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Nutrient dynamics in the western Canadian Arctic. I. New production in spring inferred from nutrient draw-down in the Cape Bathurst Polynya

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ABSTRACT: Ice-retreat from the Cape Bathurst Polynya occurred in late May and early June 2004, and was quickly followed by a decrease in dissolved nutrient concentration at the sea surface. Concentration plots of NO_3^- versus PO_4^{3-}, and $Si(OH)_4$ versus NO_3^- showed the ratios of nutrient uptake in the surface layer were in proportions expected for diatom growth (N:P 13.1:1; Si:N 1.8:1) and that water-column NO_3^- was depleted before PO_4^{3-} and $Si(OH)_4$. The temporal changes in integrated nitrate, phosphate and silicate concentrations were well described by logistic models that showed maximum consumption rates of 11.8, 0.82, and 17.8 mmol m^{-2} d^{-1}, respectively, and a total seasonal draw-down of 210 ± 19 mmol NO_3^- m^{-2}. If we include estimates of NO_3^- supply by advection, nitrification and freshwater dilution, then the amount of NO_3^- consumed could be 25–33% higher. Uptake of NO_3^- above the 1% isolume was balanced by an equivalent (94%) increase in particulate N over a 15 d period beginning at ice break-up. Thus, the amount of particulate spring new production associated with NO_3^- disappearance was estimated to be 16.1 ± 1.5 g C m^{-2}.

KEY WORDS: Phytoplankton production · Nutrient consumption · New production · Polynya · Nitrate · Phosphate · Silicate · Amundsen Gulf · Arctic Ocean

INTRODUCTION

Polynyas occupy a small fraction of the Arctic Ocean, but are regions of high primary and secondary production and play a disproportionate role in the flow of energy and cycling of nutrients. They remain ice-free for extended periods of time, so the pelagic community receives considerably greater inputs of solar radiation than in adjacent ice-covered environments. For this reason, some polynyas achieve high levels of phytoplankton biomass and production (Tremblay et al. 2006), which in turn provides an abundant supply of food for many pelagic and benthic consumers (Ashjian et al. 1995). Invertebrates, fish, sea birds, and marine mammals congregate in polynyas to exploit this production (Harwood & Stirling 1992, Dickson & Gilchrist 2002).

The seasonal cycle of primary production in ice-covered Arctic Ocean ecosystems begins with ice algal growth initiated by the increase in solar radiation during spring (Leu et al. 2011). Sun angle, sea-ice thickness and amount of snow cover influence the penetration of light (Mundy et al. 2005) and affect the timing of this initial phase of the annual production. Pelagic phytoplankton blooms generally occur later, immediately following ice breakup, so that their development is restricted to a relatively short period in summer before the onset of polar night (Hsiao 1992).

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New observations (Arrigo et al. 2012) show under some circumstances that phytoplankton blooms also begin under ice and are developing earlier across the Arctic as ice thickness declines (Kahru et al. 2011).

In Arctic polynyas, the phytoplankton bloom develops in April-May (e.g. Tremblay et al. 2002, 2006), considerably earlier than surrounding areas. Cumulative production within these systems appears to be regulated by the initial nitrate (NO_3^-) inventory, which is positively related to the duration of the ice-free season (Tremblay & Gagnon 2009). Some polynyas such as the North Water (NOW) Polynya, however, have a greatly enhanced growing season, with high levels of primary production sustained well into autumn (Arrigo & van Dijken 2004) by continual nutrient input from mixing and advection (Wallace et al. 1995).

Quantifying production of phytoplankton blooms is generally accomplished using one of 2 approaches. Temporal change in nutrient inventory due to biological consumption has been used in several cases in the Arctic to infer primary production using Redfield stoichiometry (e.g. Macdonald et al. 1987, Wallace et al. 1995, Wong et al. 2002, Honda & Watanabe 2007). Alternatively, isotopic tracers such as ^{14}C and ^{15}N have been used to estimate total production, and the *f*-ratio used to compute new and regenerated production. Tremblay et al. (2002) found both methods estimated a production of ~1.4 g C m^{-2} d^{-1} in the NOW Polynya during ice-free periods. At times of high productivity, rates in other polynyas are typically 0.5 to 1.1 g C m^{-2} d^{-1} (Harrison et al. 1982, Smith 1995, Tremblay et al. 2002), considerably faster than in neighboring regions, such as Baffin Bay (0.12 g C m^{-2} d^{-1}) and areas that experience prolonged ice cover (0.01 g C m^{-2} d^{-1}; Wheeler et al. 1996, Lee & Whitledge 2005). The daily rates of production in polynyas can be as high as those measured in more temperate environments during spring blooms (Bender et al. 1992).

The Cape Bathurst Polynya, one of the large polynyas in the Canadian Arctic, is located approximately 150 km east of the Mackenzie River in the Amundsen Gulf (Fig. 1). It experiences large interannual variation in ice cover, but generally opens rapidly in mid-May to early June and remains ice-free for an average of 4 mo before refreezing in October or November (Arrigo & van Dijken 2004). Our knowledge of the dynamics and rates of primary production in the Amundsen Gulf have thus far been inferred from studies of satellite images (e.g. Arrigo & van Dijken 2004). No time series measurements of phytoplankton production in this region exist although early autumn estimates are of about 75 mg C m^{-2} d^{-1} (Brugel et al. 2009).

Under the auspices of the Canadian Arctic Shelf Exchange Study (CASES), we participated in a quasi-annual study of nutrient dynamics and cycling in the Cape Bathurst Polynya. Here, we examine temporal changes in nutrient concentrations during phytoplankton growth and construct a simple 1-dimensional closed model to estimate the rate and total amount of spring new production.

MATERIALS AND METHODS

All samples were obtained during the 2003–2004 expedition of the Canadian Arctic Shelf Exchange Study (CASES) aboard the CCGS 'Amundsen' (Fig. 1). Ice conditions throughout the region were monitored by the Moderate Resolution Imaging Spectroradiometer (http://rapidfire.sci.gsfc.nasa.gov/realtime). The ship overwintered in Franklin Bay (70° 02.74′ N, 126° 18.08′ W) and the site was sampled every 3rd day between 15 May (day of year [DOY] 136) and 27 May 2004 (DOY 148). On 28 May, the ship left the overwintering station, and on 4 June (DOY 156) began sampling ice-free sites in the Cape Bathurst Polynya (centered at approximately 71° N and 126° W). From 4 June to 21 June (DOY 173) we sampled 15 stations throughout the polynya. The ship then moved onto the Mackenzie Shelf to complete a related part of the study. Sampling in the Cape Bathurst Polynya only resumed once the ship returned to the site on 16 July (DOY 198) and continued until 1 August (DOY 214). A total of 69 vertical profiles were obtained from stations occupied in the polynya during these time periods; these results are presented here. Fourteen of the 69 stations were revisited at some point during the cruises and sampled twice. Profiles of ammonium (NH_4^+) and nitrite (NO_2^-) were also obtained from an autumn cruise (9 Oct to 19 Nov 2003; DOY 282–323) and are included here for comparison to pre-bloom conditions measured in spring 2004. The autumn samples were collected in open waters, although pancake and frazil ice was common in the region at the beginning of November 2003.

Nutrient samples

Nutrient samples were collected using 12 l Niskin bottles mounted on a Seabird Carousel rosette system equipped with a Seabird 911+CTD (Sea-Bird

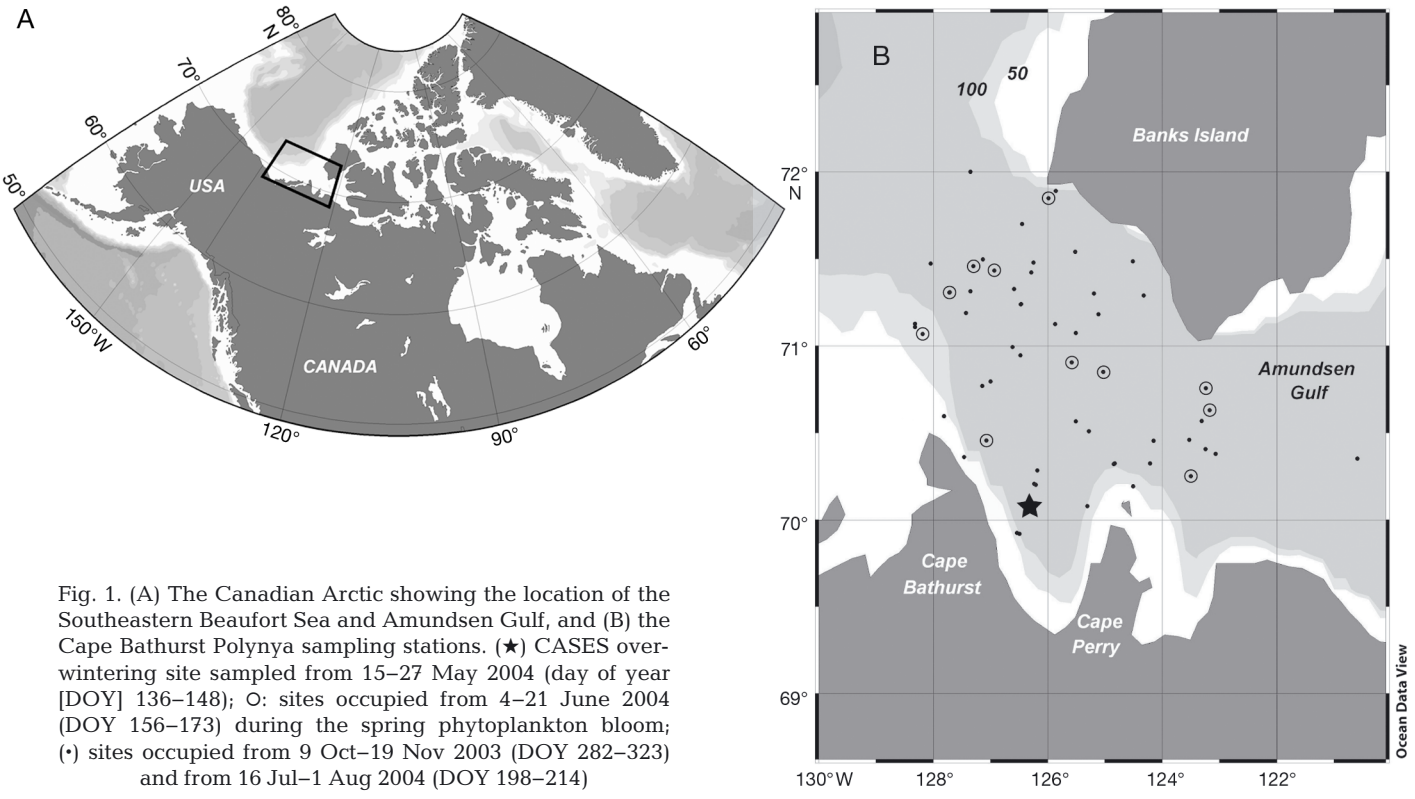

Fig. 1. (A) The Canadian Arctic showing the location of the Southeastern Beaufort Sea and Amundsen Gulf, and (B) the Cape Bathurst Polynya sampling stations. (★) CASES overwintering site sampled from 15–27 May 2004 (day of year [DOY] 136–148); ʘ: sites occupied from 4–21 June 2004 (DOY 156–173) during the spring phytoplankton bloom; (•) sites occupied from 9 Oct–19 Nov 2003 (DOY 282–323) and from 16 Jul–1 Aug 2004 (DOY 198–214)

Electronics) and fluorometer (Sea-Point). The water samples were gravity filtered through a 5 µm polycarbonate filter connected to the outlet spigot of the Niskin bottle (Tremblay et al. 2008). They were dispensed into acid-cleaned (10% HCl), 15 ml polypropylene tubes (Sarstedt), stored at 4°C in the dark and analyzed within 1 h of collection. Concentrations of nitrate [NO_3^-], nitrite [NO_2^-], ammonium [NH_4^+], phosphate [PO_4^{3-}], and silicate [$Si(OH)_4$] were measured with a Bran and Luebbe Auto-Analyzer 3 (AA3) using standard colorimetric methods. Details of the analytical procedures and detection limits for each nutrient are presented in Simpson et al. (2008). Particulate N samples were collected on combusted (24 h at 500°C) 25 mm Whatman GF/F filters. All filtrations were performed under reduced light. The filters were rinsed with 0.2 µm filtered sea water, dried at 50°C for 48 h, stored in cryovials and then analyzed by a Europa Scientific Integra isotope ratio mass spectrometer (UC Davis Stable Isotope Facility).

Statistics and calculations

Water-column nutrient inventories (mmol m^{-2}) were computed using trapezoidal integration of vertical profiles of dissolved concentrations measured at 5 or 6 sampling depths (0, 5, 10, 25, 40, 50 m) in the upper 50 m. In the absence of surface samples, we assumed that the water was well mixed down to the first sample depth and that the nutrient concentration was uniform within this layer. Particulate N inventories were calculated likewise from samples taken at depths corresponding to 100, 50, 10 and 1% of sea surface irradiance. The chlorophyll *a* (chl *a*) fluorescence maximum was shallower than 50 m during the sampling period consistent with observations reported by Martin et al. (2012) (mean ± SD depth of chlorophyll max. = 35 ± 16 m). Average NH_4^+ and NO_2^- inventories measured in autumn 2003 were computed from 21 and 12 independent vertical profiles, respectively. These data were pooled for convenience, to allow comparison with the individual profiles obtained in spring and summer of 2004.

Statistical analyses were performed using Systat v11.00.01 and curve fits were made using Sigmaplot v9.01. Samples containing less than 1.5 µmol NO_3^- l^{-1} were not used to compute nutrient draw-down ratios by regression analysis. These samples were excluded to avoid biases of non-Redfield uptake at limiting nutrient concentrations and the possibility of greater analytical error at low concentrations.

RESULTS

Nutrient draw-down

The Cape Bathurst Polynya opened in late May 2004 and nutrient concentration declined very quickly in the surface layer. A time series of vertical profiles showed within a span of roughly 18 d that NO_3^- was consumed down to a depth of approximately 30–50 m and that $[PO_4^{3-}]$ and $[Si(OH)_4]$ decreased (Fig. 2). The observed decrease in $[NO_3^-]$ above the 1% isolume was balanced by an increase in particulate N (PON) concentration (Fig. 3). Using linear models to describe the decrease and increase in $[NO_3^-]$ and PON between DOY 156 and 171, respectively, we calculated that 94% of the NO_3^- removed from the surface waters could be accounted for in the PON. Variability in the amount of nutrient

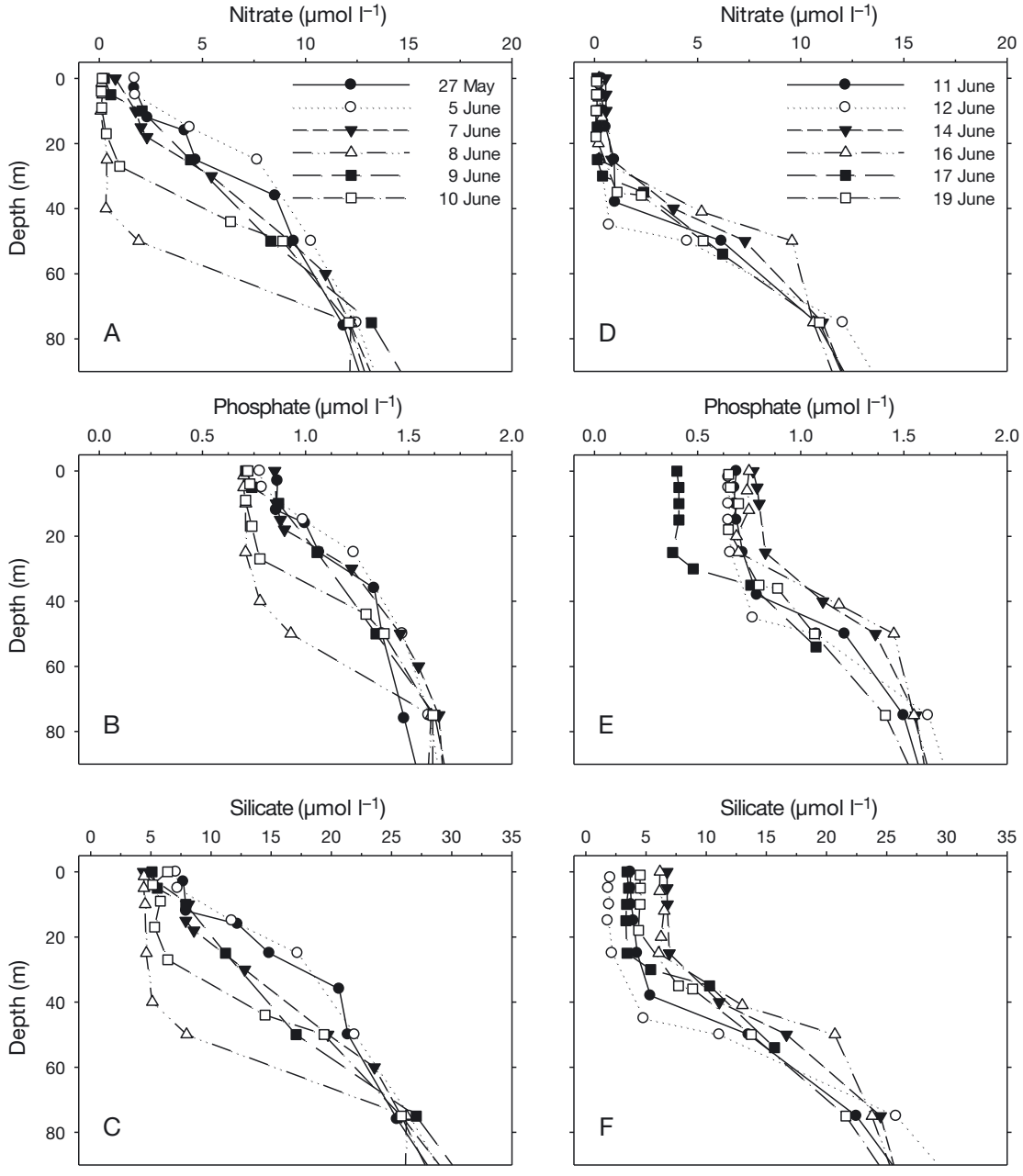

Fig. 2. Vertical profiles of nutrient concentration in open water stations showing the progressive draw-down of (A,D) nitrate, (B,E) phosphate, and (C,F) silicate during 27 May–19 June 2004 (day of year 136–171). The 27 May profile was obtained from the overwintering station immediately prior to departure to ice-free waters of the Amundsen Gulf

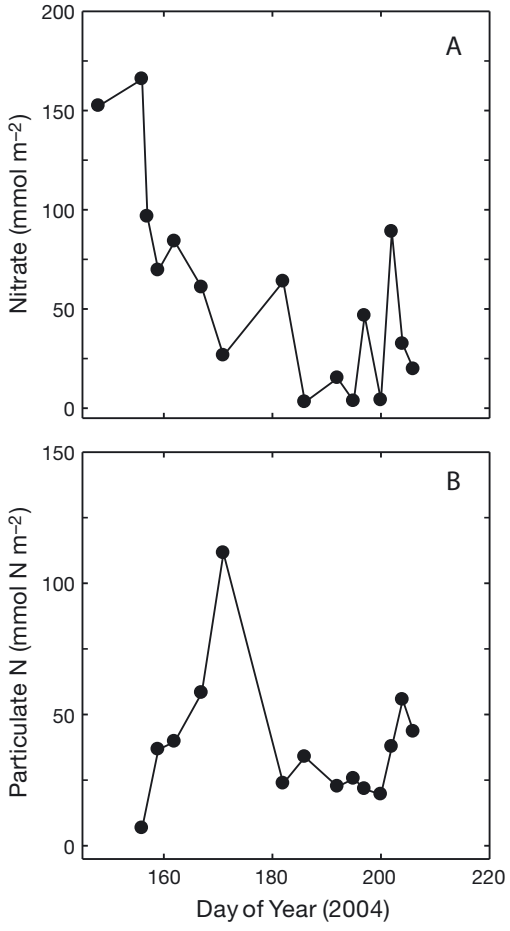

Fig. 3. Time series of water column inventories of (A) dissolved nitrate and (B) particulate nitrogen integrated to the 1% isolume. Sampling for particulate nitrogen began on 4 June 2004 (day of year 156)

draw-down observed in the NO_3^- profiles (Fig. 2; cf. 8 and 10 June) was likely due to patchy ice cover in the polynya, which influenced the rate and timing of phytoplankton growth. The thickness of the NO_3^- depleted layer (30–50 m) remained unchanged from mid-June until the final samples were obtained in August. Thus, the vast majority of the water-column nutrient consumption occurred early in the season. We note that some small decrease in $[NO_3^-]$ may have occurred between 50 and 80 m, but we could not accurately estimate this amount because of a lack of sampling between these depths.

Nitrite and ammonium

$[NO_2^-]$ was uniformly low throughout the water column between 15 and 27 May 2004 (DOY 136–148) (Fig. 4). As $[NO_3^-]$ declined, sea surface $[NO_2^-]$ increased to as much as 0.2 µmol l^{-1}. Slowly, the surface $[NO_2^-]$ decreased to ~0.05 µmol l^{-1} by the end of June 2004, and a well-defined NO_2^- maximum developed between 40 and 50 m in the nitracline. During the period of NO_3^- draw-down, water-column integrated inventories of NO_2^- and NO_3^- were inversely correlated ($p < 0.01$; Fig. 5).

In the late autumn of 2003, prior to and shortly after ice began forming in the polynya, integrated $[NO_2^-]$ and $[NH_4^+]$ were high, with mean (±SD) values of 9.4 ± 2.8 and 18.3 ± 10.3 mmol m^{-2}, respectively (Fig. 6). Volumetric $[NH_4^+]$ were about 0.35 µmol l^{-1} at all depths, with maximum values as high as 4.3 µmol l^{-1}. By the time we resumed sampling in spring, the $[NO_2^-]$ had declined to near zero and then gradually increased over the next 30 d. The increase in $[NO_2^-]$ from 15 May 2003 (DOY 136) represented about 2.5% of the decrease in total $[NO_3^-]$ (see below). There was considerable variation in integrated $[NO_2^-]$ and $[NH_4^+]$ from 16 July 2003 (DOY 198) until the end of the sampling period, but these measurements were not correlated (ANOVA, $p > 0.05$).

Relative nutrient consumption

Nutrient–nutrient plots were derived from surface water measurements within the polynya (Fig. 7). Model 2, geometric mean regression analysis (Sokal & Rohlf 1995) yielded NO_3^-:PO_4^{3-}, $Si(OH)_4$:NO_3^-, and $Si(OH)_4$:PO_4^{3-} molar utilization ratios of 13.1:1, 1.8:1, and 23.3:1, respectively. The N:P ratio was significantly different than the Redfield ratio of 16:1 (ANCOVA, $p = 0.0001$). The *y*-intercept of the N:P and Si:N plots indicated that as NO_3^- was drawn down to zero, $[PO_4^{3-}]$ and $[Si(OH)_4]$ were 0.72 µmol l^{-1} and 3.80 µmol l^{-1}. Nutrient-consumption ratios at the end of the bloom phase, when $[NO_3^-] \leq 1.5$ µmol l^{-1}, were significantly different (ANCOVA, $p < 0.05$) from the ratios determined at non-limiting concentrations and showed evidence for luxury uptake of Si and P with Si:N and N:P ratios of 6.8 and 2.0 (Fig. 7). The $Si(OH)_4$:PO_4^{3-} ratio, however, was statistically indistinguishable from the utilization ratio at high NO_3^- ($p > 0.05$).

Logistic model of nutrient consumption

We considered the nutrient inventory prior to ice retreat (15–27 May 2004) at the CASES over-wintering site in Franklin Bay (70° 02.74′ N, 126° 18.08′ W; Fig. 1) to be representative of pre-bloom conditions and used it to create a simple nutrient budget and model

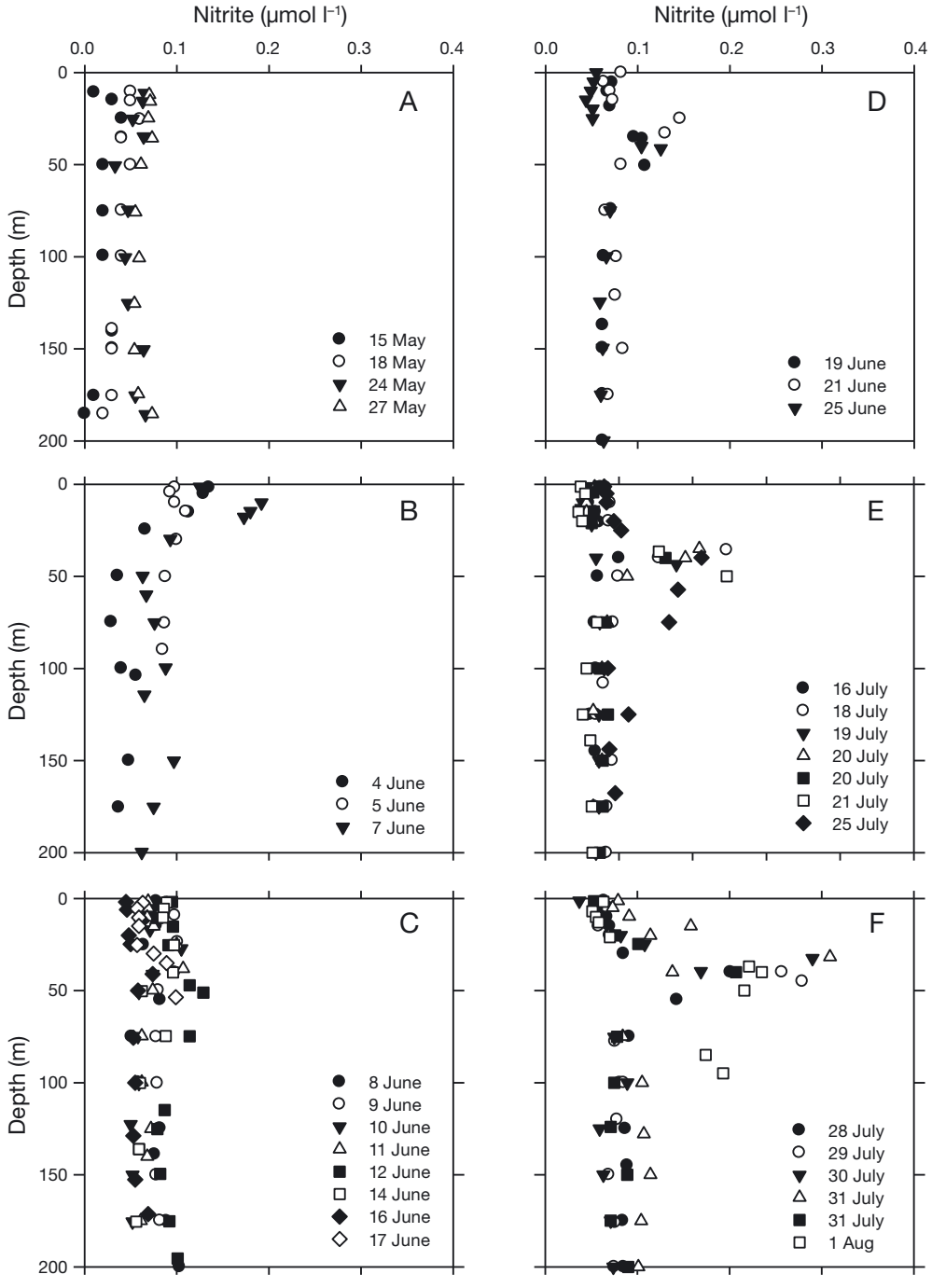

Fig. 4. Temporal variation in vertical profiles of nitrite concentration measured at stations occupied from (A) 15–27 May (day of year [DOY] 136–148), (B) 4–7 June (DOY 156–159), (C) 8–17 June (DOY 160–169), (D) 19–25 June (DOY 171–177), (E) 16–25 July (DOY 198–207), and (F) 28 July–1 Aug 2004 (DOY 210–214)

of the nutrient dynamics. The $[NO_3^-]$, $[PO_4^{3-}]$ and $[Si(OH)_4]$ measured in Franklin Bay were similar to those observed within the polynya shortly before ice break up and just prior to ice formation in autumn (e.g. station 300, 70° 59.54′ N; 127°81.30′ W = 250 mmol NO_3^- m^{-2}). Water column-integrated concentrations were computed for each nutrient profile and plotted as a function of DOY (Fig. 8). The best fit ($r^2 = 0.88$; $p < 0.001$) to the integrated nutrient data was a logistic curve ($y = y_0 + \{a / [1 + (x/x_0)^b]\}$), where a = max.–min. and b = hill slope. The asymptotes yielded the maximum and minimum inventories for NO_3^- (265.2 mmol NO_3^- m^{-2} and 55.6 mmol NO_3^- m^{-2}) and their difference (ca. 210 ± 19 mmol m^{-2}) the total NO_3^- consumed. The slope at the inflection point, corresponding to the maximum nutrient draw-down rate, equalled 11.8 mmol NO_3^- m^{-2} d^{-1}. The time for complete NO_3^- consumption was estimated to be

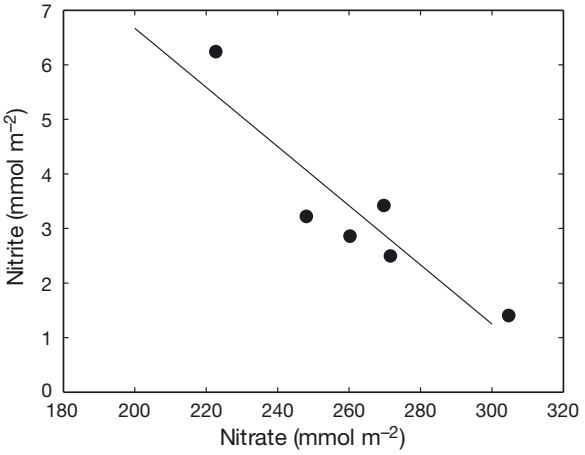

Fig. 5. Inverse relationship between water column-integrated nitrite and nitrate concentrations (mmol m^{-2}) before and during spring nitrate draw-down. Data points follow a chronological sequence beginning on 15 May 2004 (day of year [DOY] 136; 305 mmol NO_3^- m^{-2}) and ending on 7 June 2004 (DOY 159; 223 mmol NO_3^- m^{-2}). Line represents a least squares linear regression fit to the data (ANOVA, $p < 0.01$, $r^2 = 0.833$)

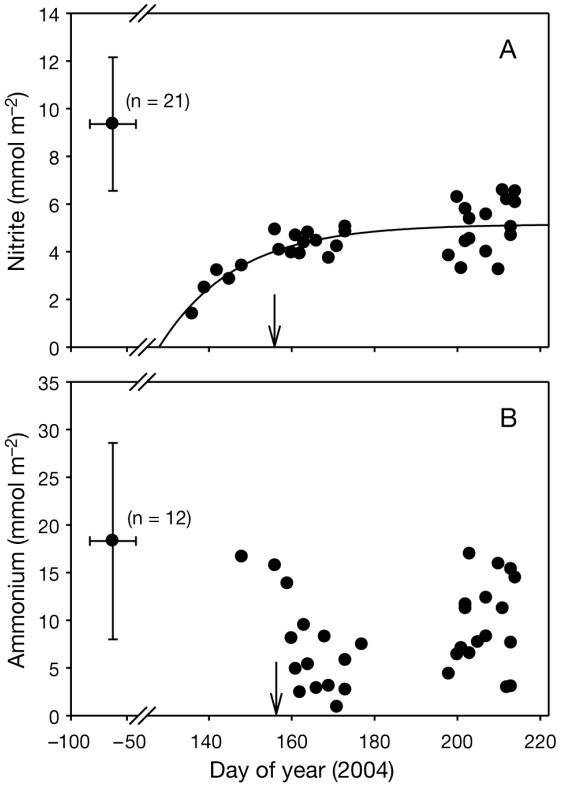

Fig. 6. Water column-integrated inventories of (A) nitrite and (B) ammonium as a function of day of year (DOY, 2004). Values measured in autumn from 9 Oct–19 Nov 2003 (DOY 282–323) are reported as mean ±1 SD. The horizontal error bars indicate when these samples were collected relative to 1 Jan 2004 (DOY 0). Arrows: start of open water sampling. The temporal change in water-column integrated nitrite was well described by an exponential rise to maximum function ($r^2 = 0.53$, $p < 0.001$)

17.6 d from the intersection of the slope with the asymptotes. Similar calculations were made using the PO_4^{3-} and $Si(OH)_4$ data (Table 1). They showed maximum draw-down rates of approximately 0.82 mmol m^{-2} d^{-1} and 17.8 mmol m^{-2} d^{-1}, respectively, and that $Si(OH)_4$ uptake continued for about 10 d after the NO_3^- and PO_4^{3-} uptake stopped. The ratios of the slopes were equivalent to the consumption ratios (mol mol^{-1}) at peak production: $Si(OH)_4$:NO_3^- = 1.5:1, NO_3^-:PO_4^{3-} = 14.4:1, and $Si(OH)_4$:PO_4^{3-} = 21.7:1.

To determine the amount of particulate new production during the spring bloom, we multiplied the nutrient consumption inventories by phytoplankton carbon:nutrient ratios (mol mol^{-1}) of C:N = 6.4:1, C:P 102:1, and C:Si = 2.9:1. The C:N ratio was measured in suspended particulate organic matter and the C:Si ratio in particulates collected in shallow sediment traps deployed during the period of maximum diatom sedimentation in the North Water Polynya (Michel et al. 2002, Tremblay et al. 2006). The C:P ratio was obtained from dissolved inorganic C:PO_4^{3-} uptake ratios in Franklin Bay adjacent to the Cape Bathurst Polynya (Tremblay et al. 2008). We assumed for the purposes of this calculation (see 'Discussion') that there was no additional nutrient input to the polynya

Table 1. Initial and final nutrient inventories and the amounts and rates of nutrient consumption during the spring bloom in the Cape Bathurst Polynya. Consumed concentrations (± SE) were calculated by subtraction of model-derived estimates of initial and final nutrient inventories (Fig. 8). Maximum uptake rates corresponded to the slopes of the inflection points of the logistic models. Spring new production and peak production were calculated from the consumed concentrations and maximum uptake rates, respectively, using C:nutrient ratios as described in 'Results: Logistic model of nutrient consumption'

Nutrient	Concentration (mmol m^{-2})			Duration of draw-down (d)	Max. uptake rate (mmol m^{-2} d^{-1})	Spring new production (g C m^{-2})	Peak production (g C m^{-2} d^{-1})
	Initial	Final	Consumed				
NO_3^-	265.2[a]	55.6	209.6 ± 19	17.6 ± 1.6	11.8	16.1 ± 1.5	0.91
PO_4^{3-}	55.3[a]	40.1	15.2 ± 2	18.5 ± 2.4	0.82	18.6 ± 2.4	1.0
$Si(OH)_4$	722.5	212.0	510.5 ± 70	28.7 ± 3.9	17.8	17.8 ± 2.4	0.62

[a]Includes the estimated contribution of sea ice (0.74 mmol NO_3^- m^{-2} and 0.78 mmol PO_4^{3-} m^{-2})

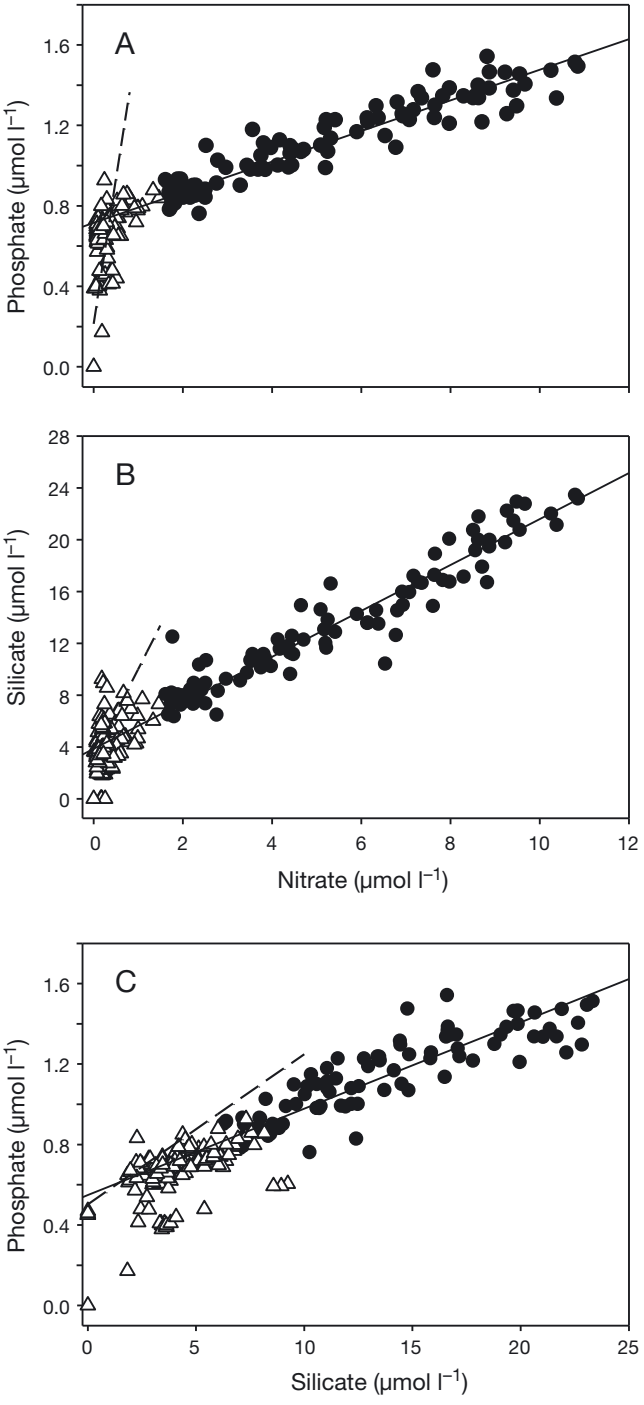

Fig. 7. Nutrient–nutrient plots derived from samples obtained from the upper 50 m in the Amundsen Gulf / Cape Bathurst Polynya between 4 and 21 June 2004 (day of year 156–173). Slopes of the model 2 regressions (solid lines), which are equivalent to the nutrient utilization ratios, were obtained for samples containing ≥1.5 µmol NO_3^- l^{-1} (●): (A) NO_3^-:PO_4^{3-} = 13.1:1, r^2 = 0.88, $p < 0.0001$, (B) $Si(OH)_4$:NO_3^- = 1.77:1, r^2 = 0.91, $p < 0.0001$, and (C) $Si(OH)_4$:PO_4^{3-} = 23.3:1, r^2 = 0.71, $p < 0.0001$. The dashed lines represent the model 2 regressions of the low-nitrate samples (Δ) (<1.5 µmol NO_3^- l^{-1})

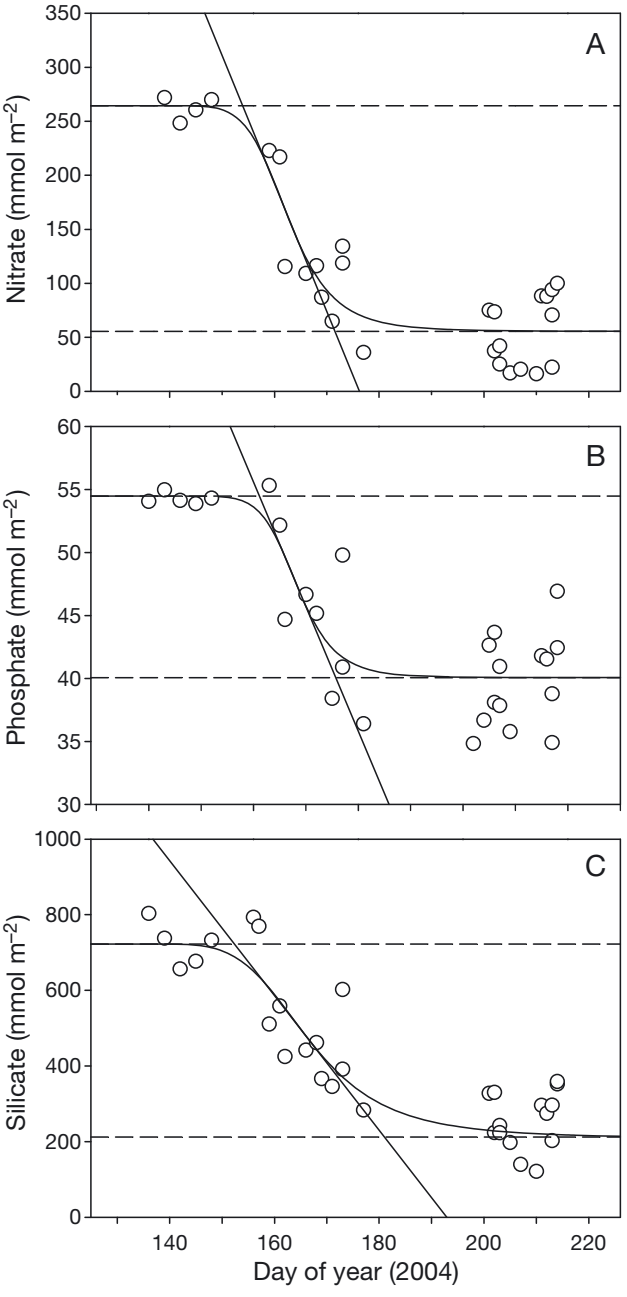

Fig. 8. Water column-integrated inventories of (A) nitrate, (B) phosphate, and (C) silicate plotted as a function of day of year. Data fitted to logistic curves: the straight lines show the slopes at the inflexion point and the dashed lines extend the asymptotes to the axes

during the period of nutrient draw-down and that there was no C overconsumption (Sambrotto et al. 1993). The NO_3^- based estimate of spring new production was thus 16.1 ± 1.5 g C m^{-2} and in good agreement with the independent estimates based on PO_4^{3-} and $Si(OH)_4$ uptake: 18.6 ± 2.4 and 17.8 ± 2.4 g C m^{-2}, respectively (Table 1). Maximum production

rates were similar for NO_3^- and PO_4^{3-}, but about 40% slower for $Si(OH)_4$ (0.91–1 g C m^{-2} d^{-1} vs. 0.62 g C m^{-2} d^{-1}).

Surface nutrient inventories of NO_3^-, PO_4^{3-} and $Si(OH)_4$ were strongly correlated (r^2 = 0.59–0.81) after 16 July 2004 (DOY 198), suggesting that wind mixing may have eroded the nutricline at this time. Indeed, the relative concentrations of NO_3^- and $Si(OH)_4$ in the surface mixed layer varied significantly (ANOVA, p = 0.02) with daily-average wind speed measured at Sachs Harbour, Banks Island (www.climate.weatheroffice.ec.gc.ca/climateData/canada_e.html), although the model only explained about 30% of the variance (data not shown). Phosphate concentration showed no relationship with wind speed (p > 0.05). The integrated quantities of NO_3^-, PO_4^{3-}, and $Si(OH)_4$ in surface waters occurred in ratios (mol mol^{-1}) of $Si(OH)_4$:NO_3^- = 2.2:1, NO_3^-:PO_4^{3-} = 10.5:1, and $Si(OH)_4$:PO_4^{3-} = 16.8:1, similar to the ratios of these nutrients in the underlying water of salinity ~33.1 (Simpson et al. 2008).

DISCUSSION

Phytoplankton nitrate consumption

Changes in population size are typically described by a logistic function in which a period of exponential increase is followed by a gradual reduction in growth as resources are depleted (e.g. Klausmeier et al. 2004). The shape of the population growth curve is sigmoidal and inversely related to the temporal change in concentration of limiting nutrient in the environment. Here, we applied a logistic function to model the change in nutrient concentration during the spring phase of phytoplankton growth in the Cape Bathurst Polynya. The model estimates spring new production and not regenerated production because it only considers net changes in nutrient concentration.

The excellent agreement between the quantities of NO_3^- consumed and PON produced (Fig. 3) provides strong evidence that changes in nutrient inventory were due to biological uptake and the development of the spring phytoplankton bloom. A time series of chl *a* fluorescence collected close to the overwintering station in Franklin Bay (70°20.35'N, 126°21.29'W), showed phytoplankton biomass began to increase on DOY 155 (3 June 2004) and reached a maximum on ~DOY 170 (18 June 2004) (Tremblay et al. 2008). These dates correspond almost exactly to the timing of nutrient depletion (Fig. 8) and PON build-up (Fig. 3) in the surface layer in the polynya which began on DOY 154 (2 June 2004) and ended on DOY 171 (19 June 2004). Thus, PON production represented the accumulation of phytoplankton biomass during the spring bloom and was quantitatively related to the amount of NO_3^- consumed at the sea surface.

Freshwater dilution could alter the NO_3^- content of the surface layer independent of biological processes and bias our estimate of new N production. For example, the Mackenzie River contained 4–5 µmol NO_3^- l^{-1} and melted sea ice water roughly 0 µmol l^{-1} (Simpson et al. 2008), which were less than the initial sea surface concentration in the polynya. We observed a 2% decrease in integrated water column salinity at the sampling stations between May and June, which would be enough to decrease the NO_3^- inventory by approximately 1–5 mmol m^{-2}. This is a small change compared to the 210 mmol m^{-2} that was taken up during the spring period (Table 1). Likewise, we calculate that the maximum input of $Si(OH)_4$ and PO_4^{3-} by freshwater dilution could be 40 mmol m^{-2} and 0.1 mmol m^{-2}, corresponding to about 8 and 0.7% of the total amounts of these nutrients consumed during the bloom. These results suggest that the changes in nutrient inventories in the polynya were primarily the result of biological uptake.

Although NO_3^- consumption was balanced by PON production (Fig. 3) and coincided with an increase in chlorophyll (Tremblay et al. 2008) some of the NO_3^- could be taken up by bacteria which compete with phytoplankton for inorganic resources (Simpson et al. 2013, this volume). Simpson et al. (2013) used stable isotopes and filter fractionation to trace the flow of N into bacteria-sized particles. The results showed that at the end of 24 h incubations about 6.6% of the particulate ^{15}N was in the <0.7 and >0.2 µm size fraction, implying that free-living bacteria assimilated little inorganic NO_3^- compared to phytoplankton. Indeed, slow rates of microbial metabolism in this region suggest that at most free-living and particle-associated bacteria could be responsible for taking up about 1 mmol NO_3^- m^{-2} d^{-1} (Simpson et al. 2013) or about 10% of the maximum rate reported here. Thus, phytoplankton appear to be responsible for most of the net NO_3^- consumption in the Cape Bathurst Polynya.

Nitrification and denitrification

Prokaryotes can alter the NO_3^- content of seawater by nitrification and denitrification which could po-

tentially affect the NO_3^- inventory. Denitrification in Arctic shelf sediments greatly reduces [NO_3^-] relative to [PO_4^{3-}] (Devol et al. 1997), but in surface waters of the Amundsen Gulf is unlikely because oxygen levels are greater than 270 µmol l^{-1} (Simpson et al. 2008) well above those that inhibit the reaction (~5 µmol l^{-1}; Codispoti et al. 2005). Although water column denitrification has been suggested to occur in sinking particles undergoing decomposition, there are little data to support it (Lehmann et al. 2005).

Evidence for the importance of nitrification at the sea surface is more compelling (Yool et al. 2007). Tremblay et al. (2008) observed a wintertime increase in the [NO_3^-] in Franklin Bay that they attributed to nitrifying bacteria. Above the pycnocline, [NO_3^-] rose steadily, but [$Si(OH)_4$] remained constant. The rate of increase was 13.2 ± 0.3 nmol NO_3^- l^{-1} d^{-1} (0.66 mmol m^{-2} d^{-1}; integrated to 50 m) (Tremblay et al. 2008), similar to the rates of nitrification measured in other cold parts of the sea (Yool et al. 2007). Our integrated NO_2^- data also shows a decrease in [NO_2^-] from winter to spring (Fig. 6), suggesting that nitrification is taking place in the upper water column. If we assume that nitrification persisted during the phytoplankton bloom period, then the amount of NO_3^- produced in the upper 50 m would be 11.9 mmol m^{-2} or roughly 5% of the amount of NO_3^- consumed over 17.6 days. This quantity is too small to greatly affect our interpretation of the NO_3^- consumption data.

Integrated NO_2^- concentration increased after the onset of polar day (Fig. 6) and reached a maximum of 5.0 mmol m^{-2} after mid-July. The increase in [NO_2^-] coincided with the decrease in [NO_3^-] due to phytoplankton uptake during the initial stages of the bloom. The inverse relationship between water-column integrated [NO_2^-] and [NO_3^-] (Fig. 5) suggested that NO_2^- was a byproduct of phytoplankton assimilatory NO_3^- reduction. This interpretation is consistent with the prevailing view that NO_2^- maxima are largely the result of phytoplankton excretion (e.g. Al-Qutob et al. 2002, Lomas & Lipschultz 2006).

The net rate of NO_2^- production during the spring rise was 0.17 mmol NO_2^- m^{-2} d^{-1} (Fig. 6). Because nitrifiers may have consumed NO_2^- at the same time it was produced, the actual rate of phytoplankton NO_2^- production may be underestimated. Assuming that the rate of nitrification was 0.66 mmol NO_2^- m^{-2} d^{-1} (see above), then production of NO_2^- by assimilatory NO_3^- reduction may have been as great as 0.84 mmol NO_2^- m^{-2} d^{-1}. This rate is about 7% of the rate of NO_3^- uptake by the phytoplankton (Table 1), implying that 93% of the NO_3^- consumed was converted into biomass. We note that this is in remarkably good agreement with quantity of PON that was produced (94% of NO_3^- converted into PON; Fig. 3). Although some assimilated NO_3^- could be released as dissolved organic N (Skoog et al. 2001, Simpson et al. 2008), our results demonstrate that during the spring phase, NO_3^- uptake was used to fuel PON production by phytoplankton.

Draw-down dynamics

Given the arguments presented above, we are confident that nutrient consumption was driven by phytoplankton growth and can use the change in water column inventory to obtain estimates of spring new production. At issue is the conversion of NO_3^- uptake to carbon assimilation. New production of C supported by NO_3^- can occur in excess of Redfield proportions (6.6 mol C mol N^{-1}) in some ocean regions (Sambrotto et al. 1993), so estimating C assimilation from NO_3^- uptake could be biased. Part of the discrepancy arises because of unbalanced growth following depletion of NO_3^- from seawater (Koeve 2004). Spring bloom production generally follows Redfield stoichiometry with C overconsumption limited to post-bloom periods (Kortzinger et al. 2001), indeed measurement of the C:N assimilation ratio (POC/PON production ratio) in Arctic phytoplankton in the NOW Polynya during the spring bloom was 5.8 mol mol^{-1} (95% CI: 5.6–6.0) (Mei et al. 2005). Tremblay et al. (2006) showed likewise that the ratio of primary production to NO_3^- uptake in the same region was 7.5 ± 0.3 mol C mol N^{-1}. Accordingly, we have chosen a C:N ratio of 6.4, because it represents the particulate C:N ratio measured in spring in the NOW (6.4 ± 0.1; Tremblay et al. 2006). We note that any DOC produced by phytoplankton would not be estimated in this way. The draw-down of 210 ± 19 mmol NO_3^- m^{-2} calculated from the model thus corresponds to a particulate phytoplankton new production of 16.1 ± 1.5 g C m^{-2}.

A straightforward approach to convert the amount of Si consumed to C equivalents would be to use an average Si:C ratio of diatoms, but these ratios are largely for warm water species grown at higher temperatures (Brzezinski 1985). Stapleford & Smith (1996) showed that the Si quota of one Arctic diatom was highly temperature dependent, increasing by a factor of 2 at temperatures less than or equal to 0°C. Because such low temperatures are typical of the Cape Bathurst Polynya, the Si:C ratio reported for most diatoms may not be applicable here. Indeed,

if we use the average value of 7.7 mol C mol^{-1} Si (Brzezinski 1985) then the amount of C production is more than double (47.2 g C m^{-2}) the N- and P-derived estimates. A more empirical approach is to use a C:Si ratio of particulates collected in Arctic waters in shallow sediment traps during a period of maximum diatom sedimentation (Michel et al. 2002). Using this estimate of diatom C:Si (2.9 mol mol^{-1}), the $Si(OH)_4$ consumption is equivalent to 17.8 g C m^{-2} similar to the amount of production estimated from NO_3^- and PO_4^{3-} (Table 1).

Consumption of regenerated nutrients

Integrated [NH_4^+] also declined coincidently with [NO_3^-] (Fig. 6) and may have supported growth of phytoplankton or ammonium-oxidizing prokaryotes (Kalanetra et al. 2009). The decrease during spring was about 10 mmol N m^{-2} and represented approximately 5% of the amount of NO_3^- consumed. This NH_4^+ likely accumulated during the autumn and winter from the decomposition of DON produced during the previous season by phytoplankton growth (Simpson et al. 2008). Because this NH_4^+ was regenerated N it has not been included in the new production inventory.

Likewise, nitrification in the surface layer would have increased the NO_3^- inventory during winter, but would really represent a regenerated form of N (i.e. DON $\rightarrow NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$) so its assimilation would not be balanced at equilibrium by export of an equivalent amount of particulate or dissolved organic N, as proposed (Eppley & Peterson 1979). This regenerated NO_3^- would have added to the 'new' NO_3^- that was supplied by vertical mixing. Tremblay et al. (2008) suggested that about 20% of the NO_3^- used by phytoplankton was remineralized in surface waters in Franklin Bay of the Amundsen Gulf, but we have not subtracted this from our new production estimate. More information is required before we clearly understand the magnitude and importance of sea surface nitrification in the Arctic.

Advection and diffusion

The 1-dimensional model applied here (Fig. 8) fails to account for the influx of 'new' N by advection, mixing or diffusion (Eppley & Peterson 1979) or from atmospheric sources. We made measurements of NO_3^- in precipitation and found average concentrations of 3.37 ± 0.17 µmol NO_3^- l^{-1} (n = 4). Aside from long storm events, pulsed atmospheric input of NO_3^- is expected to be small relative to the euphotic zone inventories. A more significant input could be horizontal advection, which in polynyas such as the NOW, sustains the bloom for much of the open water period (Tremblay et al. 2002). To further evaluate the supply of nutrients to the Cape Bathurst Polynya during the spring bloom, we calculated the amount of NO_3^- entering by currents flowing from the northwest. Current speeds determined by acoustic Doppler current profilers moored near the northern side of the mouth of the Amundsen Gulf from May–July 2004 were 3.1 and 5.8 cm s^{-1} above and below 30 m, respectively (G. Ingram pers. comm.). Using the initial NO_3^- inventory from Franklin Bay (Table 1) and a liberal estimate of the size of the advective flow (~64 km or about half the distance from Banks Island to Cape Bathurst at the 50 m isobath), we calculate 46 mmol NO_3^- m^{-2} could be introduced to the upper 50 m of the polynya (25 000 km^2) over ~18 d of the spring nutrient draw-down. This N input is about 17% of the initial NO_3^- inventory.

Deep waters could also supply NO_3^- to the surface by eddy diffusion which would not be detected by our analysis. The approach of King & Devol (1979) can be used to estimate this vertical flux. The mean slope of the nitracline was 0.34 mmol m^{-4} (Fig. 2). If we assume a vertical eddy diffusivity of 1–5 × 10^{-5} m^2 s^{-1} (C. Sévigny & Y. Gratton pers. comm.), then the vertical NO_3^- flux was between 5.4 and 26.4 mmol NO_3^- m^{-2} corresponding to about 2–10% of the initial inventory. Nitrate input by advection and vertical diffusion could potentially increase the amount of new production in the polynya by about 19–27%. Collectively, if we consider all sources of uncertainty in our estimate of the NO_3^- inventory (including freshwater dilution and nitrification), then the amount of NO_3^- consumption could be 25–33% higher than is reported here.

Spring production

The computed nutrient consumption in the Cape Bathurst Polynya is based on measurements at stations located within 100 km of each other (Fig. 1). The model (Fig. 8) estimate is thus applicable to the polynya as a whole. The good fit of the data to the model suggests that phytoplankton growth and draw-down of nutrients occurred more or less simultaneously in the polynya. At the periphery of the ice-free waters, i.e. at the overwintering station, the phytoplankton growth was likely impaired by sus-

tained ice cover (observed by MODIS satellite imaging), as high [NO_3^-] persisted at these sites for longer. We note however, that a similar deficit in NO_3^- developed at the over-wintering site by the beginning of August so that the amount of seasonal new production (but not its rate) was similar to that in the polynya. In mid-July, for example, the nitrate deficit at this site equaled ~126 mmol NO_3^- m^{-2}, and by August increased to ~190 mmol NO_3^- m^{-2}, roughly equal to the total draw-down derived by our model (Table 1, Fig. 8). Nitrate deficits of 200 and 291 mmol m^{-2} were measured in the adjacent Mackenzie Shelf in 1974 and 1975 (Macdonald et al. 1987) suggesting that NO_3^- draw-down in ice free waters of the southeastern Beaufort Sea may be comparable at even larger spatial scales.

In conclusion, our data show a tight coupling between integrated NO_3^- consumption and PON production during the phytoplankton spring bloom in the Cape Bathurst Polynya. Spring new production is estimated to be about 16.1 g C m^{-2} based on a seasonal NO_3^- draw-down of 210 mmol m^{-2} during an 18 d period. Advection, dilution and sea surface nitrification could increase the [NO_3^-] in the polynya by 25–33% during the bloom period, which would further increase production.

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