An annual study of inorganic and organic nitrogen and phosphorus and silicic acid in the southeastern Beaufort Sea

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[1] Water column samples from the Mackenzie Shelf, the Beaufort Sea, and the Amundsen Gulf were obtained during 2003–2004 to investigate nutrient dynamics in an Arctic ecosystem influenced by a large river and flaw lead polynya. Nutrient inventories in the upper water column showed a significant seasonal drawdown of nitrate (NO$_3^-$) and silicic acid (Si(OH)$_4$) (1:1.75 mol/mol) and subsequent accumulation of nitrite (NO$_2^-$) and ammonium (NH$_4^+$). Dissolved organic nitrogen and phosphorus concentrations (DON and DOP) were elevated in surface waters during the time of peak phytoplankton growth (bloom and postbloom phases) and covaried in a 17:1 molar ratio. Vertical profiles showed the typical middepth maxima in NO$_3^-$, PO$_4^{3-}$, and Si(OH)$_4$ at salinity 32–33.1. The concentration of DOP (0.76 ± 0.27 μmol P L$^{-1}$) was also 2 times higher in this layer compared to the surface average and inversely correlated with the water mass tracer N* [N* = (NO$_3^-$ − 16 × PO$_4^{3-}$ + 2.9) × 0.87], suggesting that Pacific-derived waters were a source of the enrichment. Below the mixed layer, DON was generally constant with depth, although averaged profiles (like those of urea) suggested the presence of subsurface maxima at 50 m and between 250 and 300 m. Regeneration ratios varied with depth and were approximately 9.0 mol −O$_2$/mol NO$_3^-$ and 122.5 mol −O$_2$/mol PO$_4^{3-}$ in shallow Pacific-derived waters (halocline layer) and 17.4 and 193.5 in deep Atlantic waters (Atlantic layer), respectively. Deep waters of the Amundsen Gulf contained an excess of 1.7 μmol NO$_3^-$ L$^{-1}$, 0.12 μmol PO$_4^{3-}$ L$^{-1}$, and 6.2 μmol Si(OH)$_4$ L$^{-1}$ and a deficit in O$_2$, relative to waters of similar density in the Beaufort Sea, in proportions consistent with the remineralization ratios derived from oxygen-nutrient regressions. Enhanced export of particulate matter from the overlying polynya and subsequent remineralization at depth are hypothesized to create this nutrient enrichment.


1. Introduction

[2] Uncertainties in ocean-atmosphere coupled feedbacks remain a complex problem in understanding the impact of future climate on ocean ecosystems [Soden and Held, 2006]. Of particular interest from a biogeochemical perspective is how changes in ocean circulation and mixing affect nutrient distribution and consequently planktonic production and regeneration. In the Arctic Ocean, for example, some oceanographic changes have either already taken place [McLaughlin et al., 1996; Dickson et al., 2000; Servзе et al., 2003; Barber and Hansesiak, 2004; Wu et al., 2004] or are very likely to occur given the complexity of Arctic water mass structure and the decline in sea ice cover.

Recent studies identify the sensitivity of the Arctic Ocean to climate change [Intergovernmental Panel on Climate Change (IPCC), 2001] and focus on features that set it apart from other oceans. These include the influence of freshwater (nutrient) input to the continental shelves [Carmack et al., 1989; Aagaard and Carmack, 1994; Shiklomanov et al., 2000; Arnell, 2005] and the importance of polynyas to biological production [Tremblay et al., 2002; Arrigo and van Dijken, 2004; Tremblay et al., 2006]. Both are predicted to be greatly affected by rising temperatures. Meaningful analysis of the impacts of oceanographic change on Arctic ecosystems and validation of models can only be accomplished if we have historical data to compare with future measurements. In some of the most biologically active regions of the Arctic, such baseline data are still lacking.

[3] The water column of the southeastern Beaufort Sea, in the western Canadian Arctic, is composed of several layers whose structure has been thoroughly examined [Carmack et al., 1989; McLaughlin et al., 1996; Codispoti et al., 2005]. According to Wang et al. [2006] and Codispoti et al. [2005],
the surface mixed layer or polar mixed layer (PML) extends from surface to 25–50 m and is highly variable in temperature, salinity, and nutrient content. Below it lies the upper halocline layer (UHL) (50–200 m), composed primarily of Pacific-derived waters from the Bering Sea with salinities less than 34.4. The lower halocline layer (LHL) below the UHL [Jones and Anderson, 1986] has a salinity range of 34.2–34.6 and originates mainly from the Atlantic [Wang et al., 2006]. The Atlantic layer (AL) occurs below the LHL between 250 and 850 m and is warmer and more saline than the halocline. Canadian basin deep water (CBDW) occupies the bottom, at depths below 850 m and with salinities of at least 34.8.

The distribution of dissolved inorganic nutrients in the Beaufort Sea of the Canadian Basin follows several well-established patterns that can be used to define the boundaries of the water masses and understand the processes that influence nutrient abundance. Nitrate concentrations in the PML are generally low and in some regions, like the outer Chukchi Shelf, undetectable and limiting to primary production [Codispoti et al., 2005]. A well-defined nutrient maximum occurs at salinity ca. 33.1, associated with UHL water. Part of the maximum originates from the Pacific Ocean, but the majority of it is created by biological and physical processes as the water passes through the Chukchi and East Siberian seas [Bauch et al., 1995, and references therein]. Lower halocline layer water can be distinguished by a minimum in the tracer NO [Broecker, 1974], while the core of Atlantic water resides below the halocline between 300 and 800 m and is characterized by a temperature maximum [Bauch et al., 1995, and references therein]. Little is known of the abundance and water mass distribution of dissolved organic nutrients in the Arctic. However, one study [Wheeler et al., 1997] measured low concentrations of DON across the Arctic (lowest over the Chukchi Shelf) and suggested that rivers, ice melt, and in situ production were the major sources.

The Mackenzie Shelf in the southeastern Beaufort Sea is small compared to the extensive shelves of the Russian Arctic. It is bounded by the Mackenzie Canyon and the Amundsen Gulf in the east and west, and by the Beaufort Sea and Mackenzie River to the north and south. Biological processes on the shelf are greatly affected by seasonal changes in freshwater input, ice coverage, and irradiance. Data on the nutrient chemistry and distribution on the Mackenzie Shelf is sparse [Macdonald et al., 1987; Carmack et al., 1989; Macdonald et al., 1989; Moore et al., 1992] and generally limited to observations of dissolved inorganic nutrients made in the mid 1970s and 1980s. In close proximity to the Mackenzie Shelf is the Cape Bathurst Polynya in the Amundsen Gulf, part of the Arctic Ocean’s circumpolar flaw lead polynya system [Arrigo and van Dijken, 2004]. To our knowledge, the only biogeochemical data for this region come from 18 vertical profiles of inorganic nutrients obtained during August–September 1977 [Macdonald et al., 1978].

From September 2003 to August 2004, a multidisciplinary research project was conducted aboard the CCGS Amundsen in the Southern Beaufort Sea, the Mackenzie Shelf and the Amundsen Gulf. Here we present the results of measurements of the concentrations and distributions of inorganic (NH$_4^+$, NO$_3^-$, PO$_4^{3-}$, Si(OH)$_4$) and organic nutrients (DON, urea, and DOP) throughout the region.

2. Materials and Methods

2.1. Study Site

Hydrographic measurements were made aboard the Canadian Coast Guard icebreaker CCGS Amundsen, during four open water legs of the 2003–2004 Canadian Arctic Shelf Exchange Study (CASES) program. A total of 120 nutrient profiles were obtained during Leg 1: 13 September to 14 October 2003; Leg 2: 15 October to 25 November 2003; Leg 7: 13 May to 24 June 2004; and Leg 8/9: 25 June to 31 August 2004, at sites located throughout the Mackenzie Shelf, Amundsen Gulf and southern Beaufort Sea (Figure 1).

2.2. Sampling

Discrete water samples for nutrients were collected using 12-L Niskin bottles mounted on a Seabird carousel rosette system equipped with Seabird 911 CTD (Sea-Bird Electronics, Incorporated). Samples were filtered through 5.0 µm polycarbonate filters (Poretics Corporation) and collected into acid-cleaned (10% HCl) and sample-rinsed polypropylene tubes (Sarstedt, Incorporated). One sample from each depth was analyzed for NO$_3^-$, NO$_2^-$, NH$_4^+$, PO$_4^{3-}$, and Si(OH)$_4$ concentration within one hour of collection. A replicate sample from each depth was stored frozen (−20°C) and analyzed later for total dissolved nitrogen and phosphorus (TDN and TDP), and urea. Temperature, salinity, and oxygen were obtained using a Sea-Bird 911 CTD. Oxygen calibration was performed using Winkler titration with a Mettler DL22.

2.3. Inorganic Nutrient Analyses

Concentrations of NO$_3^-$, NO$_2^-$, NH$_4^+$, PO$_4^{3-}$, and Si(OH)$_4$ were measured using standard colorimetric methods [Grasshoff, 1999] adapted for use on a 4-channel (multitest 18 and 19) continuous flow Bran + Luebbe Auto-Analyzer 3 (AA3). Nitrite concentrations were low and generally represented <10% of the combined NO$_3^-$ + NO$_2^-$ concentration. Nitrate concentrations reported here include NO$_2^-$ unless otherwise noted.

The accuracies of the measured concentrations (reported as percent relative deviation or coefficients of variation) of NO$_3^-$, PO$_4^{3-}$, and Si(OH)$_4$ were ±0.9% at 15 µmol L$^{-1}$, ±1.5% at 1.0 µmol L$^{-1}$, and ±0.8% at 10 µmol L$^{-1}$, and the detection limits were 0.012 µmol L$^{-1}$, 0.016 µmol L$^{-1}$, and 0.020 µmol L$^{-1}$, respectively. Sampling error was assessed by analyzing the nutrient concentrations in five water samples collected at the same time from the same sampling depth. The coefficients of variation of NO$_3^-$, PO$_4^{3-}$, and Si(OH)$_4$ concentrations in these samples were 0.45, 0.56, and 0.57%, respectively. Standard curves were run with each batch of samples using freshly prepared standards that spanned the range of concentrations in the samples. The r$^2$ values of all the standard curves, including the analyses of the nutrients described below, were greater than or equal to 0.99.

Salinity varied from 5 to 35 in the study area because of regional differences in ice melt, river input, and water mass stratification. A correction factor was thus applied to
calculate nutrient concentrations in these samples to compensate for the salt matrix effect as described [Grasshoff, 1999].

2.4. Total Dissolved and Organic Nutrient Analyses

[12] Total dissolved nitrogen (TDN) and phosphorus (TDP) concentrations were determined using persulphate oxidation [Valderrama, 1981]. The efficiency of this method was calculated to be 98% on the basis of the conversion of a number of different amino acids and phosphate monoesters to NO$_3^-$ and PO$_4^{3-}$, respectively. Frozen samples were thawed in a tepid water bath upon return to the laboratory and centrifuged at 3500 g for 20 min to remove particulate material. The supernatant was transferred directly to precombusted (500°C for 24 h) and acid-cleaned (10% HCl) borosilicate reaction vials with Teflon-lined screw-cap lids for hydrolysis. Concentrations of DON and DOP were calculated by subtracting the ambient concentrations of NO$_3^-$, NO$_2^-$, and NH$_4^+$, and PO$_4^{3-}$ from the TDN and TDP concentrations, respectively. A subset of samples was filtered through precombusted GF/F filters prior to hydrolysis. The DON and DOP concentrations in these samples were not significantly different from the centrifuged samples. The coefficients of variation of replicate samples of TDN and TDP were ±1.2% at 16 µmol L$^{-1}$ and ±2.7% at 1.5 µmol L$^{-1}$, respectively. Errors in the calculations of DON and DOP concentrations were computed using error propagation to be ±2.1% at 15 µmol L$^{-1}$ and ±3.0% at 1.5 µmol L$^{-1}$, respectively.

[13] Urea concentration was measured using the room temperature diacetylmonozime method of Goeyens et al. [1998], with an analytical detection limit of 0.2 µmol N L$^{-1}$. Urea-N concentration was also subtracted from the DON concentration for one set of analysis to calculate the DON minus urea concentration.

2.5. Water Mass Characterization

[14] Data were grouped spatially and temporally. For the purpose of regional analysis, samples obtained east of 128.35°W (approximately the tip of Cape Bathurst) were considered to be from the Amundsen Gulf (East stations) and samples obtained west of 128.35°W were considered to be from the Mackenzie Shelf or Beaufort Sea (West stations) (see Figure 1). Stations in the western region of the CASES site were further divided according to bottom depth: Beaufort Sea (≥250 m) and Mackenzie Shelf (≤249 m).

[15] Depth strata corresponding to unique water masses in the CASES study region (Canadian Basin–Beaufort Sea) were identified from temperature-salinity plots, which were analyzed in a piecewise manner (data not shown) [Carmack et al., 1989]. This approach was expanded to include separation of the water masses on the basis of property-property plots of nutrient concentrations. The water masses were mostly restricted to the following depths: 0–50 m; 50–200 m; 200–275 m; 275 m to bottom, as previously described [Carmack and Kulikov, 1998; McLaughlin et al., 2002; Codispoti et al., 2005; Wang et al., 2006]. They corresponded to: the polar mixed layer (0–50 m); the upper halocline (50–200 m), which was further subdivided according to nutrient content; the lower halocline (200–275 m); and the Atlantic layer (>275 m).

2.6. Temporal Characterization

[16] The data were partitioned into four temporal phases on the basis of seasonal changes in phytoplankton biomass (chlorophyll a) (S. Brugel, personal communication, 2007),
2.7. Statistical and Data Analyses

[17] Statistical analyses were performed using Systat v11.00.01. For predictive purposes, the linear (model 1), least squares regression analysis was employed. Direct stoichiometric comparisons utilized the geometric mean (model 2) regression [Sokal and Rohlf, 1995]. Samples containing low NO$_3^-$ (<1.5 $\mu$mol L$^{-1}$) or low PO$_4^{3-}$ (<0.5 $\mu$mol L$^{-1}$) were excluded from regression analyses to avoid potential bias caused by non-Redfield uptake kinetics due to nutrient exhaustion and greater analytical error at low concentrations. Ammonium concentrations measured between 6 and 27 November 2003 were unreliable because of a methodological artifact and were thus excluded from the analyses.

[18] Water column nutrient inventories were calculated using standard trapezoidal integration. All comparative analyses that utilized derived variables employed propagation of error in the calculation of standard deviations. Spatial differences between the Beaufort Sea and Amundsen Gulf deep water (200–500 m) were calculated from weighted, average, vertical profiles. Seasonal differences in concentrations were assessed using 1-way ANOVA and Tukey post hoc comparison at a significance level of $p \leq 0.05$.

[19] We used the N* parameter as a water mass tracer to identify modified Bering Sea water in the upper halocline layer at the CASES study site. N* calculates the deficit or excess of NO$_3^-$ relative to PO$_4^{3-}$ assuming that regeneration produces NO$_3^-$ and PO$_4^{3-}$ in a 16:1 molar ratio, viz. N* = ([NO$_3^-$ − 16 × PO$_4^{3-}$] + 2.9) × 0.87 [Gruber and Sarmiento, 1997]. Denitrification decreases the NO$_3^-$ concentration in the water column of the Bering Sea so that seawater values of N* are between −7 to −3 $\mu$mol L$^{-1}$ [Lehmann et al., 2005]. As the Bering water flows over the continental shelf into the Arctic Ocean it undergoes further modification that reduces N* to −15 to −10 $\mu$mol L$^{-1}$ [Codispoti et al., 2005]. Vertical profiles in the Canadian Basin show highly negative N* in the upper halocline that represents water that originated from the Bering Sea [Wheeler et al., 1997; Tremblay et al., 2002].

2.8. Terminology

[20] For simplicity, we used the terms phosphate (PO$_4^{3-}$) and silicic acid (Si(OH)$_4$) to describe soluble, molybdate-reactive phosphorus (orthophosphate) and soluble, molybdate-reactive silicate (silicic acid), respectively. All dates described are in day of year (DOY) format beginning day 1 on 1 January.

3. Results

3.1. Nitrate, Phosphate, and Silicic Acid–Salinity Relationships

[21] Property-salinity plots were used to characterize the dominant water masses in the study area and their depth distribution (Figure 2). A nutrient-rich subsurface layer with salinity of ca 33.1 and sigma-t ($\sigma_t$) of 26.6 occupied depths between 125 and 200 m. On the basis of its salinity, this was Pacific-derived water from the Bering Sea [Jones and Anderson, 1986; Carmack et al., 1989; McLaughlin et al., 1996]. It contained 1.9 $\mu$mol PO$_4^{3-}$ L$^{-1}$, 17.3 $\mu$mol NO$_3^-$ L$^{-1}$ and 33.5 $\mu$mol Si(OH)$_4$ L$^{-1}$ and was thus relatively enriched in PO$_4^{3-}$ (N:P = 9.1) compared to Redfield proportions. The Si:N ratio was 1.9, slightly lower than the Bering Sea outflow but similar to waters composing the 50 to 250 m depth layer on the Chukchi slope [Cooper et al., 1997]. There was little regional difference in the depth and density of the water containing these nutrient maxima (Table 1). In the Amundsen Gulf, however, the peak NO$_3^-$ concentration occurred at roughly 200 m depth (at a salinity of 34.2), well below the PO$_4^{3-}$ and Si(OH)$_4$ maxima in this region and below the NO$_3^-$ maximum observed in the Beaufort Sea/Mackenzie Shelf. Mixing of the Bering water with deeper Atlantic-derived waters (salinity 34.6, depth 275 m) and with surface Arctic water (salinity 30, depth < 50 m) yielded two well-defined mixing lines (Figure 2, insets). The deep Atlantic water contained less PO$_4^{3-}$ and Si(OH)$_4$ than the Bering layer but an equivalent concentration of NO$_3^-$, so that its N:P ratio was considerably greater than observed at the nutrient maximum. A low salinity surface lens occupied the upper 50 m, and was generated primarily by freshwater dilution by the Mackenzie River and to a lesser extent by ice melt. Extrapolation of the mixing line from 30 to zero salinity showed that the Mackenzie River contributed roughly 40 $\mu$mol Si(OH)$_4$ L$^{-1}$ and 4–5 $\mu$mol NO$_3^-$ L$^{-1}$ to the Shelf waters. As expected, river supply of PO$_4^{3-}$ to the Mackenzie Shelf was very small. Independent measurements at sites near the Mackenzie River discharge yielded concentrations of 56 $\mu$mol Si(OH)$_4$ L$^{-1}$ and 4–5 $\mu$mol NO$_3^-$ L$^{-1}$, and <0.1 $\mu$mol PO$_4^{3-}$ L$^{-1}$. High variability in nutrient concentration of the surface waters (Figure 2) reflected seasonality in freshwater input, mixing, and phytoplankton consumption.

3.2. Seasonal Patterns of Inorganic and Organic Nutrients

[22] Seasonal trends in dissolved nutrient concentrations were evaluated by dividing the data according to the timing of the peak and decline in phytoplankton growth. We used changes in the integrated surface NO$_3^-$ concentration to determine the onset and duration of the bloom and thereby defined four distinct phases during the study: prebloom, bloom, postbloom and autumnal (K. G. Simpson et al., Nutrient dynamics in the Amundsen Gulf and Cape Bathurst Polynya: 1. New production in spring inferred from nutrient drawdown, submitted to Marine Ecology Progress
The timing of these phases was independently confirmed by measurements of phytoplankton biomass (chlorophyll $a$) (S. Brugel, personal communication, 2007). Temporal and spatial differences in phytoplankton growth in each phase likely contributed to the variation in nutrient concentration regionally and consequently introduced noise to the data.

Nitrate and Si(OH)$_4$ inventories were significantly lower during the bloom and postbloom phases than during the prebloom, reflecting net phytoplankton consumption (Table 2). Silicic acid drawdown in the Amundsen Gulf stations east of 128.35°W was most pronounced in the postbloom period after the majority of the NO$_3^-$ had been consumed. Seasonal changes in PO$_4^{3-}$ inventory were not apparent. Ammonium concentration declined during the bloom and then rose steadily from the spring to fall periods. Nitrite concentration varied greatly, increasing threefold from low prebloom levels to the end of the study. Significant changes were observed in DON concentrations east of 128.35°W and in DOP concentrations west of 128.35°W. Elsewhere in the study area, average concentrations of DON and DOP were generally higher during the period of active algal growth than during the prebloom and autumnal phases. There was no variation in urea concentration at this coarse level of analysis.

3.3. Regional Variation in Nutrient Concentration

Regional differences in nutrient content were apparent in vertical profiles obtained during leg 8/9 when the spring phytoplankton growth had subsided (Figure 3). Depth-averaged vertical profiles showed that the waters overlying the Amundsen Gulf were depleted in NO$_3^-$ to approximately 25 m depth, whereas PO$_4^{3-}$ and Si(OH)$_4$ concentrations were detectable. Surface NO$_3^-$ concentrations were higher and more variable in the Mackenzie Shelf region than in the Gulf and the nitracline was shallower. These differences were likely due to the input of NO$_3^-$ from the Mackenzie River and high turbidity that restricted phytoplankton growth to near the sea surface. Silicic acid was also influenced by input from the river and was greatest during the time when freshwater discharge was at or near its maximum. The low PO$_4^{3-}$ content of the river water was also evident by comparing the differences in the profiles in the upper 20 m (Figure 3). Below the nutrient maxima, the Amundsen Gulf samples were more enriched in NO$_3^-$, PO$_4^{3-}$ and Si(OH)$_4$ than those from the Beaufort Sea and deep Mackenzie Shelf stations by roughly 1.7 $\mu$mol L$^{-1}$, 0.12 $\mu$mol L$^{-1}$, and 6.2 $\mu$mol L$^{-1}$, respectively.

3.4. Regenerated N and DON

The concentrations of NH$_4^+$ and urea were generally higher in the surface waters than at depth (Figure 4). Most samples contained less than 0.5 $\mu$mol NH$_4^+$-N L$^{-1}$ and less than 1 $\mu$mol urea-N L$^{-1}$. Average concentrations were 0.38 and 0.94 $\mu$mol N L$^{-1}$, respectively. Urea concentration was the most variable, ranging from undetectable to 9.6 $\mu$mol N L$^{-1}$. High concentrations of NH$_4^+$ were also present between 50 and 125 m depth and urea was at times...
abundant at all depths except in the most saline, deep water. The NH$_4^+$ concentration-salinity plot showed a significant decrease in NH$_4^+$ concentration as salinity increased from 22 to 28 (p = 0.0182).

Dissolved organic nitrogen concentration was largely independent of salinity although it decreased significantly from salinity 22 to 28 (p = 0.0029), as observed for NH$_4^+$. Because urea was detected as part of the DON pool during analysis, we subtracted its concentration from the total to see if it influenced the DON-salinity relationship. The resulting plot differed little from that shown in Figure 5, although the decrease in DON concentration as salinity increased from 22 to 28 was more striking. As reported below, urea concentration was proportional to the DON concentration. At salinities less than 22, DON concentrations remained constant at about 5 $\mu$mol L$^{-1}$, suggesting a substantial contribution by the Mackenzie River. This contribution was confirmed by measurements.

<table>
<thead>
<tr>
<th>Region</th>
<th>Nutrient</th>
<th>Concentration ($\mu$mol L$^{-1}$)</th>
<th>Depth (m)</th>
<th>Salinity</th>
<th>Sigma-T ($\sigma_t$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gulf</td>
<td>NO$_3^-$</td>
<td>17.3</td>
<td>197.8</td>
<td>34.21</td>
<td>27.49</td>
</tr>
<tr>
<td>Shelf</td>
<td>NO$_3^-$</td>
<td>17.3</td>
<td>152.5</td>
<td>33.23</td>
<td>26.73</td>
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<tr>
<td>Gulf</td>
<td>PO$_4^-$</td>
<td>1.9</td>
<td>131.2</td>
<td>33.08</td>
<td>26.61</td>
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<td>PO$_4^-$</td>
<td>1.8</td>
<td>133.3</td>
<td>33.04</td>
<td>26.56</td>
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<tr>
<td>Gulf</td>
<td>Si(OH)$_4$</td>
<td>33.5</td>
<td>146.5</td>
<td>33.12</td>
<td>26.68</td>
</tr>
<tr>
<td>Shelf</td>
<td>Si(OH)$_4$</td>
<td>36.8</td>
<td>151.1</td>
<td>33.10</td>
<td>26.60</td>
</tr>
</tbody>
</table>

Table 2. Water Density, Salinity, and Concentrations of Nitrate, Phosphate, and Silicic Acid in the Nutrient Maxima of the Beaufort Sea/Mackenzie Shelf and the Amundsen Gulf Region

<table>
<thead>
<tr>
<th>Region</th>
<th>Nutrient</th>
<th>Concentration ($\mu$mol L$^{-1}$)</th>
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Table 2. Average Integrated Nutrient Concentration ± Standard Deviation of Surface Waters With Salinity 31.6 or Less

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<tbody>
<tr>
<td>NO$_3^-$ E</td>
<td>108.6 ± 20.4 a</td>
<td>44.9 ± 20.5 b</td>
<td>31.9 ± 17.8 b</td>
<td>39.9 ± 19.6 b</td>
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<tr>
<td>NO$_3^-$ W</td>
<td>48.1 ± 35.5</td>
<td>54.7 ± 30.8</td>
<td>70.4 ± 31.1</td>
<td>73.6 ± 39.9</td>
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<td>NO$_3^-$ W *</td>
<td>28.7 ± 40.9</td>
<td>3.4 ± 1.0 a</td>
<td>3.7 ± 1.0 a</td>
<td>5.6 ± 1.18 c</td>
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<tr>
<td>PO$_4^-$ E</td>
<td>1.8 ± 0.5 a</td>
<td>2.5 ± 1.4 a</td>
<td>3.5 ± 1.0 a</td>
<td>6.0 ± 2.7 b</td>
</tr>
<tr>
<td>PO$_4^-$ W</td>
<td>1.8 ± 1.5 a</td>
<td>3.7 ± 1.2 a</td>
<td>4.9 ± 2.1 b</td>
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</tr>
<tr>
<td>PO$_4^-$ W *</td>
<td>28.5 ± 4.3</td>
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<td>28.3 ± 7.0</td>
<td>28.2 ± 6.6</td>
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<tr>
<td>Si(OH)$_4$ E</td>
<td>321.3 ± 51.2 a</td>
<td>251.7 ± 79.4 a</td>
<td>179.2 ± 46.1 b</td>
<td>172.0 ± 78.5 b</td>
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<tr>
<td>Si(OH)$_4$ W</td>
<td>163.4 ± 97.9 a</td>
<td>252.8 ± 115.4 ab</td>
<td>299.5 ± 109.7 b</td>
<td>295.2 ± 90.9</td>
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<tr>
<td>NH$_4^+$ E</td>
<td>18.1 ± 11.7 a</td>
<td>4.3 ± 2.7 b</td>
<td>7.4 ± 3.7 b</td>
<td>14.6 ± 5.1 a</td>
</tr>
<tr>
<td>NH$_4^+$ W</td>
<td>2.7 ± 1.8 a</td>
<td>12.4 ± 5.5 ab</td>
<td>16.8 ± 11.9 b</td>
<td></td>
</tr>
<tr>
<td>NH$_4^+$ W *</td>
<td>3.0 ± 2.6 #</td>
<td>11.7 ± 2.3</td>
<td>20.7 ± 13.0</td>
<td></td>
</tr>
<tr>
<td>TDN E</td>
<td>182.7 ± 8.1 #</td>
<td>240.2 ± 55.6</td>
<td>241.3 ± 83.1</td>
<td>187.7 ± 84.5</td>
</tr>
<tr>
<td>TDN W</td>
<td>251.2 ± 75.0</td>
<td>260.9 ± 77.9</td>
<td>252.3 ± 90.5</td>
<td>230.3 ± 88.7</td>
</tr>
<tr>
<td>DON E</td>
<td>117.2 ± 10.4 ab#</td>
<td>201.1 ± 42.8 a</td>
<td>200.8 ± 66.6 a</td>
<td>102.4 ± 32.7 b</td>
</tr>
<tr>
<td>DON W</td>
<td>216.4 ± 50.4</td>
<td>195.8 ± 30.7</td>
<td>213.9 ± 96.4</td>
<td>157.7 ± 74.1</td>
</tr>
<tr>
<td>DON W *</td>
<td>201.8 ± 32.4</td>
<td>201.8 ± 59.4</td>
<td>201.8 ± 59.4</td>
<td>201.8 ± 59.4</td>
</tr>
<tr>
<td>TDP E</td>
<td>26.2 ± 0.2 #</td>
<td>43.6 ± 18.5</td>
<td>46.2 ± 11.2</td>
<td>31.2 ± 6.6</td>
</tr>
<tr>
<td>TDP W</td>
<td>56.9 ± 17.7 a</td>
<td>59.2 ± 19.7 a</td>
<td>59.2 ± 19.7 a</td>
<td>29.0 ± 11.1 b</td>
</tr>
<tr>
<td>TDP W *</td>
<td>39.9 ± 31.1</td>
<td>57.5 ± 22.6</td>
<td>25.7 ± 8.6</td>
<td></td>
</tr>
<tr>
<td>DOP E</td>
<td>7.5 ± 0.2 #</td>
<td>18.6 ± 6.7</td>
<td>18.9 ± 6.7</td>
<td>11.3 ± 6.8</td>
</tr>
<tr>
<td>DOP W</td>
<td>23.0 ± 7.7 a</td>
<td>24.4 ± 13.8 a</td>
<td>9.1 ± 5.2 b</td>
<td></td>
</tr>
<tr>
<td>DOP W *</td>
<td>17.1 ± 15.3</td>
<td>20.0 ± 9.0</td>
<td>8.0 ± 4.6</td>
<td></td>
</tr>
<tr>
<td>Urea-N E</td>
<td>25.7 ± 13.5 #</td>
<td>23.6 ± 13.7</td>
<td>21.9 ± 17.9</td>
<td>15.0 ± 10.5</td>
</tr>
<tr>
<td>Urea-N W</td>
<td>48.8 ± 24.0</td>
<td>26.0 ± 15.1</td>
<td>52.8 ± 33.4</td>
<td>35.1 ± 24.5</td>
</tr>
</tbody>
</table>

Table 2. Average Integrated Nutrient Concentration ± Standard Deviation of Surface Waters With Salinity 31.6 or Less

- Units are mmol m$^{-2}$. Data obtained during the study were pooled according to time of collection relative to the spring bloom (see text for details).
- Asterisk indicates nutrient inventory of stations with bottom depth of >250 m (Beaufort Sea stations removed). Different letters (a, b, c) indicate significant differences (ANOVA and Tukey p ≤ 0.05).
- Pound sign (#) indicates samples are limited, n = 2. Subscripts E and W denote the sampling location: E, east of 128.35°W (Amundsen Gulf); W, west of 128.35°W (Beaufort Sea/Mackenzie Shelf).
taken near the eastern and western outflows, which contained 2–4 and 5–10 μmol DON – N L⁻¹, respectively. Dissolved organic nitrogen concentrations were variable but generally highest in surface waters and lower at depth. Concentrations ranged from 0.2 – 35.8 μmol DON – N L⁻¹, and averaged 4.6 ± 3.7 μmol DON – N L⁻¹. The highest values (>10 μmol DON – N L⁻¹) were found at the shelf sites and within the Amundsen Gulf. Waters deeper than 200 m contained 3.6 ± 2.64 μmol DON – N L⁻¹.

3.5. DOP Concentrations

Vertical profiles of DOP concentration showed a pronounced middepth enrichment at around 150–200 m that was absent in the DON plot (Figure 5). The high DOP concentrations (averaging 0.76 ± 0.27 μmol DOP-P L⁻¹) were associated with waters of salinity ca. 33.1 and were roughly twofold greater than average surface levels. Below the DOP maximum, concentrations declined to 0.65 μmol DOP-P L⁻¹. Mixing lines between Bering Sea water and deep Atlantic-derived water, and between Bering Sea water and Arctic surface water were evident, but the data showed considerable scatter (Figure 5b, inset).

High variability in the low salinity samples made it difficult to accurately estimate the river contribution of DOP; however, regression analysis yielded an intercept at zero salinity of 0.1 m mol DOP-P L⁻¹. This concentration was higher than we measured in the Mackenzie River, but consistent with values observed from the Mackenzie Delta at salinity 15–25 [Emmerton, 2006]. Dissolved organic phosphorus concentration ranged from detection limit to 2.3 μmol L⁻¹ and averaged 0.65 ± 0.38 μmol P L⁻¹.

3.6. Water Mass Distribution of DOP

We evaluated the contribution of the Bering water to the subsurface DOP enrichment by examining the relationship between DOP concentration and N* in samples of 30–33.1 salinity. Modified Bering Sea water contributes to the upper halocline in the Arctic Ocean and is characterized by a highly negative N* [Codispoti et al., 1991] that can be used to trace its flow. A highly significant relationship (p < 0.0001) existed between DOP concentration and N* (Figure 6). The concentration of DOP was highest in the most NO₃⁻-depleted (most negative N*) seawater samples and lowest in the least NO₃⁻-depleted (least negative N*) samples. Thus, Bering-derived water was more enriched in DOP than either Arctic or deep Atlantic water (Figure 6). The DON:DOP ratio also decreased with decreasing N*, as expected from the DOP – N* relationship and the apparent constancy of DON concentration with depth (Figure 6). In water of salinities between 33.1 and 34, DOP and DON concentrations did not change and were independent of N* (data not shown).

3.7. Vertical Profiles of DON and DOP

Depth-averaged vertical profiles of urea and DON were similar during all seasons (Figure 7). In these plots, the DON concentration has been corrected to remove the contribution of urea. As illustrated in Figures 4 and 5, both N-containing compounds were abundant in the surface waters and then declined with depth. Vertical profiles of the average values showed a remarkable correspondence.
between both nitrogen forms and revealed some subsurface maxima, notably at 50 m and between 250 and 300 m depth in the Beaufort Sea/Mackenzie Shelf and the Amundsen Gulf (Figure 7). Regression analysis of urea-N against DON showed a highly significant correlation (p < 0.0001) and a slope of 0.31 mol urea/C0_N: mol DON/C0_N.

Total dissolved nitrogen to total dissolved phosphorus ratio (TDN:TDP) increased from near 5 in surface waters to 10 at 400 m depth (Figure 8). The low surface value was consistent with a shallower concentration maximum of PO4^3- than of NO3^- and limited vertical mixing during fall and winter. Surface water variability was attributed to regional differences in nutrient inventories and to seasonal drawdown by phytoplankton that reduced DIN concentration to zero. The DON:DOP ratio ranged from 2 to 200 in surface waters and averaged 4.9:1 at depth. In surface waters (0–50 m), linear regression analysis of DON on DOP concentration showed a highly significant relationship (p < 0.001) and a DON:DOP production/utilization ratio of ~17.1, r^2 = 0.38 (data not shown). No discernable trend between DON and DOP concentrations was found in waters deeper than 50 m (but see Figure 6). Nitrate:phosphate ratios were typically low in the surface layer, between 0 and 8, gradually increased to ~15 at 300 m, and remained relatively constant below this depth.

3.8. Nutrient Consumption and Regeneration

Nutrient-nutrient concentration plots were used to infer consumption and regeneration ratios of the inorganic nutrients. Samples were pooled according to depth strata chosen on the basis of their temperature-salinity characteristics to correspond to different water masses (Figure 9). Ratios (mol mol^-1) determined from the slopes of regression analysis (model 2) were significantly different from one another (ANCOVA, p < 0.001). In surface waters (0–50 m), NO3^- and PO4^3-, and Si(OH)4 and NO3^- were consumed in the following proportions: 13.3 NO3^-:1 PO4^3-, r^2 = 0.78 and 1.75 Si(OH)4:1 NO3-, r^2 = 0.87, while samples from depths of 50 to 125 m had ratios of 15.7:1, r^2 = 0.49, and 2.11:1, r^2 = 0.82, respectively. In the deep water, below 275 m, the NO3^-:PO4^3- ratio was ~7.6:1, r^2 = 0.33 and the Si(OH)4:NO3^- ratio was 4.6:1, r^2 = 0.60.
Remineralization ratios derived from regression analyses of nutrient and oxygen concentrations reveal two significantly distinct relationships (Figure 10). The relatively shallow Pacific-derived water mass (25–200 m) had NO\textsubscript{3} and PO\textsubscript{4}\textsuperscript{3-} remineralization ratios of 9.0 and 122.5, respectively. Deeper waters (\geq 275 m) had higher ratios (NO\textsubscript{3} and PO\textsubscript{4}\textsuperscript{3-} ratios were 17.4 and 193.5, respectively) indicating that more oxygen was utilized per mol of nutrient regenerated (Figure 10).

4. Discussion

4.1. Salinity-Nutrient Distributions

The salinity-nutrient relationships reported here follow well established patterns described elsewhere in the Canadian Basin and Beaufort Sea [Jones and Anderson, 1986; Macdonald et al., 1987; Moore et al., 1992; McLaughlin et al., 1996; Codispoti et al., 2005; Wang et al., 2006]. They show nutrient maxima in the upper halocline that was composed of water derived from the Pacific Ocean. Phosphate concentration peaked at salinity 33.04–33.08 at roughly 130 m depth, shallower than the NO\textsubscript{3} and Si(OH)\textsubscript{4} maxima (Table 1). In the Amundsen Gulf, the NO\textsubscript{3} maximum occurred in deeper more saline water than in the Mackenzie Shelf and Beaufort Sea. As described below, we believe this feature was created by remineralization of diatom production exported from the overlying polynya.

A number of mixing lines between the different water masses were clearly evident. Of particular note was the transition between the upper and lower halocline, which showed a sharp decline in Si(OH)\textsubscript{4} and PO\textsubscript{4}\textsuperscript{3-} concentrations, but not in NO\textsubscript{3}, as salinity increased. On the basis of the NO\textsubscript{3}:PO\textsubscript{4}\textsuperscript{3-} and NO\textsubscript{3}:Si(OH)\textsubscript{4} ratios of these two water masses it appears that the upper halocline has lost NO\textsubscript{3} through denitrification [Lehmann et al., 2005] so that it now contains roughly the same concentration of NO\textsubscript{3} as the lower halocline.

The surface layer near the Mackenzie Shelf showed strong evidence of Si(OH)\textsubscript{4} input from the Mackenzie River but little input of NO\textsubscript{3}. Salinity plots demonstrated a
significant decrease in NH$_4^+$ concentration during the transition from river-influenced sites to full seawater between salinity 22 to 28. A decrease in concentration of DON was also observed over the same salinity range (Figure 5). Both trends suggest the presence of a frontal zone where changes in resource availability may cause the phytoplankton community to shift from phosphorus (or light) to nitrogen limitation. Phosphate limitation is widespread in freshwater ecosystems and within estuaries gradually gives way to nitrogen limitation, which is typical of marine systems [Yin et al., 2001]. We observed that surface waters of the Mackenzie Shelf contained higher concentrations of NO$_3^-$ than the Amundsen Gulf following the phytoplankton bloom. As N became more limiting to phytoplankton growth in this transitional zone the concentrations of NH$_4^+$ and DON would be expected to decline as NO$_3^-$ became less available seaward. Similar salinity-nutrient gradients have been noted for other Arctic river systems [Cauwet and Sidorov, 1996] and to co-occur with dramatic changes in the plankton community [Garneau et al., 2006; Parsons et al., 1988, 1989].

Figure 6. (a) Dissolved organic phosphorus (DOP) concentration and (b) the ratio of dissolved organic nitrogen to dissolved organic phosphorus (DON/DOP) concentrations regressed against N* in samples of salinity between 30 and 33.1. The equations of the linear regressions (model I) were (Figure 6a) DOP = $-0.097 \times N^* - 0.15 r^2 = 0.16, p < 0.0001$ and (Figure 6b) DON/DOP = $1.39 \times N^* + 19.43 r^2 = 0.17 p < 0.0001$.

Figure 7. Depth-averaged nutrient concentrations and standard deviations of dissolved organic nitrogen (DON) and urea for (a) the Beaufort Sea/Mackenzie Shelf derived from 37 vertical profiles (below 600 m, n = 3) and (b) the Amundsen Gulf region derived from 55 vertical profiles. Regression analysis (model I) of DON concentration versus urea concentration (c) shows a strong positive relationship: urea = $0.31 \times [DON-urea] - 0.337, r^2 = 0.65 p < 0.0001$. An outlier (labeled with an asterisk) was identified by Systat and not included in the regression analysis.
4.2. Urea and DON

Dissolved organic nitrogen concentration averaged about 5 \( \mu \text{mol N L}^{-1} \) throughout the study area, similar to values measured elsewhere in the Arctic [Wheeler et al., 1997]. We observed much greater variability in DON concentration than the earlier measurements, likely because of the proximity of our stations to the river outflow, which is expected to be a significant source of organic nitrogen to the nearshore. Indeed, in other Arctic rivers DON concentration averages 27.0 \( \pm \) 5.0 \( \mu \text{mol N L}^{-1} \) [Cauwet and Sidorov, 1996; Gordeev et al., 1996] and is considerably higher than the typical 3–4 \( \mu \text{mol N L}^{-1} \) that prevails in the deep ocean [Berman and Bronk, 2003].

High and variable concentration of urea reported here is common in Arctic regions [Harrison et al., 1985; but see Codispoti et al., 2005]. Concentrations are known to range from undetectable to 13.0 \( \mu \text{mol N L}^{-1} \) and often to exceed those of \( \text{NH}_4^+ \). Zooplankton excretion is thought to be a major source of urea to marine environments and is dependent on food quality [Bidigare, 1983]. In the Arctic, urea has been hypothesized to replace \( \text{NH}_4^+ \) as a waste byproduct possibly because it is less toxic than \( \text{NH}_4^+ \) to producing organisms that reside in confined habitats within sea ice [Conover et al., 1999]. Microbial oxidation of DON is also known to contribute urea to the environment [Antia et al., 1991; Berman et al., 1999; Conover and Gustavson, 1999; Conover et al., 1999; Berg and Jørgensen, 2006].

Our observations point to a close association between DON and urea (Figure 7) and suggest that these compounds

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**Figure 8.** Molar ratios of (a) total dissolved nitrogen and phosphorus (TDN/TDP), (b) dissolved organic nitrogen and phosphorus (DON/DOP), and (c) nitrate and phosphate (\( \text{NO}_3^-/\text{PO}_4^{3-} \)) plotted as a function of depth.

**Figure 9.** Nutrient-nutrient concentration relationships delineated by depth: (a) phosphate against nitrate and (b) silicic acid against nitrate. Color coding indicates depth strata: green, 0–50 m; yellow, 50–125 m; red, 125–200 m; gray, 200–275 m; and blue, 275+ m. Samples with low \( \text{NO}_3^- \) or low \( \text{PO}_4^{3-} \) concentrations (<1.5 \( \mu \text{mol N L}^{-1} \) and <0.5 \( \mu \text{mol P L}^{-1} \)) were excluded from analysis as were samples with anomalous salinity signatures for the depth of collection. Lines drawn through the data represent model II geometric mean regressions: solid line, 0–50 m; dashed line, 50–125 m; dotted line, 275+ m.
DOP concentrations were comparable to those of PO$_4^{3-}$ and within the range reported for other ocean regions [Karl and Björkman, 2002], including the Mackenzie River Delta [Emmerton, 2006]. Analysis of water from the lower reaches of the Lena River showed summer values of 1.2–1.3 µmol DOP L$^{-1}$ and roughly 0.2 µmol DOP L$^{-1}$ within parts of the Laptev Sea (chlorinity < 20) [Cauwet and Sidorov, 1996]. The relationship between DOP and salinity showed features similar to those seen with PO$_4^{3-}$, particularly over the salinity range of 26–32 where the average concentration of both increased (p < 0.01). As argued above, this increase in DOP concentration could reflect the transition from phosphorus (or light) limited primary production in the river-affected sites to nitrogen-limited primary production in the marine-dominated sites off the shelf.

The maximum DOP concentration in the upper halocline suggests that Pacific-derived waters may be a source of the enrichment. Indeed, inverse correlation (p < 0.0001) between DOP and N* provides some support for this hypothesis, because low N* is a signature of Bering-derived water. The large amount of scatter in the relationship may be caused by local processes that modify the DOP concentration and N* signature of the water as it moves from the Bering Sea to the Amundsen Gulf. Supply and decomposition of particulate matter could vary regionally which would add DOP and DON to the Bering water thereby modifying its composition. Mixing with water above and below would also erode the N* signature.

The question that naturally arises is how this water may have acquired a high DOP concentration? One possible answer is by phytoplankton production and release during nutrient-limited growth. Phytoplankton in the Bering Sea and over Arctic shelves are known to be limited by iron [Peers et al., 2005] and nitrogen [Codispoti et al., 2005; Tremblay et al., 2006] and may take up and assimilate excess amounts of nonlimiting resources including PO$_4^{3-}$. Organic phosphorus may thus accumulate intracellularly and be released either directly or indirectly by grazing and decomposition. Dissolved organic nitrogen would not be expected to be produced in Redfield proportions by Fe or N-limited phytoplankton, consistent with the low DON/DOP ratio in the water of the 33.1 salinity layer (Figure 6). Regeneration of DOP from sinking particulate matter could also produce the DOP enrichment.

4.4. Seasonal Cycle of Nutrients

Measurements of the prebloom integrated nutrient concentrations were confined to the eastern portion of the study site where the ship overwintered (70°02.74' N 126°18.08' W). These measurements are likely representative of the entire study area, judging from the constancy of calculated NO and PO tracers [Broecker, 1974] (data not shown) integrated over the upper 50 m in the Amundsen Gulf and Mackenzie Shelf/Beaufort Sea region. The prebloom nutrient inventories measured by Macdonald on the Mackenzie Shelf [Macdonald et al., 1987] were higher than we report, but they likely included measurements of high nutrient concentrations in the nitracline, which were not always included in our analysis. Recharging of the surface nutrient inventory was limited by the strength of the halocline and the rapid onset of ice that minimized wind

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**Figure 10.** Oxygen-nutrient concentration relationships delineated by depth: (a) oxygen against nitrate; (b) oxygen against phosphate. Color coding indicates depth strata: green, 0–50 m; yellow, 50–125 m; red, 125–200 m; gray, 200–275 m; and blue, 275+ m. Lines drawn though the data represent model II, geometric mean regressions. Shallow samples (0–50 m) were excluded from regression analysis. The slopes of the regression in shallow waters (solid lines) are $-O_2/N_0^- = 9.0$ and $-O_2/PO_4^{3-} = 122.5$. In deep water (dashed lines), the slopes are $-O_2/N_0^- = 17.4$ and $-O_2/PO_4^{3-} = 193.5$. 

4.3. Dissolved Organic Phosphorus

The DOP concentrations reported here are the first determined for the Arctic Ocean. In the near surface, values were variable, ranging from undetectable to 2.3 µmol DOP-P L$^{-1}$, and highest at the river-affected sites. Gener-
mixing. The resulting surface values (0–15 m) of NO$_3^-$ reached a maximum of 3.3 $\mu$mol L$^{-1}$ [Tremblay et al., 2008] roughly 1/5th of the deepwater concentration.

[45] The concentrations of NO$_3^-$ and Si(OH)$_4$ decreased significantly following ice breakup and the onset of phytoplankton growth. Phosphate concentrations did not vary, likely because dissolved values were well above those required to sustain the biomass of phytoplankton produced. At both the western and eastern sites, approximately 1/2 of the NO$_3^-$ was consumed and its concentration increased (at least in the west) as autumnal mixing ensued. The decline in Si(OH)$_4$ concentration appeared to be more rapid in the western side, and like NO$_3^-$, its inventory rose in the fall. Large increases in water column NO$_3^-$ from the prebloom to the autumnal phases were consistent at all sites. The appearance of NO$_3^-$ was correlated with the drawdown of NO$_3^-$ in the surface (Simpson et al., manuscript in preparation, 2008) and was most pronounced at the depth of the nitracline. Since NO$_3^-$ uptake and assimilation by phytoplankton were fastest at this depth, we believe that the NO$_3^-$ was produced as a byproduct of assimilatory NO$_3^-$ reduction.

[46] A similar mass balance of phosphorus cannot be obtained from our data. We calculate that approximately 4.8 ± 1.9 mmol P m$^{-2}$ would be consumed by phytoplankton during the bloom on the basis of the decrease in integrated NO$_3^-$ concentration and the NO$_3^-$:PO$_4^{3-}$ consumption ratio. This decrease in PO$_4^{3-}$ concentration is too small for us to detect given the error in our seasonal measurements (Table 2). The measured increase in DOP concentration, however, shows some seasonality, particularly in the west where values were significantly greater during the spring and summer than in the fall. A similar trend is evident in the eastern sites as well; that is, the mean values are greater during the active phytoplankton growth phase than before and after. A rough calculation shows a seasonal change in DOP of about 10 mmol P m$^{-2}$ throughout the region. Although subsurface waters contain higher DOP concentrations, they are unlikely to contribute to the seasonal surface enrichment because surface concentrations are the lowest during the fall when mixing is greatest. At present, we are unable to adequately explain this seasonal increase in DOP.

4.5. Nutrient Consumption Ratios

[47] Nitrate and PO$_4^{3-}$ drawdown was 13.3:1 mol mol$^{-1}$ in surface waters (upper 50 m) and lower than Redfield stoichiometry, as reported in other Arctic regions influenced by Pacific-derived water [Jones et al., 1998; Codispoti et al., 2005]. A model 2 (geometric mean) regression of PO$_4^{3-}$ on NO$_3^-$ concentration yielded a positive PO$_4^{3-}$ intercept (0.69 $\mu$mol L$^{-1}$). Surface Si(OH)$_4$ concentration also declined linearly with NO$_3^-$, and roughly 3.8 $\mu$mol L$^{-1}$ remained when the entire NO$_3^-$ reservoir had been exhausted. Thus, NO$_3^-$ was the biomass-limiting nutrient, consistent with the observations from the vertical profiles obtained during leg 8/9 that showed complete consumption of NO$_3^-$ in the surface layer (Figure 8).

[48] The decrease in Si(OH)$_4$ concentration during the bloom phase suggests that diatoms made up a portion of the phytoplankton community. The slope of the sea-surface Si(OH)$_4$ to NO$_3^-$ regression, the utilization ratio, was 1.75 mol Si:1 mol N (Figure 9) within the range of values seen in pure diatom cultures (range 0.28–4.38; mean 0.95 ± 0.23) [Brzezinski, 1985] and roughly twice that observed in North Water Polynya [Tremblay et al., 2002]. Diatoms are well known to be important producers in Arctic habitats [Booth and Horner, 1997; Lovejoy et al., 2002] that dominate ice and pelagic environments during bloom phases. They are a major export flux to the ocean interior in other Arctic polynyas settling as intact cells, empty frustules, resting spores and in the feces of zooplankton [Michel et al., 2002].

4.6. Excess Nutrients in the Amundsen Gulf

[49] Deep waters of the Amundsen Gulf bear the signature of diatom export production. Elevated nutrient concentrations are found in this region compared to source waters in the southern Beaufort Sea (Figure 3) and along the western side of Banks Island [McLaughlin et al., 2004] and are most pronounced for Si(OH)$_4$. The integrated difference ($\int_{(200–500m)}^{(200–500m)}$ [Amundsen gulf] $-$ $\int_{(200–500m)}^{(200–500m)}$ [Beaufort Sea]) in nutrient inventories shows that NO$_3^-$ is enriched by 512.02 ± 8.65 mmol m$^{-2}$, PO$_4^{3-}$ by 35.24 ±
19.66 mmol m$^{-2}$, and Si(OH)$_4$ by 1865.72 ± 254.15 mmol m$^{-2}$. The ratios of the excess nutrient inventories vary like the surface drawdown ratios for NO$_3$ and PO$_4^{3-}$ (14.5 mols:1 mol), but are twofold higher for Si(OH)$_4$ and NO$_3$ (3.6 mols:1 mol). They are consistent with enhanced export of primary production in the Amundsen Gulf and its subsequent remineralization at depth. We note that the higher Si:N ratio in the deep than in the near surface waters implies shallower regeneration of N, an observation made previously in the North Water Polynya by Michel et al. [2002]. Sediment trap collections at the North Water site contained particulates with Si:N ratios of 4.6:1, similar to the deepwater enrichment described here and to the remineralization ratios calculated from the slope of the dissolved nutrients in this layer (4.6:1) (Figure 9). Although we have limited measurements, our data set also shows that some of the Si(OH)$_4$ remineralization occurs in or near the sediments as the Si(OH)$_4$ concentration is consistently highest in the deepest samples.

[50] Oxygen concentrations in the Amundsen Gulf also differed as expected if there has been more remineralization: they were depleted relative to the Beaufort Sea by 7664 ± 830 mmol O$_2$ m$^{-2}$. The deep nutrient excess suggests that the Cape Bathurst Polynya, like the North Water Polynya, may preferentially export Si(OH)$_4$ to depth [Tremblay et al., 2002]. The nutrient excess can also be expressed in terms of C, assuming its assimilation in surface waters followed the C:N ratio of 6.6 – 8.9 [Redfield et al., 1963; Daly et al., 1999]. Although the timescale of deepwater replacement is unknown and so a rate of export cannot be derived, the NO$_3$ enrichment is equivalent to 40–50 g C m$^{-2}$, roughly the amount of annual new production in the overlying polynya (Simpson et al., manuscript in preparation, 2008).

4.7. Remineralization Ratios

[51] The stoichiometry of remineralization deduced from balancing the equation of organic matter production using traditional Redfield ratios shows a C$_{org}$/N/P = O$_2$ of 106/16/1/138 (–O$_2$/N = –39) [Anderson and Sarmiento, 1994]. The equation is thought to generally represent organic matter decomposition in the world ocean although recent analyses document its latitudinal variations [Li and Peng, 2002] and suggested changes with depth [Boulahdid and Minster, 1989; Shaffer et al., 1999]. Analysis of our data shows that organic matter is remineralized as predicted with –O$_2$/N and –O$_2$/P 0.9 and 122.5, respectively. The slightly lower than expected –O$_2$/P ratio in our data set (depth 50 – 200 m) suggests a shallower PO$_4^{3-}$ maximum and preferential remineralization of phosphorus compared to NO$_3$, as observed (Figure 3 and Table 1). At depth (250 m), the –O$_2$/N and –O$_2$/P ratios increased remarkably to 17.4 and 193.5. We are less confident in the accuracy of these ratios, however, because they were derived from a smaller data set than the shallow samples and the type-2 regression explained less of the variation [r$^2$ = 0.44 (–O$_2$/N) and r$^2$ = 0.74 (–O$_2$/P)].

[52] An alternative approach to calculate the deepwater remineralization is to use the integrated O$_2$ deficit and the nutrient excess in the Amundsen Gulf deep waters. The –O$_2$/P and –O$_2$/N ratios obtained in this way (217.5 ± 123.6 and 15.0 ± 1.64) are roughly equal to the ratios calculated from the oxygen-nutrient regressions suggesting that the high values are correct. They may reflect an unusual composition of the sinking POM, possibly caused by the high lipid content [Smith et al., 1997] or C:N ratio [Daly et al., 1999] of Arctic phytoplankton.

5. Conclusions

[53] Salinity-nutrient relationships showed NO$_3^-$, PO$_4^{3-}$ and Si(OH)$_4$ maxima in the upper halocline layer at salinity ca. 33.1 throughout the CASES study area. Concentrations of all nutrients were most variable in the surface layer, reflecting the seasonal drawdown by phytoplankton and discharge from the Mackenzie River. Over the salinity range of 22 – 28, ammonium and DON concentrations decreased significantly possibly indicating a transitional zone where phytoplankton became progressively more N-limited. Dissolved organic phosphorus and phosphate concentrations in surface waters increased over a slightly higher salinity gradient (26 – 32).

[54] Seasonal drawdown of NO$_3^-$ and Si(OH)$_4$ concentrations were detected on the Mackenzie Shelf and in the Amundsen Gulf and coincided with the onset of phytoplankton growth. Ammonium concentration also declined during the phytoplankton bloom and then increased during the remainder of the year. The decrease in NO$_3^-$ and NH$_4^+$ concentrations was accompanied by a roughly equivalent increase in DON concentration. Water column integrated DOP concentration was also higher during the bloom and postbloom periods compared to the early spring and fall.

[55] Dissolved organic phosphorus concentration showed a middepth enrichment in upper halocline waters of salinity 33.1. Within this layer the concentration of DOP was inversely correlated with N*, suggesting that water originating from the Bering Sea may be an important source of DOP to the Arctic.

[56] In surface waters, nutrients were consumed in near Redfield proportions with N:P = 13.1:1 and Si:N = 1.75:1 indicative of diatom diatom growth. Urea concentrations were typically high and covaried with the concentration of DON, suggesting a common source or that urea was derived from the breakdown of the DON pool.

[57] Vertical profiles of nutrients showed regional variability. Higher concentrations of NO$_3^-$, PO$_4^{3-}$ and Si(OH)$_4$ (and lower concentration of O$_2$) were present in deep water of the Amundsen Gulf compared to waters of similar depth in the Beaufort Sea. Our analysis suggests that the residence time of waters in the Amundsen Gulf is sufficiently long to allow the accumulation of nutrients derived from remineralization of exported diatom material. Regeneration ratios appeared to vary with depth and were approximately 9 mol –O$_2$/mol NO$_3$ and 122.5 mol –O$_2$/mol PO$_4^{3-}$ in shallow Pacific-derived waters (halocline layer) and 17.4 and 193.5 in deep Atlantic waters (Atlantic layer), respectively.

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