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Historical changes in trace metals and hydrocarbons in nearshore sediments, Alaskan Beaufort Sea, prior and subsequent to petroleum-related industrial development: Part II. Hydrocarbons

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ABSTRACT

Composition and concentration of hydrocarbons (normal and isoprenoid alkanes, triterpenoids, steranes, and PAHs) in nearshore surface sediments from Elson Lagoon (EL), Colville Delta–Prudhoe Bay (CDPB) and Beaufort Lagoon (BL), Alaskan Beaufort Sea, were assessed for spatio-temporal variability. Principal component analysis of the molecules/biomarkers concentrations delineated CDPB and BL samples into two groups, and cluster analysis identified three station groups in CDPB. Overall there was no geographic distribution pattern in the groups. The diversities between groups and individual samples are attributed to differences in *n*-alkanes and PAHs contents, which are influenced predominantly by sediment granulometry and sitespecific fluvial input. The predominant hydrocarbon source is biogenic, mainly terrigenous, with hardly any contribution from natural oil seeps, oil drill effluents and/or refined crude. The terrigenous source is corroborated by $\delta^{13}C$, $\delta^{15}N$, and OC/N of sediment organic matter. Time interval (1976–1977, 1984 and 1997) changes in hydrocarbon compositions and concentrations in CDPB are not significant.

1. Introduction

The Alaskan Arctic has been historically considered a relatively pristine environment free of metal and hydrocarbon contaminants. However, industrial growth has increased in the coastal region of the North Slope of Alaska during the past four decades as a result of exploration and development of onshore and offshore petroleum reserves (NAS, 2003). Concurrently urbanization of the villages along the coast (e.g., Barrow, Kaktovik) has increased. Long-range transport of anthropogenic contaminants [i.e., trace metals, organochlorines, polycyclic aromatic hydrocarbons (PAHs)] from Eurasia over the arctic region including Arctic Ocean via vapor phase or aerosols has been reported in recent decades (Welch et al., 1991; Barrie et al., 1992; Gubala et al., 1995; Chernyak et al., 1996; AMAP, 1997; Valette-Silver et al., 1999; Macdonald et al., 2000). Additional environmental changes are expected in the near future. For example, in the 1.5 million acres of coastal plain (titled the 1002 area) of the Arctic National Wildlife Refuge (ANWR) which has potential petroleum reserves, future oil drilling activities could contaminate the adjacent nearshore region with industrial trace metals and hydrocarbons. A related concern especially is that the lipid-rich food webs in the fragile arctic ecosystem could efficiently biomagnify contaminants in the region (Johansen et al., 2000; Chapman and Riddle, 2005) with deleterious implication on subsistence food source (Douglas et al., 2002).

Several investigations were initiated in Arctic Alaska to provide baselines on the composition and concentration of hydrocarbons in the nearshore (Shaw et al., 1979; Venkatesan et al., 1981; Venkatesan and Kaplan, 1982; Boehm et al., 1987; Steinhauer and Boehm, 1992; Naidu et al., 2001, 2003, 2006; Macdonald et al., 2004; Brown et al., 2005, 2010). The emphasis was on sediments because they serve as potential sink and/or source of particle-reactive contaminants including hydrocarbons (Valette-Silver et al., 1999; Lee and Wiberg, 2002; Currie and Isaacs, 2005). The ability of Alaskan arctic nearshore sediments to sequester hydrocarbons, by adsorption, was demonstrated empirically by Terschalk et al. (2004). However, all of the above studies were limited to site-specific areas and little effort was made to draw correlations between the content of hydrocarbons and associated sediment parameters [(i.e., grain size, organic matter and their C/N ratios, and carbon and nitrogen isotopes ($\delta^{13}C$ and $\delta^{15}N$ respectively)]. An integration and statistical analysis of the available data will improve our

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understanding of the factors that control the regional differences in sediment hydrocarbons and their potential sources (natural and anthropogenic, terrigenous versus marine).

This paper presents a synthesis of the hydrocarbons data [normal and isoprenoid alkanes, triterpenoids, steranes, and polycyclic aromatic hydrocarbons (PAHs)] on nearshore surface sediment samples from the North Slope of Arctic Alaska for 1977–2010. An emphasis is placed here on unpublished data sets (Naidu et al., 2001, 2003, 2006) with particular reference to the Colville Delta–Prudhoe Bay (CDPB) region where longer time-interval information is available. Statistical analysis was directed to identify regional differences in the hydrocarbon distribution pattern(s) and to deduce the possible sources of hydrocarbons in the nearshore sediments. The composition of $\delta^{13}C$ and $\delta^{15}N$ in organic matter of selected sediment samples are discussed to supplement the inference on the hydrocarbon sources. This paper constitutes part II of a two-part series of studies; a detailed treatise of sources and dynamics of trace metals in the three study areas from the same samples considered in the current report was published as part I (Naidu et al., 2012). These syntheses will provide regional database to the ongoing studies in nearshore region by the Alaska Monitoring and Assessment Program (AKMAP, 2005) on current status, trends, and changes in chemical contaminants.

1.1. Area of study and environmental setting

The study area extends from the North Slope shore of the Alaskan Beaufort Sea to about 30 km seaward including the US Federal Outer Continental Shelf (OCS) zone. The study was focused on three disjointed nearshore regions in the North Slope (Fig. 1). These regions were selected as they have been exposed to different ongoing or past anthropogenic activities. For example, the Colville Delta–Prudhoe Bay (CDPB, Fig. 2a) is currently exposed to petroleum related industrialization (currently operating, future oil prospects and slated oil lease sale sites) and Elson Lagoon (EL, Fig. 2b) to municipal and local community recreational and subsistence activities. The Beaufort Lagoon (BL, Fig. 2c) was exposed to now defunct Distant Early Warning (DEW) line military station's operations. Natural oil seeps adjacent to Beaufort Lagoon may be additional source of hydrocarbons to that area.

The regions studied are sheltered by the mainland coast and chains of barrier islands and are thus, located in an environment generally devoid of intense wave-current and tidal (amplitude 16 cm) turbulence (Barnes et al., 1984; Naidu et al., 1984). Wide seasonal disparity occurs in the cryogenic-dominated environment. Extreme frigid winter conditions (−40 to −46 °C) extend for eight to nine months (mid October–mid June), with sea-ice or shore-fast ice covering the Beaufort Sea. At this time sea floor reworking by ice gouging is pervasive. In spring (mid June), the nearshore region is exposed to the unique phenomenon of turbid fluvial overflow on sea ice extending up to 10 km offshore. Spring primary production (<10 g C m^{-2} y^{-1}) is dominated by sea ice algae (Gradinger, 2009). In the summer (July–August) open water season, water column primary production increases to ~10–20 g C m^{-2} y^{-1}. Intense wave action during occasional summer storms results in sediment resuspension and coastal erosion 1–10 m y^{-1}. Presence of mixed sediment types (poorly sorted gravelly sand to sandy mud) is typical and organic matter is predominantly terrigenous (Naidu et al., 2000; Macdonald et al., 2004).

2. Material and methods

2.1. Samples and database

Sediments were collected by van Veen grab sampler or by Haps corer with a stainless steel barrel. The upper 2-cm oxidized surficial sediment layer was subsampled and placed in a pre-baked

Fig. 1. Area of study: Elson Lagoon, Colville Delta–Prudhoe Bay, and Beaufort Lagoon from North Slope of Arctic Alaska.