Estuarine, Coastal and Shelf Science 181 (2016) 170–181

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

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

Annual cycle and spatial trends in fatty acid composition of suspended particulate organic matter across the Beaufort Sea shelf

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ARTICLE INFO

Article history:
Received 11 September 2015
Received in revised form
28 June 2016
Accepted 15 August 2016
Available online 18 August 2016

Keywords:
Essential fatty acids
Polyunsaturated fatty acids
Overwintering
Amundsen Gulf
Polar oceanography

ABSTRACT

Fatty acid profiles of suspended particulate organic matter (POM) were determined over an annual cycle (September 2003 to August 2004) on the Beaufort Sea shelf, Canadian Arctic. Special emphasis was placed on the nutritional quality of the fatty acid pool available to zooplankton by examining spatial and temporal patterns in the proportions of total polyunsaturated fatty acids (PUFA) and the essential fatty acids 22:6n−3 (DHA) and 20:5n−3 (EPA). EPA and DHA were the two most abundant PUFA throughout the study period. A log-ratio multivariate (LRA) analysis revealed strong structure in fatty acid profiles related to season and depth. Dominant fatty acids accounting for the observed trend included 18:5n−3, 18:4n−3, 16:1n−7, 20:5n-3, 18:0 and 20:3n−3. We observed a shift in fatty acid profiles from summer to autumn (e.g., from 16:1n−7 and EPA to 18:5n−3 and 18:4n−3) that likely corresponded to a shift in the relative importance of diatoms *versus* dinoflagellates, prymnesiophytes and/or prasinophytes to the POM pool. Fatty acid composition during winter was dominated by more refractory saturated fatty acids. A surprising finding was the depth and seasonal trend of 20:3n-3, which was higher in winter, aligned with 18:0 in the LRA, but behaved differently than other n−3 PUFA. We interpret fatty acid profiles during summer to be predominantly driven by phytoplankton inputs, whereas fatty acid profiles in winter were dominated by fatty acids that were left over after consumption and/or were generated by heterotrophs. The highest diatom inputs (EPA, the diatom fatty acid marker), n−3/n−6 ratios, and C_{16} PUFA index were located in an upwelling region off Cape Bathurst. This study is the first annual time series of fatty acid profiles of POM in Arctic seas, expanding our knowledge of the composition of POM throughout the dark season.

1. Introduction

The transfer of carbon and energy through a food web is not only regulated by the quantity of organic matter, but also by its biochemical composition (Brett and Müller-Navarra, 1997; Anderson and Pond, 2000; Perhar et al., 2013). Specifically, certain essential fatty acids have been shown to predict the transfer of carbon from primary producer to primary consumer (Müller-Navarra et al., 2000) and impact reproduction, growth and development of marine invertebrates and fish (Parrish, 2009). Fatty acids are considered *essential* when consumers cannot synthesize them in sufficient quantities to meet their nutritional needs, thus those needs must be met through diet. Essential fatty acids are polyunsaturated fatty acids (PUFA), which, in the marine environment, are primarily produced by algae. Availability of essential fatty acids may also control community structure of fish on climatic and interannual time scales (Litzow et al., 2006; Litz et al., 2010). Consequently, production of essential fatty acids at the base of the food web can impact ecosystem structure and function.

Seasonal studies of fatty acid composition of particulate organic matter (POM) in the Arctic Ocean and elsewhere have shown strong temporal patterns associated with community composition of phytoplankton and bacteria, nutrient availability, light intensity, and proportion of fresh to older material (Reuss and Poulsen, 2002; Parrish et al., 2005; Leu et al., 2006; Mayzaud et al., 2013b). Thus, fatty acid profiles, certain fatty acids, and fatty acid markers have been used to trace sources, diagenesis, and age of organic matter. In the Arctic Ocean, fatty acid profiles and markers have been successfully applied to organic matter in sediments (Belicka et al., 2004) and near-bottom waters of the Beaufort Sea (Connelly et al., 2012), and to suspended POM in the Canada Basin (Shah et al., 2013), waters of Greenland (Reuss and Poulsen, 2002),

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http://dx.doi.org/10.1016/j.ecss.2016.08.016
0272-7714/

lagoons of the Beaufort Sea (Connelly et al., 2015) and fjords of Svalbard (Leu et al., 2006; Mayzaud et al., 2013a, 2013b). However, few Arctic studies have focused on the dynamics of fatty acid composition of POM on annual time scales. Recent empirical and modeling studies suggest that conditions during winter and early spring can regulate food web structure and function later in the year (Schroeder et al., 2013; Saba et al., 2014). Yet, published studies of the seasonality of POM fatty acid profiles in the Arctic have not included months between October and April and had low temporal resolution (≤11 time-points per study) (Leu et al., 2011; Mayzaud et al., 2013a, 2013b; Connelly et al., 2015).

In this study, we determined fatty acid profiles of suspended POM from the Canadian Beaufort Sea shelf over an annual cycle from September 2003 to August 2004, including stations near the Mackenzie River and an overwintering station in the Amundsen Gulf. A primary goal was to assess spatial and temporal patterns in the nutritional quality of the fatty acid pool for zooplankton by comparing proportions of PUFA, saturated fatty acids, n−3/n−6 ratios, and certain essential fatty acids, such as docosahexaenoic (DHA, 22:6n−3) and eicosapentaenoic acid (EPA, 20:5n−3). We expected proportions of PUFA and essential fatty acids to reflect phytoplankton growth, and thus be greater during summer and in surface waters. In contrast, we expected fatty acid profiles during winter and at depth to be dominated by saturated fatty acids and be of low nutritional quality. We believe this time series POM data, which includes winter, is the first annual report for fatty acids in Arctic seas.

2. Methods

Water samples for fatty acid analysis of POM were collected continuously from 30 September 2003 through 10 August 2004 on the Beaufort Seas shelf, Canadian Arctic, from a single cruise on the CCGS *Amundsen* as part of the Canadian Arctic Shelf Exchange Study (CASES, Fig. 1). CASES incorporated two primary components: an overwinter time series station in Franklin Bay, Amundsen Gulf where the ship was immobile, occupying a single station continuously (Table S1), and a regional-scale array of stations covering the Mackenzie shelf and Amundsen Gulf when the ship was mobile during fall and summer (Table S2). We consider stations west of Cape Bathurst as the Mackenzie shelf and those east of Cape Bathurst as the Amundsen Gulf (Table S2). The overwinter site (70°03′N, 126°18′W, 232 m deep), when the ship was immobile, was located in landfast ice, ~23 km northeast of the Horton River outflow. Water samples were collected at this site *ca* weekly for 25 weeks from 10 December 2003 through 27 May 2004 (Table S1). Before and after the overwinter time series, the ship moved across the region and water samples were collected at stations on the regional grid, from 30 September to 14 November 2003, and again from 7 June through 10 August 2004 (Table S2). During the regional sampling, we revisited the overwinter station once on 16 July 2004 and sampled a station that was only 16.5 km from the overwinter station twice, on 4 November 2003 and 7 August 2004.

We determined fatty acid profiles of POM from a total of 34 stations during the overwinter time series, and 39 stations from the regional grid. Water samples were collected from 2 to 3 depths with 12-L Niskin bottles attached to a rosette frame with a CTD (Seabird SBE-911+). Samples generally came from surface waters, the depth of the chlorophyll maximum, and the maximum depth of the CTD-rosette cast (Tables S1–S2). Depth profiles of salinity, temperature, and fluorescence (converted to μg-chlorophyll L^{-1} using manufacturer coefficients) were collected with the CTD, which was deployed twice daily during the overwinter period and at each station on the regional grid. We also collected samples for ice algae from the overwinter site on 28 May 2004, near the time of the peak ice algae bloom (Rózanska et al., 2009). The colored section (near the ice-water interface) of two ice cores was melted into filtered seawater. Water was also collected at the mouth of the Mackenzie River from three stations on 30 September and 8 October 2003 by zodiac deployed from the CCGS *Amundsen,* and from four stations on 28 July, 30 July and 1 August 2004 from the CCGS *Nahidik* during the Arctic River Delta Experiment (ARDEX). There is no corresponding temperature, salinity or fluorescence data for these 7 river stations.

Niskin bottles on the rosette were drained into 10-L carboys, which were gently shaken before pre-filtering the seawater through a 300 μm Nitex mesh into 1-L graduate cylinders. Seawater was then filtered through combusted 47 mm GF/F filters under gentle vacuum and the total volume of seawater filtered was recorded. Generally, 4–12-L of seawater were filtered for fatty acid analysis. Filters were immediately put into 15 mL vials containing chloroform (~2 mL), which were sealed under N_2 and stored at −20 °C for about 2–4 months before further processing.

Total lipids were extracted in chloroform:methanol:water

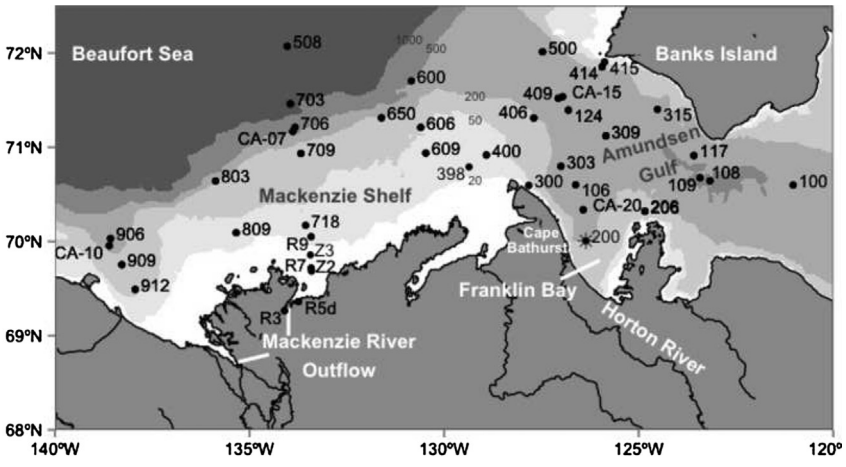

Fig. 1. Station locations and labels for suspended particulate organic matter collected from September 2003 to August 2004 from the Beaufort Sea shelf as part of the Canadian Arctic Shelf Exchange Study (CASES). The overwinter station (St. 200), which was occupied from 10 December 2003 to 27 May 2004, is marked with an asterisk (70°03′N, 126°18′W). Isobaths are shown in shades of grey (20, 50, 200, 500 and 1000 m). Stations labels beginning with 'Z' and 'R' were sampled from zodiac and the *Nahidik* (ARDEX), respectively (see text). Stations labels beginning with 'CA' were also sites of current meter moorings.