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Nutrient and organic matter patterns across the Mackenzie River, estuary and shelf during the seasonal recession of sea-ice

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Abstract

Suspended material, nutrients and organic matter in Mackenzie River water were tracked along a 300 km transect from Inuvik (Northwest Territories, Canada), across the estuarine salinity gradient in Kugmallit Bay, to offshore marine stations on the adjacent Mackenzie Shelf. All particulates measured (SPM, POC, PN, PP) declined by 87–95% across the salinity gradient and levels were generally below conservative mixing. Organic carbon content of suspended material decreased from 3.1% in the river to 1.7% in shelf surface waters while particulate C:N concurrently decreased from 17.1 to 8.6. Nitrate and silicate concentrations declined by more than 90% across the salinity gradient, with nitrate concentrations often below the conservative mixing line. Phosphate concentrations increased from 0.03 μmol/L in the river to 0.27 μmol/L over shelf waters, thereby changing the inorganic nutrient regime downstream from P to N limitation. Dissolved organic carbon decreased conservatively offshore while dissolved organic N and P persisted at high levels in the Mackenzie plume relative to river water, increasing 2.7 and 25.3 times respectively. A deep chlorophyll-*a* maximum was observed at two offshore stations and showed increases in most nutrients, particulates and organic matter relative to the rest of the water column. During river passage through the Mackenzie estuary, particulate matter, dissolved organic carbon and inorganic nutrients showed sedimentation, dilution and biological uptake patterns common to other arctic and non-arctic estuaries. Alternatively, inorganic content of particles increased offshore and dissolved organic N and P increased substantially over the shelf, reaching concentrations among the highest reported for the Arctic Ocean. These observations are consistent with the presence of a remnant ice-constrained ('stamukhi') lake from the freshet period and a slow flushing river plume constrained by sea-ice in close proximity to shore. Nutrient limitation in surface shelf waters during the ARDEX cruise contributed to the striking deep chlorophyll-*a* maximum at 21 m where phytoplankton communities congregated at the margin of nutrient-rich deep ocean waters.

Regional index terms: Canada; Northwest Territories; Mackenzie estuary
Geographic bounding coordinates: 68–71°; N; 133–135°; W
Keywords: Arctic; Estuary; Nutrients; Organic matter; Particulates, Salinity gradient

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1. Introduction

The Arctic Ocean is the most river-influenced of the world's oceans and supports a productive aquatic ecosystem despite a short growing season and extensive sea ice coverage (Wheeler et al., 1996; Opsahl et al., 1999). Rivers draining to the Arctic Ocean deliver considerable freshwater, nutrient and organic matter fluxes that exert strong controls on the productivity, salinity and water circulation in the Arctic Ocean (Aagaard and Carmack, 1989; Holmes et al., 2001). This flux of material is proportionally more important to coastal arctic biota compared to more temperate regions since strong freshwater stratification across marine shelves limits the upwelling of nutrient-rich deep waters (Macdonald et al., 1987). Nutrient and organic matter processing across arctic estuaries is therefore an essential control on the shelf ecosystem. However, arctic estuarine biogeochemistry remains relatively understudied despite rapid progressing climate changes in the region (Moritz et al., 2002).

Most biogeochemical studies in arctic rivers and estuaries have focused on the source and fate of organic carbon due in part to its massive stores in the Arctic Ocean basin (Whitehouse et al., 1989; Cauwet and Sidorov, 1996; Kohler et al., 2003; Amon and Meon, 2004). Fewer data are available for nitrogen and phosphorus patterns downstream (Cauwet and Sidorov, 1996; Holmes et al., 2001; Dittmar et al., 2001). The Mackenzie River, the largest North American river draining to the Arctic Ocean, has among the least available data regarding estuarine processing of nutrients and organic matter (Brunskill et al., 1973; Macdonald et al., 1987; Whitehouse et al., 1989; Macdonald and Yu, 2006). Most attention on the lower Mackenzie River has been directed toward its substantial sediment load (Carson et al., 1998), the potential for hydrocarbon development in the region (Yunker et al., 1993) and hydrography and biological processes in the adjacent coastal ocean (Macdonald et al., 1987; Parsons et al., 1988; Carmack et al., 2004; Garneau et al., 2006).

Though open water patterns of river material across arctic estuaries are expected to be similar to lower latitude counterparts (Lisitsyn, 1995; Macdonald and Yu, 2006), the role of offshore pack ice and freshwater stratification over arctic shelves remains unclear. Ice-free estuaries and ocean shelves often process river water by sequestering particulate matter and converting inorganic nutrients to biogenic particles and dissolved organic matter, before offshore mixing and dilution (Lisitsyn, 1995). Upstream migration of brackish water driven by tides, an extended freshwater-saltwater transition zone and a general three-layer structure over oceanic shelves (freshwater layer-mixing layer-seawater layer) are also common characteristics (Lisitsyn, 1995). In the case of the Mackenzie, we postulated the above structure and nutrient patterns could differ significantly due to several characteristics. A coastal ice dam ('stamukhi') forms along the edge of the landfast ice each winter, and this delays the release of river water into the coastal shelf environment until after the period of maximum discharge in late spring (Carmack and Macdonald, 2002; Galand et al., in press). After the break-up of the stamukhi and release of constrained river water in late June, the proximity and persistence of the Arctic pack ice, combined with recirculation processes over a small, shallow shelf, inhibit the wider dispersal and circulation of river-water into the coastal ocean (Macdonald et al., 1987; Carmack et al., 2004; Retamal et al., 2007a). Additionally, the tidal range along the Beaufort coast, and the potential for back-surging of coastal seawater beneath the surface layer of river-water, is low relative to many estuaries.

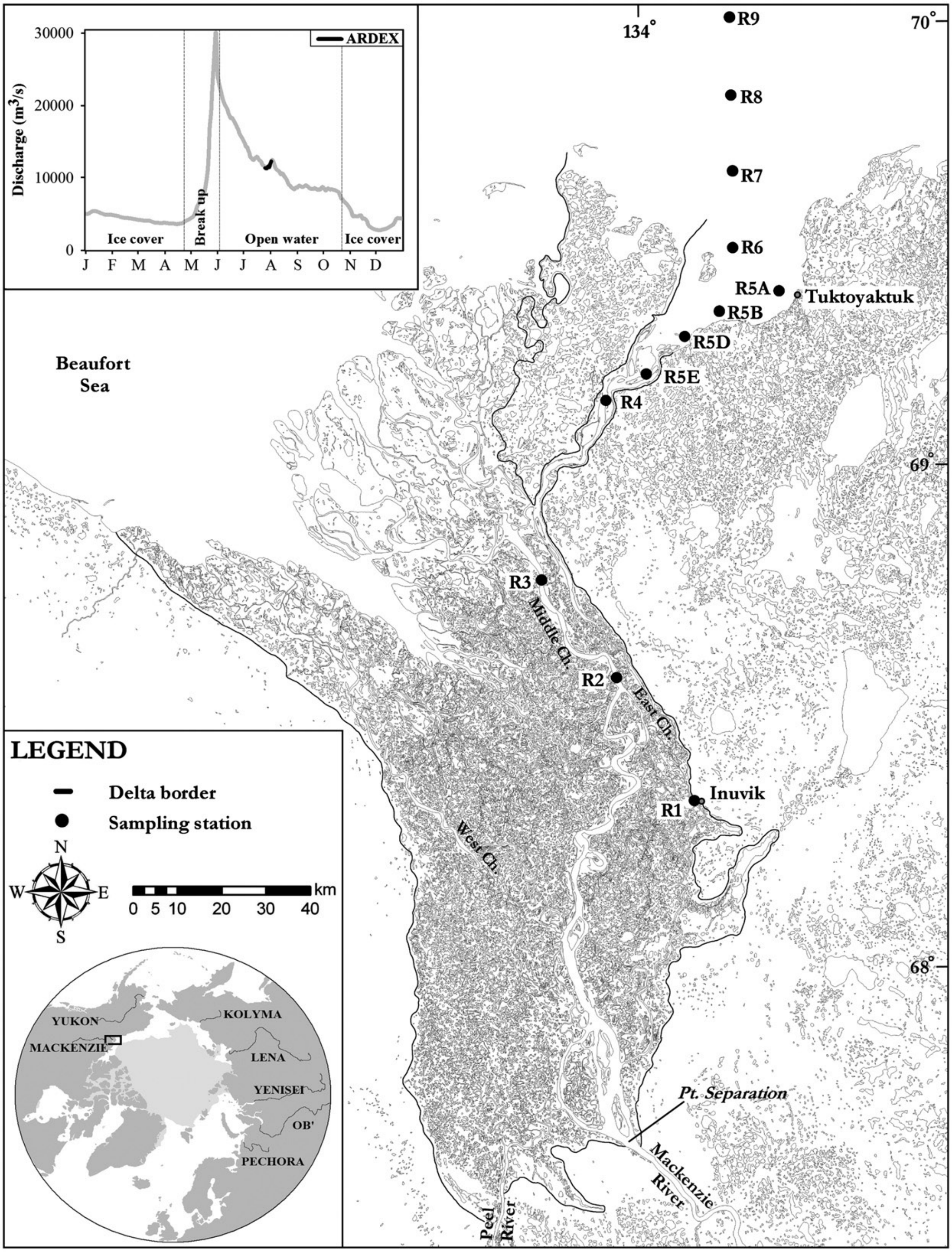
The goals of the present study were to determine the downstream and vertical patterns of nutrients and organic matter across the Mackenzie estuary during the seasonal recession of sea-ice in the coastal Beaufort Sea, and to assess the degree that the Mackenzie structure and nutrient patterns may differ from other arctic estuaries. We addressed these goals by way of a 300 km sampling transect down a series of freshwater river stations, across the freshwater-saltwater transition zone to 100 km beyond the river mouth on the coastal shelf. This study was a component of the Arctic River-Delta Experiment (ARDEX), a research program focused on bridging the Canadian Arctic Shelf Exchange Study (CASES) to the coastal inshore and riverine environments.

2. Methods

2.1. Study area

The Mackenzie River is the fourth largest river draining to the Arctic Ocean (284 km^3) and represents the largest single riverine source of sediments to the Arctic Ocean (Holmes et al., 2002). The Mackenzie drains to the Beaufort Sea (Mackenzie Shelf) through several branches of the Mackenzie Delta in Canada's western

Fig. 1. The Mackenzie River Delta and sampling stations during the ARDEX cruise, 26-July to 2-August, 2004. R1–R4 were river sites, R5 sites were estuarine while R6–9 were shelf sites. Daily 2004 discharge of the Mackenzie River above Arctic Red River (upstream of the delta) and circumpolar sea ice conditions for 2004 are shown inset.



ARDEX
Discharge (m3/s)
30000
20000
10000
0
Ice cover
Break up
Open water
Ice cover
J F M A M J J A S O N D
134°
70°
69°
68°
R9
R8
R7
R6
R5A
R5B
R5D
R5E
R4
R3
R2
R1
Tuktoyaktuk
Inuvik
Beaufort Sea
Middle Ch.
East Ch.
West Ch.
Pt. Separation
Mackenzie River
Peel River
LEGEND
Delta border
Sampling station
N
W
E
S
km
0 5 10 20 30 40
YUKON
MACKENZIE
KOLYMA
LENA
YENISEI
OB'
PECHORA

Arctic (Fig. 1). Winters in the region are cold and long (October-June) and river and shelf waters are covered with thick ice for much of the period. Local heating and a snowmelt driven river hydrology breakup river and shelf ice in late spring before a short open water season during the summer. Strong storms occur occasionally across the

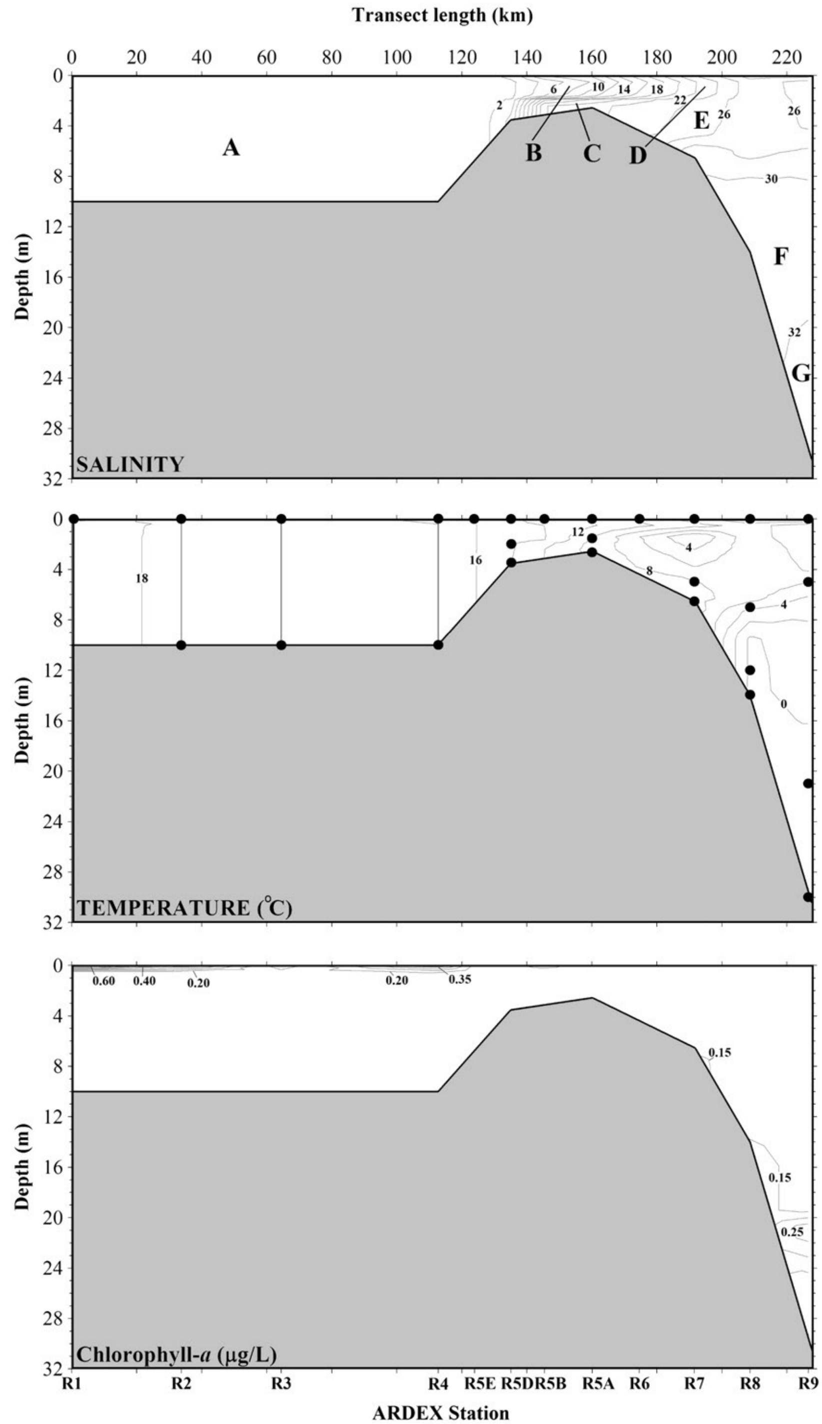


Fig. 2. Salinity, temperature and chlorophyll-*a* profiles of the Mackenzie ARDEX cruise track. Several water masses were delineated by the salinity profile: A. Mackenzie River; B. Estuary–River; C. Estuary–Shelf; D. Shelf–River; E. Shelf–MP (Mackenzie Plume); F. Shelf–LM (Lake Mackenzie); and G. Shelf–Deepwater. Note: R1–R4 depths represent mean river depth and dots represent sampling depths on the temperature plot.

shelf and tide influences are negligible due to the high latitude and open coastline. The Mackenzie River discharges to a relatively small offshore area during the summer compared to other large arctic rivers (Fig. 1; inset) and thus exerts a strong freshwater influence on shelf waters (Macdonald et al., 1987). This influence generally limits vertical mixing across the shelf and subsequent deep water nutrient inputs are restricted to small upwelling events (Carmack et al., 2004; Garneau et al., 2006). Across the estuary and shelf, nutrients are mostly supplied by the Mackenzie River or recycled throughout the water column. Autotrophic and heterotrophic production is generally highest across the estuary and shelf after ice-off in late spring when irradiance and nutrient inputs from the river peak (Parsons et al., 1988). During the decrease in river discharge over the summer, productivity decreases as surface waters become depleted in nutrients and primary producers are forced deeper in the water column (Carmack et al., 2004).

2.2. Field and analytical methods

Water samples were collected across a 12-station transect from the research vessel CCGS *Nahidik* from 26-July to 2-August, 2004 (Figs. 1, 2; Supplementary Table S1). Salinity, temperature and chlorophyll-*a* were measured at each site using a conductivity-temperature-depth profiler (RBR model XR-620). River samples (R1–4) were collected from surface and bottom waters, as well as the entire water column, using a plastic bucket, peristaltic pump or column-integrating sampler. Estuarine (R5 sites) and shelf (R6–9) water was collected from surface and bottom waters with additional samples at pycnocline and chlorophyll-*a* maximum layers, where applicable. Samples were collected by plastic bucket, peristaltic pump or 6.2 L Kemmerer sampler. All water samples were transferred to new, sample-rinsed 1 L HDPE bottles and stored in cool and dark conditions until on-board filtration, sample splitting and preservation was performed as soon as possible after collection.

All samples were passed through pre-combusted Whatman GF/C filters (1.2 µm; 16 h at 550 °C) in order to comply with historical datasets at Fisheries and Oceans Canada's Freshwater Institute as well as to more efficiently deal with high sediment loads in the river and estuary. Filters were dried (24 h at 100 °C) and retained for analyses and filtrate was split into several clean 60 mL or 125 mL HDPE bottles before preservation. Particulate matter (suspended particulate matter, particulate organic carbon, particulate nitrogen and particulate phosphorus; SPM, POC, PN and PP), dissolved inorganic nutrients (nitrate, ammonium, phosphate and silicate) and dissolved organic matter (dissolved organic carbon, dissolved organic nitrogen and dissolved organic phosphorus; DOC, DON and DOP) were measured as described in Table 1.

3. Results

3.1. Environmental conditions

The annual hydrology of the Mackenzie River follows a pattern typical of most northern latitude rivers. Low flow during winter (November–April) is followed by basin snowmelt additions resulting in the annual peak discharge (May–early June) followed by an extended recession period throughout the open water season (June–October). ARDEX sampling occurred after annual peak discharge in the Mackenzie River during the latter part of the

Table 1
Description of analytical methods used in the present study

Constituent	Preservation	Storage	Analytical method	CV (%)	MDL (µmol/L)
SPM[a]	Room temp.	24 h	Gravimetric	0.2	0.2*
POC[b]	Room temp.	1–4 weeks	Elemental analysis	3.6	1
PN[b]	Room temp.	1–4 weeks	Elemental analysis	4.0	0.1
PP[b]	Room temp.	1–4 weeks	Digest-molybdate blue spectroscopy	12.5	0.01
Nitrate[c]	Frozen	2–4 months	Ion chromatography/colorimetric	0.9	0.2
Ammonium[a]	4 °C	24 h	Indophenol blue spectroscopy	2.1	0.5
Phosphate[a]	4 °C	24 h	Molybdate blue spectroscopy	1.0	0.01
Silicate[c]	4 °C	2–4 months	Acid molybdate spectroscopy	2.9	0.1
DOC[c]	Frozen	2–4 months	Combustion/infrared gas analysis	2.3	13
TDN[b]	4 °C	1–2 weeks	High temperature photo-oxidation	2.0	0.6
TDP[b]	4 °C	1–2 weeks	High temperature photo-oxidation	12.3	0.01

Phosphate = soluble reactive phosphorus.
MDL indicates method detection limit and CV is the coefficient of variation of the method. *measured in mg/L.
Samples analyzed at: [a]Aurora Research Institute, Inuvik, Canada; [b]Freshwater Institute, Winnipeg, Canada; [c]SFU Limnology Lab, Burnaby, Canada.
Estimates: DON = TDN–Nitrate–Ammonium; DOP = TDP–Phosphate.
All samples analyzed using Freshwater Institute methods for the analysis of freshwater (Fisheries and Oceans Canada, 2004).

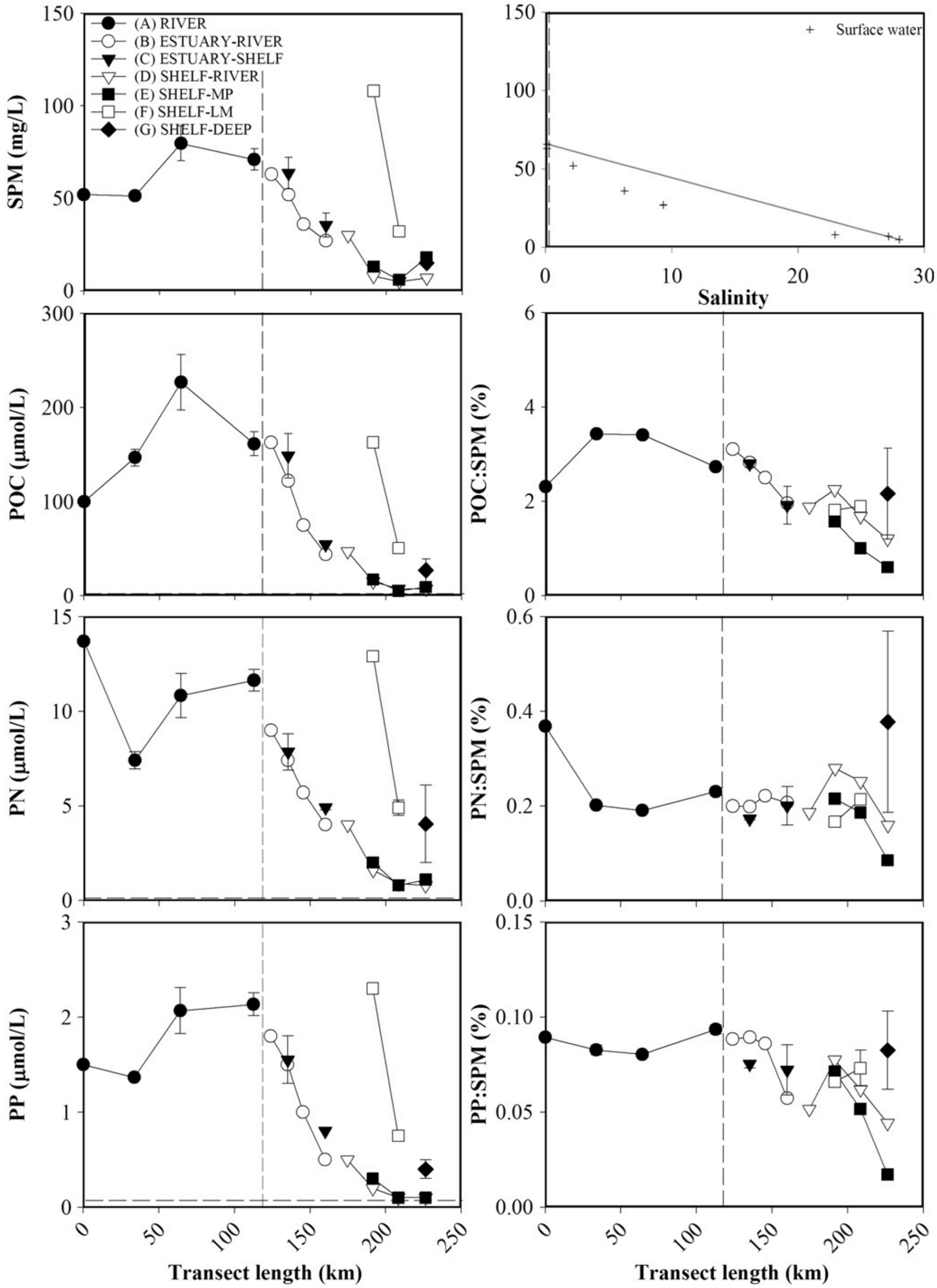


Fig. 3. Particulate measures and organic content of SPM across the ARDEX transect with water masses delineated. Surface SPM relative to the conservative mixing line is shown (river data averaged) in the upper right panel and is consistent with all particle patterns. Vertical broken lines indicate the start of brackish waters. Horizontal broken lines are analytical limits of detection. Error bars are ±1 S.E.

hydrograph recession, approximately halfway through the open water season (Fig. 1; inset). Total discharge from the Mackenzie River during 2004 was an estimated 251 km^3, 12% below the annual historical mean estimate of 284 km^3 (Water Survey of Canada, 2005).

At the time of sampling, the salinity transition zone occurred over approximately 50 km, beginning at station R5E and stabilizing by station R8. Using salinity and temperature profiles, several water masses were delineated (Fig. 2). Mackenzie River water (A) was well mixed

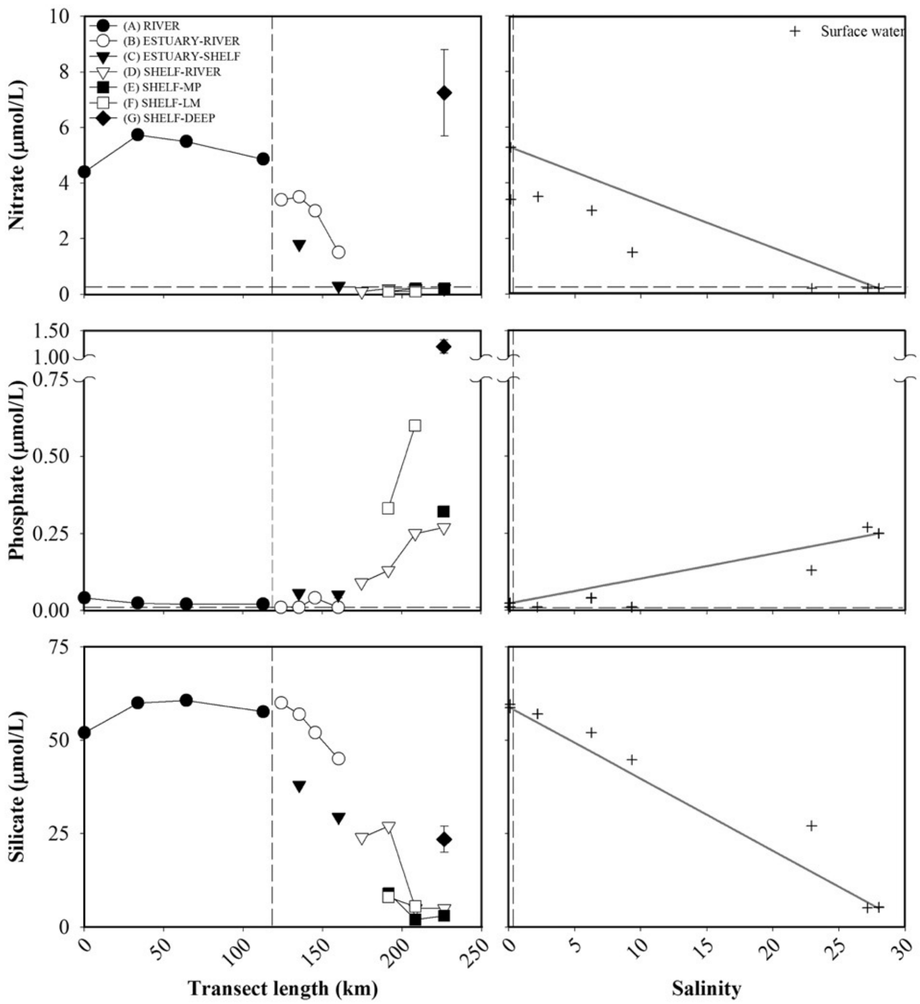


Fig. 4. Inorganic nutrients across the ARDEX transect with water masses delineated (left panels) and surface water concentrations against the conservative mixing line (river data averaged; right panels). Vertical broken lines delineate the start of brackish water. Horizontal broken lines are analytical limits of detection. Error bars are ±1 S.E.

throughout its water column, low in salinity and relatively high in temperature. Across the estuary, lower salinity, high temperature river water (B) flowed above deeper waters of higher salinity and lower temperature (C). The river water layer continued over the shelf up to 2 m in thickness (D). Below this layer were higher salinity shelf waters from approximately 2–5 m (E) and comparable to layer C and possibly reflective of older, mixed Mackenzie plume waters (MP). Between 5–20 m were higher salinity waters (F), possibly a remnant of stamukhi-constrained winter and freshet water from Lake Mackenzie (LM) (Carmack et al., 2004). Below this depth, cold, high salinity deep ocean waters (G), consistent with Pacific Ocean intrusion (Carmack et al., 2004) or Arctic Ocean water, were observed. Deep chlorophyll-*a* maximum layers were evident at stations R8 and R9 at 12 m and 21 m respectively.

The open-water portion of the Beaufort Sea was more extensive than normal during the cruise period (Canadian Ice Service, 2004) and the sea ice front at the time of R9 sampling was 50–100 km north of this station. From 29 to 30-July and 1 to 2-August, frontal storms from the northwest were experienced creating storm surges toward the south and increased water levels throughout the coastal and upstream delta areas. Tides were generally weak during the cruise measuring between 0.3 and 0.7 m (at Tuktoyaktuk, NT; Canadian Hydrographic Service, 2004) and increased during R5 sampling.

3.2. Particulate matter

All particulate measures followed a predictable change from the particle-rich riverine environment through to the depleted shelf stations (Fig. 3). Particulate concentrations decreased by 87% to 95% in surface waters and these downstream changes were generally below the conservative mixing line. Across the entire transect, most particles measured increased with depth. Particles from layer (F) were at notably high concentrations, driven mostly by increases in particles just above the sea bed. At the chlorophyll-*a* maximum layer of station R9, all particulates were higher than at the bottom of the water column. Riverine material was mostly inorganic in composition (~97%) and the organic content of all particles (Fig. 3) decreased from the riverine environment (POC, 3.10; PN, 0.22; PP, 0.09%) toward shelf waters (1.46; 0.18; 0.06%) with increases at chlorophyll-*a* maximum layers (2.48, 0.39, 0.09%). Particulate C:N:P ratios were variable but shifted towards the classic Redfield ratio for phytoplankton (106:16:1; Redfield, 1958) in the deep offshore waters.

3.3. Dissolved inorganic nutrients

Silicate and nitrate were the most abundant of the measured inorganic nutrients throughout the transect (Fig. 4). Silicate in surface waters decreased over an order of magnitude in concentration from river to shelf sites while surface nitrate concentrations declined similarly, from 4–6 μmol/L in the river to levels below detection (<0.2 μmol/L) across shelf stations. Silicate showed relatively strong conservative decreases downstream in surface waters ($r^2=0.96$, $n=12$,

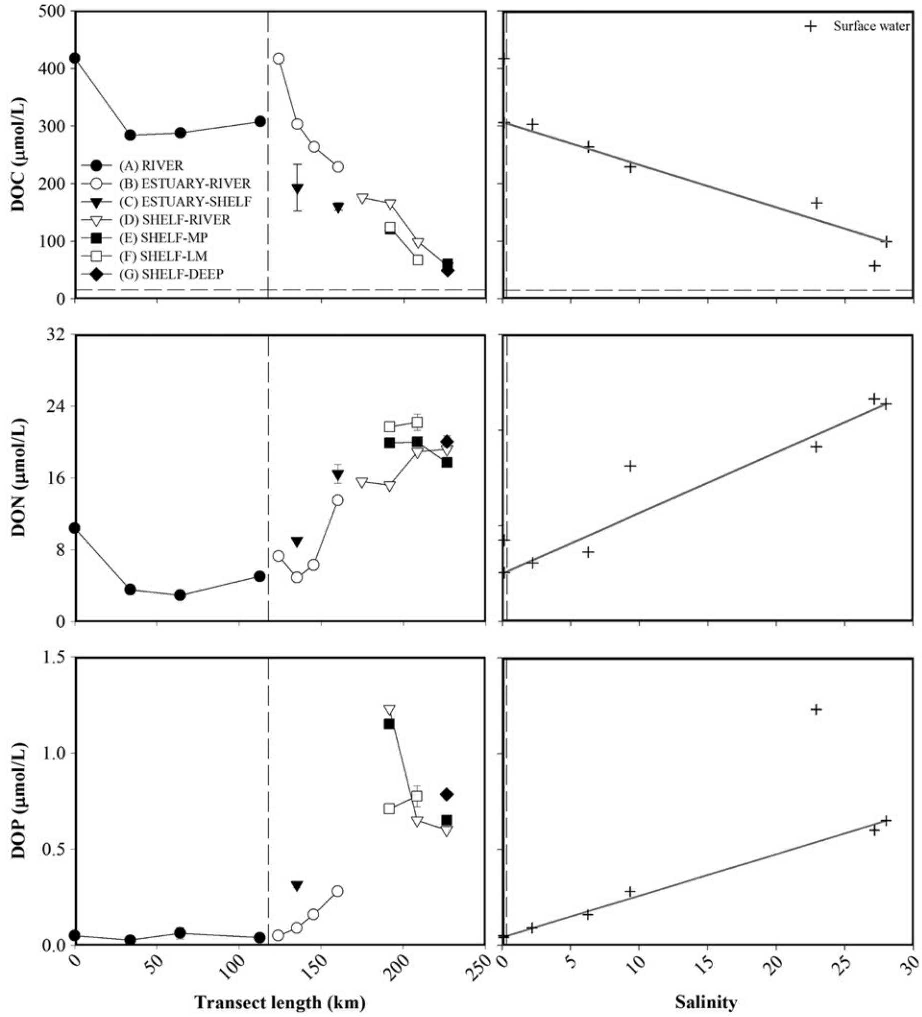


Fig. 5. DOC, DON and DOP concentrations across the ARDEX transect with each water mass delineated (left panels) and surface water concentrations against the conservative mixing line (river data averaged; right panels). Vertical broken lines indicate the beginning of brackish waters while horizontal broken lines indicate the analytical detection limit. Error bars are ±1 S.E.

$p<0.001$) whereas nitrate was less conservative ($r^2=0.86$, $n=12$, $p=0.001$), showing several data points below the predicted mixing line. Both nutrients showed well-mixed patterns through the river before stratification effects in the estuary, where relatively nutrient-rich river water overtopped depleted shelf waters. Over the shelf, deep ocean water showed elevated concentrations of silicate and nitrate but were otherwise depleted in the surface waters over the shelf.

Ammonium across the transect (not shown) was low in concentration and only detectable within error at R5D below the pycnocline (1.1–1.2 μmol/L). Surface phosphate (Fig. 4) increased from the river to shelf stations in a somewhat conservative fashion with several data points showing slightly lower levels than expected through mixing ($r^2=0.86$, $n=12$, $p=0.001$). Stratification was observed through the estuarine sites while the river sites were well mixed. Across the shelf, phosphate levels began to increase with depth, with large increases observed in the last shelf site, within the deep marine waters.

3.4. Dissolved organic matter

DOC showed conservative decreases across the transect ($r^2=0.89$, $n=12$, $p<0.001$; Fig. 5). Surface concentrations showed steady seaward declines after the river with some stratification effects where DOC was higher in surface waters. There were no observed changes in DOC levels at the chlorophyll-*a* maximum layers. Further details concerning DOC and colored dissolved organic matter (CDOM) during the ARDEX sampling period are given in Retamal et al. (2007b) and Vaillières et al. (2008-this issue). DON and DOP increased approximately four-fold and ten-fold respectively in the surface waters downstream from the Inuvik R1 station, however caution should be exercised when using DOP data as errors are often high using the subtraction method (Table 1). Each measure showed roughly conservative behavior ($r^2=0.90$ and 0.69, $n=12$, $p<0.001$ and 0.01) downstream with an outlier at station R7 for DOP. DON was well mixed throughout the water column in the river before stratification patterns appeared in the estuary and shelf regions. Deep water samples were slightly elevated in DON compared to other measures in the water column at R8 and R9. The vertical distribution of DOP was similar to DON with well-mixed river sites and stratified estuarine stations with a relatively organic rich layer underneath a depleted upper layer. Shelf stations showed well mixed to slight increases with depth except for the R7 site, which had a high surface measurement. Deepwater

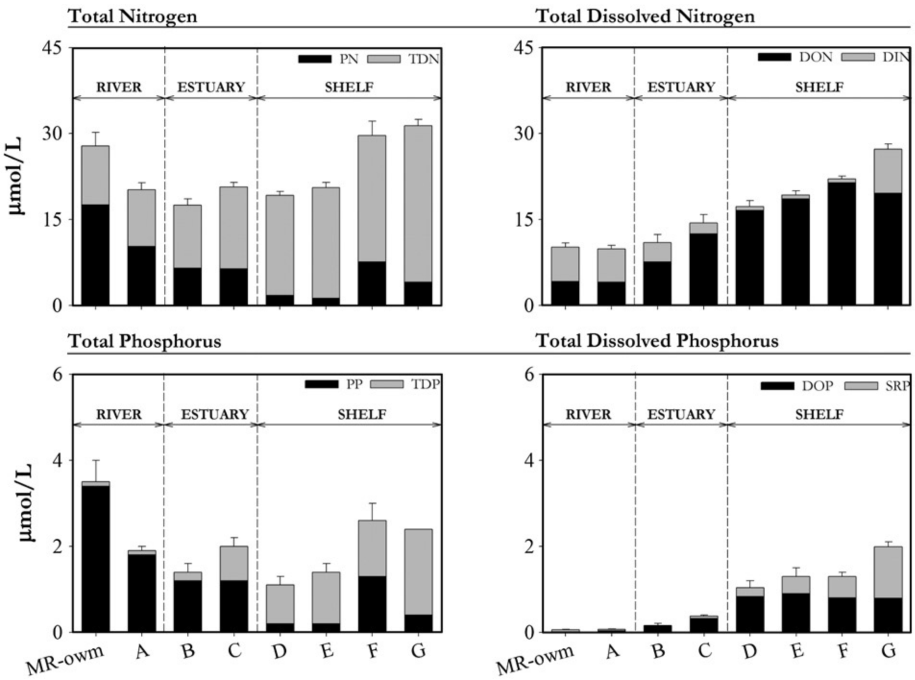


Fig. 6. Composite nitrogen and phosphorus measures for several water masses along the ARDEX transect. Errors indicate +1 S.E. 'MR-owm' is Mackenzie River open water mean composition at the Arctic Red River discharge station during 2004 (Emmerton et al., in press). A: Mackenzie River–ARDEX; B: Estuary–River; C: Estuary–Shelf; D: Shelf–River; E: Shelf–MP; F: Shelf–LM; G: Shelf–Deep.

Table 2
Mean nutrient ratios of each water mass across the ARDEX transect and 2004 mean open water data from rivers inflowing to the Mackenzie Delta

Ratios	River–open water mean [a]	River–ARDEX (A)	Estuary–river (B)	Estuary–shelf (C)	Shelf–river (D)	Shelf–MP (E)	Shelf–LM (F)	Shelf–deep (G)
TOC:TN	23.7	24.0	23.1	13.5	7.6	4.6	5.6	2.4
TOC:TP	195.7	261.8	302.0	175.7	96.0	66.0	64.8	31.9
TN:TP	8.4	11.1	14.4	10.4	17.1	14.9	12.0	13.1
POC:PN	20.1	17.1	14.7	15.0	9.4	7.6	11.1	6.9
POC:PP	105.8	94.2	83.7	82.0	77.3	65.6	69.0	64.0
PN:PP	5.3	5.7	5.9	5.6	8.3	8.6	6.3	9.4
TDN:TDP	229.2	172.4	92.0	34.6	20.0	15.6	17.9	13.8
DOC:DON	82.6	84.9	46.7	15.6	7.9	4.6	3.9	2.5
DOC:DOP	3.1E+4	8.7E+3	4.4E+03	506.1	179.8	98.8	114.1	62.6
DON:DOP	421.8	112.4	81.8	34.4	24.9	21.4	28.7	25.0
POC:SPM(%)	3.4	3.1	2.6	2.4	1.8	1.1	1.9	2.2
PN:SPM(%)	0.20	0.22	0.21	0.19	0.22	0.16	0.20	0.38
PP:SPM(%)	0.08	0.09	0.08	0.07	0.06	0.05	0.07	0.08

All ratios are mol:mol except for SPM ratios which are mass percent.
[a] 2004 open water flow-weighted mean concentrations from the 3 primary inflow rivers to the delta (Emmerton et al., in press).

concentrations were slightly higher than concentrations in the upper water column.

3.5. Total nutrients and nutrient ratios

TDN through the entire transect was largely composed of organic nitrogen (~75%), changing from 42% in river sites to approximately 90% in the shelf region. A notable increase in DIN relative to DON was observed in deep layer G waters (Fig. 6). Total nitrogen in river water was split evenly into the particulate and dissolved forms, consistent with similar measures in the Mackenzie River (Anema et al., 1990a,b). Through to the shelf waters, this fraction decreased sharply to approximately 20% particulate nitrogen with a notable increase in TDN in deep ocean waters. DOP made up about 50% of river TDP and increased to 67% in the estuarine and shelf waters. Similar to nitrogen, an increase in inorganic forms was apparent in deep marine waters (Fig. 6). Particulate phosphorus composed a much higher fraction of TP when compared to nitrogen through all stations. Over 95% of all phosphorus in the Mackenzie River was in particulate form dropping to 41% in the estuary and shelf stations. Similar to N, deep ocean waters were elevated in TDP relative to other sites. TOC in the river (not shown) was comprised of approximately 65% DOC during the time of sampling. Toward shelf waters, this proportion increased to as high as 89% in surface waters and decreased with depth.

The C:N:P ratios deviated from the classic Redfield ratio at many sites (Table 2). River water was usually furthest away from unison with Redfield values, often exhibiting high carbon-related ratios typical of terrestrial signatures. DON:DOP showed a progression toward the Redfield ratio from R1-R9. Through the water column, chlorophyll-*a* maximum layers usually showed ratios closer to the Redfield value compared to other depths.

4. Discussion

4.1. Biogeochemical and hydrological context

Several factors need to be considered to place the ARDEX results into appropriate biogeochemical and hydrological context. First, river chemistry changes substantially over the annual cycle and is strongly coupled with basin hydrology (Macdonald and Yu, 2006). ARDEX results provide a detailed snapshot of one period during seasonal recession of coastal sea-ice. The river at this time was likely most influenced by runoff derived from liquid precipitation plus lake water outflows, which translated into high nitrate and silicate levels, lower DOM concentrations and reduced turbidity compared to the freshet (Emmerton et al., in press). The freshet period delivers larger water volumes and is more influenced by runoff from surface soils and organic matter resulting in dilute nutrient concentrations, high DOM levels and peak turbidity (Finlay et al., 2006). Though the open water nutrient regime of the Mackenzie River is known relatively well (Telang et al., 1991; Emmerton et al., in press), less is known during the rising discharge phase of the freshet period due to the difficulty of sampling the river during breakup.

Second, the ARDEX cruise sampled the Middle and East channels of the river and then tracked the estuarine transition through the Mackenzie East Channel into

Kugmallit Bay. While the flows are considerable through the East Channel, the largest discharges to the sea from the Mackenzie River system occur in the Middle Channel at Langley Island and in the Reindeer Channel below Lewis Channel (Carson et al., 1999). Annual discharges from the outer delta channels are not presently known with appreciable precision because of coastal backwater effects. However, based on using the Environment Canada 1-D channel model, the percentage of total annual Mackenzie sediment load discharged from the outer delta is about 40%, 34%, and 11% from Middle Channel, Reindeer Channel, and East Channel, respectively (Carson et al., 1999). Though sediment transport is not necessarily in direct proportion to water discharge, sediment estimates provide an indication of relative importance for nutrient fluxes. Prior work (Lesack et al., 1998; Pipke, 1996) has shown that the East Channel may be reasonably similar in nutrient composition to the Middle Channel, while western channels of the delta may differ somewhat because of influence from the Peel River.

Third, upstream penetration of brackish water in the form of a tidal salt wedge can be an important control on river mouth biogeochemistry, especially when considering turbidity maxima (Dodson et al., 1989). In the Mackenzie East Channel, relatively little up-channel brackish migration was observed. Using station R5D as a conservative location of the river mouth, less than 5 km of upstream migration occurred. Prior work has shown that coastal storm surges can be detected as far upriver as the Arctic Red River gauging station above the delta (Marsh and Schmidt, 1993), and suggests the possibility that seawater could move substantial distances into the delta. The results here indicate actual up-channel movement of estuarine water may be relatively modest because of the low tidal range and the strong river influence throughout the estuary.

Finally, whereas estuaries often develop a three-layer stratification structure (i.e., freshwater overlying the halocline and seawater layers), the Mackenzie system during ARDEX sampling was configured closer to a four-layer structure. The additional layer between the typical mixing (E) and true ocean water (G) layers is possibly a remnant of “Lake Mackenzie”, the ice-constrained (stamukhi) reservoir of Mackenzie winter and freshet waters (Carmack and Macdonald, 2002; Galand et al., in press). This water is released in late June and dominates shelf waters, eventually mixing with salinity rich ocean waters to depth. Open water river flow then establishes the fresher upper waters (D–E). This four-layer structure, built from several time-dependent sources, is a notable feature of the biogeochemistry of this coastal region.

4.2. River and delta controls on nutrient patterns

Some arctic rivers show relatively little downstream variation in their nutrient content as extensive biological activity is largely limited because of turbidity, turbulence, water color and temperature (Lara et al., 1998; Gordeev et al., 2004). A similar environment was apparent in the Mackenzie River (R1-R4) as dissolved and particulate material showed patterns consistent with physical influences, rather than biological. Suspended material was variable as expected between different river channels (Middle vs. East) and with possible effects of storm surges. Organic matter changed little down to the estuarine stations, likely because the residence time of the water between the stations was relatively short and with high turbidity there is limited opportunity for DOC photochemistry that would facilitate microbial processing (Febria et al., 2006). Primary production was also severely light-limited in the river (Retamal et al., 2007b). C:N:P ratios of suspended and dissolved material were consistent with terrestrially-derived material and similar to results from prior studies (Telang et al., 1991). There was no evidence of uptake-related losses of inorganic nutrients and releases of dissolved organic compounds.

Though the water column of the Mackenzie River may not play an important role in the control of nutrients and organic matter, the Mackenzie’s large freshwater delta does provide a setting suitable for significant biological activity. There are about 45,000 floodplain lakes in the delta (Emmerton et al., 2007), covering about 25% of its surface area, and these are environments where sedimentation is considerable, primary productivity is substantial and nutrient uptake is intense. Data from these ‘ovens’ of biological activity revealed that annually flooded lakes transform river-derived inorganic nutrients to particulate and dissolved organic forms before draining back to delta rivers (Emmerton et al., in press). Thus, floodplain lakes represent an important control on river material ultimately delivered to the Mackenzie estuary. However, large lake-induced downstream changes across river sites were not observed during ARDEX as lake drainage would have been modest at that time relative to the peak river discharge period.

4.3. Nutrient patterns relative to other arctic rivers

Our results here have filled an important data gap for circumpolar arctic estuaries (Table 3). Prior work on the river-to-shelf nutrient gradients in the Mackenzie had not included a full suite of dissolved organic nutrients. Some aspects of the Mackenzie nutrient patterns are

Table 3
River-shelf coupled data during the summer open water period from large rivers of the circumpolar arctic

	Eurasia[abcde]		Mackenzie[fgh]		Mackenzie[i]	
	Rivers	Shelf	River	Shelf	River	Shelf
Particulate matter						
SPM (mg L^{-1})	104–106	28	58	0–2	66	7
POC	112–115	13	104	7–17	170	9
PN	10.9–11.4	1.2	–	–	10.3	1.1
PP	–	–	–	–	1.82	0.13
Dissolved inorganic nutrients						
Nitrate	1.8	1.5	2.9	0.5	5.3	0.2
Silicate	16–45	5–15	54	3	59	12
Phosphate	0.25–0.29	0.18–0.45	0.15	0.47	0.03	0.22
DIN	2.5–2.6	2.9	–	–	5.8	0.7
Dissolved organic matter						
DOC	553–688	155–160	253–375	49.9	306	107
DON	11.5–14.3	7.4–8.0	–	–	4.1	17.1
DOP	–	–	–	–	0.04	0.83
Total nutrients						
TDN	15–37	15	–	–	10	18
TDP	0.35	0.6	–	–	0.07	1.04
Nutrient ratios						
DOC:DON	48.2–51.6	20.9–23	–	–	84.9	6.6
POC:PN	11.0–11.1	15.1	–	–	17.1	9.4
POC:SPM%	4	10–20	5	–	3.1	1.7

Rivers represent freshwater (salinity <0.3) while shelves are marine waters in the salinity range 20–30. All values are in μmol/L unless stated otherwise.
a-Dittmar et al., 2001; b-Lobbes et al., 2000; c-Cauwet and Sidorov, 1996; d-Kohler et al., 2003; e-Dittmar and Kattner, 2003; f-Macdonald et al., 1987; g-Whitehouse et al., 1989; h-Yunker et al., 1993; i-This study.

consistent with those previously reported for other arctic rivers, while other aspects appear to differ appreciably. The Mackenzie generally followed patterns for suspended particulate matter and dissolved inorganic nutrients commonly found in other estuaries, both arctic and non-arctic. Suspended material (SPM, POC, PN, PP) rapidly declined seaward across a relatively short estuarine mixing zone of about 50 km (extent of R5 stations). This was accompanied by increases in water transparency and declines in nitrate and silicate. These nutrient declines likely reflect a combination of mixing with more dilute shelf waters plus, consistent with the concurrent results of Vallières et al. (2008-this issue), uptake by phytoplankton and heterotrophic microbial communities in the estuary.

Other nutrient measures deviated substantially from patterns that are commonly found in other estuaries. Most conspicuous is the substantial increase in dissolved organic forms of nitrogen and phosphorus from the river fully into the estuarine shelf zone. Estuaries often show an increase in such organic compounds within biologically productive areas of the freshwater-saltwater transition zone but then rapidly decline as they are diluted and mixed with offshore waters (Lisitsyn, 1995; Dittmar et al., 2001). The Mackenzie shelf levels of DON and DOP during the ARDEX cruise appear to be among the highest thus far reported for the Arctic Ocean. This contrast is particularly striking for DON by comparison with patterns in the Lena (Dittmar et al., 2001), another arctic estuary where detailed nutrient data are available. A second deviation in the Mackenzie is that the pattern of phosphate concentrations, to some degree, mirrored the pattern of DON and DOP, rather than being diluted or drawn down biologically to low concentrations similar to nitrate and silicate. Macdonald et al. (1987) have previously noted this pattern in the Mackenzie. A third deviation is an apparent seaward enrichment in the inorganic content of suspended particulate material. Particles across the freshwater-saltwater transition zone are generally expected to become organically enriched as inorganic-rich river sediments are gradually replaced by living and dead biogenic particles offshore. The Lena has shown such organic enrichment of particles offshore (Dittmar et al., 2001) in contrast to the Mackenzie.

4.4. Effects of Lake Mackenzie

The novel patterns above each can be explained to some degree by the incompletely dispersed water mass of Lake Mackenzie that appeared to be present during the time of the ARDEX cruise. In the case of DON and DOP, these high concentrations may represent (a) a direct remnant of freshet river discharge earlier in the year, or alternatively, may represent (b) an in situ buildup of N- and P-rich organic compounds trapped within the non-dispersing water mass over the period of open water. Consistent with explanation (a), the synchronous fluorescence scans reported by Retamal et al. (2007a) showed shelf water spectra in October that were more similar to river freshet signatures than to the river signature at the time of sampling over the shelf. However, the DOC:DON:DOP ratios in river freshet water are inconsistent with the ratios observed in shelf waters during ARDEX (Table 2).

In support of explanation (b), it is well established that DON and DOP concentrations are often released as a by-product of grazing plus primary and secondary production (Lopez-Veneroni and Cifuentes, 1994; Fang, 2004). During ARDEX, dense zooplankton populations were observed through the estuary stations (A. Casper, unpublished data) while bacterial abundance and production varied little throughout the transect (Vallières et al., 2008-this issue). On the other hand, abundance and productivity of phytoplankton communities was lower in the estuary relative to the river at that time (Retamal et al., 2007b). These observations suggest that Mackenzie river water supported a more productive esturarine/shelf community when the large pulse of nutrient-rich Mackenzie freshet water first arrived. However by the time of ARDEX, levels of inorganic nutrients, and possibly photoreactive DOC, may have become depleted within the incompletely dispersed Lake Mackenzie. Also consistent with this hypothesis is the pattern of decline in DOC concentration along the gradient from river-water to the shelf waters, as might be expected if microbial communities had metabolized much of the DOC. Moreover, the DOC:DON:DOP ratios decline markedly from C-rich high-values in the river (i.e., humic-rich C) to roughly the Redfield ratio in case of DOC:DOP in Lake Mackenzie water, and N-rich values relative to the ratio in the case of DOC:DON and DON:DOP. These changes in ratios are consistent with C being respired away while N and P are conserved within the microbial plankton communities and eventually excreted or released via cell lysis into the water mass.

A possible explanation of the unusual gradient in the inorganic particle content is that Lake Mackenzie waters may still have contained some residual clay colloids derived from freshet waters that had not yet sedimented out or been otherwise dispersed into the ocean. In fact, measurements of particulates in the surface, ice-covered waters of Lake Mackenzie in June 2004 showed that the lake contained high concentrations of particulate inorganic material, and mostly in the small (<3 μm) fraction (Galand et al., in press). If colloidal clays are still indeed present in Lake Mackenzie waters, it is possible that some portion of the measured phosphate concentration is actually derived from small clay colloids that pass through the filtration step prior to chemical analysis. Alternatively, nitrogen limitation of phytoplankton communities in the constrained Lake Mackenzie waters may have allowed phosphate levels to build up. A third possibility is that because Mackenzie waters are calcium-rich, phosphate may release from fine carbonate particles upon mixing with seawater (Fox et al., 1985).

The striking deep chlorophyll-*a* maximum in the pycnocline is consistent with similar features in many other parts of the Arctic (Retamal et al., 2007b and references therein). However it contrasts with estuarine phytoplankton communities elsewhere, which most commonly proliferate in surface waters at the point in the salinity gradient where enough river sediment settles out to enhance water transparency and to allow nutrients from the river water to be exploited. Though light levels at 21 m depth were modest at the time of ARDEX, inorganic nutrient supply at the boundary with the deep water mass was considerably improved, particularly in nitrate, relative to the overlying low salinity waters. Compared to the Lena/Laptev Sea region which does not show strong stamukhi effects (Reimnitz et al., 1994), the coastal shelf region of the Mackenzie may be favored by the inshore retention of the remnant low nutrient, low salinity stamukhi lake water. The presence of the deep phytoplankton maximum may also draw down nutrients in the pycnocline, and thereby further restrict the upward transfer of nutrients from deeper nitrate-rich waters to the surface mixed layer.

5. Conclusions

The Mackenzie River contains high particulate N and P concentrations, and moderate levels of dissolved inorganic and organic nutrients. During open water passage through the Mackenzie estuary, suspended particulates and most inorganic nutrients follow sedimentation and biotic uptake patterns common in other arctic estuaries. Unexpectedly, however, the organic content of suspended particles declined from river to shelf waters. Furthermore, DON and DOP concentrations increased substantially from the river to the shelf, reaching concentrations among the highest reported for the Arctic Ocean. At the same time, DOC concentrations simultaneously declined from the river to the shelf and DOC:DON:DOP ratios changed from highly C-rich (terrestrial) values to near Redfield values. These striking patterns over the Mackenzie Shelf are consistent with the residual effects of the ice-constrained stamukhi lake. At the time of ARDEX, the surface layer over the shelf was poor in nitrate (despite high DON) and silicate. Thus, phytoplankton concentrations were low in these surface waters, and much of the biomass was located in a well-developed deep chlorophyll-*a* maximum at the boundary with deeper ocean water where nutrient supply was improved. The apparently strong influence of stamukhi lake waters over the shelf well after ice break-up implies that the stamukhi dam is a critical feature regulating the biogeochemistry of the Mackenzie shelf ecosystem, not only during the peak discharge period of the river (Galand et al., in press). but also during the coastal open-water period as sampled in the present study. The seasonal extent and duration of this ice-dependent feature are likely to change in response to ongoing climate warming in this region (ACIA, 2005) and the associated loss of summer sea ice and rise in relative sea level (Manson and Solomon, 2007). Such changes would have considerable impact on the biogeochemical properties of shelf waters in this arctic coastal ecosystem.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmarsys.2007.10.001.

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