



Distributions and characteristics of colored dissolved organic matter in the Western Arctic Ocean

Céline Guéguen*, Laodong Guo, Noriyuki Tanaka

International Arctic Research Center, University of Alaska Fairbanks, Fairbanks, AK 99775, USA

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Abstract

Terrigenous dissolved organic matter (DOM) is continuously discharged by rivers into the ocean, yet its distribution and reactivity within ocean basins remain poorly defined. With high concentrations of terrestrial DOM in arctic rivers and a disproportionate share of global riverine discharge on a volume basis to the Arctic Ocean, the influence of terrigenous DOM on marine carbon budgets and the global carbon cycle can be significant. In this paper, we report the detection of terrestrial DOM using optical properties of surface waters in the Western Arctic Ocean. The distribution of absorption and fluorescence of colored dissolved organic matter (C-DOM) and dissolved organic carbon (DOC) were recorded. Mixing of C-DOM was conservative at low and mid-salinity ($S > 25\text{‰}$), indicating a terrestrial origin for this material and the absence of strong in situ sources and sinks. However, at higher salinities ($> 25\text{‰}$), C-DOM distribution was highly scattered due to the mixing of water masses of statistically different optical properties. Higher absorption coefficients and C-DOM and DOC concentrations reflect the higher contribution of terrigenous DOM. The region most influenced by land-derived DOM is the Mackenzie Shelf where the 3D excitation/emission matrix spectra show a strong signature of continental inputs. Furthermore, the absence of a typical marine DOM signal indicates that a terrigenous component dominated C-DOM composition throughout the entire Western Arctic Ocean.

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1. Introduction

Dissolved organic carbon (DOC) in marine and freshwater ecosystems is one of the Earth's largest actively cycled reservoirs of organic matter (Bushaw et al., 1996) and thus plays an important role in the global carbon cycle (Cauwet, 1978; Mopper and Degens, 1979; Hansell and Carlson,

*Corresponding author. Present address: Earth and Ocean Sciences, University of British Columbia, 1461-6270 University Boulevard, Vancouver, BC, Canada V6T 1Z4.

Tel.: +1 604 822 1493; fax: +1 604 474 2679.

E-mail address: cgueguen@eos.ubc.ca (C. Guéguen).

2002). Furthermore, the amount of DOC in the ocean is comparable to the amount of carbon found in the atmosphere as carbon dioxide (CO₂). Thus, changes in the sources and sink of marine dissolved organic matter may significantly influence levels of the important greenhouse gas CO₂ in the atmosphere.

The Arctic Ocean Basin, with about 1% of the global ocean volume, receives about 10% of the global river discharge mainly from large arctic rivers such as the Mackenzie River in Canada, and the Ob, Yenisey and Lena Rivers in Siberia. Recent studies have shown that concentrations of organic carbon in Arctic river waters are high (e.g., Lobbes et al., 2000). Thus, the disproportionate share of global river discharge into the Arctic Ocean and the high DOC concentrations in arctic rivers highlight the importance of freshwater and terrestrial organic matter in the biogeochemical cycles of the Arctic Ocean (Stein and Macdonald, 2004 and references therein). Furthermore, evidence has shown an increase of arctic river discharge by ~7% (e.g., Peterson et al., 2002). Under warming conditions, increased river discharge and the export of terrestrial organic carbon (Benner et al., 2004; Guo et al., 2004) may significantly affect the carbon cycle in the Arctic Ocean. Due to its remoteness, the Arctic Ocean remains the least studied ocean, and yet its importance to climate is immense. For example, the circulation of water into and out of the Arctic Ocean and Nordic Seas plays a major role in controlling global thermohaline circulation. Despite its key roles in global change, the biogeochemical processes and carbon cycles in the Arctic Ocean remain poorly understood.

Colored dissolved organic matter (C-DOM), the fraction of the dissolved organic carbon pool that absorbs light in the ultraviolet and visible ranges (Kirk, 1994), represents a significant fraction of the bulk DOC (up to 60%; Ertel et al., 1986). C-DOM plays a major role in the biogeochemistry of natural waters through its influence on light transfer (Vodacek et al., 1997), the production of reactive oxygen species (see review of Mopper and Kieber, 2002) and metal bioavailability (Koukal et al., 2003; Guéguen et al., 2004). The presence of C-DOM may also protect organisms against

damaging from light effects. Terrestrially derived C-DOM from river runoff is the main source of natural C-DOM to the oceans in nearshore areas, where runoff mixes with seawater. As the fluorescence signal can be sensitively determined, C-DOM has been extensively used for studies of riverine water dispersal (Coble, 1996; Mounier et al., 1999; Del Castillo et al., 2000) and DOC concentration (Vodacek et al., 1995; Ferrari et al., 1996; Guay et al., 1999). Although the Arctic Ocean is influenced to a great extent by terrestrial organic matter, studies on the distribution and transport of C-DOM and terrestrial organic carbon are still scarce (Guay et al., 1999; Opsahl et al., 1999; Amon et al., 2003), especially in the western arctic region.

Since C-DOM can be responsible for a significant but variable fraction of the total absorption of light in the water column, C-DOM is particularly important for the application of remote sensing techniques, such as ocean color models related to organic carbon cycling and chlorophyll-a (Chl-a) as an indicator of primary productivity. In areas influenced by riverine inflow, C-DOM contribution is significant and can result in an overestimation of Chl-a by satellite sensors (e.g., Carder et al., 1991; Arrigo and Brown, 1996).

In this study, we focus on the Western Arctic Ocean where the river discharge inputs come mainly from the Mackenzie River, the fourth largest Arctic river, discharging about 330 km³/yr (Macdonald et al., 1998), most of it (70%; Carmack et al., 1989; Macdonald et al., 1995) between May and September. Mackenzie River waters flow out onto the largest shelf on the North American side where they mix with seawater and are eventually exported to the Canada Basin. Here, we report the optical properties of C-DOM in relation to physical parameter distributions. Results support the use of C-DOM to track the surface circulation at low and mid-salinity on the shelf as a surrogate measure of the salinity, and also document the changes in bulk C-DOM characteristics and composition during the water mass mixing on the shelf. The significance of the terrigenous origin of C-DOM in relation to excitation–emission matrices (EEMs) is also discussed.

2. Methodology

2.1. Study area and sampling

Seawater samples were collected during the MR02-K05 cruise, onboard the R/V Mirai, from 2 September to 10 October 2002 in the Western Arctic Ocean. Fig. 1 shows the location of sampling stations. Eighty-two discrete hydrocast samples were collected for C-DOM and DOC measurements, and 59 additional stations were visited for measurements of conductivity–temperature–depth (CTD) and other hydrographic parameters. Hydrocast samples (6–8 L) were collected into a pre-washed PET container and filtered immediately through precombusted (400 °C for 6 h) GF/F filters mounted in PET holders that were connected directly to the PET container. The first liters of filtrate were discarded. The C-DOM samples were stored in precombusted (550 °C for 5 h) amber glass bottles. The DOC samples were immediately acidified. All samples were stored in darkness at 4 °C until analysis.

2.2. Dissolved organic carbon measurement

Concentrations of DOC were analyzed by the high temperature catalytic combustion method on a Shimadzu TOC-V analyzer (Guo et al., 1995). Samples (~20 mL each) were pre-acidified with 2 drops of concentrated HCl to a $\text{pH} \leq 2$ to remove inorganic carbon by purging with ultra-pure air before the analysis. Three to five replicate injections (150 μL each) were performed for each sample, which resulted in a typical coefficient of variation <2%.

Overall, concentrations of suspended particulate matter were low in the western Arctic Ocean, judging from POC concentrations from the same sample set (Guo et al., 2005). Therefore, the difference in DOC concentrations between 0.7 and 0.2 μm should be minimal. Besides, dissolved and particulate phases are highly operationally defined. Most DOC measurements in the literature are based on 0.7 μm GF/F filtrates. For comparison purposes, we consistently used 0.7 μm GF/F filters in this study.

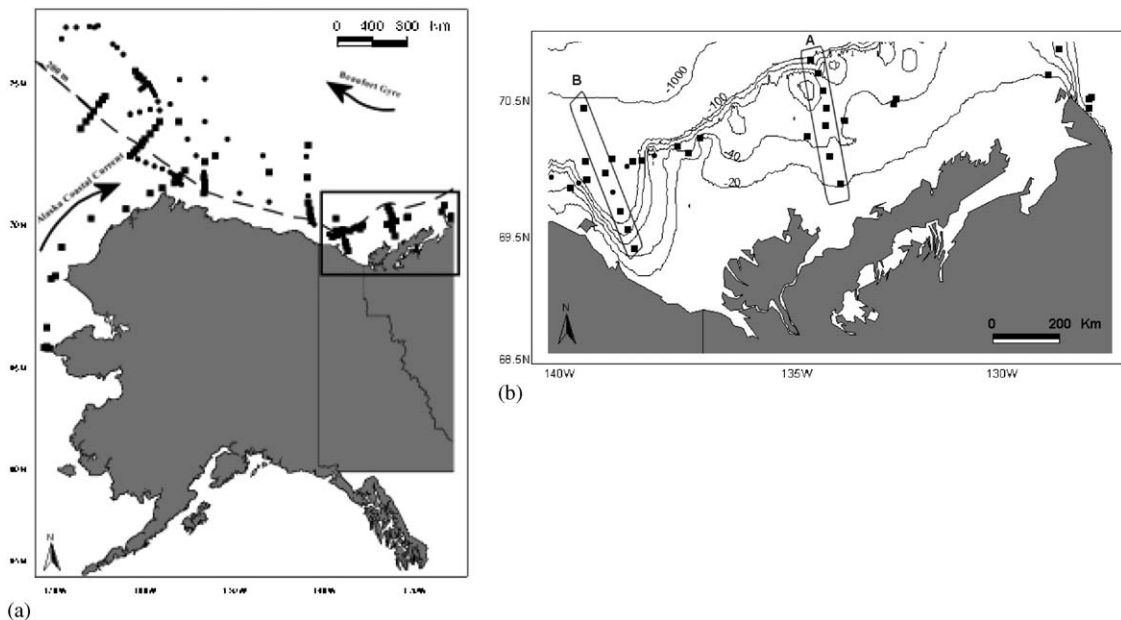


Fig. 1. (a) Map of the Western Arctic Ocean showing the hydrocast (■) and CTD-only (●) stations. Dotted line represents the 200-m isobath. (b) Bathymetry of the Mackenzie Shelf with the sampling sites.

2.3. Absorbance and fluorescence analysis

Absorbance of DOM was measured on an UV-Visible spectrophotometer (Agilent 8453) with a 5 cm quartz cuvette using Milli-Q water as a reference (Guéguen et al., 2005). In all cases, absorbance values were adjusted by dilution with MilliQ water to <0.1 at 370 nm and for 5 cm path-length. This was done to minimize both reabsorption and inner filter effects (Ewald et al., 1984), and to work in the linear domain of the fluorescence intensity variation with concentration. Values of average absorbance at 700 nm were set to zero to correct the spectra for refractive index effects (Green and Blough, 1994). The measured absorbance was converted to absorption coefficient (m^{-1}) according to the equation: $a(\lambda) = 2.303 A(\lambda)/L$, where $A(\lambda)$ is the absorbance and L the path-length of the optical cell in meters. The spectral slope coefficient S (nm^{-1}) was obtained using the non-linear fitting (NFL, Stedmon et al., 2000) over the range from 250 to 400 nm. However, most previous studies calculated S through a linear fitting (LF) of the log-linearized absorption spectra (Blough and Del Vecchio, 2002 and references therein; Del Vecchio and Blough, 2004), making the comparison difficult. For this reason, both fitting procedures were employed and showed a consistent upward bias of values of S (average value of 0.002 nm^{-1}) acquired by NLF, which is consistent with that given by Blough and Del Vecchio (2002). In this study, the reported values of S were obtained using NLF.

Fluorescence measurements were made with a FluoroMax 3 Jobin Yvon fluorometer equipped with two monochromators for both the excitation and the emission (Guéguen et al., 2005). Samples were contained in 1 cm path-length quartz cells. The recorded spectra were corrected for instrumental response (Ewald et al., 1993; De Souza Sierra et al., 1994a). Milli-Q water was used as a blank and subtracted from sample spectra. Three-dimensional EEMs were generated by concatenating the emission spectra from 260 to 700 nm at 40 separate excitation wavelengths ranging from 255 to 455 nm. Final EEMs were interpolated (4Ex/2Em) and smoothed (Savitsky-Golay, second order polynomial over 5 points) using GRAMS/

32 software (version 4.14, Galactic Industries) (Coble et al., 1993; Coble, 1996). To determine $\text{Ex}/\text{Em}_{\text{max}}$ of the visible humic-like region, the maximum slope at each grid node of the EEM was calculated using the Terrain Slope function of Surfer (version 7, Golden Software) (Komada et al., 2002). All fluorescence intensities were converted to fluorescence units (F.U.), based on measurement of the corrected fluorescence intensity of 1 ppb quinine sulfate dihydrate (NIST 936a) in 0.105 M perchloric acid. Terrestrial derived C-DOM is reported as fluorescence maximum measured in the visible-terrestrial humic fluorophore region (Ex/Em 320-360/420-460; Coble et al., 1998).

3. Results and discussion

3.1. Physical properties and C-DOM distribution

There exists a constant inflow of Pacific-origin waters entering the Western Arctic Ocean via the Bering Strait (Coachman et al., 1975; Macdonald et al., 2002). As shown in Fig. 2, warm ($T > 4^\circ\text{C}$) and salty ($>29.5\text{‰}$) water masses flow north along the Alaskan coast (Fig. 2a,b). The Pacific-origin water mass undergoes considerable modification in the Chukchi Sea, becoming colder ($T < 2^\circ\text{C}$) and fresher ($<29.5\text{‰}$). Moreover, T - S diagram (Fig. 4a) showed two distinctive warmer end-members in the high-salinity range located on the Chukchi Plateau ($\sim 28.5\text{‰}$) and off the North Slope of Alaska ($\sim 27\text{‰}$). The large gradient of water temperature decreasing westward (from 9.7 to $\sim 2^\circ\text{C}$) should be noted.

Distributions of salinity and temperature (Fig. 3a,b) were highly altered on the Mackenzie Shelf by the inputs of freshwater from the Mackenzie River. The mixing of shelf waters with freshwater was evidenced by a temperature maximum ($T \sim 4.5^\circ\text{C}$) and salinity minimum ($\sim 8\text{‰}$) near the river mouth. These warm and fresh waters entered into the Beaufort Sea mostly through two channels: Reindeer channel at the West and Kugmallit channel at the East. It can also be noticed that the flow path of freshwater entering the shelf was mostly through the East channel in

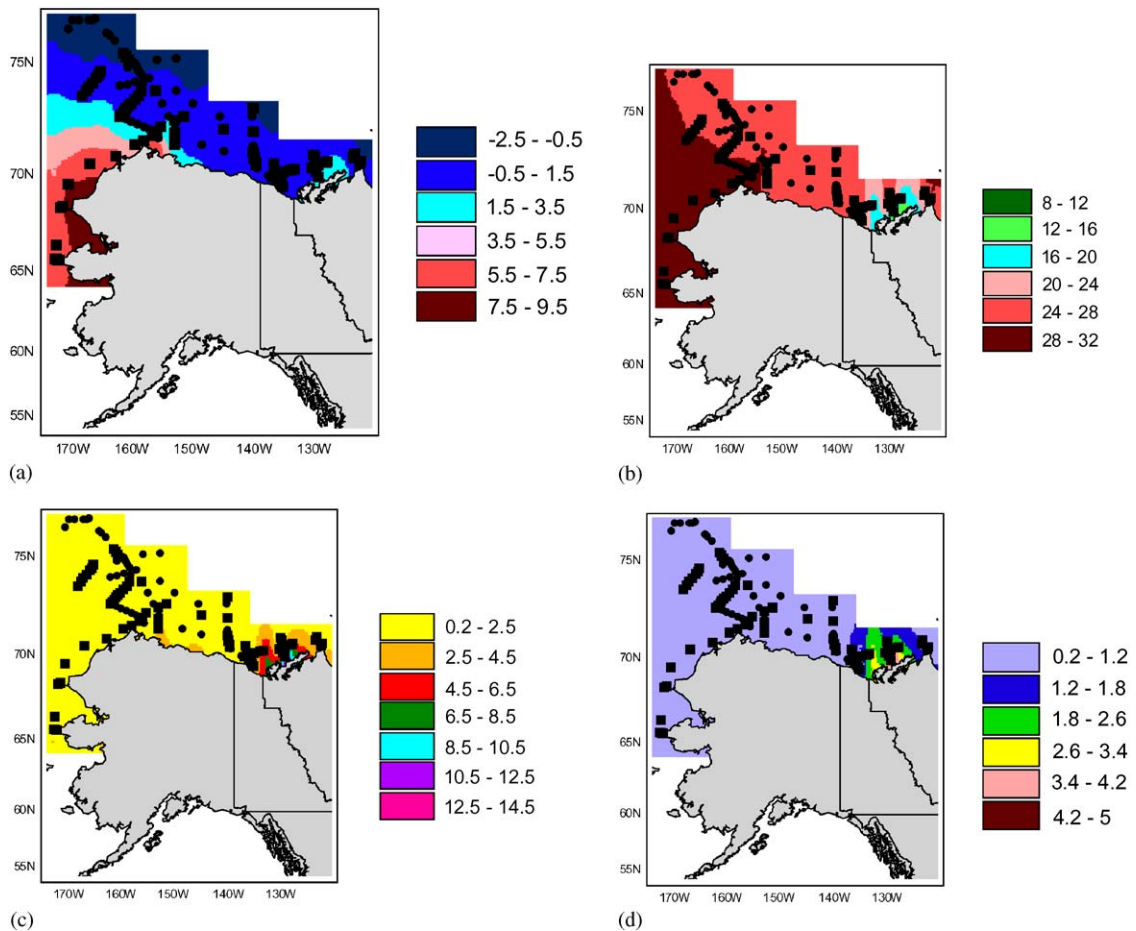


Fig. 2. Distributions of (a) temperature, (b) salinity, (c) C-DOM (Fl.U.) and (d) a_{355} (m^{-1}) at 10 m in the Western Arctic Ocean.

the Kugmallit Bay. The incoming freshwater was noticeable as far as the shelf waters progressed offshore into the Arctic Ocean. The shallow and wide shelves east of the study area allowed the incoming freshwater mass to spread far away from the source. On the other hand, the presence of a canyon to the west of the study area (Fig. 1) induced a rapid mixing with cooler and saltier waters, and a swift loss of the freshwater signal.

Dissolved organic matter had a distribution similar to that of the hydrographic parameters discussed above (Figs. 2–3). Surface waters in the Chukchi Sea contained relatively low C-DOM concentrations in terms of fluorescence (1.60 ± 0.68 Fl.U., Fig. 2c), but were two times higher than

fluorescence reported in Antarctic surface waters (Mopper et al., 1995). However, three zones with high C-DOM concentrations can be identified: north of the Seward Peninsula, shelf waters off the North Slope of Alaska, and the Mackenzie Shelf. These three high C-DOM areas coincided with the presence of river inputs from the Kobuk, Colville and Mackenzie Rivers, respectively. Higher concentrations of DOC and abundance of C-DOM (up to $310 \mu M-C$ and 14.6 Fl.U., respectively) were found on the Mackenzie Shelf (Fig. 3c, d). These plumes with high DOC and C-DOM concentrations on the Mackenzie Shelf (Fig. 3c, d) were largely the result of terrestrial inputs. Indeed, a significant inverse correlation between C-DOM

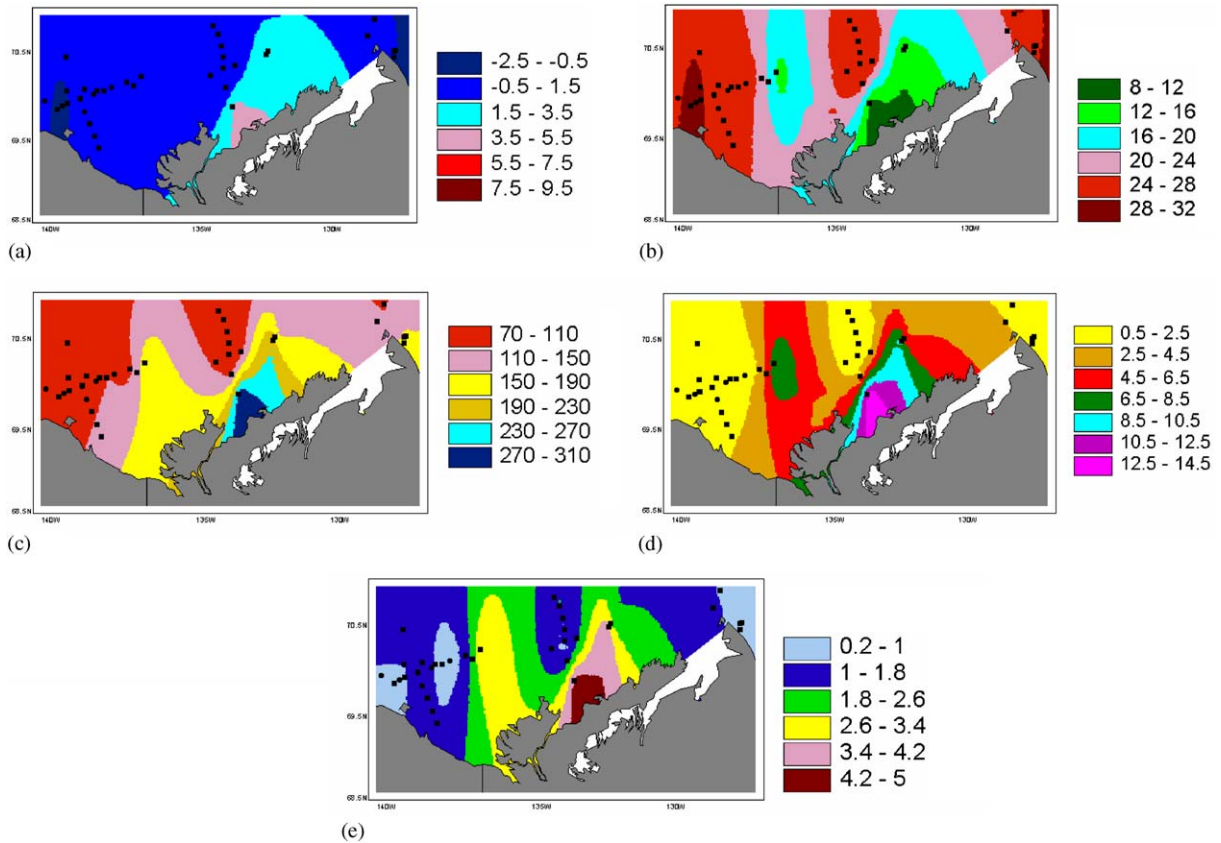


Fig. 3. Distributions of (a) temperature, (b) salinity, (c) DOC ($\mu\text{M-C}$), (d) C-DOM (Fl.U.) and (e) a_{355} (m^{-1}) at 10m on the Mackenzie Shelf.

Table 1

Correlation matrix ($p < 0.05$, $n = 11$) in the range of salinity between 5 and 25‰ in the Mackenzie Shelf

| | Temp | Salinity | C-DOM | a_{355} | DOC |
|-----------|-------|----------|-------|-----------|-----|
| Temp | 1 | | | | |
| Salinity | -0.95 | 1 | | | |
| C-DOM | 0.78 | -0.87 | 1 | | |
| a_{355} | 0.79 | -0.84 | 0.77 | 1 | |
| DOC | 0.71 | -0.83 | 0.95 | 0.76 | 1 |

Temp, temperature; C-DOM, colored dissolved organic matter (in Fl.U.); a_{355} , absorbance coefficient (m^{-1}) at 355 nm; DOC, dissolved organic carbon ($\mu\text{M-C}$).

and salinity in Mackenzie Shelf waters ($r = -0.87$, $p < 0.05$; Table 1) points to a terrigenous source for the C-DOM, and a somewhat conservative mixing of C-DOM between fresh water and seawater. This

linear relationship also indicates a terrestrial origin of DOM and the absence of strong in situ sources and sinks.

Fluorescence intensity increased from the west channel to the east channel where the strongest signal was measured. The highest sedimentation rate found on the Mackenzie Shelf was measured in the Kugmallit Bay (Harper and Penland, 1982), indicating that the Kugmallit channel was likely the main channel for freshwater export to the Mackenzie Shelf, which is consistent with the highest C-DOM values measured near the Kugmallit channel. Fluorescence appeared conservative in the salinity range from 5 to 25‰ due to rapid mixing (Fig. 4a). At higher salinities ($> 25\%$), fluorescence signatures and their relation to water mixing cannot be described by a simple two-end-member mixing model, likely resulting

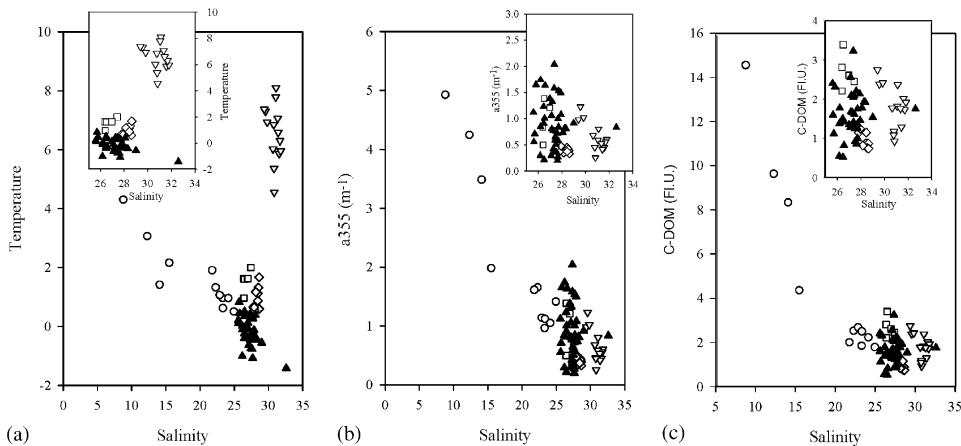


Fig. 4. Variation of (a) temperature, (b) a_{355} (m^{-1}) and (c) C-DOM (FLU.) vs. salinity the Western Arctic Ocean. Note that at low- to mid-salinity (\circ), the water column was well mixed, whereas at high salinity ($>25\text{‰}$, Δ) different water masses were distinguished: (∇) Pacific-origin, (\diamond) Chukchi Plateau, and (\square) off the North Slope of Alaska.

from multiple DOM sources from ice algae, marine plankton, and preexisting DOM. The fluorescence intensity was linearly correlated to the DOC concentration in the Mackenzie Shelf ($r^2 = 0.89$, $p < 0.05$), suggesting a common terrigenous C-DOM source and the possibility of making high-resolution DOC measurements using optical properties.

3.2. Characterization of DOM

Plots of the natural log of absorption coefficients vs. wavelength for some representative samples are showed in Fig. 5. Absorption coefficient values increased from the Chukchi Sea to the Mackenzie Shelf region, with the highest values observed near the river mouth of the Mackenzie Shelf. The rest of the study area generally exhibited lower absorption coefficients. For example, values of a_{300} , a_{355} and a_{370} ranged from 0.7 to 12.2, 0.20 to 4.9 (see also Figs. 2d–3e) and 0.13 to 3.8 m^{-1} , respectively. The a_{355} values were up to 24 times higher than those measured in the western part of the Chukchi Sea ($0.62 \pm 0.32 \text{ m}^{-1}$). In addition, the absorption coefficients measured off the Mackenzie delta were consistent with those generally observed near the mouth of large rivers (Blough and Del Vecchio, 2002), but significantly higher than those reported for open seawater in

the Sargasso Sea ($a_{355} \sim 0.05 \text{ m}^{-1}$; Nelson et al., 1998) and South Pacific Ocean (a_{355} 0.117– 0.326 m^{-1} ; Shooter et al., 1998). The steady decrease in absorption coefficient values with salinity and distance offshore on the Mackenzie Shelf indicates again the influence of river inputs and the export of terrestrial C-DOM through the shelves into the Arctic Ocean. High levels of C-DOM absorbance in some parts of the western arctic may have a substantial impact on the optical properties of ocean waters (e.g., control of light penetration into the ocean and its impact upon phytoplankton and bacterial activity). Significant correlations (Table 1, $p < 0.05$) between absorption coefficients and salinity (or fluorescence) at low and mid salinity waters (salinity $< 25\text{‰}$) suggest that the optical properties can be considered as conservative properties of water masses. Previous work on the Mississippi plume indicates a strong correlation between a_{350} and lignin phenol concentration (Hernes and Benner, 2003), relating a_{350} to terrigenous material. That would suggest that measurements of optical properties of DOM provide a powerful tool in studying the dynamics of terrigenous DOM in coastal regions.

The mean value for the spectral slope coefficient (S) was $0.018 \pm 0.002 \text{ nm}^{-1}$ (Fig. 6a), which is in the same range as previously reported values in the Greenland Sea (Stedmon and Markager, 2001)

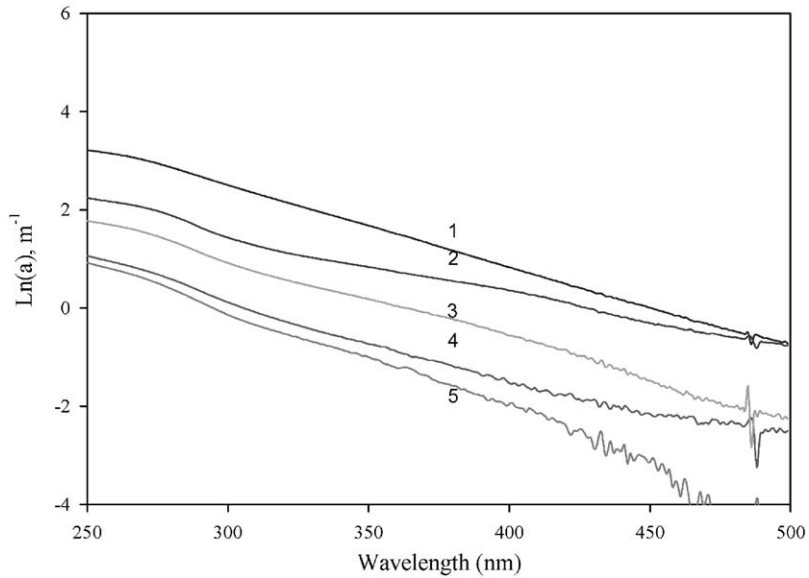


Fig. 5. Plots of the natural log-normalized spectral absorption of C-DOM. (1–2) Near-shore station (Mackenzie Shelf), (3) Off-shore station (Mackenzie Shelf), (4–5) Chukchi Sea.

and other regions (Bricaud et al., 1981; Babin et al., 2003). On the Mackenzie Shelf, S values ranged from 0.014 to 0.023 nm^{-1} ($0.018 \pm 0.002 \text{ nm}^{-1}$), characteristic of coastal waters influenced by river inputs (Blough et al., 1993; Green and Blough, 1994; Vodacek et al., 1997). Overall, these values were significantly lower than those observed for open ocean waters, where typical values are $0.025\text{--}0.030 \text{ nm}^{-1}$ (Blough and Del Vecchio, 2002). It has been shown previously that a general decrease in fluorescence intensity of the visible region peak and a blue-shift in the wavelength of the emission maximum in near-shore regions occur as river water mixes with seawater. An appreciable range in the emission maximum at excitation 313 nm (from 408 to 438 nm, Fig. 6b) was observed in the surface waters, indicating a large variety of coastal C-DOM (Donard et al., 1989; de Souza Sierra et al., 1994b) in the Western Arctic Ocean. The large red-shift (up to 438 nm) measured on the Mackenzie Shelf was suggestive of highly terrestrial-derived C-DOM. Except for stations near the Bering Strait, the absence of a typical marine signal ($\lambda_{\text{ex}} \leq 410 \text{ nm}$; Donard et al., 1989; de Souza Sierra et al., 1994b) is noticeable, indicating the surface

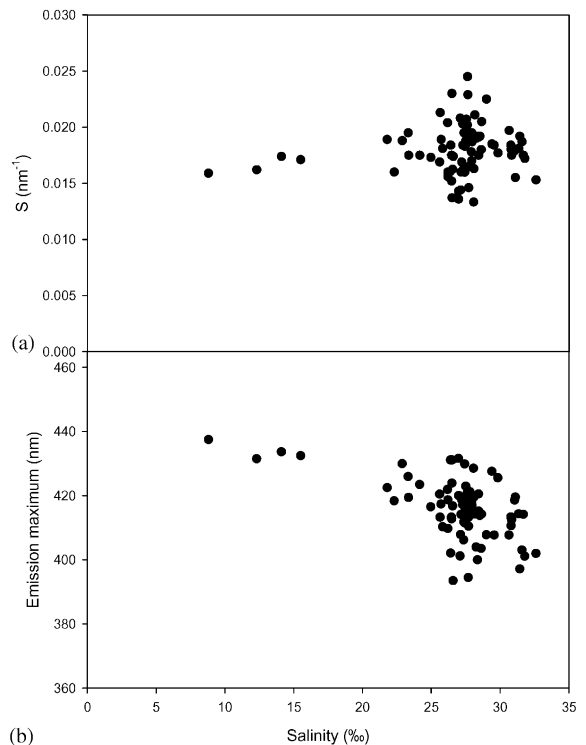


Fig. 6. Variations of (a) spectral slope coefficient (S) and (b) C-DOM fluorescence emission maximum ($\text{Ex} = 313 \text{ nm}$) with salinity.

waters of the western arctic were markedly influenced, but to differing degrees by terrestrial C-DOM. At low- and mid-salinity (<25‰), the values of S and the excitation/emission maxima remained relatively unchanged. In contrast, at higher salinity (>25‰), S begins to increase and the excitation/emission maxima blue-shifted, concomitant with a larger variability of C-DOM and a_{355} (Fig. 4b, c). The water masses of Pacific-origin, Chukchi Plateau, and off the North Slope of Alaska showed statistically different characteristics (ANOVA, $p < 0.05$), and the variation at high salinity reflected the mixing of several mid- to high-salinity water masses (Fig. 4a). However, recent studies (Vodacek et al., 1997; Moran et al., 2000) indicated that photobleaching dominantly

occurring when the river waters are sufficiently diluted within the surface layer (Del Castillo et al., 1999) can produce the same effects and may account in part for the observed gradient in optical properties from near- to off-shore waters. The photooxidation of terrigenous organic matter was also suggested in the alteration of DOM at high salinity (Hernes and Benner, 2003) but it is challenging to determine the relative importance of photochemical versus mixing of several water masses.

3.3. Dispersal of terrestrial C-DOM

To further explore how fluorescence properties can be used as a tracer of water mixing and

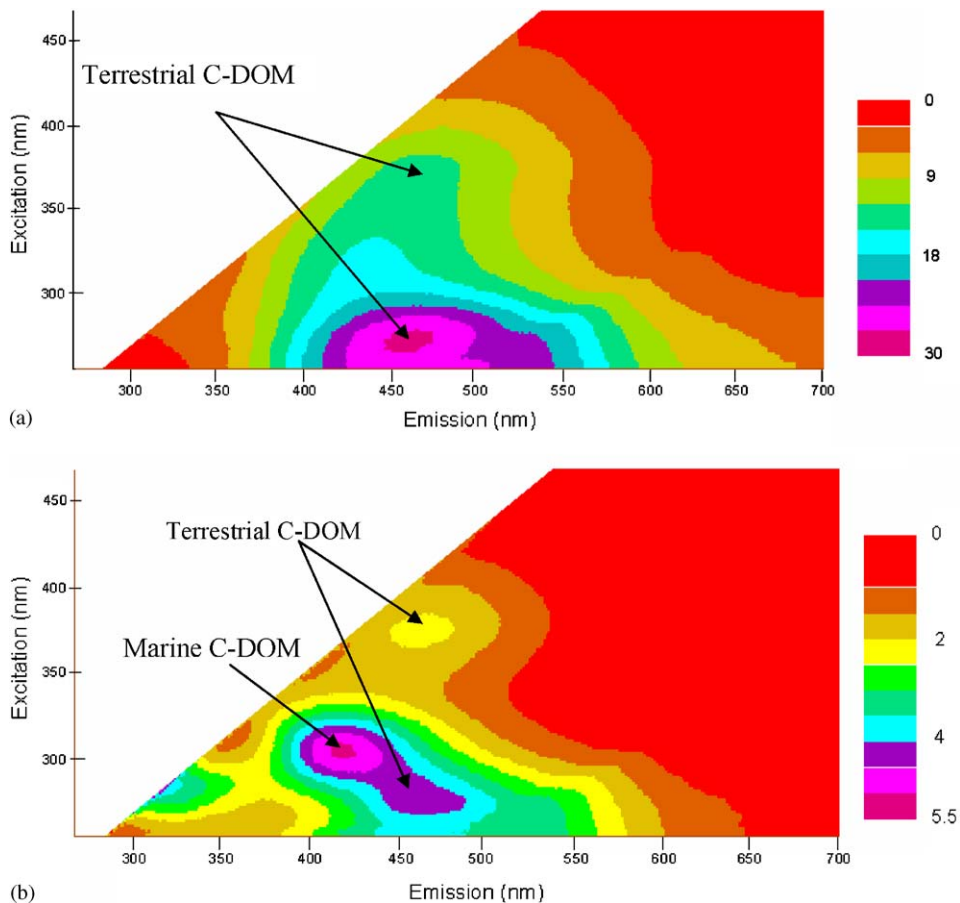


Fig. 7. Contour plots of fluorescence excitation/emission matrices of (a) near-shore (salinity 8.8‰) and (b) off-shore (salinity 26.3‰) samples collected on the Mackenzie Shelf. Fluorescence is expressed in quinine sulfate units (F.U.).

material transport in the Arctic Ocean, EEMs were measured for water samples in the transect A and B (Fig. 1). The contour plot for most near-shore stations (Fig. 7a) showed a fluorescence pattern with characteristics that are similar to those of other rivers (Coble, 1996; Coble et al., 1998), which thus carries an unambiguous terrigenous signature. Mean values for Ex_{max}/Em_{max} (365/458 nm) were in the same range as for C-DOM from other rivers (325–355/438–455; Coble, 1996). The characteristics of the off-shore C-DOM (Ex_{max}/Em_{max} 314/420 nm, Fig. 7b) were similar to those of the marine transitional group defined by Coble et al. (1998). The wavelengths at which the maximum emission and excitation occurred were blue-shifted to shorter wavelengths for the stations furthest offshore. The visible region peak was blue-shifted by 57–66 nm along the excitation axis and by 31–44 nm along the emission axis (Fig. 8). Similar results have been observed for freshwater vs. marine C-DOM samples (Coble, 1996), attributable to changes in the degree of humification of DOM (Kalbitz et al., 2000) and in the nature of the fluorophore (Coble, 1996). Off-shore C-DOM molecules are usually smaller and less aromatic than riverine and near-shore C-DOM. Their large range in emissions was also indicative of a great

modification of terrestrial C-DOM occurring in the water column over the shelf.

There was a negative correlation between salinity and terrestrial C-DOM (visible-terrestrial humic fluorophore; Coble et al., 1998) on the Mackenzie Shelf ($r^2 = 0.82$ and $p < 0.05$, Fig. 9), which could be expected if terrestrial input is the

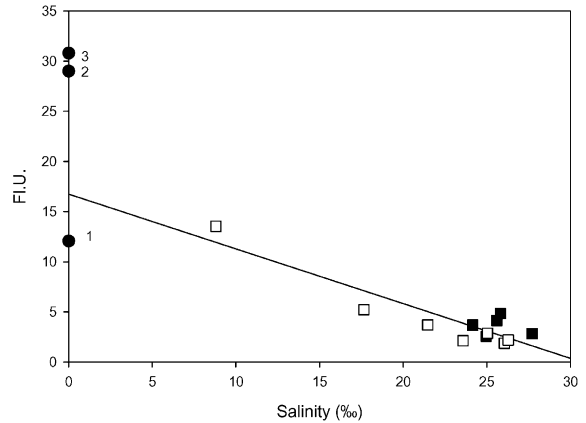


Fig. 9. Terrestrial C-DOM (visible-terrestrial humic fluorophore, Ex/Em 320–360/420–460; Coble et al., 1999) vs. salinity for the transect A (□) and B (■) (see Fig. 1) and river samples (●). 1—Mackenzie (winter), 2—Mackenzie (summer; Amon et al., 2003), 3—Yukon (summer).

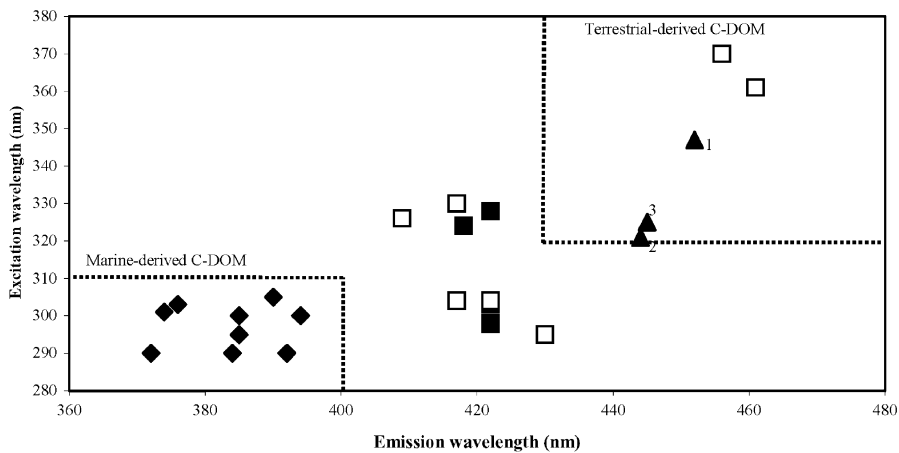


Fig. 8. Characteristics of wavelength-independent Ex_{max} and Em_{max} for transect A (□) and B (■) (see Fig. 1), river (▲) and marine samples (♦; Coble, 1996). 1—Mackenzie (winter), 2—Mackenzie (summer; Amon et al., 2003), 3—Yukon (summer). The blue-shift for the offshore samples compared to the near-shore samples can be seen.

dominant source. Using this relationship, the fluorescence intensities of terrestrial C-DOM in the river and in the Beaufort Sea were roughly calculated. Extrapolation to zero salinity would result in an intercept of 16.7 Fl.U. This value for terrestrial C-DOM in the Mackenzie River is within the range between the mid-summer data (Amon et al., 2003) and the winter data, which could constitute the minimum of C-DOM found in the river. Extrapolation to a salinity of 27 (typical surface salinity in Beaufort Sea in summer; Macdonald et al., 2002) would give rise to a C-DOM concentration of 2.0 Fl.U. in the Beaufort Sea. Such concentrations are way above the fluorescence detection limit (0.05 Fl.U.), which would allow tracking the riverine input further into the Canada Basin using C-DOM properties.

4. Conclusions

Distributions of C-DOM and absorption coefficients in the Western Arctic Ocean showed similar patterns as those of salinity. C-DOM fluorescence and a_{355} appeared conservative in low- and mid-salinity (<25‰). However, at higher salinity, the presence of several water masses with distinctive optical properties was responsible for the non-conservative behavior of C-DOM. The effect of photobleaching on C-DOM may also explain in part the variability observed offshore, as indicated by the large variability in the C-DOM spectral slope parameter. The high absorbance coefficients and C-DOM characteristics reported here were all related to coastal waters influenced by terrigenous DOM sources. The region most influenced by terrestrial inputs was the Mackenzie Shelf, with higher concentrations of DOC and C-DOM and absorption coefficient values. EEMs of the most near-shore stations (Ex_{max}/Em_{max} 365/458 nm) confirmed a strong signature of terrestrially-derived C-DOM. The blue-shift in Ex_{max}/Em_{max} with increasing salinity and offshore distance were also indicative of export and mixing of terrestrially-derived C-DOM through the shelves into the Arctic Basin. The inverse relationships of salinity with both absorption coefficients and C-DOM abundance confirmed these dilution processes.

Moreover, warmer and fresher water mass associated with a high C-DOM concentration characterizing freshwater inflow from the Mackenzie River was found mostly through the east channel during our sampling season in 2002. These findings were consistent with results derived from other hydrographic data. The fact that signatures of typical marine C-DOM were not observed in many offshore samples further suggested that terrestrial DOM overwhelmingly influenced carbon cycles and other biogeochemical processes in the Western Arctic Ocean.

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