Deep-Sea Research Part II 144 (2017) 52–62

Contents lists available at ScienceDirect

Deep-Sea Research Part II

journal homepage: www.elsevier.com/locate/dsr2

Alkane and polycyclic aromatic hydrocarbons in sediments and benthic invertebrates of the northern Chukchi Sea

H. Rodger Harvey*, Karen A. Taylor

Department of Ocean, Earth, and Atmospheric Sciences, Old Dominion University, 4600 Elkhorn Avenue, Norfolk, VA 23529, USA

ARTICLE INFO

Keywords:
Polycyclic aromatic hydrocarbon
Alkane
Chukchi Sea
Mussel
Whelk
Sediment

ABSTRACT

The Hanna Shoal region represents an important northern gateway for transport and deposition in the Chukchi Sea. This study determined the concentration and distribution of organic contaminants (aliphatic hydrocarbon and polycyclic aromatic hydrocarbons, PAHs) in surface sediments from 34 sites across Hanna Shoal. Up to 31 total PAHs, including parent and alkyl homologues were detected with total concentrations ranging from a low of 168 ng g^{-1} the western flank of Hanna Shoal (station H34) to 1147 ng g^{-1} at station in Barrow Canyon (station BarC5). Alkyl PAHs were more abundant than parent structures and accounted for 53–64% of the summed concentrations suggesting overall at background levels (< 1600 ng g^{-1}) in sediments. Alkane (C_{15}–C_{33}) hydrocarbons ranged from 4.3 μg g^{-1} on the southern flank of Hanna shoal to 31 μg g^{-1} at a northern station. Sediments were often dominated by short chain (C_{15}–C_{22}) alkanes with overall terrestrial aquatic ratios (TAR) for the region averaging 0.20. Based on the ratio of Fl/(Fl + Py) and BaF/(Baf + BeP) verses (BA/BA + Ch) in sediments, PAHs are largely derived from petrogenic sources with minor amounts of mixed combustion sources. A diversity of PAHs were detected in the northern whelk *Neptunea heros* foot muscle with total concentrations ranging from 0.14 to 1.5 μg g^{-1} dry tissue wt. Larger (and presumably older) animals showed higher levels of PAH per unit muscle tissue, suggesting that animals may bioaccumulate PAHs over time, with low but increasing concentrations also present in internal and external eggs. Alkane hydrocarbons were also higher in whelks with distributions similar to that seen in sediments. The mussel *Muscularus discors* collected in Barrow Canyon showed constrained distributions and substantially lower concentrations of both PAHs and alkanes than the surrounding surface sediments.

1. Introduction

The interest in resources and ecosystem processes in the Arctic Ocean has led to a crucial need to carry out baseline assessments of the distribution and concentration of key organic compounds as well as their potential to document organic matter cycling and sources in this changing system. Located between northern Alaska and the Siberian coast, the Chukchi Sea is one of the largest continental shelves in the world and its northern location puts it at the crossroads of recent observed changes in global climate. As an inflow shelf (Carmack et al., 2006) the Chukchi sustains a large primary production and export flux of organic matter due to the import of nutrients from the Pacific Ocean. As a consequence of high production and organic flux to sediments, a rich benthic community is present. Recent decadal scale observations of warming temperatures makes the region highly susceptible to the effects of sea-ice retreat, ecosystem shifts in both benthic and pelagic realms and with reduced sea ice increased interest in offshore energy development (Grebmeier et al., 2010). In that context the distribution and composition of organic materials in bottom sediments reflect multiple sources arriving from the overlying waters, physical processes operative during mobilization and transport, and the largely biological processes acting within sediments themselves. Hydrocarbons found in the Arctic represent a mixture of natural background and petroleum hydrocarbons from multiple sources with concentrations of aliphatic n-alkanes typically greater than those of PAHs (e.g. Yunker et al., 2011). Major contributors to the elevated n-alkane signal (C_{27} and C_{29}) in Arctic Ocean sediments are varied but largely derived from persistent inputs of terrigenous material from rivers and coastal erosion (Belicka et al., 2002; Belicka and Harvey, 2009; Yamamoto et al., 2008; Yunker et al., 2005 Guo et al., 2007). Although PAHs represent only a small (0.2–7%) fraction of the total composition of crude oil, their aromatic structures represent one of the major contributors to its toxicity (Neff, 2002; NRC, 2003).

The initial Chukchi Sea Offshore Monitoring in Drilling Area (COMIDA) program documented the suite of both biotic and chemical inventories in the southern region of the Chukchi Sea (see Dunton et al.,

* Corresponding author.
E-mail address: rharvey@odu.edu (H.R. Harvey).

http://dx.doi.org/10.1016/j.dsr2.2017.08.011

Available online 19 August 2017

2012; Dunton et al., 2014 and references therein). A portion of that program established inventories of important organic molecules and their possible sources including measures of aliphatic *n*-alkane and polycyclic aromatic hydrocarbons (PAHs) and their toxicological impact on one fish species (Harvey et al., 2014). The combination of aliphatic alkanes and PAH's as the two hydrocarbon classes of focus were based on their ability to trace specific sources of anthropogenic contamination (i.e. fossil fuel combustion) and natural inputs (i.e. oil seeps, terrestrial debris) and to establish the baseline of toxicologic responses to the native fish *B. saida*. Results of that work in the southern region of the Chukchi Sea observed low levels of PAH and alkane hydrocarbons and only minor toxicological responses (Harvey et al., 2014). This study was designed to compare measures of the suite of organic molecules in surface sediments in the southern Chukchi Sea with the more Northern Hanna Shoal region to document sources of hydrocarbon biomarkers across important areas of whale migration and increased benthic pelagic coupling. In addition, it examines the potential for trophic transfer of hydrocarbons in two benthic invertebrates through analysis of eggs and muscle tissues of the Neptune whelk *Neptunea heros* and muscle tissue of the mussel *Musculus discors*.

2. Methods

2.1. Field collections

Sampling in the Chukchi Sea in both 2012 and 2013 was accomplished aboard the USCGC HEALY in late summer during largely ice free periods. Collections included a suite of sediments and associated biota across 34 stations of the Hanna Shoal region as shown in Fig. 1. Sediments were collected using several types of samplers, predominantly a 0.25 m^2 stainless steel box core (KC Denmark), which was subsequently sectioned shipboard into 1 cm intervals. On occasion a stainless steel double Van-Veen sampler was used where undisturbed sediment samples were available. Sediment sections were stored in precleaned (as purchased) plastic I-Chem jars with Teflon-lined screw cap lids and immediately frozen until analysis in the shore based laboratory. Sample collectors were protected from stack smoke exhaust, oils from winches and wire, and other potential sources airborne contamination during sampling. Contamination blanks for deck and laboratory processing of all samples were collected and processed as described in the QA/QC section to account for artifacts.

2.2. Invertebrates

Previous work documented concentrations of PAHs and alkanes hydrocarbons from the foot muscle in 35 individuals of the *Neptunea* whelk which had been pooled into three size classes based on shell length (0–5, 5–8, and > 8 cm) in the southern Chukchi sea (see Harvey et al., 2014). That analysis showed a diversity of PAHs in muscle tissues with alkyl-substituted compounds dominating over parent species among all size classes. What was unexpected, however, was that the total concentration of PAHs decreased in larger organisms while aliphatic n-alkanes in *Neptunea* muscle showed the opposite trend. To further assess body burdens in muscle tissue and possible trophic transfer implications for organic contaminants, additional female Northern Neptune whelk (*Neptunea heros*) with attached eggs cases were collected when observed in benthic trawls. Four female *Neptunea* whelks ranging in size from 4.8 to 11.4 cm were collected from stations CBL-11, H6, and H17 during the 2013 Hanna Shoal Ecosystem Study cruise. Several individual *Neptunea* carried both internal (with albumen) and external eggs (removed from their casings) among those collected through bottom trawls. Sterile stainless tools were used for the

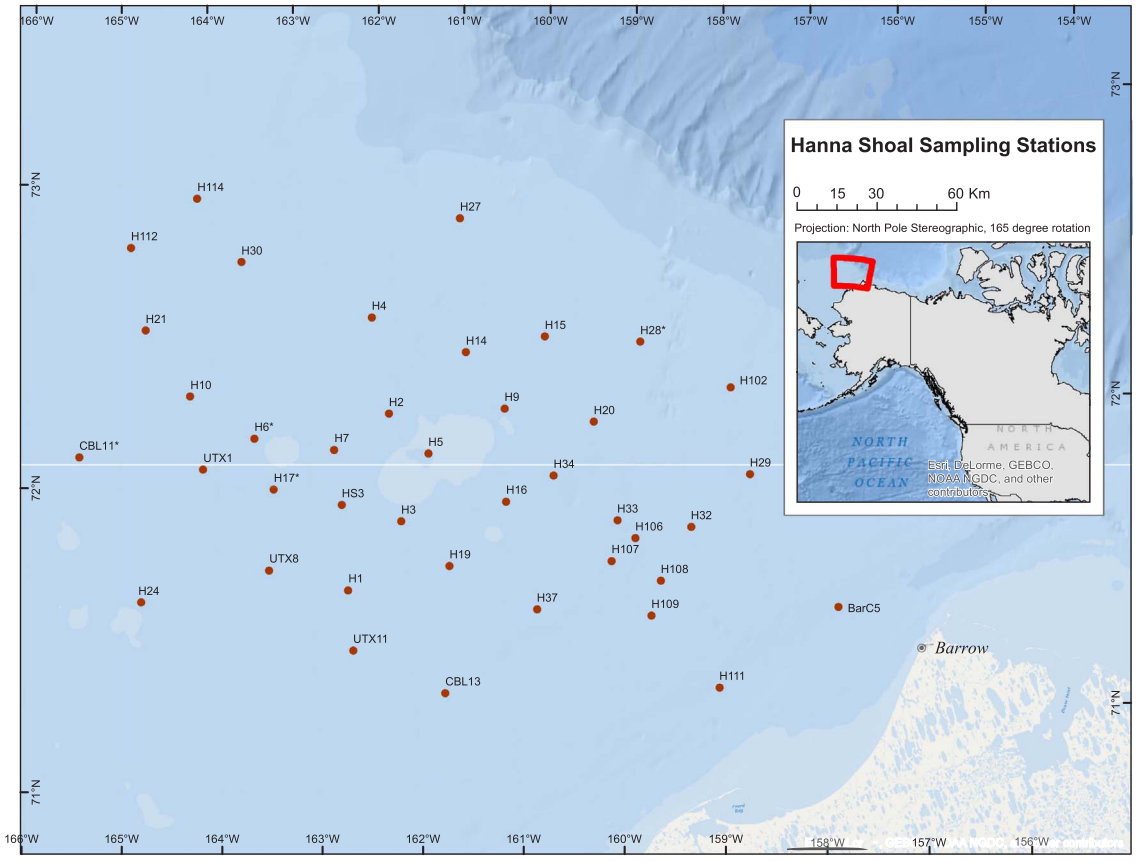

Fig. 1. Station map illustrating sites where sediments were collected for hydrocarbon analysis. Stations where benthic invertebrates (*N. heros* and *M. discors*) were also obtained by trawling are shown as *. Summary information including location and hydrocarbon totals for all stations is described in Table 3.