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High-resolution measurements of dissolved organic carbon in the Arctic Ocean by *in situ* fiber-optic spectrometry

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Abstract. Here we report results from an extensive survey of dissolved organic carbon (DOC) in the Arctic Ocean, which was achieved by means of a high-resolution, *in situ* UV fluorometer deployed on a nuclear submarine. Based on a strong linear correlation observed between fluorescence (320 nm excitation, 420 nm emission) and organic carbon concentrations determined directly by high-temperature combustion, a continuous record of DOC was produced at a keel depth of 58 m along a 2900-km transect north of the Beaufort, Chukchi, East Siberian and Laptev seas. The DOC record, combined with other physical and chemical measurements, identifies areas where river waters cross the shelves and enter the circulation of the Arctic interior. Fluvial sources were found to account for 12-56% of the total DOC in parts of the upper Makarov and Amundsen basins.

Introduction

Recent investigations of the Arctic Ocean [*Cota et al.*, 1996; *Wheeler et al.*, 1996] revealed larger and more active biological communities, higher levels of primary productivity and more dynamic carbon cycling than previously believed to exist in the region [*Apollonio*, 1959; *English*, 1961]. The large oceanic reservoir of dissolved organic carbon (DOC) in the Arctic remains poorly characterized despite its significance to the Arctic food web [*Rich et al.*, 1997] and global organic carbon cycling [*Lundberg and Haugan*, 1996; *Sarmiento et al.*, 1995]. Relatively few data exist for the interior Arctic Ocean due to its remoteness and the operational difficulties posed by its ice coverage and extreme weather conditions. Investigators working from drifting ice camps [*Gordon and Cranford*, 1985; *Kinney et al.*, 1971; *Melnikov and Pavlov*, 1978] and icebreakers [*Anderson et al.*, 1994; *Wheeler et al.*, 1997] observed high concentrations of DOC in the Eurasian and Canadian basins (typical values ranged from 65 to 125 μmol C L^{-1} at depths above 200 m and from 50 to 80 μmol C L^{-1} in deeper waters); much lower concentrations of particulate organic carbon (POC) were observed (0.2-0.8 μmol C L^{-1}, with values up to 3.6 μmol C L^{-1} occurring during periods of ice melt).

Primary sources of DOC to the Arctic Ocean include fluvial discharge, inflow from the North Atlantic and North Pacific and *in situ* production by phytoplankton and ice algae, but much uncertainty exists regarding the relative contributions from these sources and their geographical distributions [*Anderson et al.*, 1998; *Lundberg and Haugan*, 1996]. The outflow of water through Fram Strait results in a net export of DOC from the Arctic to the North Atlantic, which may play an important role in sustaining deep-ocean DOC gradients and turnover of the marine DOC pool [*Hansell and Carlson*, 1998].

Sample Collection

The SCICEX-97 cruise aboard the nuclear submarine *USS Archerfish* provided direct access to the ice-covered interior of the Arctic Ocean and allowed collection of quasi-synoptic data on an unprecedented scale and degree of resolution. The data reported in this paper were obtained between 12 and 21 September 1997, while the submarine maintained a keel depth of 58 m along an approximately 2900-km transect north of the Beaufort, Chukchi, East Siberian and Laptev seas (Fig. 1).

Water samples for total organic carbon (TOC) and barium (Ba) analyses were collected from a sampling line inside the submarine supplied by an intake valve located 3 m above the keel (TOC samples were collected roughly every hour and Ba samples were collected roughly every 2 hours). *In situ* measurements of temperature, salinity and chlorophyll-*a* were obtained by a Seabird Electronics SBE-19 conductivity-temperature-depth (CTD) probe mounted in the sail of the submarine 15 m above the keel (sampling rate: 4 Hz). *In situ* measurements of fluorescence (320 nm excitation, 420 nm emission) were obtained by a zero angle photon spectrometer (ZAPS) [*Klinkhammer et al.*, 1997] installed in a compartment in the bow of the submarine located 8 m above the keel (sampling rate: 1.7 Hz). Previous work with the ZAPS instrument in mid-latitude coastal surface waters has shown that its response at these wavelengths is closely related to the humic-rich terrestrial component of dissolved organic matter.

In the following discussion, we have assumed that the difference in sampling heights for the various parameters is negligible. While this assumption may have resulted in some degree of uncertainty (particularly in areas of strong vertical gradients), it is not sufficient to invalidate our conclusions.

Results and Discussion

The SCICEX-97 expedition provided the first comparison between ZAPS response and direct measurements of organic carbon by high-temperature combustion [*Benner and Strom*, 1993]. A strong positive correlation ($r^2 = 0.84$, least-squares linear regression) was observed between ZAPS response and TOC along the transect (Fig. 2). These results are contrary to the negative correlations between fluorescence (320 nm/420

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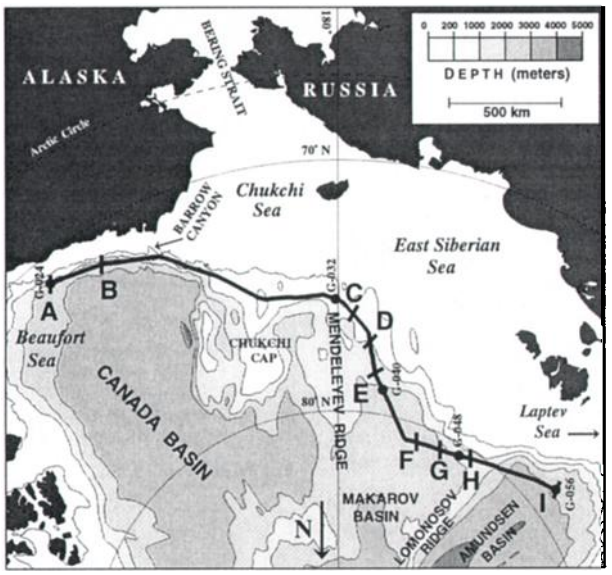

Figure 1. Transect occupied by the *USS Archerfish* from 12 to 21 September 1997. Letters A-I indicate points of reference discussed in the text. Black dots indicate locations of 5 samples for which excitation-emission matrices were constructed.

nm) and DOC documented in open ocean environments at lower latitudes [e.g., *Chen and Bada*, 1992], which were attributed to the combined effects of primary production, remineralization and photooxidation of organic material. Ice cover, seasonally limited insolation and low temperatures presumably diminish the influence of these processes in the Arctic Ocean. Our data are similar to observations made in estuaries and nearshore waters at lower latitudes [e.g., *Smart et al.*, 1976], consistent with the sizeable fluvial discharge to the Arctic Ocean (roughly 10% of global river runoff and fluvial organic carbon flux enters the Arctic Ocean and its marginal seas).

Since particles accounted for a very small portion of the organic carbon in these samples (POC concentrations for 11 samples collected during the transect ranged from 1.1 to 3.4 μmol C L^{-1}, or ≤ 4.2% of TOC), TOC ≈ DOC and the concentration of DOC can be estimated from the response of the ZAPS instrument by the relation $DOC_{ZAPS} = 94.8 \times V$, where DOC_{ZAPS} has units of μmol C L^{-1} and V is the voltage measured at the photomultiplier detector of the ZAPS instrument. Excitation-

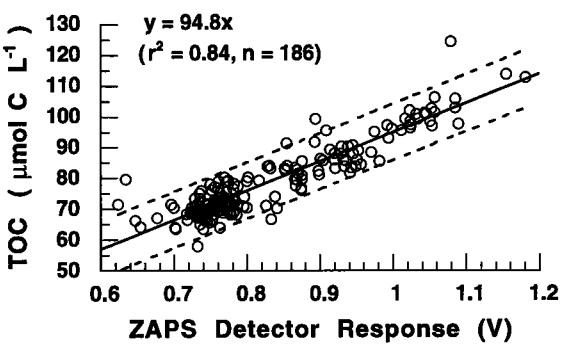

Figure 2. Calibration plot for the ZAPS instrument using TOC concentrations determined by high-temperature combustion. Dashed lines indicate the 95% prediction interval (± 9 μmol C L^{-1}). An empirically-derived correction factor of 0.5413 V was subtracted from the raw ZAPS detector response to account for reflectance from the walls of the compartment in which the ZAPS instrument was installed.

Table 1. Comparison of Organic Carbon Concentrations Measured by High-Temperature Combustion and the ZAPS Instrument to Total Integrated Fluorescence Signals (330 to 700 nm Emission) Produced by Excitation at 320 nm.

Sample Number	Julian Day	TOC (μmol C L^{-1})	DOC_{ZAPS} (μmol C L^{-1})	Integrated Fluorescence (ppb•nm)
G-024	255.840	80	82	1017
G-032	259.766	66	68	616
G-040	261.595	89	90	1209
G-048	263.218	81	83	1028
G-056	264.626	64	67	542

emission matrices [*Coble*, 1996] for 5 water samples collected along the transect showed that the peak signal occurred at or near the excitation/emission wavelengths selected by the ZAPS instrument. The total integrated fluorescence signals (emission wavelengths 330-700 nm) produced by excitation at 320 nm are positively linearly correlated with DOC_{ZAPS} concentrations ($r^2 = 0.997$; Table 1), further corroborating the ZAPS measurements based on detection at a single wavelength.

A plot of DOC_{ZAPS} versus salinity (Fig. 3) reveals three distinct groups of data: (*i*) a complex regime in the Canada Basin and over the Chukchi Cap (points A-C on Fig. 1) suggestive of mixing between Pacific inflow, ice-melt and discharge from the Mackenzie River; (*ii*) a transition zone over the Mendeleyev Ridge (points C-D) corresponding to the front between waters of Pacific and Atlantic character; (*iii*) a linear ($r^2 = 0.76$) regime in the Makarov and Amundsen basins (points D-I) dominated by discharge from Eurasian Arctic rivers (fresh, high-DOC) and marine waters of Atlantic origin (saline, low-DOC). This latter trend is consistent with previous observations of a quasi-linear inverse relationship between fluorescence (320 nm/420 nm) and salinity in nearshore waters strongly influenced by terrestrial organic material [*Klinkhammer et al.*, 1997]. Ice melting and formation, phytoplankton production, microbial respiration and photooxidation likely account for much of the scatter in the data.

To a first-order approximation, the data from the Makarov and Amundsen basins suggest conservative mixing between Eurasian river discharge and Atlantic inflow. The zero-salinity

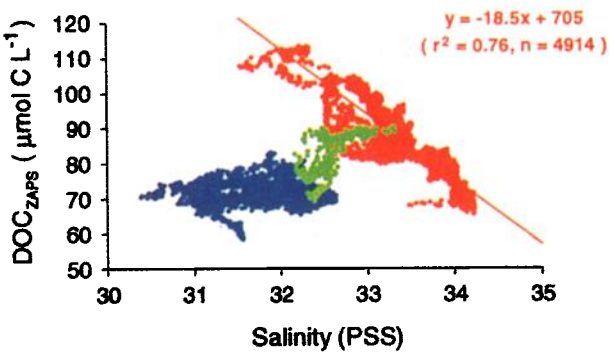

Figure 3. Relationship between DOC_{ZAPS} and salinity for data collected along the transect. Blue symbols correspond to data from the Canada Basin and over the Chukchi Cap (points A-C), green symbols correspond to data from the transition zone over the Arlis Plateau (points C-D), and red symbols correspond to data from the Makarov and Amundsen basins (points D-I). The red line was fit to the data from the Makarov and Amundsen basins by least-squares linear regression.

intercept of the best-fit line (705 μmol C L^{-1}) is comparable to DOC concentrations reported for the major Eurasian Arctic rivers (550-760 μmol C L^{-1}) [*Gordeev et al.*, 1996]. Extrapolating to a salinity characteristic of the Atlantic layer in the Eurasian Basin (34.9) results in a value (58 μmol C L^{-1}) comparable to DOC concentrations reported for Atlantic source waters to the Arctic (50-60 μmol C L^{-1}) [*Wheeler et al.*, 1997].

Assuming linear combinations of these fluvial and marine end-members, the waters encountered along the transect on the Atlantic side of the front contain 90-99% Atlantic inflow and 1-10% fluvial discharge; these results are consistent with previous estimates of the fluvial component of upper waters (depth < 300 m) in the Eurasian Basin based on a salinity/^{18}O mass balance [*Bauch et al.*, 1995]. Between 12 and 56% of the total DOC in these waters is calculated to be derived from fluvial sources. The upper limit of this range is somewhat higher than other estimates of the relative fluvial DOC contribution to the Arctic based on a budget approach [*Wheeler et al.*, 1997] and measurements of terrestrial biomarkers [*R. Benner*, unpublished data, 1999]. This partly reflects the ability of high-resolution, *in situ* DOC measurements to capture narrow, intense fluvial features (see discussion below) that are not representative of the average composition of DOC in Arctic surface waters and would likely be missed by less densely sampled discrete bottle measurements.

Distributions of salinity, temperature, Ba, DOC_{ZAPS}, TOC and chlorophyll-*a* observed along the transect are consonant with known hydrographic features of the Arctic Ocean (Fig. 4). The relatively low salinity (30.4-32.6) observed between the Beaufort Sea and Mendeleyev Ridge (points A-C on Fig. 1) is characteristic of surface waters in the Canada Basin, reflecting the influx of Pacific water through Bering Strait [*Carmack*, 1990]. Peaks in chlorophyll-*a* (3-6 μg L^{-1}) suggest local phytoplankton growth and/or advection of water from high-productivity regions over the Bering, Chukchi and Beaufort shelves [*Cota et al.*, 1996]. The high Ba concentrations (60-81 nmol Ba L^{-1}) encountered in this area are due to the influence of the Mackenzie River [*Guay and Falkner*, 1997].

The transect was punctuated by warm (T > 0 °C), relatively fresh (S < 32) waters over the slope north of Alaska. Particularly notable is the feature observed east of Barrow Canyon (point B) having an intense temperature maximum (5 °C) and local minima in salinity (31.5), Ba (54 nmol Ba L^{-1}), DOC_{ZAPS} (62 μmol C L^{-1}) and TOC (64 μmol C L^{-1}). These features are associated with the Beaufort Undercurrent, a strong (≈10 cm s^{-1}), bathymetrically-steered mean eastward flow that typically extends from near-surface to the bottom between the 50-m and 2500-m isobaths in the southern Beaufort Sea [*Aagaard*, 1984]. The Beaufort Undercurrent is an extension of the Alaskan Coastal Current, which originates in the Bering Sea and becomes seasonally warmed by solar insolation and freshened by fluvial discharge and ice-melt during its northward transit through Bering Strait and the Chukchi Sea. The observed Ba minimum is a consequence of biological uptake occurring along the advective pathway of these waters in the summer [*Falkner et al.*, 1994]. The observed minima in DOC_{ZAPS} and TOC likely resulted from microbial respiration [*Rich et al.*, 1997] and/or photooxidation [*Vodacek et al.*, 1997].

The location of the hydrographic front separating waters of Pacific and Atlantic character (points C-D) is consistent with other studies indicating a recent (late 1980's) shift from its historical position over the Lomonosov Ridge to a position aligned along the Mendeleyev Ridge [*Morison et al.*, 1998].

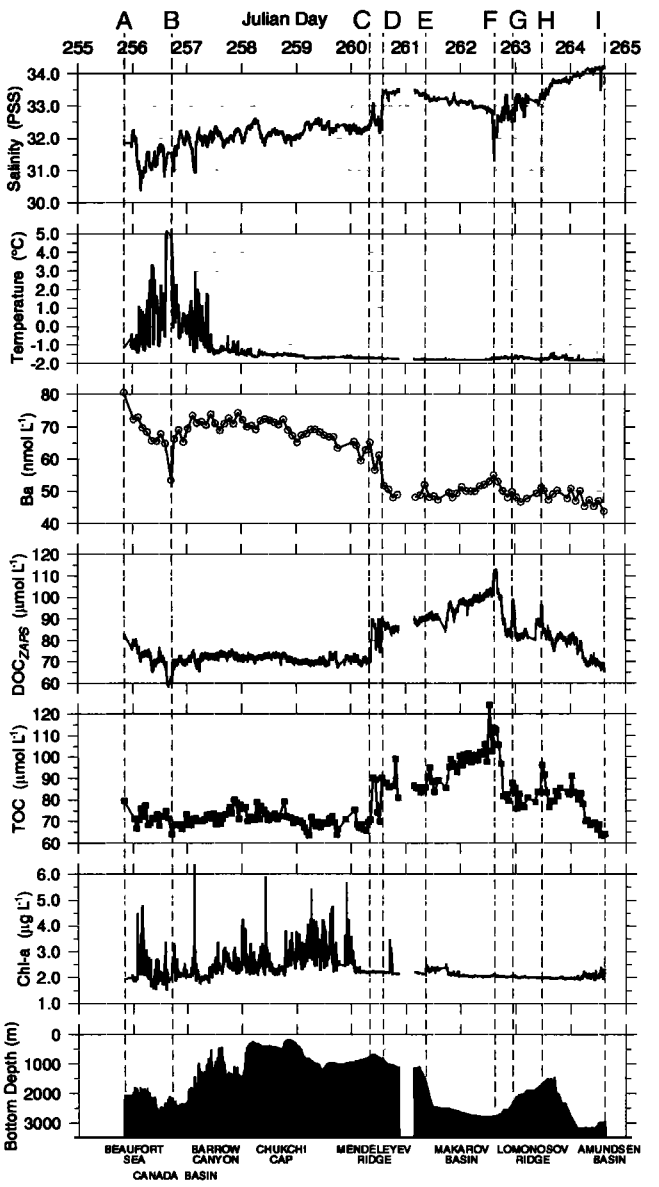

Figure 4. Distributions of salinity, temperature, Ba, DOC_{ZAPS}, TOC and chlorophyll-*a* along the transect at a keel depth of 58 m. Salinity, temperature and chlorophyll-*a* were measured by a Seabird Electronics SBE-19 conductivity-temperature-pressure (CTD) probe equipped with a Wet Star 95-1000-1 chlorophyll sensor (precision: ± 0.01, ± 0.01 °C, ± 0.03 μg L^{-1}, respectively). Analyses for Ba were conducted in the laboratory by isotope-dilution inductively coupled plasma quadrupole mass spectrometry (precision: ± 3 nmol Ba L^{-1} or better) [*Guay and Falkner*, 1997]. Analyses for TOC were conducted in the laboratory by high-temperature combustion (coefficient of variation: ≤ 2%) [*Benner and Strom*, 1993]. Values of DOC_{ZAPS} were determined from fluorescence measurements obtained by the ZAPS instrument as described in the text. Data obtained by the CTD and ZAPS instruments were averaged over 1-min time intervals. The data gap around Julian Day 261 corresponds to a 5.5 hour period when the submarine had surfaced through the ice and was not acquiring data.

The higher salinity (31.5-34.2) in the Makarov and Amundsen basins (points D-I) reflects source waters of Atlantic origin [Jones *et al.*, 1998], while the high concentrations of DOC_{ZAPS} (65-114 μmol C L^{-1}) and TOC (64-124 μmol C L^{-1}) observed in these waters reflect contributions from Eurasian Arctic rivers.

Eurasian Arctic rivers are low in Ba and the Mackenzie River is low in DOC with respect to each other, but both sources of fluvial discharge are enriched in DOC and Ba relative to the marine waters into which they flow [*Gordeev et al.*, 1996; *Guay and Falkner*, 1997]. Thus local minima in salinity coincident with local maxima in Ba, DOC_{ZAPS} and TOC (points A, E-H) indicate points along the transect strongly influenced by fluvial discharge and identify areas where river waters cross the shelves and enter the Arctic interior. The high Ba associated with the feature observed at point A and its location in the southern Beaufort Sea suggest that it is part of the Mackenzie River plume, while the high DOC_{ZAPS} associated with the features observed at points E-H and their locations over the Makarov Basin and the flanks of the Mendeleyev and Lomonosov ridges suggest that they are associated with discharge from Eurasian Arctic rivers. These fluvial features are accompanied by low chlorophyll-*a* concentrations (2.0-2.5 $\mu g\ L^{-1}$), which indicate low phytoplankton biomass and suggest that *in situ* productivity was not a major source of DOC in these waters.

The intensity of the observed fluvial signals is somewhat surprising, given that strong density stratification in the Arctic Ocean tends to inhibit vertical mixing and the depth occupied by the submarine was generally below the base of the summer surface mixed layer. The fact that these attenuated signals were still clearly detectable underscores the importance of Arctic fluvial inputs and illustrates the sensitivity of the high-resolution, optical DOC measurements. Our data suggest that DOC and Ba serve as complementary tracers for distinguishing between contributions from North American and Eurasian rivers and thus provide new information about circulation in the Arctic Ocean.

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