



RESEARCH ARTICLE

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Key Points:

- Particulate C:N ratios were well below the Redfield ratio in low-productivity Arctic waters
- Heterotrophic microbial biomass may have contributed to the low-particulate C:N measured
- Particulate C:N ratio is positively correlated with phytoplankton size and biogenic silica

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Low particulate carbon to nitrogen ratios in marine surface waters of the Arctic

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Abstract During the Canada's Three Oceans and Joint Ocean Ice Study projects in the summers of 2007 and 2008, we measured particulate organic carbon to nitrogen ratios (POC:PON) throughout the euphotic zone in Subarctic and Arctic waters. Average depth-integrated values (2.65 ± 0.19) in the Beaufort Sea and Canada Basin (BS-CB domain) were much lower than both the Redfield ratio (6.6) and the average ratios (3.9 to 5.6) measured across other Arctic-Subarctic domains. Average uptake ratios of C and N ($\rho_C:\rho_N$) were also lower (0.87 ± 0.14) in BS-CB than in the other four domains (2.10 to 3.51). Decreasing POC:PON ratios were associated with low concentrations of phytoplankton C, reduced abundance of biogenic silica (bSiO₂), a smaller relative contribution of the $>5 \mu\text{m}$ fraction to total chlorophyll *a* and a larger relative contribution of small flagellates ($<8 \mu\text{m}$) to total phytoplankton C. In the subsurface chlorophyll *a* maximum (SCM) within the BS-CB domain, phytoplankton C represented only ~13% of POC; and therefore, the presence of heterotrophic microbes may have decreased POC:PON. These ratios are supported by data obtained during other Arctic programs in 2006, 2008, and 2009. Previous work has suggested a link between freshening of surface waters and increasing dominance of picophytoplankton and bacterioplankton in the Canada Basin, and the low POC:PON ratios measured during this study may be a consequence of this shift. Our results have ramifications for the conversion between C- and N-based estimates of primary productivity, and for biogeochemical modeling of marine Arctic waters.

1. Introduction

The Arctic Ocean encompasses a unique assemblage of contrasting ecosystems where highly productive areas such as the Chukchi Sea sit alongside barren areas such as the Canada Basin in which extremely low levels of primary productivity have been recorded [Varela *et al.*, 2013]. As Arctic sea ice melts, a fundamental question for oceanographers is how biological communities and associated biogeochemical processes respond to these physical changes. In the highly productive waters of the Bering and Chukchi Seas, the retreat of sea ice has already caused a shift in biological boundaries [Grebmeier *et al.*, 2006]. In the less productive waters of the Canada Basin, recent sea ice retreat and surface freshening have resulted in a deepening of the nutricline and subsurface chlorophyll *a* maximum (SCM) [McLaughlin and Carmack, 2010], and a shift toward a community dominated by picophytoplankton ($<2 \mu\text{m}$) and bacterioplankton [Li *et al.*, 2009]. In the southern Beaufort Sea, this stratification and deepening of the SCM appears to have resulted in increased nitrate uptake at the bottom of the euphotic zone and a concomitant increase in net community production in the water column [Bergeron and Tremblay, 2014]. In northern Baffin Bay, however, nitrate consumption in the upper 100 m has declined some 65% in the once highly productive North Water Polynya (NOW), which has resulted from surface freshening and stratification and an apparent decrease in the productivity of diatoms [Bergeron and Tremblay, 2014]. How the biological carbon pump will operate in a warmer fresher Arctic is therefore unclear and dependent on region [Tremblay and Gagnon, 2009; Tremblay *et al.*, 2012; Varela *et al.*, 2013] and was one of the questions addressed by the Canada's Three Oceans (C3O) program (a Canadian component of the International Polar Year, IPY) [Carmack and McLaughlin, 2011].

A cornerstone assumption in studies on the biological carbon pump is that the molar ratio of particulate organic carbon (POC) to nitrogen (PON) at least approximates the Redfield ratio of 6.6 [Redfield, 1958], although variations on the order of 15 to 20% have been observed [Copin-Montegut and Copin-Montegut, 1983; Martiny *et al.*, 2013a]. With regard to Arctic marine waters, a fundamental question that has received

little attention is whether assumptions of Redfield ratio are robust when interconverting between various production estimates across these highly contrasting environments. The extensive reviews of oceanic elemental ratios of *Copin-Montegut and Copin-Montegut* [1983] and *Martiny et al.* [2013a] presented no data for Arctic marine waters, and most published POC:PON ratios in Arctic seas have come from isolated studies in the more productive regions. For example, POC:PON ratios tend to be close to, or higher than, the Redfield ratio of 6.6 for the NOW in northern Baffin Bay [*Mei et al.*, 2005], the Northeast Water Polynya on the northeastern Greenland shelf [*Daly et al.*, 1999], and in the Fram Strait and Barents Sea [*Tamelander et al.*, 2012].

The Canada's Three Oceans (C3O) and Joint Ocean Ice Study (JOIS) projects during the summers of 2007 and 2008 provided an opportunity to compare a large set of C:N ratios in suspended particulate organic matter (POM) in the euphotic zone across Arctic/Subarctic regions surrounding northern North America. Observations from other sampling programs during 2006, 2008, and 2009 are also used in this study to validate the C3O and JOIS POC:PON data. Spatial variations in particulate C:N ratios are further interpreted using C:N uptake ratios in the euphotic zone, as well as taxonomic analysis and C content of dominant groups of phytoplankton from the SCM.

2. Methods

In 2007, stations extending from the Labrador Sea in the Northwest Atlantic to the Canada Basin in the Arctic Ocean were sampled in July (C3O cruise 2007-19) and August (JOIS cruise 2007-20) aboard the Canadian Coast Guard Ship (CCGS) *Louis S. St. Laurent*. In 2008, stations were sampled from the west coast of Vancouver Island (Canada) in the eastern North Pacific Ocean to the southern Beaufort Sea in the Arctic Ocean in July (C3O cruise 2008-02) aboard the CCGS *Sir Wilfrid Laurier*. Further details of these three cruises and the stations sampled are presented elsewhere [*Carmack and McLaughlin*, 2011; *Varela et al.*, 2013; *Wyatt et al.*, 2013]. The stations were grouped into five regional domains coinciding with distinct water masses as revealed by temperature/salinity (T/S) correlations [*Carmack and McLaughlin*, 2011; *Varela et al.*, 2013; *Wyatt et al.*, 2013]. These domains (see numbers 1–5 on Figure 1a) consist of (1) the Eastern Subarctic North Pacific Ocean (ESNP), (2) the Bering and Chukchi Seas (BE-CH), (3) the Beaufort Sea and Canada Basin (BS-CB), (4) the Canadian Arctic Archipelago (CAA), and (5) Baffin Bay and Labrador Sea (BB-LS). The distribution of individual sampling stations is shown in Figure 1a, but for further information on station characteristics and domain classification see Table 1 in *Varela et al.* [2013] and Figure 1 in *Wyatt et al.* [2013]. It should be noted that the stations in the southern Beaufort Sea were located off the shelf [*Varela et al.*, 2013].

Seawater samples were collected vertically from the ocean surface to the base of the euphotic zone at 44 stations (referred to as full-profile stations, see Figure 1a) [*Varela et al.*, 2013; *Wyatt et al.*, 2013]. Surface seawater samples were obtained from an additional 14 stations, at the depth of 50% incident surface irradiance, usually 2–10 m depth [see *Varela et al.*, 2013]. At each full-profile station, seawater samples were collected with a rosette sampling system equipped with Niskin bottles, a Seabird SB911+ conductivity-temperature-depth profiler, and a sensor for photosynthetically active radiation (PAR). The PAR sensor was used to determine the depths of sampling at 100, 50, 30, 12, 1, and 0.1% of surface irradiance.

From each depth, seawater samples were collected from the Niskin bottles for POM measurements: biogenic silica (bSiO₂), particulate organic carbon (POC) and nitrogen (PON), and total and size-fractionated chlorophyll *a* (chl *a*). Seawater samples (0.5–2.3 L) were filtered through precombusted 25 mm diameter 0.7 μm pore size glass fiber filters for POC and PON analysis, and through 0.6 μm pore size polycarbonate filters for bSiO₂ analysis. In areas with low suspended POM (e.g., the BS-CB domain), samples of >2 L were generally filtered. Filters were then dried at 60°C for 48 h and stored in a desiccator until analysis. Glass fiber filters for POC and PON were fumed with concentrated hydrochloric acid (HCl) for 24 h to remove inorganic C [*Intergovernmental Oceanographic Commission*, 1994], and total organic C and N content measured on a PDZ Europa Automated Nitrogen-Carbon elemental analyzer as described by *Wyatt et al.* [2013]. Precombusted glass fiber filters were run as filter blanks. Polycarbonate filters were processed for bSiO₂ using alkaline hydrolysis, and the resulting Si(OH)₄ was measured with a Beckman DU 530 UV/Vis spectrophotometer as described by *Wyatt et al.* [2013]. Size-fractionated chl *a* concentrations were used to evaluate the biomass of phytoplankton greater and smaller than 5 μm in size. Seawater samples (0.8–2.3 L) were serially filtered through 5 μm pore size polycarbonate filters and 0.7 μm pore size glass fiber filters. Chl *a* on the filters was extracted with 90% acetone, analyzed with a Turner Designs 10 AU fluorometer, and corrected for phaeopigment interference

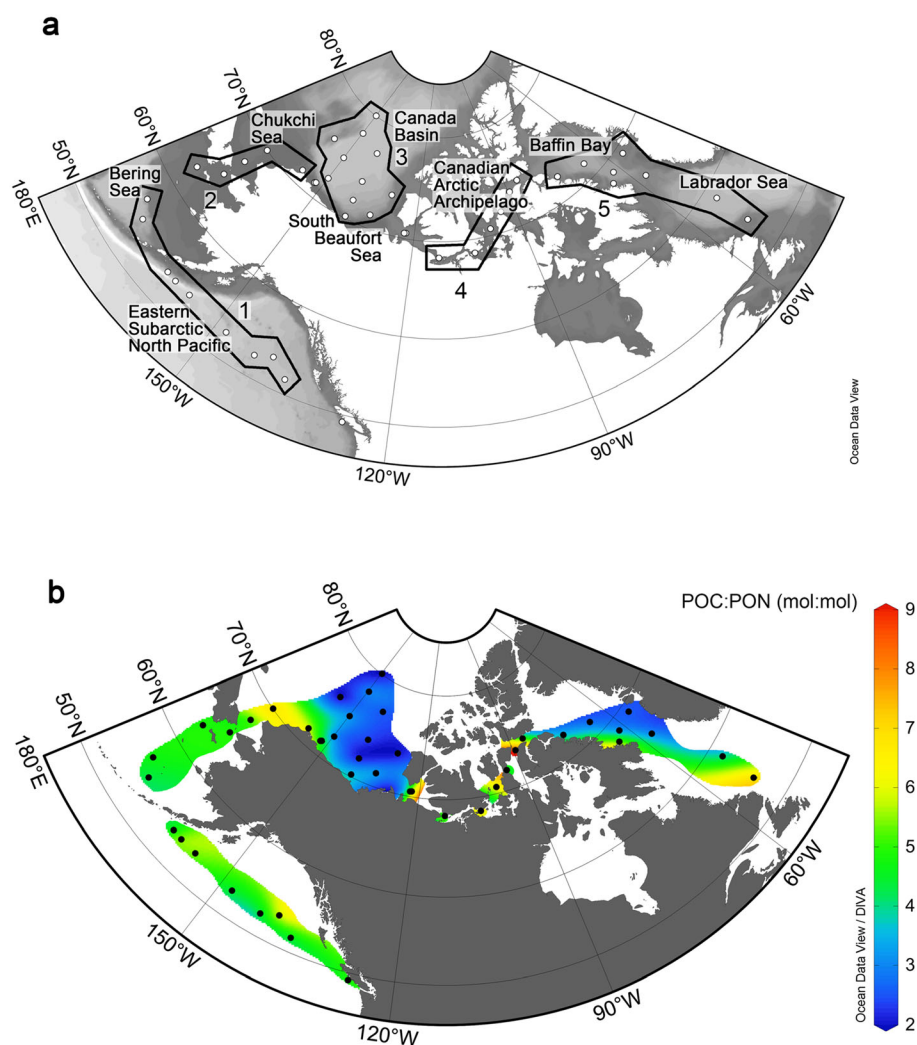


Figure 1. (a) Study areas in Arctic and Subarctic seas showing the sampling stations during summers of 2007 (eastern sector; C30/JOIS cruises) and 2008 (western sector; C30 cruise), and the oceanographic domains adopted. See Carmack and McLaughlin [2011], Varela *et al.* [2013], and Wyatt *et al.* [2013] for details of stations, cruises, and domains. These domains consist of (1) the Eastern Subarctic North Pacific Ocean (ESNP), (2) the Bering and Chukchi Seas (BE-CH), (3) the Beaufort Sea and Canada Basin (BS-CB), (4) the Canadian Arctic Archipelago (CAA), and (5) Baffin Bay and Labrador Sea (BB-LS). The map includes 44 full-profile stations for depth-integrated totals (used in Figures 1b and 2). (b) C:N ratios in suspended particulate matter integrated through the euphotic zone for each station sampled during C30/JOIS cruises. Color of contours should be used as an indication of broadscale spatial variation in POC:PON ratios and is not intended for detailed extrapolation between stations, or between stations and the coast.

[Parsons *et al.*, 1984; Wyatt *et al.*, 2013]. The particulate C:N ratios and further analyses of C30/JOIS data presented in this study are based upon data for PON, POC, bSiO_2 , and size-fractionated chl *a* that were originally presented in Wyatt *et al.* [2013].

Samples (~1 L) for C and N uptake rates were collected from each depth and inoculated with $\text{NaH}^{13}\text{CO}_3$ isotope tracer stock with the target ^{13}C enrichment of each sample being <10% of the total ambient dissolved inorganic C (DIC) [Varela *et al.*, 2013]. Samples for N uptake rates were inoculated with sodium nitrate ($\text{Na}^{15}\text{NO}_3$), ammonium chloride ($^{15}\text{NH}_4\text{Cl}$), or urea ($(^{15}\text{NH}_2)_2\text{CO}$) with the final ^{15}N enrichment target for each being approximately 10% of ambient concentrations [Varela *et al.*, 2013]. Spiked samples were incubated on deck for 24 h at surface water temperature and processed as described by Varela *et al.* [2013]. Carbon uptake rates (also referred to as “primary productivity” or ρ_C in this manuscript) were calculated according to Hama *et al.* [1983]. Specific (V_N) and absolute (ρ_N) uptake rates of the three N forms were calculated according to equations (2) and (3) of Dugdale and Wilkerson [1986] using the PON at the end of the incubation. The specific

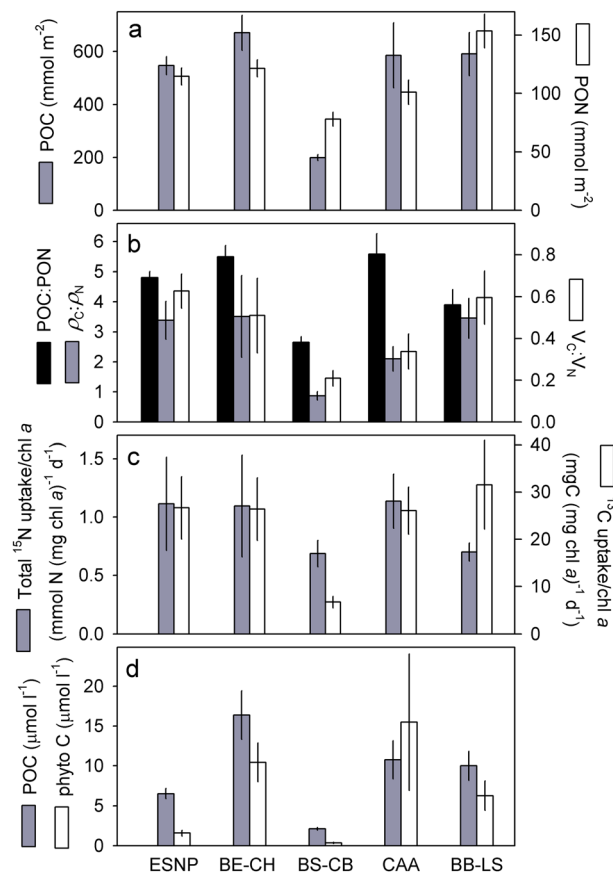


Figure 2. Euphotic-zone particulate concentrations, ratios, and uptake ratios of C and N for the five oceanographic domains during C30/JOIS. (a) POC and PON concentrations (\pm SE) integrated through the euphotic zone for each station and averaged for each oceanographic domain (adapted from Wyatt *et al.* [2013]). (b) POC:PON ratio, absolute C:N uptake ratio ($\rho_C:\rho_N$), and specific C:N uptake ratio ($V_C:V_N$), where ρ_N and V_N refer to total uptake of NO_3^- , NH_4^+ , and urea-N. Ratios are depth integrated through the euphotic zone for each station, and averaged for each oceanographic domain (\pm SE). The maximum of the POC:PON axis represents the Redfield ratio of 6.6. (c) Depth-integrated uptake rates of total N and C, both normalized by chl *a* concentration (C uptake/chl *a* is also known as the assimilation number) and averaged for each oceanographic domain (\pm SE). (d) POC concentration averaged through the euphotic zone, and estimated phytoplankton C concentration from samples taken within the SCM. Data were further averaged for each oceanographic domain (\pm SE).

uptake rate of N (V_N) is a measure of the N taken up per unit of biomass and is normally considered as an indicator of the intrinsic ability of the phytoplankton cell to take up N, similar to a growth rate. When ambient concentrations of NO_3^- , NH_4^+ , or urea-N were at the detection limit, a value equal to the detection limit ($0.05 \mu\text{mol L}^{-1}$) was used in the uptake rate calculations. Absolute C:N uptake ratios ($\rho_C:\rho_N$), and specific C:N uptake ratios ($V_C:V_N$) were calculated, where ρ_N and V_N refer to total uptake of NO_3^- , NH_4^+ , and urea-N. It should be emphasized that in contrast to most other studies in Arctic waters, these total uptake rates of N not only included the uptake of NO_3^- and NH_4^+ but also urea-N which was significant in many areas [Varela *et al.*, 2013]. Additional ^{13}C and ^{15}N size-fractionated experiments were conducted for samples from the 50% irradiance depth (2–10 m) from all 44 full-profile stations and from the 14 surface stations [see Varela *et al.*, 2013]. After incubation, these samples were fractionated between smaller ($<5 \mu\text{m}$) and larger ($>5 \mu\text{m}$) size fractions using $5 \mu\text{m}$ polycarbonate filters and precombusted $0.7 \mu\text{m}$ glass fiber filters [Varela *et al.*, 2013]. The data for C and N uptake rates from C30/JOIS cruises used in this manuscript for calculations of C:N uptake ratios were originally presented in Varela *et al.* [2013].

Additional samples (0.25–0.5 L) were collected from the Niskin bottles from the depth of the SCM and preserved with Lugol's iodine solution for identification and enumeration of phytoplankton. Since these samples were only taken from the SCM, taxonomic data are not available on a depth-integrated basis. An aliquot (0.1 L) from each sample was settled for 48 h in a settling chamber and examined at 600X

magnification using an Olympus inverted microscope [Utermöhl, 1958]. At least 300 individuals, all containing full chloroplasts, were counted in random fields and data were converted to cells per liter. Cell volume was calculated by assuming the geometric shapes suggested by Hillebrand *et al.* [1999] for each identified taxon and converted to cell C according to Montagnes *et al.* [1994]. Cellular C for all taxa within a sample was then summed to give total phytoplankton C for each sample.

We also present here a limited data set of particulate C to N ratios for the BE-CH and BS-CB domains from other field programs: the Institute of Ocean Sciences/Fisheries and Oceans Canada cruises 2006-01 in July 2006 and 2008-04 in October 2008 aboard the CCGS *Sir Wilfrid Laurier*, and the Canadian IPY-GEOTRACES cruise (ArcticNet 0903) aboard the CCGS *Amundsen* from 27 August 2009 through 12 September 2009. Particulate C and N from these cruises were also measured at discrete light depths from the surface to the base of the euphotic zone, and sample and data analyses were conducted mostly as specified above for C30 and JOIS.

Table 1. Particulate C to N Ratios Integrated From the Ocean Surface to the Base of the Euphotic Zone From Other Field Programs in the Bering/Chukchi Seas (BE-CH) and Beaufort Sea/Canada Basin (BS-CB) Domains

Cruise ID ^a	Date	Station	Latitude °N	Longitude °W	Depth-Integrated C:N Particulate Ratio	
					BE-CH	BS-CB
2006-01	12 Jul 2006	BS-6B	60.70	174.27	6.44 ^b	
	13 Jul 2006	BCS-6	64.04	171.84	6.71 ^b	
	16 Jul 2006	BRS-4a	65.67	168.34	6.27 ^b	
	18 Jul 2006	PH-2	68.09	168.37	5.96 ^b	
	19 Jul 2006	MO-4	70.64	168.24	7.39 ^b	
2008-04	3 Oct 2008	BF-7c	71.03	133.75		3.67 ^c
	6 Oct 2008	BF-5	70.23	140.01		3.82 ^c
	7 Oct 2008	BF-3	71.02	145.75		3.57 ^c
	12 Oct 2008	CS-08	72.12	164.37	5.97 ^c	
	13 Oct 2008	CCL-4	70.00	168.04	5.85 ^c	
ArcticNet 0903	30 Aug 2009	S2	70.00	138.51		3.81 ^b
	31 Aug 2009	L1	71.09	139.01		4.23 ^b
	4 Sep 2009	L2	74.59	137.12		4.79 ^b
	7 Sep 2009	L3	75.28	137.56		4.02 ^b
	9 Sep 2009	L1.1	72.52	136.79		5.50 ^b

^aInstitute of Ocean Sciences/Fisheries and Oceans Canada cruises, except for ArcticNet 0903 which was an International Polar Year Canadian GEOTRACES cruise.

^bParticulate C and N from cruises 2006-01 and ArcticNet 0903 were measured on nonacidified filters; and therefore, the ratios represent total PC:PN, which could be higher than PON:POC ratios if particulate inorganic C was present.

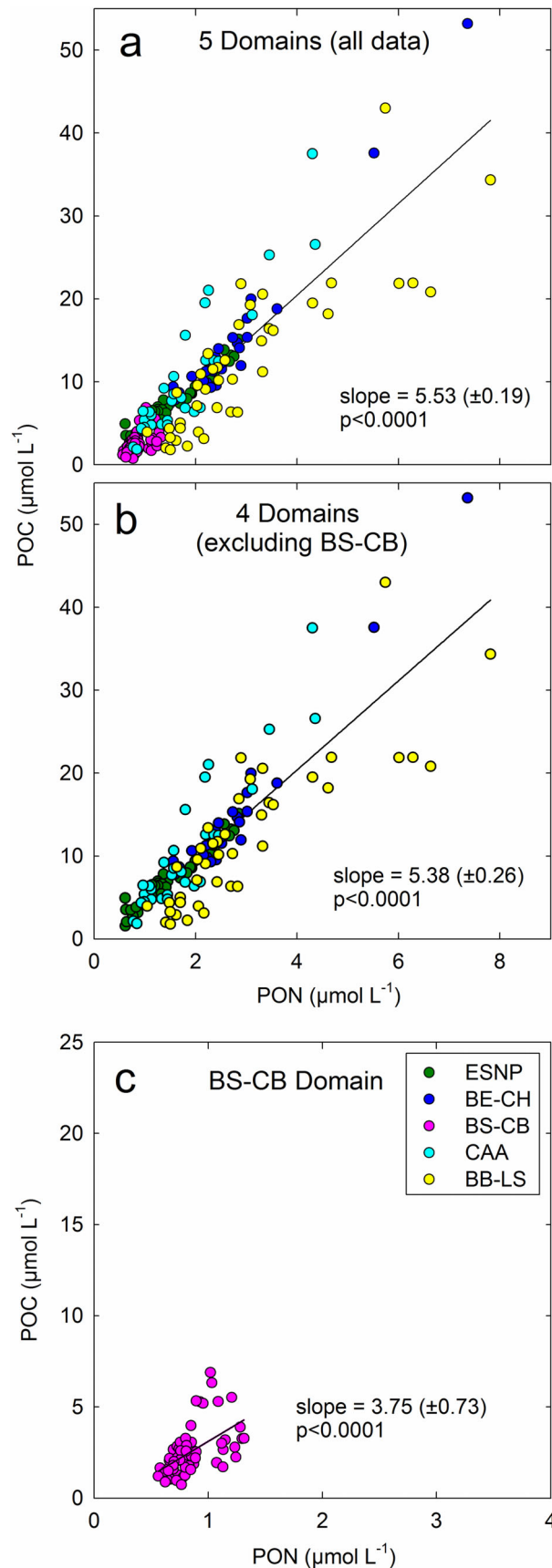
^cParticulate C and N from cruise 2008-04 were measured on acidified filters; and thus, the ratios represent POC:PON as with the rest of the C3O and JOIS data presented in this paper.

Discrete data for POC, PON, and uptake rates collected at full-profile stations were depth integrated from the ocean surface to the depth of 0.1% surface irradiance, or euphotic zone depth, using trapezoidal integration. Throughout the manuscript, statistical error is reported as standard error (i.e., \pm SE).

3. Results

The spatial distribution of depth-integrated POC:PON ratios is shown in a map of the study area (Figure 1b). These ratios are calculated for each full-profile station from depth-integrated POC and PON concentrations [see Wyatt *et al.*, 2013] that are summarized in Figure 2a as domain averages. In ESNP, BE-CH, and CAA (Domains 1, 2, and 4 in Figure 1a), depth-integrated POC:PON ratios averaged between 4.8 and 5.6, whereas for the BB-LS domain the ratio averaged 3.9 (\pm 0.51) (Figures 1b and 2b). In contrast to these four domains, the integrated POC:PON in BS-CB (Domain 3 in Figure 1a) averaged only 2.65 (\pm 0.19) (Figure 2b), with some stations in the Canada Basin as low as 1.9 (Figure 1b). These measurements in 2007 and 2008 during C3O/JOIS were supported by measurements of low depth-integrated particulate C:N ratios in the BS-CB in October 2008 and August/September 2009 and higher ratios in the BE-CH domain in July 2006 and October 2008 (Table 1). Only one station in the BS-CB domain (station L1.1) had a C:N ratio of over 5 (Table 1). It should be noted that the C:N ratios in July 2006 and in August/September 2009 were based on nonacidified filters; and therefore, these ratios represent total PC:PN, which could be elevated by the presence of particulate inorganic C.

During C3O/JOIS studies in 2007 and 2008, the $\rho_C:\rho_N$ ratios were also considerably lower in BS-CB than in the other domains (Figure 2b); average $\rho_C:\rho_N$ was 0.87 (\pm 0.14) in BS-CB and ranged from 2.10 to 3.51 in the other domains. It should be noted that the $\rho_C:\rho_N$ ratios were derived independently from the POC:PON data presented in Figures 1b and 2b. The calculation of $\rho_C:\rho_N$ used particulate C and N content measured on filters taken at the end of the incubation in which ^{13}C and ^{15}N were also measured. Furthermore, the specific $V_C:V_N$ ratios, which are calculated completely independently of particulate C and N, showed the same trends as those for POC:PON and $\rho_C:\rho_N$, with lower ratios in the BS-CB domain than elsewhere in the study region (Figure 2b). The low $\rho_C:\rho_N$ and $V_C:V_N$ ratios in the BS-CB domain were driven by a relatively lower efficiency of C uptake rather than N uptake. This is demonstrated by the much greater decrease in chl *a*-specific uptake of C (assimilation number) than chl *a*-specific uptake of N for the BS-CB domain compared to other



domains (Figure 2c). Estimated phytoplankton C at the depth of the SCM was also lowest in the BS-CB domain (Figure 2d) as also observed for both depth-integrated total POC (Figure 2a) and averaged total POC concentration throughout the euphotic zone (Figure 2d). Phytoplankton C estimates were of the same order as the average concentrations of POC in the euphotic zone for the BE-CH, CAA, and BB-LS domains but represented a lower proportion of POC in the ESNP and BS-CB domains.

All of our POC and PON data represent blank corrected values, but it is instructive to examine the raw sample signals (i.e., total amount on precombusted filter, uncorrected for filter blank and volume filtered) in comparison to filter blanks to assess the potential issue of low signal to noise ratio where POM is low. On the precombusted filter blanks, the average raw POC and PON signals were $2.51 (\pm 0.06) \mu\text{mol C}$ and $0.08 (\pm 0.01) \mu\text{mol N}$ ($n = 11$), respectively. For the BS-CB domain, the average raw sample signals for POC and PON were $7.87 \mu\text{mol} (\pm 0.34)$ and $1.91 \mu\text{mol} (\pm 0.06)$, respectively ($n = 64$), and were therefore \sim threefold and \sim 24-fold higher than the average signals for filter blanks. The minimum raw sample signals within the BS-CB domain were $4.41 \mu\text{mol C}$ and $0.89 \mu\text{mol N}$; these values were \sim 1.75 and \sim 11 times higher than average signals for filter blanks. However, out of a total of 64 samples in the BS-CB domain, only five POC samples and no PON samples had raw signals that were less than twice the filter blank signal.

To confirm the validity of our low ratios, we compared depth-integrated POC:PON ratios (Figures 1b and 2b) with those calculated using other approaches: from a regression of all POC and PON discrete data (all depths) for all stations and

Figure 3. Linear regressions of PON on POC for the different domains using data from all depths and stations. (a) All data from the five domains, (b) ESNP, BE-CH, CAA, and BB-LS domains (excluding BS-CB), and (c) BS-CB data alone; note the change of scale. Slope of regression (\pm SE) gives the POC:PON ratio.

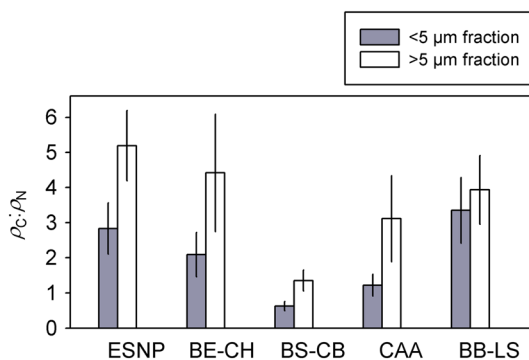


Figure 4. Average absolute uptake ($\rho_C:\rho_N$) ratios in the small (<5 μm) and large (>5 μm) size fractions measured in surface samples at 2–10 m depth for all stations ($\pm\text{SE}$). ρ_C refers to the uptake rate of inorganic C, and ρ_N refers to total combined uptake rate of NO_3^- , NH_4^+ , and urea-N. Maximum on $\rho_C:\rho_N$ axis represents the Redfield ratio of 6.6.

(Figure 3c). In the BS-CB domain, the average POC and PON concentrations for discrete depth samples were $2.53 \pm 0.17 \mu\text{mol L}^{-1}$ and $0.84 \pm 0.02 \mu\text{mol L}^{-1}$, respectively, with POC:PON ratios averaging $2.94 (\pm 0.15)$ ($n = 64$). Clearly, the POC:PON ratios in the BS-CB domain depend to some extent on the method of calculation, with variation between average depth-integrated ratios (2.65 ± 0.19), the slope of the regression for all depth samples (3.75 ± 0.73), and the average for all depth samples (2.94 ± 0.15). However, all approaches point to low ratios with an average of the order of ~ 3 .

An analysis of uptake ratios in different size fractions provided evidence that lower ratios were associated with smaller cells. The $\rho_C:\rho_N$ ratios in the < 5 μm fraction were lower than in the > 5 μm fraction for all domains

domains (Figure 3a), and from the average of all discrete data (all depths) for each domain. The slope of the regression between POC and PON for all data (5.53 ± 0.19 , Figure 3a) is close to the average depth-integrated POC:PON ratios (5.5 and 5.6) for the BE-CH and CAA domains, respectively (Figure 2b), suggesting that the slope of this regression is strongly influenced by the more productive domains. When the discrete data for the BS-CB domain is removed from Figure 3a, the slope (5.38 ± 0.26) for the other four domains is not significantly different (Figure 3b) from that when all domains are included (Figure 3a). In contrast, the slope of the POC:PON regression for the BS-CB domain alone was much lower at $3.75 (\pm 0.73)$

(Figure 4). Furthermore, when data for the discrete depths from all stations are pooled, it was evident that lower biomass of the large cell fraction (chl *a* in >5 μm) and lower concentrations of bSiO_2 were associated with decreased POC:PON ratios (Figure 5). Low POC:PON ratios in the BS-CB (Figure 2b) were mainly observed when total phytoplankton C was < $1 \mu\text{mol L}^{-1}$ (Figure 2d).

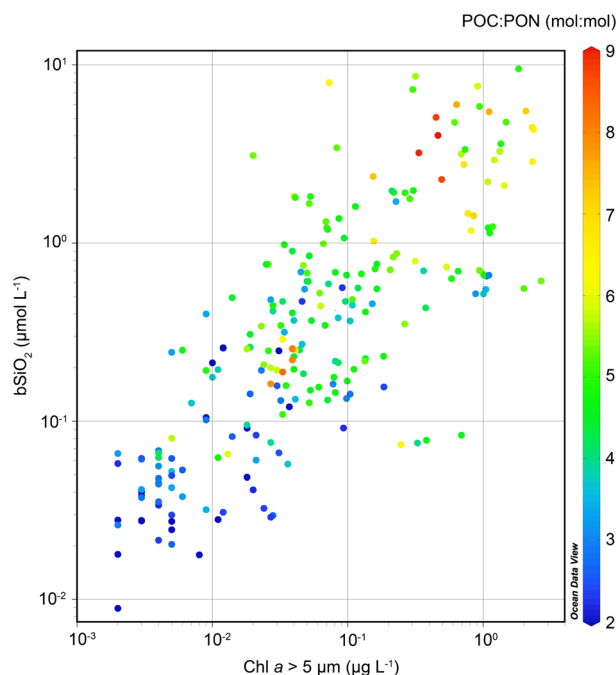


Figure 5. Biogenic silica (bSiO_2) concentration versus large fraction (>5 μm) chl *a* concentration at all depths for all C30/JOIS stations. Color of contours (indicated on vertical scale) represents the POC:PON ratio.

Taxonomic analysis revealed that the relative contribution of small flagellates (<8 μm) to total phytoplankton C has a significant negative relationship ($p < 0.0001$) with depth-integrated POC:PON ratio (Figure 6). The POC:PON ratios of between 2 and 3 (Figure 6) observed within the BS-CB were associated with an assemblage where almost 50% of phytoplankton C was contributed by small flagellates < 8 μm in size (Figure 6). In contrast, POC:PON ratios approaching Redfield ratio (6.6) were associated with a phytoplankton assemblage where >90% of C was contributed by larger cells (principally diatoms, dinoflagellates, and cryptomonads) and <10% by small flagellates < 8 μm in size.

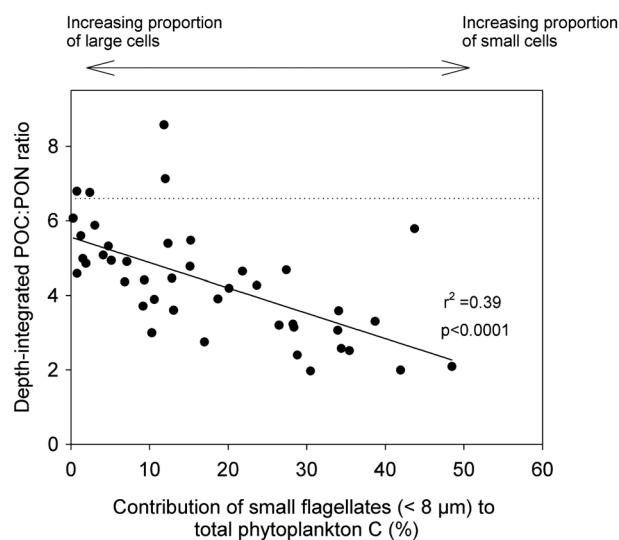


Figure 6. Relationship between the depth-integrated POC:PON ratio within the euphotic zone and the relative contribution of small flagellates ($< 8 \mu\text{m}$) to total phytoplankton C within the SCM for all full-profile C30/JOIS stations. Dotted line denotes Redfield ratio of 6.6.

[Martiny *et al.*, 2013a]. Our data for the BE-CH and CAA domains are also in good agreement with studies in more productive Arctic waters where POC:PON ratios of around Redfield, or higher, have been observed [e.g., Mei *et al.*, 2005; Daly *et al.*, 1999; Tamelander *et al.*, 2012]. For the BB-LS domain, POC:PON averaged 3.9 (Figure 2b), which is considerably lower than Redfield but still within the wide range (3.8 to 17) for marine organic matter and phytoplankton reviewed by Geider and La Roche [2002]. However, our BB-LS domain did not include stations in the more productive waters of the NOW polynya in northern Baffin Bay; inclusion of which would probably have raised the observed ratio [e.g., see Mei *et al.*, 2005]. The average depth-integrated ratio observed in the BS-CB domain (2.65 ± 0.19) is much lower than both the Redfield ratio and the average ratios in the reviews discussed above [Copin-Montegut and Copin-Montegut, 1983; Martiny *et al.*, 2013a; Geider and La Roche, 2002].

The average depth-integrated $\rho_C:\rho_N$ ratios showed a similar pattern across domains as did the POC:PON ratios, with much lower values in the BS-CB. These $\rho_C:\rho_N$ ratios were lower than POC:PON ratios, as expected, because they reflect short-term uptake rates rather than accumulated community biomass. In addition, $\rho_C:\rho_N$ ratios were lower than other published C:N uptake ratios because our data include uptake of urea as well as NO_3^- and NH_4^+ [Varela *et al.*, 2103], rather than uptake of NO_3^- only (and sometimes NH_4^+), as in most studies.

The C30/JOIS data presented here represent a summer “snapshot” of POC:PON ratios across Arctic and Subarctic seas and did not include other periods of the year. However, low ratios seem to persist seasonally at least to some extent. In the Beaufort Sea in October 2008 (cruise 2008-04), depth-integrated POC:PON averaged 3.7 at three stations compared to an average of 5.9 at two stations in the BE-CH during the same period (Table 1).

4.2. Methodological Artifacts Potentially Affecting Determinations of C:N Ratios

Because of the apparently unprecedented low ratios observed in some areas, a careful examination is required of methodological issues that may impact upon the accuracy of the data. A high signal to noise ratio is critical when collecting relatively small volumes of water in regions of low POM [Moran *et al.*, 1999; Martiny *et al.*, 2014]. In the central Arctic Ocean, Wheeler *et al.* [1997] did not report data where raw POC signals were less than twice that of the filter blank. We did analyze filter blanks, and in the region of lowest biomass (BS-CB domain), the raw signals for the majority of our samples (59 out of 64 POC samples and all PON samples) were more than twice the filter blank signal, with average signals for POC and PON of ~ 3 and ~ 24 times the filter blank signal, respectively. This suggests that low signal to noise is unlikely to be at the root of these observed low ratios. In fact, raw sample signals too close to filter blank signals are likely to result in increased noise and high variability, rather than consistently low ratios. In the BS-CB domain, a significant relationship was

4. Discussion

4.1. Spatial and Temporal Variations in C:N Ratios

In the present study we used standard and consistent methodology over an extensive geographic area and observed low POC:PON ratios in the largely oligotrophic BS-CB domain but much higher ratios in other domains. We have also supported these measurements with similar variations in depth-integrated C:N uptake ratios ($\rho_C:\rho_N$ and $V_C:V_N$) which were derived independently of the particulate ratios.

The average depth-integrated POC:PON ratios of between 4.8 and 5.6 observed in the ESNP, BE-CH, and CAA domains were lower than the Redfield ratio (6.6) but in reasonable agreement with the averages of 5.6 for marine organic matter [Copin-Montegut and Copin-Montegut, 1983] and 6 for cold, nutrient-rich waters at high latitudes

evident with a POC:PON slope of 3.75 ± 0.73 , deviating considerably from the slope for the other domains (Figure 3). The slope is independent of the filter blank correction which only influences the intercepts. In addition to the BS-CB domain, we also observed a smaller number of similarly low POC:PON ratios in the BB-LS domain (Figure 3a) where raw uncorrected signals on sample filters for POC and PON tended to be higher than in the BS-CB domain. If POC:PON ratios are similarly low when raw sample signals are higher, then signal to noise issues are unlikely to be the cause of low ratios.

POC:PON ratios can also be potentially influenced by adsorption of dissolved organic material (DOM) onto filters [e.g., Gardner *et al.*, 2003; Moran *et al.*, 1999]. Relatively high levels of dissolved organic carbon (DOC) in Arctic basins [e.g., Gosselin *et al.*, 1997] could artificially elevate apparent POC signals. Using large-volume pumps in the Arctic Ocean, Moran *et al.* [1999] obtained lower deep-water POC values ($0.25\text{--}1 \mu\text{mol L}^{-1}$) than those measured from water samples taken with small Niskin and Go-Flo bottles ($2\text{--}3 \mu\text{mol L}^{-1}$) [Wheeler *et al.*, 1997]. Moran *et al.* [1999] argued that adsorption of DOC onto filters could have significantly elevated the low POC signals obtained from the low filtration volumes (1 L) used by Wheeler *et al.* [1997]. We did not carry out adsorption blanks [Wyatt *et al.*, 2013], and sampling logistics did not allow us to collect and filter the recommended 4 L. While we cannot rule out adsorption of DOC onto our filters, the risk would be offset because we filtered >2 L for all but two stations in the BS-CB domain where POC:PON ratios were lowest. In the BS-CB domain, the POC concentrations of our deeper samples (>80 m) were $\sim 1 \mu\text{mol L}^{-1}$ and sometimes less, closer to the values reported by Moran *et al.* [1999] than those of Wheeler *et al.* [1997] for the central Arctic Ocean. If significant adsorption of DOC was contaminating our filters, this would suggest that the actual POC:PON ratios would be lower than those measured in this study, unless accompanied by relatively greater adsorption of PON. In fact, C:N ratios of DOM in the central Arctic are typically twice as high as the C:N ratio of POM [Wheeler *et al.*, 1997], suggesting that elevated adsorption of DON relative to DOC is unlikely.

Uptake rates were not corrected for isotope dilution [Varela *et al.*, 2013], which may result in an underestimation of N uptake rates [e.g., Glibert *et al.*, 1982], mainly in low N waters. However, because isotope additions under undetectable ambient N concentrations are inevitably $>10\%$ of ambient concentrations [e.g., Garneau *et al.*, 2007], the higher than expected ^{15}N enrichment can overestimate rates in some cases, and the resulting uptake rates represent a potential maximum uptake. However, this effect is unavoidable and is accepted in oligotrophic waters [Legendre and Gosselin, 1996]. In the present study, excess enrichment in areas of low N was not limited to the BS-CB region; and therefore, potential overestimation in the rates does not seem to explain the differences in the $\rho_{\text{C}}:\rho_{\text{N}}$ and $V_{\text{C}}:V_{\text{N}}$ between regions. These potential effects of isotope dilution and enrichment may have balanced each other to some extent [Garneau *et al.*, 2007; Varela *et al.*, 2013] and probably had little effect on the accuracy of our data. In fact, the low $\rho_{\text{C}}:\rho_{\text{N}}$ and $V_{\text{C}}:V_{\text{N}}$ in the BS-CB appeared to be associated with a greater relative decrease of C uptake rather than N uptake; and because of generally high DIC levels in seawater, uptake of ^{13}C would not be influenced significantly by isotope dilution or enrichment, as might be the case for ^{15}N uptake. The lower $V_{\text{C}}:V_{\text{N}}$ was driven by sharp decreases in both V_{C} and V_{N} in the BS-CB but much greater relative decrease in V_{C} rather than an inflated V_{N} .

4.3. Supporting Evidence of Low C:N Ratios From Other Arctic Studies

Although there are few available data for POC:PON and C:N uptake ratios for low-productivity Arctic marine waters, there is some evidence to support our findings. Relatively low POC:PON ratios in the BS-CB compared to the BE-CH were also measured in several other of our field programs between 2006 and 2009 (Table 1). Some of these ratios were based upon nonacidified filters and therefore represent total PC:PN ratios; the true POC:PON ratio might have been even lower if calcified phytoplankton were present since particulate inorganic C inflates the numerator in the PC:PN ratios. In fact, coccolithophores are being increasingly reported in Arctic waters [e.g., Balch *et al.*, 2014], suggesting that acidification of filters is required when measuring POC. Relatively low C:N uptake ratios of around 3 were sporadically noted in 2005 in the Canada Basin [Lee *et al.*, 2010], although POC:PON ratios were much higher in Lee *et al.* [2010] than in the present study. Yun *et al.* [2012] reported even lower C:N uptake ratios of 1.6 g/g based on NO_3^- and NH_4^+ uptake in the Canada Basin during the late summer of 2009. The rates reported by Lee *et al.* [2010] and Yun *et al.* [2012] excluded urea uptake, the inclusion of which would have decreased the C:N uptake ratios even further. Mass C:N ratios as low as ~ 3 have also been reported in copepods in the nearby Amundsen Gulf [Forest *et al.*, 2011], whereas values close to Redfield ratios were observed for exported copepod fecal pellets in the Fram Strait and Barents Sea [Tamelander *et al.*, 2012].

Although the low ratios averaging 2.65 observed for the BS-CB domain would appear to be unprecedented, a close examination of some reviews of POC:PON ratios in POM and phytoplankton [e.g., *Martiny et al.*, 2013b; *Geider and La Roche*, 2002; *Schneider et al.*, 2003] reveals that a very small number of ratios of the order of 2–4 are typically observed, although their exact geographical locations and depths are not specified. These low ratios are not discussed in detail in these reviews, and in some studies may be “lost” within the regression slopes of larger bodies of data, as observed in the present study (Figures 3a and 3b). *Schneider et al.* [2003] not only reported small numbers of POC:PON ratios as low as 3 but also briefly mentioned 45 data points with values below 3 that were omitted from further analyses because the authors were not aware of any organisms possessing such low ratios. Similarly, in a review of POC:PON ratios in globally distributed samples above 200 m depth, *Martiny et al.* [2013b] included small numbers of POC:PON ratios as low as 2 but omitted values below 2 as unrealistic. In the present study, rather than omitting data as outliers, we have attempted to highlight this phenomenon and address the validity of observed low ratios.

4.4. Mechanisms Driving Low C:N Ratios in Arctic Waters

POC:PON ratios of 2–4 have been observed in natural POM [*Schneider et al.*, 2003; *Martiny et al.*, 2013b] and in phytoplankton cultures [*Geider and La Roche*, 2002]. Ratios as low as 3.4 and 2.7 (wt/wt) were measured for a phototrophic dinoflagellate [*Menden-Deuer and Lessard*, 2000] and a diatom [*Harrison et al.*, 1977], respectively. The physiological basis for such low cellular ratios is unknown, although light limitation has been linked with reduced C:N ratios [*Martiny et al.*, 2013b]. Our observed values are at the lower end of the range reported for marine phytoplankton, and within the range for natural POM [*Schneider et al.*, 2003; *Martiny et al.*, 2013b].

The reduced POC:PON ratios in BS-CB (Figure 2b) were driven by greater decreases in the concentration of depth-integrated POC than PON compared to other domains (Figure 2a). Moreover, lower $\rho_C:\rho_N$ and $V_C:V_N$ ratios in the BS-CB domain (Figure 2b) were driven by a relatively greater decrease in chl *a*-specific uptake of C (assimilation number) than chl *a*-specific uptake of N in the BS-CB domain (Figure 2c) compared to other domains. This is supported by observations of low C:chl *a* ratios in phytoplankton in the BS-CB domain. Within the SCM in the BS-CB domain, estimated phytoplankton C averaged $0.34 \pm 0.07 \mu\text{mol L}^{-1}$ (Figure 2d) and concentration of chl *a* averaged $0.17 \pm 0.02 \mu\text{g L}^{-1}$. The C:chl *a* ratio of phytoplankton averaged 25.41 ± 4.84 compared to a C:chl *a* ratio of >50 in the other domains. This average C:chl *a* ratio for the BS-CB is lower than, but in reasonable agreement with, ratios of 28 to 31 for other Arctic basins [*Booth and Horner*, 1997; *Sherr et al.*, 2003] and can be indicative of phytoplankton acclimated to low irradiance [*Smith and Sakshaug*, 1990; *Sherr et al.*, 2003]. The low C:chl *a* ratios and low chl *a*-specific C uptake rates (Figure 2c) suggest inefficient C production by phytoplankton in the BS-CB domain. Low phytoplankton C and productivity in the BS-CB [*Varela et al.*, 2013] is consistent with previous studies [e.g., *Lee and Whitledge*, 2005; *Yun et al.*, 2012] and is probably the result of colimitation by light, nitrate, and possibly iron [e.g., *Taylor et al.*, 2013].

POC:PON ratios reflect the composition of the whole planktonic community together with detrital matter. Within the SCM, POC averaged $2.55 \pm 0.32 \mu\text{mol C L}^{-1}$, and so our phytoplankton C of $0.34 \pm 0.07 \mu\text{mol L}^{-1}$ represented only ~13% of total POC, and possibly less above or below the SCM (we only have taxonomic data for the SCM). This is supported by observations that phytoplankton C within the SCM is much lower than estimates of total heterotrophic C within the planktonic community in Arctic basins. For example, bacterial C averages $0.53 \mu\text{mol C L}^{-1}$ in the upper 40 m of the central Arctic Ocean [*Sherr et al.*, 2003] and $0.42 \mu\text{mol C L}^{-1}$ in the upper 50 m of the western Canada Basin [*He et al.*, 2012], and heterotrophic protists average $0.65 \mu\text{mol C L}^{-1}$ in the central Arctic [*Sherr et al.*, 2003]. Moreover, mesozooplankton represents around 48% of POC in the central Arctic Ocean [*Wheeler et al.*, 1996]. These data strongly support the notion that phytoplankton C represents a relatively small proportion of the total POC present in Arctic basins.

The composition of POM and the uptake of C and N in the BS-CB domain must therefore be influenced by the presence of both phytoplankton and heterotrophs, and our ratios will therefore reflect this. The amount of bacterial biomass retained by a glass fiber filter is variable, but is typically around 40–50% or greater [*Lee and Fuhrman*, 1987; *Kirchman et al.*, 1994], and larger microbes such as flagellates and ciliates will also be retained. POC:PON ratios in marine bacteria are lower and less variable than those of phytoplankton, but do nevertheless show some variation, with ranges of, for example, 4.5–6.7 [*Bratbak*, 1985] and 3.2–4.2 [*Lee and Fuhrman*, 1987], and some “outliers” with ratios <3 [*Lee and Fuhrman*, 1987]. *Vrede et al.* [2002] reported average POC:PON ratios of 5.2 for exponentially growing bacteria that dropped to 3.6 under

C-limited conditions. For larger microbes, POC:PON ratios as low as 3 (wt/wt) have been reported in heterotrophic and mixotrophic ciliates [Putt and Stoecker, 1989], and clearly our observed ratios of ~ 3 are consistent with the lower end of the published range of ratios for heterotrophic microorganisms.

Arctic basins are typically limited by NO_3^- supply, irradiance [Sherr *et al.*, 2003, Taylor *et al.*, 2013], and possibly iron availability [Taylor *et al.*, 2013]. Whereas NO_3^- limitation may be offset to some extent by the use of urea [Varela *et al.*, 2013], light limitation appears to be worsening as sea ice melt and consequential stratification deepens the SCM [McLaughlin and Carmack, 2010]. Phytoplankton situated below the pycnocline can be physically prevented from mixing into illuminated surface layers, thus potentially limiting photosynthetic C production in these stratified waters. Notably, the low POC:PON ratios in the BS-CB domain were largely collected in the summer of 2007, coincident with very low sea ice coverage and presumably increased stratification of surface waters.

Carbon fixation is low in the BS-CB domain [Varela *et al.*, 2013], but it is unknown to what extent this impacts on the cellular stoichiometry of heterotrophs. DOC release by phytoplankton in Arctic basins is significant [Gosselin *et al.*, 1997] and has been estimated to be responsible for $\sim 56\%$ of DOC in the central Arctic [Wheeler *et al.*, 1997]. However, because of the potential allochthonous lateral supply of DOC [Kirchman *et al.*, 2009], uncoupling of bacterial and primary production in time and space complicates the question of whether low primary production might influence the growth and elemental composition of bacteria and heterotrophic microbes [Kirchman *et al.*, 2009].

4.5. Wider-Scale Implications of Low C:N Ratios in the Arctic Ocean

Although largely restricted to the BS-CB domain, low POC:PON values were also measured elsewhere, particularly in parts of the BB-LS (Figures 1b and 2b). Our observations could therefore be of wider significance in Arctic waters and for modeling efforts. For example, models on the influence of sea ice retreat on productivity assumed a C:N ratio of 7.6 [Slagstad *et al.*, 2011], and estimates of the f ratio and new production have been extrapolated simply from NO_3^- uptake using the Redfield ratio [Cota *et al.*, 1996]. New production has been estimated from nutrient drawdown using a molar C:N ratio of 7.1 for the coastal Beaufort Sea [Tremblay *et al.*, 2011], and the same ratio has been used to estimate net community production (NCP) from NO_3^- uptake in the southern Beaufort, and the NOW polynya in northern Baffin Bay [Bergeron and Tremblay, 2014]. Recent pan-Arctic estimates of primary productivity from in situ and remotely sensed data, and from nutrient changes, have agreed reasonably well for the more productive Arctic regions, but the agreement was poorer for the unproductive ice-covered areas [Hill *et al.*, 2013; Codispoti *et al.*, 2013; Matrai *et al.*, 2013; Varela *et al.*, 2013]. For example, Codispoti *et al.* [2013] assumed a constant Redfield ratio to estimate NCP across the Arctic from net changes in nutrient concentration in the water column; these NCP data were therefore inherently influenced by the presence of sea ice. Using these data of Codispoti *et al.* [2013], Varela *et al.* [2013] estimated an average of $14.4 \text{ mg C m}^{-2} \text{ d}^{-1}$ for NCP within the BS-CB domain, which was much higher than the average new production of $5.5 \text{ mg C m}^{-2} \text{ d}^{-1}$ from direct measurements of ^{13}C and ^{15}N uptake from on-deck incubations, and corrected for the presence of ice [Varela *et al.*, 2013]. Correcting the Codispoti *et al.* [2013] NCP estimate for this domain with an average POC: PON ratio of 2.65 (as measured in this study) instead of the Redfield ratio (6.6), gives an average NCP of $5.8 \text{ mg C m}^{-2} \text{ d}^{-1}$, which is in excellent agreement with the estimated ice-corrected new production of $5.5 \text{ mg C m}^{-2} \text{ d}^{-1}$ from Varela *et al.* [2013] for the BS-CB domain. Clearly, the choice of POC:PON ratios is critical to productivity estimates and models in Arctic marine waters, and our data question the widespread use of the Redfield ratio in these areas. We also suggest that the relative contributions of both phytoplankton and heterotrophs to these ratios need to be clarified with reference to interconverting between C- and N-based estimates of primary productivity.

The low POC:PON ratios observed in the BS-CB domain are likely driven by a combination of reduced C:N uptake rates, a shift in the size composition of phytoplankton assemblages, and increased relative abundance of heterotrophic plankton. In addition to generally reduced levels of C uptake by the entire community in BS-CB waters, the smaller cell fraction ($< 5 \mu\text{m}$) has a lower $\rho_{\text{C}}:\rho_{\text{N}}$ than the larger fraction ($> 5 \mu\text{m}$) and the uptake of C and N by bacteria could be contributing to observed shifts in ratios. Our observations of low POC:PON in the BS-CB occurred in conjunction with low abundance of $> 5 \mu\text{m}$ chl *a*, low bSiO_2 concentrations, reduced abundance of larger ($> 8 \mu\text{m}$) cells (diatoms, dinoflagellates, and cryptomonads), and a greater

relative contribution of small (<8 μm) flagellates. This evidence supports the concept of planktonic communities dominated by small phytoplankton, bacterioplankton, and other heterotrophs, as in other Arctic basins [Sherr et al., 2003; Kirchman et al., 2009; He et al., 2012]. If there has indeed been a recent shift in the Canada Basin toward a community dominated by picophytoplankton (<2 μm) and bacterioplankton [Li et al., 2009] in response to sea ice melt, freshening, and stabilization of the water column [McLaughlin and Carmack, 2010], then our findings point to the intriguing possibility that decreasing POC:PON ratios may be a consequence of this shift.

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