00	23.85	56.96	14.49	71.45

Table 21. Correlation coefficients for alkanes, PAHs, total organic matter (OM) and granulometry of sediments from the Beaufort Sea nearshore, north arctic Alaska (N=20 except for OM where N=19; only significant correlations [P<0.005 are shown])

	Depth (m)	Total n-alkanes	C12-C19	C20-C33	Pr/Ph	Odd/Even	4,5 PAH	tPAH	OM %	Gr %	Sd %	St %	Cl %	Mud %
<b>Depth (m)</b>	1.00													
<b>Total n-alkanes</b>		1.00												
<b>C12-C19</b>		0.93	1.00											
<b>C20-C33</b>		0.96	0.87	1.00										
<b>Pr/Ph</b>		0.49	0.57	0.47	1.00									
<b>Odd/Even</b>		0.49	0.47		0.18	1.00								
<b>4,5 PAH</b>		0.92	0.91	0.87	0.54		1.00							
<b>tPAH</b>		0.88	0.90	0.76	0.50		0.95	1.00						
<b>OM %</b>									1.00					
<b>Gr %</b>										1.00				
<b>Sd %</b>		-0.75	-0.90	-0.66	-0.56	-0.47	-0.80	-0.84			1.00			
<b>St %</b>		0.71	0.69	0.65		0.64	0.62	0.66			-0.77	1.00		
<b>Cl %</b>		0.53	0.68	0.45	0.45		0.74	0.74			-0.74		1.00	
<b>Mud %</b>		0.77	0.84	0.68	0.47	0.54	0.86	0.86	-0.48		-0.93	0.83	0.80	1.00

Table 22. Stable carbon isotope ratios ( $\delta^{13}\text{C}$  ‰) and OC/N (wt/wt) of carbonate-free gross sediments from the study area [after Naidu et al. 2000]. na – not applicable

Sample #	$\delta^{13}\text{C}$ ‰	OC/N
1D	-25.4	na
2E	-25.3	na
2F	-26.1	11.2
3A	-26.0	11.8
3B	-25.3	7.3
4A	-25.9	8.4
WPB	-25.4	8.4
5(1)	-24.5	7.7
5(10)	-25.7	8.8
5A	-26.3	10.9
5F	-26.9	17.7
5G	-25.9	9.6
SL	-26.	12.9
6A	-26.4	12.6
6B	-26.3	9.5
6C	-25.6	10.5
6D	-25.7	11.3
6G	-26.3	12.9
7E	-25.7	15.4

Table 23. Summary of the stepwise multiple discriminant analysis among the station groups formed by cluster analysis of selected hydrocarbons and sediment granulometry data (Table 20).

Statistica Discriminant Stats	Discriminant Function Analysis Results		
Stepwise analysis – Step 2 (final step)			
Number of variables in model: 2			
Last variable entered: tPAH		F(2, 16) = 1.676846	p < .2182
Wilks' Lambda: .1057733		approx. F(4, 32) = 16.59813	p < 0.0000

Statistica Discriminant Stats	Discriminant Function Analysis Summary					
	Step 2		Number of variables in model: 2		Grouping: GR3 (3 grps)	
	Wilks' Lambda: .10577		approx. F(4, 32) = 16.598		p < 0.0000	
N = 20	Wilks' Lambda	Partial Lambda	F-remove (2, 16)	p-level	Tolerance	1-Tolerance (R-Square)
CL %	.1871374	.5652173	6.153849	.0104165	.9752235	.0247765
tPAH	.1746661	.6055740	5.210608	.0180858	.9752237	.0247763

Statistica Discriminant Stats	Standardized Coefficients for Canonical Variables	
	Root 1	Root 2
CL %	-.676382	-.753600
tPAH	-.637740	.786571
Eigenvalue	7.781033	.076660
Cumulative Properties	.990244	1.000000

Table 24. Comparison of concentration ( $\mu\text{g/g}$ ) and selected parameters of hydrocarbons in gross sediment samples collected 1984–1986 [Boehm et al. 1987; Steinhauer and Boehm 1992] and in 1997 (this study).\*

Region (Station)	TALK <sup>#</sup>	LALK <sup>+</sup>	Pristane	Phytane	LALK/TALK	$\Sigma\text{PAH}^{\#\#}$	N/P <sup>**</sup>	References
Camden Bay area: 1D, 2E, 2F	0.26–1.88 0.1–3.16	0.01–0.38 0.24–0.49	0.01–0.05 0.01–0.03	0.001–0.02 0.005–0.02	0.02–0.22 0.08–0.3	0.06–0.70 0.01–0.05	0.58–1.64 0.8	this study Boehm et al. 1987
Foggy Island Bay area: 3A, 3B, 4A, 5G	0.49–3.07 2.2–5.79	0.06–0.80 0.43–0.88	0.006–0.08 0.03–0.06	0.003–0.03 0.02–0.03	0.12–0.36 0.15–0.39	0.1–1.0 0.07–0.09	0.75–0.95 1.0	this study Boehm et al. 1987
Endicott Field stations: WPB <sup>**</sup> , 5(1), 5(2), 5(5), 5(10)	0.2–1.3 0.8–2.81	0.02–0.19 0.2–0.46	0.001–0.02 0.01–0.03	0.001–0.008 0.004–0.03	0.1–0.17 0.13–0.26	0.02–0.24 0.03–0.08	0.25–0.89 1.0	this study Boehm et al. 1987
Kuparuk River bay area: 5A, 5F	2.3–7.1 4.8–7.2	0.28–0.98 0.78–0.96	0.02–0.09 0.05–0.06	0.03–0.04 0.03	0.11–0.14 0.13–0.16	0.37–1.96 0.13	0.49–1.51 1.2	this study Boehm et al. 1987
East Harrison Bay area: SL <sup>**</sup> , 6A, 6B, 6C, 6D, 6G	0.8–11.8 3.1–19.4	0.08–1.2 0.6–2.50	0.007–0.1 0.04–0.2	0.003–0.05 0.02–0.1	0.10–0.19 0.10–0.18	0.29–1.78 0.08–0.64	0.59–1.59 1.5	this study Boehm et al. 1987

\* Range from this study and Boehm et al. [1987]; geometric mean for N/P from Table 7, Steinhauer and Boehm [1992]

\*\* Not sampled by Boehm et al. [1987]

# Sum of n-C<sub>10</sub>–n-C<sub>38</sub> (this study); n-C<sub>10</sub>–n-C<sub>34</sub> [Boehm et al. 1987]

+ Sum of n-C<sub>12</sub>–n-C<sub>19</sub> (this study); n-C<sub>10</sub>–n-C<sub>20</sub> [Boehm et al. 1987]

## Sum of parent and methylated PAHs from naphthalene to coronene including methylated homologs of 4,5 PAH (this study)  
Sum of parent and methylated PAHs from 2- and 3-ring and parent 4,5-ring PAH [Boehm et al. 1987]

\*\* Naphthalenes/phenanthrenes + anthracenes

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A set of 35-mm slides showing sampling tasks in the field was also submitted to the CMI office at the University of Alaska Fairbanks.

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### **The Department of the Interior Mission**

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



### **The Minerals Management Service Mission**

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

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

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