

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

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BACKGROUND:

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. 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). 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. 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. 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:

The 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 since 1977. 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.

DESCRIPTION:

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. 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. 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. Another of the synthesis's objectives was 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.

SIGNIFICANT CONCLUSIONS:

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.

A few temporal changes in the metal concentrations are noted. Time-interval comparisons of metals in surficial mud of the Colville Delta-Prudhoe Bay region (CDPB) indicate significant increases in vanadium in 1985 and 1997 compared to 1977, and in barium contents in 1997 compared to 1985. In Beaufort Lagoon mud a significant increase in Copper and manganese and a decrease in vanadium is noted in 2003 compared to 1977. The reason for the increases in vanadium and barium in CDPB are unknown. The elevated barium could be due to accumulation of barite (BaSO_4) derived from effluents discharged in the region since the 1970s from petroleum-related drilling activities, whereas the increase in vanadium could possibly be from local gas combustion products. 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. However, the significant positive correlations between the alkane $n\text{-C}_{29}$ and both THg and MeHg portend that large portion of the sediment Hg is entrained in the terrigenous hydrocarbon analog.

The overall composition of the hydrocarbon profiles in gross sediments is very similar in widely separated regions of the North Slope nearshore (Elson Lagoon, Colville Delta-Prudhoe Bay and Beaufort Lagoon). The molecular hydrocarbon markers are predominantly biogenic and terrigenous-derived, with little input, if any, from natural oil seeps and/or anthropogenic hydrocarbons.

STUDY RESULTS:

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. 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.

STUDY PRODUCTS:

Data on trace metals and hydrocarbons on sediments have been tabulated in an 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 Presentations were made in 2007 and 2008. The following presentations were also made and a final report was submitted:

Misra, D., A.S. Naidu, J.J. Kelley, M. I. Venkatesan, and F.J. Mueter, 2006. A Synthesis of Three Decades of Investigations On Heavy Metals in Coastal Sediments of North Arctic Alaska, presented 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.

Naidu, A. Sathy, Debasmita Misra, John J. Kelley, Arny Blanchard and M. Indira Venkatesan. 2009. Synthesis of time-interval changes in trace metals and hydrocarbons in nearshore sediments of the Alaskan Beaufort Sea: Final Report, OCS Study MMS 2009. Submitted to Coastal Marine Institute, University of Alaska Fairbanks, and the US DOI/MMS, OCS Office, Anchorage.

STUDY AREA

