Coastal
Marine
Institute

University of Alaska

# Synthesis of Time-interval Changes in Trace Metals and Hydrocarbons in Nearshore Sediments of the Alaskan Beaufort Sea: A Statistical Analysis

A. Sathy Naidu
Principal Investigator

Debasmita Misra
John J. Kelley
Co-Principal Investigators

Additional Researchers:
Arny Blanchard
M. Indira Venkatesan

Final Report
OCS Study BOEMRE 2011-031

June 2011

**Bureau of Ocean Energy Management, Regulation and Enforcement**
**Department of the Interior**

and the

**School of Fisheries & Ocean Sciences**
**University of Alaska Fairbanks**

This study was funded in part by the U.S. Department of the Interior, Bureau of Ocean Energy Management, Regulation and Enforcement (BOEMRE) through Cooperative Agreement No. 1435-01-02-CA-85294, Task Order No. 39921 between BOEMRE, Alaska Outer Continental Shelf Region, and the University of Alaska Fairbanks.

This report, OCS Study BOEMRE 2011-031, is available from the Coastal Marine Institute (CMI), School of Fisheries and Ocean Sciences, University of Alaska, PO Box 757220, Fairbanks, AK 99775-7220. Electronic copies can be downloaded from the BOEMRE website at www.alaska.boemre.gov/alaska/ref/akpubs.htm. Hard copies are available free of charge, as long as the supply lasts, from the above address. Requests may be placed with Ms. Sharice Walker, CMI, by phone (907) 474-7208, by fax (907) 474-7204, or by email at skwalker@alaska.edu. Once the limited supply is gone, copies will be available from the National Technical Information Service, Springfield, Virginia 22161, or may be inspected at selected Federal Depository Libraries.

Coastal
Marine
Institute

University of Alaska

# Synthesis of Time-interval Changes in Trace Metals and Hydrocarbons in Nearshore Sediments of the Alaskan Beaufort Sea: A Statistical Analysis

A. Sathy Naidu
Principal Investigator

Debasmita Misra
John J. Kelley
Co-Principal Investigators

Additional Researchers:
Arny Blanchard
M. Indira Venkatesan

Final Report
OCS Study BOEMRE 2011-031

June 2011

**Bureau of Ocean Energy Management, Regulation and Enforcement**
**Department of the Interior**

and the

**School of Fisheries & Ocean Sciences**
**University of Alaska Fairbanks**

**Contact information**

email: skwalker@alaska.edu
phone: 907.474.7208
fax: 907.474.7204
Coastal Marine Institute
School of Fisheries and Ocean Sciences
University of Alaska Fairbanks
P. O. Box 757220
Fairbanks, AK 99775-7220

# TABLE OF CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

# LIST OF PLATES

# ABSTRACT

The nearshore sediment trace metals and hydrocarbons data, generated by Dr. Naidu and associates, pertaining to three regions [Elson Lagoon (EL), Colville Delta-Prudhoe Bay (BS) and Beaufort Lagoon (BL), Alaskan Beaufort Sea] are consolidated, statistically analyzed and synthesized. The data comprise of the concentrations in the mud fraction of sediments (<63µm size), normalized and not normalized to Fe, of a suite of metals [Iron (Fe), arsenic (As), barium (Ba), cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), manganese (Mn), nickel (Ni), tin (Sn), vanadium (V) and zinc (Zn), and in gross sediments of total mercury (THg), methyl mercury (MeHg)] and hydrocarbons [normal and isoprenoid alkanes, triterpenoids, steranes, and polycyclic aromatic hydrocarbons (PAHs)]. The above analytes are selected because they are commonly associated with contaminant inputs from petroleum-, municipal- and/or military-related activities.

Generally, the concentrations of the trace metals in the study area are below or comparable to those in world's unpolluted nearshore marine sediments. Cluster analysis on the composite database of either all the metals (both normalized and not normalized to Fe basis) or hydrocarbons show lack of discrete grouping of stations confined to the individual three regions. Significant regional differences in some individual analyte's concentrations are noted, though. Time-interval comparisons of the concentrations of metals (not normalized to Fe) in surficial muds of Colville Delta-Prudhoe Bay indicate significant increases in vanadium in 1985 and 1997 compared to 1977, and in barium contents in 1997 compared to 1985. In Beaufort Lagoon sediments a significant increase is noted in copper and manganese accompanied by a decrease in vanadium in 2003 compared to 1977. The reason for the time-interval increases in vanadium and barium in Colville Delta-Prudhoe Bay are unknown. The elevated barium could possibly be due to accumulation of baryte ($BaSO_4$) derived from increased discharge of effluents in the region in post 1977 from petroleum-related drilling activities, whereas the increase in vanadium could possibly be from local gas combustion products. The time-interval variations on metals on surface muds do not match with the metal stratigraphy, which in Colville Delta-Prudhoe Bay demonstrate a significant net decrease up core during the past 15-30 years in zinc, cadmium, lead and methyl mercury. In contrast, in Elson Lagoon there are significant net increases up core in the past ~70 years in barium, chromium and manganese accompanied by decrease in total mercury. These trends are likely due to stratigraphic variations in granulometry rather than regional temporal changes in the metals input. Correlation coefficient analysis suggests that most metals are bound to organic matter, clay and iron-manganese compounds in mud. The mean concentrations in mud of As, Cr, Cu and Ni in Elson Lagoon, of As, Cu and Ni in Beaufort Lagoon, and of As and Ni in Colville Delta-Prudhoe Bay are above the Effects Range-Low (ERL) guideline level (Long et al., 1995, 1998). This implies that incidences of possible adverse effects could occasionally be expected on ten percent of the benthic organisms, consequent to chronic exposure and bioaccumulation of the above metals vis a vis within the respective regions. The suggested implication is based on the assumption that the total content of each of the above concerned metals in sediment can be readily mobilized and made available for bioaccumulation. However, our laboratory experiments suggest that only minor portions of the metals investigated would likely be mobilized from sediments when subjected to environmental changes in redox and/or pH conditions. Therefore, the application of the above guidelines to the study area must be considered with caution.

The overall composition of the hydrocarbons profiles in gross sediments is very similar in Elson Lagoon, Colville Delta-Prudhoe Bay and Beaufort Lagoon, and the hydrocarbon concentrations are generally equal or lower to those recorded for world's unpolluted marine nearshore. The molecular hydrocarbon markers are predominantly biogenic and terrigenous-derived with little input from natural oil seeps and/or refined crude. A comparison of the time-interval data on selected hydrocarbons in sediments from Colville Delta-Prudhoe Bay indicates a relative increase in ΣPAHs from 1984-1986 to 1997 accompanied by no change in ΣPAHs from 1997 to 2000 or 2002. One of the possible reasons for the ΣPAHs increase could be the additional depositional flux in post-1984 resulting from petroleum-related drilling activities. The mean concentrations of selected 14 PAHs in gross sediments of Beaufort Lagoon, are below the ERL level (Long et al., 1995, 1998), whereas in

Elson Lagoon the concentrations of 2-methylnaphthelene in one of the three samples is within the ERL. Additionally, in Elson Lagoon the detection of small amounts of coprostanol and coprostanone indicates minor sewage inputs in sediments.

In summary, the nearshore sediments have remained generally uncontaminated of metals and hydrocarbons during the past 35 years following petroleum-, municipal- , and defense-related activities. This conclusion is consistent with those on regional studies conducted in the North Slope nearshore. The database synthesized should be a baseline for contaminant monitoring for the North Slope nearshore.

# INTRODUCTION

In recent years, there has been great concern about the Arctic marine environment, especially relating to the presence of anthropogenic contaminants and their possible biological effects. Until recently the Alaskan Arctic seas were considered generally free of contaminants, but organic and inorganic contaminants from local and far away (Eurasia) sources, through long-distance transport, have found their way into the above so-called ‘pristine’ environment (Rahn and Lowenthal, 1986; Barrie et al., 1992; Chernyak et al., 1996; AMAP, 1997; Fitzgerald et al, 1998; Garbarino et al., 2002; Molnia and Taylor, 1994; Valette-Silver et al., 1999; Macdonald et al., 2000, 2005). During the past four decades there has been increasing industrial growth in the North Slope coastal region of northern Arctic Alaska, relating to the activities of exploration and development of the onshore and offshore petroleum reserves. Concurrent to this growth there has been increasing urbanization of the villages along the North Slope coast (e.g., Barrow, Kaktovik). Additionally, in the past there were military-related operations [hazardous waste discharge by Distant Early Warning (DEW) Line stations (Lackenbauer et al., 2005) and rocket firing experiments], and more recently there have been enhanced municipal activities (sewage-treatment, power-generation, and gravel mining). The petroleum-related developmental tasks include seismic surveys, drilling from onshore and offshore platforms, marine boat traffic, building of causeways, and laying of submarine pipelines, among others. These activities have affected the natural environment. There is a concern that such anthropogenic activities may lead to contamination of the environment with metals and hydrocarbons, which could have a deleterious impact on marine biota and subsistence users. More recent concern relates to the Arctic National Wildlife Refuge (ANWR), particularly the 1.5 million acre coastal plain, which has potential petroleum reserves (titled the 1002 area). This region is one of the most contentious areas for oil drilling, because of the presence of a variety of wildlife habitats (Douglas et al., 2002). The major goal of this study is to assess the regional differences and historical changes in a suite of trace metals and hydrocarbons in the mud fraction and gross sediments respectively, with an objective to identify the extent of contamination in the nearshore of the Alaskan Beaufort Sea following recent anthropogenic activities. Data on selected biomarkers [i.e., individual *n*-alkanes from $n$-$C_{13}$ to $n$-$C_{33}$, pristane, phytane, naphthalene and its monomethyl isomers, phenanthrene, fluoranthene, pyrene, benzanthraacene, chrysene, benzofluoranthenes, indenopyrene, perylene, benzo(ghi) perylene, 17α(H),21β(H)- and 17β(H),21β(H)-hopanes, diploptene], and the stable carbon and nitrogen isotopes of sediments (Naidu et al., 2000) are available from Dr. Naidu’s MMS-funded projects for 2001, 2003b and 2005. This database has a potential use to help assess the input of hydrocarbons into the nearshore from various natural and anthropogenic sources (land and marine plants, crude and refined petroleum, natural oil spill and fossil fuel combustion).

Recognition of chemical contamination is of particular concern in the Arctic in light of the theory that polar food chains are relatively sensitive and susceptible to contaminant bioaccumulation (Chapman and Riddle, 2005). Several environmental factors unique to the Arctic may specially contribute to higher levels of contaminant accumulation and biomagnifications of toxic metals and organics. For example, the arctic marine organisms which are lipid-rich are especially prone to accumulate lipophilic (fat loving) contaminants and the relatively short/simple linear food chains of the Arctic can transfer contaminants readily from the lower to the higher trophic levels resulting in contaminant biomagnifications in marine subsistence food sources (Ayotte et al., 1995; Mulvad et al., 1996; Johansen et al., 2000 and references therein). Additionally, extended period in the sensitive early life stages of organisms including brooding, resulting from slow development time, and “the consequences of the epontic (under ice) life style to contaminant exposure pathways"-- in conjunction with summer phototoxicity-- has a potential to especially lead to higher contaminant bioaccumulation in the Arctic (Chapman and Riddle, 2005).

# BACKGROUND AND RATIONALE

Responding to the above concern, several investigations have been conducted since early 1970s to gather time-intervals data on the composition and concentrations of trace metals and hydrocarbons in nearshore sediments of north Alaskan Arctic, with an objective to monitor contaminants. Marine sediments are traditionally preferred for the monitoring of pollutants as they represent a suitable environmental integrator and sink for particle-reactive contaminants (Forstner and Witmann, 1979; Chapman et al., 1998). Impacted sediments could be a major source of contaminants to the benthos (Geffard et al., 2002; Lee and Wiberg, 2002; Mountouris et al., 2002), demersal fish and other organisms, which have a close link with sediments (Naidu et al., 2001 and references therein). The earliest quantitative data on trace metals available for the nearshore sediments of the Alaskan Beaufort Sea are those collected under the auspices of the projects funded by the EPA-Alaska Sea Grant, U.S. Geological Survey, and Outer Continental Shelf Environmental Assessment Program (OCSEAP) (Naidu, 1982; Sweeney, 1984; Sweeney and Naidu, 1989). Subsequent regional investigations (Elson Lagoon, Colville Delta-Prudhoe Bay, and Beaufort Lagoon) on sediment trace metals, funded by the Minerals Management Service (MMS) and Coastal Marine Institute (CMI), were by Boehm et al. (1987), Crecelius et al. (1991), Naidu et al. (2001, 2003a, 2000b and 2005), Brown et al. (2005); and Misra et al. (2006). Trace metals inventories on snow samples are available for the North Slope coast (Snyder-Conn, 1997). Additional site-specific studies were conducted to assess the environmental impact of discharge of metals entrained in drilling effluents (Northern Technical Services, 1981; Snyder-Conn et al., 1990) and of activities near offshore drilling platform (Trefry et al., 2003). Investigations funded by the OCSEAP, MMS and CMI provide baseline and post-industrial time-intervals data on hydrocarbons (*n*-alkanes, polycyclic aromatic hydrocarbons, triterpanes and steranes) in nearshore sediments of the North Slope (Shaw et al., 1979; Venkatesan and Kaplan, 1982; Boehm et al., 1987; Steinhauer and Boehm, 1992; Naidu et al., 2001, 2003b, 2005; Macdonald et al., 2004; and Brown et al., 2005).

It is clear from the above review that substantial high quality database exist on the concentrations of trace metals and hydrocarbons in the nearshore sediments of the Alaskan Beaufort Sea. This is a region of intense industrial and municipal activities relating to ongoing and prospective oil fields. However, no effort has been made to compile and consolidate all the available data on trace metals and hydrocarbons into a Metadata form, and conduct rigorous statistical analysis on the database. Attempts made so far to understand the sources (anthropogenic and natural) of metals and hydrocarbons and geochemical processes/pathways are limited to specific project areas. It is possible that regional differences exist in nearshore sediment metal and hydrocarbon chemistries along the North Slope nearshore, but this has not been verified statistically. Further, no attempt has been made to assess if there are any significant correlations between the contents of the individual trace metals, hydrocarbon biomarkers and associated physicochemical sediment parameters (for example, grain size distribution, organic carbon, organic matter contents and carbon and nitrogen isotope compositions). This information would be important to the better understanding of the concentrations, distribution, sources and geochemical partitioning of the metals and hydrocarbons. Also, regional disparities in the sediment chemical data have not been examined in context of the regional differences in the chemical composition of various sediment sources, such as coastal snow samples (proxy for atmospheric contaminant source inputs, Snyder-Conn et al., 1997) and several possible terrigenous sources [i.e., fluvial outflow, Rember and Trefry (2004)]. Without a systematic statistical analysis of the existing chemical data on site-specific and regional scale it will be difficult to evaluate any regional differences in the database in context of potential sources, extent of anthropogenic contaminants and their possible provenances, and to understand the geochemical factors that govern the differences. This study addresses some of the above concerns.

# OBJECTIVES

Our overall objective was to complete a limited scope synthesis and analysis of trace metals and hydrocarbons data previously generated on nearshore surface sediment samples from the North Slope of Arctic Alaska. Data for this synthesis were limited to those gathered since 1977 by Dr. Naidu and associates on three CMI/MMS funded projects.

The specific objectives were to (i) to evaluate quality of the data, in context of the guidelines stipulated by NOAA, (ii) to conduct statistical analysis of the data on metals (normalized and not normalized to iron) and hydrocarbons (normalized to organic matter), to identify regional differences and distribution pattern(s) and assess the time-intervals and historical changes in the trace metals concentrations and profiles of selected hydrocarbons, and (iii) assess the possible sources of trace metals and hydrocarbons, in context of natural inputs and anthropogenic contamination.

# HYPOTHESES

The overall hypothesis of the synthesis is that the nearshore region of the North Slope has remained a relatively pristine environment and free of trace metal and hydrocarbon contaminants, despite the military activities in the decades past and followed by accelerated petroleum-related industrial and municipal activities since the early 1970s. An additional hypothesis is that there are no significant regional differences in the trace metal and hydrocarbon concentrations in sediments.

# METHODS/STATISTICAL ANALYSES

## *Sample locations and Database (Source and Normalization)*

The areal extent for this synthesis are limited to the marine region extending from the shore to about 30 km seaward including the Federal Outer Continental Shelf (OCS) zone that begins 5.56 Km beyond the coast (Fig.1). This region in particular encompasses either operating or future oil prospects, and slated oil lease sale areas, and has been subjected to various anthropogenic activities (petroleum-, municipal- and military-related). The area considered for this synthesis includes three disjointed regions within the North Slope nearshore, namely the Colville Delta-Prudhoe Bay, Elson Lagoon and Beaufort Lagoon (Fig.1). Figures 2, 3, and 4 show the locations of the sediment samples within the above regions for which data on trace metals and hydrocarbons were available. In Figure 4 the location of the natural oil seep sample (Plate 1) is depicted by OS, which is on the bank of a small unnamed creek opening into southwestern Beaufort Lagoon. The individual regions [in parenthesis are included the acronym and year of sampling, the number (N) of samples and the sources of the database for the trace metals considered in this synthesis] are as follows: Colville Delta-Prudhoe Bay (BS97, N= 62, Naidu et al., 2001), Elson Lagoon (EL99, N=5; Naidu et al., 2003a and b), and Beaufort Lagoon (BL03, N=20). Likewise, the regional database for the synthesis of the information on hydrocarbons in gross sediment was as follows: Colville Delta-Prudhoe Bay (Beaufort Sea, BS97, N=21, Naidu et al., 2001); Elson Lagoon (EL99, N=3, Naidu et al., 2003b), and Beaufort Lagoon (BL03, N=21, Naidu et al., 2006). The statistical analysis on trace metals in the mud fraction (<63μm size) was treated in two ways. One considered the trace metal concentrations not normalized to any of the sediment parameters, and the second approach was based on the individual trace metal concentrations normalized to the iron (Fe) content in mud (i.e., expressed as metal content/Iron content). The hydrocarbon concentrations in gross sediments were normalized to the organic matter content of the gross sediment. It was ascertained that for the statistical analysis (regional and time-interval comparison, trend analysis, PCA) the data from all the above investigations of Dr. Naidu are compatible with each other, as discussed in the following section relating to statistical analysis.

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

The raw data on the concentrations of the individual trace metals and hydrocarbons considered in this synthesis, are tabulated in the Microsoft Access database, delineating the database by study areas and years of collection [cf. ftp://ftp.sfos.uaf.edu/naidu/cmistat2007/]. The above information lists the concentrations of a suite of metals [Iron (Fe), arsenic (As), barium (Ba), cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), manganese (Mn), nickel (Ni), tin (Sn), vanadium (V) and zinc (Zn) in the mud fraction, and the concentrations in gross sediments of total mercury (THg), methyl mercury (MeHg) and selected hydrocarbons [normal and isoprenoid alkanes, triterpenoids, steranes, and polycyclic aromatic hydrocarbons (PAHs)]. The database corresponding to each of the samples analyzed, includes station coordinates, water depths, and selected ancillary sediment variables (sediment grain size, organic matter and water contents, stable isotopes of carbon and nitrogen) that have proved useful factors in the interpretation of the concentrations, geochemistry, and sources of trace metals and hydrocarbons (Refer to final reports relating to Dr. Naidu's CMI/MMS projects on regional studies; Naidu et al., 2001, 2003b, 2006). The database on the above website also specifies sampling precision (based on analyses of triplicate samples from each location) and the mean concentration and percent coefficient of variation calculated on the results of the replicate analyses for each metal. The database also includes the mean concentrations of the metals and percent coefficient of variation for all the samples analyzed from any one of the three regions investigated (Elson Lagoon, Colville Delta-Prudhoe Bay and Beaufort Lagoon). Additionally, the tabulated data include for the individual samples the total, ranges, and ratios between selected *n*-alkanes ($\Sigma C_{12}$-$C_{19}$, $\Sigma C_{20}$-$C_{33}$, pristane/phytane, odd/even, lower molecular weight alkanes/total alkanes, LALK/TALK).

The first task for this synthesis was to undertake a search, using online computer and library survey, of published and unpublished reports and database on the concentrations of trace metals and hydrocarbons mentioned above in nearshore sediments and of representative fluvial systems, crude and natural oil seeps of the north arctic Alaska. The above analytes were selected for the statistical analysis, because of their association generally with potential inputs of contaminants from relatively recent (since early 1970s) petroleum- and municipal-related activities and past (1950-1960) military projects (e.g., DEW Line stations, rocket firings). In particular, the analytes mentioned are constituents invariably of crude, as of Prudhoe Bay (Coleman et al., 1978), drilling mud and associate hazardous waste (Costlow et al., 1983; National Academy of Sciences, 2003).

As mandated by the CMI/BOEMRE contract, this synthesis on trace metals and hydrocarbons is restricted to the database generated solely by Dr. Naidu and associates on the nearshore sediments of the North Slope region, and data that were gathered under the three CMI/MMS-funded projects (Naidu et al., 2001, 2003b, 2006). It was also stipulated that Dr. Naidu consider normalizing the trace metal concentrations to aluminum (Al) or iron (Fe), and those on hydrocarbons to organic matter or organic carbon, which was presumably meant to conform to the approaches followed in earlier MMS-sponsored monitoring studies relating to "Arctic Nearshore Impact Monitoring in the Development Area (ANIMIDA)" (Brown et al., 2005) and "Beaufort Sea Monitoring Program (BSMP)". In our synthesis normalization of the concentrations of individual trace metals to aluminum was not possible because aluminum was not measured in Dr. Naidu's sediment samples. However, on a few selected mud samples for which iron concentrations were available, the concentrations of the individual trace metals were normalized to their iron contents. The statistical analysis, as mentioned in the following, was based on 20 pairs of trace metal/iron data sets each (total N=40) from the Colville Delta-Prudhoe Bay and Beaufort Lagoon, respectively. It is to be noted that the trace metal database, gathered by Dr. Naidu and associates, was on the mud fraction (<63 μm size) of gross sediments, and the justification to do so is discussed in the following.

**Figure 1. The three regions (Elson Lagoon, Colville Delta-Prudhoe Bay and Beaufort Lagoon) for which database is synthesized.**

Monitoring contaminants in the marine environment using gross sediment are beset with difficulties. Marine lithogenous sediments are generally a composite of a complex mixture of several subcomponents derived from genetically different sources and of contrasting compositions [e.g., particulates with a range of grain sizes (gravel to clay) with wide differences in mineralogy and chemistry (contents of organic carbon/matter, oxides/hydroxides of iron and manganese, among others)]. The relative fractional differences in the abundances of these subcomponents can drive significant disparities in the trace metal and hydrocarbon concentrations in gross sediments. Thus, comparison of the chemistries of genetically different gross sediment types are of limited practical application in contaminant monitoring, unless the chemistries of sediments of various compositions are normalized to concentrations of any one of the dominant constituents that is common to all of the samples. In this context, several sediment subcomponents (contents of aluminum, lithium, oxides of iron and manganese, mud, organic matter, granulometry, among others) have been used for normalizing trace metal and hydrocarbon abundances (Finney and Huh, 1989; Loring, 1991; Daskalakis and O'Connor, 1995; Naidu et al., 2001; Trefry et al., 2003; Brown et al., 2005; Mucha et al., 2005). Specific examples of normalizing the trace metal concentrations to aluminum in nearshore sediments of the North Slope are included in Trefry et al., (2003) and Brown et al. (2005). The use of aluminum is based on the premise that it is a measure of the clay/mud (aluminosilicate) content and, thus, also a proxy for granulometric variation between sediments (Brown et al., 2005). The underlying logic is that more aluminum would mean a higher fraction of clay or mud in the gross sediment which, in turn, will lead to possible greater scavenging of particle-reactive trace metals. Although aluminum has been used widely for normalizing sediment chemistry there can be short falls occasionally in its sole application, such as in the case when there are significant contents of other subcomponents in sediments (organic matter and/or oxides/hydroxides of iron and/or manganese) equally or more appropriate for normalizing to. The sole use of iron is also beset with problems. The use is based on the assumption that most of the sediment iron is bound in oxide/hydroxide phase which is also prone to adsorbing particle-reactive metals. This may not be true invariably as significant amount of the total iron in sediment can be tightly bound in crystal lattice of relatively 'inert' refractory minerals (magnetite, hematite, ilmenite, ferromagnesian silicates), which have relatively low capacity to adsorb and concentrate trace metals. To resolve the problems Naidu et al. (2001, 2003b, 2006) and Boehm et al. (1987) in their Beaufort Sea Monitoring Program (BSMP), preferred to analyze trace metals in the mud fraction (<63µm size) of nearshore sediments from the North Slope region. The justification is that the mud fraction, which invariably concentrate iron oxide/hydroxide, organic matter, aluminum, clay minerals, will also have the largest capacity to bind particle-reactive trace metal contaminants relative to coarser particles (>63µm size). The strong positive correlation (r=0.89) between percents silt + clay (mud) and aluminum in coastal marine sediments of the North Slope (Brown et al., 2005), suggests that trace metals data based either on the mud fraction of gross sediments or on an aluminum-normalized basis on gross sediments are equally useful for metal contaminant monitoring. Most of the databases in this synthesis are on the mud fraction. However, in compliance with the ongoing contract with the Coastal Marine Institute we have also normalized, for as many numbers of samples for which data are available, the metal data to iron. The iron-normalized database thus obtained was statistically treated and the results from this analysis were compared with those obtained on the mud fraction but not normalized to iron.

One of the synthesis's objectives is to assess the time-interval changes in the concentrations of as many of the heavy metals and selected hydrocarbon components for which temporal data are available for the nearshore Beaufort Sea. This task was addressed in two ways. One way was to compare the time-interval (1975 to 1997) sets of data on surface grab sediment samples. The pre-1997 data on metals in mud of surface sediments are from Dr. Naidu's past projects funded by the Outer Continental Shelf Environmental Assessment Program, OCSEAP (Naidu, 1982; Sweeney, 1984; Sweeney and Naidu, 1989). The trace metal data subsequent to 1997 are from Dr. Naidu's CMI/MMS projects. The second approach to assess temporal changes was by elucidating the net trends in the stratigraphic variations in the concentrations of metals in representative sediment gravity core samples, two from Colville Delta-Prudhoe Bay and one from Elson Lagoon. Because of funding constraints no core sample was collected and analyzed from Beaufort Lagoon. Each of the cores was sectioned at 1-cm intervals from the top of the core to the bottom. The geochronology of the sediment cores was established by the age-depth model using $^{210}$Pb dating (Weiss and Naidu, 1986; Naidu et al., 2001, 2003b). To make the time-interval comparison valid, it was made sure that the levels of variability of data within samples, sites, and regions were made integral to the statistical analysis. Further, at the very beginning of the synthesis it was recognized that the comparison between regions (and within a region) will be logical only if all the data are normalized against any one common variable that significantly influences the sediment chemistry. We have minimized this concern relating to both surface and core samples by restricting the comparisons on the concentrations of trace metals in the sediment mud fraction or muddy sediments (>75% mud in OCSEAP samples) and, alternatively as in selected case, by normalizing the metal to iron contents, and the hydrocarbon data to organic matter in sediments

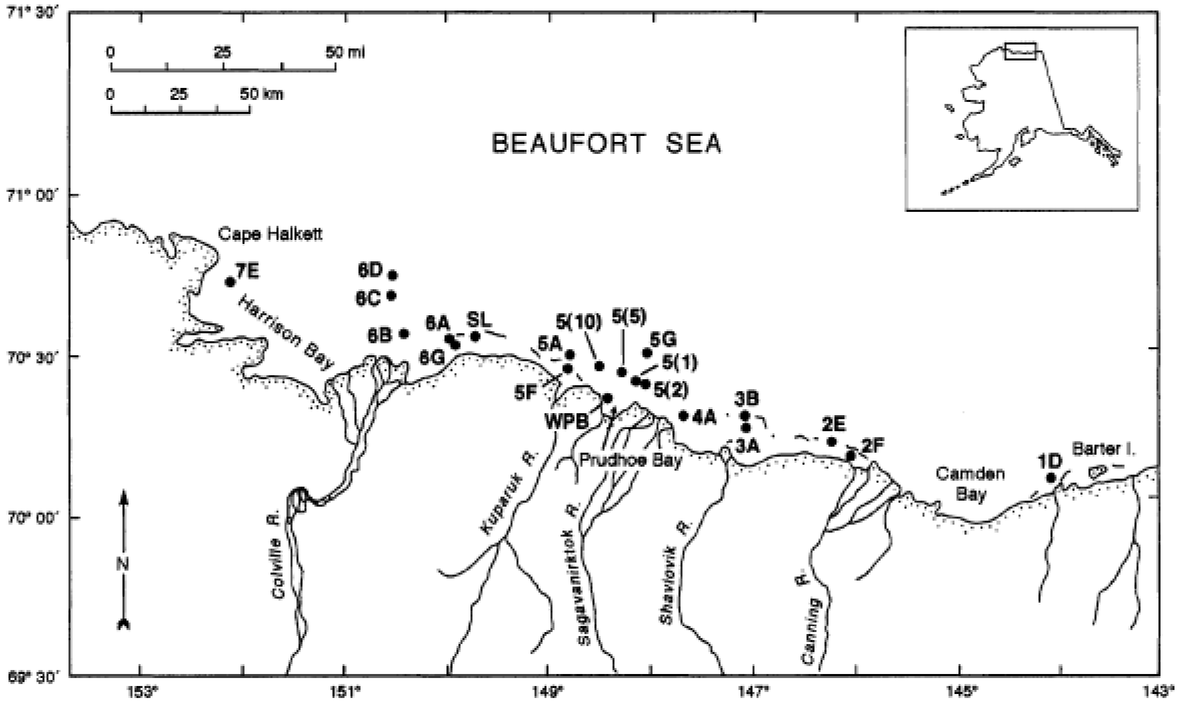


**Figure 2. Map showing the locations of sediment samples in the Colville Delta-Prudhoe Bay region.**

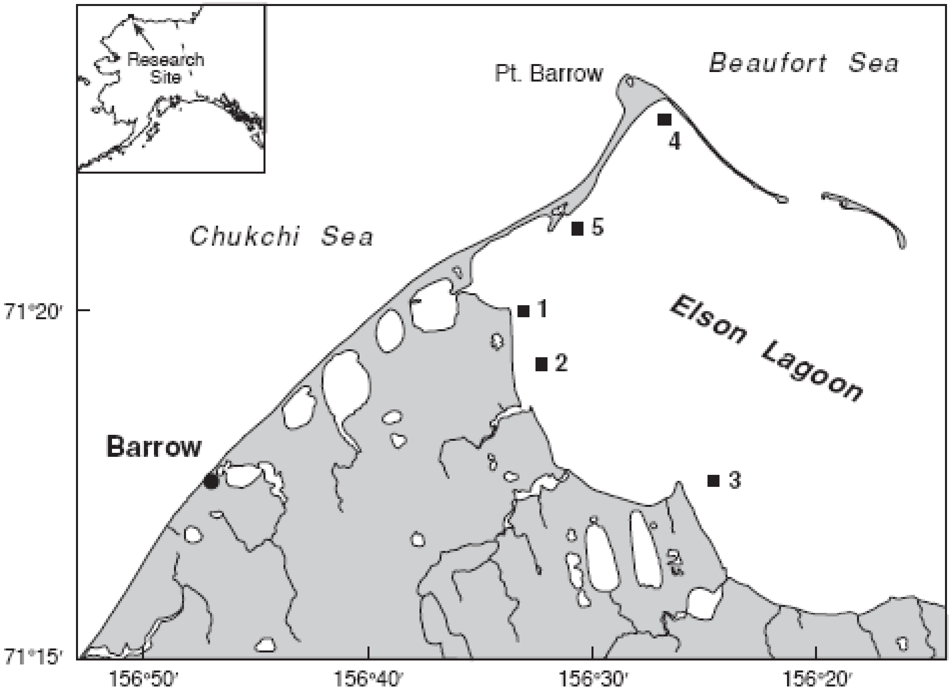


**Figure 3. Map showing the locations of sediment samples in the Elson Lagoon region.**

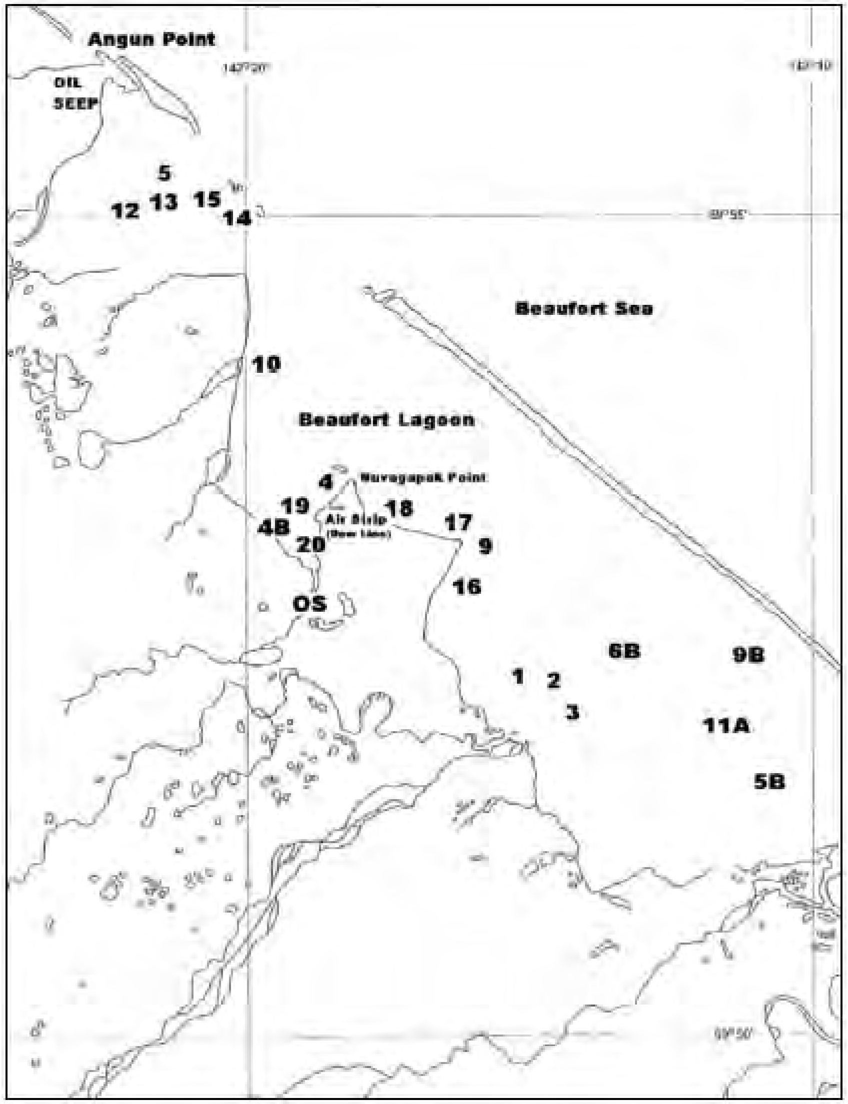


**Figure 4. Map showing the locations of sediment samples in the Beaufort Lagoon region.**

## *Analytical Methods and QA/QC*

Details on the specific methods followed for the analyses of trace metals and hydrocarbons are included in Naidu et al. (2001, 2003b, 2006) and, therefore, a brief description of the methods follows. Each of the sediment samples was sieved through a 230-mesh nylon screen to obtain the mud fraction (<63μm size). A portion of the dry mud was taken into solution by digestion in concentrated HF-$HNO_3$ acid in a Teflon bomb placed in a microwave oven. The diluted solution was analyzed for all the metals, except total and methyl mercury, either using an inductively coupled plasma/mass spectrometer (ICP/MS) or atomic absorption spectrometry (AAS). The analysis on gross sediments of total mercury was by cold vapor atomic absorption (CVAAS), and that of methyl mercury was by using cold vapor atomic fluorescence detector following cryogenic GC separation (Bloom, 1992, 1999). The analysis of the hydrocarbons included successive extraction of them from gross sediments with methanol and methylene chloride respectively. The final extract was run through a series of chromatography columns to separate the various hydrocarbon targets which were analyzed using GC/FID and GC/MS (Venkatesan et al., 1980, 1982, 1987; Venkatesan, 1994). The contents of organic carbon and nitrogen and their stable isotope ratios ($\delta^{13}C$ and $\delta^{15}N$) were determined on carbonate-free mud, following the methods outlined in Naidu et al., (2000) and using a Thermo-Finnigan Model Delta Plus XP isotope ratio mass spectrometer (IRMS). The carbon isotope ratios ($^{o}/_{oo}$) are referenced to the V-PDB standard and the nitrogen isotope ratios ($^{o}/_{oo}$) to air standard. The standard error of the isotope analysis is ± 0.2%.

It is contended that the Quality Assurance/Quality Control (QA/QC) of the analytical methods adopted for the determinations of the contents of sediment trace metals and hydrocarbons is of excellent order, based on the protocols followed in the sample collection and laboratory analysis (Naidu et al. 2001, 2003b and 2006). Presumably the QA/QC procedures initially established in 1997 are equally applicable to all of Dr. Naidu's CMI/MMS projects. These procedures included successful participation by the analytical laboratories for trace metals (Frontier Geosciences, Inc., Seattle) and hydrocarbons (University of California Los Angeles) in the round robin inter-laboratory calibration exercises NOAA/11, conducted in 1997 by the National Research Council of Canada (NRC) for the NOAA Status and Trends Program (NOAA/NS&T). Further, each of these laboratories conducted the conventional protocols to ensure the QA/QC requirements (e.g., analytical accuracy using US Geological Survey and/or National Research Council of Canada certified reference sediment standards (NIST 2709, IAEA 405), precision, maintaining low minimum detection levels, analysis of spiked blanks, using high purity chemicals and clean laboratory glasswares, among others). It is further contended that the regional data gathered in Dr. Naidu's various CMI/MMS studies and, which are included in this synthesis, are intercomparable statistically because of their equal high quality and that the analytical methods in all the studies were identical.

The relative abundance of the various sources of hydrocarbons (natural oil seep, refined petroleum, fresh crude and natural terrestrial and marine biogenous origin) was assessed in each of the sediments analyzed. This assessment was based on the guidelines stated below, which are similar to those outlined in Yunker and Macdonald (2003) on sediments of the Fraser River Basin and Strait of Georgia, in Brown et al., (2005) for nearshore sediments of the Beaufort Sea, and in Galperin and Camp (2002) with special reference to fuel-specific homologous series of hydrocarbons.

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

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

Biogenic hydrocarbons: Alkane gas chromatogram normally has baseline resolved peaks and does not have a bump (unresolved complex mixture of branched and cyclic components) (Venkatesan and Kaplan, 1982). $C_{15}$, $C_{17}$ indicates dominant *n*-alkanes from marine plankton, whereas dominance of $C_{25}$ to $C_{31}$ *n*-alkanes indicates terrestrial plant wax, with $C_{25}$, $C_{27}$, $C_{29}$, $C_{31}$ and $C_{33}$ more dominant than the even carbon *n*-alkanes (resulting in a high odd/even ratio) and with the maximum at $C_{29}$ or $C_{31}$ *n*-alkane (Simoneit and Kaplan, 1980; Venkatesan et al., 1980). The presence of perylene is a strong biomarker of biogenic components (Venkatesan, 1988). There was a presence of significant levels of alkanes from marine biota (Blumer et al., 1971). Triterpenoids are of low thermal maturity, characterized by the presence of predominantly 17β-hopanes and hopanes (Dastillung and Albrecht, 1976). There were not many alkylated PAHs.

## *Statistical Analyses*

The database for the statistical analysis on the trace metals were as follows. For the Beaufort Lagoon region, data on fourteen metals (chromium, copper, iron, manganese, nickel, vanadium, zinc, arsenic, cadmium, tin, barium, lead, total and methyl mercury) for year 2003 were available for all the stations. For the Colville Delta-Prudhoe Bay and Elson Lagoon regions, data on all the above metals except tin were available for years 1997 and 1999 respectively.

The statistical treatments presented here are based separately on metal concentrations that have been normalized to iron (Fe) and on metal concentrations that have not been normalized to iron, to compare the results of the two approaches. The analysis relied largely on multivariate procedures to discern large-scale trends and analysis of variance (ANOVA) to draw inferences about regional and temporal changes in the concentrations for individual metals. The multivariate methods used to elucidate similarities and trends among stations for the concentrations of metals were cluster analysis and principal components analysis (PCA). Cluster analysis provides a dendrogram presenting station similarities as a tree diagram where similar stations are grouped within similar branches. The first step in this process is to estimate a distance measure for each station. The Euclidean distance coefficient is calculated as the sum of differences in metals concentrations between each possible pair of stations. The distance coefficient indicates similarity of two stations when the distance is small and a lack of similarity when the coefficient is large. Thus, in the dendrogram sample locations that are similar will be grouped more closely than sites that are not similar so sites within a similar branch of a dendrogram can be interpreted as being similar with respect to the variables measured. The Euclidean distance coefficient is appropriate when the number of missing values is not large, as was the case for the chemical concentration data of this study. In PCA, the data are reduced to a few derived variables, called the axes that capture the greatest portion of variability. The results from the PCA are summarized as a scatterplot of the new variables with each station plotted as a point. The resulting ordination or “map” of similarities reveals station associations as similar stations are positioned closely in the plot. Similarity (correlations) of variables can also be assessed in PCA through the variable projection plot which summarizes the correlation of each variable to the derived PCA axes. Variables that are positioned more closely together in the projection plot are more closely correlated than variables that are positioned apart. Data were *ln*(X+1) transformed for the multivariate analyses to reduce the influence of extremely large values as would be expected for log-normally distributed data. For a weight-of-evidence approach, demonstration of similar trends in the output of multiple multivariate procedures provides greater support for the conclusions of similarities between groups of stations.

ANOVA was performed to compare between regions and years for metals data available to all the regions. To elucidate temporal changes for a region in the mean concentrations of individual metal statistical comparison of the time-interval database was restricted to a specific region (i.e., Colville Delta-Prudhoe Bay or Beaufort Lagoon). In addition, the statistical significances in net temporal trends in changes in the concentrations of the metals, as manifested in the stratigraphic record of sediment cores, were verified using regression analysis. For this purpose representative sediment core samples were collected from Colville Delta-Prudhoe Bay and Elson Lagoon. The geochronology of the cores was established via the estimation of the linear and mass accumulation rates of sediments, applying the age-depth model based on $^{210}$Pb dating (Naidu et al., 2001, 2003b). Results of ANOVA were summarized in tables. Metals concentrations were *ln*-transformed prior to ANOVA and multivariate analyses. Spearman’s rank correlations were obtained to identify levels of inter-element and element-granulometry-organic matter correlations. Such correlations provide clues to the understanding of the geochemical partitioning of the metals (Naidu et al., 1997). Additionally, scatter plots and correlations were also constructed between the various trace metals and the *n*-alkane $C_{29}$, (a typical marker for land-derived plant waxes) to get insight into whether or not the major source of the metals were terrigenous.

The statistical analysis of the hydrocarbon data was restricted to the concentrations of major homologs/biomarkers. The analysis included using univariate and multivariate statistics. To deduce the sources of hydrocarbons (Naidu et al., 2001) binary correlations were generated between Σ*n*-alkanes and *n*-$C_{29}$, total polycyclic aromatic hydrocarbons (ΣPAHs) vs organic matter (OM) contents, selected *n*-alkanes against PAHs (e.g., $C_{29}$ vs perylene), and ΣPAHs vs OM. Principal component analysis was performed to distinguish the extent of natural and anthropogenic sources of inputs of hydrocarbons (Macdonald et al., 2004). In this context, Pearson's correlation coefficient was used where relationships were linear. Where associations between variables were nonlinear, Spearman's nonparametric correlation coefficient was used as it assumes that ranks increase or decrease monotonically (Townend, 2002). Principal component analysis was also used to elucidate spatial trends among stations for the hydrocarbon data. Analyses of the hydrocarbon data were also separated by the three regions investigated on Dr. Naidu's CMI projects [Colville Delta-Prudhoe Bay/Beaufort Sea (BS97), Elson Lagoon (EL99) and Beaufort Lagoon (BL03)]. To assess temporal changes in the mean concentrations of selected hydrocarbon homologs/biomarkers and their ratios [lower molecular weight alkanes/total alkanes (LALK/TALK), naphthalene/phenanthrene (N/P), ΣPAH, pristane and phytane] the hydrocarbon data for two time-intervals [1987 (Boehm et al., 1987) and 2001 (Naidu et al. 2001)] were qualitatively compared. This comparison was restricted to five subregions in Colville Delta-Prudhoe Bay which were the only areas for the Beaufort Sea nearshore for which the database was available. To this comparison, data from limited three subregions were also added on ΣPAH in sediments that were collected in years 2000 and 2002 (Brown et al., 2005). Concentrations of the major hydrocarbon homologs were *ln*(X+1) transformed prior to multivariate analyses. The value "1" was added due to zero values in the data set. Data were standardized to percent organic matter and the PCA results are presented for both standardized and non-standardized data so that sites with no organic matter recorded could be considered in the analyses.

We have also synthesized the database on the mean concentrations of selected metals and hydrocarbons in sediments for the individual three regions (Colville Delta-Prudhoe Bay, Elson Lagoon and Beaufort Lagoon) with a goal to assess the concentration levels of the above chemicals for potential adverse effects on resident benthic and demersal organisms. In this assessment the mean concentrations were compared to the threshold guideline values proposed by Long et al., (1995) in terms of an effects range- low (ERL) and an effects range-medium (ERM).

All the above statistical analyses were performed using the statistical programs R and Statistica. The statistical procedures described in this report are widely accepted and have been applied to environment monitoring studies in arctic and subarctic Alaska (Naidu et al., 1997; Blanchard et al., 2002) and as in case of hydrocarbons [for example, by Yunker and Macdonald (2003) on sediments from Fraser River Basin and Strait of Georgia, Canada].

# RESULTS

The raw data on the sediment trace metals incorporated into this synthesis are available at the website ftp://ftp.sfos.uaf.edu/naidu/cmistat2007/. Table 1 summarizes the mean concentrations (ng/g MeHg and THg, % Fe, and μg/g rest of the metals) and related statistics for the sediment trace metals (values not normalized to Fe) by regions and year of sampling. In the table the acronym 'n' stands for the number of samples for which data are available, BL77 and BL03 refer to samples collected in Beaufort Lagoon in 1977 (after Naidu, 1981, 1984) and 2003 (Naidu et al., 2006) respectively, BS85 and BS 97 for samples collected in the Colville Delta-Prudhoe Bay nearshore in 1984 (After Trefry, per.comm.) and 1997 (Naidu et al., 2001) respectively, and EL99 for samples collected in Elson Lagoon in 1999 (Naidu et al., 2003b).

Data in Table 1 show that the mean concentrations of none of the metals differ in a consistent pattern between the three regions.

**Table 1. Summary of ANOVA comparing the Arithmetic Mean ± standard deviation, concentrations of metals (not normalized to Fe) between regions/year combinations. n = sample size, and nd = not determined. Data were log transferred, and significant difference (P-value) at α = 0.05, and F is the ANOVA f-statistics. Multiple comparisons performed using Bonferroni corrected values. Supplemental statistics on the ANOVA are included below.**

| | **BL77** | **BL03** | **BS85** | **BS97** | **EL99** | **F** | **p** | **Multiple comparisons** |
|---|---|---|---|---|---|---|---|---|
| **As (µg g$^{-1}$)** | | 14.2 ± 3.2 | | 16.0 ± 6.4 | 20.8 ± 6.4 | 3.08 | 0.056 | nd |
| **Ba (µg g$^{-1}$)** | | 504.5 ± 84.6 | 354.0 ± 119.9 | 570.5 ± 95.2 | 553.2 ± 46.2 | 20.67 | <0.001* | BL03>BS85; BS85<BS97 & EL99 |
| **Cd (µg g$^{-1}$)** | | 0.26 ± 0.1 | 0.19 ± 0.1 | 0.27 ± 0.1 | 0.17 ± 0.0 | 6.59 | <0.001* | BL03>BS85; BS85<BS97 |
| **Cr (µg g$^{-1}$)** | 67.8 ± 11.3 | 73.0 ± 7.0 | 79.2 ± 9.3 | 62.5 ± 11.6 | 120.8 ± 41.4 | 22.57 | <0.001* | EL99>BL03 & BL77 & BS97; BL77<BS85; BS85>BS97 |
| **Cu (µg g$^{-1}$)** | 22.3 ± 4.3 | 36.8 ± 8.9 | 23.0 ± 4.7 | 26.6 ± 6.3 | 34.3 ± 2.2 | 15.52 | <0.001* | BL03>BL77 & BS85 & BS97; EL99>BL77 & BS85 |
| **Fe (%)$^{a}$** | 2.88 ± 0.4 | 2.98 ± 0.4 | | 3.41 ± 0.9 | | 2.64 | 0.082 | nd |
| **MeHg (ng g$^{-1}$)** | | | | 0.06 ± 0.1 | 0.06 ± 0.04 | nd | nd | nd |
| **Mn (µg g$^{-1}$)$^{a}$** | 360.5 ± 65.1 | 607.9 ± 643.5 | | 545.1 ± 354.2 | 557.2 ± 465.8 | 0.91 | 0.445 | nd |
| **Ni (µg g$^{-1}$)** | 47.4 ± 5.9 | 39.3 ± 6.8 | | 33.8 ± 6.3 | 49.6 ± 2.9 | 13.52 | <0.001* | BL03<BL77 & EL99; BL77>BS97; BS97<EL99 |
| **Pb (µg g$^{-1}$)** | | 17.3 ± 4.1 | 13.0 ± 3.3 | 15.1 ± 5.4 | 19.1 ± 3.9 | 7.08 | <0.001* | BL03>BS85; BS85<EL99 |
| **Sn (µg g$^{-1}$)** | | 2.2 ± 1.0 | | | 2.5 ± 0.4 | nd | nd | nd |
| **THg (ng g$^{-1}$)$^{a}$** | | 56.6 ± 37.3 | | 17.2 ± 16.3 | 74.4 ± 18.8 | 4.62 | 0.015* | BS97<EL99 |
| **V (µg g$^{-1}$)** | 137.1 ± 16.6 | 119.8 ± 13.1 | 115.6 ± 20.0 | 116.6 ± 21.7 | 173.8 ± 25.6 | 9.37 | <0.001* | BL03<EL99; BL77>BS85; EL99>BS85 & BS97 |
| **Zn (µg g$^{-1}$)** | 79.9 ± 11.3 | 93.7 ± 17.3 | 91.2 ± 12.9 | 96.5 ± 15.6 | 129.2 ± 13.5 | 7.89 | <0.001* | EL99>BL03 & BL77 & BS85 & BS97; BL77<BS97 |
| | **n = 10** | **n = 20** | **n = 39** | **n = 62*** | **n = 5** | | | |

NOTE: The number of samples analyzed for Fe and Mn were 22, and for THg 21

**Table 2. Summary of the mean concentrations (ng/g THg, % Fe, and μg/g rest of the metals) and related statistics for the sediment trace metals (values normalized to Fe) by regions and year of sampling. Data in Table 2 show that the mean concentrations of none of the metals (normalized to Fe) differ in a consistent pattern between the three regions, a inference similar to the one drawn on the database in Table 1 (not normalized to Fe). The normalized metal values are metal contents/Fe contents x $10^{-4}$**

| | BL-03 | BS-97 | BL-77 | BS-77 | F | p | df1 | df2 | Multiple Comparisons |
|---|---|---|---|---|---|---|---|---|---|
| **As (μg/g)** | 4.7 ± 0.7 | 4.6 ± 1.4 | | | 0.93 | 0.342 | 1 | 38 | nd |
| **Ba (μg/g)** | 170.9 ± 24.2 | 174.9 ± 43.0 | | | 0.02 | 0.882 | 1 | 38 | nd |
| **Cd (μg/g)** | 0.09 ± 0.03 | 0.08 ± 0.04 | | | 0.75 | 0.394 | 1 | 38 | nd |
| **Cr (μg/g)** | 24.7 ± 1.8 | 18.9 ± 3.9 | 23.5 ± 1.8 | 21.7 ± 6.4 | 3.12 | 0.033* | 3 | 58 | BL03>BL77>BS77>BS97 |
| **Cu (μg/g)** | 12.3 ± 2.2 | 8.0 ± 2.1 | 7.8 ± 1.8 | 8.2 ± 1.7 | 16.12 | <0.001* | 3 | 58 | BL03>BS77>BS97>BL77 |
| **Fe (%)** | 2.98 ± 0.4 | 3.41 ± 0.91 | 2.88 ± 0.42 | 2.58 ± 0.22 | 5.26 | 0.003* | 3 | 58 | BL03>BL77<BS97>BS77 |
| **Mn (μg/g)** | 204.4 ± 207.4 | 159.3 ± 88.7 | 125.2 ± 15.6 | 143.1 ± 35.4 | 0.82 | 0.489 | 3 | 58 | nd |
| **Ni (μg/g)** | 13.2 ± 1.5 | 10.2 ± 1.9 | 16.5 ± 1.3 | 11.5 ± 0.8 | 33.78 | <0.001* | 3 | 58 | BL77>BL03>BS77>BS97 |
| **Pb (μg/g)** | 5.8 ± 0.9 | 4.3 ± 1.1 | | | 22.6 | <0.001* | 1 | 38 | BL03>BS97 |
| **Sn (μg/g)** | 0.7 ± 0.3 | 0 ± 0 | | | nd | nd | nd | nd | nd |
| **THg (μg/g)** | 0.02± 0.01 | 0.01 ± 0.01 | | | 5.76 | 0.021* | 1 | 38 | BL03>BS97 |
| **V (μg/g)** | 40.5 ± 2.9 | 34.9 ± 6.5 | 48.0 ± 5.1 | 33.8 ± 1.9 | 21.72 | <0.001* | 3 | 58 | BL77>BL03>BS97>BS77 |
| **Zn (μg/g)** | 31.3 ± 3.5 | 29.1 ± 6.0 | 27.8 ± 2.3 | 36.7 ± 3.6 | 9.54 | <0.001* | 3 | 58 | BS77>BL03>BS97>BL77 |

**[a] NOTE: Sample size of n = 20**

Table 2 also summarizes the time-interval differences in the mean concentrations (see Table 1 for units) in surficial mud samples of selected metals for the Colville Delta-Prudhoe Bay (BS-sets) and the Beaufort Lagoon (BL-sets), but the concentrations are normalized to Fe in the samples. The differences identified for the limited data available on Fe-normalized basis of metals indicate that significant increases (at 99% confidential level) are noted only in Mn

Table 3 summarizes the time-interval differences in the mean concentrations (see Table 1 for units) in surface mud samples of selected metals (not normalized to Fe) specifically referring to two regions: the Colville Delta-Prudhoe Bay (BS-sets) and the Beaufort Lagoon (BL-sets). Sediment sample series BS77, BS85, BS97, BL77 and BL03 were collected in 1977, 1985, 1997, 1977 and 2003 respectively. The concentration differences identified by comparing data on regionwise were as follows. In Colville Delta-Prudhoe Bay significant increases (at 99% confidential level) are noted in vanadium (V) in 1985 and 1997 compared to 1977, and in barium (Ba) from 1985 to 1997 (Table 3). No significant changes are noted in the concentrations of other elements. In Beaufort Lagoon a significant decrease in vanadium (V) and increases in manganese (Mn) and copper (Cu) concentrations are noted in 2003 compared to 1977.

**Table 3. Time-interval differences in the mean concentrations of trace metals [not normalized to iron (Fe)] in mud of Colville Delta-Prudhoe Bay and Beaufort Lagoon. The concentrations of iron (Fe) are in %, whereas those of other metals in µ/g.**

| REGION/YEAR | STATISTICS | V | Cr | Cu | Ni | Zn | Cd | Pb | Ba | Fe | Mn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Colville-Prudhoe, BS77 | Mean | 87 | 60 | 21 | 30 | 94 | | | | 2.58 | 368 |
| | SD | 3 | 5 | 4 | 2 | 10 | | | | 0.22 | 96 |
| | N | 12 | 12 | 12 | 12 | 12 | | | | 12 | 12 |
| | | | | | | | | | | | |
| Colville-Prudhoe, BS85 | Mean | 116 | 79 | 23 | | 91 | 0.187 | 13 | 354 | | |
| | SD | 20 | 9 | 4.65 | | 12.89 | 0.053 | 3.3 | 120 | | |
| | N | 39 | 39 | 39 | | 39 | 39 | 39 | 39 | | |
| | | | | | | | | | | | |
| Colville-Prudhoe, BS97 | Mean | 117 | 63 | 27 | 34 | 96 | 0.264 | 15 | 569 | 3.40 | 540 |
| | SD | 23 | 13 | 7 | 7 | 18 | 0.115 | 6 | 114 | 0.88 | 337 |
| | N | 62 | 62 | 62 | 62 | 62 | 62 | 62 | 62 | 22 | 22 |
| | | | | | | | | | | | |
| Beaufort Lagoon, BL77 | Mean | 139 | 69 | 22 | 48 | 81 | | | | | 359 |
| | SD | 17 | 12 | 4 | 6 | 11 | | | | | 69 |
| | N | 10 | 10 | 10 | 10 | 10 | | | | | 10 |
| | | | | | | | | | | | |
| Beaufort Lagoon, BL03 | Mean | 120 | 73 | 37 | 39 | 94 | | | | | 608 |
| | SD | 13 | 7 | 8.9 | 6.8 | 17 | | | | | 643 |
| | N | 20 | 20 | 20 | 20 | 20 | | | | | 20 |

Figure 5 displays the stratigraphic variations of the metal concentrations (not normalized to iron) in the mud fraction of two sediment cores (3B and SL) sampled in 1997 from Colville Delta-Prudhoe Bay (Fig. 2). In core sample 3B net increases are noted only in arsenic (As) and barium (Ba) toward the core top from about midway of the core (since ~1989). In core sample SL the trend within the upper ~2-cm (since ~1995-1996) shows increased concentrations in all metals toward the core top. However, regression analysis extended to the entire core indicate significant decreases (at the 99% confidence level) up core in Zn, Cd, MeHg and Pb in core 3B and in MeHg in core SL (Figs. 5 and 6), accompanied by no significant stratigraphic net changes in the remaining metals.

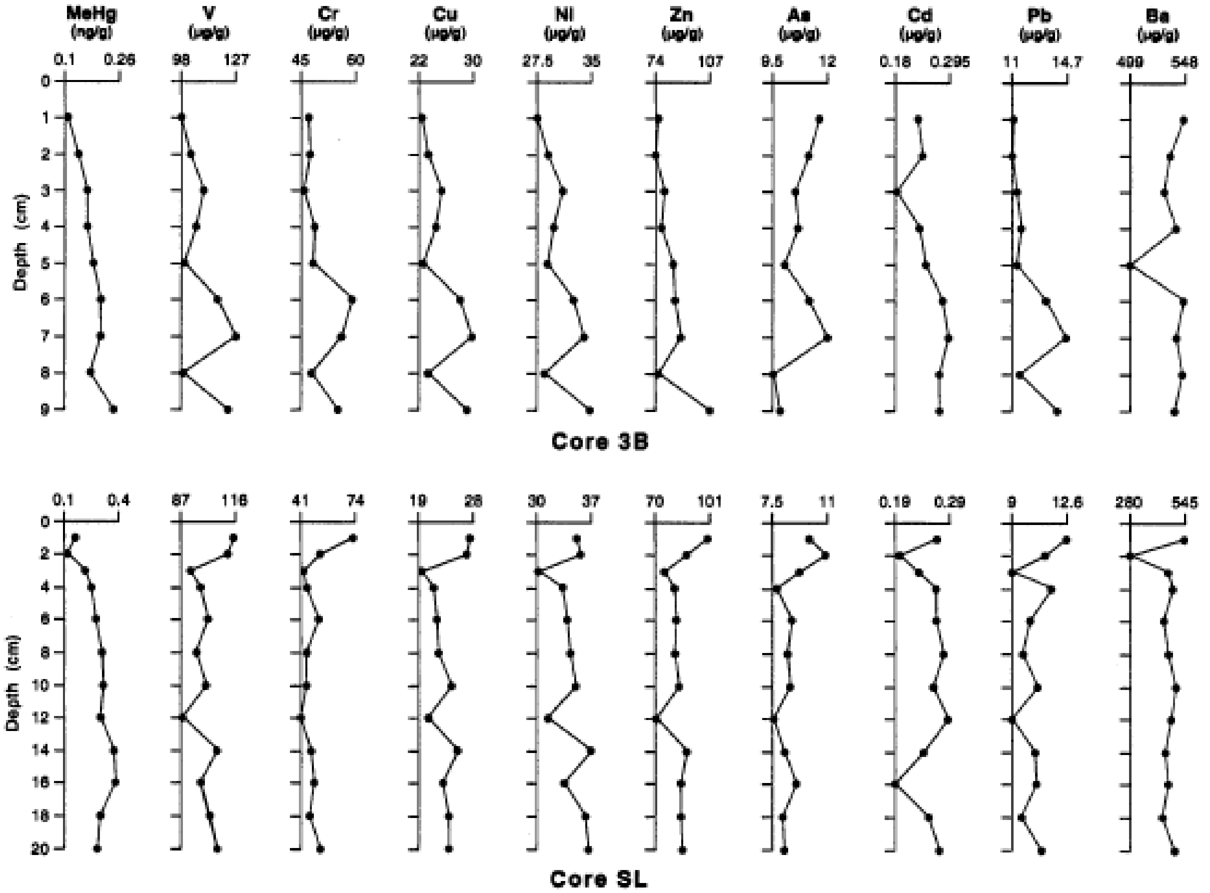


**Figure 5. Stratigraphic variations (after Naidu et al., 2001) in trace metal concentrations in sediment cores 3B and SL from Colville Delta-Prudhoe Bay**

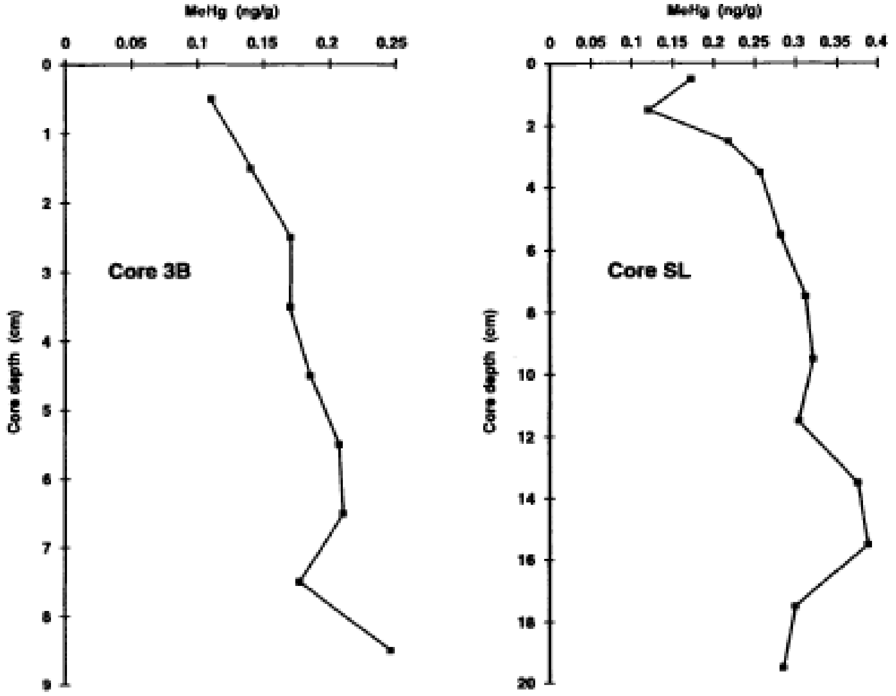


**Figure 6. Stratigraphic variations (after Naidu et al., 2001) in the concentrations of MeHg (ng/g) in cores 3B and SL from Colville Delta-Prudhoe Bay.**

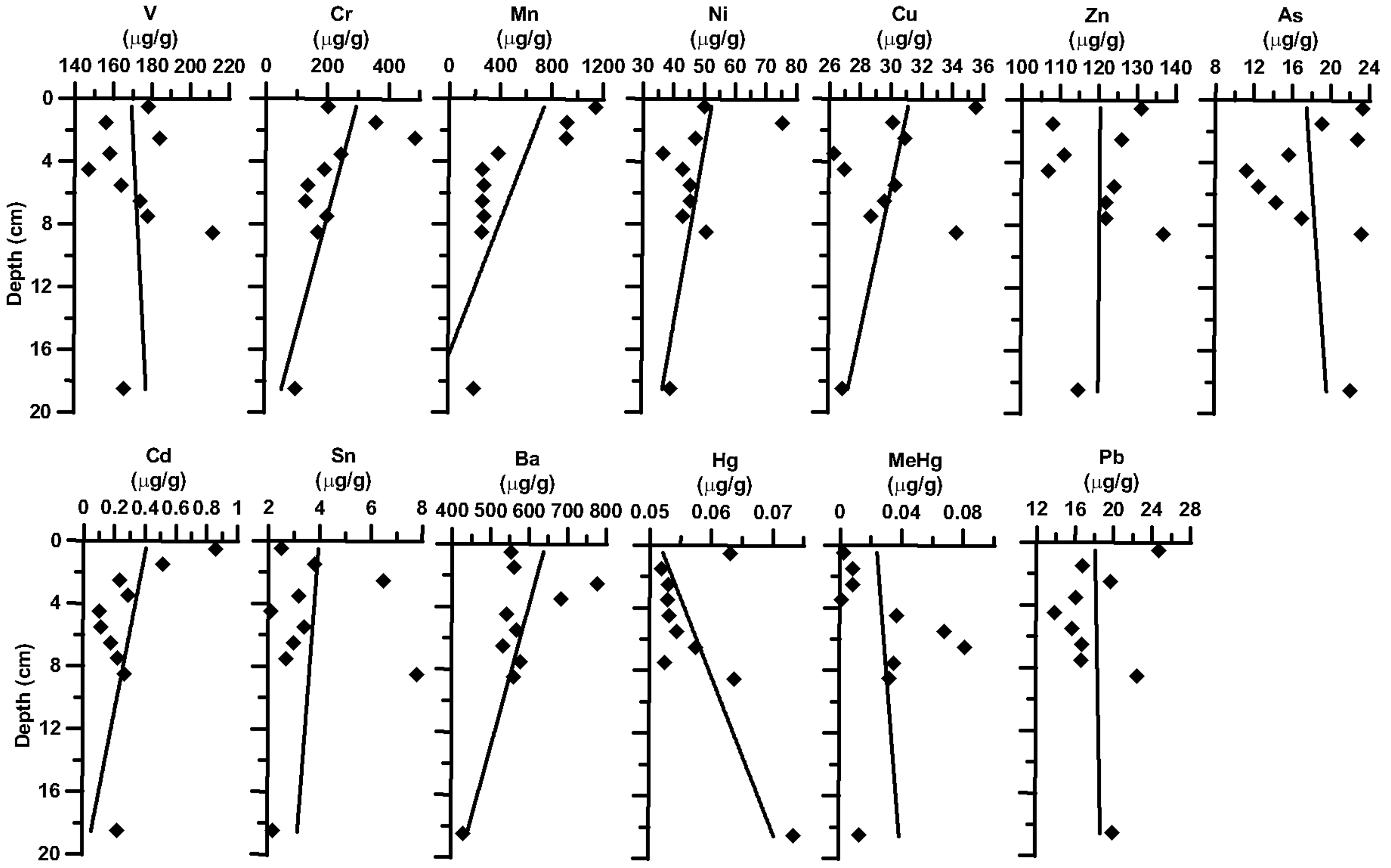


**Figure 7. Stratigraphic variations (after Naidu et al., 2001) in trace metal concentrations in sediment core EL-3 from Elson Lagoon. MeHg concentrations are in ng/g and not μg/g as in the figure above.**

Figure 7 displays the stratigraphic variations in the concentrations of the metals of one core collected in Elson Lagoon in 1999. Regression analyses of the metals stratigraphies, spanning over the past 70-83 years, demonstrate significant net increases ($p<0.05$) up core in Cr, Mn and Ba, and an up core decrease in THg, accompanied by no significant variations in the remaining metals (Fig. 7).

Figures 8 and 9 are dendrograms illustrating results of the cluster analyses, of *ln*-transformed metal concentrations, not normalized and normalized to iron, respectively for the study area [Colville Delta-Prudhoe Bay/Beaufort Sea (BS97), Elson Lagoon (EL99) and Beaufort Lagoon (BL03)]. Note that in Figure 9 there is no plot corresponding to Elson Lagoon because there were no data on iron (Fe) available for that area. Both the dendrograms demonstrate clustering of station groups delineated by each of the regions. Although some discrete clustering of sites is apparent in the cluster dendrogram, significant overlapping of clusters of different regions is illustrated in the PCA plot of metal data that are not normalized to Fe (Fig. 10). The plots corresponding to Elson Lagoon, though, stand out as a discrete cluster. Thus, broad regional distributional trends in metals concentrations are present, at best. However, the strengths of regional trends are not clear due to the inconsistencies among the multivariate methods. In slight contrast, the principal component analysis (PCA) of the metal data for 1997 through 2003 when normalized to Fe (Fig. 11) suggests that the cluster of plots display relatively minor overlapping relating to the plots for Beaufort Lagoon (BL03) and Colville Delta-Prudhoe Bay (BS97).

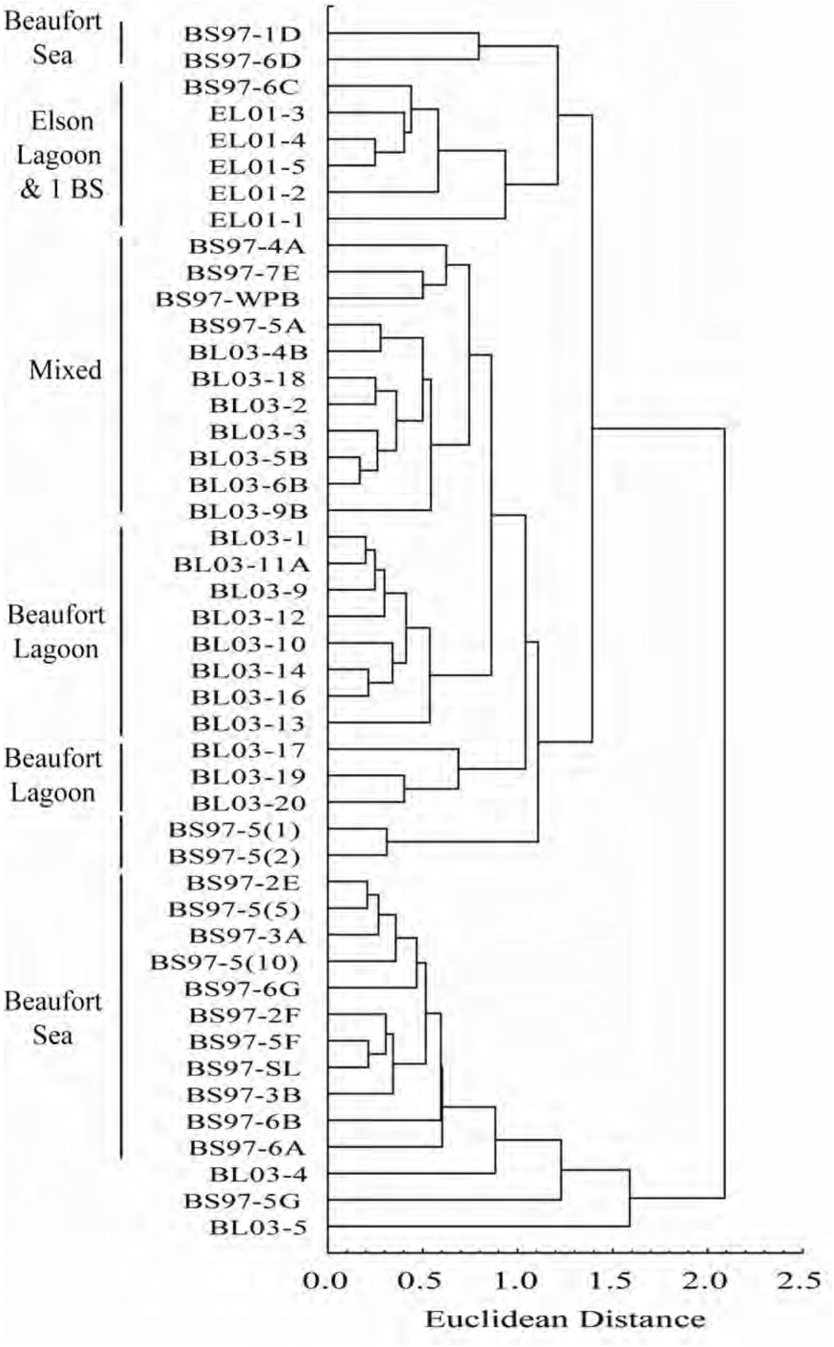


**Figure 8. Cluster analysis of *ln*-transformed metals data (not normalized to Fe) for the study area, 1997 to 2003.**

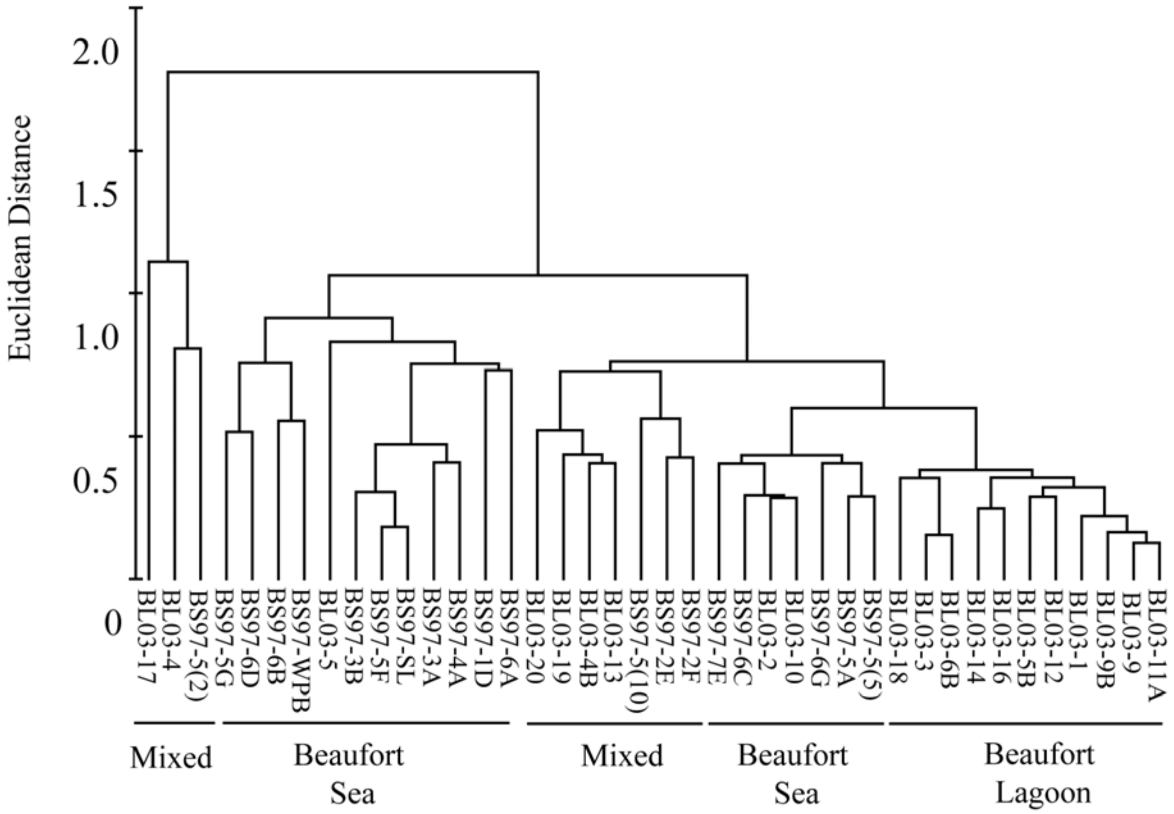


**Figure 9. Dendrogram illustrating the results of the cluster analysis on *ln*-transformed metal concentrations normalized to iron (Fe), for Colville Delta-Prudhoe Bay (Beaufort Sea, BS97) and Beaufort Lagoon (BL03).**

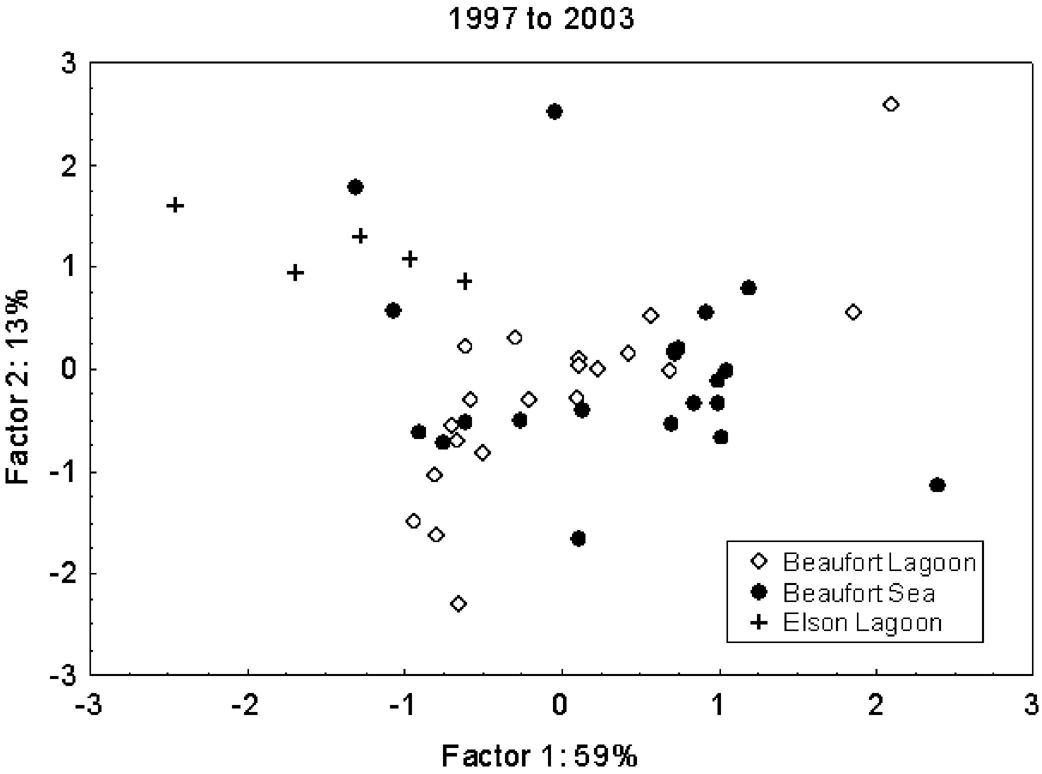


Figure 10. Score plots from PCA of the metals data (not normalized to Fe) for 1997 to 2003 period.

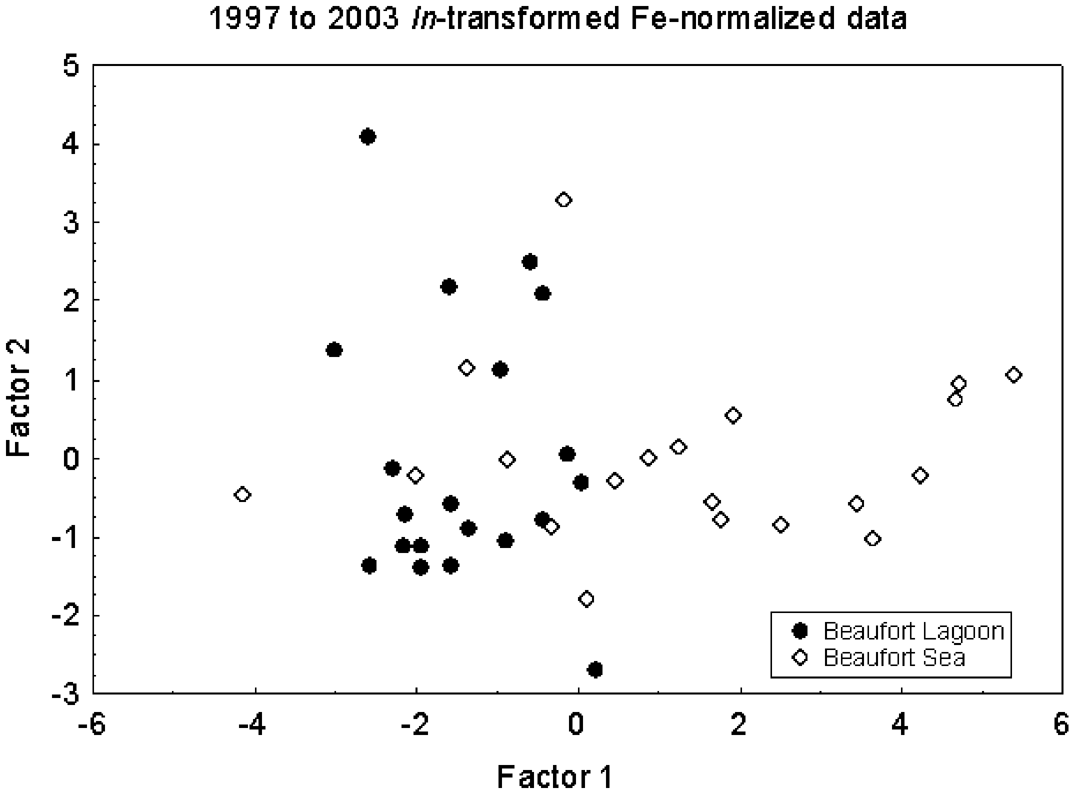


Figure 11. Score plots from PCA of the metal data (normalized to Fe), for the period 1997 to 2003. The Beaufort Sea plots correspond to BS97 (Colville Delta-Prudhoe Bay)

The variable projections from PCA of the metal data (not normalized to Fe) and metal data normalized to Fe are illustrated in Figures 12 and 13, respectively. Most of the variables in common with the BS97 sampling locations from metal data (not normalized to Fe) collected in 1997 to 2003 are highly correlated as indicated by their similar positions in the PCA variable projection (Fig. 12). The exceptions are Ba and Cd. In Fig. 13, the only exception was Cd.

Correlations between the factor scores from PCA and metal concentrations (not normalized to Fe), OM, and location coordinates, for the time period of 1997 to 2003 are provided in Tables 4 and 5. The correlation structure of the data indicate that most variables are highly correlated with PCA factor 1 with the exception of Ba and Cd which appear to be independent of the other variables. PCA factor 2 is highly correlated with Cd. The PCA axes appear to be moderately correlated with Latitude and Longitude suggesting weak regional trends in the measured variables.

The factor scores from the principal component analysis (PCA) relating to metal concentrations (normalized to Fe), OM, and location coordinates, for the time period of 1997 to 2003 are provided in Tables 6 and 7. The correlation structure of the data indicates that most variables are highly correlated with PCA factor 1 with the exception of Ba, Cd, and Mn which appear to be independent of the other variables. PCA factor 2 is highly correlated with Mn. Mn is also highly correlated with percent Mud. PCA factor 1 is correlated with Latitude and Longitude suggesting moderate regional trends in the measured variables. PCA factor 2 is highly correlated with % mud. Stations from the Beaufort Sea are spread along the x-axis of the PCA plot representing Factor 1 which is highly correlated with Latitude and Longitude while stations from Beaufort Lagoon are spread along the y-axis in association with percent mud (Fig. 11 and Table 7). These associations of the PCA plot of Fe-normalized data with environmental variables suggest that the metals concentrations for sites in the Beaufort Sea stations are associated with spatial trends but that the metals concentrations for sites in the Beaufort Lagoon stations vary based on percent mud.

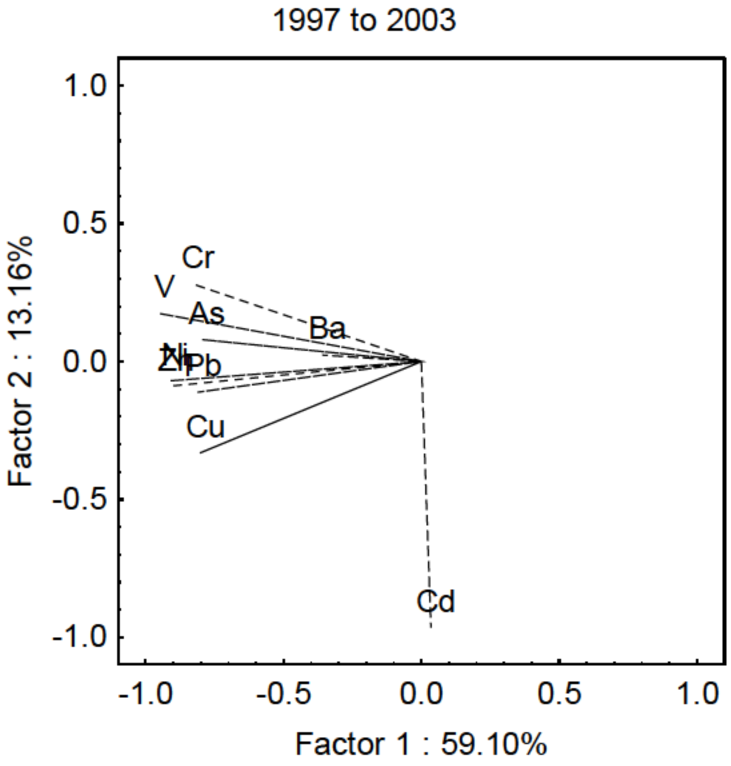


**Figure 12. Variable projection from PCA of the metals data (not normalized to Fe) for the period 1997 to 2003**

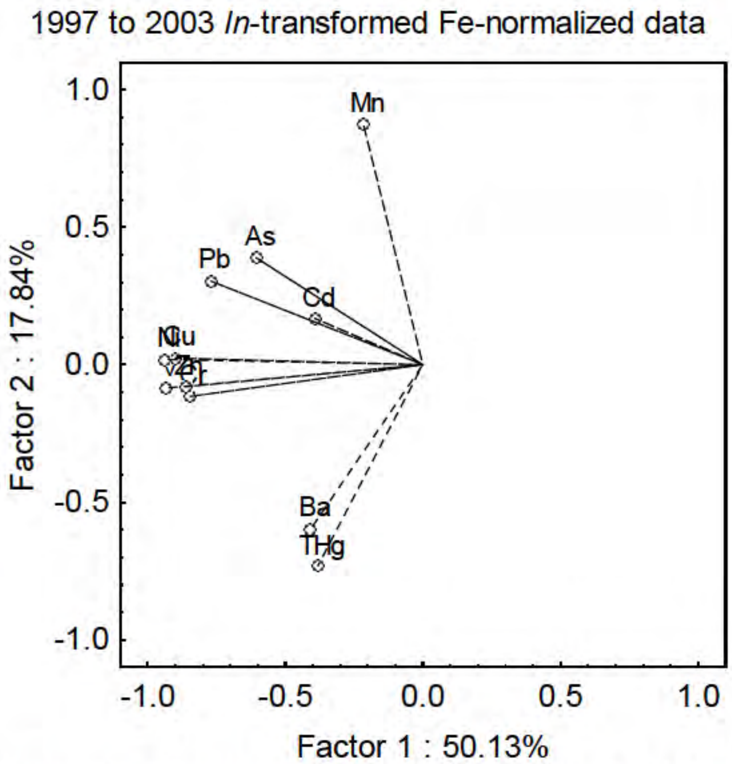


**Figure 13. Variable projection from PCA of the metals data (normalized to Fe) for the period 1997 to 2003**

**Table 4. Correlations between environmental parameters, PCA factor scores, and metals concentrations (not normalized to Fe) for the combined three coastal regions for the time-interval 1997 to 2003. Correlations significant at α = 0.05 are marked in bold.**

| Metal | Latitude | Longitude | Mud (%) | OM(%) | Factor 1 | Factor 2 |
|---|---|---|---|---|---|---|
| Cr | **0.40** | **-0.35** | -0.06 | 0.01 | **-0.83** | 0.28 |
| Cu | -0.22 | 0.25 | 0.13 | -0.04 | **-0.80** | **-0.33** |
| V | **0.49** | **-0.44** | -0.00 | **0.34** | **-0.95** | 0.17 |
| Zn | **0.47** | **-0.45** | 0.13 | **0.41** | **-0.91** | -0.09 |
| As | **0.35** | **-0.31** | -0.23 | **0.46** | **-0.80** | 0.08 |
| Ba | 0.24 | -0.27 | **0.33** | 0.32 | **-0.36** | 0.02 |
| Cd | **-0.31** | 0.26 | -0.08 | 0.16 | 0.03 | **-0.97** |
| Ni | 0.21 | -0.17 | 0.07 | 0.09 | **-0.91** | -0.07 |
| Pb | 0.02 | 0.04 | -0.17 | 0.19 | **-0.81** | -0.11 |

**Table 5. Correlations between PCA factor score and environmental parameters for the coastal three regions combined for the time-interval 1997 to 2003. Correlations significant at α = 0,05 are marked in bold.**

| PCA Factor | Latitude | Longitude | Mud (%) | OM(%) |
|---|---|---|---|---|
| Factor 1 | **-0.31** | 0.26 | -0.01 | -0.26 |
| Factor 2 | **0.48** | **-0.43** | 0.01 | -0.10 |

**Table 6. Correlations between environmental parameters, PCA factor scores, and metals concentrations (normalized to Fe) for the combined coastal regions for the time-interval 1997 to 2003 (BS 97 and BL03 samples). Correlations significant at α = 0.05 are marked in bold.**

| | Latitude | Longitude | Mud (%) | OM(%) | Factor1 | Factor2 |
|---|---|---|---|---|---|---|
| V | **-0.44** | **0.42** | -0.10 | -0.23 | **-0.87** | -0.08 |
| Cr | **-0.59** | **0.58** | -0.06 | **-0.45** | **-0.81** | -0.19 |
| Cu | **-0.77** | **0.72** | 0.09 | **-0.40** | **-0.93** | -0.12 |
| Zn | **-0.36** | 0.30 | 0.21 | -0.18 | **-0.80** | -0.21 |
| Mn | 0.05 | -0.07 | **-0.73** | 0.25 | -0.22 | **0.80** |
| Ni | **-0.64** | **0.60** | -0.02 | **-0.39** | **-0.94** | -0.11 |
| As | -0.17 | 0.15 | -0.23 | 0.00 | **-0.56** | **0.36** |
| Cd | -0.17 | 0.17 | -0.15 | -0.03 | **-0.37** | 0.16 |
| Ba | -0.12 | 0.11 | **0.38** | -0.20 | **-0.34** | **-0.63** |
| Pb | **-0.67** | **0.64** | -0.18 | -0.28 | **-0.77** | 0.08 |

**Table 7. Correlations between PCA factor score based on Fe-normalized metals concentrations and environmental parameters for the two coastal regions combined for the time-interval 1997 to 2003. Correlations significant at a = 0.05 are marked in bold.**

| | Latitude | Longitude | Mud (%) | OM(%) |
|---|---|---|---|---|
| Factor1 | **0.65** | **-0.60** | 0.03 | **0.33** |
| Factor2 | 0.24 | -0.23 | **-0.85** | **0.35** |

Result of the Spearman's rank correlation analysis relating to the matrix of inter-element variances of metal concentrations (not normalized to iron) and element-granulometry-organic matter contents for Colville Delta Prudhoe Bay, Elson Lagoon and Beaufort Lagoon are presented in Table 8. The bolded numbers indicate significant r-value (prorated to N, the sample number, analyzed for the individual elements) at least at 95% confidence level.

Results of similar Spearman's rank correlation analysis based on metal data normalized to iron (Fe) are included in Table 9. The highlighted numbers indicate significant r-value (prorated to N, the sample number, analyzed for the individual elements) at least at 95% confidence level.

Results of the Spearman's correlation coefficient analysis run between granulometry and contents of THg, MeHg and organic matter in gross sediments are presented in Table 10. The results indicate that THg and MeHg are positively correlated (r=95%) with the per cent of silt, clay and mud but not with organic matter (OM) per cent.

Correlations between concentrations of sediment metals (Cr, Fe, Mn, Pb, Ni, Cd, Ba, Zn, As, Cu, and V, THg, and MeHg and the hydrocarbon *n*-$C_{29}$ (a typical terrestrial biomarker) are illustrated in Figure 14. The scatterplots illustrate that against *n*-$C_{29}$ no significant positive correlations are identified for all the metals except for total mercury (THg, r=0.769) and methyl mercury (MeHg) (in Beaufort Lagoon and Colville Delta-Prudhoe Bay r=0.83; and in Elson Lagoon r=0.97).

**Table 8. Spearman’s rank analysis showing the correlation coefficient matrix for element-granulometry- organic matter on mud samples from Colville Delta-Prudhoe Bay, Elson Lagoon and Beaufort Lagoon, based on trace metal data not normalized to iron. Values in bold are significant at α = 0.05.**

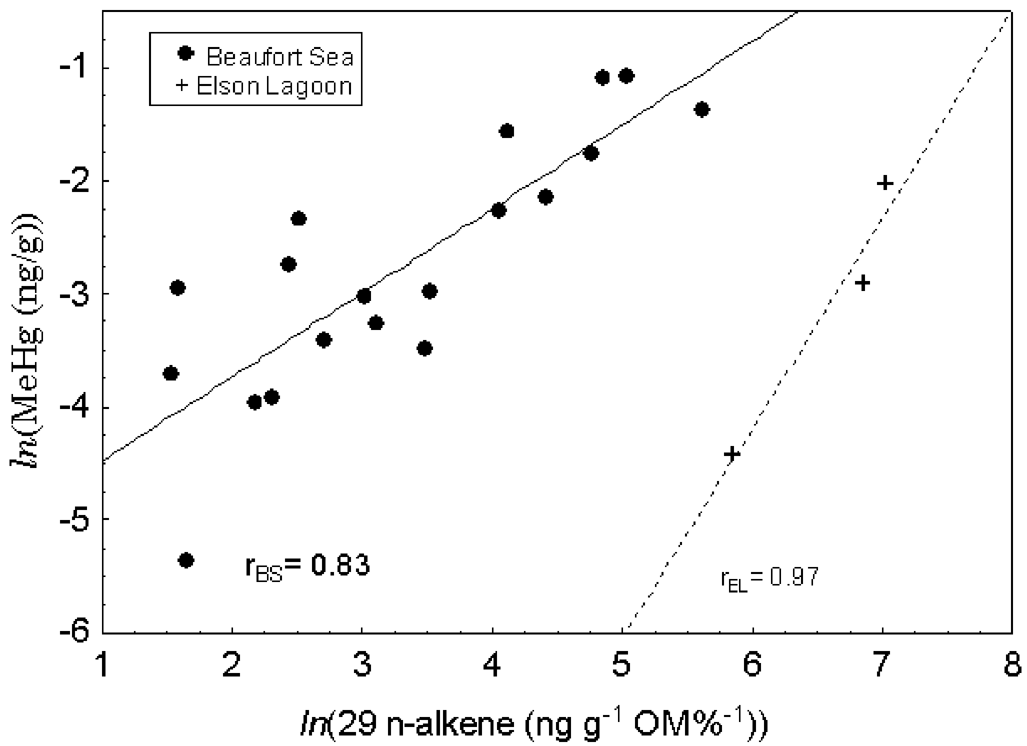
| | Silt (% in Mud) | Clay (% in Mud) | OM(%)) | V | Cr | Cu | Zn | Mn | Ni | As | Cd | Ba | Pb | Sn | Fe (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Silt (% in Mud) | 1.0 | | | | | | | | | | | | | | |
| Clay (% in Mud) | -1.0 | 1.0 | | | | | | | | | | | | | |
| OM(%) | **-0.3** | **0.3** | 1.00 | | | | | | | | | | | | |
| V | **-0.3** | **0.3** | **0.42** | 1.00 | | | | | | | | | | | |
| Cr | -0.1 | 0.1 | **0.46** | **0.88** | 1.00 | | | | | | | | | | |
| Cu | 0.1 | -0.1 | **0.36** | **0.83** | **0.79** | 1.00 | | | | | | | | | |
| Zn | -0.1 | 0.1 | **0.45** | **0.82** | **0.73** | **0.80** | 1.00 | | | | | | | | |
| Mn | **-0.6** | **0.6** | 0.24 | 0.01 | 0.03 | -0.26 | -0.13 | 1.00 | | | | | | | |
| Ni | **-0.3** | **0.3** | **0.47** | **0.89** | **0.79** | **0.85** | **0.73** | 0.11 | 1.00 | | | | | | |
| As | **-0.3** | **0.3** | **0.34** | **0.76** | **0.55** | **0.58** | **0.64** | 0.15 | **0.63** | 1.00 | | | | | |
| Cd | **-0.5** | **0.5** | **0.57** | **0.56** | **0.55** | **0.55** | **0.58** | **0.37** | **0.73** | **0.38** | 1.00 | | | | |
| Ba | **0.3** | **-0.3** | 0.10 | **0.45** | **0.47** | **0.56** | **0.70** | **-0.47** | **0.31** | 0.24 | 0.23 | 1.00 | | | |
| Pb | **-0.3** | **0.3** | **0.39** | **0.88** | **0.76** | **0.86** | **0.90** | 0.00 | **0.89** | **0.68** | **0.71** | **0.51** | 1.00 | | |
| Sn | **-0.5** | **0.5** | **0.43** | **0.74** | **0.71** | **0.60** | **0.65** | **0.39** | **0.83** | **0.57** | **0.69** | 0.15 | **0.83** | 1.00 | |
| Fe (%) | -0.2 | 0.2 | **0.45** | **0.81** | **0.83** | **0.70** | **0.80** | 0.15 | **0.71** | **0.76** | **0.56** | **0.57** | **0.79** | **0.65** | 1.00 |

**Table 9. Results of the Spearman's rank analysis showing correlations between Fe-normalized heavy metal concentrations (metal/Fe x $10^{-4}$). Significant values ($\alpha$ = 0.05) are marked in bold.**

| | Silt (%) | Clay (%) | OM(%) | V | Cr | Cu | Zn | Mn | Ni | As | Cd | Ba |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Silt (%) | 1.00 | | | | | | | | | | | |
| Clay (%) | **0.68** | 1.00 | | | | | | | | | | |
| OM(%) | -0.32 | -0.23 | 1.00 | | | | | | | | | |
| V | -0.13 | 0.00 | -0.23 | 1.00 | | | | | | | | |
| Cr | -0.05 | -0.02 | **-0.45** | **0.89** | 1.00 | | | | | | | |
| Cu | 0.07 | 0.16 | **-0.40** | **0.71** | **0.68** | 1.00 | 0.70 | | | | | |
| Zn | 0.18 | 0.18 | -0.18 | **0.64** | **0.58** | **0.70** | 1.00 | | | | | |
| Mn | **-0.69** | **-0.70** | 0.25 | 0.19 | 0.11 | 0.12 | 0.13 | 1.00 | | | | |
| Ni | -0.04 | 0.06 | **-0.39** | **0.84** | **0.83** | **0.90** | **0.68** | 0.18 | 1.00 | | | |
| As | -0.29 | -0.17 | 0.00 | **0.52** | 0.31 | **0.46** | **0.54** | **0.39** | 0.41 | 1.00 | | |
| Cd | -0.22 | -0.17 | -0.03 | 0.18 | 0.16 | **0.33** | **0.38** | 0.29 | 0.30 | 0.06 | 1.00 | |
| Ba | 0.33 | 0.31 | -0.20 | **0.39** | **0.42** | 0.20 | **0.46** | -0.27 | 0.23 | 0.06 | 0.10 | 1.00 |
| Pb | -0.19 | -0.15 | -0.28 | **0.60** | **0.57** | **0.72** | **0.52** | 0.17 | **0.71** | **0.57** | 0.22 | 0.07 |

**Table 10. Spearman's rank analysis showing correlation coefficient matrix for total mercury (THg), methyl mercury (MeHg), granulometry and organic matter (OM) on gross sediments from Colville Delta-Prudhoe Bay, Elson Lagoon and Beaufort Lagoon.**

| | Gravel (%) | Sand (%) | Silt (%) | Clay (%) | Mud (%) | OM(%) | THg(ng/g) | MeHg(ng/g) |
|---|---|---|---|---|---|---|---|---|
| Gravel (%) | 1.00 | | | | | | | |
| Sand (%) | 0.02 | 1.00 | | | | | | |
| Silt (%) | -0.30 | **-0.76** | 1.00 | | | | | |
| Clay (%) | -0.20 | **-0.75** | **0.60** | 1.00 | | | | |
| Mud (%) | -0.29 | **-0.87** | **0.90** | **0.87** | 1.00 | | | |
| OM(%) | 0.21 | 0.22 | -0.30 | -0.22 | 0.11 | 1.00 | | |
| THg(ng/g) | -0.18 | **-0.59** | **0.64** | **0.78** | **0.78** | -0.37 | 1.00 | |
| MeHg(ng/g) | -0.14 | **-0.71** | **0.77** | **0.62** | **0.83** | 0.06 | **0.47** | 1.00 |



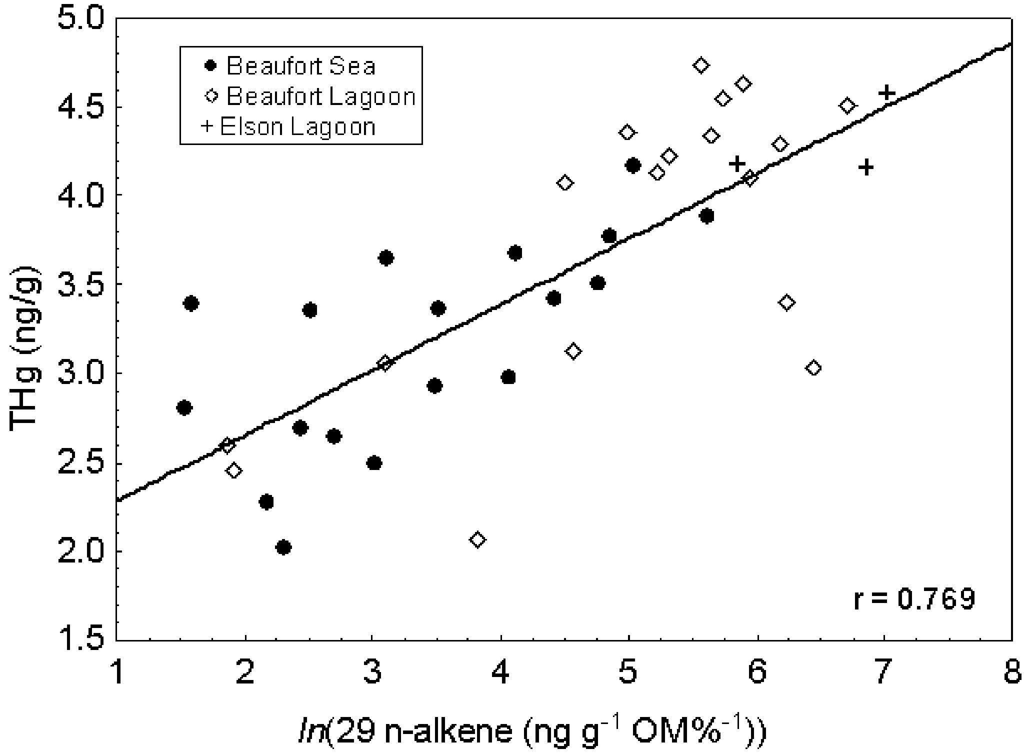
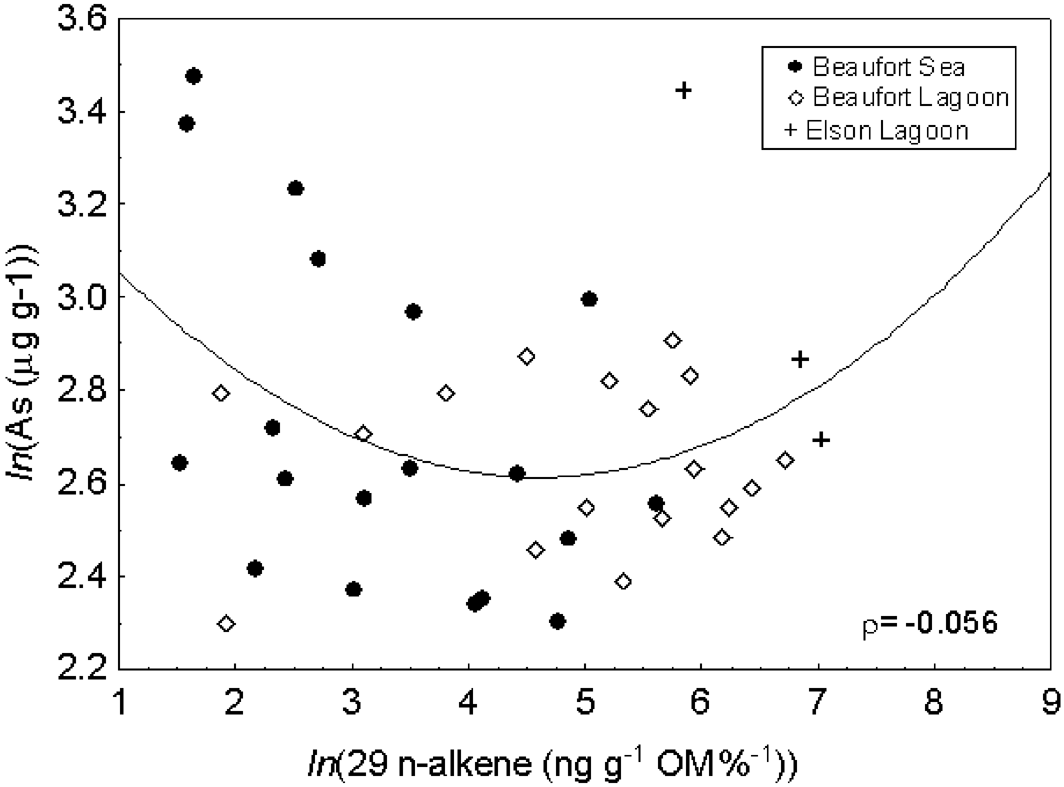


**Figure 14. Scatterplots of trace metal concentrations against $C_{29}$ *n*-alkane. All variables are *ln*-transformed. Pearson's correlations are presented but Spearman's nonparametric correlation coefficients are presented where nonlinearity is present.**



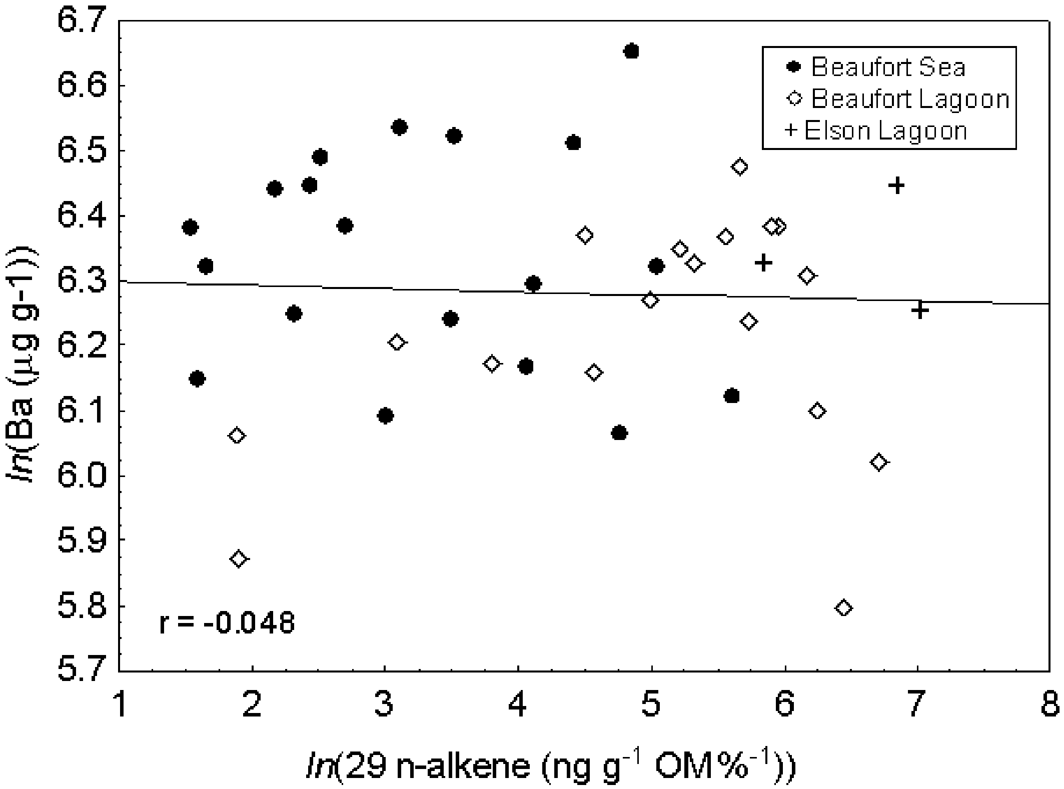
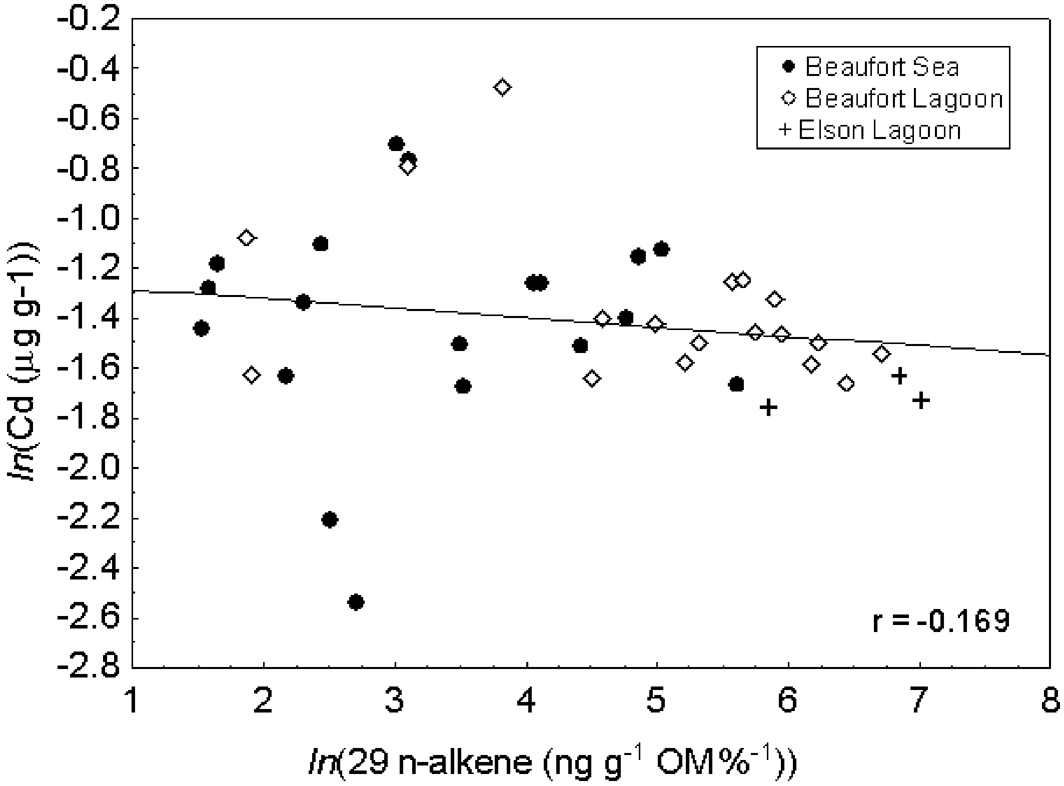


**Figure 14 Continued. Scatterplots of trace metal concentrations against $C_{29}$ *n*-alkane. All variables are *ln*-transformed. Pearson's correlations are presented but Spearman's nonparametric correlation coefficients are presented where nonlinearity is present.**



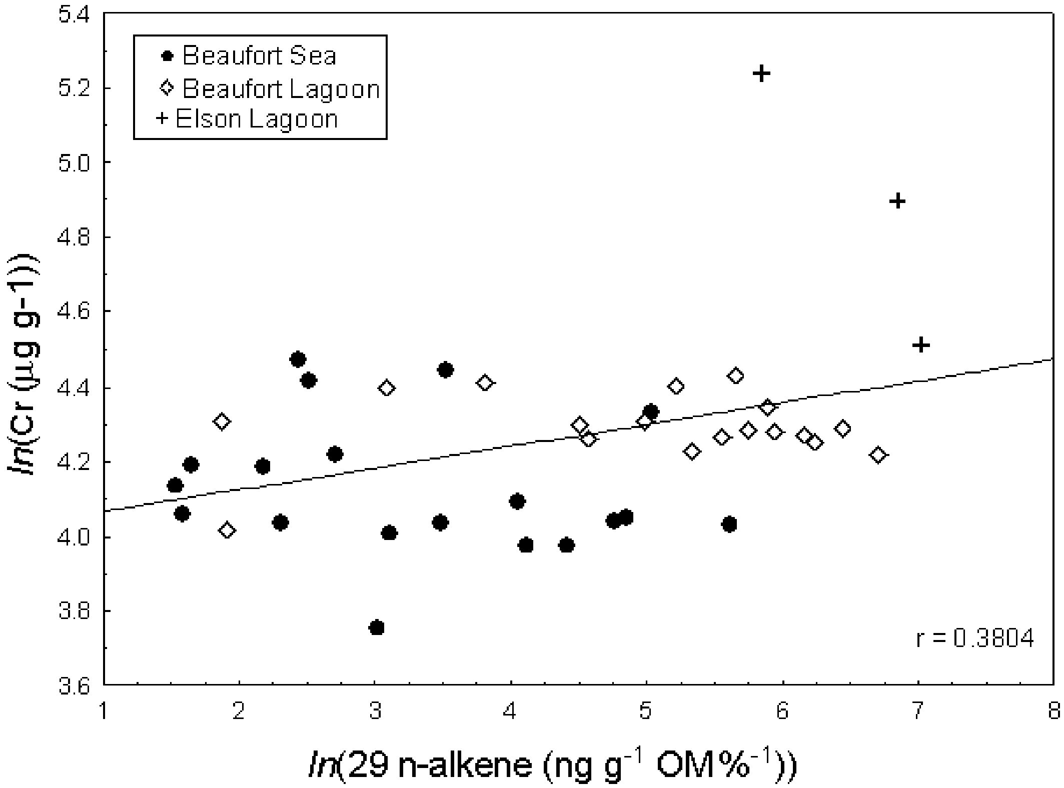
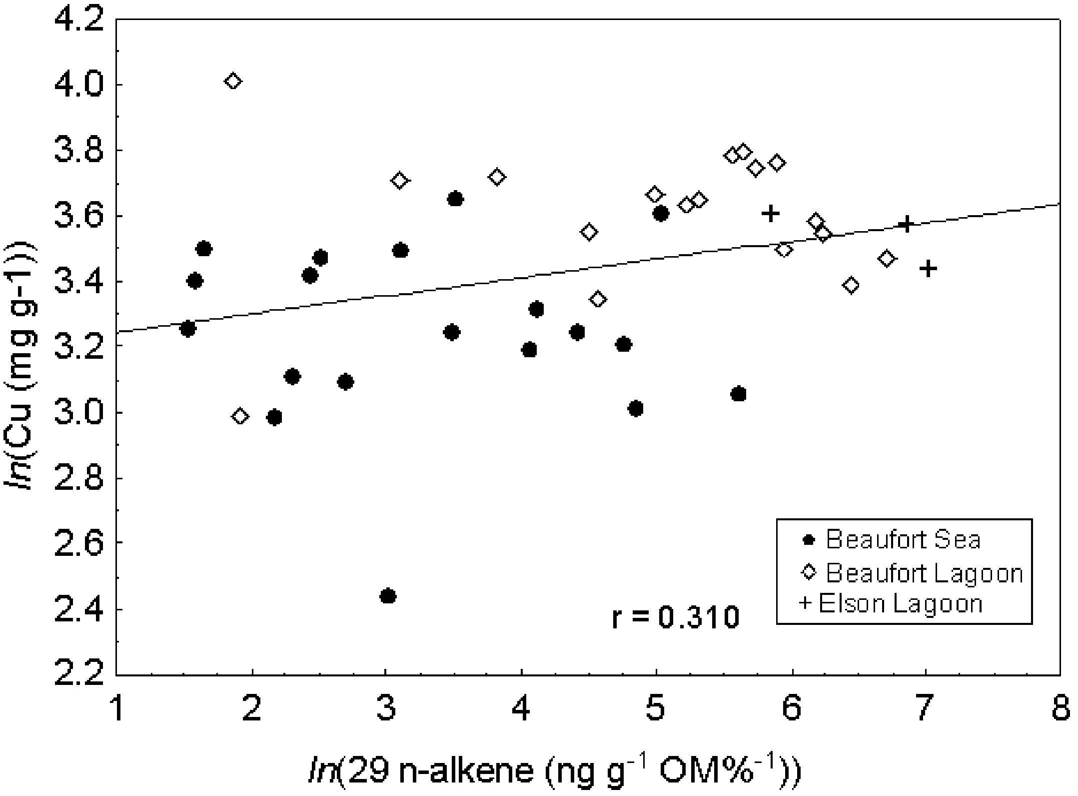


**Figure 14 Continued. Scatterplots of trace metal concentrations against $C_{29}$ *n*-alkane. All variables are *ln*-transformed. Pearson's correlations are presented but Spearman's nonparametric correlation coefficients are presented where nonlinearity is present.**



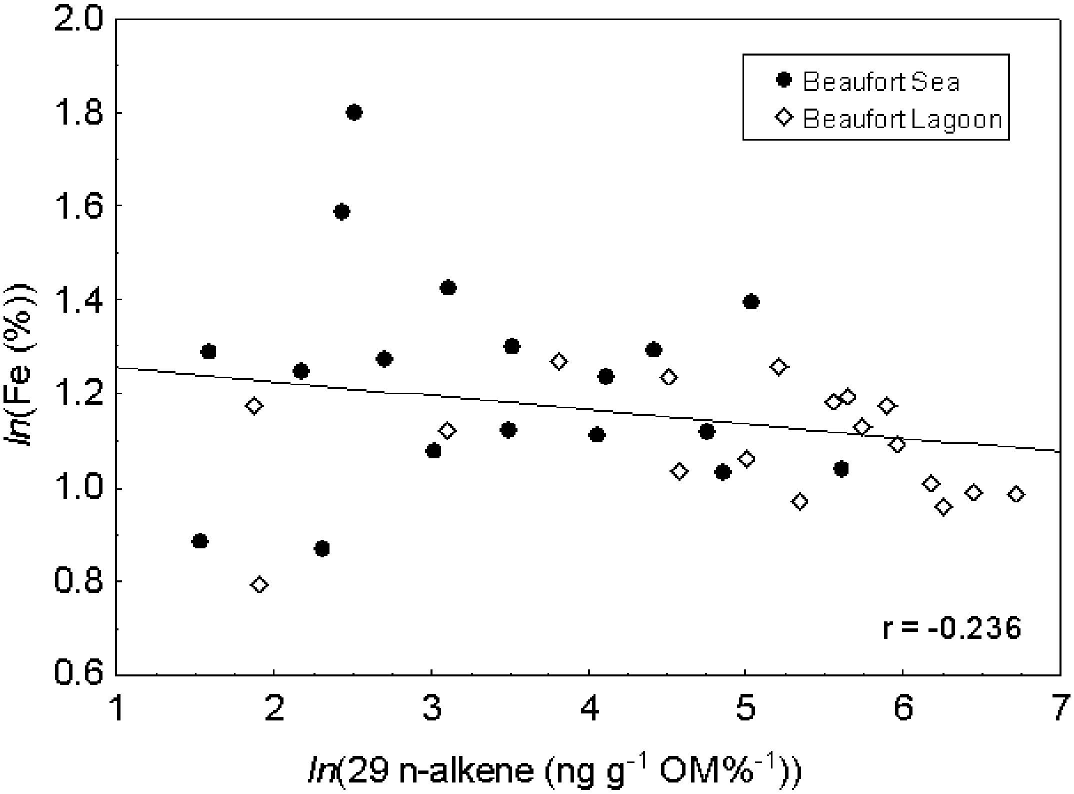
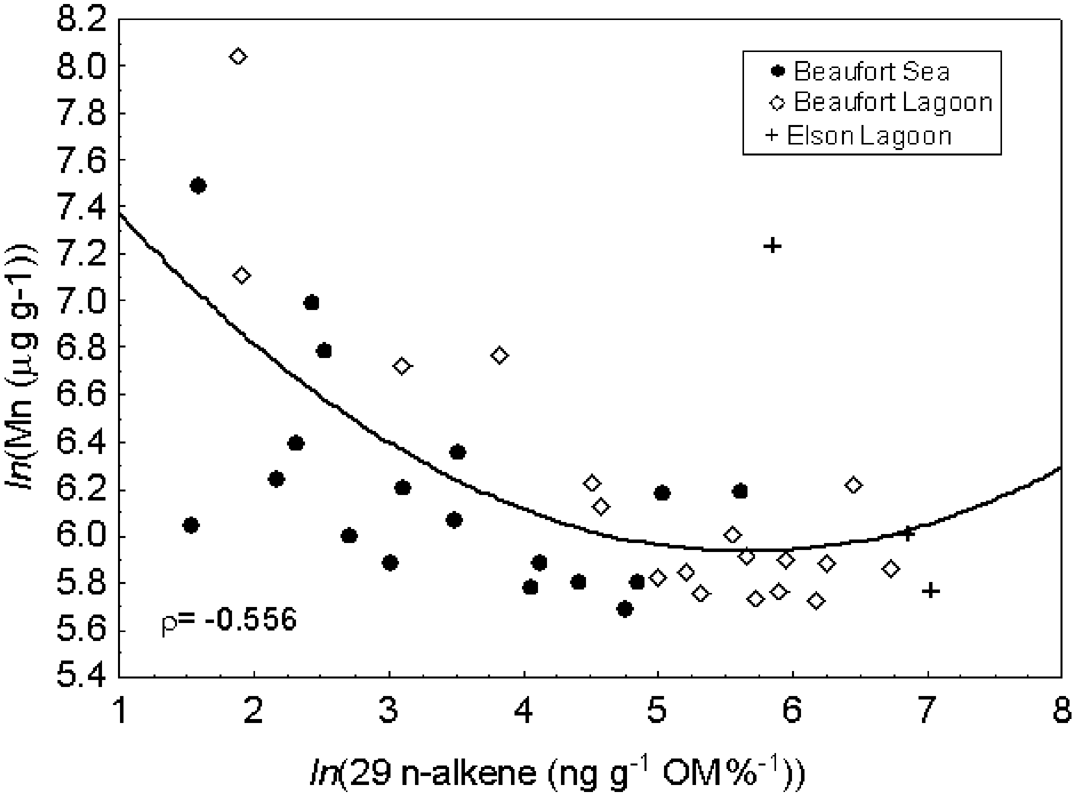


**Figure 14 Continued. Scatterplots of trace metal concentrations against $C_{29}$ *n*-alkane. All variables are *ln*-transformed. Pearson's correlations are presented but Spearman's nonparametric correlation coefficients are presented where nonlinearity is present.**



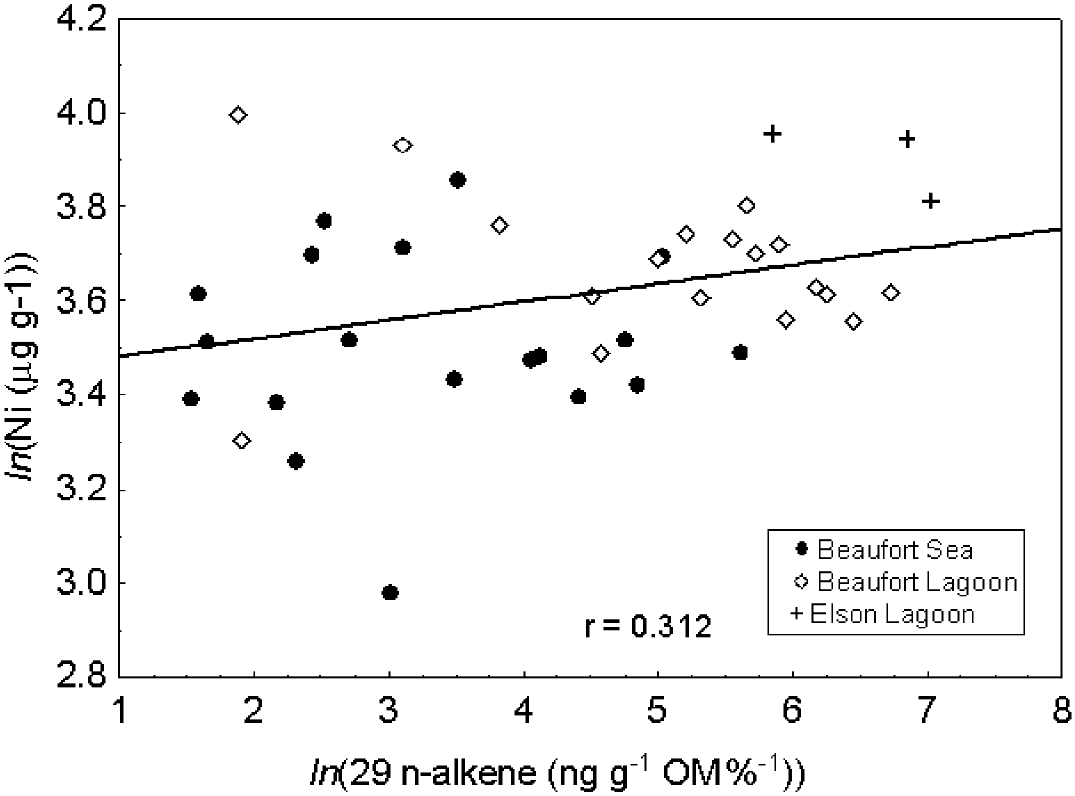
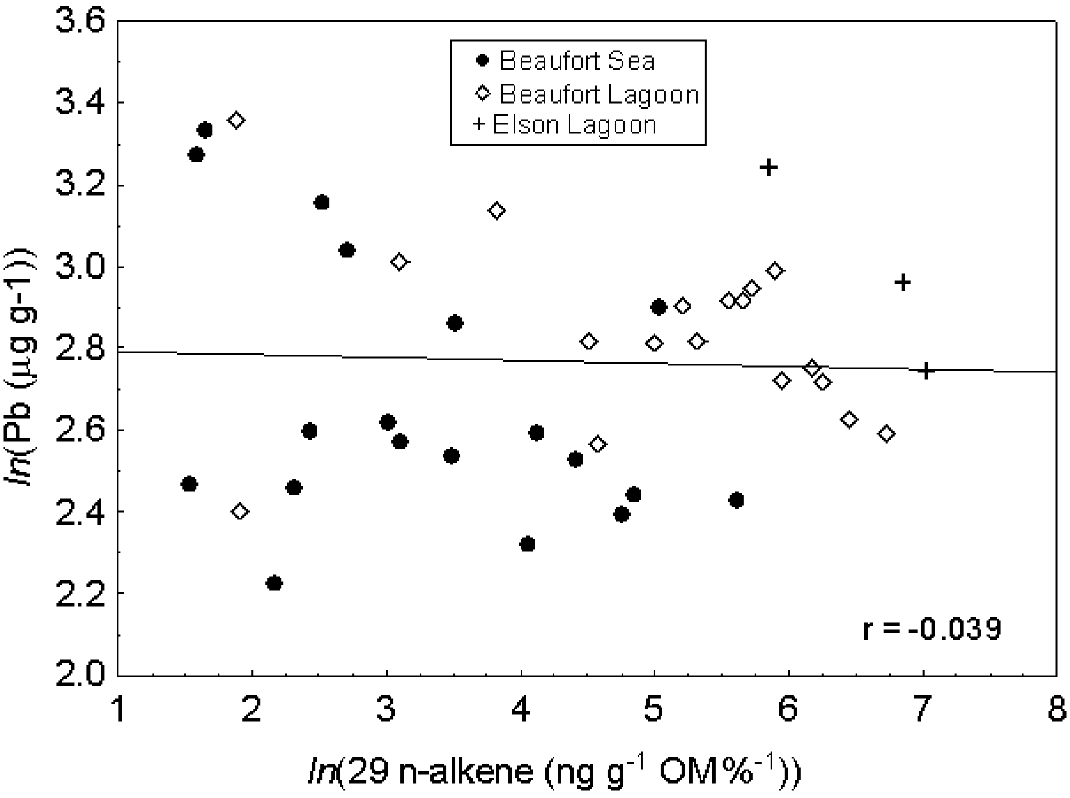


**Figure 14 Continued. Scatterplots of trace metal concentrations against $C_{29}$ *n*-alkane. All variables are *ln*-transformed. Pearson's correlations are presented but Spearman's nonparametric correlation coefficients are presented where nonlinearity is present.**



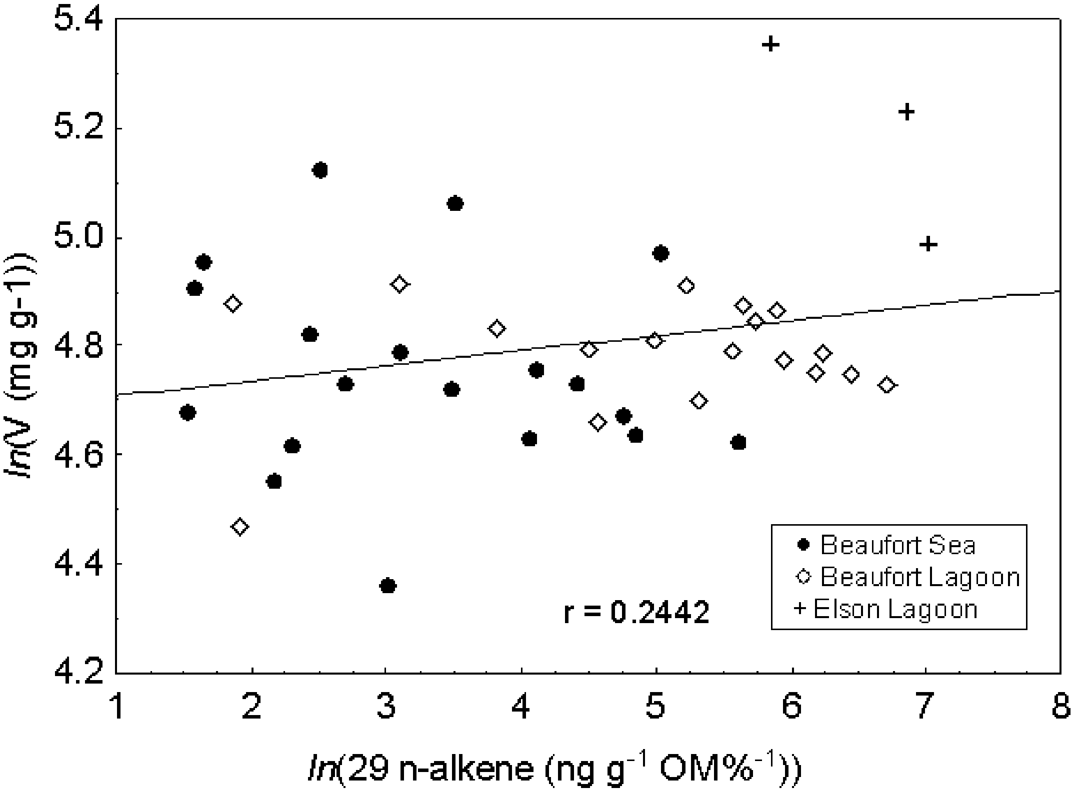


**Figure 14 Continued. Scatterplots of trace metal concentrations against $C_{29}$ *n*-alkane. All variables are *ln*-transformed. Pearson's correlations are presented but Spearman's nonparametric correlation coefficients are presented where nonlinearity is present.**

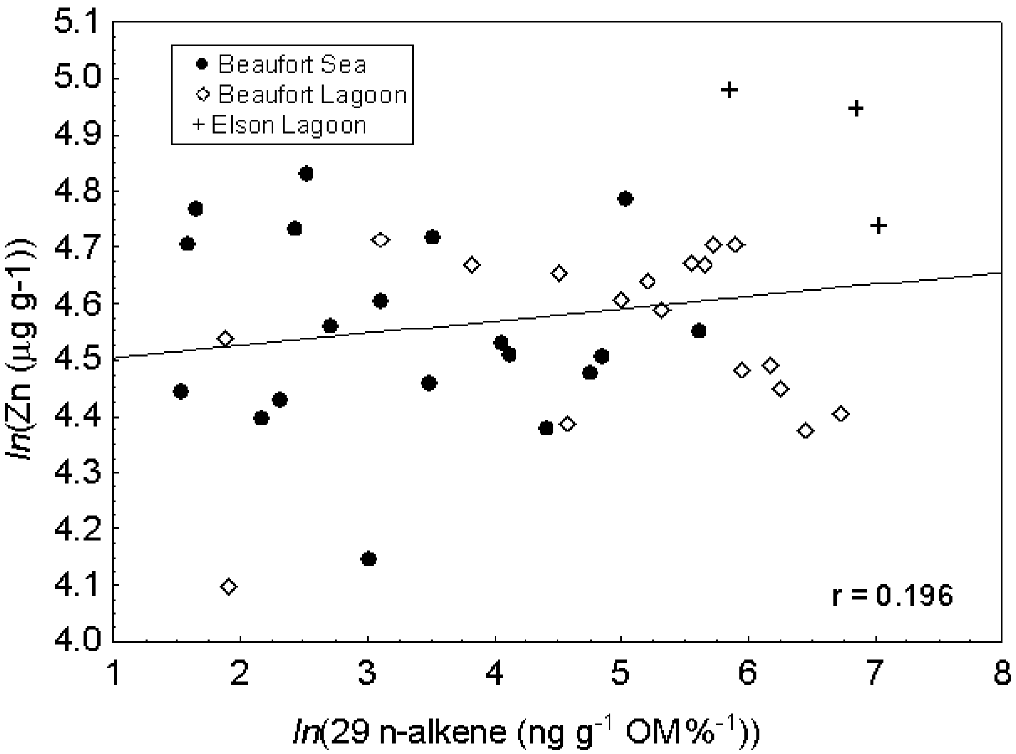


**Figure 14 Contd... Scatterplots of trace metal concentrations against $C_{29}$ *n*-alkane. All variables are *ln*-transformed. Pearson's correlations are presented but Spearman's nonparametric correlation coefficients are presented where nonlinearity is present.**

The nomenclatures of various hydrocarbon homologs/biomarkers appearing in the following text and figures are referred to by corresponding abbreviations as listed in Table 11 and 12. Table 13 lists the overall-means of PAHs sorted by their individual mean.

Box (Whisker) plots of selected hydrocarbons are presented in Figure 15 to identify if there are any significant differences in the hydrocarbon contents between the three study regions.

Scatter plots between total *n*-alkanes (∑*n*-alkanes) and total polycyclic aromatic hydrocarbons (∑PAHs) vs percent organic matter (OM) are presented in Figure 16. The nonlinear relationship between alkanes and PAH is moderate (Spearman's ρ=0.50), and significant to weak negative correlations are exhibited between ∑*n*-alkanes and ∑PAHs respectively with percent organic matter (OM). The scatter plot of perylene against $C_{29}$ alkane indicate a strong correlation (r = 0.75).

Sediment data from all the three regions (Colville Delta-Prudhoe Bay/Beaufort Sea, Beaufort Lagoon and Elson Lagoon) considered in this synthesis were used in the principal component analysis (PCA). Hopanes were only qualitatively identified in the Elson Lagoon sediments. Therefore, two sets of PCAs for the hydrocarbons variables were constructed one including Elson Lagoon but, without hopanes (Fig.17) and the other, Figure 18, including hopanes data of Beaufort Lagoon and Colville Delta-Prudhoe Bay (Beaufort Sea) for comparison, but excluding that for Elson Lagoon.

**Table 11. List of the set of hydrocarbon variables (with corresponding abbreviations) in sediments used in principal component analysis (PCA) for Colville Delta-Prudhoe Bay, Elson Lagoon and Beaufort Lagoon (as referred to in Fig. 18, for the PCA).**

| **Compound/Parameter** | **Abbreviation** |
|---|---|
| Sum *n*-alkanes (∑*n*-alkanes) | TALK |
| Sum 15-23 *n*-alkanes (∑15-23) | T1523 |
| 24 *n*-alkane | $C_{24}$ |
| 25 *n*-alkane | $C_{25}$ |
| 26 *n*-alkane | $C_{26}$ |
| 27 *n*-alkane | $C_{27}$ |
| 28 *n*-alkane | $C_{28}$ |
| 29 *n*-alkane | $C_{29}$ |
| 30 *n*-alkane | $C_{30}$ |
| 31 *n*-alkane | $C_{31}$ |
| 32 *n*-alkane | $C_{32}$ |
| 33 *n*-alkane | $C_{33}$ |
| Pristane | pr |
| Phytane | phCC |
| 27α hopane | 27a |
| 27β hopane | 27b |
| 29αβ hopane | 29ab |
| 30αβ hopane | 30ab |
| 30ββ hopane | 30bb |
| diploptene | dip |
| naphthalene | Na |
| 1 methylnaphthalene | 1Na |
| 2 methylnaphthalene | 2Na |
| phenanthrene | Pn |
| anthracene | An |
| fluoranthene | Fl |
| pyrene | Py |
| chrysene/triphenylene | Ch |
| benzanthracene | BaA |
| benzofluoranthenes | BF |
| benzo(e)pyrene | BeP |
| benzo(a)pyrene | BaP |
| perylene | Per |
| benzo(ghi)perylene | Bghi |

**Table 12. List of the set of hydrocarbon variables (with corresponding abbreviations) used for PCA for Colville Delta-Prudhoe Bay and Beaufort Lagoon (Excluding Elson Lagoon). Refer to Fig. 18 for the PCA plots.**

| Compound/Parameter | Abbreviation |
|---|---|
| naphthalene | Na |
| C1(or monomethyl) naphthalenes | N1 |
| C2 (or dimethyl) naphthalenes | N2 |
| fluorene | F |
| phenanthrene | Pn |
| anthracene | An |
| C1(monomethyl)phenanthrenes/anthracenes | P1 |
| C2 (dimethyl)phenanthrenes/anthracenes | P2 |
| fluoranthene | Fl |
| pyrene | Py |
| C1 (monomethyl) fluoranthenes/pyrenes | Fl1 |
| chrysene/triphenylene | Ch |
| benzoanthracene | BaA |
| benzofluoranthenes | BF |
| benzo(e)pyrene | BeP |
| benzo(a)pyrene | BaP |
| perylene | Per |
| benzo(ghi)perylene | Bghi |

**Table 13. Overall means of PAHs sorted by their means. Refer to Table 11 and 12 for the nomenclature of the PAHs variables.**

| Variable | Mean |
|---|---|
| An | 0.11 |
| BaP | 0.22 |
| BaA | 0.32 |
| F | 0.47 |
| Bghi | 0.53 |
| Fl | 0.54 |
| Py | 0.72 |
| Na | 0.75 |
| Fl1 | 0.83 |
| BeP | 0.87 |
| BF | 0.89 |
| 1Na | 0.98 |
| 2Na | 1.07 |
| Ch | 1.07 |
| N1 | 1.41 |
| Pn | 1.46 |
| P2 | 1.77 |
| N2 | 1.86 |
| Per | 1.88 |
| P1 | 2.45 |

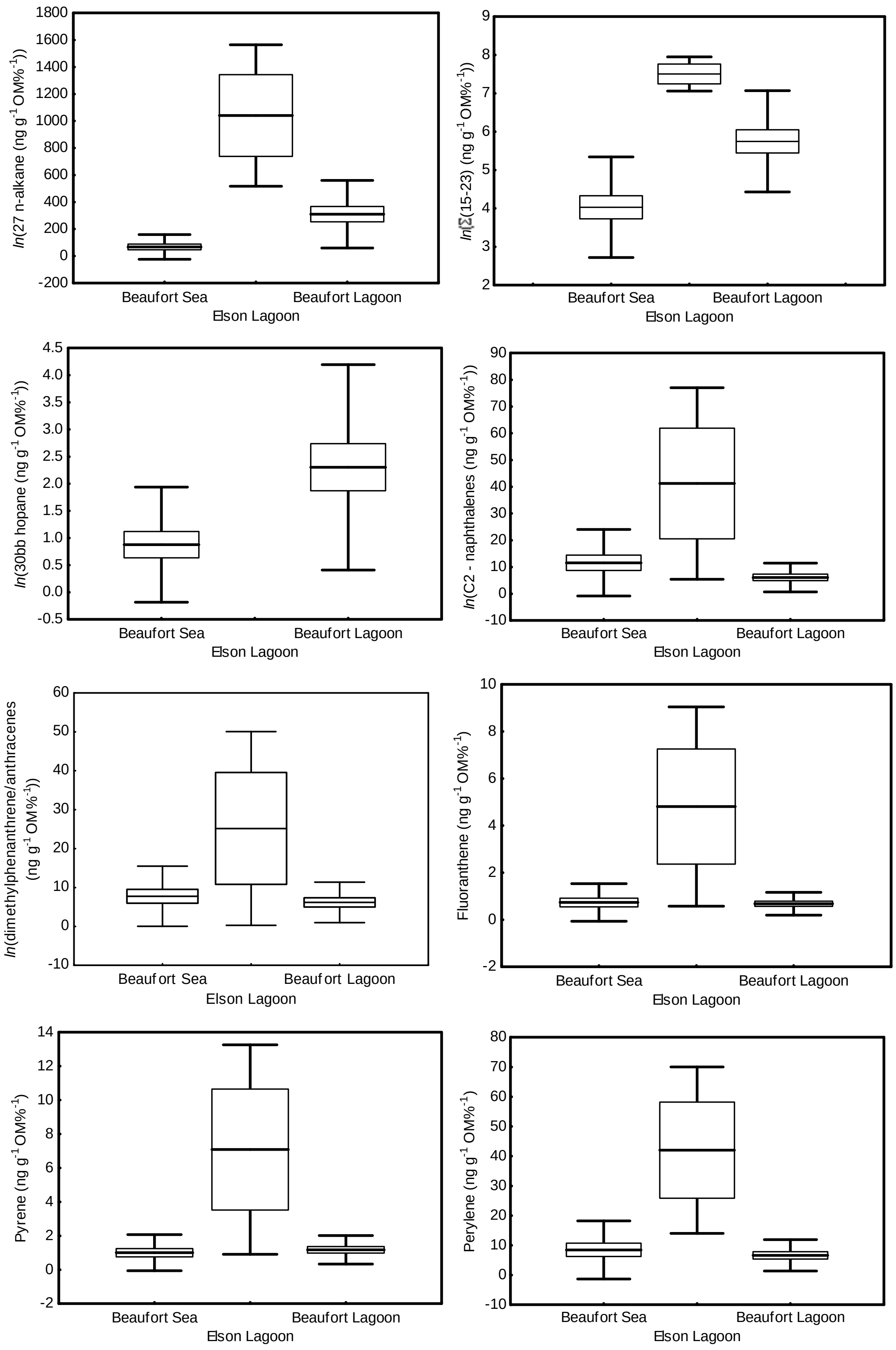
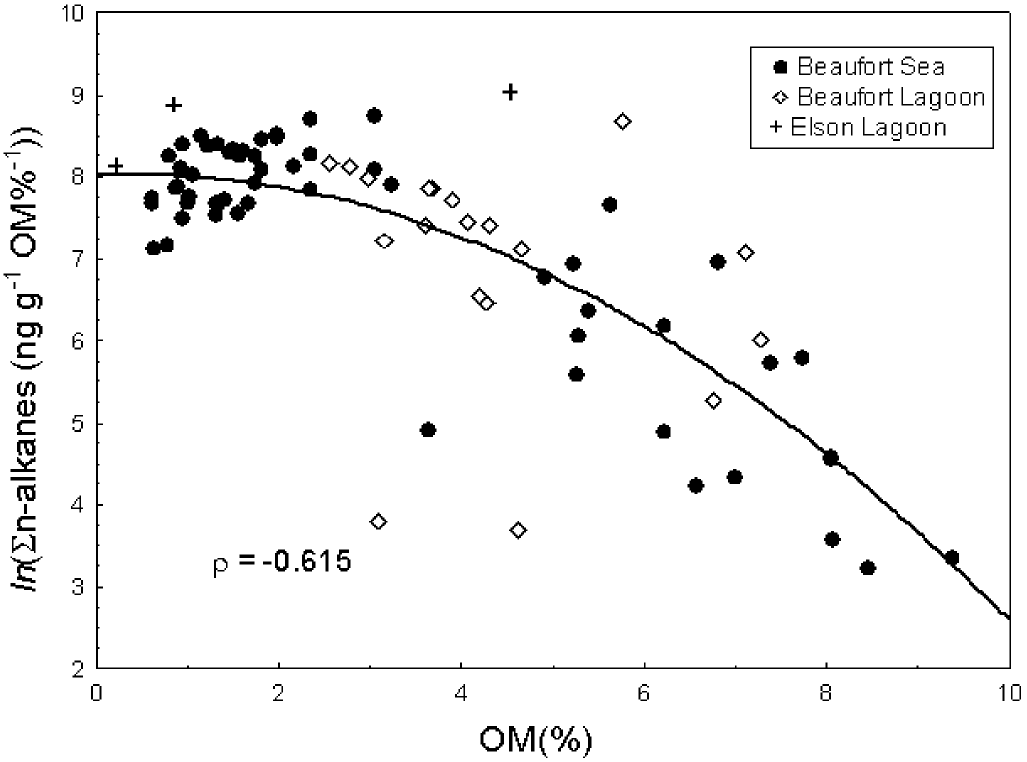


Figure 15. Box (Whisker) plots of selected hydrocarbons in sediments from Colville Delta-Prudhoe Bay (Beaufort Sea, BS97), Elson Lagoon (EL99) and Beaufort Lagoon (BL03). All variables are *ln*-transformed. The horizontal lines represent the mean, the boxes represent ±1 standard error, and the whiskers represent ±1 standard deviation.



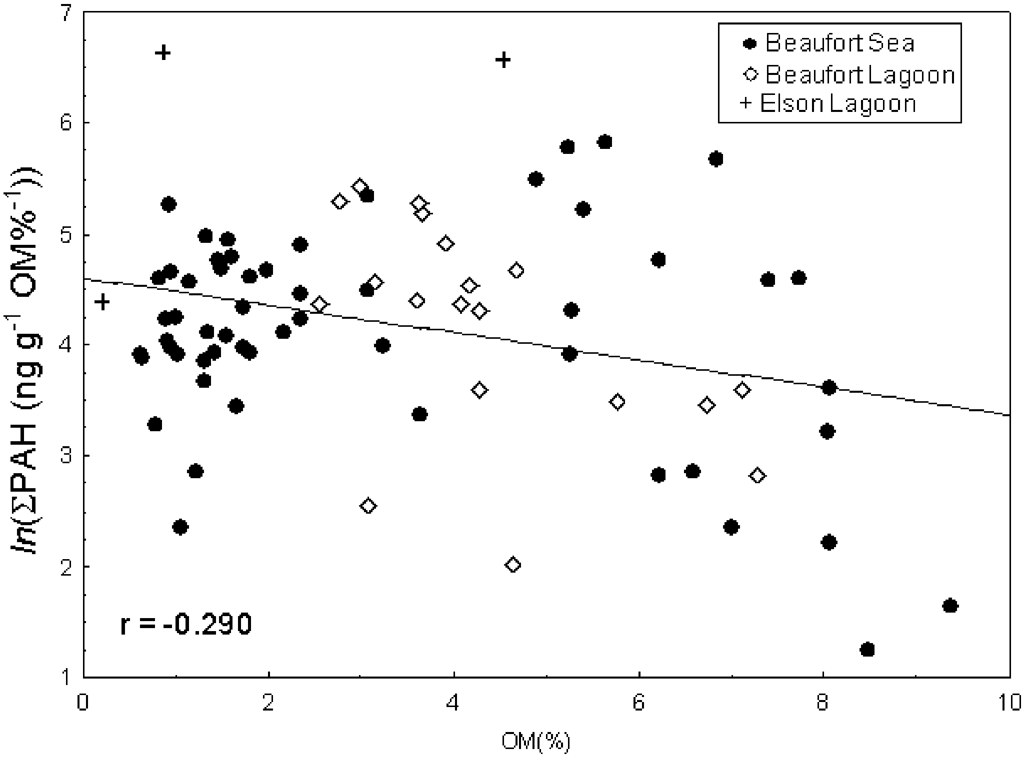
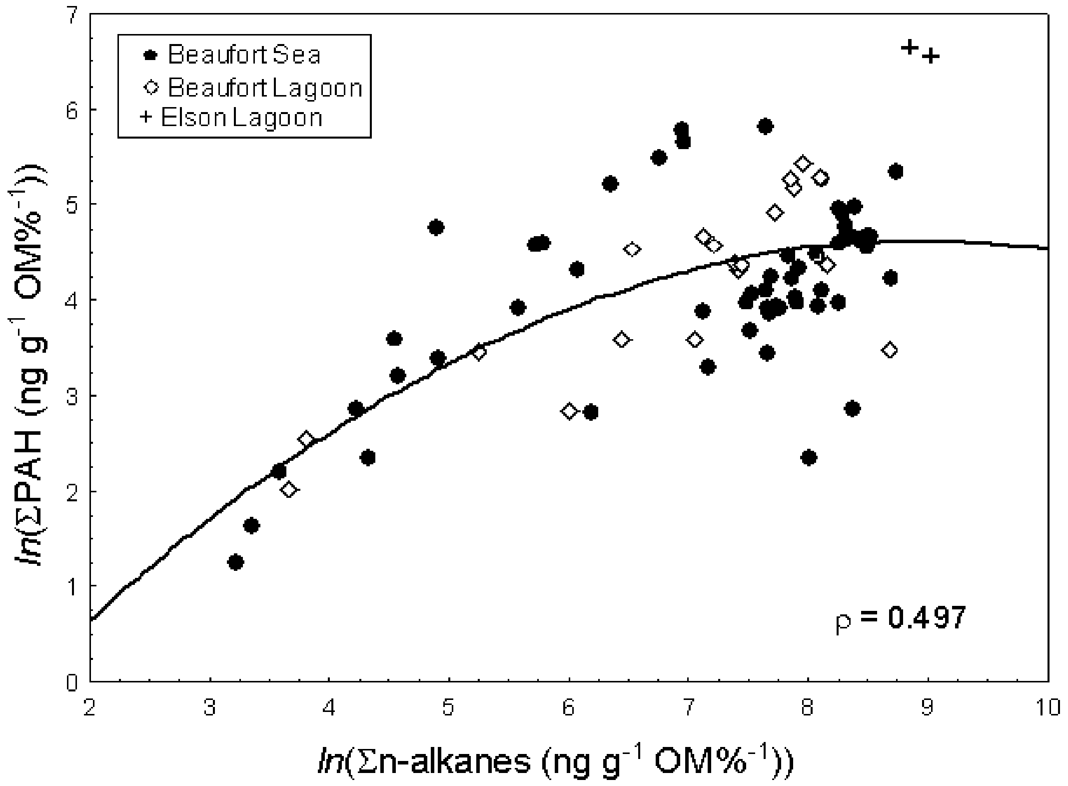


**Figure 16. Scatterplots of total polycyclic aromatic hydrocarbons (∑PAH) and total *n*-alkanes (∑*n*-alkanes) vs organic matter (OM %) and perylene against $C_{29}$ *n*-alkane. All hydrocarbon variables are *ln*-transformed. Pearson's correlations are presented for most variables but Spearman's nonparametric correlation coefficients are presented where nonlinearity is present. Beaufort Sea plots correspond to Colville Delta-Prudhoe Bay (BS97).**



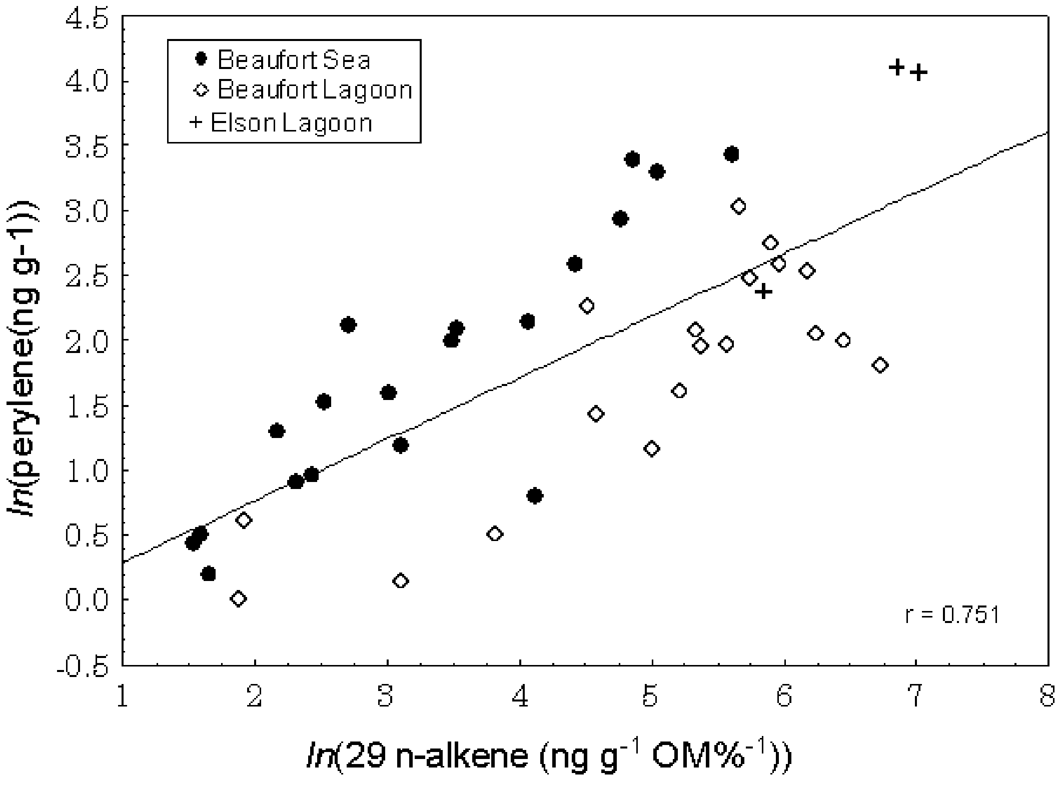


**Figure 16 Continued. Scatterplots of total polycyclic aromatic hydrocarbons (∑PAH) and total *n*-alkanes (∑*n*-alkanes) vs organic matter (OM %) and perylene against $C_{29}$ *n*-alkane. All hydrocarbon variables are *ln*-transformed. Pearson's correlations are presented for most variables but Spearman's nonparametric correlation coefficients are presented where nonlinearity is present. Beaufort Sea plots correspond to Colville Delta-Prudhoe Bay (BS97).**

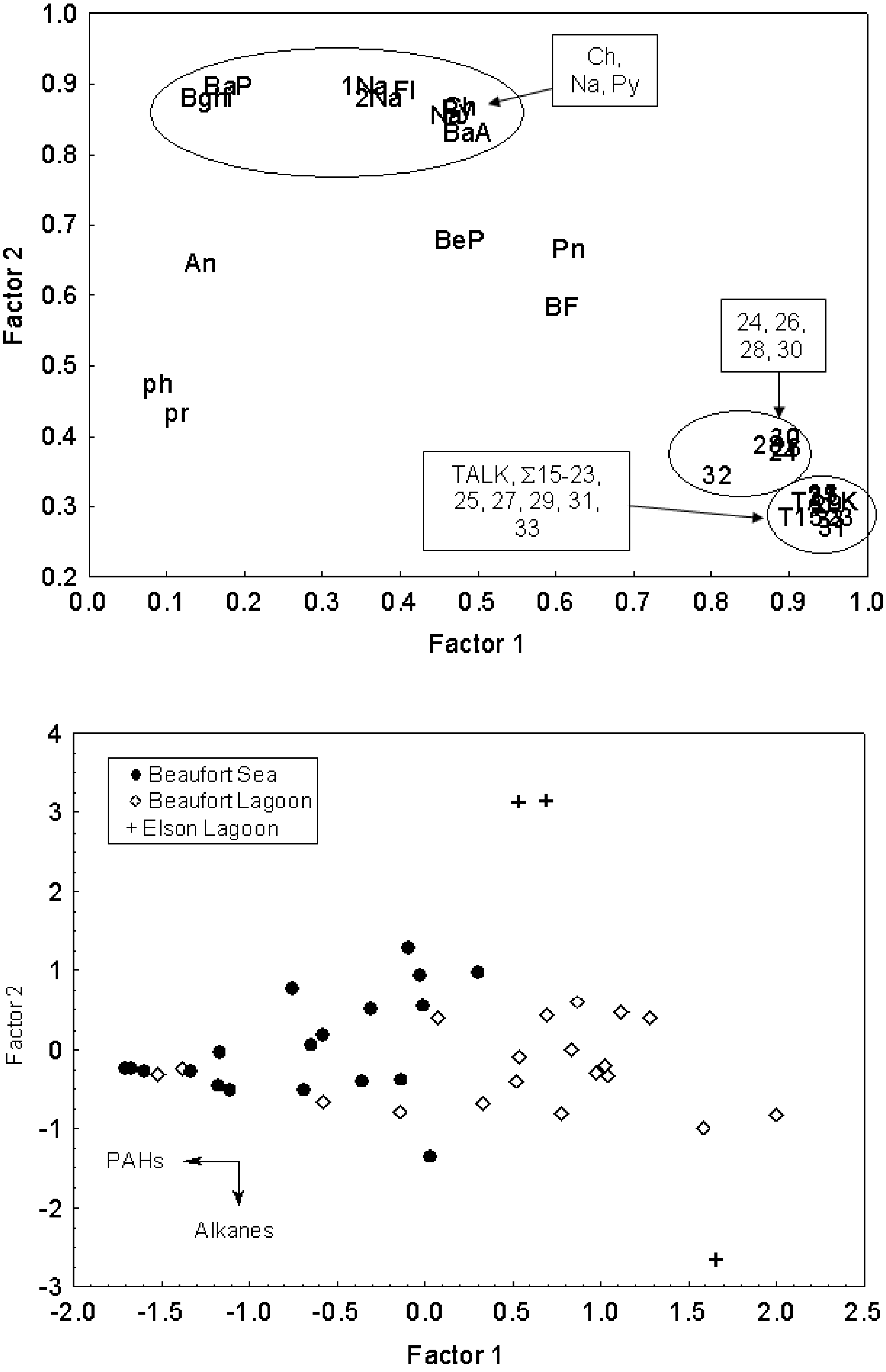


**Figure 17. Results of PCA on selected hydrocarbons (excluding hopanes) on sediment samples from Colville Delta-Prudhoe Bay (Beaufort Sea, BS97) Elson Lagoon (EL99), and Beaufort Lagoon (BL03) . Data were *ln*-transformed following normalization to percent organic matter. Circles represent clusters of variables with high correlations.**

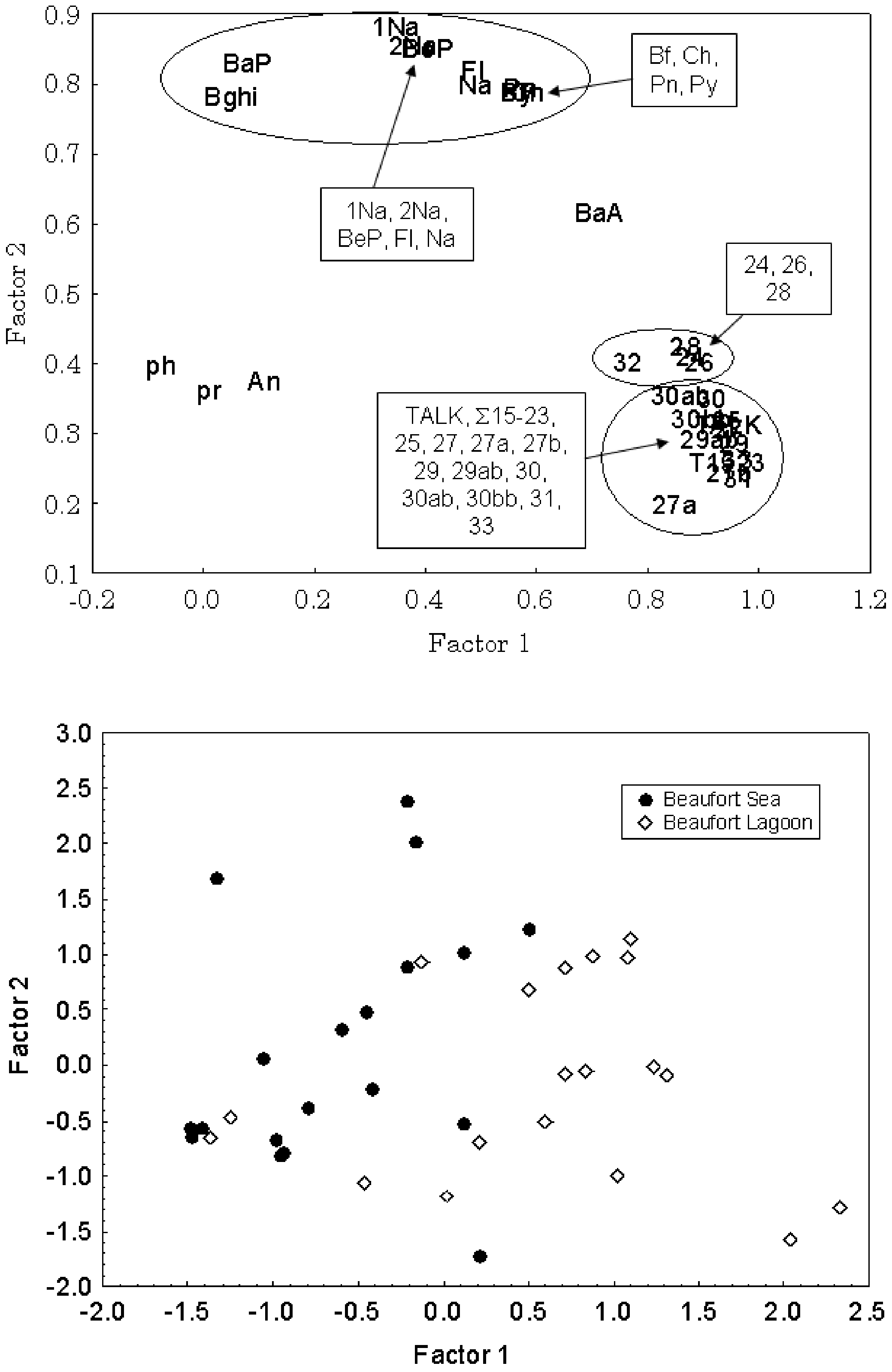


**Figure 18. Results of PCA on selected hydrocarbons (including hopanes) restricted to sediment samples from Colville Delta-Prudhoe Bay (Beaufort Sea, BS97), and Beaufort Lagoon (BL03). Data were *ln*-transformed following normalization to percent organic matter. Circles represent clusters of variables with high correlations. Data from Elson Lagoon samples are not included due to absence of hopanes in those samples.**

Figures 17 and 18 show the PCA loadings of hydrocarbons. The first two PCs account for 74% and 15% (Fig. 17) without hopanes and 72% and 14% (Fig. 18) with hopanes respectively, contributing to a total of 89% and 86% of the original data variance. The higher plant wax *n*-alkanes, i.e., odd carbon from 25 to 33, maximizing at *n*-$C_{29}$ or *n*-$C_{31}$ are highly correlated with X axis and exhibit the strongest positive contribution to the first PC (factor 1) and thus, contribute most to sample separation in the X axis (circled in Fig. 17). Alkanes with even carbon from 24 to 32 contribute slightly lower than the odd carbon alkanes as evident from the factor loadings (circled in Fig. 17).

Most of the PAHs form a loose cluster and correlate highly with factor 2 (circled) while BeP, Per, Pn and BF correlate to a lesser extent, yet still showing relatively stronger correlation with factor 2 (Figs. 17 and 18). Anthracene (An) is either absent in many samples or present at the level of 10 to ~70X less than phenanthrene. Its remote placement in the PCA doesn't contribute to the real separation of samples. Pristane and phytane form a separate group and contribute only weakly to the second PC (Figs 17 and 18). Pristane and phytane were present in only 4 samples out of 20 investigated from Beaufort Lagoon (BL) and 2 out of 3 samples from Elson Lagoon (EL). However, they are present in all the sediments from the Colville Delta-Prudhoe Bay (Beaufort Sea), with the ratio of pristane/phytane uniformly around 2.0.

PCA loadings depicted in Figure 17 are very similar to that shown in Figure 18 with strong correlations of alkanes to factor 1 and high correlation of PAHs to factor 2. All of the hopanes (Fig. 18) cluster along with the plant wax alkanes contributing strongly to factor 1.

The scores plot of hydrocarbon variables are depicted in Figures 17 and 18. In the scores plot (Fig. 17), all but one sample from the Colville Delta-Prudhoe Bay (Beaufort Sea) cluster in the left half, and all, but 4 of the Beaufort Lagoon samples cluster about the right half. These sediment samples exhibit only a small variation in the second PC (Y axis). In the scores plot shown in Figure 17, one Elson Lagoon sample (EL-1) is placed at the lower right quadrant (filled square) and the other two at topmost right quadrant. Figure 18 (where Elson Lagoon sample data are not included) exhibits similar sample separation between Colville Delta-Prudhoe Bay (Beaufort Sea) and Beaufort Lagoon sediments as illustrated in Figures 17 and 18.

The PCA loadings of polycyclic aromatic hydrocarbons (PAHs) are shown in Figure 19. The first two PCs account for 82% and 6% amounting to a total of 88% of the original data variance. The monomethylphenanthrenes/anthracenes (P1) are highly correlated with X axis and exhibit the strongest positive contribution to the first PC (factor 1) and thus, contribute most to sample separation in the X axis (Fig. 19). Monomethylphenanthrenes always dominate among the phenanthrenes and among all other PAHs except for perylene in some cases. The remaining components are not well differentiated although a close examination reveals certain trends in the PAH loadings. It is also shown that there is a strong contribution of Per, Pn and P2 to factor 1. BF has a similar strong loading. BeP, Na, N1, N2, F, Py, Fl, Fl1 and Ch show moderately strong correlation to factor 1 while F and F1 show stronger correlation to factor 2 (Fig. 19).

Further, BaA, Bghi and BaP contribute strongly to factor 2 (Fig. 19), and Anthracene (An) is either absent in many samples or present at the level of 10 to ~70X less than phenanthrene. Its weak contribution to factor 2 of the PCA doesn't influence the real separation of samples.

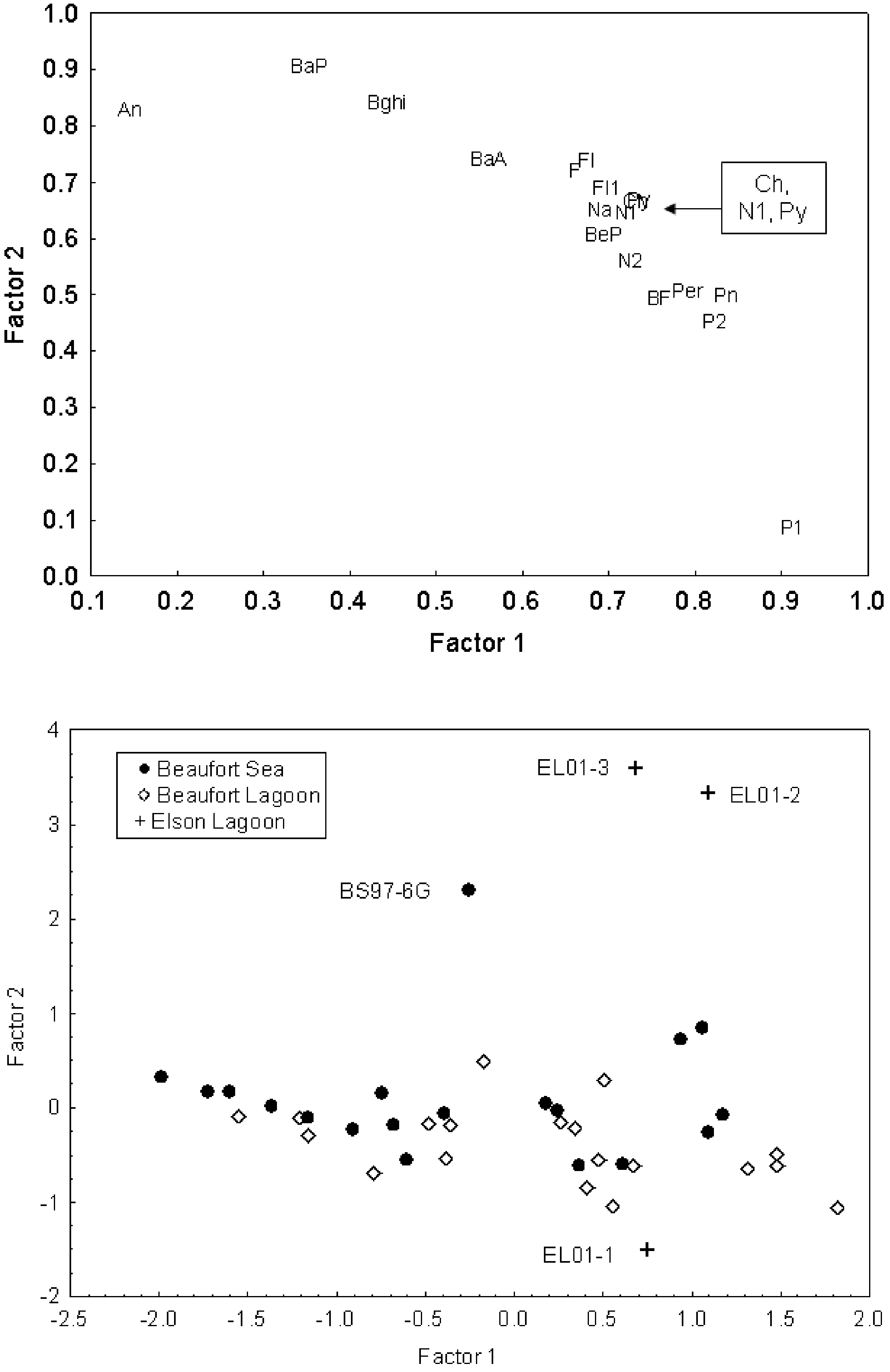


**Figure 19. PCA ordination of PAH hydrocarbon variables without alkanes. Data were *ln*-transformed following normalization to percent organic matter. The Beaufort Sea plots correspond to those of the Colville Delta-Prudhoe Bay (BS97).**

**Table 14. Comparison of the regional and time-interval concentrations ( g/g) of selected hydrocarbons and ratios in gross sediment samples collected in Alaska's Beaufort Sea nearshore [after Boehm et al. (1987), Steinhauer and Boehm (1992), Naidu et al. (2001), and Brown et al. (2005)].* Station names and locations are included in the reports corresponding to the references. Note that Boehm et al.'s samples were collected in 1984-1986, by Naidu et al. in 1997, and by Brown et al. in 2000 and 2002. Comparisons are restricted to selected stations generally occupied by all the above investigators.**

| Region (Station) | TALK[#] | LALK[+] | Pristane | Phytane | LALK/TALK | ΣPAH[##] | N/P[++] | References |
|---|---|---|---|---|---|---|---|---|
| Camden Bay<br>1D, 2E, 2F | 0.1-3.16 | 0.24-0.49 | 0.01-0.03 | 0.005-0.02 | 0.08-0.3 | 0.01-0.05 | 0.8 | I |
| | 0.26-1.88 | 0.01-0.38 | 0.01-0.05 | 0.001-0.02 | 0.02-0.22 | 0.06-0.70 | 0.58-1.64 | II |
| Foggy Island Bay<br>3A, 3B, 4A, 5G | 2.2-5.79 | 0.43-0.88 | 0.03-0.06 | 0.02-0.03 | 0.15-0.39 | 0.07-0.09 | 1.0 | I |
| | 0.49-3.07 | 0.06-0.80 | 0.006-0.08 | 0.003-0.03 | 0.12-0.36 | 0.1-1.0 | 0.75-0.95 | II |
| | | | | | | 0.03-0.06 | | III(2000) |
| | | | | | | 0.04-0.05 | | IV(2002) |
| Prudhoe Bay<br>5(1), 5(5), 5(10) | 0.8-2.81 | 0.2-0.46 | 0.01-0.03 | 0.004-0.03 | 0.13-0.26 | 0.03-0.06 | 1.0 | I |
| | 0.2-1.3 | 0.02-0.19 | 0.001-0.02 | 0.001-0.008 | 0.1-0.17 | 0.02-0.24 | 0.25-0.89 | II |
| | | | | | | 0.03-0.05 | | III(2000) |
| | | | | | | 0.00-0.03 | | IV(2002) |
| Bay off Kuparak River<br>5A, 5F | 4.8-7.2 | 0.78-0.96 | 0.05-0.06 | 0.03 | 0.13-0.16 | 0.13 | 1.2 | I |
| | 2.3-7.1 | 0.28-0.98 | 0.02-0.09 | 0.03-0.04 | 0.11-0.14 | 0.37-1.96 | 0.49-1.51 | II |
| | | | | | | 0.04-1.80 | | III(2000) |
| | | | | | | 0.04-0.81 | | IV(2002) |
| East Harrison Bay<br>6A, 6B, 6C, 6D, 6G | 3.1-19.4 | 0.6-2.50 | 0.04-0.2 | 0.02-0.1 | 0.10-0.18 | 0.08-0.64 | 1.5 | I |
| | 0.8-11.8 | 0.08-1.2 | 0.007-0.1 | 0.003-0.05 | 0.10-0.19 | 0.29-1.78 | 0.59-1.59 | II |

[*] Ranges are from Boehm et al. (1987), Naidu et al. (2001), and Brown et al. (2005) corresponding to I, II, III and IV respectively under the Reference column. Parenthesized number in III and IV correspond respectively to the year samples were collected. Geometric Mean for N/P from Table 7 of Steinhauer and Boehm (1992).

[#] Sum of n-C$_{10}$-n- C$_{36}$ (Naidu et al., 2001); n-C$_{10}$-n- C$_{34}$ (Boehm et al., 1987)

[+] Sum of n-C$_{12}$-n- C$_{19}$ (Naidu et al., 2001); n-C$_{10}$-n- C$_{20}$ (Boehm et al., 1987)

[##] Sum of parent and methylated PAHs from naphthalene to coronene including methylated homologs of 4.5 PAH (Naidu et al., 2001)

Sum of parent and methylated PAHs from 2- and 3-ring and parent 4,5-ring PAH (Boehm et al., 1987)

[++] Naphthalenes/phenanthrenes + anthracenes

In the scores plot of the polycyclic aromatic hydrocarbons (PAHs), there is no decided separation between locations except for one sample in Colville Delta-Prudhoe Bay (Beaufort Sea) and two samples from Elson Lagoon (Fig. 19). These sediment samples exhibit only a small variation in the second PC (Y axis). The two Elson Lagoon samples (EL-2 and EL-3) are clearly differentiated from the other samples along the y-axis reflecting the increased relative abundance of the PAHs. The third Elson Lagoon sample (EL-1) has PAHs at levels comparable to those of the Colville Delta-Prudhoe Bay (Beaufort Sea) and Beaufort Lagoon samples. Although Elson Lagoon sediments are compositionally very similar to those from the Colville Delta-Prudhoe Bay (Beaufort Sea) and Beaufort Lagoon, the large separation in the two samples from Elson lagoon (EL-2 and EL-33) reflects their higher PAHs content. The third 'anomalous' (outlying) station is 6G in Colville Delta-Prudhoe Bay (refer to Fig. 2 for location) which indeed shows similarly, the maximum PAH content of all the samples collected from Colville Delta-Prudhoe Bay (Beaufort Sea) and Beaufort Lagoon. Thus, Axis 2 of this PCA is apparently associated with higher PAH contents.

Data collected during two time-intervals (1984-1986 and 1997) on selected hydrocarbons and their ratios in gross sediments for the Colville Delta-Prudhoe Bay region are presented in Table 14. No such data sets were available for the Elson Lagoon or Beaufort Lagoon. The ratios correspond to low molecular weight alkanes (LALK)/total alkanes (TALK), and naphthalenes (N)/phenanthrenes (P).

# DISCUSSION

## *Regional distributions of trace metals and hydrocarbons*

The dendrograms illustrating the results of the cluster analyses based on the concentrations of metals not normalized against iron (Fig. 8) and those normalized to iron (Fig. 9), show some disjointed clusters of station groups corresponding specifically to the Colville Delta-Prudhoe Bay (BS97) and Beaufort Lagoon (BL03) regions. The BS and BL stations display significant overlapping of stations in the PCA ordination with trends in the Fe-normalized data reflecting associations with spatial and environmental factors. For Elson Lagoon (EL03) the stations cluster separately relative to the other two areas (Fig. 8). However, cluster analysis when run solely either for the Colville-Prudhoe Bay area (CDPB) or Beaufort Lagoon (BL) demonstrate presence of three and two significant station clusters, respective to the two regions (Naidu et al., 2001; 2006). Such an analysis was not extended to Elson Lagoon because of limited stations (N=5) investigated (Naidu et al., 2003b). In the CDPB region one cluster of stations was around Prudhoe Bay and immediate vicinity and the other cluster was in the lagoon farther east and west of Prudhoe Bay. In BL, one group of geographically coherent cluster of stations was identified adjacent to the former Dew Line onshore site, whereas the second and third clusters of stations were located off the Angun Point in the northwest and southeastern portions of BL, respectively. These station clusters are explained to possible relative differences in the metal inputs from natural sources, past anthropogenic activities (Naidu et al., 2001, 2006; Misra et al., 2006), and the natural oil seeps located onshore (e.g. the second station cluster off Angun Point).

Comparing the trace metal concentrations (not normalized to iron) for all the three regions (Naidu et al., 2001, 2003b, 2006), as summarized in Table 1, it becomes apparent that some broad regional differences exist in the concentrations of a suite of metals in mud. Generally, a west to east gradient (Elson Lagoon to Beaufort Lagoon through Colville Delta-Prudhoe Bay) is recognized which is marked, with some exceptions, by a net W-E decreasing concentrations in arsenic (As), barium (Ba), chromium (Cr), copper (Cu), Nickel (Ni), total mercury (THg), vanadium(V) and zinc (Zn); Table 1. These regional disparities have been explained in terms of several factors (Naidu et. al., 2003b). One explanation is the possible west to east progressive decreased depositional flux of the six metals from local natural sources, resulting from a net W-E decrease in sediment accumulation rate. It is also possible that the gradient in metal concentrations is controlled by the local differences in the natural terrigenous inputs in metals, in dissolved and particulate forms. That this could be a significant factor is supported by the database reported for the Colville Delta-Prudhoe Bay region (Trefry et al., 2003; Rember and Trefry, 2004), showing close correlations between site-specific/local concentrations of a suite of metals in nearshore marine sediments and waters and suspended particulates of rivers draining into the site. However, there is no such database for the coastal region west of the Colville Delta to clarify this possibility. A third reason invoked is decreased input successively eastward of anthropogenic metal contaminants entrained in a west to east traversing atmospheric plume originating in Eurasia. It is suggested that following the atmospheric wet or dry fall out in the north Alaskan Arctic the metal contaminants are accumulated in the North Slope coastal snow, and are eventually recycled into the nearshore sediments at spring thaw. The latter supposition is consistent with the general west to east decrease in several metal concentrations in snow samples of the North Slope coast (Snyder-Conn et al., 1997; Garbarino et al., 2002). It is to be noted that all along the coast the annual accumulation rates of snow and rain are uniformly the same, which precludes the influence of these factors (precipitation) influencing the metal fluxes in snow. Yet, there could be an additional factor that has a bearing on the W-E net decrease in the concentrations of the metals in sediments. The comparison of the mean concentrations of metals normalized to iron by region (Table 2) shows no apparent geographic trends. From this it is implied that the lateral variations in the iron contents could have expunged the regional trends that were identified based on metal data not normalized to iron (Table 1). It is widely known that oxides/hydroxide of iron in marine sediments have a tendency and capacity to scavenge metals by adsorption, which on a local scale has indeed been demonstrated on sediments from the Colville Delta and Beaufort Lagoon (Sweeney, 1984; Sweeney and Naidu, 1989; Misra et al., 2006).

The statistical analysis of the hydrocarbon data has assisted in clarifying the regional distribution of the alkanes and PAHs in sediments. The score plots of hydrocarbons as depicted in Figures 17 and 18, generally exhibit only a small variance in alkane contents in sediments from the Colville Delta-Prudhoe Bay (Beaufort Sea) and Beaufort Lagoon, especially the plant wax component which is dominant in this PC. However, all the three Elson Lagoon samples are clearly differentiated from the above two regions, by having relatively elevated abundance of the higher alkanes and PAHs, although the hydrocarbons in all the three regions are compositionally very similar. Likewise, the PCA loadings of polycyclic aromatic hydrocarbons (PAHs) as shown in Figure 19 is generally similar in all the regions. The exception to this is the loading corresponding to the Elson Lagoon, reflecting there the relative abundance of the PAHs. Barring these differences the overall composition and relative abundance of hydrocarbons in the three regions are quite similar, despite the fact that the three regions have been exposed to different anthropogenic activities of varying intensities.

## *Sources of sediment trace metals and hydrocarbons*

To get insight into the possible source(s), marine versus land-derived, of the metals in sediments of the North Slope nearshore, Pearson's correlations were run between concentrations of individual metals [Chromium (Cr), iron (Fe), manganese (Mn), lead (Pb), nickel (Ni), cadmium (Cd), barium (Ba), zinc (Zn), arsenic (As), copper (Cu), and vanadium (V), total mercury (THg), and methyl mercury (MeHg)] and the hydrocarbon *n*-alkane $C_{29}$ (a typical terrestrial biomarker). Figure 14 illustrates the results of the analysis. Against *n*-$C_{29}$ no significant positive correlations were identified for all the metals except THg (r=0.769) and MeHg (in Beaufort Lagoon and Colville Delta-Prudhoe r=0.83; and in Elson Lagoon r=0.97). A simple inference from the above could be that the two forms of sediment Hg likely have a predominant terrestrial organic source and specially bound to the *n*-$C_{29}$ biomarker of the organic matter. Consistent with the predominant terrestrial source of the nearshore sediments in question is the fact that the organic matter (OM) associated with sediments have uniformly lighter (generally -25$^{o}/_{oo}$ or lower) carbon stable isotope ratios ($\delta^{13}C$) and relatively high carbon/nitrogen ratio (C/N= >12). These latter values are typical for terrigenous-dominated organic matter in sediments of the Beaufort Sea nearshore (Naidu et al., 2000). However, it is not yet resolved whether or not the two mercury forms are actually partitioned (by complexation) in *n*-$C_{29,}$ and the specific hydrocarbon uniquely serves as a transport carrier for mercury from land to nearshore. That the entire organic matter (OM) in the North Slope nearshore sediments plays a minor role to form organic complex with THg and MeHg is implied by the lack of covariance between OM and the two Hg forms (Table 10). This was surprising as the association of THg or MeHg with living tissue or dead OM is widely known (Bloom, 1992; Gagnon et al., 1997; Ravichandran, 2004; Shoham-Frider et al., 2007 and references therein). Alternatively, it is possible that the observed co-variances between THg, MeHg and *n*-$C_{29}$ simply exemplify that both Hg and the hydrocarbon marker *n*-$C_{29}$ have a common source in land and that they have a parallel but independent particulate transport pathway seaward from land are co-deposited in the nearshore. The possibility that both forms of mercury (THg and MeHg) are bound in mud to a significant extent, is supported by the high positive correlations between silt, clay, total mercury (THg) and methyl mercury (MeHg) contents in gross sediments (Table 10).

The criteria enumerated in the method section and the PCA plots were used to infer the sources of hydrocarbons in the study area. The results of the statistical analysis indicate that hopanes in all the sediment samples considered in this synthesis group into a cluster associated with the plant wax alkanes, which reflects their biogenic source rather than petrogenic (thermogenic) origin. This is also corroborated by results of an earlier study on biomarkers in the Beaufort Sea sediments, where mostly biogenic (thermally immature) hopanes were detected with notable absence of petrogenic (thermally mature) hopanes (Venkatesan and Kaplan, 1982).

The strong positive loading of monomethylphenanthrenes clearly confirms its major source in the coastal peats. The strong contribution of Per, Pn and P2 to factor 2 (Fig. 19) can also be attributed to significant contribution of peat to sediments of the study regions (Venkatesan, 1988). This is also corroborated, for example, by high correlation of perylene content with *n*-$C_{29}$. On the other hand the moderately strong loading of BaA, Bghi, and BaP at factor 2 (Fig. 19) are commonly characteristic of hydrocarbons being a product of combustion. However, such PAH combustion product (perhaps derived from long-distance transport from Eurasia and/or from gas combustion plant at Deadhorse) is at such low concentration levels that they do not contribute to significant sample separation in the factor plots (Fig. 19). Their overall loadings suggest only a concentration gradient in the combustion input.

The above deductions are not surprising because onshore peat can be a ready source of hydrocarbons in the Beaufort Sea. Peat is a dominant component of the shoreline and coastal plain deposits in the North Slope. Through thermo-erosion of the coast (Plate 2 showing permafrost coastal bluff with overlying peat deposit) and peat particles entrained in fluvial outflow it is conceivable that large fluxes of terrigenous peat debris eventually get deposited in the nearshore. Consistent with this is coastal erosion rate in the north arctic Alaska being among the highest in the world (Naidu et al., 1984, 2000; Macdonald et al., 2004). That the sediment organic matter in the Alaskan Beaufort Sea nearshore is predominantly terrigenous is also supported by the region's mass balance of particulate organic carbon (Macdonald et al., 2004) and, as mentioned above, by the carbon isotope ($\delta^{13}C$) and organic carbon/nitrogen (C/N) signatures of sediment organic matter (Naidu et al., 2000).

Petroleum hydrocarbons are either absent or insignificant if detected in the sediments from the entire study area. This inference is consistent with those of Boehm et al. (1987) and Brown et al. (2005) on sediments of the Colville Delta-Prudhoe Bay region. Even in the Beaufort Lagoon sediments collected in the vicinity of onshore natural oil spills (refer to Fig. 4 for sample locations taken off Angun Point and site OS) there is no evidence of contribution of hydrocarbons there from petroleum. This suggests that the lagoon region has not been impacted by natural oil seeps or oil contamination from anthropogenic activities.

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

## *Historical changes in trace metal and hydrocarbon concentrations*

We discuss first the time-interval changes in the mean concentrations of trace metals in muds and then follow with a consideration of factors for the temporal changes in hydrocarbons. Temporal changes (on approximately decadal intervals) for the past ~30-35-year time span were assessed in the mean concentrations of the trace metals, based on data not normalized to iron (Table 1 and 3) and also on data normalized to iron (Table 2). This assessment was on the database of individual metal in surficial mud in two coastal regions, namely Colville Delta-Prudhoe Bay (Naidu et al., 2001) and Beaufort Lagoon (Naidu et al., 2003b) as listed in Tables 1, 2 ands 3. Additionally, stratigraphic changes in the metal concentrations in Pb-210 dated sediment core samples (Figs. 5 and 6; after Naidu et al., 2001, 2003b) have provided evidence to the metals' temporal variations. As mentioned, the historical changes identified by comparing data on surficial mud were as follows. In Colville Delta-Prudhoe Bay, data not normalized to Fe, indicate significant increases (at 99% confidence level) in V both in 1984-1985 as well in 1997 samples compared 1977; increase in Ba in 1997 compared to 1977 samples (Table 1 and 3). No significant changes were noted in the concentrations of other elements. In Beaufort Lagoon a significant decrease in V and an increase in Mn and Cu are noted in 2003 compared to 1977 samples. However, no significant temporal variations were identified in the concentrations of any of the metal when normalized to iron (Table 2).

Figures 5 and 7 display the stratigraphic variations of the metal concentrations in three cores from two study regions. In Colville Delta-Prudhoe Bay core 3B (Fig. 5) exhibits net increases only in As and Ba toward the core top from about midway of the core (since ~1989). In core SL within the upper ~2-cm (since ~1995-1996) the trend is increased concentrations in all metals toward the core top. However, regression analysis extended to the entire core indicates a significant decrease (at the 99% confidence level) up core in Zn, Cd, MeHg and Pb in 3B and in MeHg in SL (Figs. 5 and 6), accompanied by no significant stratigraphic changes in the remaining metals, including V and Ba. In Elson Lagoon regression analyses of the metals stratigraphies (recorded for the past 70-83 years), indicate significant net increases ($p<0.05$) up core in Cr, Mn and Ba, and an up core decrease in THg, accompanied by no significant variations in the remaining metals (Fig. 11).

From the above it is surmised that there are no unambiguous temporal trends that are common throughout the three regions in the metal concentrations extending over different time-intervals. Further, in a specific region (i.e., Colville Delta-Prudhoe Bay or Beaufort Lagoon) the two-decade time-interval metal variations on surficial muds are not in concordance with the net long-term trends suggested by the metal stratigraphic record. The exceptions to the latter are the time-interval increases in V and Ba in Colville Delta-Prudhoe Bay, and in Mn and Cu in Beaufort Lagoon. A discussion follows to explain the temporal variations in the exceptional cases stated above.

Naidu et al. (2001, 2006) have discussed at length the several possibilities for the recent increased concentrations in vanadium (V) and barium (Ba). Some of the possibilities suggested are: 1) increased anthropogenic contamination resulting from petroleum-related activities (including V entrained in aerial products derived from onshore gas combustion plants) especially in the Colville Delta-Prudhoe Bay region, and contaminants lingering from past operations linked to a disbanded Distance Early Warning (DEW)–Line station located at the Beaufort Lagoon shore, and 2) temporal variations in granulometry (variation in contents of clay relative to silt in mud), iron and organic matter in samples analyzed. Iron (bound in oxide/hydroxide form) has the potential to scavenge vanadium to varying capacity to form Fe-V hydroxide/oxide complexes. It would seem that the natural differences in iron contents in mud are a possible determining factor for the temporal differences in vanadium. This is supported by the data based on the iron-normalized vanadium concentrations (Table 2), which show no significant temporal differences.

Further, it is suggested that the progressive increased concentrations in Ba in successive decades in Colville Delta-Prudhoe Bay are related to a cumulative effect of successive depositional fluxes of Ba derived from discharge of baryte ($BaSO_4$)-enriched mud during oil drilling operation. Baryte is an important constituent of drilling fluids used in the Alaskan and other OCS regions (Boehm et al., 1987; National Academy of Sciences, 2003). Exploratory drilling for oil has occurred frequently (~348 coastal sites drilled in 1970-2001) and widely in the Beaufort Sea nearshore including the Colville Delta-Prudhoe Bay region (Fig. 20). It is to be expected that deposition of any intended or inadvertent discharge of baryte-rich particulates associated with drilling mud effluents, from a point source in the Beaufort Sea, will be confined to a limited area local to the drilling site (Northern Technical Services, 1981; Macdonald, 1982). However, if time-wise successively several sites are drilled adjacent to each other and within the confines of a limited region, such as in the study area (Fig. 20), there can be a cumulative effect from the effluents eventually leading to temporal increase in barium (Ba). It is to be noted that baryte is a relatively durable (refractory) mineral and it can linger long in the marine environment.

Likewise, it is conceivable that the increased concentration since 1977 in vanadium [a common trace constituent in Prudhoe Bay crude (Coleman et al., 1978) and Alaskan OCS drilling fluid [Boehm et al. (1987); National Academy of Sciences (2003)] in Colville Delta-Prudhoe Bay could possibly result from the pervasive, but marked by occasional years of intense drilling activities related to oil exploration in the North Slope nearshore (Figure 20). It is possible that chronic small fluxes of vanadium into the sediments from drilling fluid effluents could build up over time, especially in the delta-bay region where the sediment accumulation rates are relatively low (Naidu et al., 2001). An additional source of the increased vanadium contents in sediments could be from an increased depositional flux of the metal entrained in aerial products originating from onshore gas combustion plants located in the Prudhoe Bay/Deadhorse area. A mass balance study including an assumption of the possible amount of input of vanadium from the drilling effluents and the combustion plant(s) will help clarify the metal's increased levels recorded in 1997. Certainly the source of the recent increased concentrations of vanadium (a trace constituent of crude) is not from any large-scale (in the order of several millions of barrels) oil spill(s) in the Beaufort Sea nearshore, because such a catastrophic event has not occurred. Thus, tracking of the precise source of the contaminants of barium and vanadium in the sediments investigated remains to be resolved.

At any rate, the recent enhanced concentrations of vanadium and barium detected and the natural levels of all other metals in the study areas are still within the ranges reported for unpolluted nearshore marine sediments, natural baseline values in underlying core sections, and in marine shales which represent lithified muddy deposits laid in paleo-pristine environment (Forstner and Wittman, 1979). This implies that the North Slope nearshore marine sediments have generally remained relatively uncontaminated in trace metals since the early 1970s when accelerated industrial and municipal developments have been carried out. This conclusion is consistent with those arrived at by Crecelius et al. (1991), Trefry et al. (2003) and Brown et al. (2005) for the region.

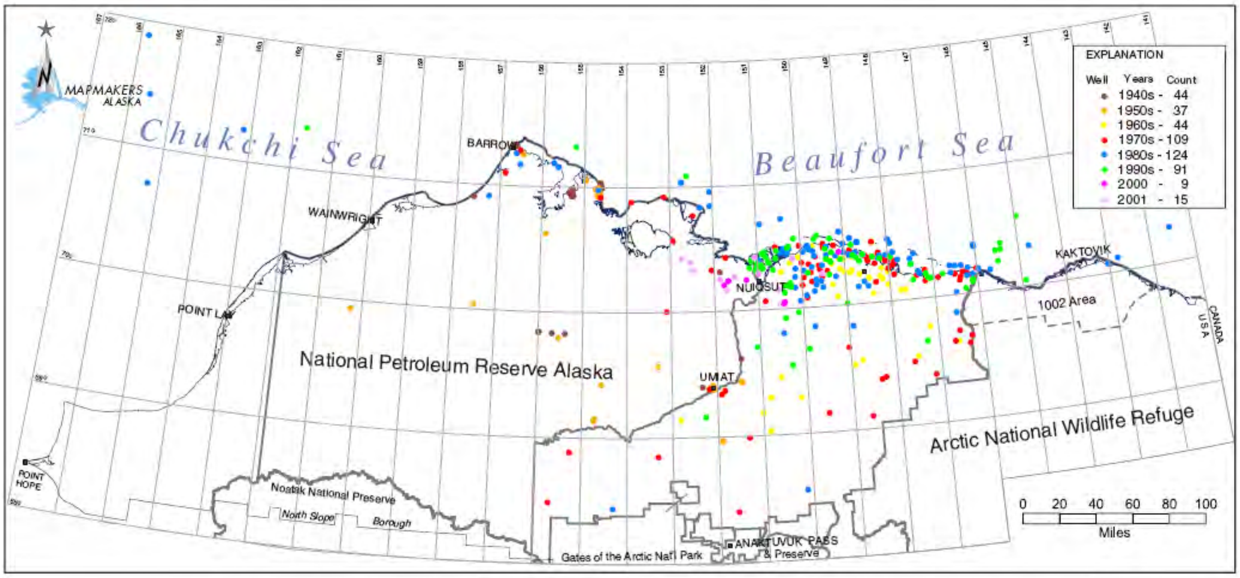


**Figure 20. Location and drilling date of exploration wells on the North Slope of Alaska. Wells drilled during the 1900s are grouped by decade and those since 2000 are depicted by year. Note the heavy concentration of exploratory drilling along the Colville Delta-Prudhoe Bay region. Map after the National Academy of Sciences (2003) and the drawing is by Mapmakers Alaska (2002).**

Comparison of the ranges of concentrations of selected hydrocarbons and their ratios in sediments of Colville Delta-Prudhoe Bay region for two time intervals (1984-1986 and 1997) indicates that, with the exception of total polycyclic aromatic hydrocarbons (ΣPAHs), there is no significant temporal difference in the concentrations of all hydrocarbon homologs listed in Table 14. In case of ΣPAHs a qualitative assessment suggests a relative increase in the concentration ranges from 1984-1986 to 1997 in the nearshore sediments collected in the bay off Kuparak River, East Harrison Bay and Camden Bay, which are located within or adjacent to the Colville Delta-Prudhoe Bay region (Table 14). Likewise, the results of two investigations that were conducted in 2000 and 2002 [Table 14, Brown et al. (2005)] indicate that generally the ΣPAHs concentration ranges corresponding to those years are relatively lower or similar to those for the 1997 ranges but higher than the 1987 ranges. It is suggested that one of the reasons for the increased levels of ΣPAHs in post-1984 period is additional deposition of relatively fresh hydrocarbons originating from the petroleum-related drilling operations. It is to be noted that PAHs are a significant constituent of the organic component of effluents associated with oil drilling in northern Alaska (Boehm et al., 1987; National Academy of Sciences, 2003).

From the data reported in this synthesis it is clear that the concentrations of trace metals and hydrocarbons in sediments within all the regions of study (Colville Delta-Prudhoe Bay, Beaufort Lagoon and Elson Lagoon) are generally similar and within the ranges considered baseline values in uncontaminated regions of the world's nearshore marine environment. Thus, the hypothesis set in this synthesis is tested to be correct.

## Geochemical Partitioning of Trace Metals

Two statistical approaches were followed to get insight into the geochemical partition of the trace metals in sediments for the investigated three regions. One approach consisted of conducting single and multiple correlation coefficient analyses on data collected from each of the above regions. These analyses included data on the concentrations of individual metals, silt, clay and organic matter (OM) on the mud samples. Results of the analysis are reported in Naidu et al. (2001, 2003b, 2006). Subsequently, as part of this synthesis, Spearman's nonparametric correlation coefficient analysis was run based on the data integrated on the trace metals, granulometry and OM in the mud samples from all the three regions. Results of the latter analysis, including metal concentrations not normalized to iron, are included in Table 9, and metal contents normalized against iron are included in Table 10. As suggested by the positive correlations (at 95% confidence level based on critical r), at least part of all metals, except barium (Ba), chromium (Cr), copper (Cu), zinc (Zn) and iron(Fe), are sequestered by adsorption on clay particles (<4µm size). Further, it would also seem that portions of all elements, except manganese (Mn) and barium (Ba), are bound in organic matter (a possible chelating agent forming metal-organic ligand bonds), and as co-precipitates with iron-oxide/hydroxide. It is to be noted that in case of barium (Ba) a weak positive correlation is restricted to per cent silt. This suggests that Ba is bound in a discrete coarse size particle in mud, perhaps barite ($BaSO_4$).

The above deductions are consistent with the investigations on metal partition conducted on representative Colville Delta-Prudhoe Bay and Beaufort Lagoon sediments, via laboratory experiments that included sequential chemical extractions of sediment metals. In this context, results on hydroxylamine hydrochloride-acetic acid (mild acidic-reducing agent) leachates on gross sediments (Chester and Hughes, 1967) are available for the two regions, Colville Delta (Naidu, 1981, 1982; Sweeney and Naidu, 1983; Sweeney, 1984) and Beaufort Lagoon (Naidu et al., 2003a; Misra et al., 2004). For example, in Beaufort Lagoon it is indicated that of the total contents in sediments, generally ~50% of manganese (Mn), 25-30% cobalt (Co), 15-20% each of zinc (Zn), copper (Cu) and nickel (Ni), 10% each of vanadium (V) and iron (Fe), and <3% chromium (Cr) are bound in the sediment non-lithogenous phase [i.e. not bound in the crystal lattice, but in phases such as organic matter (OM), clay exchange surfaces and Fe/Mn oxide/ hydroxide adsorbent]. In contrast, it would seem almost all of chromium (Cr), cadmium (Cd) and barium (Ba) are held in the crystal lattice, and <1% of the total mercury (THg) is in the methylated form. The environmental implication of the results of the above experiments is apparent. It is contended that the fractions of metals that were mobilized into the extracts would be the likely portions from the total metal held in gross sediment that potentially would be available from benthic sediments from Colville Delta-Prudhoe Bay and Beaufort Lagoon for bioaccumulation. Further, it is implied based on the experimental design that the above fractions would be mobilized from sediment consequent to significant perturbations in environmental pH and redox (reducing-oxidation potential) conditions. Changes in the environmental conditions could be from several conceivable anthropogenic activities (e.g., sea floor dredging and disposal of dredge spoils, drilling effluent discharge, oil spill) or natural events (i.e., reworking of subsurface anoxic sediment by storm, ice-gouging or bioturbation). Some of the related issues especially pertinent to the Arctic are discussed by Chapman and Riddle (2005).

To understand the geochemical partitioning of mercury in sediments Spearman's correlation coefficient analyses were run between granulometry and contents of total mercury (THg), methyl mercury (MeHg) and organic matter (OM) in gross sediments. The results (Table 10) indicate that THg and MeHg are positively correlated (r=95%) with the per cent of silt, clay and mud but not with per cent organic matter (OM). It is to be emphasized that the mercury data in this synthesis was on total rather than mud fraction, unlike for rest of the metals. It would thus, seem, that either fine aluminosilicate particles (i.e., clay minerals) are adsorbing mercury, and/or that THg and MeHg, held in some other discrete mineral(s) (fine-grained cinnabar, for example) is co-deposited with hydraulically equivalent clay or silt size particles. The lack of covariance between organic matter (OM) and THg or MeHg (Table 10) was surprising, as particulate OM generally serves as a major host for Hg (Bloom, 1992; Gagnon et al., 1997; Ravichandran, 2004; Shohan-Fridar et al., 2007 and references therein).

Further detailed investigation in the region will assist in the better understanding of the geochemical partitioning of mercury.

A pilot stratigraphic study in Colville Delta-Prudhoe Bay (Naidu et al., 2001) demonstrated a net increase down two sediment cores in the concentrations of methyl mercury (MeHg) (Fig. 6). The patterns of MeHg profiles in the cores are generally similar to those reported by Gagnon et al. (1997) for the Saguenay Fjord, Quebec and for THg in Lavaca Bay, Texas (Bloom et al., 1999), but are in contrast to the trends exhibited in the nearshore but deep water sediment cores from the Greenland fjords (Asmund and Nielsen 2000). We discuss below the possible reasons for the MeHg profiles recorded in Colville Delta-Prudhoe Bay study.

Several possible biogeochemical factors may control the stratigraphic variations in the concentrations of methyl mercury (MeHg) and total mercury (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 sections is due to a narrowly constrained redox cycle (Bloom et al. 1999). The up core decreases in Hg concentrations from a subsurface maximum in Lavaca Bay and the Saguenay Fjord are attributed to progressive decrease in the discharge of Hg contaminants from old chlor-alkali plants (Gagnon et al. 1997; Bloom et al. 1999). In the Colville Delta-Prudhoe Bay region, where there have been no chlor-alkali plants, no such Hg contamination could have occurred in the past. It is unlikely that the up core decrease in MeHg in Colville Delta-Prudhoe Bay (Fig. 6) is due to a net historical decrease in the atmospheric flux of anthropogenic mercury. Rather, during the last century anthropogenic emissions have led to a significant increase in mercury concentrations in ocean waters, arctic ice sheets and sediments (Weiss et al. 1971; Mason et al. 1994; AMAP, 1997; Boutron et al. 1998; Macdonald et al., 2000).

A more likely explanation for the stratigraphic trends in the concentrations of methyl mercury (MeHg) in Colville Delta-Prudhoe Bay (Fig. 6) is that there is a progressive increase down the core in the methylation of THg, mediated by anaerobic bacteria as suggested for other study areas by Jernelov (1974), Gagnon et al. (1997), Bloom et al. (1999), Jay et al. (2000) and Schippers and Jorgensen (2001). Such an explanation will, of course, have to be clarified by further detailed laboratory and site-specific field studies on sediment mercury in the above delta-bay region.

Naidu et al. (2001) have speculated the potential effect of the sediment-held methyl mercury (MeHg) on the North Slope nearshore ecology. It is suggested that at freeze up if there is reworking of subsurface anoxic sediments by storm waves, the MeHg associated with the underlying sediments could be released into overlying water and eventually entrained in freezing sea ice. Subsequently, during spring thaw and close to onset of primary production the ice-held MeHg could be released back into surface water with possible deleterious impact on the spring phytoplankton bloom. Additionally, there is the possibility that by spring time some of the ice-bound MeHg is converted to $Hg^o$ and mobilized to the boundary-layer. At polar sunrise the $Hg^o$ can be subjected to rapid photochemical oxidation, subsequently accumulated in the residual snowpack, and that this oxidized mercury can potentially be bioaccumulated (Fitzgerald et al., 1998; Lindberg et al., 2002). The impact of any MeHg mobilized into sea ice on epontic algae is unknown.

## *Predicting toxicity in sediments with numerical trace metal and hydrocarbon quality guidelines*

There is a growing concern that as a result of past, ongoing and predicted anthropogenic activities in North Alaskan Arctic there is a potential for metal pollution of the sensitive nearshore environment. Addressing this concern we discuss here the status of our monitoring program under the CMI/BOEMRE projects relating to toxic metals in sediments. Long et al. (1995, 1998) have proposed numerical quality guidelines to determine the potential for adverse effects by selected metals in sediment on resident marine benthic organisms and demersal fish. Based upon empirical analysis of a wide database consisting of equilibrium-partitioning modeling, laboratory bioassays and field studies on gross sediments, Long et al. (1995, 1998) developed two sediment quality guideline (SQG) values [an effects range-low (ERL), and an effects range-medium (ERM)]. The database specifically consisted of concentrations of selected trace metals and hydrocarbons in gross sediments and biological effects on numerous benthic taxa. Further, "The two values defined concentration ranges that were: (1) rarely, (2) occasionally or (3) frequently associated with adverse effects." In this context, the mean (geometric) concentrations of selected metals in mud samples collected in 1997, 1999 and 2003 from Colville Delta-Prudhoe Bay (Naidu et al., 2001), Elson Lagoon (Naidu et al., 2003b) and Beaufort Lagoon (Naidu et al., 2006) respectively were compared with the above ERL and ERM and the three ranges for the metals listed in Long et al. (1995). It is indicated that the mean concentrations of As and Ni in Colville Delta-Prudhoe Bay, of As, Cr, and Ni in Elson Lagoon, and of As, Cu and Ni in Beaufort Lagoon fall into the ERL category. The rest of the metals in all the three regions are below the ERL. An initial interpretation of this would be that incidences of adverse effects on benthos could occasionally occur as a result of the mobilization and bioaccumulation of the metals which are held in sediments and are in concentrations within the threshold level of ERL.

However, whether the extrapolation of the guidelines for trace metals suggested by Long et al. (1995) is relevant and applicable to the three regions of the North Slope investigated is a question that needs to be further investigated. At the outset, to some it would seem that the above comparisons are incompatible, because our metal data are on the mud fraction (<63 μm size) of gross sediments whereas Long et al's guidelines are based upon trace metals in gross sediments. Any infiltration of coarser materials such as gravel or sand size particles tends to dilute the overall concentration of trace metals in gross sediment. Compared to gross sediments the mud fraction invariably is enriched chemically more reactive components (e.g., clay minerals and organics) which have high ability to preferentially concentrate metals by adsorption and/or formation of organic-clay-metal ligands or complexes. So, in sediments which have relatively little mud, the concentrations of metals will likely be relatively low. Nonetheless, Naidu et al. (2003b, 2006) contend that the above comparison offer some qualitative basis for predicting potential sediment toxicity in our study area. The contention is based on the general premise that most benthic organisms selectively ingest fine particles (Lee et al., 2000). Therefore, by implication, any high concentration of metal(s) bound to the fine particles could expose the animals to possible adverse effects. From the above discussion it is apparent that any conclusions based on the Long et al.'s guidelines must be substantiated by detailed site-specific cause-effect investigations on individual resident benthic species specific to the three regions of our study. Further, it is to be noted that a lack of consensus exists as to which fractions (phases) of the sediment (e.g., adsorbed, organic and inorganic complexes, interstitial fluids, acid volatile sulfides) binding the metals drive the adverse effect [Grant and Briggs (2002); Mucha et al. (2005), and references therein]. Thus, in order to assess the potential availability of metals for bioaccumulation it is suggested that investigations should be extended to estimate the amounts of individual metals partitioned in various sediment phases (rather than gross sediments). As mentioned earlier, our laboratory experiments indicate that only minor proportions of the total of each of the metals in sediment can be released with relative ease and likely available for bioaccumulation. The unique problems relating to polar marine toxicology and the future special research needs for the region have been discussed by Chapman and Riddle (2005).

As in case of the trace metals, the mean concentrations of a group of selected 13 PAHs and ΣPAHs in sediments have been examined for two regions: Elson Lagoon (Naidu et al., 2003b) and Beaufort Lagoon (Naidu et al., 2006) in the context of Long et al.'s (1995, 1998) numerical guidelines for identifying potential hydrocarbon pollution in terms of Effects Range-Low (ERL) and Effects Range-Medium (ERM) (refer to the above text relating to trace metals). It is indicated that the mean concentrations of all the individual 13 PAHs in gross sediments of Beaufort Lagoon are below the threshold ERL level. In Elson Lagoon the mean concentration of 2-methylnaphthalene in one of the three samples analyzed is between ERL and ERM threshold levels, implying that in case of chronic exposure of the hydrocarbon potential deleterious effect could result to the resident benthos. This must, of course, be clarified by site-specific investigations.

# CONCLUSIONS: TRACE METAL AND HYDROCARBON SYNTHESIS

The following major conclusions are made based on the synthesis of the database of our previous studies on a suite of trace metals and hydrocarbon molecular chemistry of sediments from Elson Lagoon (EL), Colville Delta-Prudhoe Bay (CDPB) and Beaufort Lagoon (BL) regions of North Arctic Alaska.

Generally, the concentrations of all trace metals in surficial mud as well as of total mercury (THg) and methyl mercury (MeHg) in gross sediment are similar or below the levels reported for nearshore marine sediments from unpolluted regions of the world. Cluster analysis and ordination, based on composite metal data available for all the regions, indicated broad regional trends. There is an apparent broad W-E gradient in the concentrations of several metals, which can be driven by several conceivable factors, such as regional and lateral differences in sediment granulometry, sediment accumulation rates, inputs from fluvial system and/or to atmospheric fluxes (originating in Eurasia and transported by long-distance transport).

A few temporal changes in the metal concentrations are noted. In Colville Delta-Prudhoe Bay (CDPB) increases in V in 1986 and 1997 have occurred compared to 1977, and an increase in Ba is identified from 1986 to 1997. Likewise, from 1977 to 2003 an increase in the concentrations of Mn and Cu, accompanied by a decrease in V are recognized in Beaufort Lagoon (BL). The temporal changes in Ba in CDPB could be a result from oil-related anthropogenic activities. Although defining the source of the V contaminant has remained elusive it is possible that at least some of the metal is derived from aerial combustion product resulting from the natural gas flare (burning) in Deadhorse near Prudhoe Bay. The significant down core increase in MeHg is likely a result of increased Hg methylation in progressively anoxic subsurface sediments rather than a net decrease recently in Hg contaminant input.

Correlation coefficient analysis between elements-granulometry-organic matter (OM) suggest that most metals are partitioned in clay, OM and/or Fe oxide/hydroxide. The exceptions are Cr, THg and MeHg, which are bound in undefined discrete particles. However, the significant positive correlations between the alkane *n*-$C_{29}$ and both THg and MeHg portend that large portion of the sediment Hg is entrained in the terrigenous hydrocarbon analog. Results of laboratory experiment, involving treatment of gross sediments with mild acid-reducing solution, have further clarified the metal partitioning. It is indicated that about 50% of Mn, 25-30% of Co, 15-20% each of Zn, Cu and Ni, 10% of V and Fe and <3% of the total in sediments are extracted into the leachate fraction; thus, implying that bulk of most metals in sediment is held relatively firmly in the sediment refractory site, the crystal lattice.

The alkanes and PAHs contents generally vary within a narrow range in the sediment samples within a given location. Sediments from CDPB and BL have comparable levels of hydrocarbons, whereas in EL higher contents of hydrocarbons are found than in the above two regions. However, the hydrocarbon overall composition is uniformly similar in all the samples from the general region investigated. Coastal peats and fluvial sediments appear to be the major source of the alkanes and PAHs. In addition to the above, PAHs reflect probably minor inputs from coal residues. Long range transported pyrolytic PAHs are present only in small amounts. Petrogenic components in the region is either not present or, negligible when detected. Thus, hydrocarbon in the sediments is characteristic of biogenic sources from marine and terrestrial carbon. It is also likely that the petroleum inputs detected in the surface sediments in the general region by others a decade ago has currently decreased to such low level that their signature is not discernable in the CDPB samples collected in 1997. In summary, the results of statistical analyses confirm earlier detailed studies of biomarkers distribution in the samples of the study area. With the background data gathered here, future assessments for possible anthropogenic petroleum inputs in the region should be possible from the contents of alkanes and PAHs and their distribution profiles in the sediments of the sites in question.

Specific findings from the statistical analyses of the hydrocarbon data are highlighted below:

A small variance among the samples in the alkanes content of the sediments from the CDPB and BL, especially the plant wax component which is dominant in all the samples, is noted. Only one station in CDPB exhibits anomalously high PAH content. The three Elson Lagoon (EL) samples are clearly differentiated from CDPB and BL samples by significant differences in the relative abundance of the hydrocarbons. This large separation reflects the higher alkanes and PAHs content in EL. Yet, they are compositionally very similar to the sediments from CDPB and BL.

The hopanes cluster along with the plant wax alkanes contributing strongly to factor 1 and thus reflect their biogenic sources rather than petrogenic origin. This is also corroborated by our earlier biomarkers study where mostly biogenic (immature) hopanes were detected with notable absence of petrogenic (thermally mature) hopanes.

The strong positive loading of monomethylphenanthrenes clearly confirms its major source in the coastal peats. The remaining PAHs are not well differentiated although a close examination reveals certain trends in their loadings. The strong contribution of perylene (Per), phenanthrenes (Pn) and C2 (dimethyl) phenanthrenes/anthracenes (P2) to factor 1 can also be attributed to significant peat contribution. This is also corroborated, for example, by the high correlation of perylene content with $n$-$C_{29}$ alkane. Benzoanthracene (BaA), benzo(ghi)perylene (Bghi) and benzo(a)pyrene (BaP) with a moderately strong loading at factor 2 are commonly characteristic of hydrocarbons derived from combustion material. The remaining PAHs appear to be derived from peat sources mixed in with contribution from combustion. In general, combustion-derived PAHs transported via long range to the north Alaskan arctic samples are at such low levels that these PAHs do not contribute to significant sample separation. Their overall loadings suggest only a concentration gradient in the combustion input.

Petroleum hydrocarbons are either absent or insignificant if detected in the sediments from the entire study region. Even in the Beaufort Lagoon (BL) sediments collected in the vicinity of an oil seep there is no evidence of contribution from petroleum hydrocarbons. This suggests that the region studied is not seriously impacted by natural petroleum seeps or oil contamination from anthropogenic activities.

A qualitative comparison of the time-interval data on selected hydrocarbons in sediments from Colville Delta-Prudhoe Bay shows a relative increase ΣPAHs level from 1984-86 to 1997. One of the interpretations for the ΣPAHs increase is the likely supplemental depositional fluxes of hydrocarbons in post-1984 as a result of sustained petroleum-related drilling activities.

Relating to Long et al.’s proposed quality guidelines for identifying potential for pollution, the mean concentrations in mud of As and Ni in CDPB, of As, Cu, and Ni in BL, and of As, Cr, and Ni in EL fall into the ERL (effects range low) category. Likewise, the mean concentration of all PAHs in gross sediments of BL are below the ERL level, in EL the mean concentrations of 2-methylnaphthalene in one of the three samples is between ERL and ERM (effect range medium). From the above it is implied that incidences of adverse effect on benthos by metals and hydrocarbons existing at the ERL and ERM ranges could potentially be expected in some of the regions investigated. However, it is to be noted that Long et al.’s implied assumption underlying their proposed guidelines is that all the metals in sediments are held in a readily mobilizable phase (s) and are, thus, potentially available for bioaccumulation. This assumption would seem inapplicable in case of the sediments investigated from the north Alaskan arctic, because most of the metals there are held tightly in crystal lattice.

In summary, the nearshore marine sediments off the North Slope of Alaska have remained relatively uncontaminated in trace metals and hydrocarbons, despite the recent accelerated petroleum-related industrialization, municipal and past defense-related activities in the region. This conclusion is consistent with our stated hypothesis.

# ACKNOWLEDGEMENTS

This synthesis was funded by the Bureau of Ocean Energy Management, Regulation and Enforcement (BOEMRE), U. S. Department of the Interior through Cooperative Agreement 1435-01-98-CA-30909 (Task Order 39921) between the BOEMRE Alaska OCS Region and the Coastal Marine Institute, University of Alaska Fairbanks. Matching funds were provided by the Institute of Marine Science and the School of Mining and Engineering both of the University of Alaska Fairbanks, and the University of California, Los Angeles. The trace metal data for 1985 on Beaufort Sea nearshore was kindly provided by John Trefry. Figure 20 is reprinted with permission from The National Academy of Sciences, courtesy of the National Academies Press, Washington, D.C.

Thanks are due to Mike Castellini, Director, CMI, and to Ruth Post, Kathy Carter and Sharice Walker of CMI for excellent cooperation throughout the project. Thanks are due to Kate Wedemeyer, Cleve Cowles, R. Prentki and Heather Crowley of BOEMRE, Anchorage for coordinating and guiding this project. The assistance of Sharice Walker in the preparation of the report is appreciated.

# STUDY PRODUCTS

- Data on trace metals and hydrocarbons on sediments have been tabulated in the Excel spreadsheet and transferred to a Microsoft Access database and is accessible from the following website, ftp://ftp.sfos.uaf.edu/naidu/cmistat2007/

- The database includes in addition to the concentrations of trace metals and hydrocarbons, the location coordinates and water depth, sediment granulometry, organic carbon/organic matter, carbon and nitrogen isotopes on organic fraction of sediment. The data sets have been delineated into study areas and year of study.

- As required by the CMI, the Quarterly Progress reports per the timeline were submitted.

- CMI Annual Research Review Presentation in 2007 and 2008.

- Presentation entitled, “A Synthesis of Three Decades of Investigations On Heavy Metals in Coastal Sediments of North Arctic Alaska” was presented by D. Misra (co-authored by A.S. Naidu, J.J. Kelley, M. I. Venkatesan, and F.J. Mueter) during the 2006 Annual Meeting and International Conference of the American Institute of Hydrology in Baton Rouge, LA (May 21-24).

- Misra, D., S.A. Naidu, J.J. Kelley, M.I. Venkatesan, and F. J. Mueter, 2006. Heavy Metals and Hydrocarbons in Beaufort Lagoon Sediments, North Arctic Alaska. In: Coastal Environment and Water Quality (eds. Xu, Y.J. and Singh V.P.), Water Resources Publications, LLC, Highlands Ranch, CO, USA, ISBN 1-887201-47-5, pp. 3-16.

# REFERENCES

AMAP (Arctic Monitoring and Assessment Programme). 1997. Arctic Pollution Issues: A State of the Arctic Environment Report. Oslo, Norway. 188 p.

Ayotte, P., E. Dewailly. S. Bruneau, H. Careau and A. Vézina. 1995. Arctic air pollution and human health: What effects should be expected? Sci. Total Environ. 160/161:529–537.

Asmund, G. and S.P. Nelson. 2000. Mercury in dated Greenland marine sediments. Sci. Total Environ., 245:61-72.

Barrie, L.A., D. Gregor, B. Hargrave, R. Lake, D. Muir, R. Shearer, B. Tracey and T. Bidleman. 1992. Arctic contaminants: Sources, occurrence and pathways. Sci. Total Environ., 122:1-74.

Blanchard, A.L., H.M. Feder and D.G. Shaw. 2002. Long-term investigation of benthic fauna and the influence of treated ballast water disposal in Port Valdez, Alaska. Mar. Pollu. Bull., 44:367-382.

Bloom, N.S. 1992. On the chemical form of mercury in edible fish and marine invertebrate tissue. Can. J. Aquatic Sci., 49:1010–1017.

Bloom, N.S., G.A. Gill, S. Cappellino, C. Dobbs, L. McShea, C. Driscoll, R. Mason and J. Rudd. 1999. Speciation and cycling of mercury in Lavaca Bay, Texas, sediments. Environ. Sci. Technol., 33(1):7–13.

Blumer, M., R.R.L. Guillard and T. Chase. 1971. Hydrocarbons of marine phytoplankton. Mar. Biol., 8(3):183–189.

Boehm, P.D., M. Steinhauer, E. Crecelius, J. Neff and C. Tuckfield. 1987. Beaufort Sea Monitoring Program: Analysis of trace metals and hydrocarbons from outer continental shelf (OCS) activities. OCS Study MMS 87-0072. Final Report to MMS, Alaska OCS region, Anchorage.

Brown, J., M.T. Jorgenson, O.P. Smith and W. Lee. 2004. Long-term rates of coastal erosion and carbon input, Elson Lagoon, Barrow, Alaska. *In* Proceedings of the 8th International Conference on Permafrost, Zürich, 21–25 July 2003.

Brown, J., P. Boehm, L. Cook, J. Trefry and W. Smith. 2005. ANIMIDA Task 2: Hydrocarbon and metal characterization of sediments, bivalves and amphipods in the ANIMIDA study area. OCS Study MMS 2004-024. Final Report to MMS, Alaska OCS Region, Anchorage. 48 pp.

Boutron, C.F., G.M. Vandal, W.F. Fitzgerald and C.P. Fenari. 1998. A forty year record of mercury in central Greenland snow. Geophys. Res. Letters, 25:3315-3318.

Chapman, P.M., F. Wang, C. Janssen, G. Persoone and H.E. Allen. 1998. Ecotoxicology of metals in aquatic sediments: Binding and release, bioavailability, risk assessment and remediation. Can. J. Fish. Aquat. Sci., 55:2221–2243.

Chapman, P.M., and M.J. Riddle. 2005. Polar marine toxicology – future research needs. Mar. Pollut. Bull., 50(9):905–908.

Chester, H., and M.J. Hughes. 1967. A chemical technique for the separation of ferromanganese minerals, carbonate minerals and adsorbed trace elements from pelagic sediments. Chem. Geol, 2:249-262.

Coleman, H.J., E.M. Shelton, D.T. Nichols and C.J. Thomson. 1978. Analysis of 800 crude oil from United States oilfields. BETC/RI-78/14. Natn'l. Tech. Info. Service, U. S. Dept. Commerce, Springfield, Virginia, 447 pp.

Chernyak, S.M., C.P. Rice and L.L. McConnell. 1996. Evidence of currently-used pesticides in air, ice, fog, seawater and surface microlayer in the Bering and Chukchi Seas. Mar. Poll. Bull., 32:410–419.

Costlow, S.D, J.M. Neff, R.C. Ayers, J.P. Ray, D.F. Boesch, H. Scott, T.R. Gilbert, J. Spiller, J.G. Gonders, J.R. Tenore, D.W. Wood, D.C. White and K.D. Jenkins. 1983. Drilling Discharges in the Marine Environment: Panel on Assessment of Fates and Effects of Drilling Fluids and Cuttings in the Marine Environment. National Academy Press, Washington, D.C., 180 pp.

Crecelius, E.A., J.H. Trefry, M.S. Steinhauer and P.D. Boehm. 1991. Trace metals in sediments from the inner continental shelf of the western Beaufort Sea. Environ. Geol. 18(1):71–79.

Currie, D.R., and L.R. Isaacs. 2005. Impact of exploratory offshore drilling on benthic communities in the Minerva gas field, Port Campbell, Australia. Mar. Environ. Res. 59(3):217–233.

Daskalakis, K.D., and T.P. O'Connor. 1995. Normalization and elemental sediment contamination in the coastal United States. Environ. Sci. Technol. 29:470-477.

Dastillung, M., and P. Albrecht. 1976. Molecular test for oil pollution in surface sediments. Mar. Pollut. Bull. 7(1):13–15.

Douglas, D.C., P.E. Reynolds and E.B. Rhode (eds). 2002. Arctic Refuge Coastal Plain Terrestrial Wildlife Research Summaries Rept., USGS/BRD/BSR-2002-0001. U. S. Geol. Survey, Reston, Va. 75pp.

Farrington, J.W. and B.W. Brown. 1977. Hydrocarbon in western North Atlantic surface sediments. Geochim. Cosmochim. Acta., 41:1627-1641.

Finney, B.P., and C-A Huh. 1989. History of metal pollution in the Southern California Bight: an update. Environ. Sci. Technol., 23:294-303.

Fitzgerald, W.F., D.R. Engstrom, R.P. Mason and E.A. Nater. 1998. The case for atmospheric mercury contamination in remote areas. Environ. Sci. Technol. 32:1–7.

Förstner, U., and G.T.W. Wittman. 1979. Metal Pollution in the Aquatic Environment. Springer-Verlag, Berlin. 486 p.

Gagnon, C., E. Pelletier and A. Mucci. 1997. Behaviour of anthropogenic mercury in coastal marine sediments. Mar. Chem. 59:159-176.

Galperin, Y., and H. Camp. 2002. Petroleum product identification in environmental samples: distribution patterns of fuel-specific homologous series. Contaminated Soil, Sediment, and Water. April/May, 2002, 27-29.

Garbarino, J.R., E. Snyder-Conn, T.J. Leiker and G.L. Hoffman. 2002. Contaminants in arctic snow collected over northwest Alaskan sea ice. Water, Air, Soil Pollut. 139:183–214

Geffard, O., H. Budzinski, E. His, M.N.L. Seaman and P. Garrigues. 2002. Relationships between contaminant levels in marine sediments and their biological effects on embryos of oysters, *Crassostrea gigas*. Environ. Toxicol. Chem. 21:2310–2318.

Grant, A., and A.D. Briggs. 2002. Toxicity of sediments from around a North Sea oil platform: are metals or hydrocarbons responsible for ecological impacts? Mar. Environ. Res., 53(1):95-116.

Jay, J.A., M.M.M. Francois and F.H. Harold. 2000. Mercury speciation in the presence of polysulfides. Env. Sci. Technol. 34:2196-2200.

Jernelov, A. 1974. Factors in the transformation of mercury to methylmercury, p. 167-172. *In* R Hartung and B.D. Dinrnan [eds.], Environmental Mercury Contamination. Ann Arbor Science, Ann Arbor, Michigan.

Johansen, P., D.C.G. Muir and R.J. Law. 2000. Contaminants in the Greenland environment. Sci. Total Env. 245:1-2.

Krantzberg, G., J.H. Hartig and M.A. Zarull. 2000. Sediment management: Deciding when to intervene. Environ. Sci. Technol. 34:22A-27A.

Lackenbauer, P.W., J.F. Matthew and J.A. Lackenbauer. 2005. The Distance Early Warning (DEW) Line: a Bibliography and Documentary Resource List. Arctic Inst.North America, Calgary, Canada, pp.133.

Lee, H.J. and P.L. Wiberg. 2002. Character, fate, and biological effects of contaminated, effluent-affected sediments on the Palos Verdes margin, southern California: an overview. Cont. Shelf Res., 22(6-7):835-840.

Lee, B.-G., S.B. Griscom, J.-S. Lee, H.J. Choi, C.-H. Koh, S.N. Luoma and N.S. Fisher. 2000. Influences of dietary uptake and reactive sulfides on metal bioavailability from aquatic sediments. Science 287(5451):282–284.

Lindberg, S.E., S.B. Brooks, C.-J. Lin, K.J. Scott, M.S. Landis, R.K. Stevens, M. Goodsite and A. Richter. 2002. Dynamic oxidation of gaseous mercury in the Arctic troposphere at Polar sunrise. Environ. Sci. Technol. 36:1245–1256.

Long, E.R., L.J. Field and D.D. MacDonald. 1998. Predicting toxicity in marine sediments with numerical sediment quality guidelines. Environ. Toxicol. Chem. 17(4):714–727.

Long, E.R., D.D. MacDonald, S.L. Smith and F.D. Calder. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manage. 19:81–97.

Loring, D.H. 1991. Normalization of heavy-metal data from estuarine and coastal sediments. ICES J. Mar. Sci. 48:101-115.

Macdonald, R.W. 1982. An examination of metal inputs to the Southern Beaufort Sea by disposal of waste barite in drilling fluid. Ocean Manage. 8(1):29–49.

Macdonald, R.W., and 28 others. 2000. Contaminants in the Canadian Arctic: 5 years of progress in understanding sources, occurrence and pathways. Sci. Total Environ. 254:93-244.

Macdonald, R.W., A.S. Naidu, M.B. Yunker and C. Gobeil. 2004. The Beaufort Sea: Distribution, sources, fluxes, and burial rates of organic carbon, p. 177–192. *In* R. Stein and R.W. Macdonald [eds.], The Organic Carbon Cycle in the Arctic Ocean. Springer, Berlin/New York.

Macdonald, R.W., T. Harner and J. Fyfe. 2005. Recent climate change in the Arctic and its impact on contaminant pathways and interpretation of temporal trend data. Sci. Total Environ. 342:5-86. Final Report to MMS.

Mason, R.P., W.F. Fitzgerald and F.M.M. Morel. 1994. The biogeochemical cycling of elemental mercury: Anthropogenic influences. Geochim. Cosmochim. Acta 58:3191-3198.

Misra, D., A.S. Naidu, J.J. Kelley, M.I. Venkatesan and F.J. Mueter. 2006. Heavy metals and hydrocarbons in Beaufort Lagoon sediments, North Arctic Alaska. In: Y.J. Xu and V.P. Singh (Eds.), Coastal Environment and Water Quality. Water Resources Publications, LLC, Highland Ranch, Colorado, 1-16.

Maxwell, J.R., C.T. Pillinger and G. Eglinton. 1971. Organic geochemistry. Q. Rev. 25:571-628.

Molnia, B.F., and K.B. Taylor [eds.]. 1994. Proc. Interagency Arctic Research Policy Committee Workshop on Arctic Contamination. 2-7 May 1993, Anchorage. 311p.

Mountouris, A., E. Voutsas and D. Tassios. 2002. Bioconcentration of heavy metals in aquatic environments: The importance of bioavailability. Mar. Pollut. Bull. 44:1136–1141.

Mucha, A.P., M. Teresa, S.D. Vasconcelos and A.A. Bordalo. 2005. Spatial and seasonal variations of the macrobenthic community and metal contamination in the Douro estuary (Portugal). Mar. Environ. Res. 60(5):531–550.

Mulvad, G., H.S. Pedersen, J.C. Hansen, E. Dewailly, E. Jul, M.B. Pedersen, P. Bjerregaard, G.T. Malcom, Y. Deguchi and J.P. Middaugh. 1996. Exposure of Greenlandic Inuit to organochlorines and heavy metals through the marine food-chain: An international study. Sci. Total Environ. 186:137–139.

Naidu, A.S. 1981. Sources, Transport Pathways, Depositional Sites and Dynamics of Sediments in the Lagoon and Adjacent Shallow Marine Region, Northern Arctic Alaska. Annual Report to NOAA–OCSEAP Office, Boulder, Colorado, 39 p.

Naidu, A.S. 1982. Aspects of size distributions, clay mineralogy and geochemistry of sediments of the Beaufort Sea and adjacent deltas, North Arctic Alaska. Final report to NOAA-OCSEAP Office, Boulder, Colorado. 114p.

Naidu, A.S., A. Blanchard, J.J. Kelley, J.J. Goering, M.J. Hameedi and M. Baskaran. 1997. Heavy metals in Chukchi Sea sediments as compared to selected circum-arctic shelves. Mar. Pollut. Bull. 35:260-269.

Naidu, A.S., L.W. Cooper, B.P. Finney, R.W. Macdonald, C. Alexander and I.P. Semiletov. 2000. Organic carbon isotope ratios ($\delta^{13}$C) of Arctic Amerasian continental shelf sediments, p. 522-532. *In* R. Stein [ed.] Circum-Arctic River Discharge and Its geological Record. Int. J. Earth Sci. Spec. Issue, Vol. 89.

Naidu, A.S., T.C. Mowatt, S.E. Rawlinson and H.V. Weiss. 1984. Sediment characteristics of the lagoons of the Alaskan Beaufort Sea coast, and evolution of Simpson Lagoon. p. 275-292. *In* P.W. Barnes, E. Reimnitz and D.M. Schell [eds.], The Alaskan Beaufort Sea: Ecosystem and Environments. Academic Press, New York.

Naidu, A.S., J.J. Goering, J.J. Kelley and M.I. Venkatesan. 2001. Historical Changes in Trace Metals and Hydrocarbons in the Inner Shelf, Beaufort Sea: Prior and Subsequent to Petroleum-Related Industrial Developments. Final Report. OCS Study MMS 2001-061, University of Alaska Coastal Marine Institute, University of Alaska Fairbanks and USDOI, MMS, Alaska OCS Region, 80 p.

Naidu, A.S., J.J. Kelley and J.J. Goering. 2003a. Three decades of investigations on heavy metals in coastal sediments, North Arctic Alaska: A synthesis. J. Phys. IV France 107:913–916.

Naidu, A.S., J.J. Kelley, J.J. Goering and M.I. Venkatesan. 2003b. Trace Metals and Hydrocarbons in Sediments of Elson Lagoon (Barrow, Northwest Arctic Alaska) as Related to the Prudhoe Bay Industrial Region. Final Report. OCS Study MMS 2003-057, University of Alaska Coastal Marine Institute, University of Alaska Fairbanks and USDOI, MMS, Alaska OCS Region, 33 p.

Naidu, A. S., J. J. Kelley, D. Misra and M. I. Venkatesan. 2006. Trace metals and hydrocarbons in sediments of the Beaufort Lagoon, Northeast Arctic Alaska, exposed to long-term natural oil seepage, recent anthropogenic activities and pristine conditions. Final Repot, OCS Study MMS 2005-041. University of Alaska Coastal Marine Institute, University of Alaska Fairbanks and USDOI, MMS, Alaska OCS Region, 57 p.

National Academy of Sciences. 2003. Cumulative Environmental Effects of Oil and Gas Activities on Alaska's North Slope. National Academies Press, Washington, D. C., 304p.

Northern Technical Services. 1981. Beaufort Sea Drilling Effluent Disposal Study. Report for SOHIO Alaska Petroleum Co., Anchorage, 329 p.

Philip, R.P. 1985. Fossil Fuel Biomarkers: Applications and Spectra. Methods in Geochemistry and Geophysics, 23. Elsevier, New York, 294 p.

Rahn, K.A., and D.H. Lowenthal. 1986. Who's polluting the Arctic? Why is it so important to know? An American perspective, p. 85–95. *In* B. Stonehouse [ed.], Arctic Pollution. Cambridge Univ. Press, Cambridge, England.

Ravichandran, M. 2004. Interactions between mercury and dissolved organic matter - a review. Chemosphere, 55:319-331.

Rember, R.D., and J.H. Trefry. 2004. Increased concentrations of dissolved trace metals and organic carbon during snowmelt in rivers of the Alaskan Arctic. Geochim. et Cosmochim. Acta, 68:477-489.

Schippers, A., and B.B. Jorgensen. 2001. Oxidation of pyrite and iron sulfide by manganese dioxide in marine sediments. Geochim. Cosmochim Acta, 65:915-922.

Shaw, D.G., D.J. McIntosh and E.R Smith. 1979. Arene and alkane hydrocarbons in nearshore Beaufort Sea sediments. Estuar. Coast. Mar. Sci., 9:435-449.

Shohan-Frider, E., G. Shelef, and N. Kress. 2007. Mercury speciation in sediments of a municipal sewage sludge marine disposal site. Mar. Environ. Res., 64:601-615.

Simoneit, B.R.T., and I.R. Kaplan. 1980. Triterpenoids as molecular indicators of paleoseepage in recent sediments of the Southern California Bight. Mar. Environ. Res., 3(2):113–128.

Snyder-Conn, E., and D. Densmore, C. Moitoret and J. Stroebele. 1990. Persistence of trace metals in shallow arctic marine sediments contaminated by drilling effluents. Oil & Chem. Pollt. 7(3):225-247.

Snyder-Conn, E., J.R. Garbarino, G.L. Hofihan and A. Oelkers. 1997. Soluble trace elements and total mercury in arctic Alaskan snow. Arctic, 50:201-215.

Steinhauer, M.S., and P.D. Boehm. 1992. The composition and distribution of saturated and aromatic hydrocarbons in nearshore sediments, river sediments, and coastal peat of the Alaskan Beaufort Sea: Implications for detecting anthropogenic hydrocarbon inputs. Mar. Environ. Res., 33(4):223–253.

Sweeney, M.D. 1984. Heavy Metals in the Sediments of an Arctic Lagoon, Northern Alaska M.S. Thesis, Univ. of Alaska Fairbanks, 256 p.

Sweeney, M.D., and A.S. Naidu. 1989. Heavy metals in the sediments of the inner shelf of the Beaufort Sea, northern arctic Alaska. Mar. Pollut. Bull., 20(3):140–143.

Townend, J. 2002. Practical statistics for Environmental and Biological Scientists. John Wiley & Sons, Inc., Hoboken, N.J., 276 pp.

Trefry, J.H., R.D. Rember, R.P. Trocine and J.S. Brown. 2003. Trace metals in sediments near offshore oil exploration and production sites in the Alaskan Arctic. Environmental Geol., 45(2):149–160.

Valette-Silver, N., M.J. Hameedi, D.W. Efurd and A. Robertson. 1999. Status of the contamination in sediments and biota from the western Beaufort Sea (Alaska). Mar. Pollut. Bull. 38:702-722.

Venkatesan, M.I. 1988. Occurrence and possible sources of perylene in marine sediments-A review. Mar. Chem. 25:l-27.

Venkatesan, M.I. 1994. Historical trends in the deposition of organic pollutant in the Southern California Bight. UCLA, Final Rept., to NOAA, 35p.

Venkatesan, M.I., S. Brenner, E. Ruth, J. Bonilla and I.R. Kaplan. 1980. Hydrocarbons in age-dated sediment cores from two basins in the Southern California Bight. Geochim. Cosmochim. Acta, 46:2135-2149.

Venkatesan, M.I., and I.R. Kaplan. 1982. Distribution and transport of hydrocarbons in surface sediments of the Alaskan outer continental shelf. Geochim. Cosmochim. Acta 46(11):2135–2149.

Venkatesan, M.I. 1987. Organic geochemistry of sediments from the continental margin off southern New England, U. S. A. Part II. Lipids. Marine Chem. 21(3):267-299.

Weiss, H.V., M. Koide and E. Goldberg. 1971. Mercury in a Greenland ice sheet: evidence of recent input by man. Science, 174:692-694.

Youngblood, W.W., and M. Blumer. 1975. Polycyclic aromatic hydrocarbons in the environment: Homologous series in soils and recent marine sediments. Geochim. Cosmochim. Acta 39(9):1303–1314.

Yunker, M.B. and Macdonald, R.W. 2003. Alkane and PAH depositional history, sources and fluxes in sediments from the Fraser River Basin and Strait of Georgia, Canada. Org. Geochemistry. 34: 1429-1454.

Zafiriou, O.C., M. Blumer and J. Myers. 1972. Correlation of oils and oil products by gas chromatography. Woods Hole Oceanographic Institution Tech. Rep. 72–55, 110 p.

MARCH 3, 1849

## 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.