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Carbon to nitrogen (C:N) stoichiometry of the spring–summer phytoplankton bloom in the North Water Polynya (NOW)

Z.-P. Mei[a,*], L. Legendre[a,1], J.-É. Tremblay[b], L.A. Miller[c], Y. Gratton[d], C. Lovejoy[a], P.L. Yager[e], M. Gosselin[f]

[a]Québec-Océan, Pavillon Vachon, Université Laval, Sainte-Foy, Canada QC G1K 7P4
[b]Université Laval, Département de Biologie, Québec, Canada QC G1K 7P4
[c]Centre for Ocean Climate Chemistry, Institute of Ocean Sciences, P.O. Box 6000, Sidney, Canada BC V8L 4B2
[d]INRS-ETE (Eau, Terre, Environnement), 2800 rue Einstein, C.P. 7500, Sainte-Foy, Canada QC G1V 4C7
[e]University of Georgia, School of Marine Programs, 220 Marine Sciences Building, Athens, GA 30602-3636, USA
[f]Institut des sciences de la mer de Rimouski (ISMER), Université du Québec à Rimouski, 310 Allée des Ursulines, Rimouski, Canada QC G5L 3A1

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Abstract

The carbon to nitrogen (C:N) stoichiometry of phytoplankton production varied significantly during the spring–summer bloom in the North Water Polynya (NOW), from April through July 1998. The molar ratio of particulate organic carbon (POC) to nitrogen (PON) production by phytoplankton (ΔPOC:ΔPON) increased from 5.8 during April through early June to 8.9 in late June and July. The molar dissolved inorganic carbon (DIC) to nitrate + nitrite (NO_3) drawdown ratio (ΔDIC: ΔNO_3) increased from 6.7 in April and May, to 11.9 in June (no estimate for July because of ice melting). The discrepancy between ΔPOC:ΔPON and $\Delta DIC:\Delta NO_3$ was likely due to dissolved organic carbon (DOC) production. Increased ΔPOC:ΔPON of phytoplankton and surface water $\Delta DIC:\Delta NO_3$ throughout the phytoplankton blooms resulted from changes in physical properties of the upper water column, such as reduced thickness of the surface mixed layer that exposed phytoplankton to increased photosynthetically available radiation (PAR), accompanied by NO_3 depletion. This is expected to have significant effects on the cycling of carbon (C) and nitrogen (N) in pelagic ecosystems, as the increased C:N ratio of organic matter decreases its quality as substrate for grazers and microbial communities. Based on ΔPOC:ΔPON, the ratio of POC to chlorophyll *a* (Chl) production (ΔPOC:ΔChl) and the relationship between Chl yields and NO_3 depletion, we estimate that $71 \pm 17\%$ and $46 \pm 20\%$ of the depleted NO_3 went to PON production in the euphotic zone over the polynya from April to early June, and late June to July, respectively. The remaining NO_3 was likely channelled to dissolved organic nitrogen (DON) and heterotrophic bacteria, which were not returned to the dissolved inorganic nitrogen (DIN) pool through recycling during the course of the study. Hence, the autotrophic production of organic N and its recycling by the microbial food web were not coupled temporally.

Keywords: Phytoplankton bloom; Stoichiometry; C:N; DIC; NO_3; Biogeochemical cycling

*Corresponding author. Current address: Institut des sciences de la mer de Rimouski (ISMER), Université du Québec à Rimouski, 310 Allée des Ursulines, Rimouski, Canada QC G5L 3A1. Tel.: +1 418 723 1986x1664; fax: +1 418 724 1842.
E-mail address: zhi-ping.mei@uqar.qc.ca (Z.-P. Mei).
[1]Current address: Laboratoire d'Océanographie de Villefranche (LOV), B.P. 28, 06234 Villefranche-sur-Mer Cedex, France.

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1. Introduction

Primary production in the North Water Polynya (NOW) is among the highest observed to date above the Arctic Circle (Lewis et al., 1996; Klein et al., 2002; Mei et al., 2002, 2003; Tremblay et al., 2002b). This high production is strongly associated with the dynamics of ice and the physical properties of the water column, which are forced by regional circulation and climate patterns (Barber et al., 2001; Mei et al., 2002; Melling et al., 2001; Tremblay et al., 2002b).

The photosynthetic fixation of carbon (C) by phytoplankton is accompanied by the uptake of major chemical elements such as nitrogen (N) and phosphorus (P), and for diatoms, silicon (Si). The long-term stoichiometry of nutrient consumption by marine phytoplankton is the same as the ratio of the principal elements in phytoplankton biomass, i.e. phytoplankton take up C, N and P at the approximate ratio of 106:16:1 (Redfield et al., 1963). Because this stoichiometry holds over large oceanic regions and long time scales, it is a critical parameter in global biogeochemical models that predict new and export production from nutrient drawdown (Fasham et al., 1990; Fennel and Neumann, 2004).

Short-term or local deviations of C:N drawdown from the Redfield ratio were discussed by Redfield et al. (1963), and have been reported frequently since then (Brzezinski, 1985; Brzezinski and Nelson, 1995; Codispoti et al., 1991; Daly et al., 1999; Sambrotto et al., 1993). Sambrotto et al. (1993) stressed that the elevated consumption of C relative to the Redfield C:N ratio causes underestimation of organic carbon export from the euphotic zone based on new production. The elevated consumption of C relative to N can result from the production of carbon-rich dissolved organic matter (DOM) (Banse, 1994; Williams, 1995), N limitation (Daly et al., 1999), N_2 fixation (Anderson and Pondaven, 2003; Lee et al., 2002), or growth limitation (Goldman et al., 1979; Goldman, 1986).

The first objective of this study is to investigate the seasonal changes in dissolved inorganic carbon (DIC) to nitrate + nitrite (NO_3) drawdown ratio (ΔDIC:ΔNO_3) and particulate organic carbon (POC) to particulate organic nitrogen (PON) production ratio (ΔPOC:ΔPON) in surface waters, and their relationships with physical, chemical and biological factors in the upper water column. Comparing ΔDIC:ΔNO_3 with ΔPOC:ΔPON would provide insights in the production of DOC and DON during phytoplankton blooms. Production and export from surface water of C-rich DOM makes carbon export more efficient than through POM, because DOM has much higher C:N ratio than POM (Hopkinson and Vallino, 2005).

It is generally assumed that the export of organic matter from the euphotic zone in a marine system is equal to the NO_3-based new production, when the system is in a long-term steady state (e.g. Eppley and Peterson, 1979). Recent studies have shown that NO_3 uptake by phytoplankton is accompanied by significant production of dissolved organic nitrogen (DON) (Bronk et al., 1994). Consistent with the steady-state assumption, the export of organic matter from the euphotic zone must be equal to total (gross) new production over the relevant space and time scales. Because most field estimates of new production (^{15}N uptake experiments, Dugdale and Goering, 1967) do not include the production of DON, the resulting values may underestimate total new production and thus the export of organic matter from the euphotic zone. The second objective of this study is to estimate the balance between NO_3 depletion and PON production, based on the stoichiometry of phytoplankton production, whereby exploring the fate of the N that is not accounted for by PON, and its implications for new and export production.

Data on the distributions of nutrients [NO_3, silicic acid ($Si(OH)_4$) and phosphate (PO_4)] (Tremblay et al., 2002a), DIC (Miller et al., 2002), new production (Tremblay et al., 2002b) and primary production (Klein et al., 2002; Mei et al., 2003) have been published elsewhere. Tremblay et al. (2002a) pointed out that during the spring–summer phytoplankton bloom, NO_3 was the limiting nutrient for primary production, and $Si(OH)_4$ and PO_4 were in extra supply in the NOW. The present paper is the first attempt to estimate ΔDIC:ΔNO_3 under complex hydrodynamic conditions and the seasonal variations in ΔPOC:ΔPON related to the physical properties of the upper water column, thus providing new insights in the response of the biogeochemical cycling of C and N in the NOW to future climate change.

2. Material and methods

2.1. Sampling

Samples were collected in the NOW (75–79°N, 66–80°W; located between Ellesmere Island, Canada, and Greenland) during a cruise from April through July 1998. The samples were taken at depths of 100%, 45%, 30%, 20%, 10% and 1% of the surface irradiance, and several depths below the euphotic zone down to the bottom. Locations of the sampling stations are shown on Fig. 1. Stations were sampled once during each of the first three 1-month legs: April (7 April–4 May), May (7–31 May) and June (4–27 June). Stations along the southernmost transect were sampled in June only, when water opened south of 76°N. During the fourth, July leg (30 June–21 July), samples were taken at mooring stations only, prefixed with the letters D, S, E and N. Stations 2 (sampled from April to June) and N2 (sampled in July only) were at the same location. A rosette equipped with a CTD (Falmouth ICTD) and 10-L bottles (Brooke Ocean Technology Limited, Dartmouth, Nova Scotia) was used to take water samples for phytoplankton chlorophyll *a* biomass (Chl), nutrients, including NO_3, PO_4, $Si(OH)_4$, DIC, POC and PON. The PO_4 and $Si(OH)_4$ data will not be used in this paper, which focuses on ΔDIC:ΔNO_3 and ΔPOC:ΔPON.

We divided the polynya into northern and southern parts for comparison purposes, as the northern and southern parts of the polynya were sampled in the first and second half of each month, respectively, and nutrient concentrations as well as phytoplankton productivity changed from the first to second half of the months (Mei et al., 2003). The southern stations are those to the south of 77°N, including the transect on 77°N. Procedures for CTD profiling and phytoplankton sampling are detailed in other papers (Bâcle et al., 2002; Melling et al., 2001). Measurements of irradiance and calculation of average photosynthetically available radiation (PAR, μmol photons $m^{-2} s^{-1}$) in the surface mixed layer and the euphotic zone were described in detail in Mei et al. (2002). Sampling and analyses for nutrients, POC and PON are described in Tremblay et al. (2002a, b), and for DIC in Miller et al. (2002). Samples for phytoplankton cell counts were taken at depths of 50% and 1% surface irradiance. Detailed procedures for phytoplankton cell counts and taxa identifications based on a combination of fluorescence, Nomarski optics and Utermöhl sedimentation are given in Lovejoy et al. (2002a). Phytoplankton carbon biomass was estimated from the relationship between cell volume and carbon content, as detailed in Lovejoy et al. (2002a). Since we used a sedimentation method to count phytoplankton, we may have missed the smallest cells because small particles have very low settling rates.

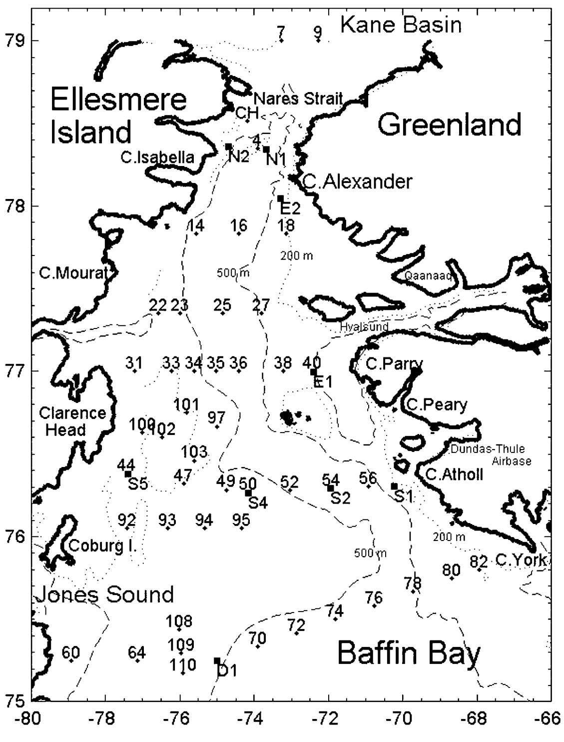

Fig. 1. Positions of the sampling stations in the NOW.

2.2. Phytoplankton drawdown of NO_3 and DIC

Surface water was defined as the 0–100 m water column for April and May, and 0–50 m for June, following the seasonal variations in maximum mixed layer depth (MLD) (Melling et al., 2001) and euphotic zone depth. Surface water in the NOW forms mainly by the mixing of two water masses in varying proportions, i.e. Arctic water, flowing southward from the Kane Basin, and Baffin Bay water, flowing northward from the North Baffin Bay, which is located southeast of the polynya (Bâcle et al., 2002; Melling et al., 2001). The two water masses have distinct salinity and nutrient, especially $Si(OH)_4$, properties when they enter the region, the Arctic water mass being fresher and colder, and having higher $Si(OH)_4$ concentration than Baffin Bay water (Bâcle et al., 2002; Melling et al., 2001; Tremblay et al., 2002a).

The observed NO_3 and DIC concentrations in surface water result from the mixing of the two main water masses, drawdown due to phytoplankton uptake, heterotrophic respiration, and air–sea CO_2 exchange for DIC. Based on the plots of NO_3 and DIC as functions of salinity (Fig. 2), we could distinguish losses of NO_3 and DIC due to phytoplankton production from that due to surface water mixing with the following approach: the data points at the two extremes of the salinity versus NO_3 and salinity versus DIC plots were selected as potential mixing end members; the line connecting the two end members represents mixing of the two water masses with different salinities and concentrations of NO_3 and DIC without biological drawdown; the concentrations of NO_3 and DIC expected from the mixing of the two water masses for a given sample was obtained by entering the salinity of the sample into the mixing line equation (Table 1). Downward deviations of NO_3 and DIC concentrations from the mixing lines represent the net result of biological processes and air–sea CO_2 exchanges. The drawdown of NO_3 or DIC was computed as the difference between the observed concentration and the concentration expected from mixing. The NO_3, DIC and salinity properties of the two end members and the equations defining the mixing lines are given in Table 1. As respiration and nutrient regeneration in the euphotic zone were not estimated, our estimates of DIC and NO_3 drawdowns in the present study represent net DIC and NO_3 utilization by phytoplankton and possibly ice algae, which may use water column nutrients when they enter the water column.

Because the air–sea CO_2 exchanges contributed to DIC changes in the water column, we examined the effects of air–sea CO_2 exchange (F_{CO_2}, $mg\,m^{-2}\,d^{-1}$) on $\Delta DIC:\Delta NO_3$ based on pCO_2 data of Miller et al. (2002) (see Section 4).

2.3. Statistics

The student *t*-test was used to test differences between two means using Statistica (StatSoft, Tulsa, USA). Model II regression (standard major axis procedure, SMA, Legendre and Legendre, 1998) was used to obtain the slope of the regression between two variables, considering that both the *X* and *Y* variables contained errors. Differences between slopes were tested based on the 95% confidence intervals (95% C.I.) of the slopes. Principal component analysis (PCA) was conducted based on the correlation matrix among variables using Statistica (StatSoft, Tulsa, USA).

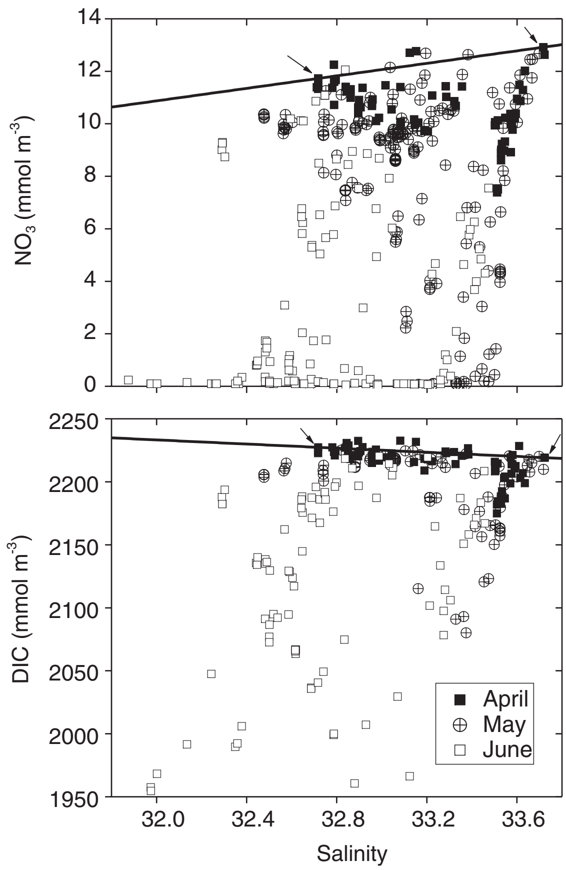

Fig. 2. Scatter plots of NO_3 (upper panel) and DIC (lower panel) as a function of salinity. Solid lines are the mixing lines for the two end members, which characterize the relationships between salinity, NO_3, and DIC due to the mixing of the two water masses with different salinity, NO_3, and DIC properties (equations in Table 1). The two arrows on the mixing lines point to the two end members. The salinities of Baffin Bay samples decreased from 33.7 (upper right) in April, when NO_3 was 12.9 $mmol\,m^{-3}$, to 33.4 (lower right) in June, when NO_3 is depleted; the salinities of most Arctic water samples decreased from 32.7 in April (upper left), when NO_3 was 11.7 $mmol\,m^{-3}$, to 32.3 (lower left) in June, when NO_3 was depleted, except for a few samples for which salinities decreased to <32.3.

3. Results

3.1. Seasonal variations of phytoplankton biomass and community structure

Detailed dynamics of the phytoplankton bloom (Mei et al., 2002) and seasonal succession of phytoplankton community structure (Lovejoy et al., 2002a) were reported elsewhere. These results are summarized in Fig. 3, which shows the seasonal

Table 1
Physical and chemical properties of the end members of the two main water masses in the NOW

Target nutrients	Properties	End member 1 (Arctic water)	End member 2 (Baffin Bay water)
NO_3 (mmol m^{-3})	Salinity	32.72 (32.29–32.72)	33.72 (33.44–33.72)
	NO_3	11.73	12.9
	Mixing line	$NO_3 = 1.19$ salinity–27.254	
DIC (mmol m^{-3})	Salinity	32.72 (32.29–32.72)	33.72 (33.44–33.72)
	DIC	2227.4	2219.4
	Mixing line	$DIC = -8.19$ salinity + 2495.4	

Ranges in seasonal variation of salinity of the two end members are in parentheses. The equations define the mixing lines of the two end members shown in Fig. 2.

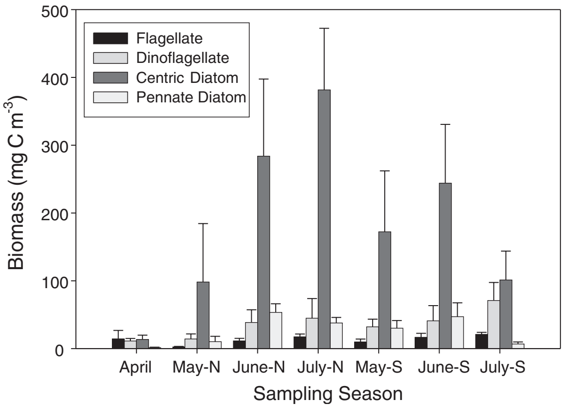

Fig. 3. Biomasses of flagellates, dinoflagellates, and centric and pennate diatoms from April through July 1998. N and S after months on *X*-axis refer to the northern and southern stations, respectively, as defined in the Section 2. Phytoplankton biomass was averaged over the whole area in April. Error bars show the standard errors of means.

and spatial changes in biomass of the major phytoplankton groups (flagellates, dinoflagellates, and centric and pennate diatoms). Briefly, phytoplankton biomasses ranged from 40 to 480 mg C m^{-3}, and were low in April. The diatom bloom was first observed in the southeast of the polynya (Station 54) in late May; it extended to the northwest of the polynya in June, and declined in June at stations where it had been first observed in May. The biomasses of flagellates and dinoflagellates slightly increased from April to June at all stations. Centric diatoms were mostly responsible for the seasonal changes in phytoplankton biomass; they varied from 30% (April) to 79% (June, northern polynya) of the total phytoplankton biomass during the investigation.

3.2. DIC to NO_3 drawdown ratio (ΔDIC:ΔNO_3)

The NO_3 to DIC drawdown ratios (ΔDIC:ΔNO_3, mol:mol) were estimated as the slopes of Model II regressions between the drawdowns of two nutrients, after correcting for the mixing of two water masses (see Section 2). Due to small dataset, and small range of nutrient drawdowns in April, the DIC and NO_3 drawdowns of April were combined with those of May.

The ΔDIC:ΔNO_3 was 6.7 (95% C.I.: 6.1–7.4) in April and May (Fig. 4, upper panel), and 11.9 (95% C.I.: 10.7–14.2) in June (Fig. 4, lower panel). ΔDIC was >100 mmol m^{-3}, at station 54 in May , and >120 mmol m^{-3} at stations 18, 36, 40, 44, 50 and 56 in June, whereas corresponding ΔNO_3 remained constant at about 11–12 mmol m^{-3}. These data points (shown as empty symbols in Fig. 4) were not included in the Model II linear regression analysis in order to avoid overestimating the regression coefficients.

In the present study, the major uncertainty in estimating the mixing of different water masses comes from changes in salinity due to ice melt during the opening of the polynya. If ice melt had accompanied the opening of the polynya from April through July, this would have compromised the use of salinity as a tracer to resolve the mixing between the Arctic and Baffin Bay waters. However, because of the advective character of the ice in the polynya (Ingram et al., 2002), most melting took place along the southern transects, where there was no significant decrease in surface salinity until late June. The salinity of end members I (Arctic Water) and II (Baffin Bay water) decreased by 0.5 and 0.3, respectively, between April and June (Table 1). Salinity decreased to <32 on the transect from

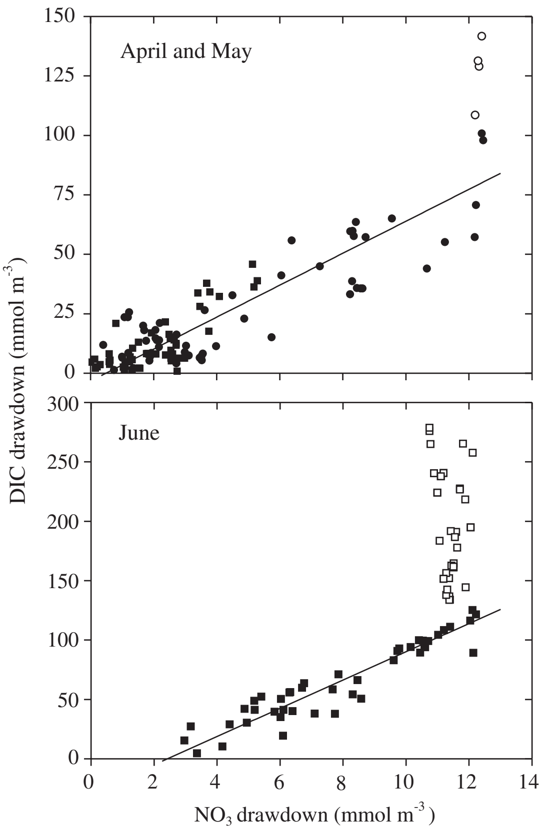

Fig. 4. Relationship between DIC and NO_3 drawdowns for (upper panel) combined April (solid square) and May (solid circle), and (lower panel) June. Empty dots were not included in the regressions to avoid biasing the regression coefficients. Line: model II linear regressions (SMA): $\Delta DIC = 6.7\ \Delta NO_3 - 3.2$ ($r^2 = 0.78$, $n = 109$, $p < 0.01$) for April and May; $\Delta DIC = 11.9\ \Delta NO_3 - 28.8$ ($r^2 = 0.89$, $n = 44$, $p < 0.001$) for June.

stations 44–54, except at station 44, in late June. By that time, nutrients had already been depleted at stations with low salinity (southern stations sampled in late June), so that the effects of melting on nutrient drawdown would have been small.

The mixing lines are defined based on salinity and nutrient concentrations of the two end members (Fig. 2). The same lines were valid over the 3 months indicating that the end members were not affected by seasonal changes in salinity due to ice melt. Based on the mixing line equations (Table 1), a decrease in salinity of 0.5 due to ice melting would have underestimated ΔNO_3 by $0.6\,mmol\,m^{-3}$, and overestimated ΔDIC by $5\,mmol\,m^{-3}$, for samples affected by ice melt. The resulting errors in ΔNO_3 and ΔDIC are close to the uncertainties in NO_3 and DIC determinations. Because ice melt became important in the northern part of the NOW when the atmospheric and water temperatures increased in July, we did not attempt to resolve the nutrient drawdown for that month.

3.3. *Chl yield and NO_3 depletion*

In order to estimate Chl yield ($mg\,m^{-3}$) corresponding to the observed NO_3 depletion ($mmol\,m^{-3}$) during the phytoplankton bloom, we regressed NO_3 on Chl based on the samples in the euphotic zone taken in April and May (including only samples with Chl$<11\,mg\,m^{-3}$, and NO_3 above depletion, i.e. $\geqslant 0.2\,mmol\,m^{-3}$), because the effects of phytoplankton losses due to sinking and grazing on the regression are negligible in that period (next paragraph). The slope of Model II regression equation (SMA) of NO_3 as a function of Chl is -1.06 (95% C.I.: -1.1 to -1.0) (Fig. 5), which is not significantly different from -1.0. That is, 1 mol of NO_3 would produce 1 g of Chl during the phytoplankton bloom, when the effects of phytoplankton losses due to grazing and sinking are ignored.

The Chl yield corresponding to a given NO_3 depletion could have been underestimated if Chl had been lost due to sinking or grazing. In April and May, export due to sinking was small ($1.5\%\,d^{-1}$) because of low sinking velocities (Mei et al., 2003). Losses due to copepod grazing accounted for $<10\%$ of phytoplankton production during the

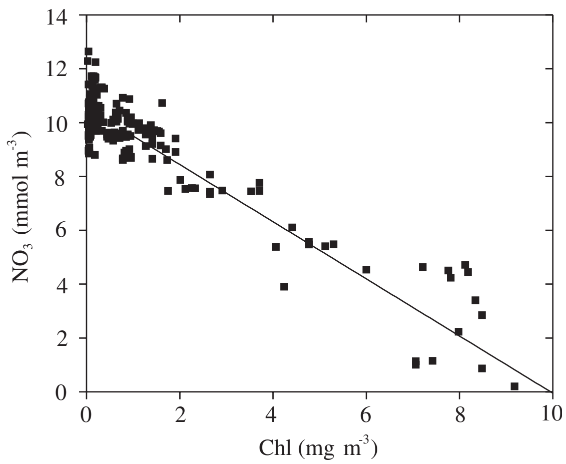

Fig. 5. Relationship between Chl and NO_3 in the euphotic zone during April and May, when the losses of phytoplankton due to grazing and sinking were small (see text). Line: model II linear regression (SMA): $NO_3 = -1.1\ Chl + 10.56$ ($r^2 = 0.85$, $n = 239$, $p < 0.001$). Note: the units for NO_3 and Chl are $mmol\,m^{-3}$ and $mg\,m^{-3}$, respectively.

phytoplankton bloom; a significant increase of 15–55% of primary production occurred only after the phytoplankton bloom ended in late June and July (Saunders et al., 2003). Given the average P^B (production normalized to Chl) of 11 g C (g Chl)$^{-1}$ d^{-1} in the NOW (Mei et al., 2003), the daily loss due to copepod grazing accounted for 0.9% of the phytoplankton standing stock. Therefore, losses of phytoplankton biomass from the euphotic zone were insignificant in April and May.

It follows that the slope based on Chl and NO_3 in the euphotic zone of April and May is not significantly biased by export. The slope of −1.06 (Fig. 5) is similar to that obtained from deck incubations in the NOW, where 1 g of Chl was produced from 1 mol of NO_3 (Lovejoy et al., 2002b), and also as frequently observed under laboratory (Caperon and Meyer, 1972; Laws et al., 1983) and field conditions (Sakshaug et al., 1981; Barlow, 1982; Marra et al., 1990).

3.4. POC to PON production ratio (ΔPOC:ΔPON)

Fig. 6 shows two groups of stations. On the one hand, ΔPOC:ΔPON = 5.8 (95% C.I.: 5.6–6.0) was observed at stations sampled in April and May (except for station 54), the northern stations in June, and stations N1 and N2 in July. This production ratio is lower than the Redfield C:N ratio of 6.6, and the corresponding samples will be referred to as N-enriched production in the remainder of this study. On the other hand, ΔPOC:ΔPON = 8.9 (95% C.I.: 8.3–9.5) was observed at station 54 in May, southern stations in June and all stations (except for stations N1 and N2, where NO_3 concentration was still high) in July. This value is higher than the Redfield ratio, and the corresponding samples will be referred to as C-enriched production in the remainder of this study.

In order to use the regression slope of POC on PON (and POC on Chl, see Section 3.5) as robust estimates of phytoplankton ΔPOC:ΔPON (and ΔPOC:ΔChl), we must assume that non-phytoplankton detrital carbon was the same over the range of PON (or Chl). This assumption is not easy to test. However, on the regional to global scale, the variation of POC over seasonal cycles and across oligotrophic to eutrophic conditions is mostly contributed from phytoplankton biomass when Chl is >0.14 mg m^{-3} (Behrenfeld et al., 2005 and references cited). For N-enriched production, the intercept of the regression is small, i.e. 2.0 mmol m^{-3} (95% C.I.: 1.4–2.7), indicating that POC contributed from detritus was small. Similarly for C-enriched production, the intercept of the regression is not significantly different from 0, i.e. −0.48 mmol m^{-3} (95% C.I.: −2.7–1.6) (Fig. 6). Therefore, we assumed a small and constant contribution of detrital carbon to POC, based on the very small intercepts.

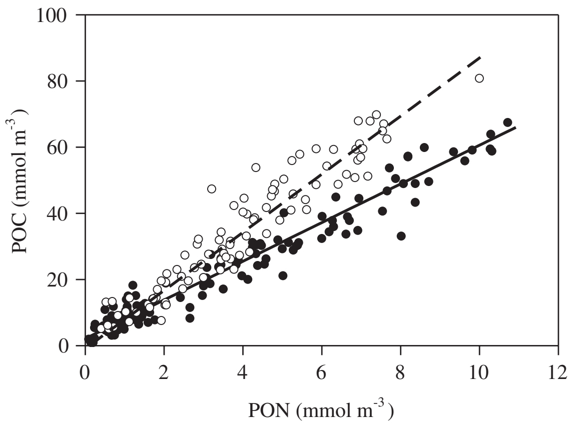

Fig. 6. Relationships between particulate organic carbon (POC) and particulate organic nitrogen (PON). Full dots represent samples taken at all stations in April and May, northern stations in June, and stations N1 and N2 in July (N-enriched). Empty dots represent samples taken at southern stations in June and all stations except N1 and N2 in July (C-enriched). Solid and dashed lines: model II linear regressions for N- and C-enriched production, respectively: POC = 5.8 PON + 2.0 ($r^2 = 0.96$, $n = 144$, $p<0.001$) for N-enriched production; POC = 8.9 PON−0.48 ($r^2 = 0.84$, $n = 96$, $p<0.01$) for C-enriched production.

Samples with N-enriched production (ΔPOC:ΔPON < the Redfield ratio) showed significantly higher NO_3 (7.2 ± 0.7 vs 2.1 ± 0.3 mmol m^{-3}, $p<0.01$) and deeper mixed layer (29 ± 4 vs 9 ± 0.8 m, $p<0.01$) than samples with C-enriched production (ΔPOC:ΔPON > Redfield ratio). The average PAR in the euphotic zone (PAR_{EU}) was not significantly different (54 ± 7 versus 60 ± 7 µmol m^{-2} s^{-1}, $p = 0.58$) between the two groups. However, average PAR in the surface mixed layer (PAR_{MLD}) (83 ± 17 versus 151 ± 24 µmol photons m^{-2} s^{-1}, $p<0.05$) in samples of N-enriched production was significantly lower than in samples with C-enriched production.

PCA of MLD, PAR_{MLD}, PAR_{EU}, NO_3 in the euphotic zone, and percent diatoms (%Diatom) showed that the first two principal components explained 70% of the total variance, with the first principal component explaining 43% of the variance (Fig. 7). Stations with C-enriched (empty dots)

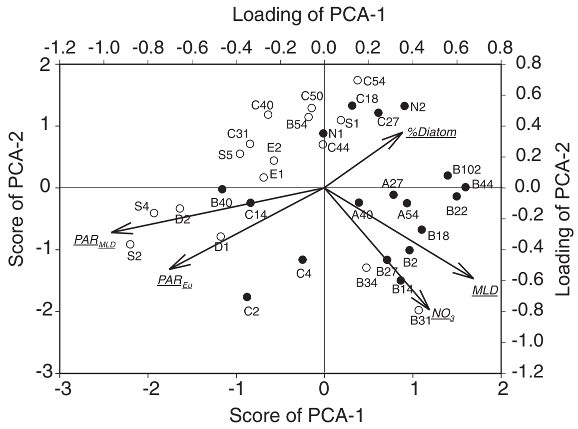

Fig. 7. Principal component analysis: biplot of scores of stations and loadings of variables (PAR_{MLD}, PAR_{EU}, MLD, NO_3, and %Diatoms) on the two principal axes. Solid dots: N-enriched production; empty dots: C-enriched production.

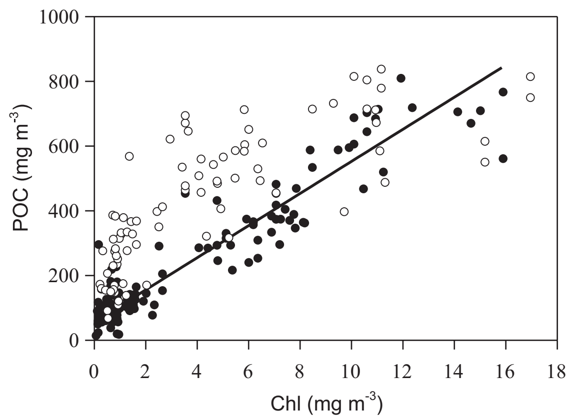

Fig. 8. Relationship between POC and Chl. Full dots represent the samples taken at all stations in April and May, northern stations in June, and stations N1 and N2 in July, where nutrients were not depleted. Empty dots represent the rest of the samples taken at the southern stations in June, and all stations except for N1 and N2 in July, where nutrients were depleted. Only the samples from nutrient sufficient stations were included in the regression analysis. Line: model II linear regression (SMA): POC = 49.6 Chl + 56.7 ($r^2 = 0.89$, $n = 129$); the 95% confidence interval (95% C.I.) for the slope ranges between 46.8 and 52.5.

and N-enriched (filled dots) production are ordinated along the first principal axis, which is highly correlated with PAR_{MLD}, PAR_{EU}, and MLD. On the first two axes, stations with C-enriched production are associated with shallow MLD and low NO_3, and those with N-enriched production, with deep MLD and high NO_3. Because %Diatom is weakly correlated with the first two principal axes, it does not explain the differences in ΔPOC:ΔPON of the two groups.

3.5. POC to Chl production ratio (ΔPOC:ΔChl)

POC was positively correlated with Chl, and the slope of model II linear regression between POC and Chl was 49.6 (95% C.I.: 46.8–52.5) (Fig. 8) for samples of N-enriched production. The calculated regression slope provides an estimate of phytoplankton ΔPOC:ΔChl, assuming that detrital carbon accounted for a small fraction of POC (see Section 3.4, on ΔPOC:ΔPON). The relationship for C-enriched production is not linear, with most of the data points falling above the regression line for N-enriched production.

4. Discussion

4.1. Discrepancies between $\Delta DIC:\Delta NO_3$ and ΔPOC:ΔPON: implications for DOC production

While ΔPOC:ΔPON increased from 5.8 from April to early June to 8.9 in late June and July, $\Delta DIC:\Delta NO_3$ increased from 6.7 in April and May to 11.9 in June. There was no estimate of $\Delta DIC:\Delta NO_3$ for July. However, the ratio should have been similar to that observed in June, given that most of the nutrients had been depleted (<0.05 μM) by the end of June. Ammonium was undetectable during the phytoplankton bloom in May and June. In summary, the increase in $\Delta DIC:\Delta NO_3$ took place earlier than that of ΔPOC:ΔPON. The discrepancies between ΔDIC: ΔNO_3 and ΔPOC:ΔPON are striking. When averaged over the whole sampling period [average $\Delta POC:\Delta PON = (5.8 + 8.9)/2 = 7.4$; average $\Delta DIC: \Delta NO_3 = (6.7 + 11.9)/2 = 9.3$], the ΔPOC:ΔPON was about 80% [$= (7.4/9.3) \times 100\%$] of ΔDIC: ΔNO_3, i.e. the production of POC was 20% lower than that of total organic carbon. Discrepancies between $\Delta DIC:\Delta NO_3$ and ΔPOC:ΔPON have been observed in many instances (e.g. Sambrotto et al., 1993; Banse, 1994), and were attributed to the production of dissolved organic carbon (DOC). Nitrogen fixation, which could be another cause for the elevated $\Delta DIC:\Delta NO_3$ (Lee et al., 2002; Anderson and Pondaven, 2003), should be of minor importance in the NOW because diazotrophs, which are the main nitrogen-fixation group, and cyanobacteria in general were not observed during our sampling (Lovejoy et al., 2002a). Wong et al. (2002) indicated that calcification might be more important than DOC production in contributing to the difference between ΔDIC:ΔNO_3 and ΔPOC:ΔPON in the Northeast subarctic Pacific. In the NOW, however, calcifying organisms such as coccolithophores were rarely observed during spring–summer 1998 (Lovejoy et al., 2002a). Preferential recycling of N over C as observed in some marine systems, when NO_3 became exhausted, (Thomas et al., 1999), might have contributed to the elevated ΔDIC:ΔNO_3 relative to ΔPOC:ΔPON. Such preferential recycling would have been possible at few stations only, such as station 54 in May and on southern transects in late June, where NO_3 became exhausted. However, the discrepancy between ΔDIC:ΔNO_3 and ΔPOC:ΔPON in April and May (except at station 54), and at northern stations in early June, before NO_3 was exhausted, cannot be attributed to preferential recycling of N, but instead to DOC production. DOC concentrations determined in the NOW during the same period as our study show substantial accumulation in the upper mixed layer, where it increased from 76–100 mmol m^{-3} in April to 120–160 mmol m^{-3} in July, depending on locations (Miller et al., 2002). This supports the idea that DOC production was mostly responsible for the discrepancy between ΔDIC:ΔNO_3 and ΔPOC:ΔPON.

If the discrepancy of 20% between ΔNO_3:ΔDIC and ΔPOC:ΔPON is attributed to DOC production, this value is lower than our previous estimate that DOC production accounted for 34% of total primary production during April–July (Mei et al., 2003). However, the value of 20% is a lower bound estimate of the contribution of DOC production to total DIC depletion, because the uptake of atmospheric CO_2 by the sea was not accounted for. Based on the pCO_2 (partial pressure of CO_2, μatm) values reported by Miller et al. (2002), CO_2 in surface water was undersaturated at stations on the Greenland side from May, and on the Canadian side from June, i.e after the initiation of phytoplankton production in those areas. CO_2 in surface water was oversaturated from April to June at a few stations only, north of 77.5°N where phytoplankton production was delayed. Therefore, influx of CO_2 from air to sea dominated the air-to-sea CO_2 exchange at stations where phytoplankton production started. The flux of atmospheric CO_2 into surface waters likely reduced the observed DIC drawdown (ΔDIC) due to phytoplankton production at most of the stations, after the initiation of phytoplankton production. It follows that our values likely underestimated the ΔDIC:ΔNO_3 due to phytoplankton production.

The 20% value is close to the global average of 17% of net primary production that is accounted for by semi- and refractory DOC (Hansell and Carlson, 1998). The observation that DIC drawdown continued to increase at NO_3 drawdown of 11–12 mmol m^{-3}, without further increase in NO_3 drawdown (Fig. 4), is a sign that some of the DIC uptake was caused by DOC production after nutrient depletion.

4.2. Stoichiometry of phytoplankton POC:PON production: seasonal changes

At temperate upwelling sites off Oregon, where diatoms dominated the phytoplankton assemblage and primary production during upwelling season was similar to that observed in the NOW, Wetz and Wheeler (2003) reported, based on deck incubation experiments, that the production of particulate organic matter was nitrogen-enriched at the beginning of the phytoplankton bloom, and became carbon-enriched at the end of the bloom, after nitrate depletion. Our results on the changes of ΔPOC:ΔPON during the development of the phytoplankton bloom in the NOW agree with this trend. In the present study, increased irradiance in the mixed layer, which was accompanied by decreased NO_3 supply, could have played a role in increasing ΔPOC:ΔPON during the later stage of the phytoplankton bloom. Indeed, PCA identified PAR_{MLD}, which correlated with the first principal axis, as the most important variable separating the stations falling into the N-enriched and C-enriched groups (Fig. 7). The increase in PAR_{MLD} as the season progressed resulted from both reduced MLD, and increased solar radiation as solar elevation increased and the ice cover diminished.

On the one hand, the range of variation in C:N is rather narrow among different species, due to the narrow range of variation in C:N of the dominant cellular components (e.g. proteins, nucleic acids and phospholipids) across a variety of phytoplankton taxa; and increased C:N can be observed when the protein content of cellular biomass decreases substantially as a result of NO_3 starvation (Geider and La Roche, 2002). On the other hand, high irradiance can contribute to increased POC:PON, when N supply is limited, by synthesizing N-poor photoprotective pigments (Levasseur and Therriault, 1987; Dubinsky and Berman-Frank, 2001).

In general, ΔPOC:ΔPON higher than the Redfield ratio is related to reduced growth rate resulting from N limitation (Goldman et al. 1979; Goldman, 1986; Sterner and Elser, 2002), whereas lower than the Redfield ratio results from light limitation (Geider et al., 1998). We conclude that phytoplankton in the NOW experienced light-limited growth in April, May, and early June (north) when ΔPOC:ΔPON was <6.6, and N-limited growth in June (south), and July, when ΔPOC:ΔPON was >6.6.

4.3. Implications of C:N stoichiometry of phytoplankton production on C cycling in marine ecosystems, and responses to climate change

Seasonally, ΔDIC:ΔNO_3 increased more (from 6.7 to 11.9) than ΔPOC:ΔPON (from 5.8 to 8.9). This suggests that the C:N ratio of DOM increased more than that of POM during the phytoplankton bloom. This is consistent with the observation of Kepkay et al. (1997) during the summer phytoplankton bloom in Bedford Basin, Canada, that the C:N ratio of POM was relatively constant, while that of DOM varied. In the NOW, ΔPOC:ΔPON started to increase later than ΔDIC:ΔNO_3, in response to reduced MLD and nutrient concentrations. The time-dependent C:N incorporation into particulate and DOM during the course of the phytoplankton bloom would have significant consequences for the carbon and nitrogen cycling in the herbivorous and microbial food webs. The increased ΔPOC:ΔPON would decrease the quality of phytoplankton as food for herbivores and thus their production (Jones et al., 2002), which would in turn reduce the efficiency in transferring carbon towards large animals in the C-enriched production regime. Hecky et al. (1993) suggested that the usually higher C:N ratios of seston in freshwater than marine systems may be one of the reasons why the yield of fisheries per unit of C fixed by photosynthesis is lower in freshwater than marine systems. Hence, reduced transfer efficiency of C in the herbivorous food web could favour export to deep water or recycling by microbial heterotrophs.

The observed seasonal increases in ΔPOC:ΔPON in the NOW were largely driven by the reduction in MLD that exposed phytoplankton to increased irradiance. Hence, on the decadal time scale, increased stratification due to ice melt, especially glacier melting expected from global warming, could result in shallower mixed layer in the NOW, as expected in other ice-covered region, where warming would increase ice melt, freshwater influx, and thus stratification (e.g. Aagaard and Carmack, 1989). As a result, phytoplankton would be exposed to increased average irradiance in the shallower mixed layer with reduced nutrient supply, thereby increasing the C:N ratio of primary production. The latter may decrease the efficiency of transferring C from primary production to large animals.

4.4. Stoichiometrically based balance between PON production and NO_3 depletion

Based on the stoichiometry of phytoplankton production (Chl:NO_3, ΔPOC:ΔPON and ΔPOC:ΔChl), which were conservative over the polynya under specific conditions such as N-enriched production or C-enriched production, we estimated PON production as a percentage of NO_3 consumption (PON/NO_3) at the spatial scale of the whole polynya, and a temporal scale that covers two periods, i.e. April to early June, and late June to July, respectively, using the following approach:

$$\frac{\mathrm{PON}}{\mathrm{NO_3}} = \frac{\mathrm{Chl}}{\mathrm{NO_3}} \times \frac{\mathrm{POC}}{\mathrm{Chl}} \times \frac{\mathrm{PON}}{\mathrm{POC}}.$$

Because $\mathrm{Chl/NO_3} = 1$ ($\mathrm{mg\,mmol^{-1}}$, minus sign was ignored for simplicity), $\mathrm{POC/Chl} = 49.6/12$, ($\mathrm{mmol\,mg^{-1}}$), and $\mathrm{PON/POC} = 1/5.8$ ($\mathrm{mol\,mol^{-1}}$) for April to early June, then, $\mathrm{PON/NO_3} = 1 \times (49.6/12) \times (1/5.8) = 0.71$ in April to early June, corresponding to N-enriched production. The estimated uncertainty resulting from the propagation of errors estimated from the 95% C.I. of individual drawdown ratios is 17%.

For the remainder of the season (late June to July), which corresponded to C-enriched production, ΔPOC:ΔPON was 8.9. Hence,

$$\frac{\mathrm{PON}}{\mathrm{NO_3}} = 1 \times (49.6/12) \times (1/8.9) = 0.46.$$

The estimated uncertainty is 20%.

The value PON/NO_3 for C-enriched production could be underestimated because we used the same ΔPOC:ΔChl as for the N-enriched production, whereas the ΔPOC:ΔChl for C-enriched production under nutrient limitation might be higher than that for N-enriched production (Fig. 8; Cloern et al., 1995).

In other words, PON produced in the water column represented only 71% of the NO_3 taken up by phytoplankton during the N-enriched phytoplankton blooms from April to early June. The value in late June and July is 46% of the NO_3 uptake in areas dominated by C-enriched phytoplankton production, corresponding to the breakdown of the phytoplankton bloom. The missing N estimated on the basis of stoichiometry should not be interpreted as PON export because the three terms of the algorithm, except for Chl/NO_3, do not contain export processes. The effect of export on Chl/NO_3 is assumed to be small based on the discussion in Section 3.3, and thus export is explicitly excluded from our algorithm.

The stoichiometrically estimated imbalance between PON production and NO_3 depletion in the present study indicates the significant losses of NO_3 to DON and heterotrophic bacteria during the phytoplankton bloom, and its breakdown (late June and July). The NO_3 going to DON is generally not included in field estimates of new production, as reported for various marine systems based on ^{15}N tracer experiment (Bronk et al., 1994). Although there is some debate as to the significance of N losses to the dissolved organic and heterotrophic pools that are not retained on the filters during most of the field filtrations (Bronk and Ward, 2000; Slawyk et al., 2000), these losses generally increase during the decline of the phytoplankton bloom (Bronk et al., 1994).

In the NOW, there are no DON data available as yet. However, the increased DON production from spring to summer estimated from the stoichiometry of phytoplankton production in the present study agrees with field observations in Northeast Water Polynya, where the percentage of inorganic N converted to DON in surface waters increased from spring to summer 1993 (Skoog et al., 2001). The seasonal pattern of DON production could have resulted from the sloppy feeding of herbivorous zooplankton (Tremblay et al., Unpublished) and microbial activities. On the same cruises as ours, Huston and Deming (2002) reported that the activity of leucine–aminopeptidase, which is one of the proteases and is associated with sinking particles, dominated the bacterial extracellular enzymes and increased as the season progressed. These studies are consistent with the trend of increased seasonal DON production that we estimated.

During the same cruise, Middelboe et al. (2002) reported that bacterial production increased when the phytoplankton bloom ended, and substrates originating from primary production increased in July 1998. N-limited bacteria tend to take up ammonium and retain N in their cells, to keep a strict C:N stoichiometry when N is limited in the environment (Goldman et al., 1987; Goldman and Dennett, 2000). During September 1999, Fouilland et al. (Pers. Comm.) estimated that heterotrophic bacteria accounted for 40–90% of the total inorganic N uptake, based on ^{15}N tracer experiments with selective inhibition of heterotrophic bacteria in the NOW. Therefore, the release of extracellular DON by phytoplankton, microbial remineralization of organic N, and incorporation of inorganic N into heterotrophic bacteria may all be responsible for the missing N, especially during the breakdown of the phytoplankton bloom.

The percentage of missing N provides a measure of the efficiency of the microbial food web at recycling organic N. The gap between PON production and NO_3 depletion in the NOW indicates that the organic N that was not recovered in PON was not recycled over the sampling period. As bacteria in cold waters (e.g. NOW) require high levels of substrate to achieve optimum growth (Pomeroy and Wiebe, 2001), bacterial production there and consequently the recycling of organic matter by the microbial food web could be decoupled from primary production. In that case, the delayed recycling of organic N would contribute to the imbalance between PON production and NO_3 depletion. This decoupling has important implications for the estimation of new production based on NO_3 depletion in cold waters. Hu and Smith (1998) reported that 8–19% of the $^{15}NO_3$ uptake was released as DON in the Ross Sea. The latter represents total (or gross) new production (i.e. NO_3-based production of both PON and DON). When the temporal scale of observations is not long enough to allow the recycling of DON by the microbial food web, export of PON based on NO_3 depletion and PON standing stock could be overestimated.

The fate of DON produced in surface waters is highly dependent on residence time and advection pathways. The residence time of surface water in the NOW is seasonally variable (Melling et al., 2001). Most of the surface water on the western side of the polynya advects southward to the Baffin Bay, and that on the Greenland coast advects northward (Melling et al., 2001). DON produced during the spring–summer phytoplankton bloom could be brought to the regions downstream, and increase primary production in these regions. It follows that determining DON production in the NOW would be fundamental to understand the regional biogeochemical cycling of N.

5. Conclusion

The present study shows that the stoichiometry of phytoplankton C:N production during the phytoplankton bloom changed with the physical properties of the water column during the course of seasonal succession. As DOM and POM are substrates for the microbial and herbivorous food webs, respectively; and increased C:N of organic matter generally reduces the quality of substrate for heterotrophic organisms, changes in the C:N production of DOM and POM will have significant effects on the cycling and transfer of organic carbon in the pelagic food webs by modifying the assimilation efficiency of heterotrophic organisms.

The constant stoichiometry of C:N phytoplankton production under specific nutrient and light conditions indicates an imbalance between PON production and NO_3 depletion integrated over the whole polynya and the sampling period. The present study shows that a significant amount of the organic N produced was not recovered in PON, and thus channelled to DON and heterotrophic bacteria. That organic N had not been recycled in the planktonic system by the end of our sampling season. Consequently, the resulting estimates of new production, and thus exports would be different from those based on NO_3 depletion.

Stoichiometric data of C:N on phytoplankton production in the present study show that the production of DOC and DON contributed to the depletion of DIC and NO_3, respectively, in the NOW during the spring–summer phytoplankton bloom. However, there remain uncertainties in the estimated contribution of DOC and DON production to DIC and NO_3 drawdown, due to uncertainties and assumptions in various components of our analysis. Additional data on the standing stocks, and production and remineralization rates of DOC and DON would be needed to reduce the uncertainties.

The upcoming global warming will increase the temperature of the upper water column, and the stratification of the upper ocean, and thus decrease the supply of new nutrients from depth (e.g., Aagaard and Carmack, 1989). The resulting changes in phytoplankton stoichiometry and thus total and new production should correspond to those we observed in the C-enriched production regime, i.e. increased C:N of primary production, reduced transfer efficiency of carbon from primary producers to large animals, and thus increased activity of the microbial food web relative to the herbivorous food web. These conditions could become prevalent under long-term (decadal and centennial) climate change.

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