



## Nutrients, organic carbon and organic nitrogen in the upper water column of the Arctic Ocean: implications for the sources of dissolved organic carbon

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**Abstract**—Particulate and dissolved organic carbon and nitrogen were analyzed for shelf, slope and basin samples collected during the 1994 Arctic Ocean Section. Concentrations of organic carbon and nitrogen were highest in the surface water and decreased dramatically below 100 m. Over the shelf 40–50% of the organic material was present in the particulate phase, while in the slope and basin waters  $\geq 90\%$  of the organic material was present in the dissolved phase. The halocline layer over the Chukchi plateau contained high concentrations of inorganic nutrients but no significant elevation of either organic carbon or organic nitrogen. Highest concentrations of total organic carbon were found in the surface water of the Makarov and Amundsen Basins between 80 and 90° N. The C:N ratio of the dissolved organic material in the upper 100 m ranged from 9 to 25, with highest ratios along the Makarov flank of the Lomonosov Ridge. We suggest that a major portion of the carbon-rich organic material in surface waters is derived from Eurasian shelf riverine inputs, which tend to flow in perimeter currents along the slope and ridges. Our preliminary dissolved organic carbon (DOC) budget suggests that the three major sources of DOC in the central Arctic are *in situ* production (56%), river run-off (25%), and Pacific water (19%). © 1998 Elsevier Science Ltd. All rights reserved

### INTRODUCTION

The Arctic Ocean is comprised of  $4.1 \times 10^6$  km<sup>2</sup> of shallow shelf seas that are seasonally ice-free and  $8.2 \times 10^6$  km<sup>2</sup> of central deep basins that are usually covered by 3–5 m of ice throughout the year. Major inflow of Pacific water through the Bering Strait is about 0.8 Sv per year, which is balanced by outflow through the Canadian Archipelago and Fram Strait to the Atlantic Ocean. Atlantic water also flows into the Arctic at surface and intermediate depths and is balanced by the outflow of deep water in the Greenland Sea. Additional input of fresh water from the MacKenzie River in the Canadian Basin and the Russian rivers on the Eurasian shelf contribute a total flow of 0.1 Sv per year.

The upper Arctic Ocean is comprised of three major layers, the surface mixed layer, the halocline (between 75 and 150 m), and the warm Atlantic layer between 200 and 500 m. The halocline stratifies the water column and isolates the mixed layer from the Atlantic layer. Surface currents have been determined from ice drift patterns (Thorndike and Colony, 1982) and more recently from density by assuming geostrophic equilibrium (Morison *et al.*, in press). The velocity pattern is dominated by currents along the Alpha–Medeleyev Ridge and the Transpolar Drift along the Lomonosov Ridge, circumarctic flows along the Eurasian and Canadian continental slopes, and the anticyclonic Beaufort Gyre in the Canada Basin.

Studies from US, Russian, and Canadian ice camps in the central basins (Kinney *et al.*, 1971; Melnikov and Pavlov, 1978; Gordon and Cranford, 1985) showed elevated concentrations (about 100  $\mu\text{M}$ ) of dissolved organic carbon (DOC) in surface water but usually low concentrations of particulate organic carbon and nitrogen. Kinney *et al.* (1971) attributed the high concentrations of DOC to slow microbial activity at cold temperatures, while Melnikov and Pavlov (1978) noted a positive correlation between zooplankton standing stocks and DOC distributions and suggested that biological activity and the vertical migration of zooplankton played an important role in the distribution of DOC. More recent studies in the Eurasian Basin (Anderson *et al.*, 1994; Olsson and Anderson, 1997) also report high DOC concentrations but conclude that most of this material is derived from river inputs. For the Canadian Basin, Walsh (1995) and Walsh *et al.* (1997) propose an influx of organic carbon from the Bering Sea and transport into the halocline layer, which could operate as a carbon sink under the ice cap.

The interdisciplinary Arctic Ocean Section was carried out aboard the CCGS Louis St Laurent and USCGC Polar Sea from 17 July–9 September 1994. The main goal of the biology program aboard the USCGC Polar Sea was to assess the major components of biological cycling of carbon in the central Arctic Ocean. Preliminary results (Wheeler *et al.*, 1996) confirmed the high concentrations of DOC in surface water but also showed that rates of primary and secondary production under the ice were significantly higher than suggested by earlier studies (English, 1961). This paper presents a detailed report of the distribution of inorganic nutrients and both particulate and dissolved organic carbon and nitrogen in the upper 300 m of the water column for stations sampled from USCGC Polar Sea. A more complete chemical hydrography including the deeper parts of the water column was conducted by colleagues aboard the CCGS Louis St Laurent (see Swift *et al.*, 1997).

We observed significant differences in the relative distribution of particulate vs dissolved organic material in shelf waters compared with slope and basin waters. We used nutrient versus salinity plots to distinguish the Pacific and Atlantic water mass assemblages and their contributions to the spatial variations in nutrient profiles across the arctic basins. Comparison of the distributions of inorganic nutrients and organic carbon and nitrogen shows no evidence of transport of organic material into the halocline layer. The C:N ratio of total organic material in the upper 100 m across the basins is examined as a possible indicator of the spatial distribution of riverine organic material and we present a comparison of the sources of DOC in the central Arctic. Finally we combine the water fluxes into and out of the Arctic with available data on DOC concentrations to evaluate the fluxes of DOC.

## METHODS

### *Cruise track and sample collection*

Samples collected from the USCGC Polar Sea (Fig. 1) started on the shelf (Stns 2–3) and slope (Stns 4–6) of the Chukchi Sea, then continued across the Chukchi Abyssal Plain and the Arlis Plateau (Stns 7–13), across the Mendeleyev Ridge into the Makarov Basin (Stns 16–24), then across the Lomonosov Ridge into the Amundsen (Stns 25–31) and Nansen (Stns 32–33) basins. The cruise track crossed a major front separating Pacific and Atlantic water assemblages (McLaughlin *et al.*, 1996; Morison *et al.*, in press) over the Mendeleyev Ridge at about 80° N. The ships exited into the Greenland Sea on 31 August 1994. Nutrients

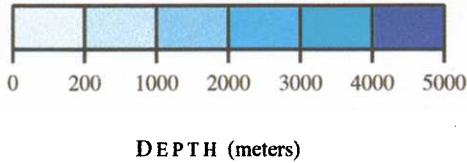
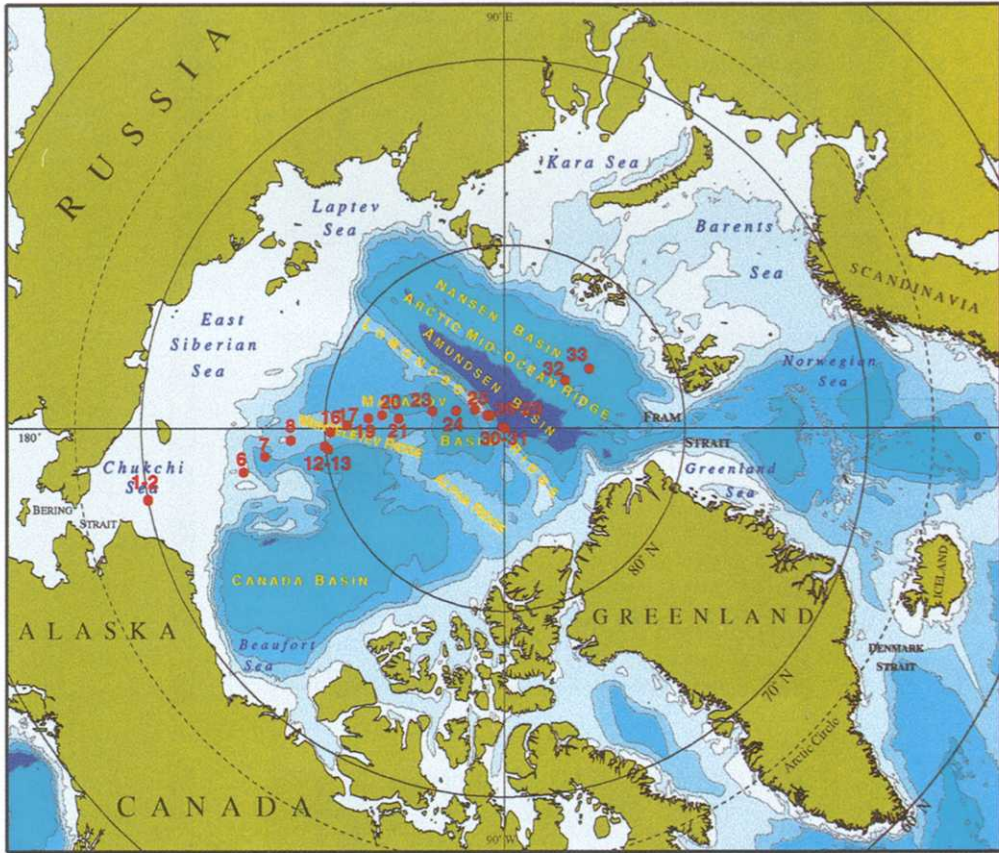


Fig. 1. Map of USCGC Polar Sea cruise tract.

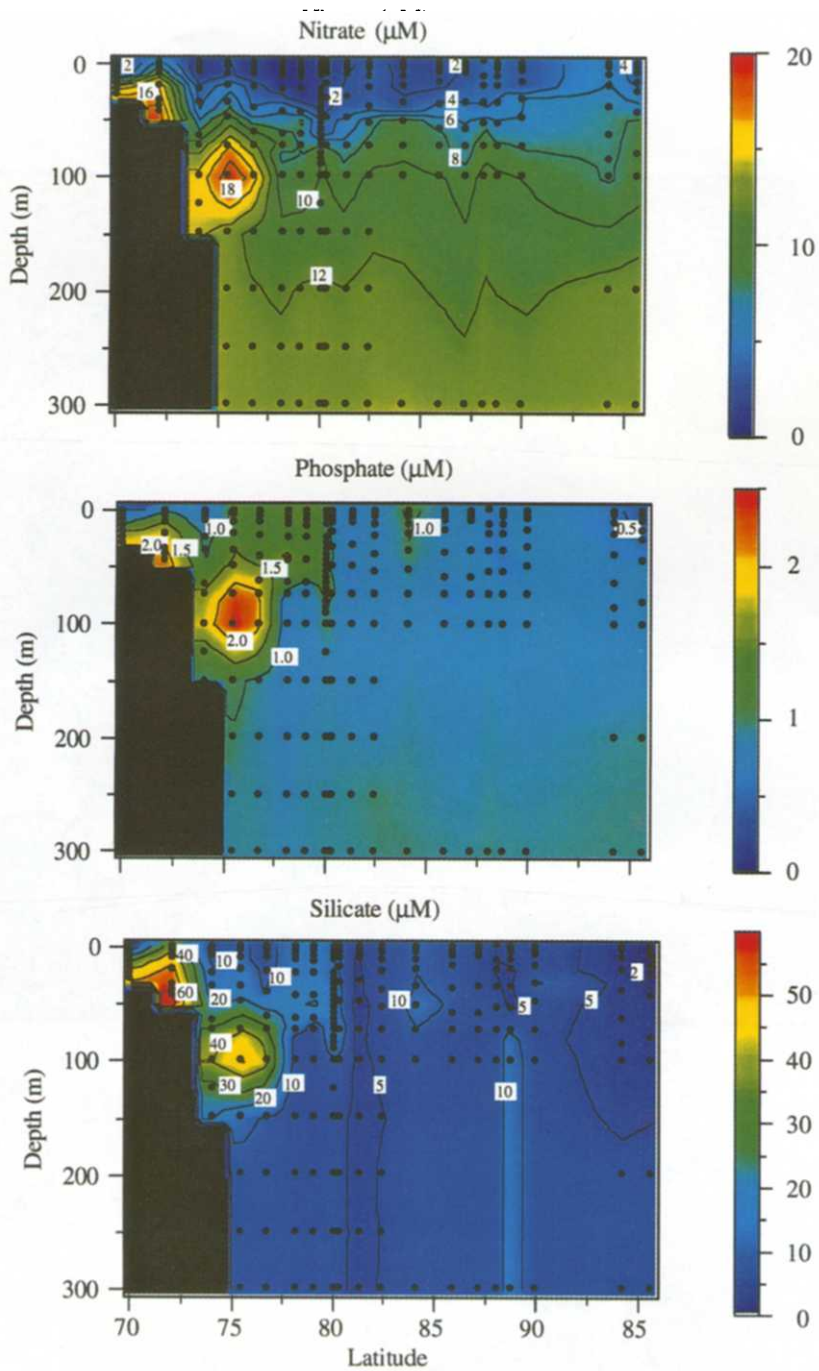


Fig. 2. Distribution of nitrate, phosphate and silicate in the upper 300 m.

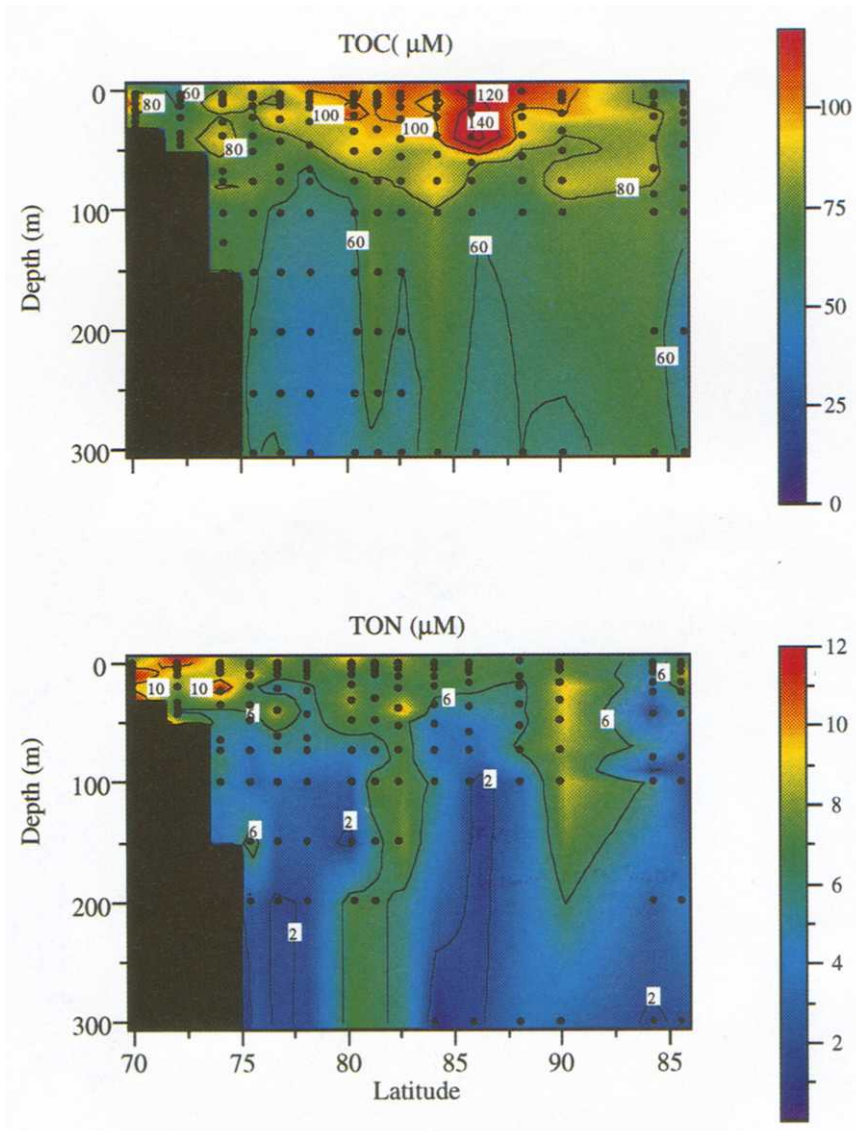


Fig. 4. Distribution of TOC and TON in the upper 300 m.

were measured at all 22 biological stations, while particulate and dissolved organic material were measured at 16–18 stations (Fig. 1).

Water samples and hydrographic data were collected with a CTD rosette. Most sampling was in the upper 300 m of the water column. Samples for nutrients were collected in 30 ml polyethylene bottles and analyzed on board for nitrate, phosphate, silicate and ammonium by standard autoanalyzer methods (Atlas *et al.*, 1971). Unfiltered duplicate samples for total organic carbon were collected in 7 ml glass vials which were acid-washed and combusted for 12 h at 500°C. Vials were capped with Teflon-coated septa and screw caps. After acidification with 50 µl 85% phosphoric acid, samples were stored at 5 °C. Samples for total nitrogen were placed in 30 ml acid washed teflon vials, then stored at –20 °C. Particulate organic carbon and nitrogen was collected by filtration of 1 l onto 25 mm precombusted glass fibre filters. Filters were dried for 48 h at 60 °C then stored in sealed tubes.

#### *Analysis of total organic carbon*

The total organic carbon of the samples was measured using a commercial high temperature combustion (HTC) instrument (Shimadzu TOC-500). Each sample was brought to room temperature, acidified (60 µl H<sub>3</sub>PO<sub>4</sub> per 6 ml sample) and sparged with compressed air (<0.1 ppm CO<sub>2</sub>) for 15 min prior to analysis to remove all inorganic carbon. Using a 100 µl syringe (Hamilton Gastight #1710), 60 µl of sample was then injected through the septum port into the vertical quartz combustion tube heated at 680 °C. The combustion tube contained two sheets of Pt gauze and quartz wool topped with Pt–Al catalyst (Shimadzu). Carbon dioxide released from the combustion was quantified by a non-dispersive infrared (NDIR) detector after passing through an electronic dehumidifier and halogen scrubber. The carbon dioxide peaks were visually inspected to monitor and correct any drifts in baseline or peak shape and were integrated by the Shimadzu electronics.

The instrument was calibrated with a four point standard curve of potassium hydrogen phthalate dissolved in Milli-Q water. Fresh standards (ranging from 80–420 µM) were prepared prior to each run by diluting a refrigerated stock solution (~8 mM) made weekly. Milli-Q water was used as the blank. Prior to running samples, we conditioned the catalyst by injecting Milli-Q water until achieving a low blank (Benner and Strom, 1993). The entire four point standard series was run before and after the analysis of samples ( $r^2 > 0.998$  for all runs). Standard and sample peak area averages are based on at least three injections. We assessed instrument drift by injecting an acidified seawater sample (collected at 9°N, 140°W on February, 1992) or standards after each set of duplicates. Sample concentrations were estimated by subtracting the entire blank (due to the instrument and Milli-Q water) from each sample and dividing by the instrument response (slope of standard curve). We assume the blank due to the water is negligible (Benner and Strom, 1993), although we may slightly underestimate sample concentrations (Sharp *et al.*, 1993).

The samples were analyzed during a three-month period (May–August, 1995) as 24 runs. Changes in the condition of the column led to some variation in the instrument response and the blank over this time period. The instrument response averaged  $71.4 \pm 6.4$  area units per µM TOC concentration. The combined instrument and Milli-Q blank averaged  $30.0 \pm 9.0$  µM over the three month analytical period, with a mean coefficient of variation ( $\pm 1$ SD) of  $9.5 \pm 4.2\%$  during individual runs. The 9° N seawater averaged  $73.0 \pm 5.9$  µM. Due to variation between runs, samples were normalized using the average value ( $n = 4$ ) of

the 9° N water samples for that day relative to the initially determined value of 68  $\mu\text{M}$ . These 9° N water replicates varied by an average of  $3.0 \pm 1.0\%$  during individual runs. Altogether 179 arctic water samples were run in duplicate for TOC (a minimum of 3 replicate injections from each of two vials). Of the 358 samples, 18 (5%) were rejected as outliers based on excessively high values ( $n = 4$ ) or lack of consistency between the duplicates ( $n = 14$ ). In the latter case the outliers were identified by comparison with the replicates samples for the bracketing water samples within the depth profile. The mean coefficient of variation ( $\pm 1$  SD) for the arctic TOC replicates was  $4.6 \pm 1.7\%$ . Dissolved organic carbon (DOC) was calculated by subtracting particulate carbon (PC) from TOC. All DOC calculations were based on samples drawn in parallel from the Niskin bottles.

#### *Analysis of total and dissolved organic nitrogen*

Samples were analyzed for total nitrogen, TN, using a persulfate oxidation method (Raimbault and Slawyk, 1991) as described in detail by Libby and Wheeler (Libby and Wheeler, 1994, Libby and Wheeler, 1997). Samples were digested for four hours under oxidative conditions using a solution prepared from twice recrystallized potassium persulfate. Digests were then analyzed for TN using standard techniques for  $\text{NO}_3^- + \text{NO}_2^-$  on a Technicon autoanalyzer II (Atlas *et al.*, 1971).

The instrument was calibrated daily using a standard curve prepared from triplicates of digested leucine standards at three concentrations. Prior to each run, fresh standards (0–30  $\mu\text{M}$ ) were made by diluting frozen primary standard (15 mM) with artificial seawater. Digested artificial seawater was used as a blank. The digested leucine standard curve was corrected for any nitrogen present in the artificial seawater by first determining the amount of nitrogen in the persulfate oxidizing solution and then calculating the amount of nitrogen in the artificial seawater. The amount of nitrogen in the artificial seawater is estimated as the difference between the total blank signal and the persulfate signal. The leucine standard curve was corrected by the small signal due to nitrogen in the artificial seawater at each concentration. Comparison of undigested nitrate and digested leucine standards yielded similar slope values under equivalent dilution conditions.

Samples were analyzed over a two month period (July–September, 1995) as 11 runs. The slope of the standard curve averaged  $24.9 \pm 0.6$  peak height units per  $\mu\text{M}$  during this time with  $r^2 > 0.991$  for all runs. Samples were analyzed in duplicate. Final duplicate TN values were screened for potentially contaminated samples. When one of the two replicates gave an anomalously high concentration ( $\text{CV} > 15\%$ ), the lower concentration was used (as was the case for 42 samples). For the remaining 144 samples, the final TN concentration is an average of two samples. Total organic nitrogen, TON, was calculated as TN minus  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{NH}_4^+$ . Dissolved organic nitrogen, DON, was calculated as  $\text{TON} - \text{PON}$ .

#### *Particulate carbon and nitrogen*

Filter samples were analyzed with a Perkin–Elmer CHN analyzer. At shelf and slope stations duplicate filters were run separately, and at deeper stations two filters were run as a single sample. Acetanilide was used as a standard, and mean filter blanks of  $7 \pm 1$   $\mu\text{g C}$  and  $0.9 \pm 0.3$   $\mu\text{g N}$  ( $\pm \text{SE}$ ,  $n = 13$ ) were subtracted from the raw data to determine particulate C and N. Precision is typically about 10%, and we only report data for samples which are at least twice as high as the filter blanks.

Our filter samples were not acid fumed and our PC values may include some inorganic carbon but are directly comparable to past POC arctic data (Loder, 1971; Kinney *et al.*, 1971; Gordon and Cranford, 1985). Our PC values are higher than the acid-fumed POC determinations for samples collected by Moran *et al.* (1997). However, the difference is small when POC is very high (i.e. shelf samples). For our central arctic samples PC overestimates POC, but greater than 95% of the TOC is present as DOC and the overestimate of POC has little effect on our conclusions.

## RESULTS

### *Distribution of inorganic nutrients*

Overall, nitrate concentrations ranged from 0.1–18  $\mu\text{M}$  (Fig. 2). Highest concentrations were found just above the sediments of the shelf stations (up to 16  $\mu\text{M}$ ) and in the subsurface nutrient maximum (up to 18  $\mu\text{M}$ ) in the halocline waters at the shelf/slope break (75–76° N). Further north along the transect across the basins, nitrate concentrations ranged from 2–4  $\mu\text{M}$  in the surface water and maximum concentrations were about 12  $\mu\text{M}$  in the Atlantic layer (below 200 m). Nitrite concentrations ranged from 0.03 to 0.34  $\mu\text{M}$  in shelf waters, but were usually  $\leq 0.1 \mu\text{M}$  with little vertical pattern in deeper water. Ammonium concentrations ranged from 0.9 to 2.6  $\mu\text{M}$  in the bottom layer of shelf water, but were always  $\leq 0.2 \mu\text{M}$  in deeper water off the shelf.

Phosphate concentrations ranged from 0.5–2.0  $\mu\text{M}$  (Fig. 2). Similar to nitrate, highest phosphate concentrations were above the shelf sediments and in the halocline waters between 75–76° N. Further north across the basins, phosphate ranged from 0.6–1.0  $\mu\text{M}$  and showed little variation with depth. The N:P ratios (calculated as  $\text{NO}_3^-/\text{PO}_4^{3-}$ ,  $\mu\text{M}/\mu\text{M}$ ) ranged from 1 to 9 in the upper 25 m, from 8 to 11 in the “halocline” layer (30–150 m) and averaged 14 in the Atlantic layer (Table 1).

Silicate concentrations ranged from 2–60  $\mu\text{M}$  (Fig. 2). Highest concentrations were also above shelf sediments and in the halocline as observed for nitrate and phosphate. Further north along the transect, silicate ranged from 5–10  $\mu\text{M}$  with little distinct vertical pattern. Surface concentrations of silicate decreased by more than one order of magnitude along the transect, while the concentrations in the Atlantic layer remained relatively constant at 6–8  $\mu\text{M}$  (Table 2).

Table 1. Inorganic nutrient N:P ratios (mean  $\pm$  1 SE) for upper water layers of the Arctic calculated from the molar ratio of nitrate and phosphate. Halocline ratios were calculated from nitrate and phosphate concentrations from 30–150 m. Number of samples used for calculations are in parentheses

Region	Surface mixed layer (0–25 m)	“Halocline” (30–150 m)	Atlantic water (200–300 m)
Shelf	6.50 $\pm$ 0.89 (11)	NA	NA
Slope	1.66 $\pm$ 0.26 (19)	8.01 $\pm$ 0.64 (21)	NA
Mendeleyev Ridge	0.98 $\pm$ 0.18 (29)	8.08 $\pm$ 0.69 (41)	14.22 $\pm$ 0.07 (18)
Makarov Basin	2.62 $\pm$ 0.24 (19)	10.69 $\pm$ 0.83 (17)	14.42 $\pm$ 0.14 (6)
Amundsen Basin	4.37 $\pm$ 0.23 (20)	10.79 $\pm$ 0.51 (15)	14.40 $\pm$ 0.02 (4)
Nansen Basin	8.68 $\pm$ 0.77 (8)	NA	14.41 $\pm$ 0.03 (2)



Table 2. Mean ( $\pm 1$  SE) silicate concentrations ( $\mu\text{M}$ ) for upper water layers of the Arctic. Number of samples used for calculations are in parentheses

Region	Surface mixed layer (0–25 m)	“Halocline” (30–150 m)	Atlantic water (200–300 m)
Shelf	37.0 $\pm$ 4.1 (12)	NA	NA
Slope	9.54 $\pm$ 0.62 (19)	27.8 $\pm$ 3.0 (21)	6.69 $\pm$ 0.22 (10)
Mendeleyev Ridge	11.3 $\pm$ 0.6 (29)	10.4 $\pm$ 0.7 (41)	5.79 $\pm$ 0.20 (19)
Makarov Basin	7.99 $\pm$ 0.33 (19)	7.26 $\pm$ 0.47 (17)	6.04 $\pm$ 0.29 (6)
Amundsen Basin	5.80 $\pm$ 0.13 (20)	7.52 $\pm$ 0.67 (15)	8.07 $\pm$ 1.53 (4)
Nansen Basin	2.04 $\pm$ 0.56 (8)	3.89 $\pm$ 0.38 (10)	6.12 $\pm$ 0.02 (2)

### Nutrient/salinity characteristics and identification of water assemblages

A clear distinction between Pacific-derived and Atlantic-derived water masses is shown in nutrient versus salinity plots. Stations 2–7 show the typical Pacific-derived (western Arctic) characteristic of high nutrients at salinity = 33.1, while Stations 23–32 show typical Atlantic-derived (eastern Arctic) characteristic of lower nutrients over a salinity range from 31.5 to 34. (Fig. 3). The front between the two water assemblages is located between Stations 8–21, which have intermediate nutrient vs salinity characteristics (Fig. 3).

### Organic carbon and nitrogen

Total organic carbon (TOC) ranged from 40–140  $\mu\text{M}$  (Fig. 4). Highest concentrations were in the surface water (upper 50 m). TOC was inversely related to salinity, and over the salinity range of 31.5 to 33.1 Atlantic-derived water had higher TOC concentrations than Pacific-derived water (Fig. 5). Mean DOC concentrations in the surface mixed layer ranged from 34.4 to 106.9  $\mu\text{M}$  across the transect, with highest concentrations over the Mendeleyev Ridge and in the Makarov and Amundsen Basins (Table 3). In contrast to silicate (Table 2), there was no evidence of elevated DOC in the halocline of the slope stations (Table 3). DOC concentrations in the Atlantic layer water (200–300 m) were relatively constant across the transect, with an overall mean ( $\pm$  SD) of 56.0  $\pm$  3.4  $\mu\text{M}$  calculated from the regional means in Table 3.

Integrated values of PC and DOC either to the bottom of the water column for shelf stations and to 100 m for all other stations are shown in Table 4. Means and SD for stations grouped according to regions of shelf, slope and basins are shown in Table 5. Integrated PC ranged from 3.53 to 15.8  $\text{g m}^{-2}$  with the highest values on the shelf and no significant difference between slope and basin stations (*f*-test,  $F_s < F_{0.05(1,12)}$ ). Integrated DOC ranged from 15.4–122  $\text{g m}^{-2}$  with the lowest values on the shelf and highest values ( $\geq 97.8 \text{ g m}^{-2}$ ) between 80 and 90° N (Table 4). It is noteworthy that a large portion (39%) of total organic carbon on the shelf is in the particulate fraction, while in the basins, particulate carbon is <7% of total organic carbon (Table 5). A plot of DOC versus PC for the entire data set (Fig. 6) clearly shows the distinction between basin/slope stations with high DOC and very low PC, and shelf stations with very low DOC but high PC concentrations.

Total organic nitrogen ranged from 2–12  $\mu\text{M}$  (Fig. 4). Highest concentrations were found over the shelf and intermediate concentrations were present over the Mendeleyev and Lomonosov Ridges. Integrated PN ranged from 0.33 to 2.88  $\text{g m}^{-2}$ , with the highest values on the shelf and no significant difference (*f*-test,  $F_s < F_{0.05(1,12)}$ ) between slope and basin

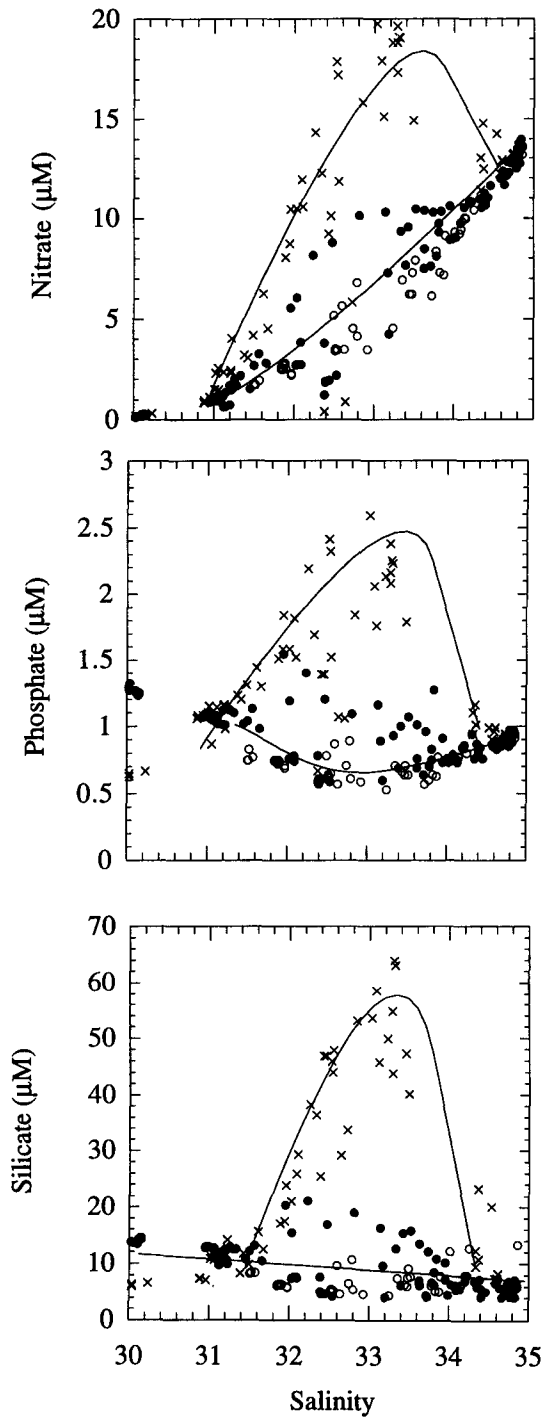


Fig. 3. Nutrient versus salinity plots. Stations 2-7 with Pacific-derived characteristics (X). Stations 8-21 with intermediate chemical characteristics (filled circles). Stations 23-32 with Atlantic-derived characteristics (open circles).

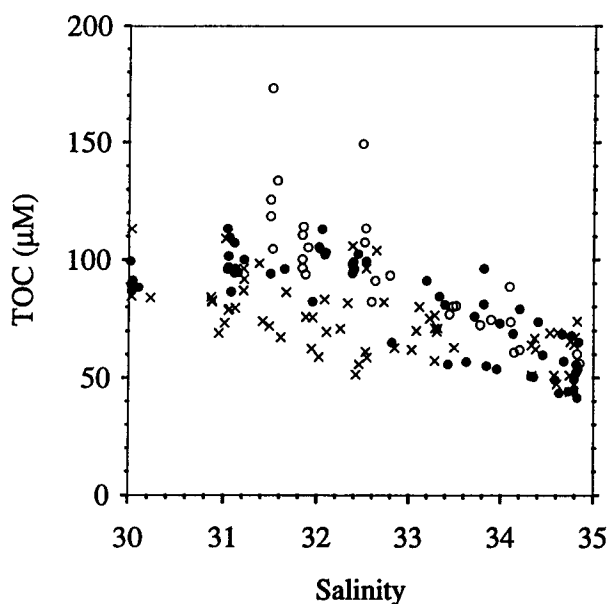


Fig. 5. TOC concentration versus salinity. Symbols as in Fig. 3

Table 3. Mean ( $\pm 1$  SE) DOC concentrations ( $\mu\text{M}$ ) for upper water layers of the Arctic. Number of samples used for calculations are in parentheses

Region	Surface mixed layer (0–25 m)	“Halocline” (30–150 m)	Atlantic water (200–300 m)
Shelf	$34.4 \pm 4.0$ (12)	NA	NA
Slope	$76.5 \pm 2.7$ (19)	$67.1 \pm 2.4$ (21)	$57.6 \pm 3.5$ (10)
Mendeleyev Ridge	$91.9 \pm 0.6$ (15)	$67.6 \pm 4.1$ (15)	$50.9 \pm 3.3$ (9)
Makarov Basin	$106.9 \pm 5.0$ (15)	$82.1 \pm 6.0$ (13)	$55.2 \pm 2.1$ (5)
Amundsen Basin	$98.8 \pm 2.7$ (9)	$74.2 \pm 2.7$ (7)	$55.8 \pm 1.6$ (2)
Nansen Basin	$65.2 \pm 3.9$ (8)	$66.2 \pm 3.3$ (10)	$60.3 \pm 3.8$ (2)

stations. Integrated DON ranged from  $1.70$  to  $11.7 \text{ g m}^{-2}$ , with the lowest values on the shelf and local maxima along the slope and the eastern flanks of the Mendeleyev and Lomonosov Ridges (Table 4). As observed for carbon, the percent organic nitrogen present in the particulate fraction is high (50%) on the shelf but low (<10%) for all other stations (Table 5).

#### C:N ratios in PM and DOM

The mean C:N (mol:mol) ratio of particulate material ranged from 4.4 to 14.6. In general the lowest values were found over the shelf and highest values in the basin (Table 5). The C:N ratio of dissolved organic material ranged from 9.2 to 25.1 and was usually twice as high as the C:N ratio of PM (Table 5). Local maxima in C:N of DOM in the upper 100 m appeared over the slope, across the Mendeleyev Ridge and especially on the Makarov flank of the Lomonosov Ridge (Fig. 7).

Table 4. Integrated particulate (PC) and dissolved organic carbon (DOC) and particulate (PON) and dissolved organic nitrogen (DON). Integrated to bottom depth (shelf stations) or to 100 m ( $g\ m^{-2}$ )

Station	Latitude	Longitude	Depth (m)	PC	DOC	PON	DON
2	70°00' N	168°45' W	40	15.82	15.4	2.88	1.70
3	72°00' N	168°51' W	55	9.27	24.8	1.80	3.14
4	74°01' N	168°50' W	120	5.19	90.9	0.66	8.84
5	75°25' N	170°44' W	900	5.74	96.7	0.88	8.33
6	75°21' N	170°30' W	525	5.84	71.8	0.84	4.83
7	76°39' N	173°20' W	2250	4.84	85.4	0.63	7.70
8	78°08' N	176°48' W	1047	5.02	82.3	0.58	6.60
13	80°09' N	173°17' W	2654	4.97	95.3	1.33	7.15
17	81°15' N	179°00' E	2255	3.53	102.8	0.37	8.19
19	82°26' N	175°50' E	2414	3.56	102.9	0.43	9.91
21	84°06' N	174°59' E	3205	4.48	106.3	0.44	6.63
23	85°54' N	166°50' E	3535	4.08	121.6	0.40	5.65
25	88°04' N	147°47' E	2191	4.14	97.9	0.33	7.65
31	89°59' N	31°45' E	4290	4.11	100.4	0.39	11.77
32	85°43' N	37°50' E	3585	4.24	92.1	0.34	4.94
33	84°16' N	34°37' E	4052	8.19	72.5	1.12	5.37

Table 5. Mean ( $\pm 1$  SD) particulate and dissolved organic carbon and nitrogen ( $g\ m^{-2}$ ) integrated to bottom depth for shelf stations (Stns 2–3), and to 100 m for slope stations (4–6) and basin stations (7–33). C:N ratios for both particulate and dissolved organic material are mol:mol

Region	PC $\pm$ SD	DOC $\pm$ SD	% PC
Shelf	12.5 $\pm$ 4.6	20.1 $\pm$ 6.6	38.9 $\pm$ 16.5
Slope	5.59 $\pm$ 0.35	86.5 $\pm$ 13.0	6.2 $\pm$ 1.2
Basin	4.63 $\pm$ 1.20	94.4 $\pm$ 14.4	5.0 $\pm$ 2.0
	PON $\pm$ SD	DON $\pm$ SD	% PON
Shelf	2.34 $\pm$ 0.76	2.42 $\pm$ 1.02	49.7 $\pm$ 18.7
Slope	0.79 $\pm$ 0.12	7.33 $\pm$ 2.18	10.4 $\pm$ 4.0
Basin	0.57 $\pm$ 0.31	7.40 $\pm$ 2.03	8.4 $\pm$ 5.1
	PM C:N	DOM C:N	
Shelf	6.77 $\pm$ 0.09	13.4 $\pm$ 6.6	
Slope	8.88 $\pm$ 0.82	15.1 $\pm$ 4.7	
Basin	9.97 $\pm$ 2.04	16.0 $\pm$ 4.0	

#### Hydrochemical characteristics of shelf and slope water

Silicate versus salinity plots for shelf stations (2–3) and slope stations (4–6) show the correspondence of high shelf nutrients for salinities of 32.5 to 33.5 and the subsurface halocline nutrient maximum at the same salinity in slope water (Fig. 8). This correspondence suggests that dense shelf water is the source of the subsurface nutrient maximum in the western Arctic halocline layer. A similar plot for DOC versus salinity in shelf and slope water (Fig. 8) shows that shelf water has low DOC concentrations compared to slope water. Moreover, the high DOC at low salinities in the slope waters (Fig. 8) and high

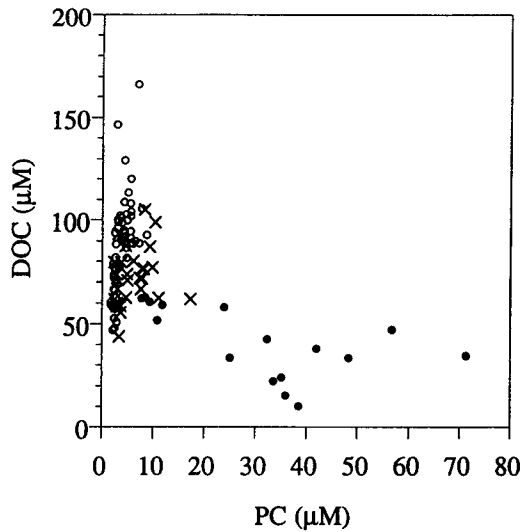


Fig. 6. DOC versus PC concentrations. Shelf stations (filled circles), slope stations (X), and basin stations (open circles).

TOC concentrations in Atlantic derived water in the salinity range of 31.5 to 32.5 (Fig. 5) suggest that the Pacific-derived Chukchi shelf water is not the primary source of DOC in the central Arctic.

### DISCUSSION

Production in the Arctic is highly seasonal, and it is important to consider the magnitude of seasonal variations in nutrients and organic material before discussing the significance of

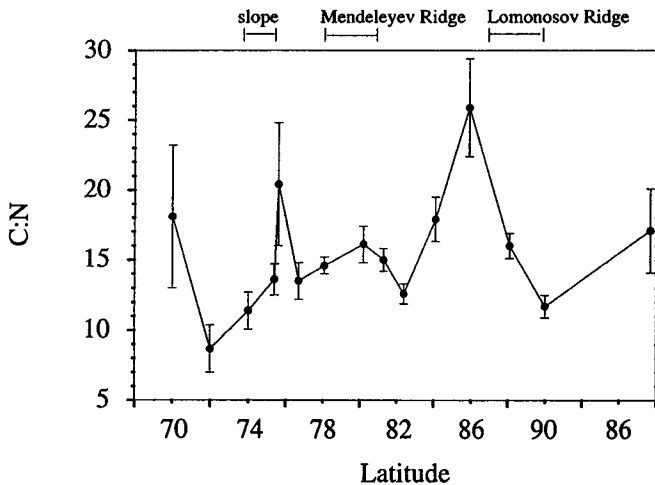


Fig. 7. Mean C:N of dissolved organic material to the bottom for shelf stations and in the upper 100 m for slope and basin stations. Error bars denotes  $\pm 1$  SE. The number of depths sampled was usually 9, but ranged from 7-10.

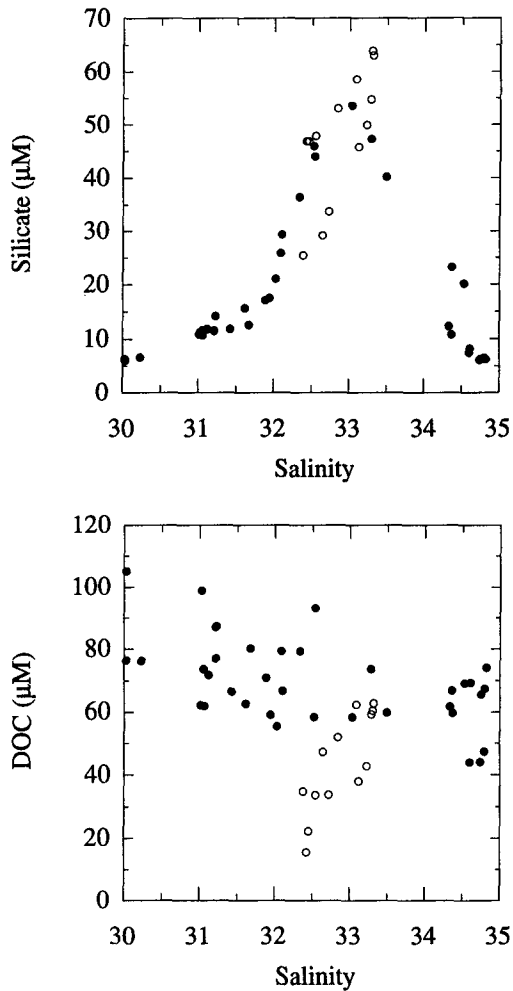


Fig. 8. Silicate and DOC versus salinity for shelf (open circles) and slope (filled circles) stations.

the broad spatial distributions observed during the 1994 transect. Ice camp studies from 1968–1975 (Pautzke, 1979, fig. 10) show low chlorophyll concentrations (about  $0.05 \mu\text{g l}^{-1}$ ) in the upper 20 m most of the year with blooms of  $0.2\text{--}2.0 \mu\text{g l}^{-1}$  for about two months during the summer but no corresponding seasonal changes in inorganic nutrients. Melnikov and Pavlov's (Melnikov and Pavlov, 1978) results from the Russian ice camp show an order of magnitude increase in POC in the surface water between May and July, but no significant seasonal variations in DOC. Thus, although significant seasonal variations in nutrients and organic material are seen in the shallow shelf seas (Harrison and Cota, 1991), only particulate organic material and chlorophyll show a consistent seasonal pattern in the central Arctic. Water mass characteristics and circulation patterns appear to be the primary factors affecting the broad scale variations in spatial distribution of dissolved constituents as described below.

*Nutrient distributions and implications for location of Pacific and Atlantic water assemblages*

Physical and chemical characteristics of the upper mixed layer and halocline waters of the Arctic show the presence of two major water assemblages which can be distinguished by Pacific versus Atlantic influences (McLaughlin *et al.*, 1996; Swift *et al.*, 1997). The characteristics of Pacific water that are demonstrated most strongly in the present data set are the low inorganic N:P ratios and elevated silicate concentrations in the mixed layer and in the halocline. The contrasting Atlantic water characteristics are higher N:P ratios, and lower silicate concentrations at all depths in the water column. Based on the distribution of these characteristics, we crossed the front separating the Pacific and Atlantic water assemblages near the southern end of the Mendeleyev Ridge, and little of the Pacific influence is seen beyond Station 13. As noted by McLaughlin *et al.* (1996) and Morison *et al.* (in press) this front has apparently shifted across the Makarov Basin from its past position over the Lomonosov Ridge to its current position over the Mendeleyev Ridge during the last decade. The causes for the shift of the front are not known.

*Comparison of particulate and dissolved organic material with past data sets*

Kinney *et al.* (1971) and Gordon and Cranford (1985) reported that Arctic Ocean POC concentrations are the lowest of any oceanic environment (about  $1 \text{ g C m}^{-2}$  in the upper 100 m); however, their samples were collected in April and May prior to the seasonal bloom of phytoplankton. Melnikov and Pavlov (1978) report maximum POC in the surface water from June through August, but do not report integrated POC concentrations. POC concentrations determined during the August 1994 Arctic Ocean Section were low in the central basins compared to the shelf, but 5-fold greater than the early spring values reported by Kinney *et al.* (1971) and Gordon and Cranford (1985). We also observed significant levels of primary and secondary production (Wheeler *et al.*, 1996) indicating that the central Arctic is biologically active during this part of the year. Moreover, the low mean C:N ratio of the particulate material in the upper water column (8.4) is indicative of marine, rather than terrestrially derived material (Schubert and Stein, 1996).

Our results confirm the high levels of dissolved organic carbon observed in earlier studies. DOC concentrations in the surface mixed layer of the central Arctic are typically  $\geq 100 \mu\text{M}$ , whereas surface water values in the Sargasso Sea, the subtropical Pacific Ocean and the Ross Sea (Antarctica) usually range from 40–60  $\mu\text{M}$  (Carlson *et al.*, 1994; Peltzer and Hayward, 1996; Carlson *et al.*, 1997). Kinney *et al.* (1971) and Gordon and Cranford (1985) attributed the high DOC in the central Arctic to low bacterial activity at polar temperatures; however, measurements during our field work demonstrated significant bacterial activity (Wheeler *et al.*, 1996; Rich *et al.*, 1997). Assuming that deep DOC levels represent a “refractory” portion of DOC, Wheeler *et al.*, 1996 estimated an average turnover time of semi-labile DOC ranging from 0.1 to 1.2 years which is significantly shorter than the mean residence time of surface water (7–14 years) in the central Arctic (Schlosser *et al.*, 1990).

*Shelf vs basin comparison of % PM.*

Few studies have examined the distribution of both PM and DOM in Arctic waters simultaneously. In oceanic waters it is generally assumed that more than 90% of total organic material is present in the dissolved phase. Chukchi shelf water with 40–50% of the

total particulate carbon and nitrogen present in the particulate fraction clearly deviates from this trend. Agatova *et al.* (1995) report a similar distribution of PM and DOM in Anadyr water, and they attribute the high relative abundance of particulate organic material to the absorption of “dissolved organic material” in coastal waters with high particle loading. Our observation of high PC and low DOC in shelf waters compared with slope and basin water is consistent with their interpretation. PC and PN on the Chukchi shelf exceed concentrations in basin waters by a factor of 2–3, while DOC and DON are 3–4 times lower than slope and basin dissolved organic material.

Recent studies in other oceanic regions (Williams, 1995; Carlson *et al.*, 1997) demonstrate the importance of examining both particulate and dissolved organic carbon phases for understanding the seasonal accumulations and transformation of organic carbon in marine waters. Understanding the organic carbon cycle in the shelf and basins of the Arctic ocean will clearly require more information on seasonal variations and rates of transformations of the major carbon pools. Nonetheless, our present results combined with past data sets provide important information for the partitioning and transport of organic carbon in the central Arctic.

#### *Shelf export of DOM to basins*

Walsh (1995) and Walsh *et al.* (1997) postulate that high production of organic carbon and nitrogen in the Bering and Chukchi Seas is exported from the shelf regions to halocline waters and serves as a sink for organic carbon and nitrogen under the permanent ice cover of the Arctic. Loder’s (Loder, 1971) measurements in the Bering Strait and Chukchi Sea show highest concentrations of POC in the southern Chukchi Sea (Table 6) where a maximum in Chl concentration is also found (Coachman and Shigaev, 1992). However, low levels of both POC and DOC in the northern Chukchi Sea (Table 6) and in the nutrient-rich halocline waters (Figs 2 and 4) argue against a large export of dissolved organic carbon from the Chukchi Sea into the central Arctic. Much of the carbon exported from the shelf appears to be remineralized and then exported as dissolved inorganic carbon (Sambrotto, 1996). Other potential sources and sinks for organic carbon in the Arctic are discussed below.

#### *Sources of DOC and DON*

Three other potential sources of organic material are river runoff, ice melt, and *in situ* production. The largest riverine inputs are from the MacKenzie (340 km<sup>3</sup> year<sup>-1</sup>) into the Canada Basin and the Lena, Yenisei and Ob (1,650 km<sup>3</sup> year<sup>-1</sup>) into the Eurasian Basin.

Table 6. Concentrations of POC and DOC (means  $\pm$  SD) in the Bering and Chukchi Seas. Data are taken from Loder, 1971 and integrated for 0–50 m using concentrations from 3–4 depths at each station

Region(Number of Stations)	POC (g C m <sup>-2</sup> )	DOC (g C m <sup>-2</sup> )
North Bering Sea (2)	11.2 $\pm$ 1.3	43.8 $\pm$ 3.8
Bering Strait (2)	18.0 $\pm$ 13.1	58.2 $\pm$ 0.8
Southern Chukchi Sea (5)	33.3 $\pm$ 23.3	47.0 $\pm$ 5.6
Northern Chukchi Sea (8)	6.2 $\pm$ 2.1	39.0 $\pm$ 11.1



Table 7. Dissolved organic carbon and nitrogen in Russian arctic rivers calculated from data reported by Gordeev *et al.* (1996). DOC was calculated from mean TOC (in their table 5) multiplied by the mean fraction of DOC/TOC=0.9 for Russian rivers (in their table 7). DON taken from their table 8

River	DOC ( $\mu\text{M}$ )	DON ( $\mu\text{M}$ )	C:N
Khatanga	472	29	16.3
Anabar	382	18	21.2
Olenjok	540	29	18.6
Lena	758	33	23.0
Yana	502	21	23.9
Indigirka	578	29	19.9
Kolyma	607	29	20.9
Mean $\pm$ SD	548 $\pm$ 118	27 $\pm$ 5	20.5 $\pm$ 2.6

River water usually contains high levels of DOC and a recent compilation for Russian arctic rivers (Gordeev *et al.*, 1996) averages 548  $\mu\text{M}$  (Table 7). Organic material in river water is primarily derived from terrestrial inputs with high C:N ratios, and this is reflected in an average C:N of 20 for Russian rivers draining onto the Eurasian shelf (Table 7).

Salinity,  $^{18}\text{O}$  and mass balance considerations (Bauch *et al.*, 1995) indicate that a major pathway for the distribution of Siberian river runoff across the Arctic is in the Transpolar Drift along the Makarov flank of the Lomonosov Ridge. Anderson *et al.*, 1994 also suggest the localized flow of river runoff over the ridges based on the distribution of total carbonate and total organic carbon. Our results show relatively high (> 90  $\mu\text{M}$ ) DOC concentrations in surface water across most of the Makarov and Eurasian basins. The large peak in C:N ratio of DOM along the edge of the Makarov Basin along with the evidence from  $^{18}\text{O}$  studies and the distribution of carbonate and organic carbon cited above support the argument for the localized distribution of terrestrial/riverine derived organic material in surface currents. Moderate elevation of the C:N ratio of DOM over the continental shelf and over the Mendeleev Ridge suggests a more diffuse distribution of riverine DOC in that region of the Arctic.

The mean concentration of DOC ( $\pm$ SD) in ice from the central Arctic is 316  $\pm$  99  $\mu\text{M}$  (Melnikov, 1997). If the lower 10 cm melts annually in the central basin, this would contribute about 32  $\mu\text{M}$  DOC to the upper  $\text{m}^3$  of the surface water. This is about 30% of ambient surface water DOC in the Makarov Basin but amounts to only 3% of DOC integrated over the upper 100 m. Ice formation appears to remove dissolved organic carbon from the surface water (Melnikov, 1997). Hence, the average net contribution of ice formation and ice melt to the DOC pool of the upper 100 m of the Arctic Ocean seems quite small.

Results from the 1994 Arctic Ocean Section indicate that primary production in the central Arctic is at least 10 times higher than English (1961) estimates, and is accompanied by significant release of DOC (Gosselin *et al.*, 1997), as well as significant bacterial production and respiration (Wheeler *et al.*, 1996; Rich *et al.*, in press). Although we have insufficient information for accurate determination of annual production, daily rates are presented here along with estimates of annual production in order to compare *in situ* production and consumption of DOC to other inputs of DOC to the central Arctic. For the purpose of this comparison, we assume a 120 day productive season for both primary

production and bacterial respiration and use the mean rates for all basin stations (shelf and slope stations were excluded). The average rate of primary production in the central Arctic was  $144 \text{ mg C m}^{-2} \text{ day}^{-1}$  ( $6.1 \text{ g C m}^{-2} \text{ year}^{-1}$ ), with  $51 \text{ mg C m}^{-2} \text{ day}^{-1}$  ( $6.1 \text{ g C m}^{-2} \text{ year}^{-1}$ ) released as DOC (Gosselin *et al.*, 1997). Bacterial biomass production was  $22 \text{ mg C m}^{-2} \text{ day}^{-1}$  ( $2.6 \text{ g C m}^{-2} \text{ year}^{-1}$ , Rich *et al.*, in press). Assuming a 30% growth efficiency for bacteria gives a total DOC consumption of  $73 \text{ mg C m}^{-2} \text{ day}^{-1}$  ( $8.8 \text{ g C m}^{-2} \text{ y}^{-1}$ ). Therefore, bacterial consumption of DOC exceeds *in situ* primary production of DOC. More extensive seasonal data will be needed before we can determine the precise balance between *in situ* production and utilization of DOC in the central Arctic. Nonetheless, the 1994 results clearly show that *in situ* production and respiration of DOC are both quantitatively important sources and sinks of DOC in the central Arctic Ocean. Further support for the importance of heterotrophy and respiration in the central Arctic is provided by the high standing stocks of heterotrophic protists (Sherr *et al.*, in press) and the high standing stocks of mesozooplankton (Wheeler *et al.*, 1996).

Three major sources of DOC to the upper layer of the Arctic Ocean are compared in Table 8; *in situ* production, Pacific water flowing through the Bering Strait, and river runoff. Mean concentrations for Pacific derived water are estimated from Loder's data for the Bering and Chukchi Seas (Table 6) and the annual flow of 0.82 Sv through the Bering Strait (Lundberg and Haugen, 1996) giving an annual flux of 16.8 Tg C or  $2.04 \text{ g C m}^{-2}$  in the central Arctic (Table 8). Similarly, river inputs are estimated from mean concentrations of DOC and annual flow of 0.11 Sv giving an annual flux of 22.8 Tg C, or  $2.78 \text{ g C m}^{-2}$ . Our 1994 estimate of *in situ* production of DOC is  $6.12 \text{ g C m}^{-2}$  as described above. Total annual input of DOC to the central Arctic from these three sources is  $10.9 \text{ g C m}^{-2}$ , with 56% from *in situ* production, 25% from rivers, and 19% from Pacific derived water.

#### Fluxes of DOC between the Arctic and Atlantic

We use the recent tabulation of water fluxes in the Arctic (Lundberg and Haugen, 1996) for a further comparison of DOC fluxes between the Arctic and Atlantic Oceans (Table 8). The largest water fluxes are the inflow of Atlantic Intermediate Water (8.4 Sv) and the outflow of water through the Fram Strait, Canadian Archipelago, and Denmark Strait (7.4 Sv). Mean concentrations of DOC in Atlantic Intermediate water are from our 1994 results using the concentrations ( $60 \mu\text{M}$ ) measured at 300 m. Inflowing DOC concentrations for the North Sea ( $50 \mu\text{M}$ ) were taken from Williams (1995). Total annual inflow of DOC

Table 8. DOC fluxes in the Arctic Ocean

Source/Sink	DOC ( $\text{mg C l}^{-1}$ )	Flow (Sv)	Annual Flux (Tg)	Annual Flux ( $\text{g C m}^{-2}$ )
Pacific	0.65	0.82	16.8	2.04
Rivers	6.58	0.11	22.8	2.78
<i>In situ</i> production			50.0	6.10
<i>In situ</i> respiration				-8.80
Atlantic inflow (including Irminger Current)	0.72	6.73	152.8	18.63
North Sea	0.60	0.67	12.7	1.55
Atlantic outflow	0.72	-8.38	-190.5	-23.23
Net flux			-7.6	-0.93

into the Arctic from the Atlantic and the North Sea is 165 Tg, while outflow is 190 Tg C (Table 8). This results in an annual export of 25 Tg DOC to the Atlantic, which within the errors of the estimates (Lundberg and Haugen, 1996) can be supported by DOC influx from the Pacific and from river water minus net *in situ* consumption (17 Tg DOC, see Table 8). It is important to note however, that this estimate assumes constant concentrations of DOC in inflowing and outflowing waters. Clearly, more data will be needed to determine the temporal and spatial variations in the distribution of DOC in these waters. Nonetheless, the present analysis does indicate that the net export of DOC from the Arctic to the Atlantic could be supported by the influx of DOC into the Arctic from the Pacific Ocean and from rivers. More data are needed on the temporal variations in rates of *in situ* production and utilization to determine if biological processes serve as a net source or sink for organic carbon in the central Arctic.

## CONCLUSIONS

New data on the distribution of organic carbon and nitrogen across the Arctic Ocean support the following conclusions. First, we found no evidence for the export of organic carbon or nitrogen from the shelf into halocline waters. Second, the major sources of DOC in the Arctic are *in situ* production (56%), river run-off (25%), and inputs from Pacific water (19%). Third, net import of DOC into the Arctic from the Pacific and rivers is sufficient to balance the net efflux of DOC from the Arctic to the Atlantic Ocean.

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