

SOURCES AND GEOCHEMICAL CONTROLS ON HYDROCARBONS IN SEDIMENTS FROM CHESTERFIELD INLET AND WAGER BAY (UKKUSIKSALIK NATIONAL PARK)

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INTRODUCTION

Sediment particles deposited on the seafloor carry a record of the environment from which the particles were sourced and the environment in which they were deposited. As particles settle to the seafloor, particularly those rich in organic matter, they scavenge contaminants such as polycyclic aromatic hydrocarbons (PAHs) from the water column [1]. Thus, well-dated sediment cores may contain a record of past contaminant sources and depositional processes. This information is valuable, particularly in the Arctic, where baseline data are often not available.

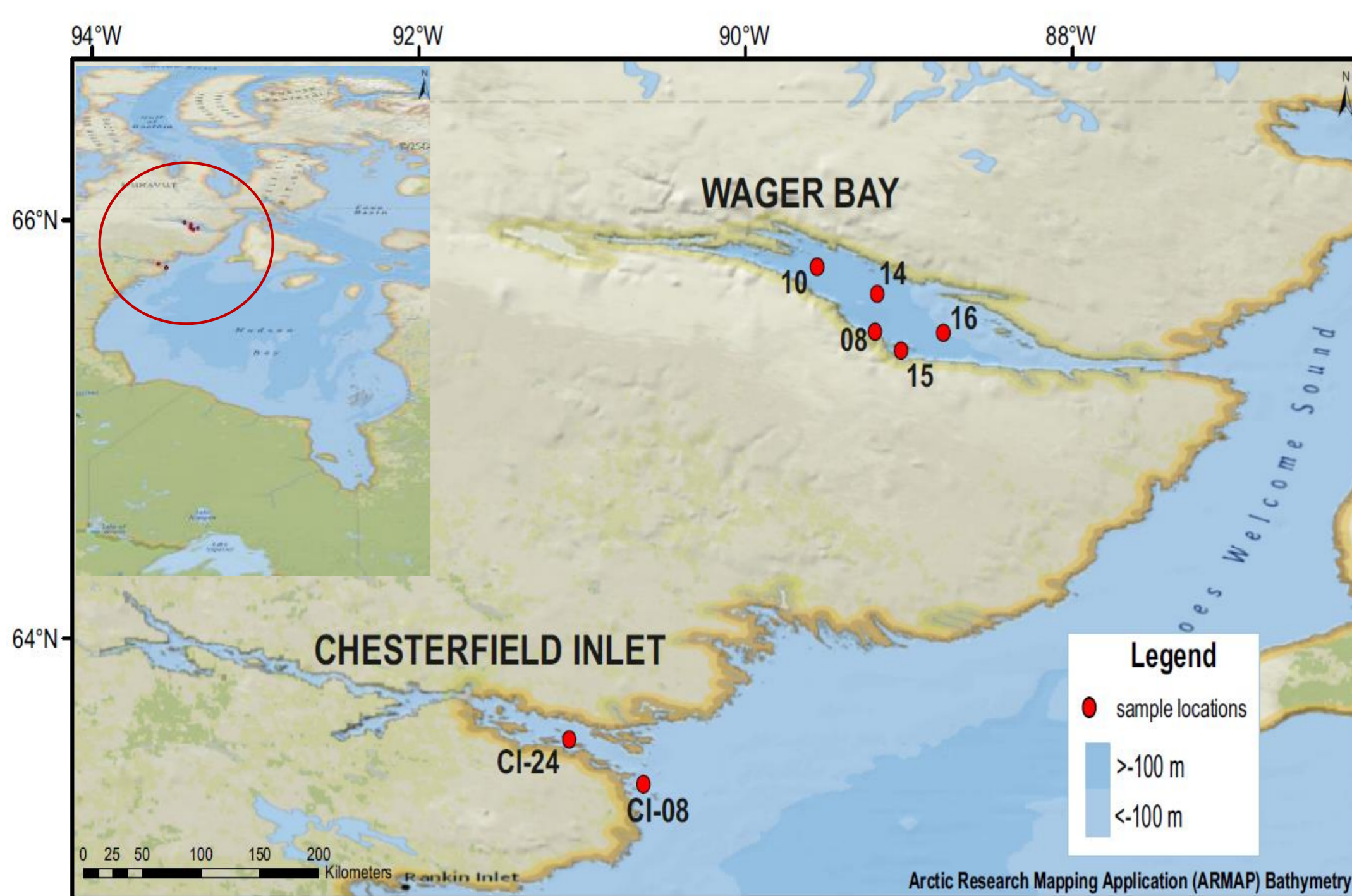
In recent years, industrial ship traffic through Chesterfield Inlet, NU has increased due to mining activities inland. Community members have expressed concerns about the potential for oil spills and impacts to food security and fisheries (e.g., Arctic Char and Scallops) near town. Wager Bay, Ukkusiksalik National Park (UNP) has not experienced industrial ship traffic. However, mining activities outside the Park could lead to shipping through Wager Bay (UNP) waters at some point in the future. To prepare for this potential future shipping in Wager Bay (UNP) and address concerns about shipping through Chesterfield Inlet, Parks Canada Agency and the Government of Nunavut Fisheries and Sealing Division supported collection of sediment cores and baseline PAH measurements in these two coastal environments.

Here we present PAH profiles in four dated sediment cores collected across Chesterfield Inlet and Wager Bay (UNP). We examine PAH composition to assess the importance of pyrogenic sources (combustion of wood or fossil fuels) vs. petrogenic sources (releases of petroleum hydrocarbons) [2]. We also describe geochemical properties of the sediments that inform us about depositional and post-depositional processes that affect PAH fluxes and profiles in sediments.

Objectives

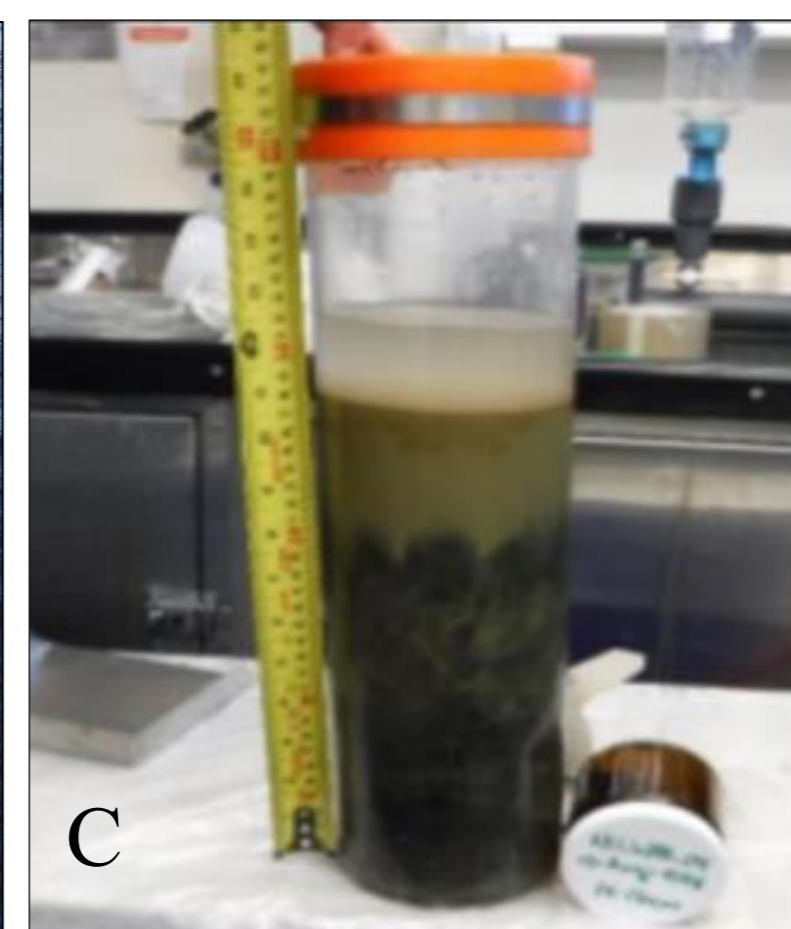
- Determine composition and concentrations of the suite of PAH compounds in dated sediment cores
- Identify the predominant sources of PAHs within the study areas
- Characterise the diagenetic conditions within the sediment cores using profiles of organic carbon and redox elements
- Interpret vertical profiles of PAHs in the cores in the context of sources and geochemical controls

SAMPLE COLLECTION AND ANALYSES



Sediment cores were collected at five sites across Wager Bay (UNP) and two sites in Chesterfield Inlet. The four cores discussed here include NU_WAB_08, NU_WAB_10, PLK_NU_15, and CI-08.

Core	Station	Bottom Depth (m)	Core Length (cm)
8	NU_WAB_08	332	27
10	NU_WAB_10	221	13
15	PLK_NU_15	131	18
CI-08	CI-08	42	21.5



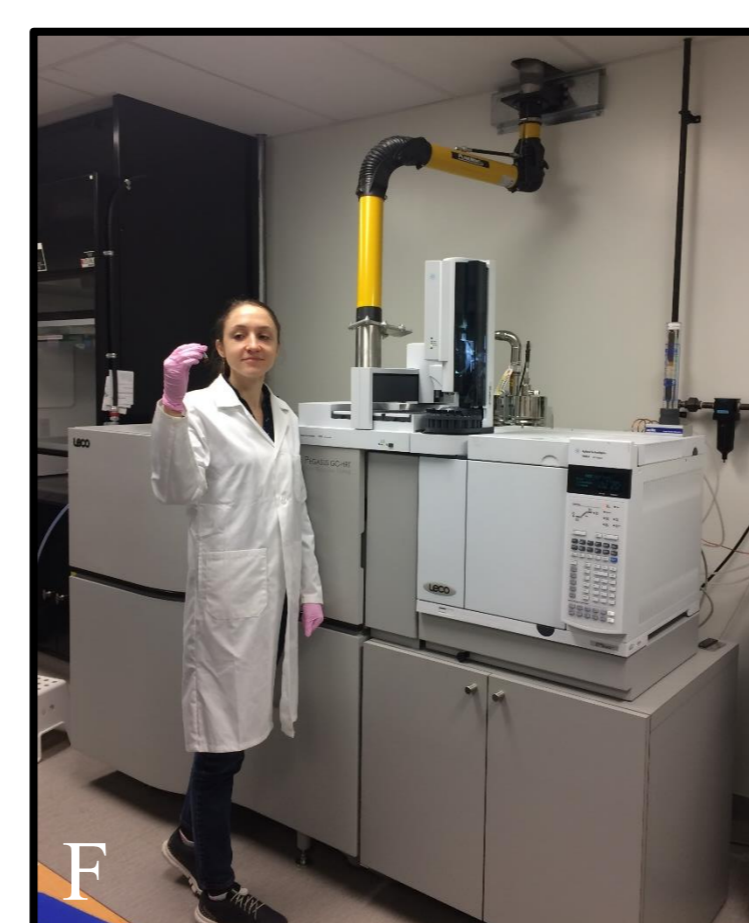
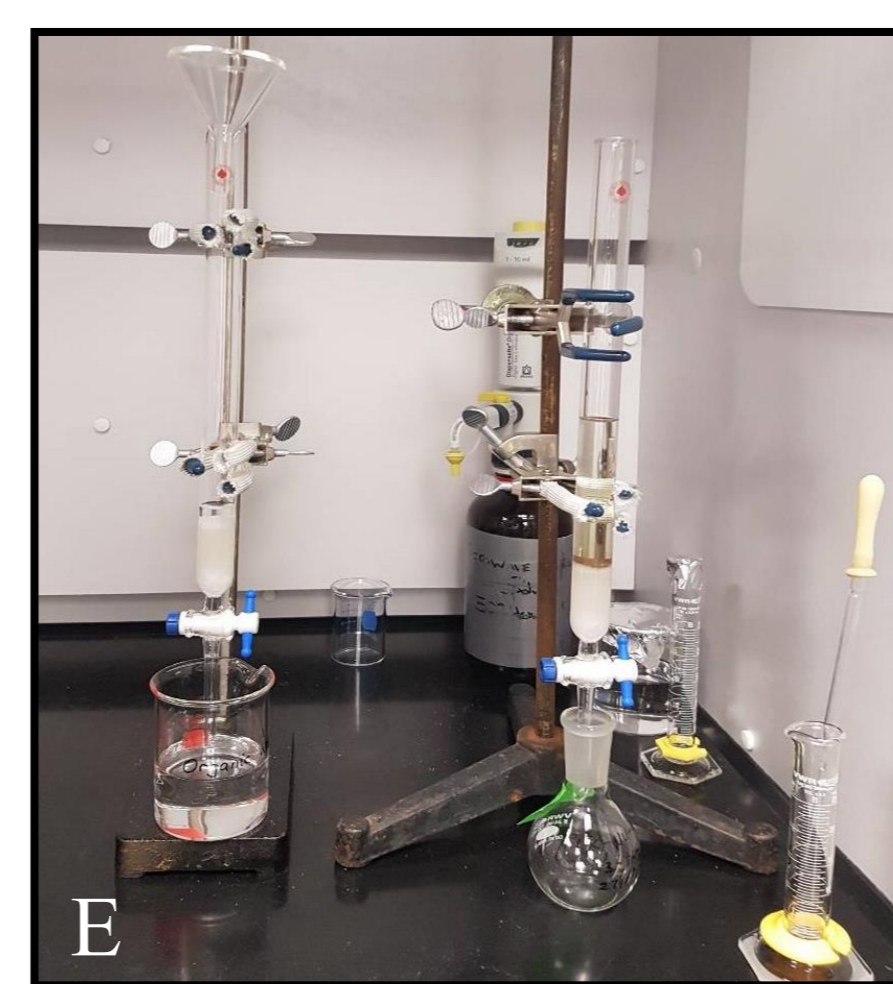
Cores were collected from F.R.V Nulijuk (A) using a box corer (B), and subsequently push cores (C). Cores were sectioned onboard into 1 cm slices for the top 10 cm and into 2 cm slices for the remainder of the core length and then immediately frozen.

PAH Analyses: PAHs were extracted from selected samples from four (4) stations according to methods outlined in US EPA 3546 (D). The extracts were fractionated using silica gel chromatography via a modified version of the US EPA method 3630C (E).

The solution was then analysed to identify the individual compounds and concentrations using a LECO Pegasus GC-HRT equipped with a high resolution time of flight mass spectrometer operated in Full Scan Mode (100-305 amu) at the CEOS PETRL Lab, University of Manitoba (F).

TOC Analyses: Total Carbon (TC) and Total Inorganic Carbon contents were analysed at the Stable Isotope Lab at the University of Manitoba using an Eltra Helios Elemental Analyser. TOC was calculated with the formula $TOC = TC - TIC$

Redox Elements Analyses: Dried and ground samples were submitted to ACME Labs (Bureau Veritas, Vancouver BC) for analyses. A total of 47 samples were analyzed following Aqua regia digestion.



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RESULTS AND DISCUSSION

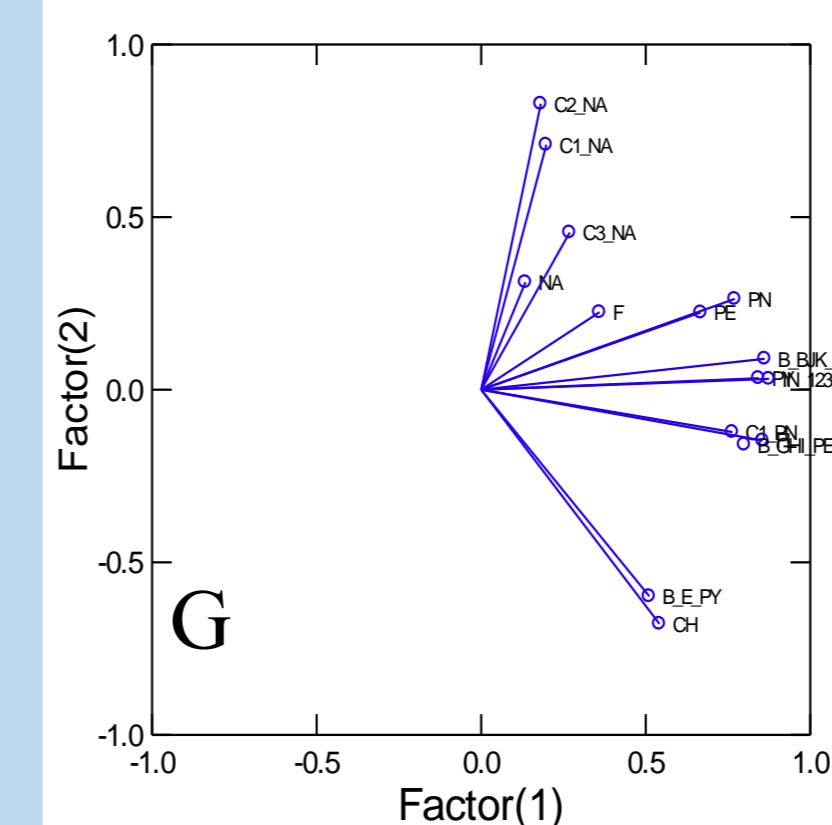
PAH Sources - Diagnostic Ratios

Diagnostic Ratios (DR)	CI-08 (ng/g dw)	Implied Sources	NU-WAB-10 (ng/g dw)	NU-WAB-08 (ng/g dw)	PLK-NU-15 (ng/g dw)	Implied Sources
Fl/(Fl+Py)	0.3	Petrogenic	0.47	0.42	0.47	Combustion sources (liquid fossil fuels)
IP/(IP+B(ghi)Pe)	0.41	Combustion sources (liquid fossil fuels and biomass)	0.54	0.46	0.49	Combustion sources (liquid fossil fuels and biomass)
B(b(jk)F / (B(b(jk)F)+B(e)P)	0.65	Combustion sources (liquid fossil fuels and biomass)	0.82	0.55	1	Combustion sources (liquid fossil fuels and biomass)
Σ(16 priority PAHs)	72.6		58.3	74.8	31.6	
Σ (PAHs)	138.2		140.9	222.9	90.6	

A total of 20 PAH compounds including several alkylated PAHs and some members of the 16 "priority" PAHs were detected at low concentrations in the samples. Total PAH concentrations (sum of detected compounds) ranged from 222.9 ng/g dw to 90.6 ng/g dw. These concentrations reflect typical background levels (uncontaminated Arctic sediments).

PAH sources assessed using diagnostic ratios and principal components analyses imply dominance of pyrogenic sources (combustion) [2].

Factor Loadings Plot



Overall, high molecular weight compounds are higher than low molecular in both Chesterfield Inlet and Wager Bay (UNP) cores, suggesting that PAH sources are locally transported or are reflecting background in-situ concentrations [3].

PAH Sources - Principal Component Analysis (PCA)

PCA was conducted on log transformed PAH data. Pyrogenic compounds on PC1 have the greatest influence on the data (40%) compared to petrogenic compounds (17%) on PC2 (G). There is some separation between Wager Bay and Chesterfield Inlet samples on PC2, which implies some subtle regional differences (H).

Geochemical Controls

Profiles of Total Organic Carbon (TOC) and redox-sensitive elements were examined in the cores to elucidate depositional and post-depositional conditions, which may affect profiles of PAHs.

TOC Composition and Profiles

TOC content is similar in cores NU-WAB-10 and PLK-NU-15 (averages of 1.68% and 1.55%, respectively), slightly higher in core NU-WAB-08 (1.93%) and very low at CI-08 (0.75%). Decrease in TOC with depth in the sediment implies TOC oxidation [4]

Redox Elements Composition and Profiles

Profiles of concentrations of redox sensitive elements (Mn, S and Fe) adjusted for variations in the lithologic component provide information about the strength of reducing conditions in the cores, which reflect the intensity of TOC oxidation [5].

Mn concentrations (and Mn/Al ratios) are high in the top 8cm of NU-WAB-08 and 3cm of CI-08, which implies oxic conditions in the surface sediment layers. (J) The low concentrations of Mn in deeper sediment sections imply reducing conditions. The Mn concentration remains unchanged throughout PLK-NU-15 and NU-WAB-10, signifying that no oxic is present and the sediments are reducing throughout. The differences in Mn profiles in the cores suggest differences in labile carbon flux, with lower fluxes at NU-WAB-08 and CI-08. These two cores came from the deepest and most shallow sites, respectively, and the sediments had the highest and lowest TOC contents, respectively.

Fe and S (and their ratios to Al) tend to increase with depth at all locations (K and L). The profiles are consistent with accumulation of authigenic Fe and S compounds, which implies strongly reducing and sulphidic conditions in subsurface sediments.

ACKNOWLEDGEMENTS

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