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## Synthesis of mycosporine-like amino acids by a size-fractionated marine phytoplankton community of the arctic beaufort sea



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#### ABSTRACT

During the RV-ARAON cruise, a comparative study on the biosynthesis of mycosporine-like amino acids (MAAs) was conducted for the size-fractionated phytoplankton of the Beaufort Sea (Arctic). The MAAs contents in the micro-phytoplankton community (> 20  $\mu m$  size) is considerably higher than that observed in the nano-(20–2  $\mu m$  size) and pico-phytoplankton (< 2  $\mu m$  size) communities. The micro-phytoplankton of the Mackenzie Shelf had a relatively higher Chlorophyll a (Chl a) concentration. Considering the total phytoplankton community, the MAAs concentration as well as net production of individual MAAs (such as shinorine and palythine) were higher at the Mackenzie Shelf rather than at the sites located beyond the Beaufort Sea; precisely, the highest net production rates of shinorine and palythine were 0.211 ( $\pm$ 0.02) ng C L $^{-1}$  d $^{-1}$  and 0.136 ( $\pm$ 0.001) ng C L $^{-1}$  d $^{-1}$  respectively (No other MAAs were detected). The micro-phytoplankton used around 0.5% of the total carbon uptake for the synthesis of MAAs. Compared to the smaller phytoplankton community, the micro-phytoplankton focused on cellular activity and had poor biosynthesis of MAAs. This clearly indicates the phytoplankton size-dependent variation in the biosynthesis of MAA in the natural phytoplankton community. This study revealed the environmental adaptation of the various sizes of phytoplankton community as well as their physiological response in the Arctic Beaufort Sea.

#### 1. Introduction

A huge quantity of particulate organic matter (POM) is exported to the coastal marine environment through the vast riverine systems [1–3]; in particular, in the Mackenzie–Beaufort system of the Arctic (where the river transports carbon and nutrients derived from the 1,787,000 km² Mackenzie River Basin, and the 12,170 km of river and delta), which is dominated by terrestrial organic matter, the riverine signature is particularly pronounced [4–6]. This shelf behaves like an estuarine system that derives water and its associated material properties from both oceanic and terrestrial sources [7,8]. Here, the Mackenzie River is responsible for the inflow of freshwater biota as well as the land-derived nutrients, especially in the upper 5–10 m waters of the coastal ocean [9]. However, as a result of the low nitrate availability and strong stratification, a shift towards

smaller-sized phytoplankton has been reported in the Canadian Arctic [10]. Marine phytoplankton in the Beaufort Sea and the Canada Basin are predominantly large-celled diatoms and dinoflagellates that account for 58% and 21% of all 555 microscopic forms recorded, respectively [11]. The diatoms dominate the regions with 50–90% ice cover; however, under thicker ice cover, autotrophic flagellates are often more abundant than diatoms [12,13]. In fact, one particular study [14] has foreseen the augmentation of nano-flagellates in the newly ice-free basins as a consequence of the deepening nitracline.

Mycosporine-like amino acids (MAAs) are a group of over 20 water-soluble compounds that absorb ultraviolet (UV) radiation ( $\lambda_{max}=310\text{--}360\,\text{nm}$ ) [15] and are present in a diverse variety of freshwater and marine organisms (e.g., macro- and microalgae, cyanobacteria, corals, marine invertebrates (sea anemones, limpets,

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shrimp, sea urchins) and vertebrates (fish and fish eggs)) where they act as sunscreens to reduce UV-induced damage [15]. Geographically, MAAs are distributed ubiquitously, occurring in tropical, temperate, and polar aquatic environments [15]. The Arctic region has direct incoming solar radiation along with enhanced back scatter (associated with the high albedo of surrounding sea ice); as a result, the surface melt ponds located there are exposed to high radiation intensities [16-18]. Therefore, in the past a few years, studies have been undertaken on the production of MAAs in this region; for example, Ha et al. [19] measured MAA concentrations in the case of phytoplankton communities in a spring near the ice edge along the Svalbard coast of the Arctic Ocean, reporting that their concentrations were lower than those of the open water (away from the ice margin) [19]. In addition, the experimental exposures to UV radiation revealed relatively high MAA concentrations in the surface of the land-fast ice (in the Baltic Sea) upon the melting of snow [20], in snow-covered ice, and, in snow-free ice [21].

The objective of this investigation was to examine the strategies of the UV-absorbing compounds of the size-fractionated phytoplankton community (in the Beaufort Sea), which in turn are influenced by freshwater from the Mackenzie River and ice-melt water. In order to understand the physiology of the phytoplankton community (exposed to rapid change of light availability) in the Beaufort Sea, the carbon

uptake and net production rates of individual MAAs of the total natural phytoplankton community (which dominate the micro-phytoplankton or nano- and pico- phytoplankton) have been undertaken and presented herein.

#### 2. Materials and methods

#### 2.1. Experimental setup

On deck incubation experiments were carried out at two stations in the Mackenzie Shelf (MS) and in the region outside the Mackenzie Shelf in the Beaufort Sea (OB) (Fig. 1). Temperature and salinity observations were conducted using a CTD-Rosette system (Sea-Bird SBE-911plus). Hydrological measurement and on-board incubations were conducted in the Beaufort Sea during an IBRV Araon cruise in summer (7–24 September 2013). Surface water samples using a rosette sampler at each station were collected and stored in Quartz bottles (6 L; HanJin Quartz Co.), which transmits natural full sunlight (UV radiation (UV-A and UV-B) and photosynthetically active radiation (PAR)); and on-board incubations were carried out under natural solar irradiation for a period of 72 h of exposure (24 h sampling interval). A LI-190 Quantum sensor (Li-Cor Biosciences, Lincoln, NE, USA) was used to measure the PAR in the 400 nm to 700 nm waveband. A pyranometer (The Eppley

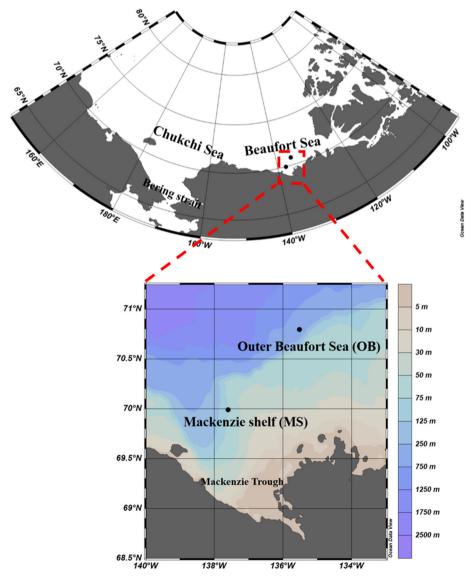


Fig. 1. Location of in situ study, i.e., the Mackenzie Shelf (MS) and the site located outside the Mackenzie Shelf in the Beaufort Sea (OB) of the Arctic.

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