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Discussions

Impact of river discharge, upwelling and vertical mixing on the nutrient loading and productivity of the Canadian Beaufort Shelf

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Abstract

The concentrations and elemental stoichiometry of particulate and dissolved pools of carbon (C), nitrogen (N), phosphorus (P) and silicon (Si) in the southeast Beaufort Sea during summer 2009 were assessed and compared with those of surface waters
5 provided by the Mackenzie river as well as by winter mixing and upwelling of upper halocline waters at the shelf break. Neritic surface waters showed a clear enrichment in dissolved and particulate organic carbon (DOC and POC, respectively), nitrate, total particulate nitrogen (TPN) and dissolved organic nitrogen (DON) originating from the river. Silicate as well as bulk DON and DOC declined in a conservative manner
10 away from the delta's outlet, whereas nitrate dropped non-conservatively to very low background concentrations inside the brackish zone. By contrast, the excess of soluble reactive P (SRP) present in oceanic waters declined in a non-conservative manner toward the river outlet, where concentrations were very low and consistent with P shortage in the Mackenzie River. These opposite gradients imply that the admixture of
15 Pacific-derived, SRP-rich water is necessary to allow phytoplankton to use river-derived nitrate and to a lesser extent DON. A coarse budget based on concurrent estimates of primary production shows that river N deliveries support a small fraction of primary production when considering the entire shelf, due to the ability of phytoplankton to thrive in the subsurface chlorophyll maximum beneath the thin, nitrate-depleted river plume.
20 Away from shallow coastal bays, local elevations in the concentration of primary production and dissolved organic constituents were consistent with upwelling at the shelf break. By contrast with shallow winter mixing, nutrient deliveries by North American rivers and upwelling relax surface communities from N limitation and permit a more extant utilization of the excess SRP entering through Bering Strait. In this context, in-
25 creased nitrogen supply by rivers and upwelling potentially alter the vertical distribution of the excess P exported into the North Atlantic.

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1 Introduction

The Arctic Ocean is currently experiencing severe and rapid physical changes that are expected to alter primary productivity as well as the structure and function of marine food webs. In the Arctic, the ability of photosynthetic algae to profit from the greater irradiance resulting from the demise of sea ice is ultimately constrained by the availability of nitrogen (N), which was shown to explain large regional differences in annual productivity at the pan-arctic scale (Tremblay and Gagnon, 2009). This condition partly results from the physical setting, whereby strong, persistent and increasing vertical stratification in the interior impedes the vertical renewal of nutrients across the halocline (Tremblay et al., 2008; Li et al., 2009; Codispoti et al., 2013).

While any process conducive to the erosion of the halocline or upwelling will inject more nutrients into the upper euphotic zone, the unusual stoichiometry (or mixture) of nutrients imposes an additional constraint on productivity in the Pacific sector of the Arctic Ocean. In these waters, a chronic deficiency of N relative to phosphorus (P) is maintained by a host of biogeochemical processes taking place upstream. In the eastern Pacific, the remineralization of P-rich organic matter exported from the surface in upwelling areas combines with denitrification and anaerobic ammonium oxidation in oxygen minimum zones to lower the N : P ratio of waters that eventually ascend in the subarctic Pacific (e.g. Mills and Arrigo, 2010; Kalvelage et al., 2011). As these waters move northward, their N : P ratio is further reduced by coupled nitrification-denitrification in the sediments of the Bering Sea (Granger et al., 2011). The ensuing N deficiency in the high Arctic limits the ability of phytoplankton to fully use P and silicon (Si), which remain in excess at the surface and are ultimately exported into the North Atlantic Ocean (Torres-Valdés et al., 2013; Yamamoto-Kawai et al., 2006). In this regard, our knowledge of the impact of rivers and marine processes in supplying different nutrient mixtures, stimulating primary production and altering the chemical composition of waters exiting the high Arctic is rudimentary.

The Canadian Beaufort Shelf is a narrow interior shelf exposed to discharge from the Mackenzie River and shelf-break upwelling (Tremblay et al., 2011; Carmack and Mac-Donald, 2002) (Fig. 1). Its location along the eastward path of Alaskan coastal water and at the southern margin of the Beaufort Gyre makes it sensitive to upstream water mass history, but also implies that it can modify the biogeochemical properties of waters exiting the Arctic through the Canadian Archipelago. The Mackenzie is the fourth largest river draining the Arctic Ocean and the largest single source of sediments to the coastal zone (Holmes et al., 2002). The region harbors vital feeding and staging areas for marine mammals and marine birds that depend on primary production at the base of the food web (Carmack and MacDonald, 2002). While significant knowledge of nutrient transport by Arctic rivers has been gained and synthesized recently (Holmes et al., 2012), the biogeochemistry of estuaries and contiguous shelves is relatively understudied by comparison with other estuarine systems at lower latitudes (Moritz et al., 2002; McClelland et al., 2012). Recent modeling studies suggest a minor influence of rivers on inorganic nutrient loading at the pan-Arctic scale (Tank et al., 2012; Le fouest et al., 2013), but field investigations considering both inorganic and organic constituents as well as their local and far-field biogeochemical impacts remain scarce and fragmentary.

Previous investigations of the Canadian Beaufort shelf focussed on brackish waters in Kugmallit Bay (Emmerton et al., 2008a, b; Retamal et al., 2008) and occurred during a year of relatively low discharge. Characteristics of the western arm in Mackenzie Bay were not established and the marine "end-member" sites considered by these studies were relatively neritic. A comparison between riverine and oceanic nutrient sources (e.g. upwelling, vertical mixing and advection) considering both quantity and stoichiometry remains to be achieved. Here we report on a comprehensive dataset acquired under the auspices of the MALINA project during the fourth International Polar Year. Measurements of inorganic and organic constituents were performed in the Mackenzie River, in the estuarine transition zones of Mackenzie and Kugmallit bays, as well as in the marine domains of the inner and outer Mackenzie Shelf and southeast Canada

Basin during spring and summer 2009. These results are compared with late-winter, pre-bloom data obtained from the adjacent Amundsen Gulf to provide seasonal and regional perspectives on nutrient availability. Finally, estimates of river nutrient deliveries to the inner shelf were compared with in vitro measurements of nitrogen uptake and primary production to elucidate some of the processes taking place in the estuarine transition zone.

2   Materials and methods

2.1   General

Oceanographic sampling took place from 2 July to 25 August 2009 during the Mackenzie Light and Carbon (MALINA) expedition of the CCGS Amundsen to the southeast Beaufort Sea (Fig. 1). High vertical resolution environmental data were collected between 0 and up to 500 m depth using a conductivity-temperature-depth-oxygen profiler (CTDO, Seabird 911 plus) with a rosette supporting 24 12 L Niskin bottles equipped with silicon rubber closures. Salinity values are reported in the Practical Salinity Scale, without units. Surface samples from the Mackenzie River plume in the shallow portions of Mackenzie Bay and Kugmallit Bay were collected with a bucket from a barge. A water mass analysis assessing the contribution of meteoric water (Mackenzie River runoff + precipitation) and sea-ice melt water to the different sampling stations was performed using alkalinity and δ^{18}O data according to procedures previously described for our sampling area (Lansard et al., 2012). This data will be presented elsewhere and here is used only to discuss the validity of salinity as a tracer of river water.

2.2   Inorganic nutrients

Ammonium concentrations were measured using the sensitive method of Holmes et al. (1999) with a detection limit of 5 nM. Samples for nitrate, nitrite, soluble reactive phosphorus (SRP) and silicic acid determination, were collected into 20 mL polyethy-

lene flasks and immediately poisoned with mercuric chloride ($10\,\mu g\,mL^{-1}$), according to Kirkwood (1992), and stored for subsequent laboratory analysis. Nitrate and nitrite concentrations in the nanomolar range (lower detection limit = 3 nM) were obtained using the sensitive method of Raimbault et al. (1990). Nitrate in deep waters (detection limit = 0.05 µM) and phosphate (detection limit = 0.02 µM) were measured according to the method of Aminot and Kerouel (2007). To ensure the reproducibility of nutrient measurements between analyses, in-house standards were used, which were regularly compared to the commercially available products (OSIL). Winter nutrient samples collected in the adjacent Amundsen Gulf during the IPY-International Circumpolar Flaw Lead Study in 2008 were determined using similar procedures as outlined in Tremblay et al. (2008). Deviations of nitrate and SRP concentrations from the N : P ratio of biological demand and remineralization (r) were assessed with the parameters N^* and P^*:

$$N^* = \text{nitrate} - (r \cdot \text{SRP}) \tag{1}$$

$$P^* = \text{SRP} - (\text{nitrate}/r) \tag{2}$$

Since the N : P ratio of biological drawdown during blooms in the Beaufort Sea (12.6–13.7; Tremblay et al., 2008; Bergeron and Tremblay, 2013) is lower than the global average of 16 (Gruber and Sarmiento, 1997), we prescribed a mean r value of 13.1 to better reflect the regional balance of nutrient losses and gains with respect to phytoplankton demand.

2.3 Organic constituents

Samples for particulate organic carbon (POC) and total particulate nitrogen (TPN) and phosphorus (TPP) were filtered onto a glass fiber Whatman GF/F (25 mm in diameter, 0.7 µm pore size). Between 250 to 1200 mL of sample was filtered depending on the

quantity of particulate matter in the sample. Following filtration, filters were washed with 100 μL of H_2SO_4 (0.5 N) to remove inorganic carbon. The filters were then stored in 25 mL Schott glass bottles for subsequent laboratory analysis. Blank filters were prepared for each set of samples by washing the filter with 200 mL of 0.2 μm-filtered seawater. Determination of POC, TPN and TPP was carried out simultaneously on the same sample using the wet-oxidation procedure described in Raimbault et al. (1999b).

Samples for total organic matter determination were collected directly from the Niskin bottles into 50 mL Glass Schott bottles. Samples were immediately acidified with 100 μL H_2SO_4 0.5N and stored for analytical determination in the laboratory. Prior to oxidation, samples were bubbled with a high purity oxygen/nitrogen gas stream for 15 min. Persulfate wet-oxidation was used to digest the organic matter in these unfiltered samples and the inorganic end-products were determined according to Raimbault et al., 1999a. The calibration was made according to the range of the marine content observed. Total organic nitrogen and total organic phosphorus were calculated as total nitrogen and phosphorus minus dissolved inorganic nitrogen (nitrate + nitrite + ammonium) or phosphate measured in the same samples. Dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) were calculated by subtracting values of POC, TPN and TPP in the > GF/F fractions (see above) from the unfiltered totals. The analytical accuracy was ca. 5.0, 0.5 and 0.05 μmole L^{-1} for DOC, DON and DOP, respectively. Deep Sargasso Sea reference water was used to verify the analytical calibration (45 μmoles C L^{-1} ± 0.5 SE, Hansell Laboratory, Bermuda Biological Station for Research). All reagents and sample blanks were prepared using fresh Millipore Milli-Q plus® water.

2.4 River discharge and nutrient transport by the Mackenzie River

Two river sites were used during our Study. Given the complex branching of the river in the delta region, discharge data were taken only from the Environment Canada station at Tsiigehtchic (http://www.wsc.ec.gc.ca/applications/H2O/), which is located 200 km inland in the main body of the river (Supplement). Water samples were obtained dur-

ing the period of peak discharge at Tsiigehtchic (25 May, 3 June and 11 June 2009) and at Inuvik (daily from 23 May to 11 June 2009). The latter is located at the head of the delta, 100 km downstream of Tsiigehtchic. Surface water was taken with a clean plastic bucket, filtered through pre-combusted Whatman GF/F filters and frozen. Inorganic and organic constituents were subsequently analysed as above. The concentrations of these constituents as well as concomitant discharge data are given in Supplement A (Table S1). To facilitate comparison with shelf data, we calculated median and discharge-weighted mean concentrations at Inuvik for the period between 25 May and 11 June (Table S1). Discharge-weighted means were obtained by multiplying daily discharge (Tsiigehtchic) by concentration (Inuvik), summing all time points and dividing by cumulative discharge. Estimates of nutrient transport for the main MALINA sampling period (July–August) and the whole year were calculated by assuming a steady decrease in concentrations from those measured at peak discharge and those measured during the MALINA sampling on the shelf. Since the main emphasis of this paper is on the estuarine transition zone and the shelf, the data pertaining to discharge and nutrient concentrations in the Mackenzie River are confined to Supplement A.

2.5 Primary production and nitrogen uptake

Rates of carbon fixation (primary production) and of nitrate and ammonium uptake were measured at a subset of stations using a dual ^{13}C-^{15}N isotopic technique (Raimbault et al., 1999c). For this purpose, 580 mL samples were collected at 6–7 depths between the surface and the depth where irradiance is 0.3 % of its surface value, and poured into acid-cleaned polycarbonate flasks. Bottles were rinsed before use with 10 % HCl, then with distilled water from a Milli-Q ion exchange unit. Radiolabelled sodium bicarbonate (NaH^{13}CO$_3$ – 6 g, 250 mL^{-1} deionized water – 99 at % ^{13}C, EURISOTOP) was added to each bottle in order to obtain ≈ 10 % final enrichment (0.5 mL per 580 mL sea water). Nitrogen ^{15}N-tracer additions, K^{15}NO$_3$ or ^{15}NH$_4$Cl (99 % at ^{15}N), were 10 % or 20 % of the ambient concentration based on real-time

measurements. In nutrient impoverished waters, when concentrations were lower than the detection limit, additions of ^{15}N were fixed at $\sim 17 \pm 3$ nmoles L^{-1} for ^{15}N-NO$_3$ and 43 ± 3 nmoles L^{-1} for ^{15}N-NH$_4$.

Incubations were started immediately following tracer addition, just before dawn in an on-deck incubator. The latter consisted of 6–7 compartments, each covered with a blue-light screen allowing the samples of a given location collected at different depths to be exposed to the light 50 %, 25 %, 15 %, 8 %, 4 %, 1 % and 0.3 % of incident sunlight. The incubator was maintained at sea-surface temperature using pumped seawater. After 24 h samples were filtered through precombusted (450 °C) Whatman GF/F filters using a low vacuum pressure (< 100 mm Hg). Following filtration, filters were placed into 2 mL glass tubes, dried for 24 h in a 60 °C oven and stored dry until laboratory analysis. These filters were used to determine the final ^{15}N / ^{13}C enrichment ratio in the particulate organic matter and the concentrations of particulate carbon and particulate nitrogen. The dual isotopic enrichment analysis was performed on an Integra-CN mass spectrometer calibrated using international reference material (glycine) every 10–15 samples.

3   Results

3.1   River discharge and nutrient transport

Historical data indicate that annual discharge during 2009 was greater than the long term mean, ranking 8th for the period 1972–2009 (Supplement, Fig. S1). For 2009, daily discharge reached a peak of 30 000 m^3 s^{-1} on 27 May, remained very high until the end of June and decreased to ca. 50 % of the peak value during July, August and September. A comparison with a year of low discharge (2004) shows that high discharge in 2009 did not result from a particularly strong freshet but from persistently elevated transport from June to September (Fig. S1).

Concentrations of DON and DOC measured at river sites during May–June and on the shelf at stations with negligible salinity (< 0.23) during August were related exponentially to daily river discharge (Table S1 and Fig. S3). By contrast, high and low concentrations of DOP alternated throughout the sampling period with no apparent rela-
5 tionship to discharge (Table S1). This relationship was also absent for nitrate and phosphate although maximum concentrations occurred during the freshet. Phosphate concentrations fluctuated widely relative to other constituents (CV > 100 %), which drove high variability in Nitrate : SRP and N^*. Roughly 25 % of the annual seaward transport occurred during July–August for all constituents (Table 1). The ratio of organic
10 to inorganic forms in the overall transport was much larger for nitrogen (5.6) than for phosphorous (2.3).

3.2 Distribution of inorganic and organic constituents on the shelf

Surface distributions of salinity and dissolved constituents on the shelf are shown in Fig. 2. The river signal was strongest in Mackenzie Bay, where salinity ranged from
15 0.15–0.23, at the two southernmost stations (collectively referred to as "river outlet" hereafter), to 15 psu in the outer bay at 69.3° N. By contrast, the minimum inshore salinity observed in Kugmallit Bay was 16.4. Relatively low salinities (15–25) west of 135° W suggest the propagation of freshwater as far north as 70.5° N. Nutrients showed strong inshore-offshore gradients. Surface concentrations of nitrate and silicate were highest
20 (3.62 µM and 64.5 µM, respectively) at the river outlet and declined seaward to low values for silicate (> 3 µM) and measurable trace levels for nitrate (0.005 to 0.02 µM).
Spatial gradients in dissolved organic constituents were similar to those of nitrate, but this time the highest concentrations were observed in Kugmallit Bay, with maxima of 26.7, and 1.33 µM for DON and DOP, respectively. Corresponding concentrations in
25 inner Mackenzie Bay were only 15.2 and 0.22 µM. Offshore concentrations were generally much lower, ranging from 4.43 to 8.0 µM for DON and from 0.09 to 0.33 µM for DOP. Phosphate showed opposite spatial gradients, with a minimum concentration of 0.02 µM observed at the river outlet and a seaward increase to concentrations rang-

ing from 0.40 to 0.67 µM offshore. Ammonium concentrations in Mackenzie Bay were low at the river outlet (0.20 µM), increased to a maximum of 1.48 µM in the central part and declined to very low but always detectable levels offshore (0.01–0.05 µM). A qualitatively similar pattern was observed in Kugmallit Bay, but the highest observed concentration was only 0.34 µM in the center of the bay.

Figure 3 shows the vertical distribution of a subset of dissolved properties along the three sections identified in Fig. 1. Seaward intrusions of freshwater from both arms of the Mackenzie River were confined to the upper 10 m on sections C and K. Sections C and M and to a lesser extent section K showed a shoreward uplifting of intermediate offshore waters, which resulted in elevated nitrate concentrations and nitrate : SRP ratios over the bottom on the outer and middle shelf. The shallow end of section C was characterized by nitrate concentrations ranging from 2 to 4 µM between 15 and 20 m as well as elevated ammonium levels over the bottom (station 170, 30 m deep). Concentrations of ammonium and DON qualitatively followed a similar pattern, with maximum surface concentrations in central Kugmallit and Mackenzie bays and bottom accumulations over the shelf and slope. Maximum nitrate : SRP ratios at the surface were observed nearshore and rapidly declined seaward, where a strong vertical gradient was present on all sections.

Since the influence of the Mackenzie river plume was confined to the upper 10 m (mixed layer depths ranged 5–10 m on the inner shelf), we investigated how the concentrations of different constituents changed as a function of salinity in this layer. Properties at the river outlet in inner Mackenzie Bay were considered as undiluted (surface salinities < 0.23) and representative of "pristine" river waters on the shelf. Inorganic nutrient concentrations in this area were highly similar to the median and discharge-weighted concentrations observed at Inuvik during May–June (Fig. 4). The agreement was better with the median, which is less affected by extreme values during the freshet (Fig. S2). On the shelf, each constituent should theoretically vary with salinity along a conservative mixing line in the absence of net gains or losses resulting from chemical or biological processes. Such conservative behaviour roughly applied to silicate,

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N^* (hence P^*) but not to DIN, DIP nor SRP. Nitrate and SRP showed opposite, non-conservative gradients, while ammonium showed a clear accumulation at intermediate salinities. The Nitrate : SRP ratio increased markedly between the river and inner Mackenzie Bay and then decreased abruptly with rising salinity. Nitrate, SRP and silicate all showed conspicuously low concentrations at the head of Mackenzie Canyon (stas. 670 and 680) with a surface salinity of ca. 15. This station was located in the outskirts of Mackenzie Bay in the west. By contrast, the concentrations of silicate and N^* at similar salinities in Kugmallit Bay loosely followed the general conservative dilution line. In this bay, daily nitrate uptake declined seaward with increasing salinity and decreasing nitrate availability (Fig. 4). No spatial gradient was discernible in ammonium uptake, which remained relatively high across the bay and accounted for 50 to 86 % of total inorganic N uptake (i.e. sum of ammonium + nitrate uptake).

Concentrations of DON and DOC in the river were higher than on the shelf and, by contrast with DOP, showed a clear conservative decrease with salinity (Fig. 5). All ratios decreased between the river outlet and marine waters with salinities > 25 psu, but the relative decrease was most pronounced for DOC : DOP (4×), followed by DOC : DON (2.6×) and DON : DOP (1.5×), suggesting a differential lowering of C relative to N and P. Only the DOC : DON ratio showed a linear decrease with salinity. The overall C : N : P stoichiometry of DOM in the river (2419 : 48 : 1, based on discharge-weighted means) and at the river outlet in Mackenzie Bay (2085 : 63 : 1) was similar but very different from the area of maximum DOM in Kugmallit Bay (149 : 13 : 1) and the average for marine stations with salinities above 25 (451 : 35 : 1).

Primary production and particulate organic constituents also showed clear inshore-offshore gradients (Fig. 6). Daily rates of primary production at the surface where generally very low across the survey area, ranging from 0.1 µg C L^{-1} d^{-1} offshore to a maximum 545 µg C L^{-1} d^{-1} in Kugmallit Bay at a salinity of 16 (Fig. 6). The estimated turnover time of the suspended POC pool (i.e. POC divided by primary production) was 2 days at this location, which also exhibited the highest concentrations of POC and TPN on the transect. An exception to this general pattern occurred in the notori-

ously upwelling-prone area to the northwest of Cape Bathurst, were primary production, POC and TPN were clearly elevated. In Mackenzie Bay, concentrations of POC, TPN and TPP were 52.02, 8.34 and 4.96 µM, respectively, at the river outlet (salinity = 0.15), rose to 72.83, 12.51 and 5.47 µM at the next station (salinity = 0.23) and

5 declined to minimum values of 1.68, 0.33 and 0.03 µM offshore. When excluding the upwelling area, TPN and POC showed a somewhat progressive decline with rising salinity across the shelf, in stark contrast the shark drop of TPP at the beginning of the estuarine transition zone (Fig. 7). Despite a tendency toward higher values at the marine end of the salinity gradient, POC : TPN values clustered around the Redfied

10 value (6.7) across the whole sampling area, which contrasted with seaward increases in TPN : TPP and to a lesser extent POC : TPP (Fig. 7). The overall stoichiometry of particulate organic matter at the river outlet (10.5 : 1.7 : 1) differed from that of marine waters with salinities > 25 (107 : 7.6 : 1). At the delta's outlet in Mackenzie Bay, nearly all (95 %) of the total phosphorus (SRP + DOP + TPP) was in the particulate pool. For

15 nitrogen the particulate fraction represented only 31 % of the total.

4   Discussion

The importance of inorganic and organic river nutrients for biological productivity on a given shelf depends on (1) the width and area of the shelf relative to river transport, (2) the extent to which these nutrients can be used by autotrophs, either directly or after

20 microbial and/or photochemical transformation, and (3) the strength of oceanic nutrient deliveries through horizontal advection, vertical mixing and upwelling. In addition to their direct effects on local productivity, different oceanic and riverine sources of nutrients to the euphotic zone impact the magnitude and composition of surface nutrient fluxes to downstream areas. Effects on composition (or nutrient ratios) are manifest

25 when the nutrient mixtures provided differ from biological demand and leave surpluses of one or more nutrients, such as the excess P and Si that are exported from the Arctic into the North Atlantic (Yamamoto-Kawai et al., 2006; Torres-Valdés et al., 2013). The

following discussion will therefore explore the implications of nutrient deliveries at both local and large scales, after assessing the quality of our river transport estimates, and considering the fate of river nutrients on the shelf and what distinguishes these nutrients from those provided by upwelling and winter convection in the area. Given the coherent patterns shown in Fig. 4, the discussion is generally simplified by considering Mackenzie and Kugmallit bays as part of a single continuum of conditions along one salinity gradient.

4.1 Nutrients: river transport and gradients on the shelf

The estimates of nutrient transports provided in Table 1 are based on measurements made in Inuvik during May–June and may not fully correspond to actual nutrient deliveries to the shelf due to seasonality and processes occurring through the delta. Based on model results and limited observations, Emmerton et al. (2008b) suggested that river waters lose inorganic nutrients and gain DOM across the delta. This pattern did not seem to apply to the upper delta during our study, where limited comparisons between Tsiigehtchic and Inuvik suggest an increase in DOC, a decrease in DOP and negligible or inconsistent changes in DON, SRP and nitrate along flow (Table S1). For the lower delta, the assessment of delta effects between Inuvik and the inner shelf is complicated by the seasonal decrease in discharge. This decrease is entirely consistent with the decline in DOC and DON concentrations between Inuvik in May–June and the inner shelf in August, based on the exponential relationships linking discharge and concentration for these two constituents (established using previously published data and ours, Fig. S2; see also spring and summer data in Fig. 3 of Holmes et al., 2012). These two constituents also followed a single linear relationship (DOC$= -578 + 71.9$ DON; $r^2 = 0.93$; not shown) when pooling all data from Inuvik and Tsiigehtchiic for May–June (Table S1) with those from the river outlet in August (Fig. 5), implying consistency in their sources and biogeochemical cycling across the region. For inorganic constituents, relatively invariant concentrations across the inner shelf and the two river sites for all sampling periods suggests minor impacts by discharge and delta processes (Table S1

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and Fig. 3). The lack of discharge effect was previously noted for nitrate (Holmes et al., 2012) and the concentrations of SRP and nitrate we measured here are on par with those reported for other years (Emmerton et al., 2008b; Holmes et al., 2012). This similitude and the apparent lack of change along the river's path is presumably
5 a consequence of very low SRP levels, which presumably impeded the consumption of nitrogen through P limitation of phytoplankton and bacterial growth in the river and delta lakes (Squires and Lesack, 2003; Spears and Lesack, 2006). A corollary to this interpretation is that DOP was a minor source of labile P in this system.

A comparison of the overall fluxes provided in Table 1 with other published values
10 was possible only for the annual estimates. It is noteworthy that the climatological DON and DOC fluxes estimated by Holmes et al. (2012) and Le Fouest et al. (2013) were half those in Table 1, which given the above considerations can be regarded as a consequence of high discharge throughout spring and summer 2009 and, possibly, changing conditions in the watershed (e.g. thawing permafrost). By contrast, transport estimates
15 for the discharge-independent constituents (i.e. nitrate, TDP) were the same or within the envelope of those published by Holmes et al. (2012) and Lefouest et al. (2013). For this reason and those discussed above we surmise that the concentrations of dissolved constituents measured in August just outside the delta were representative of river deliveries and that the nutrient transports in Table 1 provide realistic estimates of
20 allochthonous supply to the inner shelf for 2009.

The interpretation of changes in dissolved constituents away from the southernmost stations in Mackenzie Bay and Kugmallit Bay depends on whether salinity is a valid tracer of river water in the upper 10 m. This condition can only be met if ice melt does not introduce large amounts of freshwater at different shelf stations, which was plau-
25 sible in 2009 since patchy ice floes persisted through July and early August. A water mass analysis based on δ^{18}O and total alkalinity showed robust, inverse linear relationships between salinity and the fraction of meteoric water and lignin content at our sampling sites (not shown). The meteoric fraction ranged from 97 % at the river outlet in Mackenzie Bay to < 5 % at stations with salinities > 30. At stations with salinities < 20,

the fraction of sea-ice melt water did not exceed 5 %, except at the head of Mackenzie Canyon (stations 670 and 680) where it reached 20 % at salinities of ca. 15 psu. These stations stand out in several figures (dashed circles), most notably in Fig. 4 where silicate concentrations show a strong negative anomaly. In this case, the surface layer must have been diluted with sea-ice melt water containing little or no nutrients and affected by diatom production. Particulate stocks were not noticeably elevated at the time of sampling but TPN : TPP ratios were consistent with the N : P drawdown ratios previously observed in diatom blooms (Tremblay et al., 2008). Apart from these two anomalous stations, all constituents would be expected to follow conservative patterns in the absence of biological processes.

4.2 Contribution of river transport an N recycling to primary production

Since there were gaps in the spatial coverage of primary production measurements, we used empirical relationships to interpolate our data vertically and across the survey area. Among static variables, the best predictor of primary production at the surface was the concentration of TPN (Fig. S3). This relationship suggests that most of the TPN was recently produced by autotrophs in the estuarine transition zone, which is consistent with the slope of the geometric mean regression of POC against TPN (6.0 ± 0.3 mol : mol, $r^2 = 0.98$; not shown) in Mackenzie and Kugmallit bays (0.15–23 salinity range) and the short turnover time of POC at the southernmost station in Kugmallit Bay. Even at the station with the highest particulate load in Mackenzie Bay (salinity of 0.15), the POC : TPN ratio did not exceed 5.82 (Fig. 7). This situation contrasted with the strong terrigenous matter inputs (POC : TPN ratios of up to 17) reported by Emmerton et al. (2008a).

At shallow stations (2–20 m) sampled from the barge, where only surface water was incubated, water-column primary production was estimated by assuming a vertical attenuation of production rates similar to observations made at station 390 on the inner shelf, noting that this may cause a slight overestimation of subsurface values at the most shallow and turbid stations (< 5 m). Spatially integrated water-column values

were calculated for the entire shelf inside the 75 m isobath (average primary production value times the area of 61 117 km^2), the western portion influenced by river discharge (i.e. west of 135° W; 35 069 km^2) and the neritic sector where nitrate declined non-conservatively at salinities < 20 (4132 km^2). Cumulative estimates of 352, 215 and 121 × 10^9 g C were obtained for July–August (62 days) in each of these three sectors. For the neritic portion, the estimated fraction of primary production occurring in the upper 10 m only (i.e. layer directly influenced by the river) was 114 × 10^9 g C.

New production in the neritic sector can be driven by the river influx of labile N or atmospheric N sources (N$_2$ fixation, deposition). Complete utilization of the nitrate supplied by the river, which clearly occurred in the upper 10 m at salinities < 20 in 2009 (i.e. Fig. 4), corresponds to an equivalent nitrate-based new production of 23.1 and 91 × 10^9 g C during July–August and the whole year, respectively, using the above C : N ratio of 6.0 ± 0.3. In the absence of direct estimates, the riverine flux of ammonium during July–August can be approximated by multiplying nitrate transport by the ammonium : nitrate concentration ratio (0.2 µM / 3.5 µM) at the river outlet in Mackenzie Bay. This addition yields a DIN-based new production of 24.5 × 10^9 g C during July–August. While the labile fraction of river DON cannot be formally assessed, the amino acid fraction (TDAA) is a viable surrogate (Benner, 2003). The mean TDAA concentration at the river outlet was 0.6 µM (4 % of total DON) during our survey (Shen et al., 2012). Adding the estimated TDAA flux (by multiplying DON transport by the TDAA/DON concentration ratio at the river outlet) to DIN-based new production yields a TDN-based new production of 29.7 × 10^9 g C during July–August. Finally, concomitant rates of nitrogen fixation decreased from 4.5 to 0.5 nmol N L^{-1} d^{-1} across the estuarine transition zone (Blais et al., 2012). Prescribing a mean N$_2$ fixation rate of 2.5 nmol N L^{-1} d^{-1} over an average depth of 5 m for 62 days rises total new production to 30.0 × 10^9 g C during July–August.

The above calculations yield a ratio of new (30.0 × 10^9 g C) to total (114 × 10^9 g; based on the ^{14}C technique) production of 0.26 for the area. Another way to estimate the ratio of new to total primary production is the f ratio, which is calculated

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by dividing nitrate uptake by the sum of nitrate and ammonium uptake (Dugdale and Goering, 1967). The average in vitro f ratio calculated using the data in Fig. 4 is 0.31, assuming that all the ammonium taken up was released by the local food web at the stations where short-term DIN uptake experiments were performed. This assumption appears reasonable given the low concentrations of ammonium at the river outlet and the maxima observed at intermediate salinities (Figs. 4 and 5). While ammonium is also provided by photochemical processes in this area, the rates estimated by Xie et al. (2012) would supply at most 1.1–3.5 % of daily ammonium uptake at the surface and presumably less underneath. The two independent estimates of the ratio of new to total production (0.26 and 0.31) can be considered equivalent given our coarse approach. This good match suggests that direct uptake of locally-recycled DON, which reached maximum concentrations in central Kugmallit Bay (and likewise TDAA; Shen et al., 2012), contributed little to phytoplankton N demand, although it is possible for algae to use labile DON in estuaries (Tarr et al., 2001; Bushaw-Newton and Moran, 1999). The strong positive relationship between bacterial production and TDAA concentration on the shelf (Ortega-Retuerta et al., 2012) implies that bacteria were major users of fresh DON, from which ammonium was presumably supplied to phytoplankton. Our analysis therefore suggests that nitrate was the main source of allochthonous riverine N supporting new production and that intense recycling supported high total primary production in the neritic sector.

The impact of the Mackenzie River on primary production during summer is localized to the nearshore estuarine transition zone during summer. A rough annual perspective can be gained by comparing with maximum winter nutrient concentrations in nearby oceanic waters. Data from the overwintering survey of the Amundsen Gulf showed maximum nitrate concentrations of $\sim 5.0\,\mu M$ in mid-March 2008 (Fig. 9, see also Forest et al., 2011). Assuming a similar winter maximum across the shelf would yield a total inventory of 3.06×10^{12} mmol in the upper 10 m inside the 75 m isobath. This amount is ca. 9 times larger than the estimated annual river delivery (Table 1) and excludes the subsurface layer where subsurface chlorophyll maxima (SCM) thrive (Martin et al.,

2012; Carmack et al., 2004). The extent to which phytoplankton consume nutrients in this layer is not fully known, but given the vertical extent of seasonal depletion in Fig. 3 and previous work in adjacent Franklin Bay (Tremblay et al., 2008), it is safe to assume that the SCM consumed at least another 3×10^{12} mmol between 10 and 20 m. In this scenario, the Mackenzie River supply would provide at most 5 % of the nitrate consumed annually on the narrow Canadian Beaufort Shelf. This contribution might rise if river discharge increases, supplies more nitrogen and reinforces vertical stratification beyond the nearshore zone. Once river nutrients are consumed, freshwater remains and propagates at much larger scales across the Arctic. The negative impact of rivers on upward nutrient supply offshore thus reinforces their overall contribution to primary production.

4.3 Significance of river N supply on the Mackenzie shelf

At present, surface marine waters of the Canada Basin and Canadian Archipelago harbor excess quantities of Si and SRP (= strongly positive P^*, Fig. 9a) that are unused due to N shortage. Based on the availability of P alone, biological productivity in the Beaufort Sea could be 3.6 times higher than it currently is (based on winter data in Fig. 9). While the realization of this potential is susceptible to changes and variability in the nitrogen balance of source waters, it is also affected by processes occurring within the high Arctic, such as river discharge and physical oceanic processes. In this regard, phytoplankton might gain access to excess P in the euphotic zone through (1) a decrease in N : P demand linked to changes in assemblage composition, (2) differential addition of labile N through nitrogen fixation, photochemistry or atmospheric deposition, and (3) the admixture of waters with a N : P ratio of labile nutrients exceeding the ratio of biological demand (otherwise the nutrient input stimulates primary production, but does not reduce the P surplus).

The current nitrate : SRP and Si : nitrate drawdown ratios of 13.1 and 1.75 during blooms in the southeast Beaufort Sea are consistent with a large contribution of diatoms with an absolute requirement for Silicon and low N : P ratios (Deutsch and We-

ber, 2012; Geider and La Roche, 2002). The nitrate : SRP ratio is higher than the value of 9 advocated for diatom blooms in other areas (e.g. Mills and Arrigo, 2010), which could be due to a difference in diatom assemblages and the greater importance of small non-diatom taxa in the high Arctic (e.g. *Micromonas*, Lovejoy et al., 2007). The
5 reported shift toward small-sized phytoplankton (Li et al., 2009) in the Canada Basin potentially increases N : P demand (possibly up to 16 or even 20), further exacerbating N limitation, decreasing new production and rising surface P^*, in agreement with the high post-bloom TPN : TPP ratios observed at the northern end of our sampling area (Fig. 7).
10 A comparison between pre-bloom nutrient inventories and the N : P drawdown ratio during blooms clearly reveals the large imbalance between demand and supply in the upper 140 m of the water column (Fig. 9a). At the height of winter, the N : P ratio of dissolved inorganic nutrients peaked at 4.5 in the upper mixed layer (35 m), indicating that blooms with an observed N : P demand of 13.1 can only use 34 % of the available
15 SRP before running out of nitrate. Since nutrient remineralization in the mesopelagic zone proceeds with the same stoichiometry as the organic matter exported from above (Simpson et al., 2008), the nutrients supplied to the surface during winter do not originate from the main decomposition horizon. This situation arises from the strong stratification that persists throughout winter, during which strong and coincident gradients
20 in salinity, Nitrate : SRP and P^* extend from 40 to 170 m. The coincidence implies that nutrients are mostly trapped where they are mineralized and those re-injected to the surface during winter come from a relatively shallow N-poor horizon, dominated by advected excesses of SRP and Si. This condition allows the surface P^* anomaly to survive for several years and to propagate over large distances, providing a unique
25 setting for nutrient deliveries by the Mackenzie River, upwelling or mixing.

A corollary to the above discussion is that nitrate : SRP ratios increase with depth in the Canada Basin of the Arctic Ocean, contrary to most other oceans where nitrate : SRP remains relatively stable (e.g. central north Atlantic) or decreases (e.g. eastern North Pacific) away from the surface. It follows that in the Beaufort Sea upwelling

or mixing events that erode the halocline will close the gap between N : P supply and demand, stimulating primary production while allowing for a more complete utilization of the P and Si in the euphotic zone. Mixing is currently limited to modest winter convection in the southeast Beaufort Sea, but can be extensive in the narrow channels of the Canadian Archipelago (Michel et al., 2006; Tremblay et al., 2002) where pre-bloom N : P ratios in the euphotic zone are twice higher than in the Beaufort Sea. Based on the profiles shown in Fig. 9, the nitrate : SRP ratio of surface waters during upwelling events should rise by 1 unit for every 17 m increment in entrainment depth. Indeed, surface nitrate : SRP ratios exceeding 10 and approaching the N : P demand of blooms have been observed during strong upwelling events (Tremblay et al., 2011). Upwelling during MALINA was relatively modest, but nevertheless increased nitrate and N : P ratios in the lower euphotic zone. Corresponding impacts on the Si : N ratio are relatively weak since the latter deviates from the demand ratio by only 17 % across the water column (Fig. 9).

Assuming a negligible sequestration of nutrients in the sediment (see Link et al, Malina special issue of BGD) and matching stoichiometry of drawdown and remineralisation in the water column, changes in the extent of P and Si utilization resulting from mixing or upwelling would not affect the overall export of these nutrients into the North Atlantic. Given the above considerations however, it would alter the vertical distribution of P^* in the salt-stratified outflow. By relieving N limitation in surface waters, greater vertical mixing, upwelling or river transport within the high Arctic would work to transfer excess P to depth when sinking particles are remineralized in the mesopelagic zone. A weakening of these processes would act to elevate P^* and Si^* in the upper mixed layer.

In the absence of intense mixing or upwelling at the shelf break, runoff provides the only source of relatively high nitrate : SRP water to the coastal Beaufort Sea. Riverine nitrate : SRP ratios are very high, starting at ca. 50 at Inuvik and exceeding 150 at the river outlet when nearly all of the small riverine SRP pool of SRP has vanished. Conditions are similar in the Yukon River (Le Fouest et al., 2013). At the opposite end of the nutrient spectrum, surface marine waters of the Canada basin are nitrate-depleted

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and show a large excess of SRP. The mixture of both water types in the coastal zone is thus necessary to support efficient consumption of river nitrogen and explains why the parameters N^* and P^* are linearly related to salinity (Fig. 4). In this context, the net loss of nitrate in upstream source waters of the Pacific Ocean and Bering Sea creates the conditions necessary to allow for the swift consumption of river nitrogen in the estuarine transition zone. This also suggests that North-American rivers contribute to restore N^* toward its mean global value, even though the total transport of nitrogen by Arctic rivers currently remains small relative to Bering Strait influx (Le Fouest et al., 2013).

5 Conclusions

Our results provide new information and insights into the interplay of riverine and oceanic processes on a narrow interior Arctic shelf, and into the biogeochemical consequence of these processes at local and larger scales. The ratio of river discharge to shelf area is much higher for the narrow Mackenzie shelf than for the vast Siberian shelves, which should maximize the overall contribution of river nutrients to overall shelf productivity. During summer 2009, river nutrients had a major impact on the nearshore zone at salinities < 20 but a much lower one at the scale of the shelf, despite the fact that winter nitrate had already been stripped from the surface in the area. This low contribution occurred partly because the narrow configuration of the shelf also magnifies the impact of upwelling at the shelf break. Although upwelling was weaker during our survey than at other times (e.g. Tremblay et al., 2011), it supported elevated primary production by providing nutrients to the lower euphotic zone where subsurface phytoplankton layers persist. Direct measurements of the uptake of different riverine DON and DOP sources were not performed in our study but indirect evidence suggests that their contribution to new production was minor and that locally produced organic nutrients indirectly supported regenerated primary production which, based on DIN uptake measurements, represented a large portion of total primary production in the estuar-

ine transition zone. The respective roles of benthic and pelagic processes on nutrient regeneration in this area remain to be assessed.

The regional impact of the Mackenzie River would be much different if (1) the waters supplied through Bering Strait did not carry such a strong P^* anomaly, and (2) Pacific-derived polar surface waters were not so strongly stratified in the interior. The first condition supplies a reservoir of excess P and the second one helps maintaining it by limiting the re-injection of mineralized nutrients with a higher N : P into the euphotic zone. The same biogeochemical processes that lower the inflow of nitrate to the interior of the Arctic also create a setting in which labile N from North American Rivers can be readily used by coastal phytoplankton. Patterns of coastal nutrient use are presumably much different on Siberian shelves, where low nitrate : SRP river waters (e.g. 3.5 and 2.2 for the Yenisey and Ob rivers, respectively; Le Fouest et al., 2013) contribute to increase P^* since there is not enough inorganic N to support the consumption of excess marine P. Beyond its immediate impact on shelf productivity, the Mackenzie River helps to rectify the nitrogen deficit of waters exported into the western North Atlantic and to rise silicate levels in this outflow (Torres-Valdés et al., 2013). It follows that variability or change in the flow, nutrient load and nutrient stoichiometry of surface waters supplied to the Arctic Ocean by rivers and through Bering Strait will impact marine productivity and biogeochemistry both locally and far downstream.

Supplementary material related to this article is available online at http://www.biogeosciences-discuss.net/10/16675/2013/ bgd-10-16675-2013-supplement.pdf.

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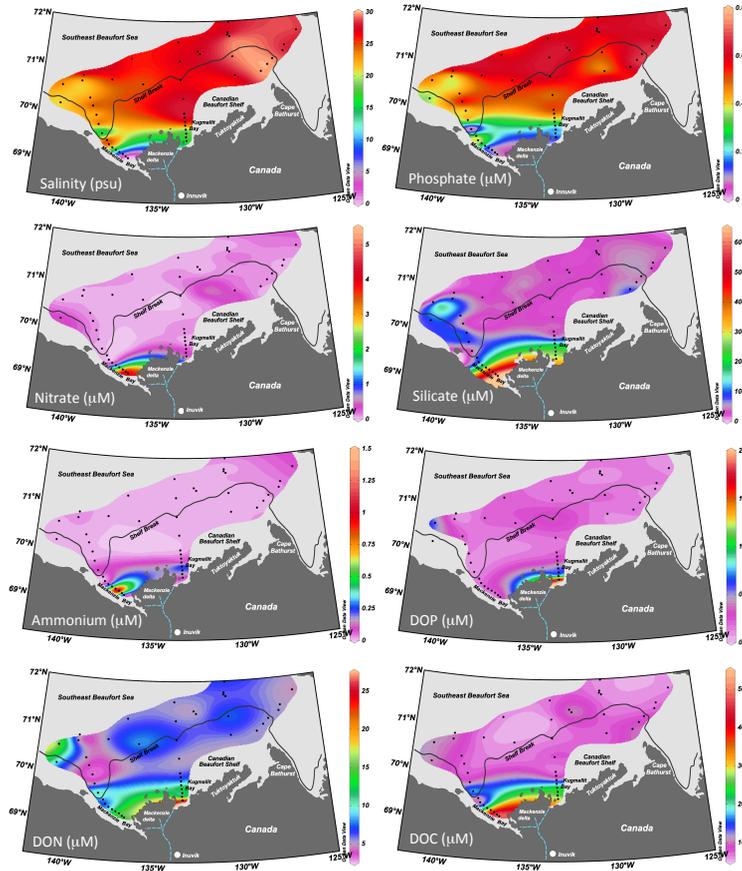| Abstract | Introduction |
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Table 1. Nutrient transports ($\times 10^9$ mmol N or P) by the Mackenzie River during 2009.

	Nitrate	SRP	TDN	TDP	DON[*]	DOP
Jul–Aug	320	8	2019	23.9	1786	17.1
Whole year	1259	31	7922	100	6993	72.0

[*] Maximum estimate calculated as TDN-NO_3^- (ignores potential contribution from NH_4^+, which is presumably small given the low concentrations observed on the inner shelf).
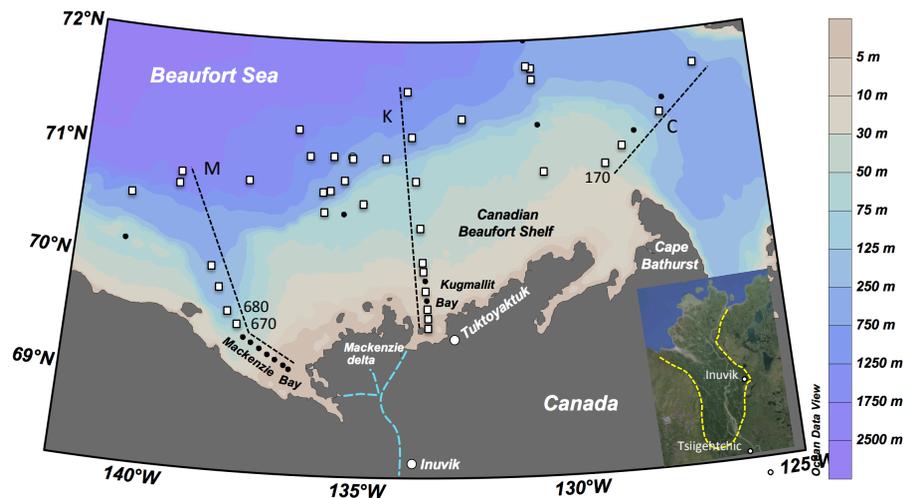
Fig. 1. Map of sampling stations in the Mackenzie River (inset) and southeast Beaufort Sea, with locations where inorganic nutrient concentrations were determined (all symbols) and were primary production and the particulate and dissolved organic pools of carbon, nitrogen and phosphorous were also quantified (squares). Samples were taken at the surface only for stations located inside the 30 m and 50 m isobaths in Kugmallit Bay and Mackenzie Bay, respectively. Black dashes and capital letters mark the vertical sections presented in the subsequent figures. Yellow dashes coarsely define the coutours of the delta region (inset). To avoid visual clutter, only the few stations discussed specifically in the text are identified.

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Fig. 2. Surface distributions of salinity, nitrate, ammonium, DON, phosphate, silicate, DOP and DOC in the coastal Beaufort Sea during July–August 2009. The mean position of the shelf break is indicated by the black line (75 m isobath) and dashed circles denote coastal stations influenced by sea-ice melt (see text).
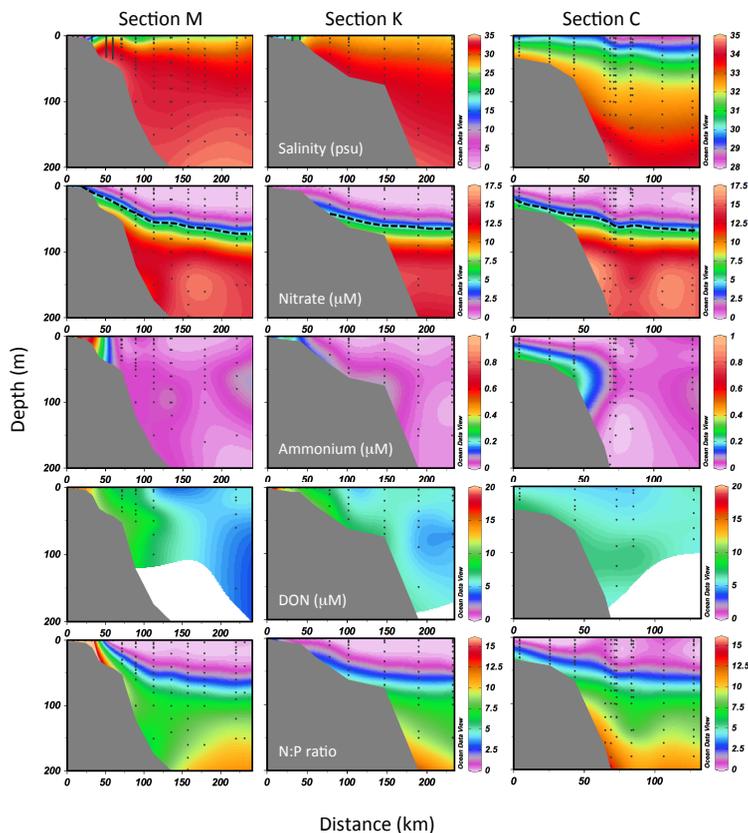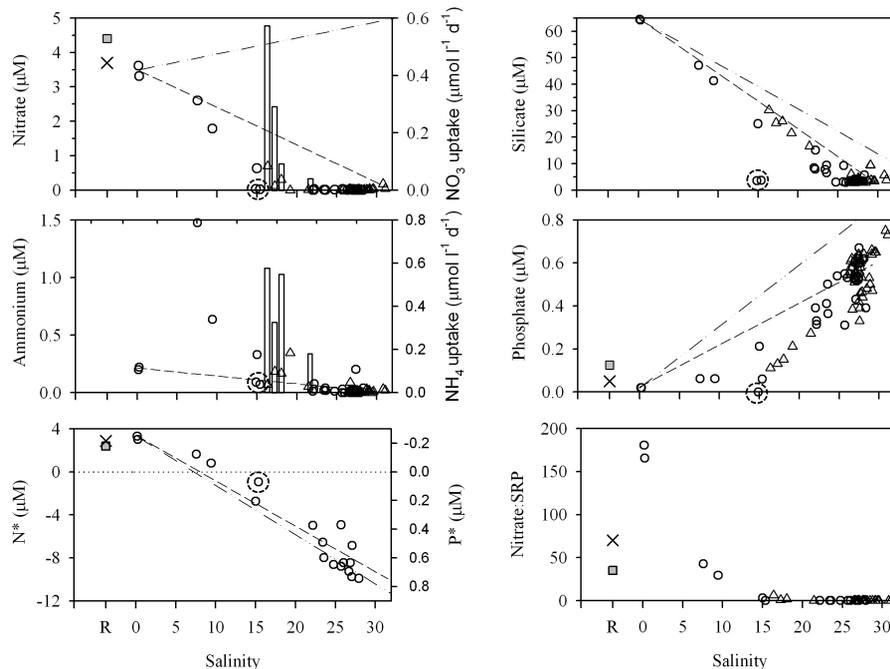
Fig. 3. Vertical distributions of salinity, nitrate, ammonium, DON and the nitrate : SRP ratio along sections M, K and C. The location of each section is given in Fig. 1. The dashed line indicates the depth where the concentration of nitrate equates 5 μM.

Fig. 4. Concentrations of nitrate, ammonium, phosphate, silicate, N^*, P^* and the N : P ratio in the Mackenzie River at Inuvik (R) and on the shelf as a function of salinity during 2009 (circles = marine stations west of 135° W; triangles = marine stations east of 135° W; squares = discharge weighted mean concentration; crosses = median concentration). Vertical bars indicate daily uptake rates of nitrate and ammonium estimated from ^{15}N tracer techniques. Oblique lines provide hypothetical conservative mixing relationships between riverine and marine water-mass end-members, excluding stations that were influenced by upwelling (salinity > 30 psu); the dashed line is the theoretical dilution line for river water mixing with summer water offshore, whereas the dash-dot-line is for river water mixing with winter offshore water (see Fig. 9b). Dashed circles indicate stations 670 and 680 (see text).

Fig. 5. Concentrations of DON, DOP and DOC and elemental ratios (DOC : DON, DON : DOP and DOC : DOP) in the Mackenzie River at Inuvik (R) and over the shelf as a function of salinity during 2009 (circles = stations west of 135° W; triangles = stations east of 135° W). Dashed lines provide hypothetical conservative mixing relationships between riverine and marine water-mass end-members, excluding stations that were influenced by upwelling (salinity > 30 psu).

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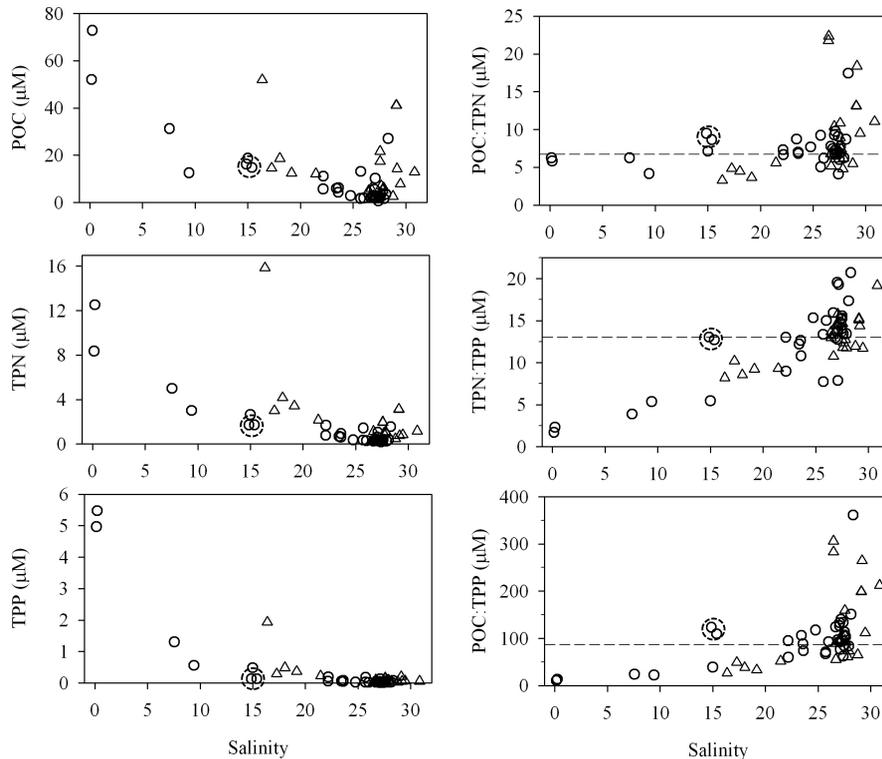
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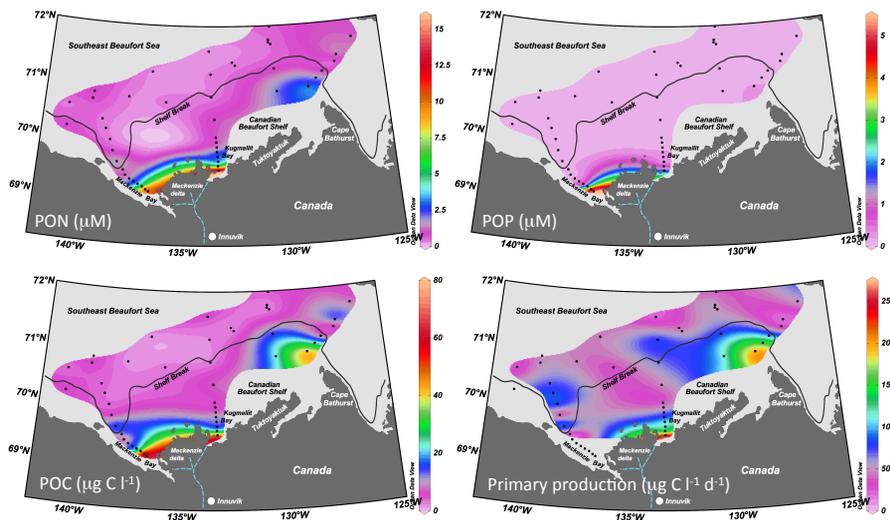
Fig. 6. Distributions of **(a)** TPN, **(b)** TPP, **(c)** POC, and **(d)** primary production at the surface in the coastal Beaufort Sea during July–August 2009.

Fig. 7. Concentrations of TPN, POC and TPP and elemental ratios (POC : TPN, TPN : TPP and POC : TPP) in the Mackenzie River (T = Tsiigehtchic, I = Inuvik) and over the shelf as a function of salinity during 2009 (circles = stations west of 135° W; triangles = stations east of 135° W). Oblique dashed lines provide hypothetical conservative mixing relationships between riverine and marine water-mass end-members, excluding stations that were influenced by upwelling (salinity > 30 psu). Horizontal dashed lines indicate elemental ratios of 6.7 for POC : TPN, 13.1 for TPN : TPP and 87 for POC : TPP based on previous observations of diatom blooms in the area (see Discussion). Dashed circles indicate stations 670 and 680 (see text).

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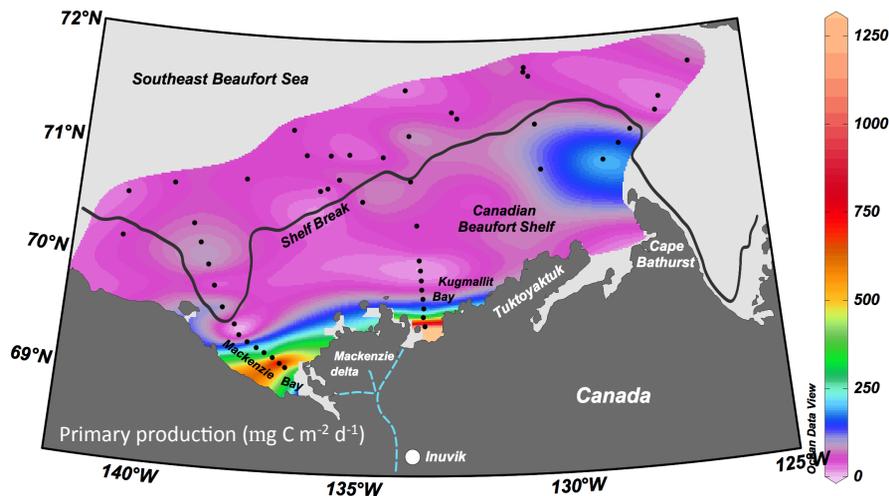
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Fig. 8. Spatial distribution of daily primary production during July–August on the shelf, based on a combination of direct measurements and empirical relationships (see text). The sites at which direct measurements were made are given by the white squares in Fig. 1.

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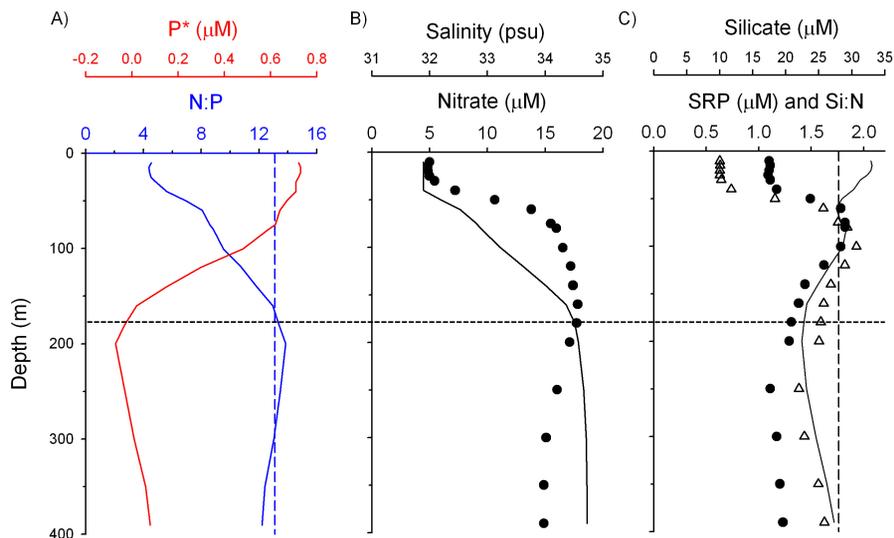
Fig. 9. Vertical profiles of **(a)** the nitrate : SRP ratio (solid blue line; dashed blue line = drawdown ratio of 13.1) and P^* (solid red line), **(b)** salinity (solid line) and nitrate (circles), and **(c)** SRP (circles), silicate (triangles) and the Si : N ratio (solid line; dashed line = drawdown ratios of 1.75) in Amundsen Gulf at the time of the winter nutrient maximum. The horizontal dashed line marks the depth of the deepest water shown to upwell at the surface on the Mackenzie shelf (from Tremblay et al., 2011).

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