Seasonal dynamics of dissolved nitrogen exports from two High Arctic watersheds, Melville Island, Canada

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ABSTRACT

This study examines the magnitude and seasonal patterns of dissolved N export during the 2006 melt season from two small watersheds on Melville Island, in the Canadian High Arctic. The dominant N species was dissolved organic nitrogen (DON), comprising >80% of the seasonal nitrogen flux from both rivers. The total DON and dissolved inorganic nitrogen (DIN, NH_4^++NO_3^-) yields from the catchments were similar (183 and 204 kg DON, and 46–42 kg DIN): however, on a per unit area basis the West catchment had greater yields of both DON and DIN. There were also differences in the temporal patterns and concentrations of the N species between the catchments, which may be a function of inter-catchment differences in vegetation cover. Low end-of-season DIN concentrations in the West river suggest there is strong biogeochemical retention of inorganic N in this catchment during the growing season relative to the East catchment, where stream NO_3^- concentrations increase through July. A decrease in DOC:DON ratios in the East river at the end of season also indicates a change in the composition of dissolved organic matter in this river that is not evident in the West river. The results illustrate that there can be large differences in the processes controlling nitrogen between two adjacent and similar catchments.

Key words | dissolved organic nitrogen, High Arctic, nitrate, nitrogen, watershed nutrient fluxes

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INTRODUCTION

Fluvial input of dissolved organic matter (DOM) represents an important source of carbon and bioavailable nitrogen (N) to freshwater and marine ecosystems (Cornell *et al.* 1995; Cole & Caraco 2001; Dittmar 2004; Pace *et al.* 2004; Mayorga *et al.* 2005). This export of nitrogen species (including DON, NO_3^- and NH_4^+) from terrestrial catchments plays an important role in aquatic elemental cycles and productivity because N is often a limiting nutrient for marine phytoplankton growth (Dittmar 2004).

Arctic catchments store a significant proportion of the world's soil organic matter (Dittmar & Kattner 2003) and Arctic rivers yield large amounts of terrigenous organic matter relative to other river basins (Hansell *et al.* 2004). In addition, observations indicate that the central Arctic has experienced substantial warming over the 20th century and especially over the last few decades, and models project this warming trend will continue over the next century (Serreze *et al.* 2000; ACIA 2005). Observations of recent changes in precipitation and snow cover suggest that precipitation in the Arctic appears to have increased, while snow cover duration and extent have decreased in most areas (Serreze *et al.* 2000; ACIA 2005). As two of the primary controls on the export of N from the land surface are the volume and the routing of catchment runoff through shallow soils (Hagedorn *et al.* 2000; Perakis 2002; Pinay *et al.* 2002; Hood *et al.* 2003*a*; Cooper *et al.* 2007), the effect of observed climate changes on runoff (timing and quantity), permafrost degradation and slope stability will exert significant influence on nutrient dynamics in Arctic catchments. There is, therefore, a pressing need to understand the response of terrestrial nutrient dynamics to changing water, permafrost and climate regimes in the High Arctic.

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The aim of this research was to determine the magnitude, seasonal patterns and composition of nitrogen exports from two small watersheds on Melville Island, in the Canadian High Arctic, as part of a broader investigation of the hydrological and catchment response to climate variability. Despite a significant interest in the climatic and hydrologic controls on N cycling and fluvial nitrogen export in the lower latitude and subarctic watersheds (Giblin *et al.* 1991; Campbell *et al.* 2000; Peterson *et al.* 2001; Williams *et al.* 2001; Boyer *et al.* 2002; Hood *et al.* 2003*a*,*b*; Weintraub & Schimel 2003; Donner *et al.* 2004), there is a dearth of research that pertains to nitrogen dynamics in the High Arctic (Chapin 1996; Stutter & Billett 2003), a region that is currently subject to substantial climate change (ACIA 2005). This study addresses the hydrologic controls on the 2006 nitrogen concentrations, yields and mass fluxes from paired adjacent watersheds, and evaluates the significance of N fluxes in these High Arctic watersheds by comparison with other alpine, northern (subarctic) and temperate environments where watershed N cycling has been more intensively studied.

METHODS

Site description

The research site is Cape Bounty (74°54′N, 109°35′W), Melville Island, Nunavut, Canada (Figure 1). This study reports on the rivers draining the two main watersheds unofficially named West (8.0 km^2) and East (11.6 km^2). The catchments are topographically similar, consisting of rolling hills and plateaus, with elevations ranging from approximately 5–125 m a.s.l. Both streams are incised into the surrounding terrain and drain into similar small lakes (Figure 1). The study area is underlain by continuous permafrost that develops an active layer ca. 0.5–1 m deep during the melt season. The geology consists of steeply dipping Devonian sedimentary sandstones and siltstones that are mantled with glacial and regressive early Holocene marine sediments (Hodgson *et al.* 1984). Vegetation and soil cover is heterogeneous and broadly varies with moisture conditions. Both catchments are dominated by polar desert soil/plant communities which are low moisture sites comprised of a mixture of rock or till (34–84%) and *bryophyte* spp. (2–42%). The next most abundant soil/plant community type is wet sedge type, where there is essentially 100% vegetation cover (dominated by *bryophytes* spp. (79%) and *eriophorum* L. (65%)) and soils remain saturated throughout the growing season (Atkinson & Treitz 2007). A third common soil/plant community is characterized by moderate soil moisture conditions and vegetation cover (dominated by blue–green algae crusts on the soil (47%) and *bryophyte* spp. (32%)) (Atkinson & Treitz 2007). A larger proportion of the West catchment is covered by the wet sedge (18%) and moderate moisture community types (11%) relative to the East where only 12% and 8% of the catchment area is covered by the same types, respectively. Also a larger fraction of the East catchment (81%) consists of polar desert type communities than the West catchment (71%) (Atkinson, D.M. unpublished data).

The climate is characterized by a cold winter with mean winter (December–February) temperatures of −32.2°C and a brief, cool summer with mean temperatures (June–August) of 1.9°C (Rea Point, 105 km northeast, 1969–1985, Meteorological Service of Canada). Mean annual precipitation is $<$150 mm and occurs primarily as snowfall. Rainfall is generally limited to trace precipitation and infrequent, low intensity events. Melt conditions occur from approximately mid-June to mid-August each year, and river discharge is dominated by snowmelt. Snow is extensively redistributed by the wind, and accumulates in concavities and channels where melt is extended long after the relatively brief snowmelt period.

Field methods

Local meteorological conditions were obtained at three stations in the catchments (Figure 1). Shielded air temperatures were collected from all stations at 1.5 m above the ground with either an Onset Hobo H8 temperature logger (0.4° accuracy, WestMet and EastMet) or a Humirel HTM2500 temperature-RH probe (±3%) logged with a Unidata Prologger (MainMet). Precipitation was recorded with Davis industrial tipping bucket gauges (0.2 mm resolution) logged with Onset Event loggers or the Unidata Prologger. Additional meteorological parameters were recorded at MainMet but are not reported in this study.

End-of-winter snowpack depth (snow water equivalent SWE) for 2005–2006 was calculated using a terrain

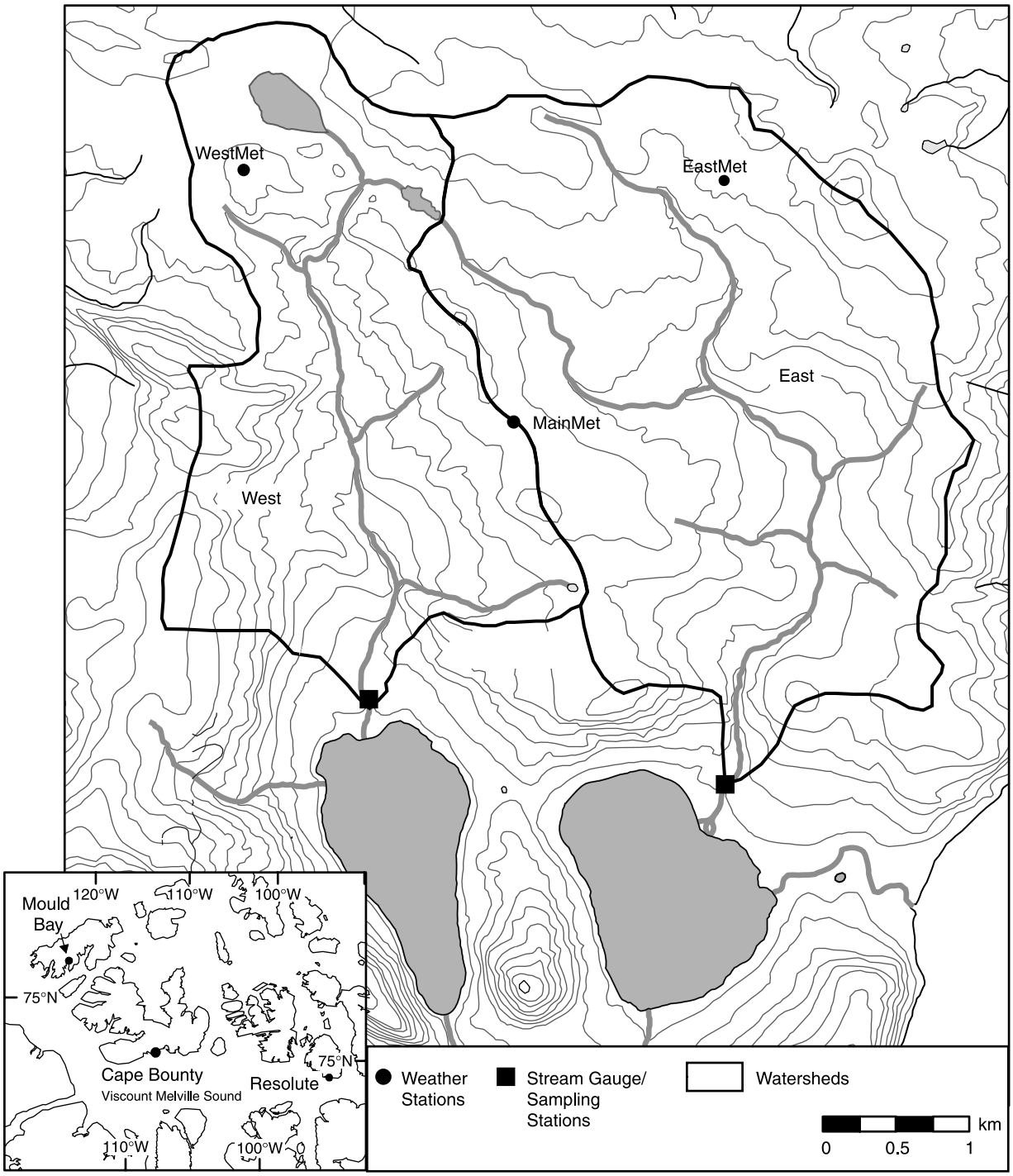

Figure 1 | Topographic map of the West and East watersheds at Cape Bounty, illustrating the locations of the weather stations and stream gauging and sampling sites. Contour interval 10 m. Source 1:50 000 NTS 78 F/15.

classification model to spatially average measurements from 42 transects (McLeod 2008). Each transect was 100 m in length, and included 11 depth and 3 density measurements. The ends of each transect were marked with fixed stakes at the time of measurement in 2005. Mean SWE was calculated for each transect and spatially averaged for each watershed on the basis of terrain type units (channel, slopes and plateau). For 2003 and 2004, end-of-winter SWE were calculated based on a network of only 13 transects (which were part of the 42 transects measured in subsequent years) (Lamoureux *et al.* 2006).

Hydrological measurements were obtained from gauging stations near the lake inlets (Figure 1). Stage was recorded at 10 min intervals with an Omega OM-CP Level 1000 logger (±0.2%, 0.5 mm, vented at West) and compensated for barometric pressure with an Omega CP-PRTEMP101 logger (±0.4%) located at MainMet. Instantaneous discharge was determined at each gauging station using manual area–velocity measurements obtained throughout the season with a Swoffer 2,100 current velocity meter (±1%) and used to construct stage–discharge rating curves. A total of 19 and 12 measurements were used to develop the stage–discharge rating curves for the West and East rivers, respectively. Discharge was recorded in the West river from 21 June to 29 July and the East river from 19 June to 29 July. Errors in the discharge measurements are estimated to be of the order of 10–15%.

Sample collection and analytical methods

Sample collection began on 18 June, 2006 (the first day of stream flow) and continued through to 29 July, 2006. Water samples were collected in amber (HDPE) bottles that were triple rinsed before field deployment with deionized (DI) water, and then triple rinsed with stream water prior to sample collection. The bottles were filled completely to eliminate headspace and transported to camp for filtration and processing within two hours (Figure 1). Processed samples were stored in snow packed coolers and refrigerated upon return to the laboratory at Queen's University. Sample aliquots for dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) analysis were vacuum filtered using pre-combusted glass fiber filters (GF/F) and glass filtration apparatus. The glass filtration apparatus was acid washed and combusted before the field season. During the season, the apparatus was soaked in 30% hydrogen peroxide overnight at the end of each day and rinsed three times with DI water and sample between each sample. A filtered sample for DOC/TDN was collected in 40 ml amber glass EPA vials with Teflon lined septa and acidified with hydrochloric acid immediately upon return to the laboratory (within 30 d of sampling). Aliquots for dissolved inorganic ion analyses were vacuum filtered through 0.45 μm nitrocellulose membrane filters, with a polysulfone filter stage. Ion samples were bottled in plastic scintillation vials.

DOC and TDN were determined simultaneously by high temperature combustion and NDIR and chemiluminescent detection using a Shimadzu TOC-VPCH/TNM system equipped with a high sensitivity catalyst. Analytical error was less than 1% (±0.020 ppm) for DOC and less than 2% (±0.01 ppm) for TDN based on duplicate analyses of replicate field samples and replicate analysis of standards.

Dissolved inorganic anions and cations (including NH_4^+, NO_3^-, NO_2^-, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, Br^-, SO_4^{2-} and PO_4^{3-}) were measured by ion chromatography. The anions and cations were determined simultaneously on separate systems using a Dionex ICS 3000 system. The anions were separated by gradient elution with 23–40 mM KOH (using an EG II KOH), with a 1.0 ml/min flow rate, AS18 analytical and guard columns, and self-regenerated suppression (ASRS-ULTRA II). Cations were measured isocratically with 23 mM methanesulphonic acid eluent, flowing at 0.5 ml/min with CS12A analytical and guard columns and self-regenerated suppression (CSRS-ULTRA II). The precision for most analyses was better than 1% based on replicate analyses of samples and standards, while errors on NO_3^-, NO_2^- and NH_4^+ were 1.7% (±0.002 ppm), 20.7% (±0.003 ppm) and 5% (±0.002 ppm), respectively. DIN is reported as the sum of the nitrogen mass from NO_3^-, NO_2^- and NH_4^+, while DON was determined as the difference between the TDN and DIN (propagated error in DON ±0.012 ppm; approximately 5%).

Mass flux calculations

The seasonal yields (kg) of the DOC and N species were estimated as the sum of the daily yields (M_d (kg/d)) determined as the product of the measured concentrations

and the mean daily discharge (Q_d (m^3/s)) over the period of measurement. Samples were collected twice daily at approximate minimum and maximum discharge from the onset of runoff until after peak discharge (at 1000 and 1800 h in the West river, and 1100 and 1800 h in East river), and then once daily (at 1000 h in the West river and 1100 h in the East river) until the end of July. West river sample collection extended from 18 June to 28 July ($n = 52$), and East river collections were between 18 June and 29 July ($n = 43$). In the case where there was only one measurement per day, the daily yield of the solute in question (e.g. M_d(TDN), M_d(DOC), $M_d(NO_3^-)$) was determined as the concentration multiplied by the total mean daily discharge (Q_d). For days where two samples were collected, the daily yield ($M_d(x)$) was determined as the product of the mean concentration and the total mean daily discharge flux. No samples were collected in either stream on 14 July, thus the mass fluxes for this day were determined by linear interpolation of the 13 July and 15 July fluxes. The total seasonal yields were calculated as the sum of the daily mass yields.

The rating curve obtained for the West river discharge is only valid after 21 June at 1200 h, approximately three days after initial flow, while the collection of the first water sample occurred on 18 June. Therefore, the mean daily discharges for the first three days of runoff (18–20 June) in the West river had to be estimated. The flow during these three days consisted of a narrow snow-lined channel. Thus, the mean daily discharges at this time must have been much lower than that recorded on 22 June ($Q_d = 0.48\ m^3/s$), which was the first day with a full 24 h discharge record. Therefore, we used the minimum hourly discharge on 22 June ($Q_h = 0.25\ m^3/s$) as a conservative estimate of the mean daily discharge (Q_d) for 18, 19 and 20 June. On 21 June hourly discharge was recorded between 1200–2300 h. Therefore, to estimate the mean daily discharge for 21 June we examined the trend and magnitude of the hourly discharges between 1200–2300 h, and the ratio of the Q_d and mean discharge between 1200–2300 h (Q_{12-23h}) over the next 5 d (22–27 June). The afternoon discharge trend and values on 21 June were similar to those observed on 23 June and 25 June. We therefore used the mean of the Q_d:$Q_{12-23\,h}$ ratios for 23 and 25 June (0.73) to estimate the Q_d for 21 June. Thus, the Q_d for 21 June was found by multiplying the $Q_{12-23\,h}$ by a factor of 0.73. The mean daily discharges values for 18–21 June are considered conservative; hence the fluxes during the first three days of runoff in the West river may be underestimated.

RESULTS AND DISCUSSION

Climate and hydrology

The snow accumulation at the end of winter 2006 was the highest observed at this site over the last four years, and yielded the highest discharges recorded over the same period (Table 1). The June air temperatures were near the mean of the past four years; however, July 2006 was warm relative to the previous three years (Cockburn & Lamoureux 2008). In most years observed, the SWE in the West catchment was higher than in the East catchment, except for the end of winter 2006 when there was a more evenly distributed snow cover across both catchments. The wind redistribution of snow over winter results in the formation of deep snow banks on the lee side of slopes and within incised stream channels. The snow depth in these drift areas is frequently deeper than the length of the snow probe (> 2.8 m) and/or too dense to penetrate fully with

Table 1 | End-of-winter snow water equivalent (SWE) for West and East catchments and mean June and July air temperatures. Data for 2003 and 2004 are from Cockburn & Lamoureux (2008) and were based on measurement from only 13 transects, while those for 2005–2006 (this study) were calculated using a terrain classification model and measurements from 42 transects

Year	West ΣQ (mm)	West SWE (mm)	East ΣQ (mm)	East SWE (mm)	June temp. (°C)	July temp (°C)
2003	69	43	>24	20	−1.0	3.6
2004	120	82	107	41	−0.1	3.1
2005	81	65	82	43	2.0	3.1
2006	155	113	118	123	1.0	6.2

the probe. Hence, we consider the high runoff to snow ratios (Table 1) to largely reflect the underestimation of SWE in channels and snow banks. Hence, we are more confident in the total river discharge reported and infer that the apparent differences between the estimated SWE and the total discharge are largely due to difficulties in SWE estimation.

Seasonal hydrographs and total discharges for the two rivers were similar in 2006 (Figure 2 (D, H)). Both streams began to flow on 18 June and reached peak discharge on 26 June. However, the East river had a higher maximum hourly discharge (3.1 m^3/s) than West (2.4 m^3/s). Most of the winter snow, except for some perennial snow banks, was exhausted by mid-July. Hence the warmer July temperatures did not lead to substantial additional runoff. Note that the area-specific flux in the West catchment was approximately 30% higher (155 mm) than in the East (118 mm). However, the total runoff values for the two catchments were similar due to the larger surface area of the East catchment, 1.37×10^6 m^3 and 1.25×10^6 m^3 for East and West, respectively.

N species concentrations and export yield

The dominant N species in both rivers was DON, which comprised 80–83% of the seasonal nitrogen yield from both rivers (Table 2). The mean DON and DIN concentrations and total mass yields for the two catchments were also similar (Table 2). In both streams nitrite (NO_2^-) was the least abundant of the inorganic N species. The West river exhibited a higher mean ammonium concentration (0.018 ppm N) than the East (0.011 ppm N), while the East river had a higher mean concentration of nitrate (0.024 ppm N) than the West (0.011 ppm N, Table 2).

These mean concentrations and total seasonal yields mask the differences between the specific mass N flux (kg/km^2) from the two catchments (Figure 2 (A, E)). Despite having a lower total discharge, the smaller West catchment exported more water, DOC and nitrogen per unit area than the larger East catchment (Table 2). Therefore, the between-catchment ratios (West:East) for the specific mass fluxes of nutrients (1.38, 1.30 and 1.59 for DOC, DON, and DIN, respectively) were similar to the ratio of specific discharge (1.32), although the West:East ratio for the specific mass flux of DIN (1.59) was disproportionately higher than the ratio of specific discharge (1.32). These results suggest that the specific yield of DON and DOC from these catchments was largely a function of the intensity of surface water runoff, and hence flushing intensity, within the catchments (Table 2). A greater specific discharge in the West catchment would likely increase the hydrological connectivity in the watershed and therefore increase the area flushed by surface water. However, the higher between-catchment ratio of specific DIN flux indicates the West catchment exported more DIN per unit area and per unit of water than the East catchment. This therefore suggests that there must be some process that makes more DIN susceptible to hydrological flushing in the West catchment, especially at the onset of melt. Potential processes that could yield more DIN include the rates of over-winter/subnival microbial respiration, mineralization and immobilization of N which are controlled by a combination of the timing and depth of snow pack development, as well as by the nature of the soil organic matter and vegetative cover (Brooks & William 1999; Elberling 2007). These over-winter processes can have significant impact on the amount of leachable DOM and N available beneath the snow pack at the onset of melt (Brook & William 1999). Without detailed knowledge of over-winter soil temperatures and microbial activity, it is not possible to pinpoint the exact process that might explain these inter-catchment differences in DIN fluxes. However, since approximately 75% of the seasonal DOC, DIN and DON fluxes occur within 14–16 d of the onset of flow, the important controls on total seasonal fluxes must be associated with processes occurring during the nival melt period, as opposed to later in the growing season when flows are low (Figure 2 (A, E)).

For most of the runoff season, the two streams generally had similar mean DIN and DON concentrations (Figure 2 (C, G)). However, NH_4^+ concentrations in the West river were frequently higher than those in the East (Figure 2 (B, F)). Concentrations of all N species and DOC in the West river were at a maximum at the onset of melt, and decreased exponentially as discharge increased to peak flow (Figure 2 (B, C, D)). After peak discharge, DON and DOC concentrations continued to decrease, then stabilized or increased towards the end of the season (Figure 2 (C, D)). The seasonal pattern of variation in DIN concentrations

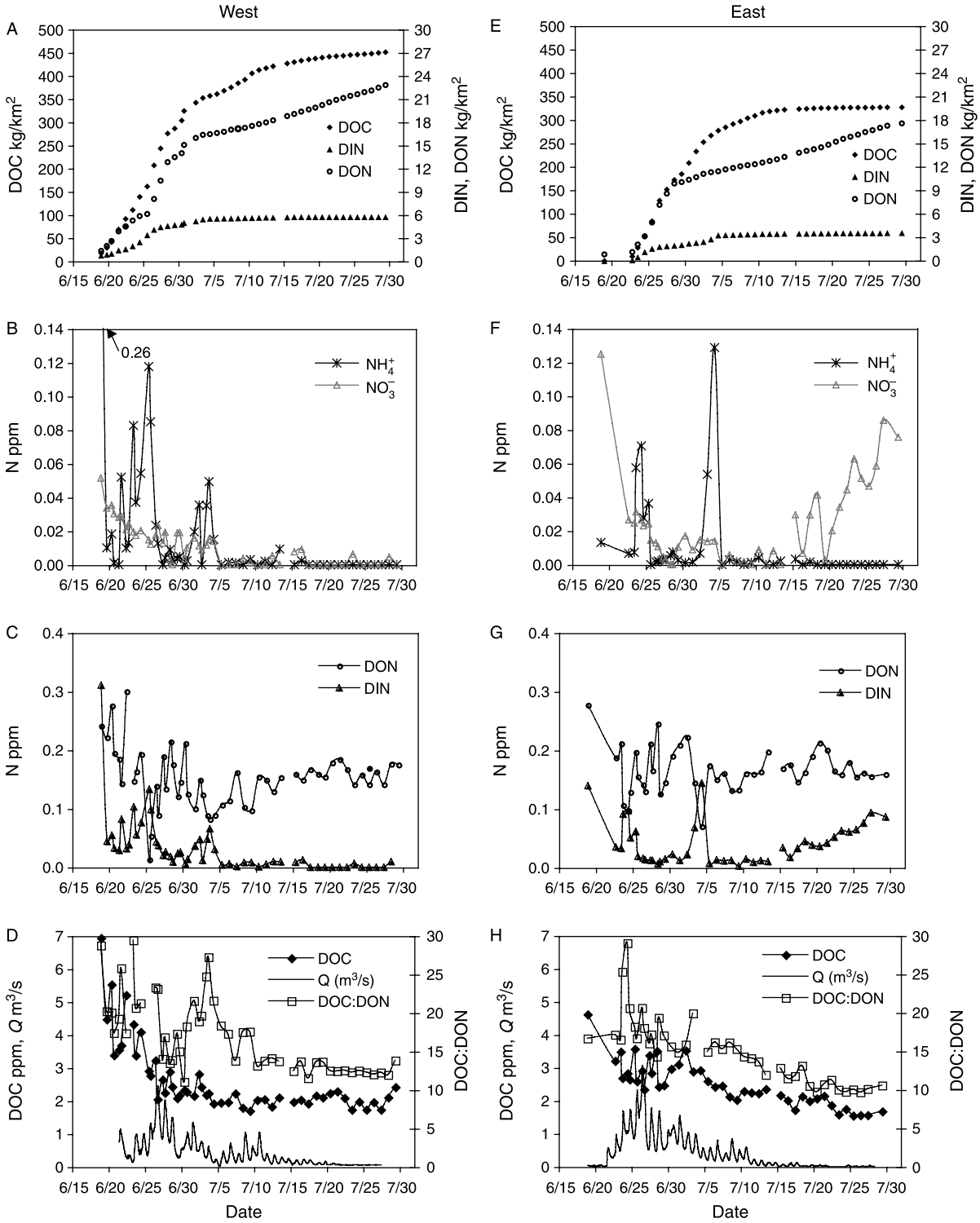

Figure 2 | Seasonal variations in dissolved solute fluxes (kg/km^2), concentrations (ppm) and discharge (m^3/s) in the West and East rivers. Cumulative specific mass fluxes of DOC, DON and DIN are shown in panels (A) and (E). Concentrations of N from NO_3^- and NH_4^+ are shown in panels (B) and (F). DIN and DON concentrations are plotted in (C) and (G). DOC concentrations are plotted with mean daily discharge and DOC:DON (secondary *y* axis) in panels (D) and (H).

Table 2 | Arithmetic mean concentrations, seasonal yields and mass fluxes of nitrogen species and DOC in the West and East rivers

	ΣQ (× 10^6 m^3)	DOC ppm	DON ppm	DIN ppm	N–NO_3^- ppm	N–NO_2^- ppm	N–NO_4^+ ppm	
West	1.24	2.63	0.152	0.031	0.011	0.002	0.018	
East	1.37	2.50	0.167	0.040	0.024	0.006	0.011	
	ΣQ (mm)	**DOC kg**	**DON kg**	**DIN kg**	**DOC: DON**	**DOC kg/km²**	**DON kg/km²**	**DIN kg/km²**
West	155	3,620	183	46	17.0	453	23	5.8
East	118	3,803	204	42	15.1	328	18	3.6
West: East	1.31					1.38	1.30	1.59

diverged from DOC and DON on several occasions. DIN concentrations were highest at the onset of runoff, but in contrast to DOC and DON, DIN concentrations dropped significantly in the second sample and then increased prior to peak discharge (Figure 2 (C, D)). Figure 2 (B) illustrates that the nitrate concentrations in the West river followed a trend similar to DOC and DON, and that NH_4^+ was the species driving the early season increase in DIN (Figure 2 (B, C)). Correlation analysis revealed that NO_3^- and NH_4^+ were relatively well correlated ($n = 52$ and $p < 0.0001$ in all cases) with DOC ($r = 0.81$ and $r = 0.69$, respectively) in the West river, while DON exhibited only a moderate correlation with DOC ($r = 0.59$). NO_3^- was most strongly correlated with DOC ($r = 0.81$) and K^+ ($r = 0.81$, not shown). Significant correlations between DOC and NO_3^- suggest that these species may share similar source areas (e.g. shallow soils) and a dependence in terms of the processes that lead to their presence in the streams (e.g. decomposition of organic matter, mineralization).

In the East river, all N concentrations were also at a maximum at the onset of melt, and although the DOC and DON concentrations are variable near the peak in discharge, they remained high on average until the end of June (Figure 2 (F, G, H)). DIN concentrations increased gradually after 14 July, while DOC concentrations declined (Figure 2 (G, H)). Figure 2 (F) shows that, while NH_4^+ was responsible for the early season spikes in DIN concentrations illustrated in Figure 2 (G), NO_3^- was responsible for the increase in DIN concentrations at the end of the season. Correlations between nitrate and other solutes were examined to better understand the likely source or pathway of the increase in NO_3^- toward the end of season. For the East river ($n = 43$) there was no significant correlation between NO_3^- and DON ($r = 0.22$, $p < 0.15$) or between NO_3^- and DOC ($r = -0.06$, $p > 0.6$). However, NO_3^- was strongly correlated with the inorganic ions Cl^- ($r = 0.92$, $p < 0.0001$, not shown), Na^+ ($r = 0.86$, $p < 0.0001$, not shown), K^+ ($r = 0.83$, $p < 0.0001$, not shown) and SO_4^{2-} ($r = 0.67$, $p < 0.0001$, not shown). The lack of correlation between nitrate and DOC and DON, and the strong correlation with the mineral-derived ions, suggest that in the East river nitrate may be derived from or follow a flow path through mineral soil horizons.

Controls on N species and seasonal variations in concentrations

Water flux exerts first-order control over the export of solutes from the terrestrial system. However, as nitrogen is a limiting nutrient in most terrestrial ecosystems, nitrogen losses in stream waters will only occur if the nitrogen cannot be utilized or controlled by the biota in the terrestrial system (Perakis 2002). In principle this means that N can be lost in forms that are unavailable to organisms, such as complex or large organic molecules, or if there is a spatial or temporal disconnect between the hydrological supply and demand of bioavailable forms of N such as organic N monomers, e.g. amino acids, nucleic acids, amino-sugars (Schimel & Bennett 2004), and NO_3^- and NH_4^+ (Perakis 2002; Pinay *et al.* 2002).

The ultimate source of DON in terrestrial ecosystems is from the leaching and decomposition of N-containing compounds in soil organic matter into soluble forms of organic nitrogen. DON yields in stream water are usually closely related to the composition of soil organic matter and the flow of water through the shallow soil horizons (Hood *et al.* 2003*a*; Cooper *et al.* 2007). The sinks for DON are primarily mineralization reactions (conversion of DON to

NH_4^+ by ammonification). Percolation of DON into mineral soil horizons also promotes the retention of DON via sorption reactions, and also losses as a result of microbial mineralization and immobilization (Hagedorn *et al.* 2000; Perakis 2002). Several studies indicate that plants may also be a sink for DON, as several Arctic tundra plant species have been shown to absorb DON (amino acids) directly (Keiland 1994; Schimel & Chapin 1996).

The NH_4^+ produced by ammonification may be taken up by plants, immobilized by microbes and/or adsorbed on clay minerals. Some remaining NH_4^+ may be subject to nitrification by chemoautrophic bacteria (Giblin *et al.* 1991). Nitrification and oxidation of NH_4^+ bearing minerals are generally the only sources of nitrate in terrestrial catchments. Nitrate is subject to 'uptake' by plants and also 'immobilization' by microbes. Both uptake and immobilization involve the incorporation of nitrogen into biomass via assimilatory nitrate reduction: however, here 'uptake' is used to refer to assimilation by plants, while 'immobilization' is taken to refer to microbial assimilation. A recent study of Arctic tundra soils illustrates that microbes can take up all forms of nitrogen (amino acids, NH_4^+ and NO_3^-) but that NH_4^+ uptake tends to be higher, especially in acidic soils (Nordin *et al.* 2004). This study and others have found that plants also have the ability to use any dissolved form of nitrogen (Keiland 1994; Schimel & Chapin 1996; Nordin *et al.* 2004). Recent research appears to suggest a model where the type of N available in soils and the dominant form taken up by plants is largely a function of the state of N limitation (Schimel & Bennett 2004). According to this conceptual model, in cases of extreme low N availability (where litter inputs and decomposition rates are low, as in Arctic systems) plants and microbes are likely to rely primarily on organic N monomers as an N source, and microbes only rarely mineralize N. As the decomposition, depolymerization and availability of N increases, so do rates of mineralization and the relative rates of uptake of NH_4^+ by plants and microbes. This model suggests that nitrate availability and uptake would only dominate in soils where N availability is high enough that microbial and plant competition for NH_4^+ is low, thus leaving 'excess' NH_4^+ that would sustain nitrification (Schimel & Bennett 2004).

The differences in the composition and specific fluxes of the N species in the two streams (Table 2), and the substantial differences in the relationship between N species and other solutes in the two streams at Cape Bounty suggest that there are different controls on N export between these catchments. The West river runoff chemistry indicates the exported N species (DON, NH_4^+ and NO_3^-) are all relatively well correlated with DOC exports. This suggests that the N sources are related to the flushing of the shallow soil horizons, which provide a source of leachable DOM and also NH_4^+ and NO_3^-. Note that the DOC and DON concentrations in the West river remain stable while the NH_4^+ and NO_3^- concentrations drop to zero for most of the summer (after 5 July, Figure 2 (B, C, D)). This suggests that, although there is continued drainage of organic matter (i.e. sustained DOC, DON) derived from surface soil horizons in the West catchment, either there is limited production of inorganic N (low rates of ammonification and nitrification) in these soil horizons, or that any NH_4^+ and NO_3^- available or released by mineralization of DON during the growing season was effectively immobilized by soil microbes, taken up by plants or denitrified (in the case of NO_3^-). Studies elsewhere in the Arctic have found that net mineralization drops to zero over the summer as soil microbes immobilize substantial quantities of N, leaving little N available for export or plant uptake (Giblin *et al.* 1991). Hence, it is likely that the low DIN concentrations in the later half of the runoff period in the West catchment reflect low net mineralization and high rates of N uptake and immobilization within soils during the growing season. It is also possible that the limited N loss in runoff is due to more effective denitrification (loss of NO_3^- as nitrous oxide (N_2O) or dinitrogen gas (N_2)) due to the higher proportion of moist and saturated soil cover types in the West catchment relative to the East.

By the end of summer, the East river exhibited different N concentration patterns. In this stream both DON and NO_3^- concentrations increased after 15 July, when ammonium concentrations were low or zero (Figure 2 (F, G)) and the DOC:DON ratio decreased from ~16 to 9 (Figure 2 (H)). The absence of NH_4^+ in the summer months is expected, as the microbial and plant demands for N is typically high in the summer. However, in order to explain the increase in the late-season NO_3^- concentrations, some excess NH_4^+ must have been available for nitrification. Ammonium could be derived from mineralization, nitrified

to NO_3^-, and subsequently lost from the catchment in runoff, if there was spatial or temporal disconnect between the sources of N and the sinks. For example, in cases where plant roots and microbes are not present in the areas where the nutrients are available, or the nutrients are available at a time when plants and microbes are not able to use them. As mentioned in the previous section, the strong correlation between NO_3^- and the mineral-derived ions, and the lack of correlation with DOC and DON, suggests that in the East river nitrate may be derived from, or follow a flow path through, deeper mineral soil horizons.

The decrease in the DOC:DON ratio (from ~16 to 9) after 15 July indicates that there was a change in the nature and/or dominant source of DOM in the East river over the course of the summer (Figure 2 (H)). The higher N content of the DOM suggests a more labile DOM, which is generally associated with higher rates of microbial productivity (McKnight *et al.* 1994). Higher microbial productivity would also be associated with higher rates of decomposition and depolymerization of soil organic N, thus higher DON concentrations. Therefore, the decrease in DOC:DON also supports the interpretation of contributions from deeper subsurface flow, as studies have shown that more hydrophobic/recalcitrant forms of DOM are preferentially adsorbed and retained by mineral soils (Kawahagashi *et al.* 2004). Therefore, results suggest there was a change in the source of nitrogen in the East river runoff at the end of summer. Although the data from this study do not permit the identification of the specific processes responsible, the results clearly indicate that there was (1) an increase in nitrate concentrations and (2) a change towards a more labile (higher N content) DOM in late summer. Percolation of meltwater and thawed soil water through the deeper zones of the thickening active layer in sparsely vegetated soils could potentially explain the correlation of NO_3^- with the geochemically derived solutes and the change in the DOC:DON ratio. The differences in the vegetation cover between the two catchments support the interpretation that the DIN in the West catchment is subject to relatively strong biogeochemical retention (or denitrification) during the growing season while the East catchment appears to be more susceptible to nitrate losses (due to lower biological demand or denitrification) at this time of year (30% of the West catchment is covered in well vegetated, moist soil/plant community types compared to only 20% of the East catchment). Regardless, this end-of-season increase in nitrate concentrations in the East river had little effect on the DIN flux due to low discharge at the time.

N structure and losses relative to other environments

The catchments had different seasonal patterns of nutrient concentrations as well as very different specific mass fluxes (Table 2). The seasonal specific mass flux of all dissolved species were 453 kg C/km^2, 23 kg N-DON/km^2 and 5.8 kg N-DIN/km^2 for the West and 328 kg C/km^2, 18 kg N-DON/km^2 and 3.6 kg N-DIN/km^2 from the East catchment. The results highlight the importance of DON as a vector for N losses from these High Arctic catchments (DON > 80% of total N) (Table 2).

The mean concentrations of DON in these High Arctic streams (0.152–0.167 ppm) were generally higher than those reported for studies in the Colorado Rocky Mountains (0.023–0.084 ppm) and the total DON fluxes from the Cape Bounty catchments (18–23 kg/km^2) were within the range reported for these alpine and subalpine catchments (18–60 kg/km^2) (Williams *et al.* 2001; Hood *et al.* 2003*b*). However, the flux of DIN from Cape Bounty streams were two orders of magnitude lower than DIN exports in the catchments in the Colorado Front Ranges (Williams *et al.* 2001; Hood *et al.* 2003*b*). The very high DIN exports in these studies are largely attributed to the high rates of atmospheric N deposition in this region of the Rocky Mountains. Compared to Alaskan watersheds with permafrost coverage varying between 3–53%, these High Arctic catchments have similar mean DON concentrations, but nitrate concentrations in the Cape Bounty streams are an order of magnitude lower than those in the Alaskan watersheds (Petrone *et al.* 2006). The area and annual runoff for the Alaskan watersheds investigated by Petrone *et al.* (2006) were of the same order of magnitude as those for the catchments investigated here. However, the total nitrate fluxes in the discontinuous permafrost subarctic catchments are 5–25 times higher than those at Cape Bounty, although the DON fluxes are within the same range in the two study areas (Petrone *et al.* 2006). In a study of nutrient concentration and export from the upper Kuparuk River (continuous permafrost) basin on the North Slope of

Alaska, Peterson *et al.* (1992) report similar DIN concentrations and fluxes as observed at Cape Bounty. The mean DON concentrations in the stream from this tundra catchment were approximately 50–60% higher than concentrations at Cape Bounty, and total annual DON flux was approximately four times higher than the seasonal fluxes from the East and West catchments (Peterson *et al.* 1992). The much higher fluxes recorded at Kuparuk relative to Cape Bounty are likely due to the combined effect of a longer runoff season (4–5 month season at Kuparuk vs. 2–3 months at Cape Bounty) and the tussock tundra vegetation. These comparisons support the results of previous studies, which report that NO_3^- and NH_4^+ concentrations tend to decrease with increased catchment permafrost coverage, while DON concentrations and fluxes vary less, but increase slightly with more extensive permafrost (MacLean *et al.* 1999; Jones *et al.* 2005).

When compared to unpolluted headwater catchments in temperate South American forests, we find that the concentrations of both inorganic and organic N in runoff at Cape Bounty were higher than in these forested watersheds (Perakis & Hedin 2002). The mean concentrations for DON, $N-NO_3^-$ and $N-NH_4^+$ for the East and West rivers combined were higher (160 ppb, 17 ppb and 15 ppb, respectively) than the mean concentrations for the same species in the 13 South American study areas (58.6 ppb DON, 1.9 ppb $N-NO_3^-$ and 4.9 ppb $N-NH_4^+$ (Perakis & Hedin 2002)). Similar to the Arctic streams where DON accounted for >80% of total N load in streams, DON represented >90% of the total N exported in streams from the unpolluted South American catchments. The high rates of precipitation (500–6,000 mm/yr) and runoff in the South American locations puts the annual net flux of DON from these areas between 20–350 kg DON/km^2/yr (Perakis & Hedin 2002). Despite the much lower precipitation, the streams at Cape Bounty delivered DON in amounts equivalent to the low end of the observed range in the South American study. This observation likely reflects the intense nature of runoff processes in the nival environment.

The discussion above demonstrates that the fluxes of N, and especially DON, from these high arctic systems are comparable to other subarctic, alpine and temperate regions. There is still very little known about the controls on watershed DON cycling, or consequences of DON exports on either the terrestrial ecosystems that are being stripped of this potential nutrient source, or the downstream aquatic systems. However, given that Arctic plants take up DON (Schimel & Chapin 1996), these high rates of DON removal could contribute to or lead to N limitation in terrestrial ecosystems (Perakis 2002). On the other hand, this DON flux may represent a substrate for both limnic and marine planktonic bacteria (Rosenstock & Simon 2003) and marine phytoplankton (Stepanauskas *et al.* 1999; Carlsson *et al.* 1993). Further research into the significance of DON for Arctic aquatic ecosystems is warranted, especially since summer terrestrial N exports are dominated by DON.

CONCLUSIONS

The study reports the seasonal mass flux and temporal variations in N species in two adjacent High Arctic catchments. The total yields from the catchments were similar. However, there were significant inter-catchment differences in the specific DOC, DIN and DON fluxes. The smaller West catchment exported approximately 30% more water, DOC and DON per unit area and approximately 60% more DIN than the larger East catchment. These differences in solute fluxes are largely explained by the differences in catchment runoff intensity (Table 2) and vegetation cover. Results indicate that greater water availability allows for increased hydrological connection of the catchment, which enables more effective flushing of the watershed and greater rates of nitrogen export. Since the majority of the seasonal fluxes occur within 14–16 d of the onset of flow, the important controls on total seasonal fluxes must be associated with processes occurring during the nival melt period.

Differences in temporal patterns and concentrations of the N species between the catchments indicate that there are also differences in the processes controlling nitrogen losses between these two adjacent towards the end of the melt season, which may be largely a function of the differences in vegetation cover between the catchments. The near-zero concentrations of inorganic nitrogen in the West river after the first week in July suggest that there was efficient retention (biological uptake or gaseous loss) of inorganic N in this catchment during the growing season. In contrast, the rise in the concentrations of NO_3^- in the East river over the month of

July suggest that biological demand for nitrogen was lower, or spatially disconnected from the N sources, allowing for end-of-summer nitrate export from this watershed.

The seasonal mass fluxes of DON from these small Arctic catchments are comparable to catchments in alpine, subarctic and more temperate environments. By contrast, DIN concentrations and yields at Cape Bounty were many times lower than in several other alpine and subarctic watershed studies. DON accounted for more than 80% of the total mass of N exported from these two Arctic catchments, suggesting that DON may be a key source of N for downstream ecosystems. The fact that the peak in the flux of DON (and DIN) species fluxes occurred before or at the beginning of the growing season suggests that the bulk of nutrient export may be well in advance of the peak of biological demand in both terrestrial and aquatic ecosystems. The potential for DON losses to lead to, or perpetuate, N-limiting conditions in terrestrial catchments, and/or for these DON inputs to serve as a nutrient source for aquatic ecosystems downstream, highlights the need for more detailed information on the hydrologic and biological controls of DON exports.

The results of this study suggest that, if DON can be used as a source of nitrogen, N should not be a limiting factor for aquatic biological productivity, but the timing and the type of the nitrogen being delivered may be the more important constraints on N availability in aquatic ecosystems downstream. There is a need to understand the extent to which the magnitude, nature and timing of the N fluxes from Arctic systems vary with changes in hydrology and climate and what they mean for downstream aquatic ecosystems.

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