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Photoreactivity of chromophoric dissolved organic matter transported by the Mackenzie River to the Beaufort Sea

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ABSTRACT

The photoreactivity of chromophoric dissolved organic matter (CDOM) transported to Arctic shelf environments by rivers has only recently been studied and its quantitative role in Arctic shelf biogeochemistry has received little attention. Sunlight exposure experiments were performed on CDOM collected over a three year period (2002 to 2004) from river, estuary, shelf, and gulf regions of the Western Canadian Arctic. Decreases in CDOM absorption, synchronous fluorescence (SF), and dissolved organic carbon (DOC) concentration were followed after 3 days of exposure, and in two experiments, six optical cutoff filters were used to incrementally remove ultraviolet radiation incident on the samples. Apparent quantum yields for CDOM photobleaching (AQY_{ble}) and for DOC photomineralization (AQY_{min}) were computed, as were two AQY spectra (ϕ_{ble} and ϕ_{min}) for the Mackenzie River and a sample from the Mackenzie Shelf. The photoreactivity of Mackenzie River CDOM was highest after break-up and peak discharge and lowest in late summer. The half-lives of CDOM and DOC were estimated at 3.7 days and 4.8 days, respectively, when Mackenzie River water was exposed to full sunlight. Photobleaching of Mackenzie River CDOM fluorescence after most UV-B wavelengths were removed increased the correlation between the river and offshore waters in the Beaufort Sea. When light attenuation from particle- and CDOM-rich river water was considered for the Mackenzie Shelf, our photodegradation models estimated around 10% loss of absorption and <1% DOC loss, suggesting that sunlight exposure does not substantially degrade CDOM on Arctic shelves.

1. Introduction

Climatic warming in the Arctic can result in the loss of sea ice and an increased riverine discharge to the surface waters of the Arctic Ocean (Peterson et al., 2006). With increased riverine flow, fluxes of terrigenous dissolved organic matter (DOM) can also increase (Dixon et al., 1994; Oelke et al., 2004). Given the proximity to large rivers, most DOM on Arctic shelves originates from terrigenous sources and is transported in river discharge.

The Mackenzie River is the 4th largest freshwater discharge and the largest source of particulates to the Arctic Ocean (Macdonald et al., 1998), dominating the western Arctic region of Beaufort Sea. Seasonal discharge historically increases after break-up in early May, when the river floods its extensive delta, and then decreases during a recession period throughout the summer (Emmerton et al., 2008). Thus river flow is largest in the late spring–early summer and lowest in the winter when much of the river remains frozen. The flux of DOM from this river to the Beaufort Sea is linked to its hydrology and thus varies considerably (Emmerton et al., 2008). Only recently has the DOM of this river been studied (Droppo et al., 1998; Retamal et al., 2007; Emmerton et al., 2008).

Terrigenous DOM strongly absorbs sunlight. The ultraviolet and visible light absorption by this chromophoric dissolved organic matter (CDOM), in addition to particulate matter, controls and structures the euphotic zones in the coastal waters of the Arctic shelves. Two important biogeochemical consequences that can result from CDOM light absorption are investigated here: the photomineralization of organic C to inorganic C (Mopper and Kieber, 2002) and photobleaching (Del Vecchio and Blough, 2002; Osburn and Morris, 2003). Photomineralization represents a source of CO_2 to the atmosphere whereas photobleaching can increase the relative depth of the euphotic zone to the mixing zone in surface waters (Del Vecchio and Blough, 2002). Photobleaching can increase the penetration of UV radiation as well as photosynthetically available radiation (PAR) into the water column, with a combination of negative and positive effects on photosynthesis, bacterial production and other marine biological processes (Vincent and Belzile, 2003). The effects on either process from reduced sea ice cover in the Arctic are still unknown.

Compared to lower latitude shelves, photodegradation of CDOM in the Mackenzie Shelf waters is restricted to just a few months in the polar summer, yet several forcing factors make the overall effect of

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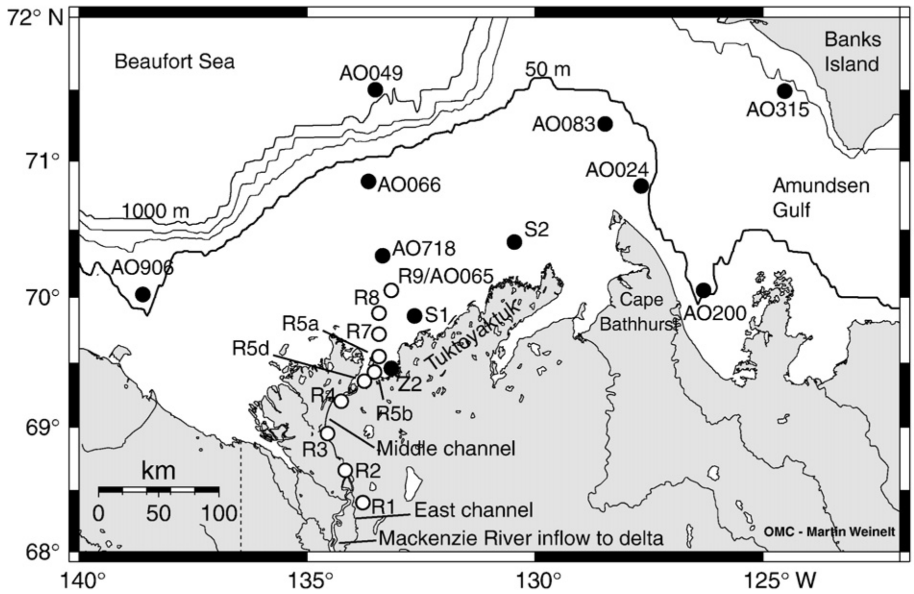

Fig. 1. Sampling locations on the Mackenzie shelf; the inlet to the Mackenzie River delta and the East and Middle channels were sampling occurred are indicated (map produced at http://www.aquarius.ifm-geomar.de/). Open circles indicate stations collected during the ARDEX cruise in July–August 2004. Closed circles indicate stations collected during the CASES2002 and CASES2003–2004 expeditions.

photodegradation unclear. First, the low sun angle at high latitudes results in a relatively lower sunlight intensity on surface waters than at lower latitudes. Second, sea ice cover and the large particulate load of the Mackenzie River reduce sunlight penetration in surface waters. However, sunlight is nearly continuous during the short polar summer, so a substantial cumulative dose is possible. Third, the changing quantity of Mackenzie River CDOM released after break-up and during free ice conditions (Emmerton et al., 2008) indicates that CDOM reactivity may change as day length increases during the polar summer. Finally, oceanographic features such as ice shoal (stamuhki) development on fast ice (Emmerton et al., 2008; Galand et al., 2008) and the anticyclonic Beaufort gyre can retain river water in the coastal zone for long periods of time (Macdonald et al., 1999). In combination, these latter factors may enable exposure of Mackenzie River CDOM to substantial photochemical processing in the very surface waters.

Bélanger et al. (2006) estimated that nearly 6% of Mackenzie River DOC can be photomineralized in the Beaufort Sea in ice free periods, yet CDOM photoreactivity varies in shelf waters and after exposure to sunlight. For example, Johannessen and Miller (2001) demonstrated that apparent quantum yields (AQY) for CDOM photomineralization can change significantly inshore to offshore, and with prior sunlight exposure. Similarly, Osburn et al. (2001) showed that AQY for CDOM photobleaching were significantly lower in the surface mixed layer of temperate lakes than at depth during summer stratification. In this report, we calculated AQY for CDOM photobleaching and photomineralization to study the CDOM photoreactivity of a series of surface samples collected from the Mackenzie River, its freshwater–saltwater transition zone through a small estuary, and across the Mackenzie Shelf to the Amundsen Gulf. We hypothesized that the most photoreactive CDOM occurs on the shelf after break-up, but that a long residence time might reduce its photoreactivity. We then used the AQY to predict photodegradation in the surface waters of the Mackenzie Shelf during the polar summer and compared our results to previous work in this region.

2. Methods

2.1. Sample collection and processing

Surface water samplings of the Mackenzie River and the Beaufort Sea were performed in October 2002 and from October 2003 to June 2004 during the Canada Arctic Shelf Exchange Study expeditions (CASES; details at http://cases.quebec-ocean.ca). During 28 July to 02 August 2004, a satellite expedition (Arctic River Delta Experiment; ARDEX, see Vincent and Pedrós-Alió, 2008) was conducted for this study. In the CASES expeditions, samples were collected from two sites (R1 and R2) upriver via helicopter, coastal sites near the river mouth, and along the shelf edge into the Beaufort Sea aboard the icebreaker CCGS *Pierre Radisson* (2002) or the icebreaker CCGS *Amundsen* (2003–2004). For the ARDEX expedition, river sampling aboard the CCGS *Nahidik* was conducted through out the delta and the river's East and Middle Channels, and along a transect extending from the river mouth at Kugmallit Bay to about 100 km offshore at station R9, which coincided with CASES station AO065 (Fig. 1).

Shipboard samples were collected from Niskin bottles affixed to a rosette or from surface grabs in cleaned plastic buckets. Riverbank sampling by helicopter involved collecting 20 L of surface water by manually filling cleaned polyethylene carboys by immersion below the water surface. Each collection procedure involved triple rinsing a container with surface water before filling with sample. All samples were vacuum-filtered through 0.2 µm filters into acid-cleaned polycarbonate and polyethylene bottles and stored in the dark at 4 °C until transport back to Washington, DC. Aliquots for DOC concentration were acidified with 85% H_3PO_4 and stored in the dark at 4 °C. CDOM absorption and fluorescence measurements were made within 3 days of receipt.

DOC concentration was measured on an OI Analytical 1010 TOC analyzer. Acidified samples were sparged for 10–15 min with UHP He to remove inorganic C. Osburn and St-Jean (2007) have modified this persulfate-based TOC analyzer to measure seawater DOC. Samples were calibrated against 0, 83, 208, 416, and 833 µM DOC standard solutions made from potassium hydrogen phthalate. The average relative standard deviation on this system was 3%, corresponding to an average standard error of 6 µM C. The limit of detection is 12–15 µM C.

CDOM absorption was measured in the laboratory on a Shimadzu UV1601 spectrophotometer in 5- or 10-cm pathlength cuvettes against 18 µM MilliQ laboratory water and converted to absorption coefficients as follows:

$$a_\lambda = A_{(\lambda)} \times 2.303 / l, \tag{1}$$