

# Dissolved organic carbon distribution and origin in the Nordic Seas: Exchanges with the Arctic Ocean and the North Atlantic

Rainer M. W. Amon<sup>1</sup> and Gereon Budéus

Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany

Benedikt Meon<sup>2</sup>

Institute of Biogeochemistry and Marine Chemistry, University of Hamburg, Germany

Received 9 August 2002; revised 26 November 2002; accepted 16 April 2003; published 9 July 2003.

[1] Dissolved organic carbon (DOC) and in situ fluorescence were measured along with hydrographic parameters in the Greenland, Iceland, and Norwegian Seas (Nordic Seas). Surface (<100 m) concentrations of DOC ranged from 60 to 118  $\mu\text{M}$  with elevated values in the East Greenland Current (EGC) which transports water from the Arctic Ocean to the North Atlantic. EGC surface waters also showed a pronounced fluorescence maximum between 30 and 120 m depth in all EGC sections indicating the abundance of Arctic river derived DOC in this current. Based on fluorescence we estimated that 20–50% of the annual river discharge to the Arctic Ocean was exported in the EGC. The fluorescence maximum was typically associated with salinity around 33 and temperatures below  $-1^\circ\text{C}$  which are characteristic of surface and upper halocline water in the Arctic Ocean. The elevated fluorescence in this water mass suggests a strong Eurasian shelf component and also suggests that in situ fluorescence could be used to trace Eurasian shelf water in the central Arctic Ocean. DOC concentrations in the Nordic Sea basins (>1000 m) were relatively high ( $\sim 50 \mu\text{M}$  DOC) compared with other ocean basins indicating active vertical transport of DOC in this region on decadal timescales. Based on existing vertical transport estimates and 15  $\mu\text{M}$  of semilabile DOC we calculated an annual vertical net DOC export of 3.5 Tg C  $\text{yr}^{-1}$  in the Greenland Sea and about 36 Tg C  $\text{yr}^{-1}$  for the entire Arctic Mediterranean Sea (AMS) including the Greenland-Scotland Ridge overflow. It appears that physical processes play a determining role for the distribution of DOC in the AMS. **INDEX TERMS:** 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4207 Oceanography: General: Arctic and Antarctic oceanography; 4552 Oceanography: Physical: Ocean optics; 4806 Oceanography: Biological and Chemical: Carbon cycling; 4808 Oceanography: Biological and Chemical: Chemical tracers; **KEYWORDS:** dissolved organic matter, dissolved organic carbon, chromophoric dissolved organic matter, fluorescence, vertical carbon transport

**Citation:** Amon, R. M. W., G. Budéus, and B. Meon, Dissolved organic carbon distribution and origin in the Nordic Seas: Exchanges with the Arctic Ocean and the North Atlantic, *J. Geophys. Res.*, 108(C7), 3221, doi:10.1029/2002JC001594, 2003.

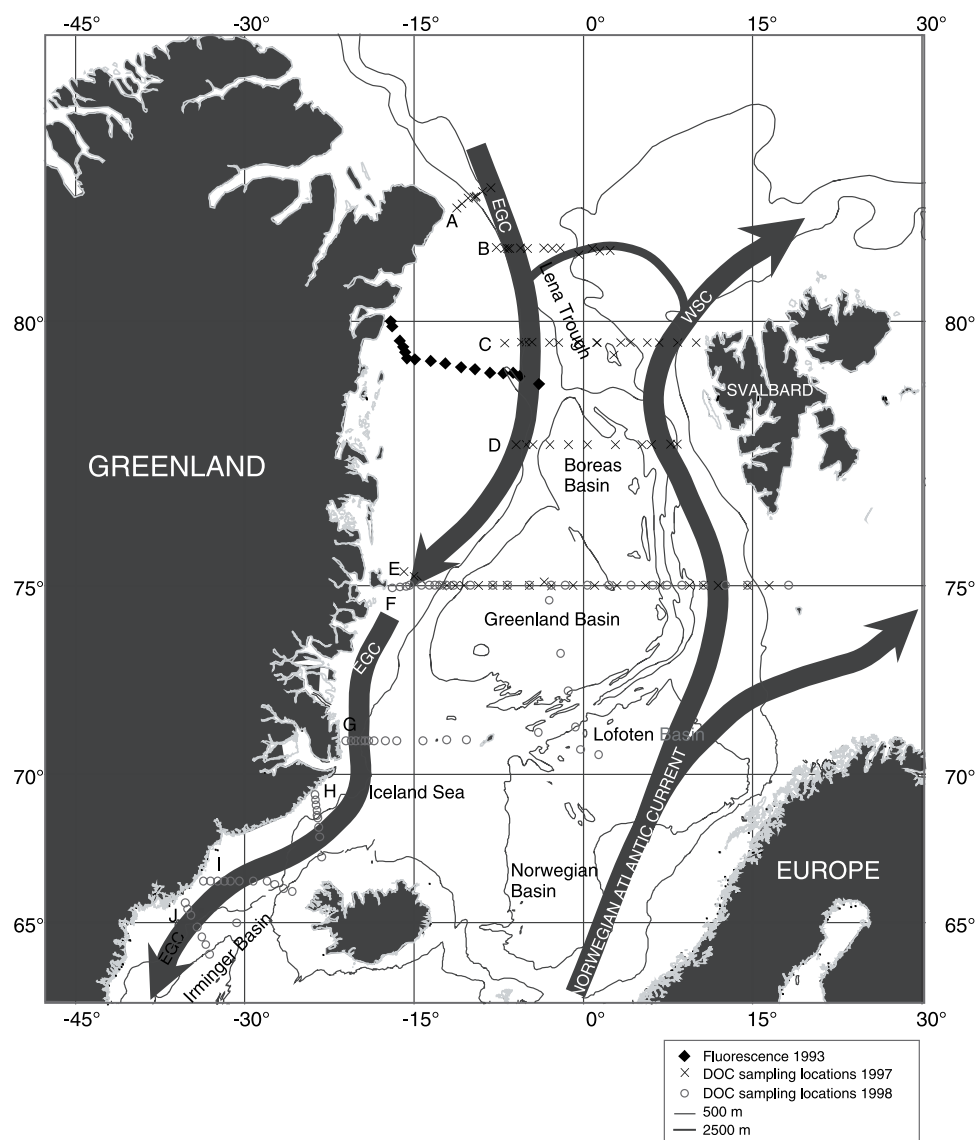
## 1. Introduction

[2] Dissolved organic matter (DOM) in the ocean represents one of the largest reservoirs of organic carbon on Earth and changes in the size of this pool would have significant consequences for atmospheric  $\text{CO}_2$  concentrations on time-scales of 1000–10,000 years [Hedges, 1992]. The potential importance of dissolved organic carbon (DOC) as part of the biological carbon pump has been realized [Ducklow *et al.*, 1995; Ducklow, 1995; Denman *et al.*, 1996; Nagata, 2000; Hansell *et al.*, 2002] but the mechanisms responsible for the

global distribution of DOC are not well understood [Hansell and Carlson, 1998; Williams, 2000]. While there are some general estimates of annual global DOC convection (>500 m) around 120 Tg C  $\text{yr}^{-1}$  [Druffel *et al.*, 1992; Hansell, 2002], only few studies [Copin-Montégut and Avril, 1993; Carlson *et al.*, 1994; Hansell *et al.*, 2002] have specifically determined vertical DOC fluxes in the ocean. The Greenland, Iceland, and Norwegian Seas (Nordic Seas) are arguably among the most important sites for deep water formation on Earth [Aagaard *et al.*, 1985], and at the same time they appear to have relatively high concentrations of DOC throughout the water column compared with other oceans [Børshiem, 2000; Anderson, 2002; Amon and Benner, 2003]. Although the Nordic Seas have been known to be an important site for deep water formation, representing a driving force for the thermohaline circulation and hence for global climate [Broecker, 1991], relatively little is known about DOC fluxes in this area.

<sup>1</sup>Now at Departments of Marine Sciences and Oceanography, Texas A & M University at Galveston, Galveston, Texas, USA.

<sup>2</sup>Also at Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany.



**Figure 1.** Study area indicating sampling stations and major currents in the region. The different sections are numbered A–J. EGC, East Greenland Current; WSC, West Spitzbergen Current.

[3] Exchanges between the Nordic Seas and adjacent ocean basins are largely restricted by bottom topography. The Greenland-Scotland Ridge with a maximum sill depth of 800 m separates the Nordic Seas from the North Atlantic, while the connection to the Arctic Ocean allows the exchange of deeper waters (<2600 m) through Fram Strait. Together, the Nordic Seas and the Arctic Ocean are referred to as the Arctic Mediterranean Sea (AMS) and in fact share a number of characteristics with respect to physical oceanography [Aagaard *et al.*, 1985] and organic geochemistry [Amon and Benner, 2003]. Lateral exchanges of the AMS with the Pacific and especially the Atlantic are disproportionately large relative to its small volume ( $13.7 \times 10^6 \text{ km}^3$ ) and would theoretically renew the entire AMS in less than 50 years. In reality, residence times for surface water (years) and deep water (decades to centuries) of the different basins are quite variable but are typically <500 years with Canadian Basin Deep Water (CBDW) representing the “oldest” water body and Greenland Sea Deep Water (GSDW) having

the most recent exchange with surface waters [Bönisch and Schlosser, 1995; Aagaard *et al.*, 1985; Östlund *et al.*, 1987; MacDonald and Carmack, 1993; Budeus *et al.*, 1998]. The large lateral exchange of water masses influences the distribution, concentrations, and flux of DOC in a variety of ways.

[4] One very important influence, the large amount of river water and terrigenous DOM in surface waters of the Arctic Ocean and the East Greenland Current (EGC), has been realized in the recent past [Opsahl *et al.*, 1999; Anderson, 2002], but geographical and temporal variability are still poorly understood. It is usually necessary to characterize a sample on the isotopic or molecular level to determine the origin of DOM. These analyses are very time consuming, and often require concentration of DOM and separation from abundant salts prior to analysis (something which cannot realistically be achieved on a large sample set typically collected during oceanographic cruises). As an alternative, electronically detectable fluorescence properties

of water samples have been used in several studies to distinguish DOM of different origin [Coble *et al.*, 1990; Coble, 1996; Parlanti *et al.*, 2000; McKnight *et al.*, 2001], to monitor estuarine mixing of riverine and marine water masses [Klinkhammer *et al.*, 1997; De Souza Sierra *et al.*, 1997; Ferrari and Dowell, 1998; Del Castillo *et al.*, 1999], and as a proxy for bulk DOC concentration [Laane and Koole, 1982; Ferrari *et al.*, 1996; Guay *et al.*, 1999]. In this study we used in situ fluorescence measurements to trace the distribution and concentration of river water and terrigenous DOM in Nordic Seas surface waters.

[5] The distribution and origin of DOC in Nordic Seas will be discussed in relation to water mass characteristics, lateral exchanges with neighboring basins, vertical transport in the convective gyres, and residence times.

## 2. Materials and Methods

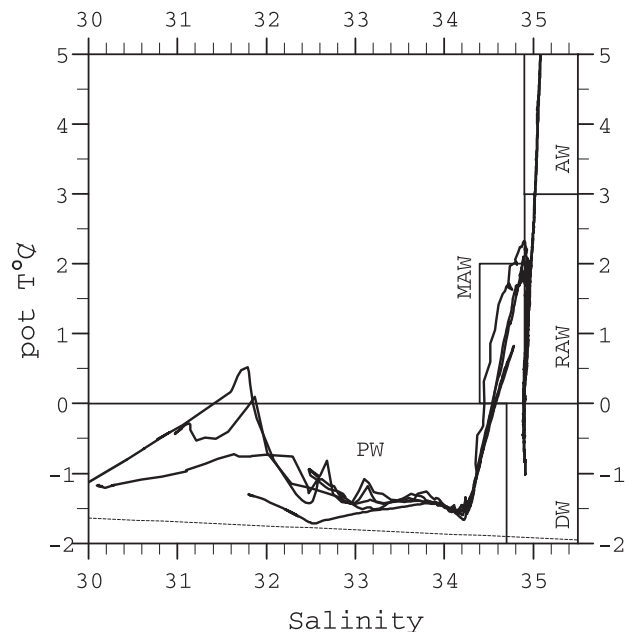
### 2.1. Sampling

[6] Hydrographic data (salinity and temperature) and samples for DOC determination were collected during cruises ARK XIII/3 (August–September 1997) and ARK XIV/2b (September–October 1998) on FS *Polarstern*. Additionally, we obtained in situ fluorescence data during cruises ARK IX (May–June 1993) along one cross section at about 79°N and during ARK XIV/2b from sections between about 65° and 76°N. During ARK XIII/3 four oceanographic sections (A–D; Figure 1) in the Fram Strait and one section across the Greenland Sea along the 75°N latitude (E; Figure 1) were sampled. During ARK XIV/2b we extended our survey to the south with cross sections at 75°N (F; Figure 1), 71°N (G; Figure 1), two sections across the Denmark Strait (H + I; Figure 1), a short section across the Greenland Shelf south of 66°N (J; Figure 1), and a less frequently sampled section crossing from the Greenland Basin into the Lofoten Basin in the Norwegian Sea (Figure 1).

### 2.2. Principal Water Masses and Currents

[7] The sampling area (Fram Strait, Nordic Seas, and Denmark Strait) is characterized by several deep basins (Figure 1) which communicate through lateral exchanges of water masses characterized by temperature and salinity (Figure 2 and Table 1). There are two main large-scale currents in the study area. The first is the Norwegian Atlantic Current (NAC; Figure 1) which transports warm and saline Atlantic water masses northward. These Atlantic Waters (AW) enter the Arctic Ocean through the Fram Strait (West Spitzbergen Current or WSC) and through the Barents Sea (Figure 1). Part of the AW recirculates (Return Atlantic Water, RAW) in the Fram Strait area, while the major portion of AW enters the polar ocean. After being modified along its way the “Modified” Atlantic Water (MAW) exits the Arctic Ocean on the western side of Fram Strait, where it can be found together with the RAW and the overlying lighter Polar Waters (PW) in the EGC (Figure 1). The EGC extends along the entire Greenland coast from Fram Strait to Denmark Strait and transports also deep waters stemming from the Arctic due to its barotropic flow component.

[8] AW is easy to identify because of its high salinity and temperature (Figure 2). In the WSC it is found between the



**Figure 2.** Characteristic temperature and salinity values for typical water masses observed in the sampling area. PW, Polar Water; DW, Deep Water; RAW, Return Atlantic Water; MAW, Modified Atlantic Water; AW, Atlantic Water. Dotted line represents the freezing points at the different salinities.

surface and about 600 m depth. RAW and MAW still form a maximum in temperature and salinity within the EGC (at roughly 250 m), but since it is often difficult to distinguish the two water masses we refer to both as RAW in the following text. The PW above RAW occupies a layer of 100–150 m depth and carries pack ice southward. PW is a pragmatic term and includes all waters with salinities below 34.0 and temperatures below 0°C (Figure 2). It contains waters of diverse origins, such as river runoff, Eurasian shelf water, ice and snow meltwaters, and Pacific waters which mix in the Arctic Ocean to form PW. The deep waters of the EGC originate in the Canadian Basin (CBDW, core at about 1500 m depth) and in the Eurasian Basin (Eurasian Basin Deep Water (EBDW), core at about 2000 m depth). Other identifiable deep water masses in the study area are GSDW and Norwegian Sea Deep Water (NSDW; Table 1).

### 2.3. Measurements

[9] Hydrographic data were collected with a SeaBird SBE 911 + CTD system with a pumped TC-duct and duplicate sensors. Water sampling was performed by a Carousel rosette sampler equipped with 24 Niskin bottles of 12 l. Calibration of hydrographic sensors included lab and in situ calibrations, for the latter a SBE35 deep sea reference thermometer has been used. Fluorescence was determined with an in situ backscatter fluorescence probe (Dr. Haardt, Optic & Mikroelektronik, Germany) mounted onto the CTD system. The in situ probe has fixed excitation (350–460 nm) and emission (550 nm) wavelengths chosen based on empirical calibrations with terrigenous humic substances. These wavelengths were found to give the optimal signal-to-noise ratio and superior resolution relative to specific narrow band excitation

**Table 1.** DOC Concentrations in Nordic Seas Water Masses

Water Mass	Depth, m	Salinity, ‰	Pot. Temperature, °C	DOC $\pm$ SD (n), $\mu\text{M}$
PW	0–200	<34.70	<0.0	75.8 $\pm$ 10.2 (160)
AW	50–600	>34.90	>3.0	58.2 $\pm$ 4.9 (54)
RAW	50–500	>34.90	>0.0	58.4 $\pm$ 5.1 (44)
Intermediate water	300–1500	<34.92	>−0.5	53.3 $\pm$ 3.6 (66)
Unspecified deep water	1500–2000	>34.70	<0.0	51.6 $\pm$ 3.6 (20)
CBDW	1500–1800	>34.92	−0.8 to −0.5	47.2 (1)
EBDW	1800–2500	>34.92	<−0.8	49.8 $\pm$ 2.0 (20)
GSDW	>2500	34.88–34.90	<−1.0	49.5 $\pm$ 2.0 (22)
NSDW	>2000	<34.92	<−0.5	47.5 $\pm$ 1.8 (4)

and emission wavelengths (Ex/Em = 340/420 nm) for the detection of terrigenous DOM. The in situ fluorescence probe used in this study was specifically designed to collect fluorescence data during CTD casts allowing real-time data collection along with other oceanographic parameters, matching their high spatial resolution.

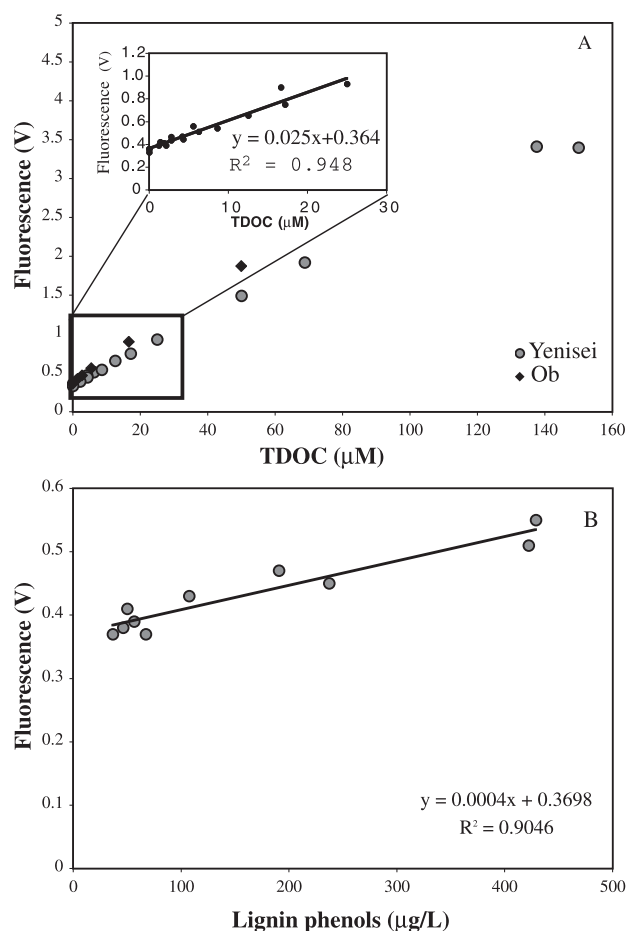
[10] To determine the response of the in situ fluorometer to various concentrations of terrigenous DOC (TDOC) and to use the collected data quantitatively, we conducted calibration experiments by mixing water from the Russian rivers, Ob and Yenisei (~650  $\mu\text{M}$  DOC), with AW (salinity = 35) from Fram Strait. We found a strong linear relationship between the concentration of TDOC and the fluorescence signal (Ex: 350–460 nm; Em: 550 nm) of the in situ probe over a broad range of concentrations (Figure 3a). In the lower concentration range (Figure 3a, insert), typically encountered in PW, the relationship ( $r^2 = 0.948$ ) is best described by the following linear equation:

$$F(350 - 460/550) = 0.025 \times \text{TDOC} + 0.364. \quad (1)$$

The in situ fluorescence measurements were also strongly related to lignin phenol concentrations determined in ultrafiltered DOM sampled in PW (Figure 3b) indicating that the in situ fluorescence probe detects DOM coming from terrestrial vegetation. The strong positive relationships between TDOC and the fluorescence signal from the probe together with detailed chemical information on DOM with elevated fluorescence values established the probe as a reliable, fast, and cost efficient solution to estimate the contribution of riverine or terrigenous DOM in PW. The y intercepts in Figures 3a and 3b also indicated the presence of a considerable background fluorescence potentially coming from marine-derived organic matter, however, the ultimate source of this fluorescence background is still unidentified. The background observed during the laboratory calibrations (Figure 3a) agreed well with the fluorescence background observed in surface waters of the Nordic Seas which showed little variation throughout the study area.

[11] Independent of the in situ probe, we used a laboratory-based high-resolution fluorescence spectrometer (QuantaMaster-1; Photon Technology International) [Coble *et al.*, 1993] to compare fluorescence characteristics of selected samples from Arctic rivers and the Nordic Seas. Fluorescence of 0.2  $\mu\text{m}$  filtered water collected from the rivers Ob (2 September 1999; 0.6 psu), Yenisei (12 Sep-

tember 2000; 0 psu), Mackenzie (31 July 1999), and the Nordic Seas was measured in 1 cm quartz cuvettes at 18°C. The instrument is equipped with a 75-watt xenon short arc lamp (Ushio Inc., Japan) as light source and monochromators for both the excitation and emission sides. The river samples were diluted twofold to threefold with water (Milli-Q-UV) prior to analysis in order to minimize quenching of fluorescence by inner filter effects. Excitation/emission matrices were generated by concatenating 42 individual emission spectra collected in ratio mode at excitation wavelengths between 260 and 465 nm using 5 nm increment steps. The first emission scan covered the spectral range from 272 to 492 nm and the last from 477 to 697 nm with data collected every 1 nm over an interval of 0.5 s. Photomultiplier voltage was set to 1000 V and band-pass widths were 5 nm for excitation and 2 nm for emission, respectively. Individual spectra were corrected for the water Raman scatter peak. Correction for excitation and emission characteristics of the instrument [Ewald *et al.*, 1983; Coble



**Figure 3.** Relationship between (a) in situ fluorescence (Ex: 350–460 nm; Em: 550 nm) and the concentration of TDOC during a calibration experiment (mixing of AW with water from the Ob and the Yenisei rivers. The insert focuses on the lower concentration range typically observed in PW of the EGC. Relationship between (b) in situ fluorescence (Ex: 350–460 nm; Em: 550 nm) and lignin phenol concentrations measured in samples from the same locations.



et al., 1993] was performed electronically by the software of the instrument. The fluorescence intensity (Ex/Em = 350/450 nm) of a standard solution of 1 ppb quinine sulfate in 0.05 M sulfuric acid (measured under sample conditions and corrected for solvent fluorescence) was used to convert sample fluorescence to quinine sulfate units (QSU).

[12] DOC samples were collected from Niskin bottles and filtered through precombusted GFF filters immediately after sampling. Samples were stored in precombusted sealed glass ampoules at  $-20^{\circ}\text{C}$  until analysis at the home laboratory. DOC was measured using the high-temperature combustion method and either a Shimadzu TOC 5000 analyzer [Benner and Strom, 1993] or MQ-1001 TOC Analyzer [Qian and Mopper, 1996] with slight modifications [Peterson et al., 2003]. To assure quality control we routinely determined deep-sea DOC standards supplied by J. Sharp (University of Delaware) or our own from Arctic Ocean deep water ( $50.5\text{ }\mu\text{M}$ , calibrated with the standard supplied by J. Sharp). The standards were used approximately on every second day of analysis and averaged  $47.5 \pm 0.7\text{ }\mu\text{M C}$  ( $n = 5$ ) for the Shimadzu TOC 5000, and  $45.4 \pm 1.4\text{ }\mu\text{M C}$  ( $n = 8$ ) for the MQ-1001 Analyzer. The deep water standard from the Arctic Ocean had an average DOC concentration of  $51.1 \pm 2\text{ }\mu\text{M C}$  ( $n = 27$ ) which was within the margin of error compared to cross calibration with Sharp's deep sea standard. The vast majority of the samples were measured with the MQ-1001 analyzer. With this instrument the relative standard deviation at the  $80\text{-}\mu\text{M}$  DOC level was on average 1.6% ( $n = 200$ ) and 2% at the  $50\text{-}\mu\text{M}$  DOC level ( $n = 309$ ). DOC values were not corrected for differences between instruments or deviations from the deep-sea standards.

### 3. Results and Discussion

#### 3.1. Distribution of DOC

[13] The horizontal and vertical distribution of DOC in the 10 cross sections (Figure 4) show locally elevated surface DOC values over the Greenland Shelf in the Fram Strait (Figures 4a–4d), and in the Greenland-Island Sea (Figures 4e–4j). In general, highest DOC concentrations were found in low-salinity water typically associated with the EGC surface layer (Figures 4 and 5). Average DOC concentrations in the upper 100 m ranged from  $81\text{ }\mu\text{M C}$  ( $60\text{--}118\text{ }\mu\text{M C}$ ) in the northernmost sections (Figures 4a and 4b) to  $59\text{ }\mu\text{M C}$  ( $53\text{--}68\text{ }\mu\text{M C}$ ) in the southernmost section (Figure 4j) indicating a general decrease of surface DOC concentrations from the north to the south. Depth profiles of DOC in the deep basins ( $>2500\text{ m}$ ; Figure 6) indicate highly variable DOC concentrations in the upper 150 m, except for the Irminger Basin. DOC decreased with depth in all deep basins to deep water ( $>1000\text{ m}$ ) values between  $45$  and  $60\text{ }\mu\text{M C}$  with no obvious latitudinal trend (Figure 6). Highest deep water concentrations were found in the Boreas Basin (Figure 6b) and lowest concentrations in the Lofoten Basin of the Norwegian Sea (Figure 6e). Compared to average DOC concentrations in ocean surface ( $<100\text{ m}$ ;  $60\text{--}90\text{ }\mu\text{M C}$ ) and deep waters ( $>1000\text{ m}$ ;  $35\text{--}45\text{ }\mu\text{M C}$ ; Benner, 2002], surface values presented in this study appear similar to the global average, while average deep water DOC concentrations are higher than the global average. The high deep water DOC values reported here

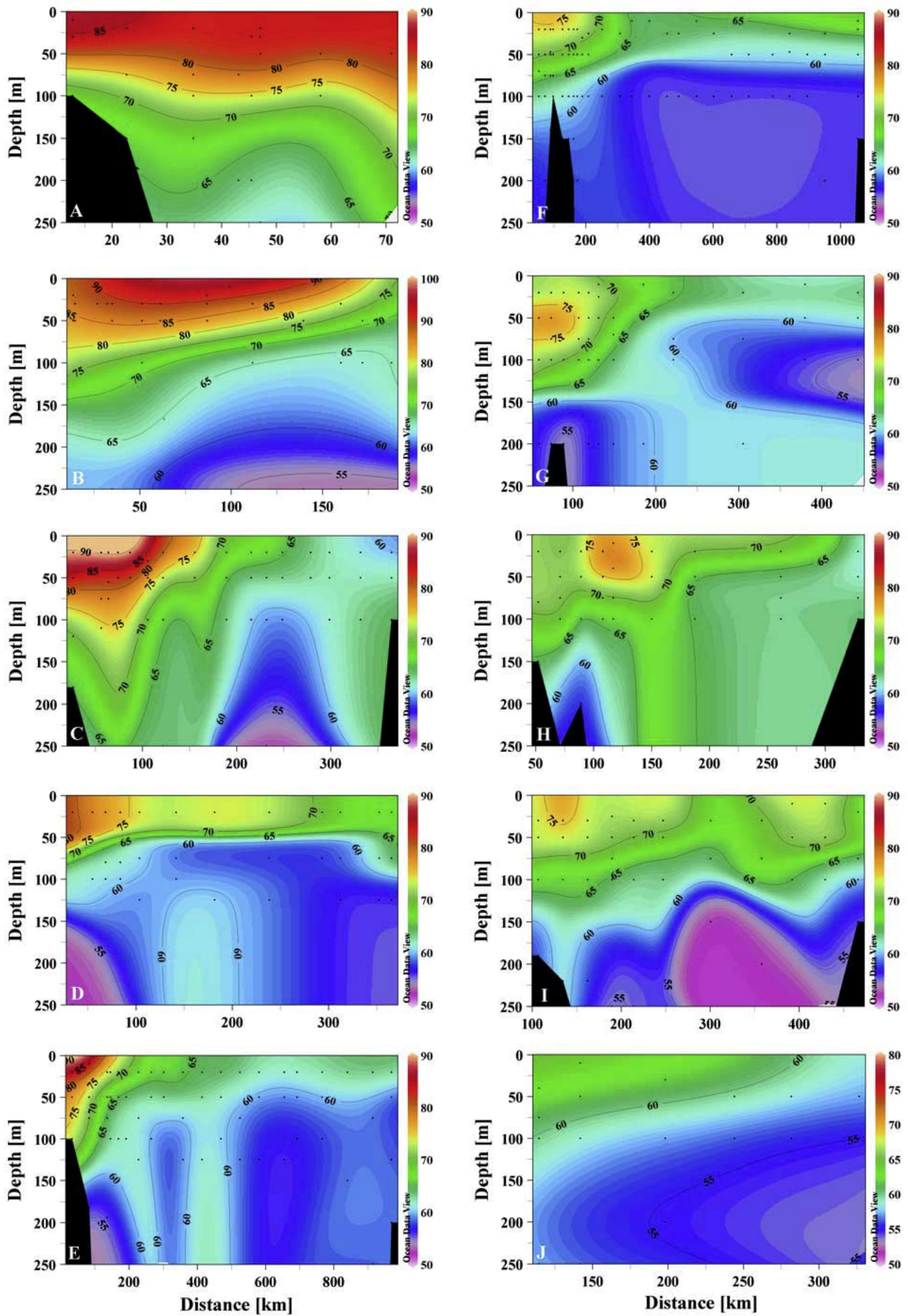
are consistent with reports of relatively high DOC concentrations in the deep basins of the central Arctic Ocean [Anderson et al., 1994; Bussmann and Kattner, 2000; Amon and Benner, 2003] and the deep Nordic Seas [Hansell and Carlson, 1998; Børshheim and Mykkestad, 1997; Børshheim, 2000; Amon and Benner, 2003], and appear to be a characteristic feature of high northern latitude ocean basins. The higher surface DOC concentrations ( $>100\text{ }\mu\text{M C}$ ) observed in the northernmost sections (Figures 4a–4c) are similar to DOC concentrations reported from surface waters of the central Arctic Ocean [Guay et al., 1999; Bussmann and Kattner, 2000; Amon and Benner, 2003]. These studies indicate that the elevated DOC concentrations were in part a result of abundant river water in Arctic Ocean surface waters consistent with the low salinities in EGC surface waters observed here (Figures 5a–5c).

[14] To get a better grasp on the distribution, fluxes, and origin of DOC we related them to specific water masses which can be distinguished based on temperature and salinity limits (Figure 2 and Table 1). As the most prominent water mass, AW is observed in most cross sections except the northernmost (Figures 5a and 5b) which did not extend far enough to the east to meet AW. AW flowing into the central Arctic Ocean can be identified by salinity ( $>34.9$ ) in the upper 600 m of the eastern parts of sections B, C, D, E, and F (Figures 5b–5f). AW entering the Arctic Ocean through Fram Strait had an average DOC concentration of  $60.6 \pm 5.4\text{ }\mu\text{M C}$  in 1997. In 1998 we sampled AW further south at  $71^{\circ}\text{N}$  and  $75^{\circ}\text{N}$  with DOC concentrations of  $57.6 \pm 4.2\text{ }\mu\text{M C}$ . DOC concentrations in AW appear to be quite consistent in the different zonal cross sections with an overall average DOC value of  $58.2\text{ }\mu\text{M C}$  for the Nordic Seas (Table 1) and a similar value ( $59\text{ }\mu\text{M C}$ ) assigned to AW in the central Arctic Ocean [Bussmann and Kattner, 2000]. AW was also collected in the Denmark Strait (Figures 5h and 5i) and was characterized by salinities  $>35$  and average DOC concentrations of  $60.1 \pm 4.9\text{ }\mu\text{M C}$ .

[15] RAW can be identified on the western side of sections C, D, E, F, and G at a depth between 50 and 500 m (Figures 5c–5g). Based on characteristic salinity ( $>34.9$ ) and potential temperature ( $>0^{\circ}\text{C}$ ) limits, RAW had an average DOC concentration of  $58.7 \pm 5.3\text{ }\mu\text{M C}$  in 1997 (transects north of  $75^{\circ}\text{N}$ ) and  $56.9 \pm 3.6\text{ }\mu\text{M C}$  in 1998 (transects south of  $75^{\circ}\text{N}$ ) with an overall average concentration of  $58.4\text{ }\mu\text{M C}$  (Table 1), closely resembling AW.

[16] Higher concentrations of DOC ( $>70\text{ }\mu\text{M C}$ ) were generally associated with PW (surface to  $75\text{--}200\text{ m}$ ) in the EGC with salinities  $<34.7$  and temperatures  $<0^{\circ}\text{C}$  (Figures 2 and 5, and Table 1). Minimum salinities of PW in summer were below 30, and lowest salinities were observed south of  $76^{\circ}\text{N}$  in 1998 (Figures 5f–5j) due to prolonged ice melt and thaw water runoff from Greenland. The horizontal extension of PW was between 200 and 300 km, and covered large portions of the northern Fram Strait (Figures 5b and 5c) and also Denmark Strait (Figures 5h and 5i). The average DOC concentration in PW was  $75.8 \pm 10.2\text{ }\mu\text{M C}$  (Table 1). Again, higher values were detected in 1997 north of  $75^{\circ}\text{N}$  ( $81.0\text{ }\mu\text{M C}$ ) than 1998 south of  $76^{\circ}\text{N}$  ( $71.2\text{ }\mu\text{M C}$ ; Figure 4).

[17] Water masses between 300 and 1500 m that do not belong to the above-mentioned water masses are referred to as intermediate water with a salinity  $<34.92$  and a potential





temperature  $>-0.5^{\circ}\text{C}$ . DOC concentration in these waters averaged  $54.3 \pm 3.9 \mu\text{M}$  in the northern sections in 1997 and  $52.6 \pm 3.1 \mu\text{M}$  in the southern sections in 1998. The overall average DOC concentration of intermediate water was  $53.3 \pm 3.6 \mu\text{M C}$  (Table 1). Deep water masses identified in Figure 2 have an average DOC concentration of  $51.6 \pm 3.6 \mu\text{M C}$  with NSDW having slightly lower values ( $47.5 \mu\text{M C}$ ) than the others (Table 1). In summary, the distribution of DOC concentrations (Figures 4 and 6, and Table 1) revealed two particular features, elevated concentration of DOC in low-salinity PW leaving the Arctic Ocean in the EGC, and relatively high concentrations of DOC in all the deep basins.

[18] Prior studies in Arctic Ocean and Nordic Seas surface waters [Guay *et al.*, 1999; Amon and Benner, 2003] have found a variable but inverse relationship between DOC and salinity, generally pointing to a freshwater (river) source of DOM in PW. The relationship between DOC and salinity observed in the upper 200 m of the EGC (Figure 7a) also showed the general trend of increasing DOC concentrations with lower salinity, however, the correlation was not very strong. The overall weak relationship, and differences between the two sampling periods and locations indicated the variable contribution of other freshwater (rivers and ice ablation) and/or DOM (rivers and marine phytoplankton) sources. Apparently, the relative importance of these factors varies greatly with location. This also explains that in situ fluorescence shows a much weaker correlation to bulk DOC concentration (Figure 7b) than to TDOC (Figure 3a). The  $y$  intercept in Figure 7b also indicates considerable fluorescence at zero DOC. This suggests that at least some of the fluorescence background is of inorganic nature.

### 3.2. Distribution of in Situ Fluorescence as an Indicator of the Origin of DOM in PW

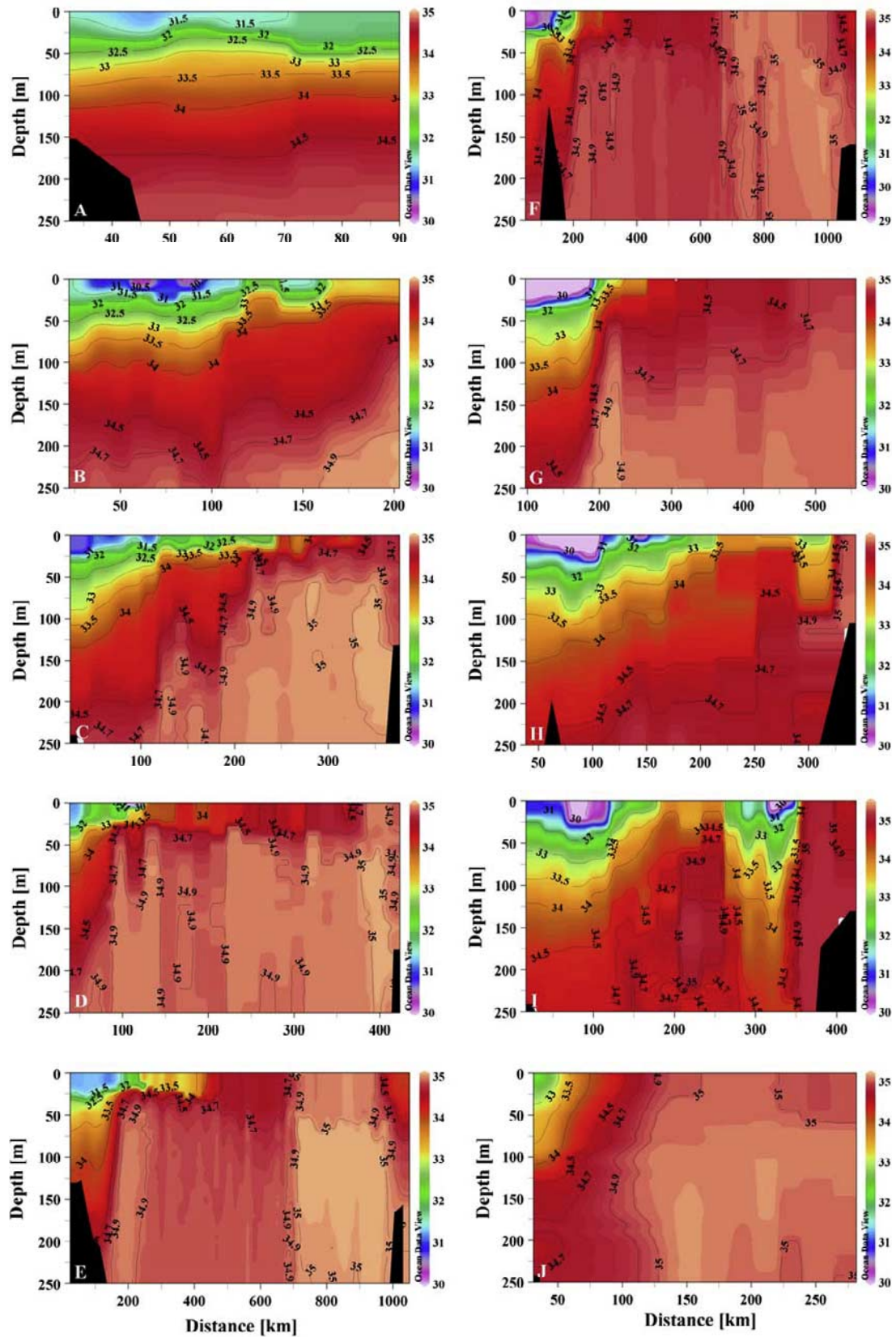
[19] In situ fluorescence data collected at  $79^{\circ}\text{N}$  in 1993 (Figure 8a) and at the sections sampled in 1998 (Figures 8b–8e) show a pronounced and reproducible pattern. A well-defined subsurface (50–100 m) fluorescence maximum observed in all sections from the northern Fram Strait at  $79^{\circ}\text{N}$  (Figure 8a) to the Denmark Strait at  $70^{\circ}\text{N}$  (Figures 8d and 8e) was the most striking feature in the fluorescence data set. At  $79^{\circ}\text{N}$  (Figure 8a) the fluorescence maximum was about 300 km away from the coast, while further south at  $75^{\circ}\text{N}$  and  $71^{\circ}\text{N}$  (Figures 8b and 8c) the core of the fluorescence was found closer to the Greenland coast, generally following the pathway of the EGC. In sections H and I (Figure 1) across the Denmark Strait (Figures 8d and 8e) we observed two patches with elevated fluorescence indicating that the well-defined single core of fluorescence observed all along the EGC was disintegrating. South of Denmark Strait in the Irminger Sea (Figure 8f), only a weak fluorescence maximum was detected in PW close to the coast. It appears that part of the high-fluorescence PW recirculated back into the Iceland Sea or drifted into the open North Atlantic at a depth level close to the surface. In general, we observed a decrease in the surface fluorescence

maximum from north ( $0.84 \text{ V}$  at  $79^{\circ}\text{N}$ ) to the south ( $0.48 \text{ V}$  in the Denmark Strait). AW was consistently characterized by low fluorescence throughout the study area (Figures 8b–8f). With the relationship between in situ fluorescence and TDOC (equation (1)), it is possible to roughly calculate the concentration of TDOC in PW and to estimate TDOC fluxes from the Arctic Ocean to the North Atlantic. We found that the concentration of TDOC in PW ranged from 1 to  $19 \mu\text{M}$  TDOC, which represents between 1.5 and 25% of total DOC.

[20] The fluorescence maximum in the EGC was associated with PW of a certain salinity (around 33) and potential temperature ( $-2^{\circ}$  to  $-1^{\circ}\text{C}$ ) in all sections from  $79^{\circ}\text{N}$  to Denmark Strait (Figures 9a–9d). This salinity and temperature range is typical for surface and upper halocline water in the Arctic Ocean, and is often associated with water originating in the Pacific Ocean because of its occasionally high silicate concentrations [Jones *et al.*, 1998]. We suggest that PW of this salinity (around 33) in Fram Strait also contains a significant amount of Eurasian river runoff and that this is responsible for most of the observed fluorescence signal. This idea is supported by the large export of TDOC observed in the EGC ( $3\text{--}10 \text{ Tg C yr}^{-1}$ ) [Opsahl *et al.*, 1999] which cannot be supplied by North American rivers alone (including Yukon and Anadyr) that annually deliver  $<3 \text{ Tg C}$  to the Arctic Ocean. Additionally, part of the North American river discharge is likely channeled through the Canadian Archipelago. Instead of proposing a new pathway for Pacific waters we suggest that there is an additional near-surface water mass in Fram Strait with very similar temperature-salinity characteristics. We believe that a large portion of the high fluorescence water observed in PW of the Fram Strait is formed on the Eurasian shelves from where it is advected into the central Arctic Ocean and on toward the Fram Strait via the Transpolar Drift where it mixes with waters originating in the Pacific Ocean. This is consistent with a recent study by Falck [2001] who argued for a 50/50 mix of AW and Pacific water in EGC subsurface waters resulting in a water mass with a salinity around 33 and high nutrient levels. A possible mechanism to produce water with high levels of fluorescence at a salinity around 33 would involve mixing of AW and river runoff under the influence of vertical mixing and sea ice formation on the Eurasian shelves [Amon, 2003]. The questions as to which processes are most important for the production of such water on the Eurasian shelves and where it happens exactly are not clear at the moment. Nevertheless, the high concentrations of terrestrially derived DOM in PW of the EGC can only be explained by a Eurasian shelf contribution. The fact that we were able to observe enhanced fluorescence in the subsurface layer of PW at various latitudes, from  $79^{\circ}\text{N}$  to  $65^{\circ}\text{N}$ , and over several years indicates that the outflow of terrigenous DOM is a characteristic feature of PW and the EGC.

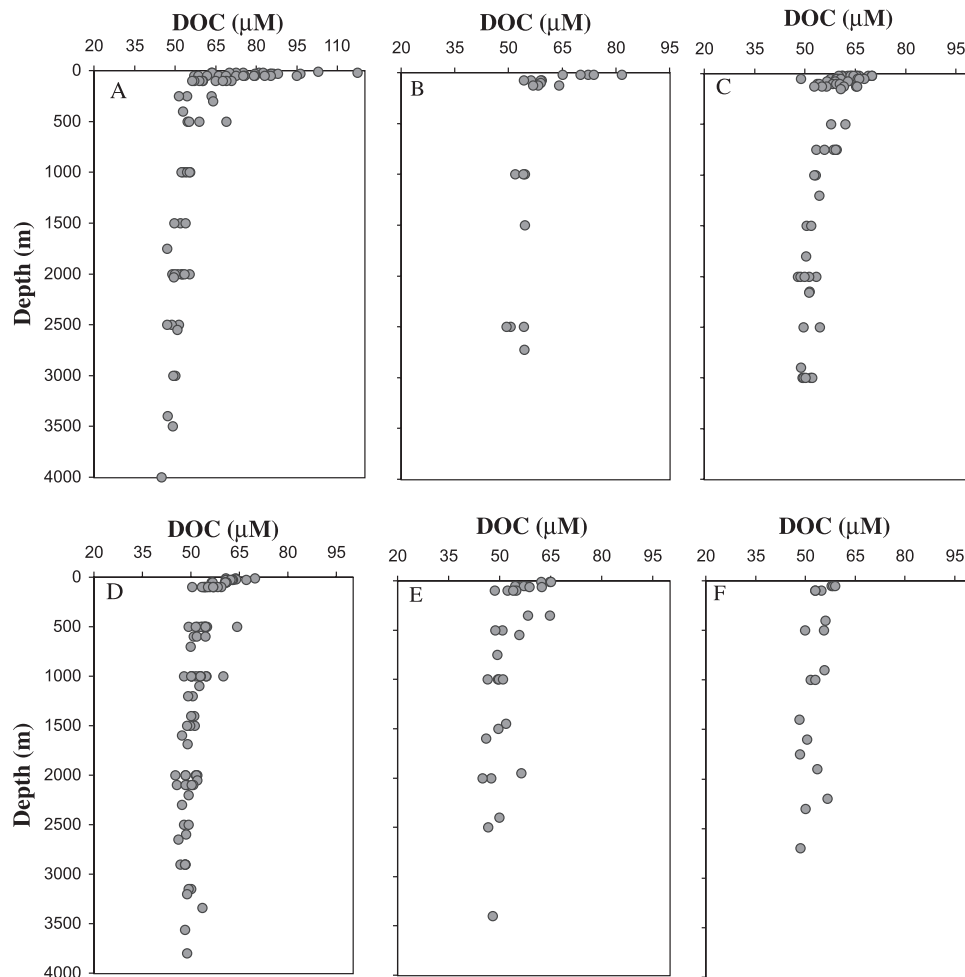
[21] To further confirm that fluorescence can be used to trace Arctic river DOM in PW of the EGC, we determined 3-D excitation/emission matrices of water samples from Ob,

**Figure 4.** (opposite) Distribution of DOC ( $\mu\text{M}$ ) in the upper 250 m of the oceanographic sections at ca.  $82^{\circ}\text{N}$  (a), at  $81^{\circ}\text{N}$  (b), at ca.  $79^{\circ}\text{N}$  (c), at  $78^{\circ}\text{N}$  (d), at  $75^{\circ}\text{N}$  (e + f), at  $71^{\circ}\text{N}$  (g), across the northern Denmark Strait (h), at ca.  $66^{\circ}\text{N}$  across the Denmark Strait (i), and at ca.  $65^{\circ}\text{N}$  (j). Figures were created with Ocean Data View (available at <http://www.awi-bremerhaven.de/GEO/ODV>).



**Figure 5.** Distribution of salinity in the upper 250 m of the oceanographic sections at ca. 82°N (a), at 81°N (b), at ca. 79°N (c), at 78°N (d), at 75°N (e + f), at 71°N (g), across the northern Denmark Strait (h), at ca. 66°N across the Denmark Strait (i), and at ca. 65°N (j). Figures were created with Ocean Data View (available at <http://www.awi-bremerhaven.de/GEO/ODV>).

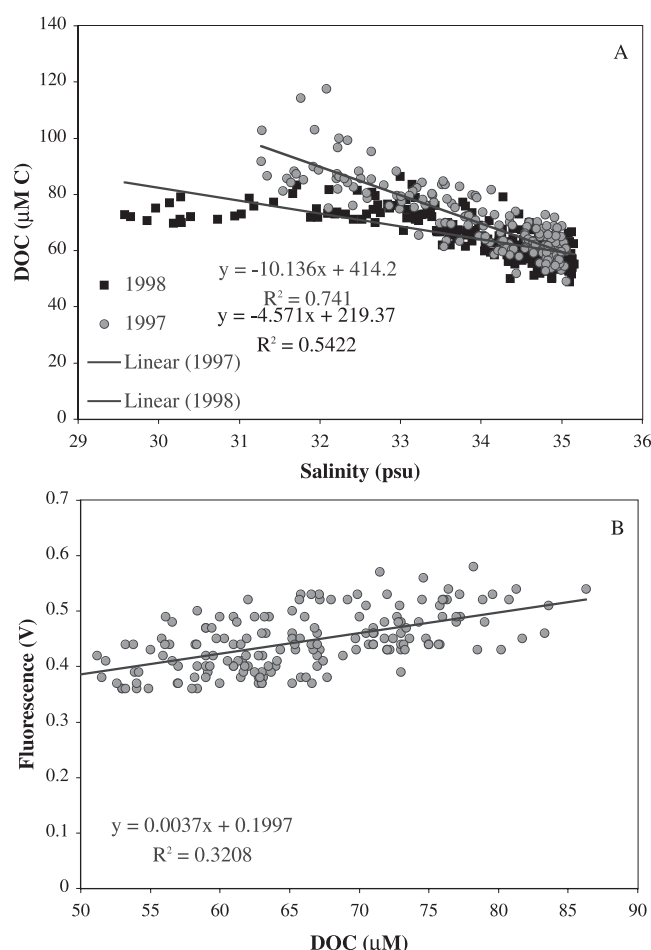




**Figure 6.** DOC depth profiles in (a) the northern Fram Strait (Lena Trough) in 1997, (b) the Boreas Basin in the northern Greenland Sea in 1997, (c) the central Greenland Sea in 1997, (d) the central Greenland Sea in 1998, (e) the Lofoten Basin in the Norwegian Sea in 1998, and (f) the Irminger Basin in 1998.

Yenisei, and the Mackenzie as well as from surface waters inside and outside PW in the EGC, and from one deep water sample (Figures 10a–10f). The contour plots (corrected for excitation and emission characteristics of the fluorometer; Figures 10a–10c) showed fluorescence patterns typical for riverine DOM with two humic-like fluorescence peaks [Coble, 1996; Del Castillo *et al.*, 1999]. The position of these peaks is very similar among the three Arctic rivers with distinct excitation/emission maxima at 270/455 and 320–325/435–445 nm for Ob and Yenisei, and a lower but still identifiable region of elevated signal intensities at an emission range of 425–440 nm upon excitation at 300–325 nm for Mackenzie, indicating a qualitatively uniform fluorescence signal for TDOM coming from different Arctic rivers. The wavelengths at which excitation/emission had their maximum in the PW sample (from section G; Figure 8) were also very similar to the river maxima (Figure 10d), only 7–24 times lower in fluorescence intensities. This indicates that the terrigenous humic-like fluorescence signal did not change qualitatively during the several years of transit from the rivers to the EGC [Schlosser *et al.*, 1995a]. Several studies report that riverine fluorescence signals

exhibit a conservative behavior upon mixing with the marine end-member over a wide salinity range, with no major qualitative and quantitative changes due to flocculation, biological degradation, or photodegradation [Klinkhammer *et al.*, 1997; Del Castillo *et al.*, 1999; Clark *et al.*, 2002]. However, both field studies in lower latitude systems and laboratory studies have demonstrated that extended exposure to sunlight can result in substantial photodegradation of terrestrially derived DOM [Amon and Benner, 1996; Vodacek *et al.*, 1997; Chen, 1999; Moran *et al.*, 2000; Chen *et al.*, 2002]. The qualitative effect of photobleaching on the fluorescence spectra appears to be modest, with a blue shift in the excitation/emission maximum of the humic-like fluorescence peak [Del Castillo *et al.*, 1999; Moran *et al.*, 2000] that still allows to match source and signal. Arguments that explain the strong terrestrially derived fluorescence signal in Fram Strait, far away from their riverine sources include (1) the intense humic-like fluorescence signal of DOC from major Arctic rivers (Figures 10a–10c), (2) the conservative mixing pattern of riverine DOC on Arctic shelves [Cauwet and Sidorov, 1996; Köhler *et al.*, 2003], (3) self-shading of photosensitive molecules



**Figure 7.** Relationship between (a) DOC concentrations and salinity in surface waters of the Nordic Seas during the cruises in 1997 (north of 75°N) and in 1998 (south of 75°N) and between (b) DOC concentrations and in situ fluorescence (Ex: 350–460 nm; Em: 550 nm) during the 1998 cruise.

due to the high light attenuation in the water column over the shelf areas, (4) partial protection of photoreactive dissolved material by sea ice, and (5) low irradiance in the Arctic on an annual scale. The contour plots of Greenland Gyre surface water (Figure 10e) and deep sea water (Figure 10f) represent background fluorescence since they contain minor amounts of TDOM based on lignin phenol and stable carbon isotope values [Opsahl *et al.*, 1999]. As mentioned before it is not known at this point where this background fluorescence, which is especially pronounced in deep water, comes from. Elevated humic-like fluorescence in deep water samples relative to surface waters was found in various oceanic regimes (e.g., Sargasso Sea, Pacific Ocean, eastern Atlantic Ocean) and was attributed to enhanced photobleaching occurring in surface waters [Chen and Bada, 1992; Mopper and Schultz, 1993; Determann *et al.*, 1996; Vodacek *et al.*, 1997]. It is noteworthy that marine water samples expressed additional emission maxima in the range of 310–334 nm upon excitation at 280 nm (Figures 10d–10f). This type of fluorescence is indicative for proteinaceous material [Coble *et al.*, 1990;

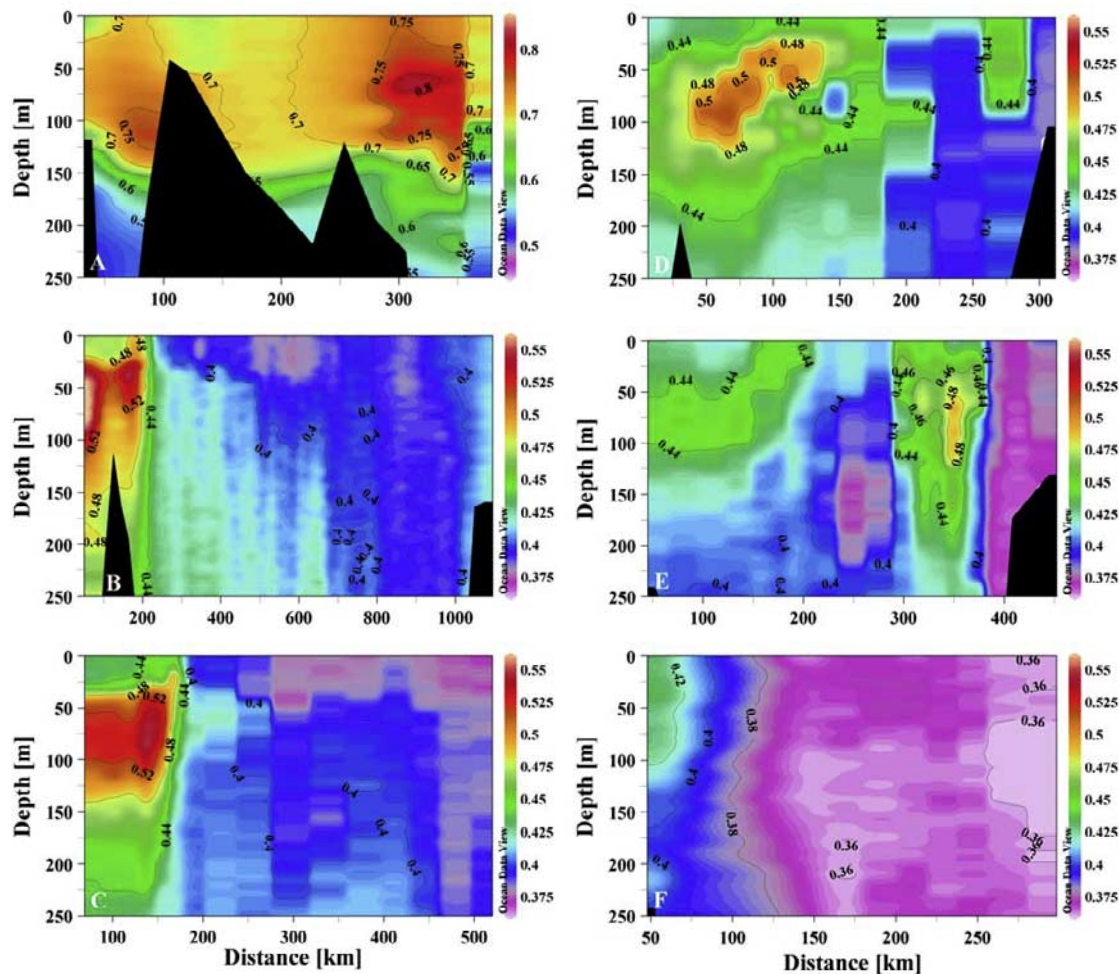
Mopper and Schultz, 1993; Coble, 1996; Determann *et al.*, 1998] and is likely derived from biological processes in the ocean thus indicating a marine source of this chromophoric material in contrast to the much higher humic-like fluorescence observed in the Arctic rivers and in PW.

### 3.3. DOC Fluxes Between the Arctic Ocean and the North Atlantic

[22] Since the 1970s a number of studies were devoted to the estimation of absolute volume transports of water masses through Fram Strait [Aagaard and Greisman, 1975; Hanzlick, 1983; Foldvik *et al.*, 1988; Mauritzen, 1996a, 1996b; Cisewski, 2001; Fahrbach *et al.*, 2001] and across the Greenland-Scotland Ridge [Dickson *et al.*, 1990; Mauritzen, 1996a, 1996b; Hansen and Østerhus, 2000; Smethie and Fine, 2001]. Although there still exist considerable uncertainties about net transports and their interannual and seasonal variation, together with the concentrations of DOC presented here, it is possible to estimate ranges of import and export of DOC to and from the Nordic Seas (Table 2). In order to simplify the discussion of lateral DOC transport, we will focus on PW and RAW in the EGC and AW in the NAC. This is reasonable since our main interest is not on the internal circulation within the Arctic Mediterranean but rather on the export of DOC out of the Arctic system into the world ocean. With respect to this, deep water transport in the Nordic Seas is poorly understood and less important due to topographic constraints in the south and was not considered here.

[23] Through Fram Strait the Nordic Seas exchange DOC with the Arctic Ocean (Table 2). The southward transport in the EGC can be partitioned in two subfractions, PW (27–49 Tg C yr<sup>-1</sup>) and RAW (53–103 Tg C yr<sup>-1</sup>; Table 2). AW northward flow with the WSC is on the order of 66–121 Tg C yr<sup>-1</sup> (Table 2), and about half that amount (41–47 Tg C yr<sup>-1</sup>) of DOC is exported to the Arctic Ocean through the Barents Sea branch of the NAC (Table 2) corresponding to the smaller volume flow there [ca. 2 Sv, 1 Sv = 10<sup>6</sup> m<sup>3</sup> s<sup>-1</sup>; Ingvaldsen *et al.*, 2002]. This would suggest that DOC exchanges between the Nordic Seas and the central Arctic Ocean are approximately in balance.

[24] In Denmark Strait the upper 600 m of the EGC deliver 90–112 Tg C yr<sup>-1</sup> to the North Atlantic (Table 2) of which 2.4–2.9 Sv [Dickson *et al.*, 1990; Smethie and Fine, 2001] or 50–60 Tg C yr<sup>-1</sup> are considered Denmark Strait Overflow, a precursor of North Atlantic Deep Water (NADW). Together with overflow water crossing the Iceland-Scotland Ridge [2.7 Sv; Dickson *et al.*, 1990] and assuming a DOC concentration of 55 μM C for overflow water (Table 2), the Nordic Seas export roughly 146–168 Tg C yr<sup>-1</sup> to the North Atlantic of which about 117 Tg C yr<sup>-1</sup> enter as precursor for NADW. In return, about 8 Sv (1 Sv through Denmark Strait) [Hansen and Østerhus, 2000], of AW enter the Nordic Seas importing 167–197 Tg C annually (Table 2). The strong relationship between TDOC and fluorescence (Figure 3) together with the high resolution of in situ fluorescence data (Figure 8) allows us to estimate also the export of TDOC in the EGC. According to the relationship in equation (1), PW and RAW export about 5 Tg TDOC through Denmark Strait into the North Atlantic (Table 2). A similar but slightly higher transport value (4.5–8.1 Tg TDOC yr<sup>-1</sup>) was calculated for the EGC at 75°N



**Figure 8.** In situ fluorescence (Ex: 350–460 nm; Em: 550 nm) in the upper 250 m of oceanographic sections at ca. 79°N in 1993 (a), at 75°N in 1998 (b), at 71°N in 1998 (c), section H across the northern Denmark Strait in 1998 (d), section I at ca. 66°N across the Denmark Strait in 1998 (e), and section J south of Denmark Strait in 1998 (f). Figures were created with Ocean Data View (available at <http://www.awi-bremerhaven.de/GEO/ODV>).

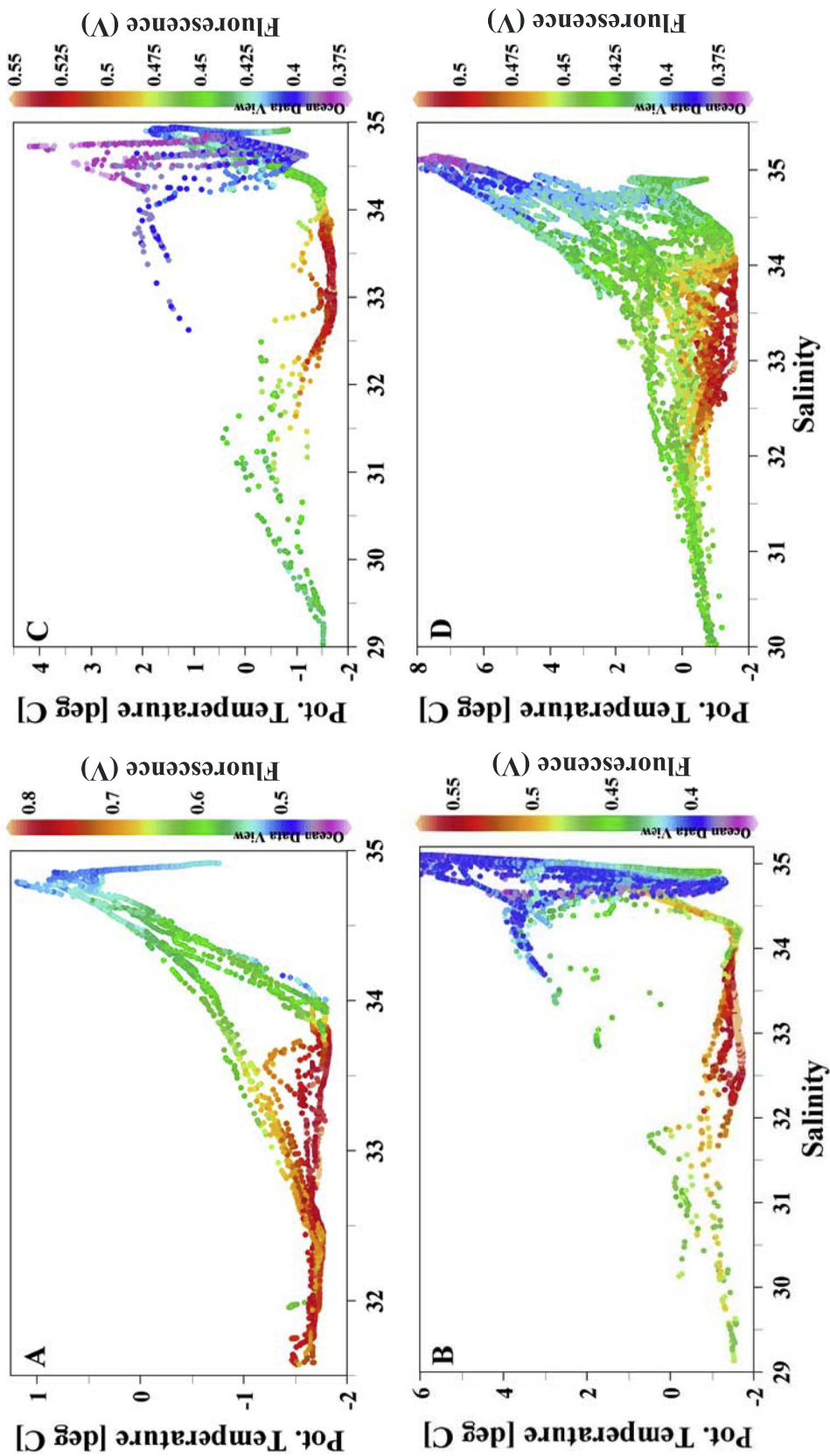
(Table 2). At the 79°N section from May 1993 (Figure 8a) higher fluorescence values ( $>0.8$  V) were observed which would translate to an export of about  $11\text{--}12\text{ Tg C yr}^{-1}$ , however, without concurrent DOC measurements and proper calibration of the probe for this year this number has to be viewed with caution. If we assume an annual river discharge of  $23\text{ Tg DOC}$  to the Arctic Ocean [Anderson, 2002] our TDOC export estimates indicate that  $22\text{--}51\%$  of this river carbon is exported from the Arctic Ocean in the EGC. This estimate is similar to a previous estimate ( $12\text{--}41\%$ ) based on detailed chemical characterization of ultrafiltered DOM [Opsahl et al., 1999].

[25] We observed considerable amounts of TDOC at several latitudinal cross sections through the EGC and over several years, and therefore consider our export estimates for TDOC to be representative, but at the same time we realize that sampling was limited to the August to October period and the relative amount of TDOC (fluorescence) could change over the course of the year as does the volume transport [Woodgate et al., 1999]. The variability of TDOC in the EGC reflects the heterogeneous distribution of river

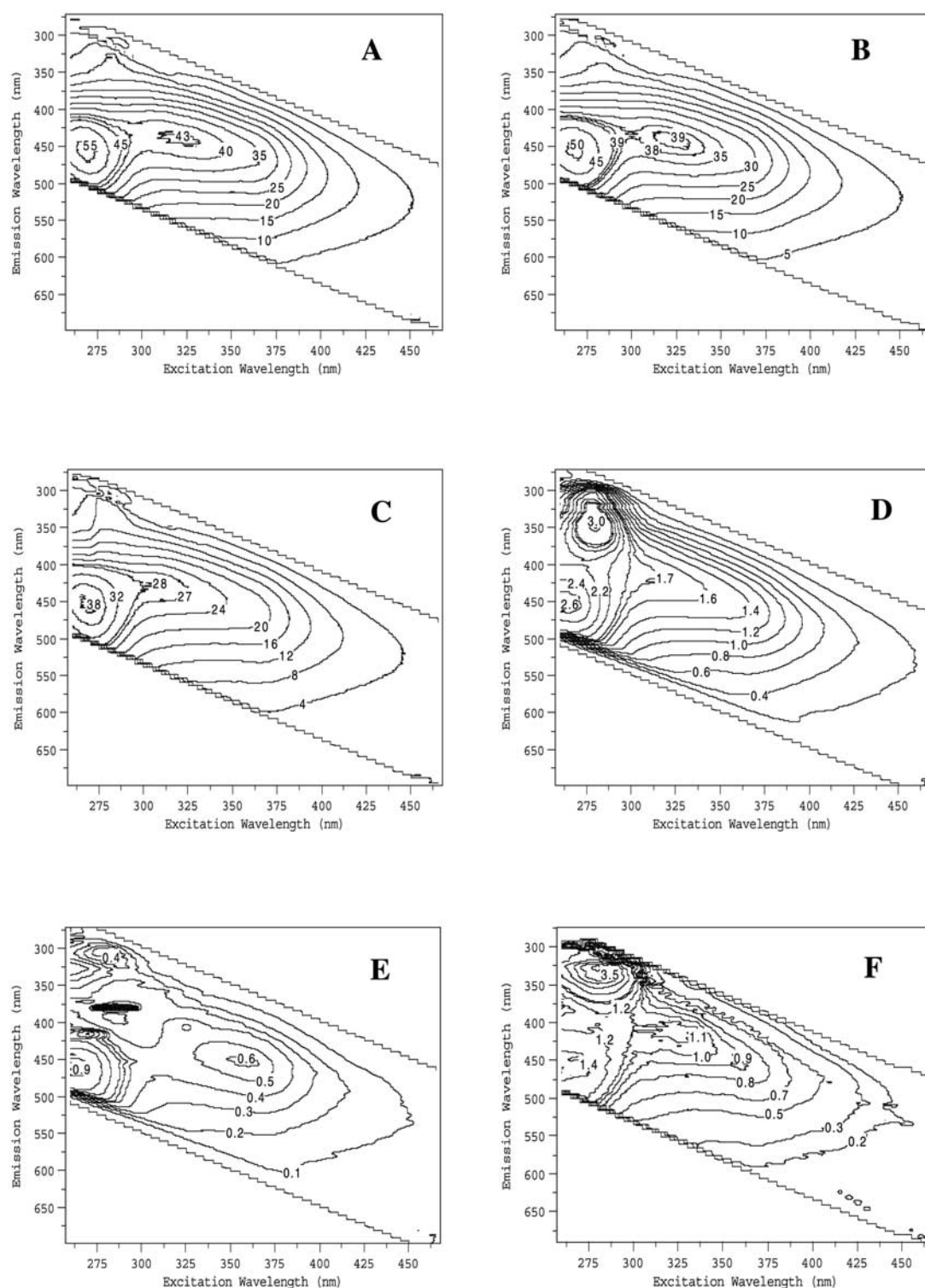
water within the Arctic Ocean surface [Opsahl et al., 1999; Amon and Benner, 2003]. The ultimate fate of Arctic river DOM is not well understood but a recent study by Jones et al. [2003] traced Pacific water, which we believe has a strong Arctic river component, deep into the North Atlantic. The fact that we find significant amounts of DOC derived from Arctic rivers far away from its source indicates that this material survived several years of transit through the Arctic Ocean [Schlosser et al., 1995a]. This is consistent with our finding that DOM discharged by the two Russian rivers, Ob and Yenisei, is largely refractory [Köhler et al., 2003].

[26] If we balance the lateral exchanges of DOC in the Nordic Seas we end up with a total annual import of  $247\text{--}349\text{ Tg C}$  and an export of roughly  $243\text{--}337\text{ Tg C}$ . Considering the error associated with these estimates the import and export fluxes are well balanced. The magnitude of the lateral DOC exchanges becomes obvious when it is compared to annual estimates of primary production in the Greenland ( $42\text{ Tg C yr}^{-1}$ ) [Sakshaug, 2003] and Norwegian Sea ( $160\text{ Tg C yr}^{-1}$ ) [Sakshaug, 2003]. Phytoplankton





**Figure 9.** Relationship between in situ fluorescence (Ex: 350–460 nm; Em: 550 nm), temperature, and salinity at (a) 79°N in 1993, (b) 75°N in 1998, (c) 71°N in 1998, and (d) in the Denmark Strait in 1998. Figures were created with Ocean Data View (available at <http://www.awi-bremerhaven.de/GEO/ODV>).



**Figure 10.** Contour plots of fluorescence excitation/emission matrices of water samples from (a) the Yenisei river (0.0 psu), (b) the Ob river (0.6 psu), (c) the Mackenzie river, (d) the EGC (fluorescence maximum), (e) Greenland Sea surface water (outside the fluorescence maximum), (f) Fram Strait deep water (2500 m). Fluorescence signals were corrected for water Raman peaks and excitation/emission characteristics of the fluorometer. Isolines represent QSU (1 QSU = 1 ppb quinine sulfate in 0.05 *M* sulfuric acid).

**Table 2.** DOC and TDOC Fluxes in the Nordic Seas<sup>a</sup>

Section	Water Mass	DOC, mg l <sup>-1</sup>	TDOC, mg l <sup>-1</sup>	Volume Flow, Sv = 10 <sup>6</sup> m <sup>3</sup> s <sup>-1</sup>	DOC Flux, Tg yr <sup>-1</sup>	TDOC Flux, Tg yr <sup>-1</sup>
Fram Strait	PW	0.99 ± 0.12	0.21	1.0–1.4 (–)	27.4–49.0 (–)	6.6–9.3
79°–81°N	RAW	0.76 ± 0.06	0.02	2.4–4.0 (–)	53.0–103.4 (–)	1.5–2.5
	AW	0.74 ± 0.06		3.1–4.8 (+)	66.4–121.1 (+)	...
75°N	PW	0.88 ± 0.12	0.07	1.3–2.4 (–)	31.2–75.7 (–)	2.9–5.6
	RAW	0.71 ± 0.05	0.02	2.6–5.2 (–)	54.1–95.9 (–)	1.6–2.5
	AW	0.70 ± 0.05		3.1–3.4 (+)	63.6–80.5 (+)	...
	AW <sup>b</sup>	0.70 ± 0.05		~2.0 (+)	40.9–47.1 (+)	...
Denmark Strait	PW	0.86 ± 0.12	0.06	~1.6 (–)	37.3–49.4 (–)	~3.1
64°–66°N	RAW	0.66 ± 0.06	0.02	~2.8 (–)	53.0–63.6 (–)	~1.8
	AW	0.73 ± 0.05		~0.9 (+)	19.3–22.1 (+)	...
Iceland-Scotland	overflow water	0.66 <sup>c</sup>		~2.7 (–)	~56.2 (–)	...
Ridge	AW	0.72 ± 0.05		~7.1 (+)	147.8–174.6 (+)	...

<sup>a</sup>Volume flux sources: *Dickson et al.* [1990], *Mauritzen* [1996a, 1996b], *Woodgate et al.* [1999], *Hansen and Østerhus* [2000], *Cisewski* [2001], *Fahrbach et al.* [2001], *Smethie and Fine* [2001], *Ingvaldsen et al.* [2002], and U. Schauer (personal communication, 2003).

<sup>b</sup>Indicates the Barents Sea branch of Atlantic Water.

<sup>c</sup>Not directly measured in this study; (–) indicates the southward flow, (+) indicates the northward flow. For the volume transport estimates that do not give a range an error of 10–28% should be assumed.

production in the Nordic Seas is efficiently remineralized during the summer and fall [Miller *et al.*, 1999] leaving little particulate organic matter for vertical export [Sauter *et al.*, 2001]. The large import of DOC from the North Atlantic (167–197 Tg C yr<sup>-1</sup>) is of the same magnitude as primary production and potentially supplies large amounts of DOC to Nordic Seas surface waters for deep convection (see below). Our samples were collected between September and October, months after the end of the spring bloom, and we think that most of the DOC (~60 µM C) found in Nordic Seas surface waters during the sampling period consists of refractory DOC and some (~15 µM) semilabile DOC (DOC which is utilized on timescales of months to a few years) left over from the productive season and/or DOC imported by the NAC.

### 3.4. Elevated Concentrations of DOC in High Northern Latitude Deep Waters and Vertical DOC Export

[27] DOC concentrations (~50 µM C) in all the deep water masses sampled in this study were 5–10 µM C higher than in deep waters of the Atlantic and Pacific Oceans [Hansell and Carlson, 1998]. Deep water DOC concentrations are a function of supply (convection and advection) and removal (largely by bacterial utilization). Since DOM sources are associated with surface waters, there needs to be a somewhat continuous supply of surface DOM to the deep basins of the Nordic Seas to counteract microbial mineralization of DOM. This happens most likely at the two deep water formation sites, the Greenland Sea and Iceland Sea convective gyres [Aagaard *et al.*, 1985]. The deep Norwegian Sea is ventilated by lateral exchanges with Greenland and Island Sea deep water.

[28] The Greenland Gyre is a relatively well-studied location for deep water renewal with recent estimates of vertical transport and flushing times of 0.6 Sv and 20–30 years, respectively [Budeus *et al.*, 1998]. From their long-term studies in the Greenland Sea, Budeus *et al.* concluded that recent deep water renewal in the Greenland Sea is a stepwise process at a rate of approximately 150 m yr<sup>-1</sup> but that deep (>1700 m) convective events were absent during the last decade. This means that surface water with elevated DOC concentration is continuously downwelled into the deep Greenland Sea. Knowing the typical prewinter surface

(<100 m) concentrations of 60.4 µM DOC and the DOC concentration of 50.3 µM C at 1500 m in the Greenland Gyre (Figures 5c and 5d) we can roughly estimate the annual vertical export of DOC (total and semilabile) as well as DOC mineralization rates in the Greenland Gyre assuming a steady state. With an approximate vertical transport of 0.6 Sv the Greenland convective gyre would produce an annual DOC export of 13.6 Tg of total DOC or 3.5 Tg of semilabile DOC, based on concentrations of 60 and 15 µM DOC, respectively. This compares to a vertical particulate organic matter flux of 0.3 Tg C yr<sup>-1</sup> in the Greenland Sea [Wassmann *et al.*, 2003]. The vertical transport of semilabile DOC contributes to the sequestration of carbon dioxide and is of a similar magnitude as a recent estimate (2.4 Tg C yr<sup>-1</sup>) for dissolved inorganic carbon sequestration in the Greenland Sea [Anderson *et al.*, 2000].

[29] The depth profiles of DOC in the Greenland Gyre (Figures 5c and 5d) show a gradient from the surface to about 1500 m depth where the DOC concentration decreased from 60 µM DOC to about 50 µM DOC. Below this depth the DOC concentrations remains fairly constant. Independent of the complex mechanisms establishing a variety of ventilation schemes for the upper 1000 m we estimate that on average it will take between 4 and 9 years for surface water to be transported to 1500 m, which would translate to a DOC mineralization rate between 1.1 and 2.5 µM C yr<sup>-1</sup>. The fact that DOC concentrations appear constant between 1500 and 3500 m (Figures 5c and 5d) indicates a much lower remineralization rate for DOM with DOC concentrations below 50 µM C. This is consistent with a deep water DOC remineralization rate of 0.05 µM C yr<sup>-1</sup> recently given by Hansell and Carlson [1998] for the deep North Atlantic. This means that in order to sustain a DOC concentration at about 50 µM C, the renewal of deep waters in the Nordic Seas needs to happen in a matter of a few decades rather than centuries.

[30] A similar vertical transport of DOM is necessary to sustain the relatively high DOC concentrations found in the Nansen, Amundsen, and Makarov Basins (no data exist for the deep Canadian Basin) in the central Arctic Ocean [Anderson *et al.*, 1994; Busmann and Katner, 2000; Amon and Benner, 2003]. Deep water formation in the Arctic Ocean is less well understood, but increasing evidence



points to deep water renewal along the continental slopes [Aagaard *et al.*, 1985; Anderson *et al.*, 1999; Rudels *et al.*, 2000a] with an estimated volume transport of 1.3–1.9 Sv [Mauritzen, 1996a, 1996b; Anderson *et al.*, 1999]. The relatively high DOC concentration (50  $\mu\text{M C}$ ) in the deep Eurasian and Makarov Basins suggest that a similar time-scale (decades) to the Greenland Gyre estimate is at work. Decadal timescales for the ventilation of the deep Eurasian Basin have also been suggested by Östlund *et al.* [1987] and Schlosser *et al.* [1995b] based on  $^{14}\text{C}$  data and other tracers. Using the above estimates for volume transport and 15  $\mu\text{M C}$  for the semilabile fraction of DOC, we estimate a vertical DOC transport of 7.4–10.8 Tg C  $\text{yr}^{-1}$  in the central Arctic Ocean. Lateral exchanges of deep waters have been shown to occur between the Eurasian, the Greenland, and the Norwegian Basins, but typical characteristics (low salinity) of Nordic Seas deep waters disappear rapidly north of Fram Strait [Rudels *et al.*, 2000b] indicating that lateral exchange from GSDW to the EBDW is not the dominating mechanism by which EBDW is ventilated. Patterns in the DOC concentrations of the deep basins (Table 1) indicate similar values for the GSDW and EBDW but lower values for NSDW. Assuming a constant remineralization rate for deep water DOC this pattern suggests that GSDW and EBDW receive comparable inputs of DOC by convection, while NSDW receives DOC by lateral input during which DOC concentration would decrease. With a volume of 986,600  $\text{km}^3$  for NSDW and a lateral exchange of about 0.7 Sv [Bönisch and Schlosser, 1995] it would take about 45 years to renew NSDW, enough time to remineralize 2–3  $\mu\text{M C}$  DOC based on a 0.05- $\mu\text{M C yr}^{-1}$  remineralization rate.

[31] Together, the Arctic Ocean and the Greenland Sea have a net DOC export between 11 and 15 Tg C  $\text{yr}^{-1}$  which is roughly 9–13% of the global vertical DOC export [Druffel *et al.*, 1992; Hansell, 2002]. Recent studies on NADW formation estimate that 5.6 Sv of NADW precursor are crossing the Greenland-Scotland Ridge [Dickson *et al.*, 1990], gaining in volume by entrainment down the continental slope to about 10.7 Sv [Dickson *et al.*, 1990], and together with deep water formation in the Labrador Sea reaching a total of 17.2 Sv [Smethie and Fine, 2001]. Assuming a concentration of 10  $\mu\text{M C}$  of semilabile DOC in NADW source waters the annual net DOC export would be around 21 Tg C for Greenland-Scotland Ridge area. As much as 36 Tg DOC  $\text{yr}^{-1}$  could be removed from the ocean surface for decades to centuries at the deep water formation sites in the Arctic Ocean, Nordic Seas, and across the Greenland-Scotland Ridge, excluding the Labrador Sea. Net DOC export of a similar magnitude (13 Tg DOC  $\text{yr}^{-1}$ ) has recently been suggested for North Pacific Intermediate Water [Hansell *et al.*, 2002].

[32] This study demonstrated that high northern latitude oceans have a significantly elevated prewinter and deep water DOC concentration compared to other ocean basins and that the higher concentrations can be sustained for decades. We believe that one reason for this is the high concentration of semilabile DOC in the NAC and downwelling of this semilabile DOC at the deep water formation sites. Changes in DOC concentrations are especially important in areas of deep water formation where semilabile DOC can be removed from the ocean surface for centuries. Most studies in Southern Ocean deep water formation areas have

reported very low concentrations of DOC, typically between 38 and 55  $\mu\text{M C}$  in surface water and deep water concentrations between 34 and 46  $\mu\text{M C}$  [Kähler *et al.*, 1997; Ogawa *et al.*, 1999; Carlson *et al.*, 2000]. Particularly, the amount of semilabile DOC is thought to be small in this area [Carlson *et al.*, 2000; Kirchman *et al.*, 2001]. It will be crucial to learn more about the mechanisms that determine the concentration of semilabile DOC in order to constrain the potential of fluctuating DOC concentrations in the global ocean. The distribution of DOM in the Nordic Seas and the central Arctic Ocean is largely determined by the physical oceanography of the region.

[33] **Acknowledgments.** We thank the captain, scientists, and crew of the R/V *Polarstern* for their help. We especially want to thank R. Benner for lignin phenol data; L. Tranvik for supplying the Mackenzie river sample; W. Schneider, S. Ronski, P. Louchuarn, B. Rost, and A. Terbrüggen for their help with sampling; K. Ohm for his help with the fluorescence probe; and U. Westernströer and C. Hartmann for their help with DOC analysis. Valuable discussions of volume transports with U. Schauer, E. Fahrbach, G. Rohardt, and R. Woodgate are also highly appreciated, and comments by R. Benner and two anonymous reviewers improved an earlier version of the manuscript. Funding during the writing of this manuscript came from the EC-project COMET and the German Federal Ministry of Education and Research (BMBF; Siberian River run-off, FKZ 03G0547A).

## References

- Aagaard, K., and P. Greisman, Toward new mass and heat budgets for the Arctic Ocean, *J. Geophys. Res.*, 80(27), 3821–3827, 1975.
- Aagaard, K., J. H. Swift, and E. C. Carmack, Thermohaline circulation in the Arctic Mediterranean Seas, *J. Geophys. Res.*, 90, 4833–4846, 1985.
- Amon, R. M. W., The role of dissolved organic matter for the Arctic Ocean carbon cycle, in *The Arctic Ocean Organic Carbon Cycle: Present and Past*, edited by R. Stein and I. R. Mac Donald, pp. 83–99, Springer-Verlag, New York, in press, 2003.
- Amon, R. M. W., and R. Benner, Photochemical and microbial consumption of dissolved organic carbon and dissolved oxygen in the Amazon River system, *Geochim. Cosmochim. Acta*, 60(10), 1783–1792, 1996.
- Amon, R. M. W., and R. Benner, Combined neutral sugars as indicators of the diagenetic state of dissolved organic matter in the Arctic Ocean, *Deep Sea Res.*, Part I, 50(1), 151–196, 2003.
- Anderson, L., K. Olsson, and A. Skoog, Distribution of dissolved inorganic and organic carbon in the Eurasian basin of the Arctic Ocean, in *The Polar Oceans and Their Role in Shaping the Global Environment*, edited by O. Johannessen, R. Muench, and J. Overland, pp. 255–262, AGU, Washington, D.C., 1994.
- Anderson, L. G., DOC in the Arctic Ocean, in *Biogeochemistry of Marine Dissolved Organic Matter*, edited by D. A. Hansell and C. A. Carlson, pp. 665–683, Academic, San Diego, Calif., 2002.
- Anderson, L. G., E. P. Jones, and B. Rudels, Ventilation of the Arctic Ocean estimated by a plume entrainment model constrained by CFCs, *J. Geophys. Res.*, 104(C6), 13,423–13,429, 1999.
- Anderson, L. G., M. Chierici, E. Fogelquist, and T. Johannessen, Flux of anthropogenic carbon into the deep Greenland Sea, *J. Geophys. Res.*, 105(C6), 14,339–14,345, 2000.
- Benner, R., Chemical composition and reactivity, in *Biogeochemistry of Marine Dissolved Organic Matter*, edited by D. A. Hansell and C. A. Carlson, pp. 59–90, Academic, San Diego, Calif., 2002.
- Benner, R., and M. Strom, A critical evaluation of the analytical blank associated with DOC measurements by high-temperature catalytic oxidation, *Mar. Chem.*, 41, 153–160, 1993.
- Bönisch, G., and P. Schlosser, Deep water formation and exchange rates in the Greenland/Norwegian Seas and the Eurasian Basin of the Arctic Ocean derived from Tracer balances, *Prog. Oceanogr.*, 35, 29–52, 1995.
- Børsheim, K. Y., Bacterial production rates and concentrations of organic carbon at the end of the growing season in the Greenland Sea, *Aquat. Microb. Ecol.*, 21, 115–123, 2000.
- Børsheim, K. Y., and S. Mykkestad, Dynamics of DOC in the Norwegian Sea inferred from monthly profiles collected during 3 years at 66°N, 2°E, *Deep Sea Res.*, 44, 593–601, 1997.
- Broecker, W., The great ocean conveyor, *Oceanography*, 4(2), 79–89, 1991.
- Budeus, G., W. Schneider, and G. Krause, Winter convective events and bottom water warming in the Greenland Sea, *J. Geophys. Res.*, 103(C9), 18,515–18,527, 1998.

- Bussmann, I., and G. Kattner, Distribution of dissolved organic carbon in the central Arctic Ocean: The influence of physical and biological properties, *J. Mar. Syst.*, 27, 209–219, 2000.
- Carlson, C. A., H. Ducklow, and A. Michaels, Annual flux of dissolved organic carbon from the euphotic zone in the northwestern Sargasso Sea, *Nature*, 371, 405–408, 1994.
- Carlson, C. A., D. A. Hansell, E. T. Peltzer, and W. O. Smith, Stocks and dynamics of dissolved and particulate organic matter in the southern Ross Sea, Antarctica, *Deep Sea Res.*, 47, 3201–3225, 2000.
- Cauwet, G., and I. Sidorov, The biogeochemistry of Lena River: Organic carbon and nutrients distribution, *Mar. Chem.*, 53, 211–227, 1996.
- Chen, R. F., In situ fluorescence measurements in coastal waters, *Org. Geochem.*, 30, 397–409, 1999.
- Chen, R. F., and J. L. Bada, The fluorescence of dissolved organic matter in seawater, *Mar. Chem.*, 37, 191–221, 1992.
- Chen, R. F., Y. Zhang, P. Vlahos, and S. M. Rudnick, The fluorescence of dissolved organic matter in the Mid-Atlantic Bight, part II, Topical Studies in oceanography, *Deep Sea Res.*, 49, 4439–4459, 2002.
- Cisewski, B., The transport of heat, mass and salt into the Arctic Ocean, *Rep. Polar Mar. Res.*, 378, 1–184, 2001.
- Clark, C. D., C. Jimenez-Morais, G. Jones II, E. Zenardi-Lamardo, C. A. Moore, and R. G. Zika, A time-resolved fluorescence study of dissolved organic matter in a riverine to marine transition zone, *Mar. Chem.*, 78, 121–135, 2002.
- Coble, P., Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy, *Mar. Chem.*, 51, 325–346, 1996.
- Coble, P. G., S. A. Green, N. V. Blough, and R. B. Gagosian, Characterization of dissolved organic matter in the Black Sea by fluorescence spectroscopy, *Nature*, 348, 432–435, 1990.
- Coble, P. G., C. A. Schultz, and K. Mopper, Fluorescence contouring analysis of DOC intercalibration experiment samples: A comparison of techniques, *Mar. Chem.*, 41, 173–178, 1993.
- Copin-Montégut, G., and B. Avril, Vertical distribution and temporal variation of dissolved organic carbon in the north-western Mediterranean Sea, *Deep Sea Res., Part I*, 40, 1963–1972, 1993.
- Del Castillo, C. E., P. G. Coble, J. M. Morell, J. M. López, and J. E. Corredor, Analysis of the optical properties of the Orinoco River plume by absorption and fluorescence spectroscopy, *Mar. Chem.*, 66, 35–51, 1999.
- Denman, K., E. Hoffmann, and H. Marchant, Marine biotic responses to environmental change and feedbacks to climate, in *Climate Change 1995: The Science of Climate Change*, edited by J. T. Houghton et al., pp. 485–516, Cambridge Univ. Press, New York, 1996.
- De Souza Sierra, M., O. Donard, and M. Lamotte, Spectral identification and behavior of dissolved organic fluorescent material during estuarine mixing processes, *Mar. Chem.*, 58, 51–58, 1997.
- Determann, S., R. Reuter, and R. Willkomm, Fluorescent matter in the eastern Atlantic Ocean, part II, Vertical profiles and relation to water masses, *Deep Sea Res.*, 43, 345–360, 1996.
- Determann, S., J. M. Lobbes, R. Reuter, and J. Rullkötter, Ultraviolet fluorescence excitation and emission spectroscopy of marine algae and bacteria, *Mar. Chem.*, 62, 137–156, 1998.
- Dickson, R. R., E. M. Gmitrowicz, and A. J. Watson, Deep-water renewal in the northern North Atlantic, *Nature*, 344, 848–850, 1990.
- Druffel, E. R., P. M. Williams, J. E. Bauer, and J. R. Ertel, Cycling of dissolved and particulate organic matter in the open ocean, *J. Geophys. Res.*, 97(C10), 15,639–15,659, 1992.
- Ducklow, H. W., Ocean biogeochemical fluxes: New production and export of organic matter from the upper ocean, *Rev. Geophys.*, suppl. 33, 1271–1276, 1995.
- Ducklow, H. W., C. A. Carlson, N. R. Bates, A. H. Knap, and A. F. Michaels, Dissolved organic carbon as a component of the biological pump in the North Atlantic Ocean, *Philos. Trans. R. Soc. London*, 348, 161–167, 1995.
- Ewald, M., C. Belin, P. Berger, and J. H. Weber, Corrected fluorescence spectra of fulvic acids isolated from soil and water, *Environ. Sci. Technol.*, 17, 501–504, 1983.
- Fahrback, E., J. Meincke, S. Østerhus, G. Rohard, U. Schauer, V. Tverberg, and J. Verduin, Direct measurements of volume transports through Fram Strait, *Polar Res.*, 20(2), 217–224, 2001.
- Falck, E., Contribution of waters of Atlantic and Pacific origin in the north-east water polynya, *Polar Res.*, 20(2), 193–200, 2001.
- Ferrari, G., M. D. Dowell, S. Grossi, and T. Cristina, Relationship between the optical properties of chromophoric dissolved organic matter and total concentration of dissolved organic carbon in the southern Baltic Sea region, *Mar. Chem.*, 55, 299–316, 1996.
- Ferrari, G. M., and M. D. Dowell, CDOM absorption characteristics with relation to fluorescence and salinity in coastal areas of the southern Baltic Sea, *Estuarine Coastal Shelf Sci.*, 47, 91–105, 1998.
- Foldvik, A., K. Aagaard, and T. Tørresen, On the velocity field of the East Greenland Current, *Deep Sea Res., Part A*, 35, 1335–1354, 1988.
- Guay, C. K., G. K. Klinkhammer, K. K. Falkner, R. Benner, P. G. Coble, T. E. Whitledge, B. Black, F. J. Bussell, and T. A. Wagner, High-resolution measurements of dissolved organic carbon in the Arctic Ocean by in situ fiberoptic spectrometry, *Geophys. Res. Lett.*, 26, 1007–1010, 1999.
- Hansell, D., C. A. Carlson, and Y. Suzuki, Dissolved organic carbon export with North Pacific intermediate water formation, *Global Biogeochem. Cycles*, 16, 77–84, 2002.
- Hansell, D. A., DOC in the global carbon cycle, in *Biogeochemistry of Marine Dissolved Organic Matter*, edited by D. A. Hansell and C. A. Carlson, pp. 685–715, Academic, San Diego, Calif., 2002.
- Hansell, D. A., and C. A. Carlson, Deep-ocean gradients in the concentration of dissolved organic carbon, *Nature*, 395, 263–266, 1998.
- Hansen, B., and S. Østerhus, North Atlantic-Nordic Seas exchanges, *Prog. Oceanogr.*, 45, 109–208, 2000.
- Hanzlick, D. J., The West Spitzbergen Current: Transport, forcing and variability, Ph.D. dissertation, Sch. of Oceanogr., Univ. of Washington, Seattle, Wash., 1983.
- Hedges, J. I., Global biogeochemical cycles: Progress and problems, *Mar. Chem.*, 39, 67–93, 1992.
- Ingvaldsen, R., H. Loeng, and L. Asplin, Variability in the Atlantic inflow to the Barents Sea based on a one-year time series from moored current meters, *Cont. Shelf Res.*, 22, 505–519, 2002.
- Jones, E. P., L. G. Anderson, and J. H. Swift, Distribution of Atlantic and Pacific waters in the upper Arctic Ocean: Implications for circulation, *Geophys. Res. Lett.*, 25, 765–768, 1998.
- Jones, E. P., J. H. Swift, L. G. Anderson, M. Lipitz, G. Civitarese, K. K. Falkner, G. Kattner, and F. McLaughlin, Tracing Pacific water in the North Atlantic Ocean, *J. Geophys. Res.*, 108(C4), 3116, doi:10.1029/2001JC001141, 2003.
- Kähler, P., P. Bjørnsen, K. Lochte, and A. Antia, Dissolved organic matter and its utilization by bacteria during spring in the Southern Ocean, *Deep Sea Res.*, 44, 341–353, 1997.
- Kirchman, D., L., B. Meon, H. W. Ducklow, C. A. Carlson, D. A. Hansell, and G. Steward, Glucose fluxes and concentrations of dissolved combined sugars (polysaccharides) in the Ross Sea and Polar Front Zone, Antarctica, *Deep Sea Res., Part II*, 48, 4179–4197, 2001.
- Klinkhammer, G. K., C. S. Chin, C. Wilson, M. D. Rudnicki, and C. R. German, Distribution of dissolved manganese and fluorescent dissolved organic matter in the Columbia River estuary and plume as determined by in situ measurements, *Mar. Chem.*, 56, 1–14, 1997.
- Köhler, H., B. Meon, V. V. Gordeev, A. Spitz, and R. M. W. Amon, Dissolved organic matter (DOM) in the estuaries of Ob and Yenisei and the adjacent Kara-Sea, Russia, *Proc. Mar. Sci.*, 6, 281–309, 2003.
- Laane, R. W. P. M., and L. Koole, The relation between fluorescence and dissolved organic carbon in the Ems-Dollart estuary and the western Wadden Sea, *Neth. J. Sea Res.*, 15, 217–227, 1982.
- Macdonald, R. W., and E. C. Carmack, Tritium and radiocarbon dating of Canada Basin deep waters, *Science*, 259, 103–104, 1993.
- Mauritzen, C., Production of dense overflow waters feeding the North Atlantic across the Greenland-Scotland ridge, part I, Evidence for a revised circulation scheme, *Deep Sea Res.*, 43, 769–806, 1996a.
- Mauritzen, C., Production of dense overflow waters feeding the North Atlantic across the Greenland-Scotland Ridge, part II, An inverse model, *Deep Sea Res.*, 43, 807–835, 1996b.
- McKnight, D. M., E. W. Boyer, P. K. Westerhoff, P. T. Doran, T. Kulbe, and D. T. Andersen, Spectrofluorometric characterization of dissolved organic matter for indication of precursor material and aromaticity, *Limnol. Oceanogr.*, 46, 38–48, 2001.
- Miller, L. A., M. Chierici, T. Johannessen, T. T. Noji, F. Rey, and I. Skjelvan, Seasonal dissolved inorganic carbon variations in the Greenland Sea and implications for atmospheric CO<sub>2</sub> exchange, *Deep Sea Res.*, 46, 1473–1496, 1999.
- Mopper, K., and C. Schultz, Fluorescence as a possible tool for studying the nature and water column distribution of DOC components, *Mar. Chem.*, 41, 229–238, 1993.
- Moran, M. A., W. M. Sheldon Jr., and R. G. Zepp, Carbon loss and optical property changes during long-term photochemical and biological degradation of estuarine dissolved organic matter, *Limnol. Oceanogr.*, 45(6), 1254–1264, 2000.
- Nagata, T., Production mechanisms of dissolved organic matter, in *Microbial Ecology of the Oceans*, edited by D. Kirchman, pp. 121–152, John Wiley, New York, 2000.
- Ogawa, H., R. Fukuda, and I. Koike, Vertical distributions of dissolved organic carbon and nitrogen in the Southern Ocean, *Deep Sea Res.*, 46, 1809–1826, 1999.
- Opsahl, S., R. Benner, and R. M. W. Amon, Major flux of terrigenous dissolved organic matter through the Arctic Ocean, *Limnol. Oceanogr.*, 44, 2017–2023, 1999.

- Östlund, G. H., G. Possnert, and J. H. Swift, Ventilation rate of the deep Arctic Ocean from carbon 14 data, *J. Geophys. Res.*, 92(C4), 3769–3777, 1987.
- Parlanti, E., K. Wörz, L. Geoffroy, and M. Lamotte, Dissolved organic matter fluorescence spectroscopy as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs, *Org. Geochem.*, 31, 1765–1781, 2000.
- Peterson, M. L., S. Q. Lang, A. K. Aufdenkampe, and J. I. Hedges, Dissolved organic carbon measurement using a modified high temperature combustion analyzer, *Mar. Chem.*, 81, 89–104, 2003.
- Qian, J., and K. Mopper, Automated high-performance, high temperature combustion total organic carbon analyzer, *Anal. Chem.*, 68(18), 3090–3097, 1996.
- Rudels, B., R. D. Muench, J. Gunn, U. Schauer, and H. J. Friedrich, Evolution of the Arctic Ocean boundary current north of the Siberian shelves, *J. Mar. Syst.*, 25, 77–99, 2000a.
- Rudels, B., R. Meyer, E. Fahrbach, V. V. Ivanov, S. Østerhus, and D. Quadfasel, Water mass distribution in Fram Strait and over the Yermak Plateau, *Ann. Geophys.*, 18, 687–705, 2000b.
- Sakshaug, E., Primary production in the Arctic Seas, in *The Arctic Ocean Organic Carbon Cycle: Present and Past*, edited by R. Stein and I. R. MacDonald, Springer-Verlag, New York, in press, 2003.
- Sauter, E. J., M. Schlüter, and E. Süß, Organic carbon flux and remineralization in surface sediments from the northern North Atlantic derived from pore-water oxygen microprofiles, *Deep Sea Res.*, 48, 529–553, 2001.
- Schlosser, P., J. Swift, D. Lewis, and S. Pfirman, The role of the large-scale Arctic Ocean circulation in the transport of contaminants, *Deep Sea Res.*, 42, 1341–1367, 1995a.
- Schlosser, P., G. Bönisch, B. Kromer, H. H. Loosli, R. Bühler, R. Bayer, G. Bonani, and K. P. Koltermann, Mid-1980s distribution of tritium,  $^3\text{He}$ ,  $^{14}\text{C}$ , and  $^{39}\text{Ar}$  in the Greenland/Norwegian Seas and the Nansen Basin of the Arctic Ocean, *Prog. Oceanogr.*, 35, 1–28, 1995b.
- Smethie, W. M., and R. A. Fine, Rates of North Atlantic Deep Water formation calculated from chlorofluorocarbon inventories, *Deep Sea Res., Part I*, 48, 189–215, 2001.
- Vodacek, A., N. V. Blough, M. D. DeGrandpre, E. T. Peltzer, and R. K. Nelson, Seasonal variation of CDOM and DOC in the Middle Atlantic Bight: Terrestrial inputs and photooxidation, *Limnol. Oceanogr.*, 42, 674–686, 1997.
- Wassmann, P., et al., Particulate organic carbon flux to the seafloor, in *The Arctic Ocean Organic Carbon Cycle: Present and Past*, edited by R. Stein and I. R. MacDonald, Springer-Verlag, New York, in press, 2003.
- Williams, P., Heterotrophic bacteria and the dynamics of dissolved organic material, in *Microbial Ecology of the Oceans*, edited by D. L. Kirchman, pp. 153–201, John Wiley, New York, 2000.
- Woodgate, R. A., E. Fahrbach, and G. Rohard, Structure and transports of the East Greenland Current at  $75^\circ\text{N}$  from moored current meters, *J. Geophys. Res.*, 104(C8), 18,059–18,072, 1999.

---

R. M. W. Amon, Departments of Marine Sciences and Oceanography, Texas A&M University at Galveston, 5007 Avenue U, Galveston, TX 77551, USA. (amonr@tamug.edu)

G. Budéus and B. Meon, Alfred Wegener Institute for Polar and Marine Research, Columbusstrasse, 27515 Bremerhaven, Germany. (gbudeus@awi-bremerhaven.de; bmeon@awi-bremerhaven.de)