Chapter 14

DOC in the Arctic Ocean

Leif G. Anderson
Analytical and Marine Chemistry
Göteborg University
Göteborg, Sweden

I. INTRODUCTION

The objective of this chapter is to summarize the present knowledge on the input of terrigenous dissolved organic matter (DOM) to the Arctic Ocean, the input of marine DOM in water masses flowing into the Arctic from the Pacific and Atlantic oceans, and the distribution of terrigenous and marine-origin DOM within the Arctic Ocean. The Arctic Ocean is, together with the Greenland, Iceland, and Labrador seas, a major area of deep-water formation in the Northern Hemisphere (Anderson *et al.*, 1999). As this deep water contributes to the global thermohaline circulation and thus adds to the deep waters of all global oceans, it is of global interest to evaluate the vertical flux of DOM within the Arctic Ocean (and the other deep-water formation sites). In order to address the above aspects of DOM it is essential to consider the water mass formation and circulation within the area.

Biogeochemistry of Marine Dissolved Organic Matter

Several rivers draining large areas of Siberia and North America flow into the Arctic Ocean. The four dominating are the Ob, Yenisey, and Lena from Siberia and the Mackenzie from North America. In addition, much of the runoff from the Yukon River reaches the Arctic Ocean after entering the Bering Sea and flowing north through the Bering Strait. Consequently, the Arctic Ocean receives much freshwater, about 10% of the global runoff (Aagaard and Carmack, 1989), while constituting only about 1% of the global ocean volume (Menard and Smith, 1966). These rivers, with the major fractions supplied by Siberian rivers, add large amounts of terrigenous DOM to the Arctic Basins (e.g. Gordeev *et al.*, 1996). A significant fraction of this DOM is dissolved organic carbon (DOC), which is the focus of this review. The large terrestrial component of DOM distinguishes the Arctic Ocean from the Southern Ocean.

A. Water Masses and Circulation

Ocean water from the Pacific enters the Arctic Ocean through the Bering Strait and from the Atlantic, through the eastern Fram Strait and the Barents Sea (Fig. 1). Fresh water, in the form of runoff and sea ice meltwater mixes with ocean water in the upper Arctic Ocean and exits the Arctic Basin mostly through the Canadian

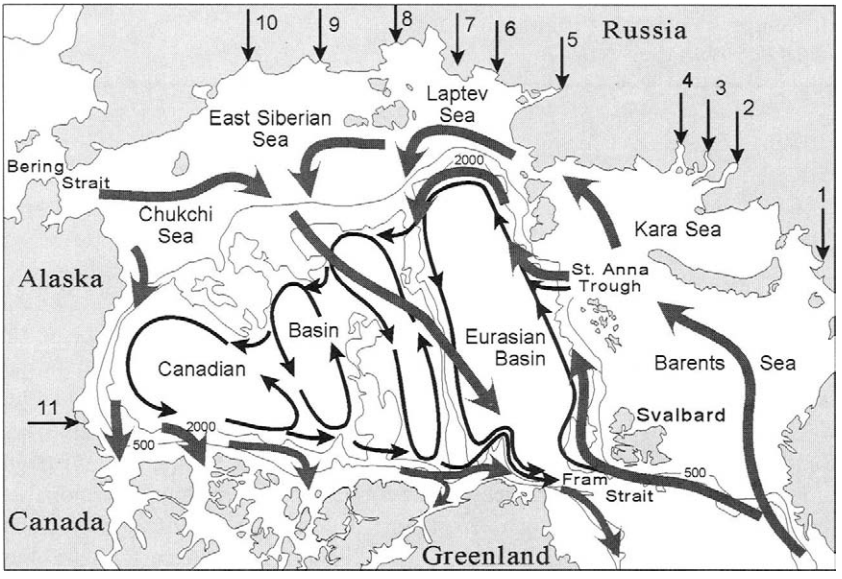

Figure 1 Map with geographic information and schematic circulation of surface water (gray arrows) and intermediate water (black arrows). The straight arrows indicate the mouths of the rivers included in Table I.

Archipelago and western Fram Strait (Jones *et al.,* 1998). Some of the upper waters are entrained and transported to deeper regions. Intermediate-depth water largely follows the topography, resulting in several large loops within the deep central Arctic Ocean (Rudels *et al.,* 1994). Deep water both enters and exits the Arctic Ocean through Fram Strait over a sill at a depth of about 2200 m.

The inflowing Pacific water is relatively fresh and contributes significantly only to the upper water masses. However, a small amount of high-salinity water formed during sea ice production penetrates to the deepest parts of the Canadian Basin (Jones *et al.,* 1995). The Atlantic water, on the other hand, has a salinity of close to 35 when entering the Fram Strait and the Barents Sea, but the temperature is high enough (around 4°C) for this water to stay at the surface. However, during the transit over the Barents Sea, heat is lost to the atmosphere and, together with brine release from sea-ice production, the density increases to form waters that penetrate to intermediate depths of the Arctic Ocean (e.g., Swift *et al.,* 1983; Schauer *et al.,* 1997). Most of this high-density water enters the Arctic Ocean through the St. Anna Trough, though some water of Atlantic origin passes through the Kara Sea into the Laptev Sea, with a fraction continuing into the East Siberian Sea before meeting water of Pacific origin (Jones *et al.,* 1998). The Atlantic water that flows through Fram Strait meets sea ice and the upper part of this warm water melts the sea ice, forming an approximately 100-m-thick surface water layer of low salinity (S ~34.2) and with temperatures close to the freezing point (Rudels *et al.,* 1996). This constitutes the formation of the lower halocline water (LHW) and prevents deep-water formation within the central Arctic Ocean. In addition, the LHW hampers the penetration of heat from the Atlantic Layer water to the overlying sea-ice cover.

The Pacific water, and to some extent the Atlantic water, transports significant amounts of nutrients into the Arctic Ocean shelf seas. The high nutrient supply and hydrographic conditions stabilizing the water column result in primary production rates that are high even in a global perspective. In the Bering–Chukchi Sea region, new production has been estimated to be 288 g C m^{-2} $year^{-1}$ (Hansell *et al.,* 1993). New productivity in the Barents Sea is also considered high, being still higher within the marginal ice zone (Sakshaug and Skjoldal, 1989). Because of the patchy productivity it is difficult to estimate a mean productivity rate, but the vertical carbon flux at 75 m, as simulated by a 3-D model, generally varied between 10 and 40 g C m^{-2} $year^{-1}$, depending on forcing conditions (Slagstad and Wassmann, 1996).

II. SOURCES OF DOC TO THE ARCTIC OCEAN

The highest concentrations of DOC in source waters to the Arctic Ocean are found in river runoff, with a mean of more than 500 μM (e.g., Gordeev *et al.,* 1996; Lobbes *et al.,* 2000). This concentration is about an order of magnitude higher than

in the inflowing Atlantic water, but the volume flux of the latter is about 50 times larger than that of the continental runoff. Nevertheless, there is a clear signature of terrigenous DOC in the surface water over the central Arctic Ocean (Opsahl *et al.,* 1999). Many of the investigations of organic carbon in the Arctic Ocean have reported data on unfiltered samples and are therefore total organic carbon (TOC) concentrations. However, often the waters of the Arctic Ocean are very low in particles, which makes the difference between DOC and TOC very little. This is not the case for samples collected during high primary productivity or in turbulent coastal waters.

A. River Runoff Sources

Numerous rivers enter the Arctic Ocean. They drain enormous areas (total drainage basin area $>10 \times 10^6$ km^2) with variable vegetation and soil conditions. Consequently, DOC concentrations vary significantly between rivers (Table I). There are also significant seasonal differences in river TOC concentration, as reported for the Lena River by Cauwet and Sidorov (1996). The maximum concentration (980 μM) was found during the maximum water discharge in early summer, followed by a lower concentration (700 μM) in the summer and autumn, and the lowest concentration (310 μM) during winter. The mean annual, discharge-weighted, concentration was 830 μM. It should be noted that several investigations were performed after maximum water discharge in summer, and not always is the date of sampling given in the literature. To get average discharge weighted concentrations, DOC concentrations were multiplied by each river discharge and divided by the total annual discharge (Table II). Another uncertainty is that around one-third of the discharge to the Arctic Ocean takes place through smaller rivers and creeks that are not included in Table I.

An alternative approach for estimating an average discharge weighted concentration for the rivers entering a given area is to sample the estuary and the surrounding sea and make a DOC versus salinity plot (Fig. 2). Assuming that DOC behaves conservatively, the intercept at $S = 0$ corresponds to a discharge weighted mean of the rivers entering the area investigated. This estimate includes the seasonal variability, as the residence time of the runoff on the Eurasian shelves has been estimated to $\sim$3 years (Schlosser *et al.,* 1994). This approach is not suitable for the Beaufort Sea area, where the Mackenzie River discharges, as the residence time of the surface water on the shelf in summer is short (Macdonald *et al.,* 1989). The Mackenzie River dominates the discharge from North America into the Arctic Ocean and it is thus more straightforward to evaluate the DOC concentration in the runoff from this continent, than from the Eurasian.

The regression lines of Figs. 2C and 2D (from the Laptev Sea region) are in excellent agreement with an intercept of 579 and 580 μM. The data of Fig. 2B fall

Table I

Reported Concentrations of DOC and TOC in Arctic Rivers

No.	River	DOC (μM)	TOC (μM)	References	Shelf seas
1	Pechora		1083	*d*	Barents
2	Ob		592 to 733	*d, g*	Kara
3	Pyr		558	*d*	Kara
4	Yenisey	711	617	*d, e, g*	Kara
5	Katanga		525	*d*	Laptev
6	Olenek	850	600	*d, e*	Laptev
7	Lena	538 to 558	792 to 842	*a, c, d, e, g*	Laptev
8	Yana	232 to 264	558 to 611	*c, d, e, g*	Laptev
9	Indigirka	404	642 to 754	*c, d, g*	East Siberian
10	Kolyma	387	389 to 675	*c, d, g*	East Siberian
11	Mackenzie	375 to 863	642 to 1050	*b, d, f, g*	Beaufort
B.S.	Yukon	357 to 733	476 to 833	*b, f, g*	Bering

Note. The Yukon river enters the Bering Sea (B.S.), outside the range of Figure 1, but most of its water enters the Arctic Ocean through Bering Strait.

[a]Cauvet and Sidorov (1996).

[b]Degens *et al.* (1991).

[c]Fitznar (1999).

[d]Gordeev *et al.* (1996).

[e]Lobbes *et al.* (2000).

[f]Pocklington (1987).

[g]Telang *et al.* (1991).

Table II

DOC Flux from Major Rivers into the Arctic Ocean (Lobbes *et al.*, 2000)

River	Discharge (km^3 $year^{-1}$)	Drainage basin area (km^2 10^3)	DOC (μM)	DOC flux (10^9 g C $year^{-1}$)
Mezen	21	56	1006	248
Ob	419	2,990	735	3,690
Yenisey delta	569	2,440	711	4,860
Olenek	32	198	850	323
Lena delta	524	2,430	538	3,380
Yana	31	244	232	85
Indigirka	50	305	404	241
Kolyma	98	526	387	458
Mackenzie	249	1,805	640	1,917
Total	1,993	10,994	636[a]	15,200

[a]The mean concentration is computed as (DOC flux)/(discharge) × (12).

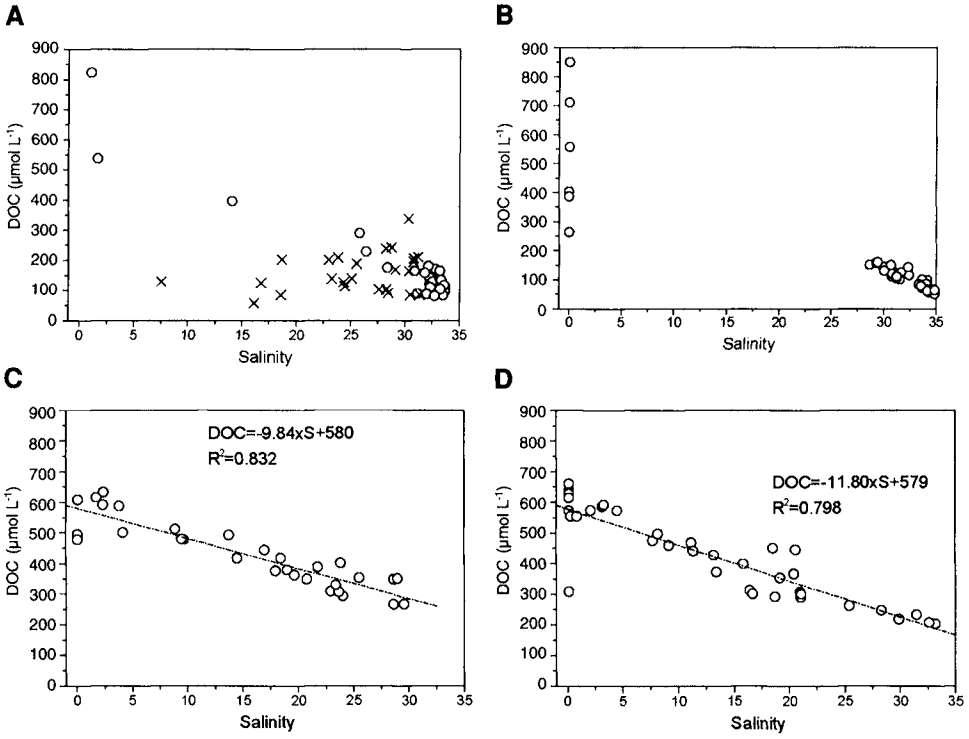

Figure 2 DOC concentration versus salinity in the Siberian Shelf Seas. (A) From Tundra 94 cruise, with o representing west of 115°E (mainly Barents and Kara Seas) and × representing east of 115°E (East Siberian and Laptev Seas) (Anderson *et al.*, 1999). (B) From ARK XI/1 and runoff data (mainly the Laptev Sea) (Fitznar, 1999). (C) SPASIBA-1, September 1989 (Cauwet and Sidorov, 1996); (D) SPASIBA-2, September 1991 (Cauwet and Sidorov, 1996), both in the Laptev Sea. The regression lines are for all data marked with circles.

around the same regression line, but without data in the salinity interval 1 to 28 it is not meaningful to make a linear regression calculation. The data West of 115°E in Fig. 2A also falls along the same regression line, but with too few low-salinity data to make a linear regression calculation. Hence, it is not possible to draw any conclusion with regard to the DOC concentration in the runoff entering the Kara Sea relative to that entering the Laptev Sea. A striking feature in Fig. 2A is the large scatter in data east of 115°E and the low DOC concentrations in the low-salinity waters. Three possible explanations for the scatter can be considered. First, these samples were not filtered prior to analysis, which might both result in higher concentration and larger scatter. Second, these samples were analyzed on board the ship, using a Shimadzu TOC 5000, which is sensitive to vibrations, and thus also likely to contributes to scatter. Finally, the low-salinity samples were mainly collected in the East Siberian Sea, where sea-ice melt contributed significantly to the freshwater (Olsson and Anderson, 1997). Since sea ice can have highly variable TOC concentrations depending on biological activity in and under the ice, this can add to the scatter. The consequence of all these uncertainties is that it is difficult to evaluate any mean runoff DOC (or TOC) concentration for the East Siberian Sea, using the available data.

Guay *et al.* (1999) used a UV fluorometer on the SCICEX-97 cruise to record a continuous *in situ* record of fluorescence at excitation 320 nm and emission 420 nm along the submarine track, at a depth of about 50 m. The fluorescence measurements can be used to estimate the concentrations of the humic-rich terrestrial component of DOM. The measured fluorescence detector response (V) gave a linear correlation to the TOC concentrations (TOC $= 94.8 \times V$, $r^2 = 0.84$, $n = 186$), the latter measured by high-temperature combustion on samples collected roughly every hour during the cruise. Also particulate organic carbon was determined on some samples and that accounted for less than 4.2% of the measured TOC, leading the authors to conclude that DOC $\approx$ TOC. The DOC and salinity data collected along the continental slope of the Makarov and Amundsen Basins, show a linear correlation of DOC $= -18.5 \times S + 705$ μM ($r^2 = 0.76$, $n = 4914$). This is interpreted as data from a region with high DOC Eurasian runoff mixing with waters of Atlantic origin with low DOC. The resulting runoff concentration of 705 μM is higher than that found from measurements in the Laptev Sea. However, there might be temporal variability in the runoff DOC concentration and also the data reported by Guay *et al.* (1999) covered a salinity range of about 32 to 34, making the computed intercept at $S = 0$ somewhat uncertain. These data help identify regions with runoff from the shelf seas to the deep central Arctic Ocean.

B. Seawater Sources

The reported DOC concentrations in the inflowing water from the Atlantic vary between 52 and 75 μM (Wheeler *et al.*, 1997; Børsheim and Mycklestad, 1997;

Opsahl *et al.*, 1999; Fransson *et al.*, 2001). Some of this variation might be a result of analytical errors, but in addition different water masses were sampled, and they were not sampled at the same time. Inflowing water from the Atlantic includes surface water flowing through Fram Strait and the Barents Sea, as well as deeper water flowing through Fram Strait. Deeper Atlantic water is modified between the Greenland–Scotland Ridge and the Arctic Ocean. The Norwegian Sea deep water, flowing north through Fram Strait, is a mixture of Eurasian Basin deep water and Greenland Sea deep water (Swift *et al.*, 1983). Some of the Eurasian Basin deep water that exits through Fram Strait flows around the Greenland Sea and mixes with the Greenland Sea deep water before it reenters the deep Arctic Ocean.

It is difficult to assign a specific DOC concentration to the water flowing in through Bering Strait as the inflow consists of several different water masses and considerable modifications take place during the transit through the Bering Sea. The Arctic Ocean Section expedition in 1994 showed a TOC concentration span of 50 to 110 μM in the waters with Pacific-derived characteristics (Wheeler *et al.*, 1997). When the particulate carbon fraction was subtracted the DOC concentrations had a span of 20 to 100 μM (their Fig. 8). The mean concentration computed for the samples at the slope stations equals $\sim 70 \pm 15$ μM. Using a Lagrangian model, Walsh *et al.* (1997) computed a monthly depth average DOC concentration of between 67 and 134 μM at positions over the 80-m isobath of the northwestern Chukchi Sea. The annual average of the monthly values is ~ 90 μM, which is in fairly good agreement with the Wheeler *et al.* (1997) mean DOC measurements of the slope stations north of the Chukchi Sea.

C. Biological Sources within the Arctic Ocean

An additional source of DOM in the Arctic Ocean is through biological processes within the Arctic Ocean and its shelves. Primary productivity over the continental shelves is substantial and results in a significant seasonal production of marine DOM. This seasonal signal can be observed in surface waters. The outflow from the Barents Sea into the central Arctic Ocean through the St. Anna Trough (containing insignificant fraction of river runoff) showed elevated surface DOC concentrations relative to waters below 150 m (Fransson *et al.*, 2001). At depths shallower than 150 m, the nutrient distribution indicated that primary production occurred in the surface water during the transit over the Barents Sea. Subtracting the deep-water DOC concentration (average of 52 μM) from surface DOC values estimates the labile, i.e., freshly produced, part of the DOC (cf. Hansell and Carlson, 1998). The labile DOC amounts to 1.4 mol C m^{-2} integrated over the top 150 m (Fransson *et al.*, 2001), which will be exported to the central Arctic Ocean. The Chukchi Sea also has a high biological productivity. In analogy with the above estimate of exported DOC, the difference between the highest (134 μM)

and lowest (67 μM) monthly depth average, DOC concentrations at the continental break of the northwestern Chukchi Sea (Walsh *et al.,* 1997) should reflect the marine DOC exported into the central Arctic Ocean from this area.

The productivity of the central Arctic Ocean is small compared to the shelf seas. Based on the computed deficit of phosphate in surface waters, Anderson *et al.* (2000) estimated an average export production of 0.04 mol m^{-2} $year^{-1}$ over the central Arctic Ocean. In contrast an *in situ* DOC production of over 0.5 mol m^{-2} $year^{-1}$ (assuming a 120-day productive season) was computed for the central Arctic Ocean in 1994 (Wheeler *et al.,* 1997). If this DOC production is distributed over the top 50 m, it will result in a concentration increase of 10 μM. In order to sustain such an annual DOC production over the residence time of the Arctic Ocean surface water, 5–10 years, an unrealistic DOC concentration would follow, indicating extensive recycling. Hence, it is essential to consider the seasonal production and degradation of marine DOC in the Arctic Ocean. Data are unfortunately not available to make such an evaluation, not even in the shelf seas.

From extensive measurements, DOC in sea ice has been attributed to ice algae production (e.g., Smith *et al.,* 1997). In shelf seas receiving much runoff, the sea ice produced will include some terrigenous DOC. In the spring (beginning of April to end of May) when the sea ice algae develops, Smith *et al.* (1997) found a good correlation between chlorophyll *a* and DOC in the bottom ice of Resolute Passage in the Canadian Archipelago. DOC concentrations were much higher in ice than in underlying water, especially in ice covered with only a thin snow layer. The highest DOC concentration (>3000 μM) was measured in the bulk of the bottom ice on May 14 (Smith *et al.,* 1997). However, the volume with this high concentration is small and thus the integrated contribution of DOC from ice to the underlying water mass is small. Measurements of DOC release rates by ice algae were performed by Gosselin *et al.* (1997) along the track of the Arctic Ocean section in 1994. The release rate varied from less than 25 μmol m^{-2} day^{-1} to 1600 $\pm$ 1500 μmol m^{-2} day^{-1}, with the highest rates in the Chukchi Sea. Thomas *et al.* (1995) collected three ice cores of more than 2 m length in the Fram Strait. In two of these the DOC concentration was mostly below 100 μM all through the core. In the third the concentration was close to 100 μM in the top $\sim$1.8 m, and increased to a maximum of $\sim$700 μM some 10 cm from the bottom. This increase was explained by a combination of DOM excretion by biota and decomposition of organisms (Thomas *et al.,* 1995). The mean bulk concentration of DOC in sea ice from the central Arctic Ocean is 316 $\pm$ 99 μM (Melnikov, 1997). If 1 m of ice melts annually, the concentration in the top 50 m (typical winter surface mixed layer (Rudels *et al.,* 1996)) would increase by just over 6 μM.

A further source of DOC from biological processes is release from the sediment surface caused by decomposition of particulate organic material. Hulth *et al.* (1996) measured DOC concentrations in the range of 500 to 8000 μM in pore

water in the Svalbard area. The lowest concentrations were found at stations east of Svalbard, where also a significant inverse linear correlation ($r^2 = 0.849$) of DOC concentrations with a sediment reactivity index (defined as sediment oxygen consumption rate normalized to the organic content) was found. This suggests a coupling between reactivity of organic matter in sediment and DOC lability in pore water. In a study of the eastern Eurasian Basin and adjacent shelves (Hulthe and Hall, 1997), DOC fluxes out of the sediment were evaluated to be in the range from close to zero to 3.6 mmol m^{-2} day^{-1}. The highest fluxes were found on the shelves and the lowest in the deep basins and on the slopes. A positive correlation of the DOC and dissolved inorganic carbon fluxes was observed, with DOC constituting up to 50% of the total benthic carbon flux at stations with the highest total benthic carbon fluxes. This indicates that the fraction of DOC that is oxidized to inorganic carbon is decreasing with increasing decomposition rates.

III. COMPOSITION AND DISTRIBUTION OF DOC WITHIN THE ARCTIC OCEAN

Before the transport of DOC to and from of the Arctic Ocean is discussed, the quality of the terrigenous DOM has to be considered. Does it flow with the water as a biogeochemically stable solute or is it available to diagenetic alteration or photochemical decomposition? Several investigations have studied the composition of DOM in rivers entering the Arctic Ocean (e.g., Gordeev *et al.*, 1996; Cauwet and Sidorov, 1996; Lara *et al.*, 1998; Lobbes *et al.*, 2000) as well as in the Arctic Ocean itself (e.g., Wheeler *et al.*, 1997; Opsahl *et al.*, 1999; Kattner *et al.*, 1999). One general conclusion is the stability of terrigenous DOC in the surface waters of the Arctic Ocean. Except for the linear mixing line of runoff and seawater in a DOC vs salinity plot, the fairly constant composition of the DOM in all of the Arctic Ocean supports this conclusion.

A. Lignin Oxidation Products and Stable Carbon Isotopes

The most useful quantitative tracers of terrestrial organic matter are lignin oxidation products, which have been determined in runoff to the Arctic Ocean (Opsahl *et al.*, 1999; Lobbes *et al.*, 2000) and in the surface waters of the Arctic Ocean (Opsahl *et al.*, 1999; Kattner *et al.*, 1999). Kattner *et al.* (1999) determined lignin in the "humic" fraction of DOM and used this as a tracer for terrigenous influence, with the result that the riverine-derived freshwater contribution to the Laptev Sea is 8 to 30%. Combining this proportion with DOC concentrations in the Lena River and Laptev Sea indicates that about 60% of the DOC in the surface layer of the Laptev Sea and adjacent Eurasian Basin would be of terrigenous

origin. In contrast, terrigenous dissolved organic nitrogen (DON) only accounted for 20 to 30% of the total DON (Kattner *et al.*, 1999). However, as stressed by the authors, the distribution of DON is generally more influenced by biological processes, making this last estimate more uncertain.

The fraction of terrigenous DOM in surface waters of the central Arctic Ocean was estimated from the carbon-normalized yields of lignin oxidation products (Λ_6) and $\delta^{13}C$ in ultrafiltered dissolved organic matter (UDOM) (Opsahl *et al.*, 1999), resulting in 5–22% and 16–33%, respectively. The UDOM represents the high-molecular-weight fraction of DOM (>1 kDa), which is about 20–30% of total DOM. In Fig. 3 the mean values (±variability) of samples from the Kara Sea (low $\delta^{13}C$), the polar surface water (medium $\delta^{13}C$), and deep Fram Strait and Greenland Sea (high $\delta^{13}C$) (Opsahl *et al.*, 1999) are plotted versus Λ_6. The polar surface water ($32.04<S<34.49$) samples in this investigation were collected from submarines at depths of 38 to 165 m, within the SICEX program. Hence, these data do not include low-salinity surface waters. The relative contribution of terrigenous DOM in the polar surface water was computed from the mixing line of Fig. 3 to 15 ± 6%, where the error represents the extreme variability of the data. This computation is based on the same hypothesis as the estimate by Opsahl *et al.* (1999), that the deep Fram Strait and Greenland Sea data represents marine-derived organic matter and the Kara Sea data represents terrigenous-derived organic matter. If Λ_6 and $\delta^{13}C$ are conservative, the data would fall along a straight line, and the estimates of Opsahl *et al.* (1999) and that from Fig. 3 would be equal.

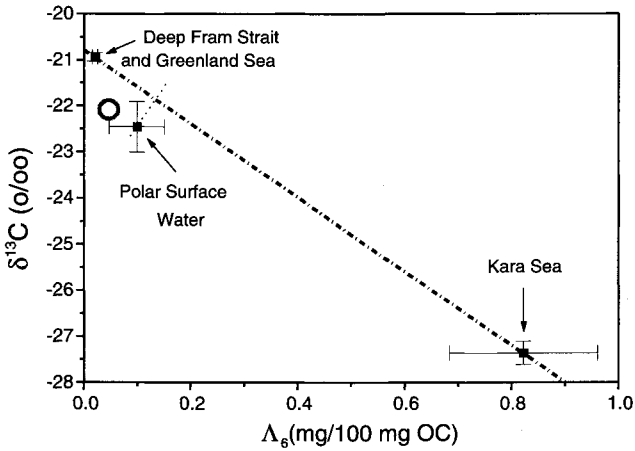

Figure 3 The mean values (± standard deviation) of carbon normalized yields of lignin oxidation products (Λ_6) versus stable carbon isotopic composition ($\delta^{13}C$) of DOM samples from the Kara Sea, the polar surface water and deep Fram Strait and Greenland Sea. The open circle indicates value from one sea ice sample. All data from Opsahl *et al.* (1999).

Syringyl and vanillyl phenols are two of the oxidation products from lignin. The ratio of syringyl and vanillyl (S/V) has been shown to be an indicator of oxidative changes. Investigations suggest that the S/V ratio is reduced by diagenetic alterations in the Atlantic and Pacific oceans (Opsahl and Benner, 1997). Likewise, photochemical degradation can selectively alter S/V of terrigenous DOM oceans (Opsahl and Benner, 1998). Lobbes *et al.* (2000) showed that the S/V ratio also is a biomarker to distinguish between DOM originating from angiosperm plants (high S/V ratios) and gymnosperms (low S/V ratios) in Russian rivers entering the Arctic Ocean. Opsahl *et al.* (1999) determined the S/V ratio in UDOM for different regions of the Arctic Ocean, showing ratios not too different in the Kara Sea (0.3–0.5; $n = 9$) and central Arctic Ocean (0.12–0.31; $n = 13$) samples. Consequently, the relatively constant S/V ratio within the Arctic Ocean indicates a limited alteration of terrigenous DOM in this region.

B. C/N Molar Ratios

The molar ratio of C/N is the most studied property of DOM and can be used as a tracer for the origin of DOM. The C/N ratio is generally high in terrigenous DOM and low in marine DOM. An average C/N ratio of 20.5 ± 2.6 was reported for seven Siberian rivers (Gordeev *et al.*, 1996, recalculated by Wheeler *et al.*, 1997). Cauwet and Sidorov (1996) found a similar value (22) for the Lena river, while significantly higher ratios (30 to 58) were reported by Lara *et al.* (1998) for different locations along the Lena River. Lobbes *et al.* (2000) reported data from several rivers, where the mean C/N ratio for Yenisey, Olenek, Lena, Yana, and Indigirka was 47 ± 10. The variability in the reported ratios is mainly a result of variable DON concentrations. The high C/N ratios of DOM in the runoff are characteristic of riverine fulvic acids (Thurman, 1985).

The C/N ratio of marine DOM is dependent on biological activity in the investigated water mass. When the C/N ratio is plotted versus salinity for samples collected in the outer Laptev Sea, at the continental margin and in the eastern part of the Eurasian Basin, two regimes can be identified (Fig. 4). At salinities below 34.5 (depth <100 m), the C/N ratio increases with decreasing salinity (o in Fig. 4) and at salinities above 34.5 (depth >100 m), the ratio varies from 12 to 30 (× in Fig. 4). The signature at $S<34.5$ is mainly a result of water of Atlantic origin mixing with runoff, supported by the intercept 49.7 at $S = 0$ of the fitted line. No trend but a large C/N span can be seen in the waters of $S>34.5$, which likely is a result of these samples being deep waters and thus have a signal affected by decay of sinking organic particulate matter. A large variability in the C/N ratio of DOM, ranging from 10 to 40 with a peak around 15, was also observed in the Fram Strait (Lara *et al.*, 1998). The variable C/N ratio in marine dominated waters is a result of variable DON concentrations. This makes the C/N ratio less useful for

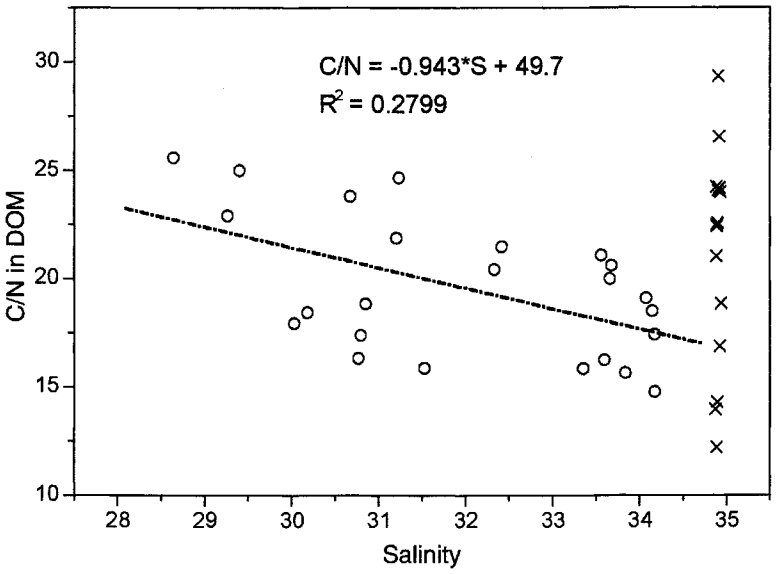

Figure 4 C/N ratio in dissolved organic matter (DOC/DON) in the eastern Eurasian Basin. Open circles represent S <34.5, crosses represent S >34.5. The linear regression line is fitted to the open circles. Data are from Fitznar (1999).

quantitative computations, but it is valuable as a qualitative tracer of terrigenous DOM.

C. Distribution

Too few DOC data are available from the central Arctic Ocean surface waters to produce a map of the concentration distribution. Several processes considerably influence the distribution by producing and consuming DOC. The relative importance of these processes can be seen in a DOC versus salinity plot of the surface waters with S<34.5 (Fig. 5). A line representing the conservative mixing of Atlantic water ($S = 34.926$ and DOC = 60 μM) and runoff ($S = 0$ and DOC = 550 μM) is included as reference. Data with S>34 (Anderson *et al.*, 1994; Opsahl *et al.*, 1999) are spread around the mixing line, showing that consumption and production of DOC balance. At salinities around 33, the Opsahl *et al.* (1999) data are below the mixing line, while the Anderson *et al.* (1994) data are above the mixing line. The latter is likely caused by biological activity as shown by Wheeler *et al.* (1997). Their data from the Arctic Ocean section 1994 show a similar trend (see Fig. 5 in Wheeler *et al.*, 1997), but with fewer data above the mixing line.

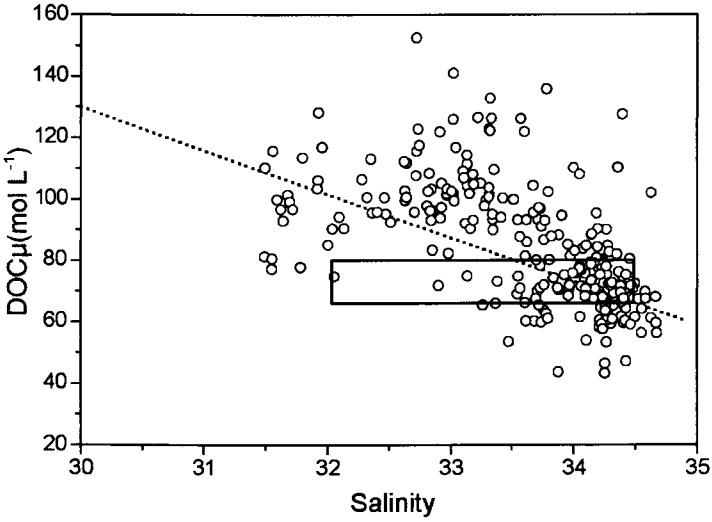

Figure 5 DOC versus salinity for the samples from the central Arctic Ocean with S <34.5. The open circles are data from the Oden 91 cruise (Anderson *et al.*, 1994), while the square illustrates the range of data from Opsahl *et al.* (1999). A line representing the conservative mixing of Atlantic water ($S = 34.926$ and DOC = 60 μM) and river runoff ($S = 0$ and DOC = 555 μM) is included as a reference.

However, sea-ice meltwater also lowers the salinity, and the DOC concentration (316 ± 99 μM; Melnikov, 1997) is lower in sea-ice meltwater than in the runoff. Nevertheless, the DOC concentration in the surface waters of the central Arctic Ocean is negatively correlated with salinity to a large degree.

The DOC concentrations in Arctic Ocean deep waters are lower than in the inflowing Atlantic water (Opsahl *et al.*, 1999; Bussmann and Kattner, 2000). Opsahl *et al.* (1999) found 61 μM in the inflowing Atlantic water of Fram Strait and 65 μM in that recirculating in Fram Strait, while Bussmann and Kattner (2000) found 59 μM ($n = 37$) in the Atlantic layer of the central Arctic Ocean. The mean deep-water concentration was 50 μM in the Nansen Basin ($n = 53$), 54 μM in the Amundsen Basin ($n = 67$), and 56 μM in the Makarov Basin (Bussmann and Kattner, 2000). These values agree well with the observations in the outflowing deep waters from the Canadian and Eurasian Basins, 53 and 49 μM, respectively (Opsahl *et al.*, 1999). The difference in DOC concentration between the inflowing Atlantic water and the Arctic Ocean deep waters is in the order of 10 μM, which is not much above the analytical range of accuracy. However, it is realistic to expect a higher DOC concentration in the Atlantic water relative to the Arctic Ocean deep waters as the former has been exposed to a larger flux of particulate organic matter from above. Furthermore, the Arctic Ocean deep waters have a long residence time (>100 years), with a limited flux of particulate organic matter from above,

resulting in a DOC decomposition rate that could be larger than the production rate by decay of particulate organic matter. The lower DOC concentrations in the Arctic Ocean deep waters do not exclude an export of terrigenous DOM to the deep waters, as this is a function of sources and sinks. However, both the low concentration of lignin oxidation products and the predominance of a marine $\delta^{13}C$ signature indicate that terrigenous DOM is a minor contribution to the DOC of the deep waters of the Arctic Ocean (Opsahl *et al.*, 1999).

IV. SUMMARY OF SOURCES AND SINKS

A budget of the fluxes to and from the Arctic Ocean is given in Table III, based on measured concentrations of DOC and reported volume fluxes of the different waters. This budget does not distinguish between terrigenous and marine DOC. Generally the terrigenous DOC is high in the surface waters and low in the deep waters (Opsahl *et al.*, 1999; Fitznar, 1999). It should be noted that the DOC budget of Table III is around 15% lower than that reported by Anderson *et al.* (1998), a result of much new high-quality data being collected during the past few years, as referred to in Section III.

The uncertainties given in Table III are based on the variability in reported DOC concentrations for the different water masses. No considerations of uncertainties in volume fluxes are included. Fortunately, the largest uncertainties are in the Atlantic and deep-water volume fluxes and these waters have a fairly constant DOC concentration. Consequently, an error in the volume influx has to be compensated by a comparable error in the volume outflux and hence have a small impact on the net DOC flux out of the Arctic Ocean. Adding the in- and outfluxes of Table III gives $-5 \pm 9 \times 10^{12}$ g C year^{-1}, indicating that the Arctic Ocean is neither a sink nor a source of DOC considering the uncertainty in the estimate.

The *in situ* production of marine DOC within the central Arctic Ocean has been estimated to 6.1 g C m^{-2} year^{-1} and the *in situ* respiration to 8.8 g C m^{-2} year^{-1} (Wheeler *et al.*, 1997). Combining these numbers with the area of the deep central Arctic Ocean (5.8×10^{12} m^2) gives a total *in situ* production of 35×10^{12} g C year^{-1} and a total *in situ* respiration of 51×10^{12} g C year^{-1}. These numbers are based on one summer investigation in a limited area and the uncertainties must be significant when applying them to a whole year and the whole central Arctic Ocean. Nevertheless, it is interesting to note that the *in situ* respiration of DOC exceeds that of *in situ* production of marine DOC, while the latter is of the same order as the added terrigenous DOC (35×10^{12} g C year^{-1} relative to 23×10^{12} g C year^{-1}). These results indicate that the *in situ* respiration of DOC in the central Arctic Ocean will quantitatively consume all marine DOC produced in the central Arctic Ocean and some of that added by river runoff. This estimate does not include the DOC produced by the biota on the shelves.

Table III

A Budget of the DOC Fluxes to and from the Arctic Ocean

Water mass		Volume flux (Sv)	DOC (μM)	Organic carbon transport, (10^{12} g C year^{-1})
In				
Atlantic water		2.5	58 ± 5^a	55 ± 5
Deep water		0.58	53 ± 5^b	12 ± 1
Pacific water		0.83	71 ± 20^c	22 ± 6
Runoff		0.11	555 ± 50^d	23 ± 2
Total in		**4.02**		**112 ± 8**
Out				
Sea ice		0.11	316 ± 50^e	13 ± 2
From EB:	- Surface mixed layer	0.165	82 ± 15^f	5 ± 1
	- Halocline	0.25	70 ± 6^f	7 ± 1
	- Atlantic layer	0.9	58 ± 4^f	20 ± 1
	- Deep water	0.42	51 ± 5^g	8 ± 1
From CB:	- Surface mixed layer	0.362	100 ± 10^f	14 ± 1
	- Halocline	0.54	75 ± 12^f	15 ± 2
	- Atlantic layer	0.698	53 ± 4^f	14 ± 1
	- Deep water	0.575	55 ± 5^g	12 ± 1
Total out		**4.02**		**107 ± 4**
Net outflow				***-5 ± 9***

Note. The volume fluxes of the water masses are from Anderson *et al.* (1998), while the DOC concentrations are means of literature values. The river runoff includes all continental freshwater input, and outflows are from the Eurasian Basin (EB) and Canadian Basin (CB), respectively. As discussed in the text, errors in the organic carbon transport figures do not include errors in the volume fluxes.

[a]Mean of Wheeler *et al.* (1997), Opsahl *et al.* (1999), and (Bussmann and Kattner, 2000).

[b]Data in the Greenland Sea at 1800 m (Opsahl *et al.*, 1999).

[c]Mean of Walsh *et al.* (1997), Wheeler *et al.* (1997), and Guay *et al.* (1999).

[d]The mean of the regression lines at $S = 0$ of Figures 2B-D.

[e]Melnikov (1997).

[f]Wheeler *et al.* (1997).

[g]Mean of Opsahl *et al.* (1999) and Bussmann and Kattner (2000).

Even if the Arctic Ocean itself is neither a sink nor a source of DOC there is a significant export of DOC to the North Atlantic. This flux (29×10^{12} g C year^{-1}) is a combined result of inflow from the Pacific Ocean (22×10^{12} g C year^{-1}), river runoff (23×10^{12} g C year^{-1}), and the difference between *in situ* production (35×10^{12} g C year^{-1}) and respiration (51×10^{12} g C year^{-1}) within the Arctic Ocean. The above arguments together with the balanced budget support the idea that terrigenous DOC is relatively stable within the Arctic Ocean.

The finding that the outflowing deep water DOC concentrations are lower than (or very similar to) the inflowing water concentrations indicate (*i*) that little terrigenous DOM is exported to deep layers (as was also concluded by Opsahl *et al.*, (1999) on the basis of lignin analysis) and (*ii*) that little net export of marine DOM occurs to deep layers. The latter statement is supported by the arguments above that most marine DOC produced in the central Arctic Ocean is respired in the surface layers. The fact that little terrigenous DOC is exported to the deep waters of the Arctic Ocean through dense plumes originating on the shelves, where they are initiated by brine drainage from sea ice production, is an important finding as it put constraints on the global DOC budget.

With regard to the total carbon budget in and out of the Arctic Ocean, the DOC fluxes are about 5% of the total carbon fluxes, calculated as the sum of inorganic and organic carbon. However, while the dissolved inorganic carbon concentration largely has a positive correlation with salinity, the DOC concentration has a negative one. Consequently, *in situ* production and respiration of DOC plays a relatively more important role for the carbon cycle in the low-salinity surface waters, relative to deeper layers, and it is the surface water that is in contact with the atmosphere linking the marine carbon cycle to climate.

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