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Composition and distribution of dissolved carbohydrates in the Beaufort Sea Mackenzie margin (Arctic Ocean)

Christos Panagiotopoulos [a,*], Richard Sempéré [a], Violaine Jacq [b], Bruno Charrière [a,c]

[a] Aix-Marseille Université, Mediterranean Institute of Oceanography (MIO), 13288, Marseille, Cedex 9, Université de Toulon, 83957, CNRS-INSU/IRD UM 110, France
[b] Université Pierre et Marie Curie, Laboratoire d'Océanographie et du climat: Expérimentations et approches Numériques (LOCEAN), CNRS-INSU/IRD/IPSL, 75005 Paris, France
[c] Université de Perpignan Via Domitia, Centre de Formation et de Recherche sur les Environnements Méditerranéens (CEFREM), UMR 5110, 66860 Perpignan, France

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ABSTRACT

The carbohydrate composition (TDCHO) of dissolved organic matter (DOM) was studied in the Mackenzie margin (southeast Beaufort Sea) in summer 2009 as a part of the MALINA project. Sampling was performed in the shelf (bottom depth ≤ 100 m), slope (100 m < bottom depth ≤ 1000 m), and basin (bottom depth > 1000 m) areas of the Mackenzie margin. Our results showed that sugar concentrations did not follow dissolved organic carbon (DOC) patterns, which decreased from shelf to basin stations (from 115 to 65 μM), but instead remained rather constant (965–900 nM), indicating an accumulation of carbohydrates in surface waters (0–80 m). TDCHO concentrations exhibited their highest values (>1000 nM) and higher relative abundance to DOC in the central sector of the studied area, especially in the zone between 130 and 135°W indicating differences in their distribution in the broader area and possible various sources. TDCHO represented 6 ± 2% and 8 ± 3% of DOC (TDCHO-C/DOC) for the shelf and basin stations, respectively. Semi-labile DOC estimated values accounted for 10–40% and 20–50% of DOC in the slope and basin areas and agreed well with the above TDCHO/DOC values suggesting a gradient of carbohydrate freshness from inshore to offshore stations. The high fucose + rhamnose relative abundances (Fuc. + Rha. 15–18%) and high C/N ratios (19–13) recorded in the surface waters of the shelf area are indicative of soil-derived matter delivered by the Mackenzie River, possibly with contributions from mainly gymnosperm terrestrial plants. The high abundance of glucose (up to 50%) suggests that the carbohydrate component of the DOM in the Mackenzie margin appears to have a more pronounced marine autochthonous origin with an important contribution of terrestrial sources, especially for the shelf stations. Overall, these results suggest a largely uniform distribution of TDCHO carbohydrates within the area with occasional patches of lower concentrations.

1. Introduction

The Arctic Ocean is considered an important site of deep-water formation in the Northern Hemisphere because it actively contributes to the global thermohaline circulation and consequently, it plays an important role to the vertical flux of dissolved organic matter (DOM) (Anderson, 2002). Despite its low volume and surface compared with other oceans (~1% of the global ocean volume), the Arctic Ocean receives the highest amount of terrestrial input in terms of freshwater discharges of particulate organic matter (POM) and DOM (POM + DOM ~ 0.22–0.336 GT C y^{-1}; Dittmar and Kattner, 2003). Therefore, it is unsurprising that DOC values recorded nearshore on the Arctic continental shelf are among the highest in the world (~100 μM; Rich et al., 1997; Wheeler et al., 1997; Skoog et al., 2001).

Although numerous rivers enter into the Arctic Ocean, the four most important in terms of discharges are the Ob, Yenisey, and Lena from Siberia, and the Mackenzie from North America. For a long time it was supposed that this terrigenous organic matter (DOM + POM) delivered by rivers was refractory compared with the organic matter freshly produced in the Arctic shelf and basin (de Leeuw and Largeau, 1993; Peulvé et al., 1996; Macdonald et al., 1998; Fernandes and Sicre, 2000). Nevertheless, recent studies in this area based on lipid biomarker analysis (Rontani et al., 2012a,b), compound specific isotopes (Drenzek et al., 2007), and $^{228}Ra/^{226}Ra$ isotopes (Hansell et al., 2004; Letscher et al., 2011) indicate that this material “disappears” rapidly via abiotic or biotic processes. In line with these results, bulk $\Delta^{14}C$ and lignin–phenol data on Arctic riverine DOM suggested that this terrestrial material exhibits modern radiocarbon ages (Benner et al., 2004; Amon et al., 2012).

The chemical composition of the Arctic rivers has been well documented in the literature in terms of amino acids (Lara et al., 1998; Amon and Meon, 2004; Unger et al., 2005), sugars (Amon and Benner, 2003; Dittmar and Kattner, 2003; Unger et al., 2005), and lipids (Goñi et al., 2000; Zou et al., 2006; van Dongen et al., 2008). However, much less is known about the sources, distribution, and bioavailability of these compounds in the Arctic Ocean. Previous studies have indicated that in the Arctic Ocean freshly produced organic matter has high turnover rates and is labile; however, these rates of production and

* Corresponding author.
E-mail address: christos.panagiotopoulos@mio.osupytheas.fr (C. Panagiotopoulos).

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consumption differ between the different areas of the Arctic because they are closely linked to the biogeochemical characteristics of each site (Rich et al., 1997; Cottrell et al., 2006; Kirchman et al., 2009; Ortega-Retuerta et al., 2012). For example, the Chukchi and Beaufort Seas, both belonging to the western Arctic Ocean, exhibit different productivities, receive different amounts of nutrients, and experience different effects from rivers (Hill and Cota, 2005; Carmack and Wassmann, 2006; Grebmeier et al., 2006; Lavoie et al., 2009). In addition, the quantity and quality of DOM in both areas appear quite different in terms of dissolved organic carbon (DOC) content (Fransson et al., 2001; Mathis et al., 2005), chromophoric-DOM properties (CDOM; Guéguen et al., 2005; Matsuoka et al., 2012), optical characteristics including fluorescence (Osburn et al., 2009; Para et al., 2013), and amino acid content (Shen et al., 2012). However, the quality and bioavailability of organic matter cannot be evaluated fully if additional measurements of other "labile" organic compounds (e.g. carbohydrates) are not taken into account.

Currently, there is a paucity of data regarding the carbohydrate component of DOM in the Arctic Ocean. Previous investigations have reported bulk carbohydrate measurements in the Chukchi Sea (Wang et al., 2006), but almost no carbohydrate data exist for the Beaufort Sea, into which the Mackenzie River discharges (Amon and Benner, 2003). Interestingly, the Beaufort Sea could be considered as an example of a shelf region with a large riverine input and narrow shelf, characterized by short transport times for the injection of terrestrially-derived organic matter into deeper waters (Macdonald et al., 1998; Davis and Benner, 2005; Mathis et al., 2007; Lalande et al., 2009). Therefore, the Beaufort Sea might serve as a model system for future climate scenarios in the Arctic Ocean, in which several features are currently observed. These features include (a) the increase in river runoff, (b) increase in UV radiation, (c) permafrost thawing, and (d) decrease in ice cover (Peterson et al., 2002; Grigoriev et al., 2004; Stroeve et al., 2005; Rawlins et al., 2010; Long and Perrie, 2013; Fichot et al., 2013). Therefore, the chemical characterization of the autochthonous and allochthonous components of Arctic-DOM appears critical, not only with regard to the evaluation of their relation with the sources and cycling pathways, but also with regard to the comprehension of the Arctic system evolution.

The MALINA (Mackenzie Light aNd cArbon) cruise was conducted in the Beaufort Sea in 2009 with the objectives assessing the impact of climate changes on the fate of terrestrially-derived organic carbon

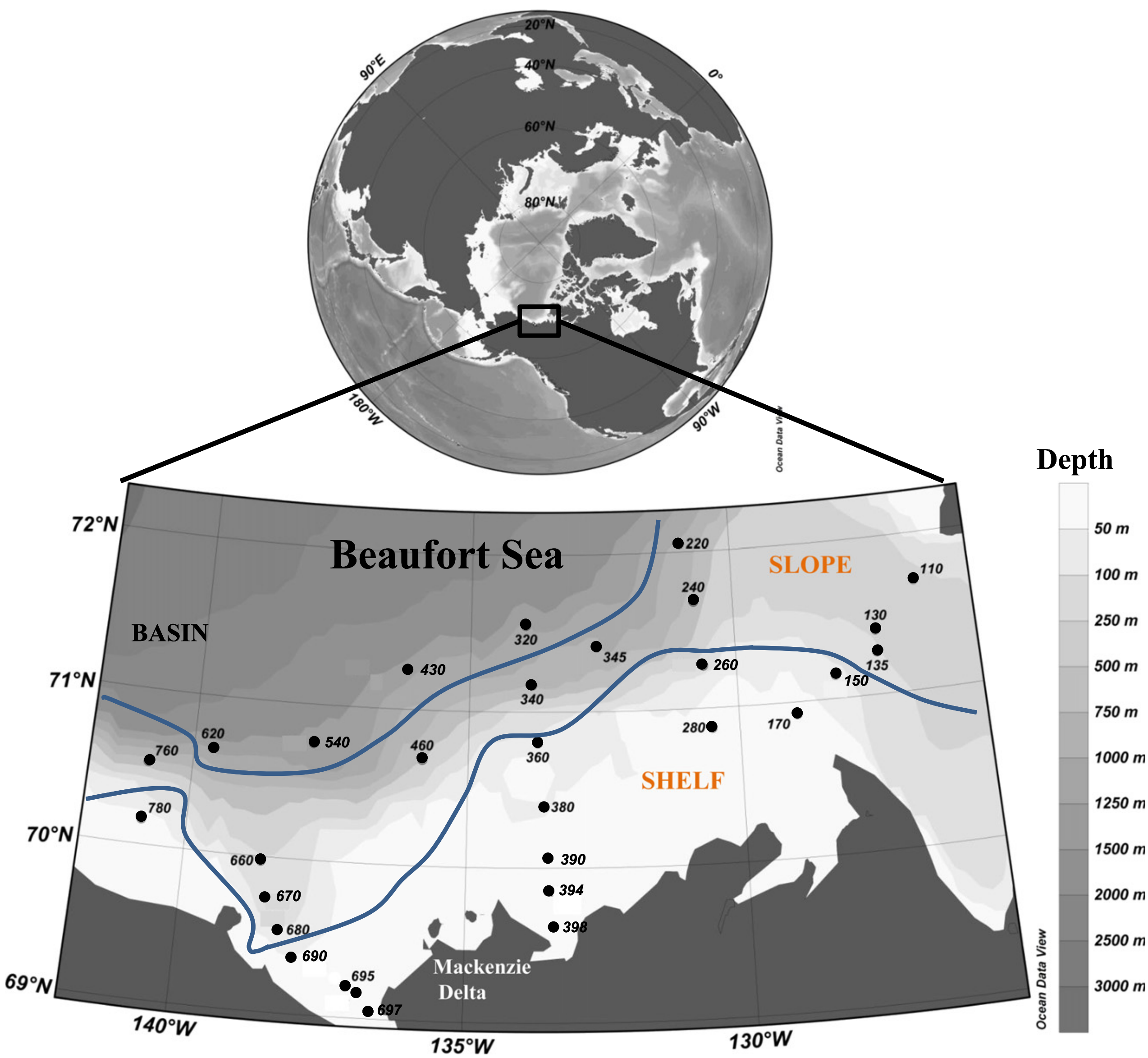

Fig. 1. Location and station numbers sampled for dissolved carbohydrates (TDCHO) during the MALINA cruise over the Canadian shelf of the Beaufort Sea. The sampling stations were divided into three areas (shelf, slope, and basin) according to bathymetry (see Table 1).