Sources, cycling and export of nitrogen on the Greenland Ice Sheet

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Abstract

Fjord and continental shelf environments in the Polar Regions are host to some of the planet's most productive ecosystems, and support economically important fisheries. Their productivity, however, is often critically dependent upon nutrient supply from upstream terrestrial environments delivered via river systems. In glacially-fed coastal ecosystems, riverine nutrients are largely sourced from melting snow and ice. The largest and most extensive glacially-fed coastal ecosystem in the Arctic is that bordering the Greenland Ice Sheet. The future primary productivity of this ecosystem, however, is uncertain. A potential increase in primary productivity driven by reduced sea ice extent and associated increased light levels may be curtailed by insufficient nutrient supply, and specifically nitrogen. Research on small valley glaciers indicates that glaciers are important sources of nitrogen to downstream environments. However, no data exists from ice sheet systems such as Greenland. Time series of nitrogen concentrations in runoff are documented from a large Greenland glacier, demonstrating seasonally elevated fluxes to the ocean. Fluxes are highest in mid-summer, when nitrogen limitation is commonly reported in coastal waters. It is estimated that approximately half of the glacially-exported nitrogen is sourced from microbial activity within glacial sediments at the

surface and bed of the ice sheet, doubling nitrogen fluxes in runoff. Summer dissolved inorganic nitrogen fluxes from the Greenland Ice Sheet (30-40 Gg) are a similar order of magnitude to those from a large Arctic river (Holmes et al., 2012). Nitrogen yields from the ice sheet (235 kg TDN km^{-2} a^{-1}), however, are approximately double those from Arctic riverine catchments. We assert that this ice sheet nitrogen subsidy to Arctic coastal ecosystems may be important for understanding coastal biodiversity, productivity and fisheries, and should be considered in future biogeochemical modelling studies of coastal marine productivity in the Arctic regions.

1. Introduction

The availability of nitrogen widely limits primary productivity in fjord (Rysgaard et al., 1999), coastal (Poulsen and Reuss, 2002;Daly et al., 1999;Nielsen and Hansen, 1999) and open ocean (Smith et al., 1985;Moore et al., 2002) waters bordering the Greenland Ice Sheet (GrIS) in summer. Hence, external sources of nitrogen to these waters, e.g. riverine runoff, may be important in sustaining the productivity of these waters and may alter in a warming climate. These Greenlandic waters are some of the most productive ecosystems in the world, and boast high socio-economic value via fisheries (e.g. shrimp, halibut) (Hamilton et al., 2000). In the North Atlantic, primary productivity also draws down CO_2 from the atmosphere and has an important regulatory effect on global climate (Sabine et al., 2004). Warmer ocean temperatures and a lengthened growing season in the Arctic are predicted in future decades. However, increases in marine primary productivity may be capped by intensified summer nitrogen limitation (Vancoppenolle et al., 2013).

The GrIS discharges >1000 km^3 of freshwater annually to the Arctic Ocean, Irminger Sea, Labrador and Greenland Seas (Bamber et al., 2012) but has yet to be evaluated as a source of nitrogen to these waters. This freshwater flux is increasing (Bamber et al., 2012), and will continue to do so as rising air and ocean temperatures enhance rates of ice sheet melting and iceberg calving (IPCC, 2007). Greenland ice core data show the ubiquitous presence of low concentrations of dissolved inorganic nitrogen (DIN) in ice and snow, sourced from the atmosphere (Wolff, 2013). Based upon findings from small glacier systems (Hodson et al., 2008;Telling et al., 2011;Boyd et al., 2011), it is plausible that this atmospheric DIN is supplemented by nitrogen cycled into bioavailable forms by glacial biota (Telling et al., 2012;Boyd et al., 2011). While there is a mounting body of literature on nitrogen cycling on

valley glaciers (Telling et al., 2011;Hodson et al., 2008), there is comparatively little data on nitrogen sources and cycling on the Greenland Ice Sheet, which is likely to be important as a nutrient source to downstream fjord and marine ecosystems. High reported rates of fjord primary productivity around the GrIS margin (Jensen et al., 1999) and coastal blooms as late as July/August (Frajka-Williams and Rhines, 2010;Nielsen and Hansen, 1999) coincident with peak meltwater fluxes (Bartholomew et al., 2011) suggest that such an evaluation will be a fruitful exercise.

This manuscript aims to examine the sources, cycling and fluxes of nitrogen and it's component species in bulk runoff exported from the GrIS during the summer melt season. We document seasonal time series of nitrogen concentrations, speciation and fluxes associated with both surface meltwaters and subglacial runoff at the large (600 km^2) land-terminating Leverett Glacier (LG) in SW Greenland during the 2012 melt season. This glacier has a bedrock (Precambrian gneiss/granite (Kalsbeek, 1982)) that is consistent with large areas of the GrIS, and covers a large altitudinal range drawing meltwaters from >100 km from the ice margin. Hence, we assert that it is representative of large sectors of the Greenland margin. This manuscript builds upon recent work by (Hawkings et al., 2015), who presented a more limited dataset of dissolved inorganic subglacial nitrogen fluxes from the same catchment. We report data from a range of contextual field and experimental samples collected from sediment-laden ecosystems on and beneath the ice sheet (basal ice and incubated basal ice, glacier surface ice, snow, moulin and cryoconite waters) and subglacial incubation experiments in order to infer the relative importance of different sources of nitrogen species in runoff. Total Dissolved Nitrogen (TDN), DIN (nitrate and ammonium) and dissolved organic nitrogen (DON) were quantified in all samples and exchangeable ammonium associated with suspended sediments ($SS\text{-}NH_4^+$) was analysed in runoff. These data were used to calculate seasonal nitrogen fluxes and yields from the catchment, and subsequently similar estimates for the GrIS.

2. Materials and Methods

2.1 Field site

Leverett Glacier is located on the south-west of the GrIS, approximately 300 km north of Nuuk (Figure 1.; 67.06°N, 50.10°W). The glacier overlies predominantly Precambrian gneiss/granitic bedrock, typical of much of Greenland as indicated by geological surveys of the non-glaciated areas bordering the ice sheet (Kalsbeek, 1982;Kalsbeek and Taylor, 1984). The subglacial sediments are primarily Quaternary deposits (e.g. paleosols) containing fresh organic matter that were buried during glacial advance in the last few thousands of years following the Holocene Thermal Maximum when the GrIS margin was positioned tens of kilometres further inland (Simpson et al., 2009). LG supplies runoff to the Watson River during the summer months, the largest of three glacially-fed rivers which supply Søndre Strømfjord (Figure 1). Søndre Strømfjord is the largest fjord system in western Greenland and comprises an inner fjord (up to 275 m deep, 4 km wide and 80 km long) and a shallow outer fjord (<100 m deep, 1km wide and 100 km long) (Nielsen et al., 2010). The inner fjord physical oceanography is influenced by meltwater, as indicated by a 50-75 m freshwater surface layer (Nielsen et al., 2010).

2.2 Sample collection, processing and storage

Two main sampling sites were established in summer 2012: one at the ice sheet margin (11th May – 15th July) 1km downstream of the glacier terminus (glacial runoff sampling site, Figure 1, black dot) and one on the ice sheet surface (8th May – 8th August) at a moulin located approximately 35 km from the ice margin (surface meltwater sampling site, Figure 1, red dot).

2.2.1 Ice sheet surface sampling

A field camp was established in 2012 in the mid ablation zone at LG at 1030 m elevation, 35 km from the western margin (66.97°N, 049.27°W). Here, samples of meltwater descending to the ice sheet bed (Chandler et al., 2013) were collected from the streams feeding a large moulin between 5th May and 9th August (Day 129 and 222). The discharge of meltwater into this moulin was also measured (Supplementary Information 1). A range of contextual samples were collected, including ice containing dispersed cryoconite debris (referred to here as “summer ice”) and cryoconite hole waters. Cryoconite holes are water-filled cylindrical melt holes, formed by radiation heating of surface sediment and subsequent melting (Podgorny and Grenfell, 1996). The debris in the base of these holes is termed “cryoconite” which may become distributed over

the glacier surface during melt out of cryoconite holes in summer. Ice samples were melted in clean/sterile Whirl-pak™ bags (Nasco) overnight in a warm water bath immediately after collection (melting typically took 2-3 hrs). All meltwater samples were filtered through 47 mm, 0.45 µm cellulose nitrate filters (Whatman™) in a plastic filter unit (Nalgene™ PES), pre-rinsed 3 times with sample, and stored in high density polyethylene plastic bottles (Nalgene™; 30 mL). Samples were frozen immediately after filtration and only thawed out immediately prior to analysis in Bristol. Procedural blanks were processed (n=5) during the course of the sampling season, where deionised water (stored in clean plastic bottles) was treated as a sample.

2.2.2 Bulk meltwater sampling

The river draining from the subglacial portal at LG was continuously monitored during the 2012 melt season (May – October) using stage measurements in a stable bedrock section ~2.2 km downstream of the terminus (Hawkings et al., 2014;Hawkings et al., 2015;Cowton et al., 2012;Tedstone et al., 2013;Hawkings et al., 2016). Stage was logged every 5-10 minutes, and converted to discharge using rhodamine dye-dilution experiments (>30 dye tracing experiments were carried out over the season using standard methods (Cowton et al., 2013)). The error in measured discharge determinations is ±10% (Tedstone et al., 2013). Suspended sediment concentrations were calculated as in previous work from bulk meltwater turbidity measurements (Cowton et al., 2012). A turbidity sensor was employed throughout the monitoring period in a similar location to stage measurements. The sensor was calibrated using manual sediment weight samples. Briefly, a recorded amount of meltwater (usually 300 mL) was filtered through a 0.45 µm cellulose nitrate filter (Whatman™), oven dried overnight at 40 °C and weighed.

Bulk meltwater samples were taken approximately 1 km downstream from the LG subglacial portal, at least once a day during the main melt period (May-July). Samples were collected daily at ~10:00 hr, with occasional additional afternoon samples taken at ~18:00 hr, mostly during subglacial outburst events. A 2 L meltwater grab sample was taken in a HDPE Nalgene™ bottle (Thermo Scientific™), which had been pre-rinsed 3 times in the meltwater stream. Samples were filtered soon after collection using a Nalgene™ reusable PES filtration stack, and a 47 mm 0.45 µm cellulose nitrate filter membrane (Whatman™). Filtered samples were stored in 28 mL HDPE bottles. Procedural blanks were processed (n=10) during the course of the sampling

146 season, where deionised water (stored in clean Nalgene™ HDPE plastic bottles) was treated as a
147 sample and filtered and bottled accordingly All samples were immediately frozen and stored in
148 the dark until analysis in Bristol.
149
150 ### 2.2.3 Basal ice sampling and incubation experiments
151 Basal ice from the Leverett/Russell Glacier catchment was collected by chain saw from an easily
152 accessible outcrop of debris-rich basal ice at the ice margin (within 5 km of the main LG bulk
153 meltwater sampling site, Figure 1) by chain saw (30 x 30 x 30 cm blocks) in spring 2008 and
154 summer 2010. The outermost ~0.5 m of ice was first removed before the blocks were cut. The
155 blocks were wrapped in large sheets of pre-combusted foil and stored at ≤ -20°C prior to
156 processing. Sub-samples of the ice were prepared for nitrogen analysis by chipping ~15 x 15 x 5
157 cm chunks from the main block using a flame sterilised chisel. The outer ~10-30 mm was
158 removed by rinsing with ultrapure (≥18.2 MΩcm^{-1}) deionized water, and the remaining ice was
159 transferred into a pre-combusted glass beaker covered with foil. The ice was allowed to melt
160 inside a laminar flow cabinet (Telstar Mini-H) at room temperature. Icemelt was filtered through
161 Whatman polypropylene Puradisc™ 0.45 µm syringe filters. Samples for nitrogen species
162 determinations were stored in clean, thrice-rinsed Nalgene™ HDPE bottles. All sediment and
163 filtered samples were stored in the dark at ≤ -20ºC until analytical processing.
164
165 Long-term incubation experiments (> 1 yr) were conducted using sediment and meltwater
166 derived from melted basal ice samples, in order to investigate microbially derived sources of
167 dissolved nitrogen in a simulated subglacial environment. Three types of experiments were
168 conducted: 1) Live control experiment with no sediment added, where the solution was
169 meltwater from basal ice; 2) Live anaerobic experiments (sediment+meltwater from basal ice);
170 and 3) Live aerobic experiments (sediment+meltwater from basal ice). The control sediment-free
171 experimental nitrogen concentrations were subtracted from the live (sediment+water)
172 experiments in order to correct for nitrogen species added from the sampling vessel and the
173 original basal ice meltwater matrix. Hence, nitrogen concentrations reported are those that have
174 evolved during the experiment via rock:water contact and *in situ* microbial activity.

Experiments were performed in the dark at 0.1 °C in modified gas-tight 500 mL borosilicate glass bottles. A sampling port towards the base of the vessel immediately above the sediment surface was used for water extraction. All incubations contained 100 mL of wet-weight sediment, 200 mL melt water and 200 mL gas headspace. Control incubation experiments contained 200 mL ice melt only. Sediment and ice melt (flushed with O_2-free-N_2 gas) required for the anaerobic incubations were melted inside a glove-bag filled with O_2-free-N_2 gas (BOC Ltd, UK). Meltwater/sediments were later flushed with O_2-free-N_2 gas for >20 minutes to ensure that the sediment and water were equilibrated with an oxygen-free atmosphere. The incubations were sampled ~2 hrs after set-up (T=0 d), on day 4, 109, 190, 294, 382 and 533 and 758 (aerobic only). At each sampling point, 30 mL (15% of the initial volume) of melt water was removed, filtered through Whatman polypropylene Puradisc™ 0.45 μm syringe filters and stored at ≤ -20ºC until analysis. Sampling of the anaerobic incubation experiments were conducted inside a glove-bag filled with O_2-free-N_2 gas. All meltwater samples were frozen immediately after collection and stored frozen prior to analysis for dissolved nitrogen species.

2.3 Analytical methods

All meltwater samples were analysed for concentrations of total dissolved nitrogen (TDN), dissolved inorganic nitrogen (DIN, comprising nitrate and ammonium), with dissolved organic nitrogen (DON) determined by difference between TDN and DIN. Concentrations of nitrite were generally below the limit of detection and are not reported. We also analysed ammonium concentrations associated with suspended sediments in runoff (SS-NH_4^+), where this component is assumed to be bioavailable. The nitrogen content of snow is taken from previous work conducted in the same catchment (Telling et al., 2012) and from Greenland ice cores (Wolff, 2013). Pre-melt surface glacier ice nitrogen concentrations were taken from previous work conducted in Leverett glacier catchment (Telling et al., 2012). The detailed sampling and analytical procedures are provided in the following sections.

2.3.1 Nitrate

Nitrate was determined using a Thermo Scientific™ Dionex™ ICS-5000 ion chromatograph fitted with an IonPac™ AS11-HC-4μm anion-exchange column. A 30 mM KOH eluent

concentration was used, with an injection volume of 0.4 μL and cell temperature of 35°C. The detection limit of the instrument was 0.08 μM N. The precision of analyses, determined via analysis of eleven replicate standards at the lower end of the sample range (1.6 μM), was 8.1%. The accuracy of the machine was determined as -6.4%, using gravimetrically weighed standards from a 1000 mg L^{-1} certified stock standard (Sigma TraceCERT®). All field nitrate data were blank corrected using field procedural blanks. The nitrate concentrations within these blanks were <0.45 μM for surface samples and below the detection limit for runoff samples.

2.3.2 Ammonium

Ammonium was determined manually using the salicylate spectrophotometric method (Bower and Holm-Hansen, 1980;Le and Boyd, 2012), adapted for a smaller sample size (1 mL). The detection limit of the method was 0.6 μM N. The precision of analyses was 4.9 %, calculated from five replicate standards (1.8 μM). Accuracy was calculated to be +0.3% (from a gravimetrically diluted certified reference standard, Sigma-Aldrich TraceCERT(R) 1000 mg L^{-1}). Ammonium concentrations in field samples were blank corrected using field procedural blanks, and were all above the limit of detection. Mean blank correction factors for ammonium were 0.75 μM N for surface samples. Runoff blank corrections were below the detection limit of the instrument.

2.3.3 Total Dissolved Nitrogen (TDN)

Total Nitrogen was determined on most runoff samples using a Lachat QuikChem® 8500 Flow Injection Analyser system, with digestion unit (method number 10-107-04-3-E). The detection limit of the instrument was 1.4 μM TDN, the precision of analyses was calculated as 11.3% from six 3.6 μM replicate reference standards (gravimetrically diluted from a certified reference standard, Sigma-Aldrich TraceCERT(R) 1000 mg L^{-1}). Accuracy was determined using the same reference standards as -0.4%. All TDN data were field blank corrected (2 μM for surface samples, and no correction for runoff samples since these were below the detection limit of the instrument).

2.3.4 Exchangeable NH_4^+ in suspended sediment (SS-NH_4^+).

Measurements were conducted using the method described by (Maynard et al., 2007). Filters containing suspended solids were placed into polypropylene centrifuge tubes and the NH_4^+ was then extracted with 10 ml of 2M KCl for 30 minutes on an automatic shaking table (160 rpm). Extracts were decanted into additional centrifuge tubes, centrifuged at 4500 rpm for 5 min, and filtered through 0.45 µm inline Whatman® polypropylene Puradisc filters. When immediate analysis was not possible, they were immediately, frozen (-20°C) until analysis. A second sequential extraction was then performed to extract any residual sediment bound NH_4^+. Extracts were analyzed on a Bran and Luebbe Autoanalyzer 3, with a detection limit in extracts of 0.9 µM N, equivalent to 0.09 µM N for a typical sediment mass of 0.1 g. The NH_4^+ concentrations from the first and second extracts were combined to give a total NH_4^+ for the suspended sediment samples. Dry weights for sediment samples were obtained by washing residual sediment from filters into centrifuge tubes with MQ water, centrifuging at 4500 rpm for 5 min, then repeating with a further MQ wash and centrifuging stage to remove any residual KCl. Sediments were then oven dried (overnight at 40°C) and weighed. This gave concentrations of exchangeable NH_4^+ of µg N g^{-1}, which were converted into units of µM N g^{-1} and then to µM N by multiplying by the instantaneous suspended sediment concentration (in g L^{-1}) at the time of sample collection. SS-NH_4^+ fluxes (µM N s^{-1}) were subsequently calculated from the product of the NH_4^+ concentration and bulk discharge (in L) at the time of sample collection.

2.4 Flux calculations

2.4.1 Nitrogen fluxes from Leverett Glacier

Nitrogen fluxes over the entire melt season (May - September) are calculated for LG for the 2012 melt season, which was a record melt year in Greenland (Tedesco et al., 2013). Discharge weighted mean concentrations of dissolved nitrogen species and SS-NH_4^+ for LG runoff were calculated for the 2012 melt season. Use of discharge weighted mean (DWM) concentrations lowers the mean nitrogen concentrations in bulk meltwaters, since high discharge values are generally accompanied by low nitrogen concentrations. Hence, this method provides a more conservative estimate of nitrogen fluxes. We use minimum and maximum concentrations of nitrogen species to illustrate the potential maximum range of nitrogen fluxes under different hydro-climatological regimes. The product of the DWM, minimum and maximum concentration

of each nitrogen species and the runoff flux for the summer discharge monitoring period in 2012 from LG (2.2 km^3, Supplementary Figure 5) generated the total seasonal fluxes of these nitrogen species. We did not measure the particulate organic nitrogen (PON) concentrations in runoff, and in previous years these concentrations have been below the detection limit of standard analytical methods. However, we did calculate the SS-NH_4^+ fluxes in the same manner as the dissolved nitrogen species. Total fluxes of dissolved and SS-NH_4^+ in LG runoff during the 2012 melt season are presented in Table 2. Errors on these estimates due to discharge uncertainty and catchment area are of the order of ±10% and ±25% respectively (Tedstone et al., 2013;Cowton et al., 2012), giving a combined uncertainty of ±27%.

2.4.2 Nitrogen fluxes from the Greenland Ice Sheet

Currently, there are no other seasonal time series of nitrogen concentrations in runoff from large Greenland outlet glaciers. Hence, nitrogen concentrations in LG runoff are used in order to generate order of magnitude flux estimates for nitrogen associated with Greenland freshwater export. We base our calculations upon the premise that LG is representative of large areas of the GrIS, for several reasons. First, LG displays a high altitudinal range (250 – 1510 m a.s.l.) and extends for > 80 km inland, like many large Greenland outlets. Hence, nitrogen supply from snow and ice melt are likely to be representative of other large catchments draining the ice sheet. Second, microbial processes (e.g. nitrogen fixation, nitrification, organic matter mineralisation), which are thought to generate approximately half of the ice sheet nitrogen in runoff (via DON, nitrate and ammonium), are reported from a wide range of other glacial systems worldwide including the Greenland Ice Sheet (Hodson et al., 2005;Boyd et al., 2011;Telling et al., 2012), a reflection of the ubiquitous nature of microbial ecosystems upon glacier surfaces and at glacier beds. Third, the bedrock geology at LG is representative of large areas of the GrIS (see Section 2.1). This suggests that the drivers for nitrogen export at Leverett Glacier are likely to be applicable to other large catchments, which account for the bulk of the freshwater flux from the ice sheet to the oceans. Our approach is widely employed for calculating solute fluxes from ice sheet systems where datasets are sparse due to the difficulty of making measurements (Wadham et al., 2010;Bhatia et al., 2013;Lawson et al., 2013;Hawkings et al., 2014;Hawkings et al., 2016).

Fluxes of nitrogen from the GrIS are calculated from the product of DWM, minimum and maximum concentrations of the different nitrogen species at LG glacier (Table 3) and the total

ice sheet runoff flux for 2012 and the mean runoff flux of 2000-2011 (Tedesco et al., 2013) (Table 3). The latter is modelled using the MAR regional climate model. Errors for meltwater runoff determinations via the MAR model are estimated 10% (Vernon et al., 2013). Hence, we might expect similar uncertainty to propagate to nutrient flux determinations. We also estimate the potential nitrogen fluxes exported to the ocean by iceberg calving, which have a potential far-field influence within the open ocean (Syvitski et al., 2001;Smith Jr. et al., 2013). Iceberg nitrogen fluxes are taken to be the product of the iceberg freshwater flux and mean nitrogen concentrations in Greenland ice cores (Table 3). We employ a freshwater flux for Greenland icebergs of 600 km^3 a^{-1}, based upon approximate average values for the last decade (Bamber et al., 2012). We assume that the mean concentrations of nitrogen in icebergs are similar to those reported in Greenland ice cores (Wolff, 2013), which are also in line with those reported in LG catchment (Telling et al., 2012). This is a conservative estimate, since additional nitrogen supply is likely associated with sediments entombed within icebergs. Results from this work indicate that the SS-NH_4 content of ice containing even trace amounts of debris may display elevated nitrogen concentrations which are five times higher than in ice with no debris (Table 1).

3. Results and Discussion

3.1 Sources of nitrogen in runoff

The LG runoff time series demonstrates that the GrIS provides a continuous supply of nitrogen to downstream ecosystems throughout the main melt period (Figure 2). Concentrations of TDN are significant (1-10μM) and mean nitrate concentrations (1.8 μM) alone are higher than those reported in surface ocean and fjord waters (<0.1-1μM) in western Greenland in summer (Nielsen and Hansen, 1999;Arendt et al., 2010;Hopwood et al., 2016). Higher concentrations of nitrate are observed in deeper ocean waters, but upward diffusion and advection are often limited by a stratified water column during the summer months (Arendt et al., 2010). DIN, which is readily available to marine phytoplankton, accounts for half of the TDN in LG runoff, supplemented by SS-NH_4^+ from the ice sheet bed. A component (~50%) of the DIN measured in LG runoff originates from natural and anthropogenic atmospheric sources, via melting of snow and ice

(Wolff, 2013) (Table 1). LG drains a large catchment (active hydrological catchment area = 600 km^2 ±25% (Cowton et al., 2012)) with a high altitudinal range (extending to >1500 m a.s.l.). New moulins open up and surface lakes drain with snow line retreat (Bartholomew et al., 2011), providing a mechanism by which new sources of DIN are fed to runoff. Water fluxes control the overall nitrogen flux, which rises through summer to attain high values during the sampling period in mid-July (Figure 2). The bulk runoff chemical sampling record did not extend beyond this point. However, we assert that runoff nitrogen fluxes will continue to be high in late July/early August, as evidenced by the sustained high fluxes of nitrogen species in moulin waters up until 9th August (Day 222, Suppl. Figure 5). This is significant given the reported nitrogen limitation of fjord and marine phytoplankton in mid-summer, once the water column becomes more stratified and deep marine sources of nitrogen become more inaccessible (Rysgaard et al., 1999;Budeus and Schneider, 1995).

A striking feature of the runoff dataset is the factor of four increase in concentrations of TDN in LG runoff (4.5 µM, 5.7 µM including SS-NH_4^+) compared with those in snow and ice (<1 µM), reflecting enhancements in dissolved organic nitrogen, ammonium and nitrate (Figure 3, Table 1). Similar findings have been reported at small valley glaciers (Hodson et al., 2008), and imply the acquisition of significant quantities of nitrogen within the glacier. A substantial proportion of this enhancement must occur in sedimentary environments at the ice sheet bed, as indicated by a significant association between TDN in moulin waters and bulk runoff, but a positive intercept of 2.5 µM (Figure 4). A range of possible sources exist for this additional nitrogen in runoff. Our wider contextual survey of the nitrogen content of basal and surface ice and meltwaters and subglacial incubation experiments allows us to conjecture on these sources. For nitrate, enhancement is likely to occur in the subglacial environment, since nitrate concentrations in moulin waters and snow/ice are similar (Table 1). The basal regions of ice sheets are viable habitats for microbial life and previous work has demonstrated the activity of nitrifying bacteria, which transform ammonium to nitrate, at small Alpine valley glaciers (Boyd et al., 2011;Wynn et al., 2007) and Subglacial Lake Whillans in Antarctica (Christner et al., 2014). In support of this, long-term incubation experiments using LG subglacial sediments (Figure 5) show the release of up to 5 µM nitrate under aerobic conditions in live sediments and an absence of this production in live controls (no sediment) and under anaerobic conditions. The

simultaneous removal of ammonium ions is consistent with nitrification as the source of this nitrate, likely in more aerobic subglacial channel-marginal sedimentary environments.

The enhancement of DON concentrations in moulin waters relative to snow and ice, and in runoff relative to moulin waters is also significant (independent t-test, p=0.05) and suggests the acquisition of DON in surface and basal ecosystems respectively. This is consistent with previous work that has suggested the presence of a significant nitrogen-rich component to dissolved organic matter exported from glacier ecosystems in runoff (Hood et al., 2009;Lawson et al., 2014;Bhatia et al., 2013). Likely surface sources are cryoconite holes and debris-rich ice, which display elevated DON concentrations relative to pre-melt ice and snow (Figure 2, Table 1). These debris-laden environments support diverse microbial communities, which actively fix carbon dioxide from the atmosphere (Stibal et al., 2012). We assert that mineralization of organic matter in such environments generates the elevated DON concentrations in surface waters by microbial activity or by leaching from allochthonous organic matter in debris. The factor of two enhancement in DON concentrations in runoff relative to moulin waters reflects an even greater subglacial input of these nitrogen species. It is notable also that, while ammonium concentrations in bulk runoff are generally low (< detection limit at 0.6 μM), both DON and ammonium concentrations in runoff are often elevated during subglacial outburst events, rising to up to 3 and 6 μM respectively (Figures 2 and 6). These events are known to expel long-term stored meltwaters and sediments from beneath the ice sheet in response to surface lakes drainage (Bartholomew et al., 2011),. A subglacial source of these waters is clearly evident from elevated sulphate concentrations, which rise during outburst events. Sulphate ions are uniquely generated in inefficient distributed drainage pathways at the glacier bed, where comminution of the underlying bedrock releases highly reactive iron sulphide minerals to meltwaters. These oxidise rapidly to give sulphate (Tranter et al., 1993). The elevated runoff DON and ammonium during such events implies a source in subglacial sedimentary ecosystems. Long-term incubation experiments presented in Figure 5 strongly support a subglacial source for DON but do not show elevated concentrations of ammonium in live experiments. We propose that the subglacial acquisition of DON reflects *in situ* microbial activity, as reported beneath smaller valley glaciers (Hodson et al., 2005). The low dissolved organic carbon (DOC):DON ratio in runoff (mean=9.5, DOC data from (Hawkings, 2015)) is similar to other world glaciers (Hood and Scott, 2008) and is consistent with a microbial source for DON. It contrasts with the higher mean DOC:DON

ratios for Arctic rivers (mean=48) which include a greater terrestrial contribution (Lobbes et al., 2000). These findings support the notion that dissolved organic matter exported from the GrIS may be highly bioavailable to marine bacteria (Lawson et al., 2014;Lawson et al., 2013;Bhatia et al., 2010), as has been suggested for glacier systems elsewhere (Hood et al., 2009).

The subglacial source of the enhanced ammonium concentrations in long-term stored subglacial waters released during outburst events is less clear. Ammonium concentrations in basal ice and outburst waters were relatively high (mean = 2-3 μM) (Table 1; Figure 6) but our subglacial incubation experiments time series showed no significant enhancement of ammonium from initial concentrations over time (Figure 5). Enhancement of ammonium concentrations in long-term stored subglacial meltwaters have been documented previously in Antarctic Subglacial Lake Whillans, inferred to reflect microbial mineralisation (Christner et al., 2014). There are several potential reasons for the static ammonium concentrations during our laboratory experiments. It may reflect the difficulty of replicating microbial processes under laboratory conditions, together with elevated starting ammonium concentrations at t=0 in experiments (basal ice mean NH_4^+=2.7 μM). Second, it may indicate that the subglacial process that generates ammonium ions is not modelled well by laboratory experiments. For example, ammonium may be released to solution directly or indirectly by crushing of the underlying bedrock (Dixon et al., 2012), as occurs for other species such as hydrogen (Telling et al., 2015). Greenland gneiss contains very small concentrations of nitrogen (9 μg N g^{-1} (Holloway and Dahlgren, 2002)), but glacial crushing and release of this nitrogen from bedrock as ammonium has the potential to generate concentrations an order of magnitude higher concentrations of ammonium that those observed in incubation experiments. Overall, data presented here suggests the operation of a suite of diverse mechanisms that supply nitrogen species from snow and icemelt, enhancing them in supra- and subglacial ecosystems prior to meltwaters being evacuated at the ice margin. This is consistent with recent work in Alpine regions that clearly demonstrated the potential for glacier-fed catchments to display enhanced nitrogen concentrations in runoff relative to snowmelt-fed systems (Saros et al., 2010).

3.2 Fluxes of nitrogen from Leverett Glacier

Total dissolved nitrogen (including SS-NH_4^+) fluxes from LG in summer are on average 0.14 t a^{-1} (Table 2). The estimated TDN yields for the Leverett Glacier catchment arising from this flux

412 are 236 kg km^{-2} (164 kg m^{-2} excluding SS-NH_4^+), which is an order of magnitude higher than the
413 typical annual TDN yields measured in large Arctic rivers (36-81 kg km^{-2}) (Holmes et al., 2012).
414 This high yield largely arises from the high specific water yield at LG (3.7 x 10^6 m^3 km^{-2} a^{-1}), in
415 comparison to the water yield (July-October) of the largest Arctic rivers, which is two orders of
416 magnitude lower (9.3 x 10^4 m^3 km^{-2} a^{-1}, calculated from a water flux for the six largest Arctic
417 rivers of 1011 km^3 a^{-1} from July to October and a gauged catchment area of 10.9 x 10^6 km^2)
418 (Holmes et al., 2012). This implies that there is a much higher continuous flux of dissolved
419 nitrogen species per unit area from the ice sheet in summer than from high Arctic River
420 catchments, reflecting the acquisition of dissolved N species from both melting snow and ice on
421 the surface and sedimentary environments at the ice sheet bed.

422 ### 3.3 Fluxes of nitrogen from the Greenland Ice Sheet

423 The estimated summer mid-range TN flux (including SS-NH_4^+) from the GrIS is ~27 Gg (2000-
424 2011) and 43 Gg (2012) (Table 3) using discharge weighted mean concentrations, with potential
425 flux ranges of 7-86 and 11-137 for 2000-2010 and 2012 respectively. The mean values are of a
426 similar order of magnitude to a large Arctic river (the average TDN flux for the Lena, Yenisey,
427 Ob Rivers, July-October is 41 Gg (Holmes et al., 2012)). The glacial nitrogen fluxes largely
428 supply different ocean basins to the Arctic rivers (Bamber et al., 2012;Holmes et al., 2012). We
429 contend that ice sheet derived nitrogen fluxes are likely to rise with enhanced melting in a
430 warmer climate and could, therefore, stimulate increased primary production in downstream
431 coastal ecosystems. Evidence from a single melt year suggests that within-season fluxes of
432 nitrogen species rise exponentially with increasing glacial water fluxes (Figure 2). The degree of
433 future nitrogen flux increase in warm melt years, however, is difficult to predict. The
434 atmospheric nitrogen flux (largely as DIN) are likely to scale with increasing melt volumes as
435 has been suggested else (Hawkings et al., 2015). However, the magnitude of increase will
436 depend upon the availability of glacial ice and snow from post-industrial times, since these
437 display elevated atmospheric DIN compared with pre-industrial ice (Olivier et al., 2006). DON
438 and non-atmospheric ammonium fluxes might also be expected to increase as the zone of melting
439 expands and there is more extensive contact of meltwater with organic matter in surface and
440 subglacial ecosystems.

441 The impact of present and future nitrogen fluxes upon fjord and coastal marine
442 ecosystems around Greenland is unknown, and requires further study. The input of nutrients
443 associated with Greenland icebergs and runoff may sustain elevated primary productivity beyond
444 the spring phytoplankton bloom, and offers one possible explanation for the reported mid-
445 summer phytoplankton bloom in Western Greenland (Frajka-Williams and Rhines, 2010;Nielsen
446 and Hansen, 1999). Nitrogen limitation is common in fjord and coastal waters in summer, and
447 hence any increase in DIN supply has the potential to enhance primary productivity.

448

449 ## 4 Conclusions

450 In summary, our findings at Leverett Glacier suggest that large glacial outlet glaciers draining
451 the Greenland Ice Sheet provide a continuous source of dissolved nitrogen in runoff through the
452 summer months, a proportion of which is likely to originate from microbial ecosystems on and
453 beneath the ice. The degree to which these nitrogen fluxes are modified by proglacial processes
454 is unknown, as are the potential impacts upon fjord and coastal marine biological productivity.
455 However, phytoplankton in coastal Greenlandic waters often become limited by nitrogen
456 availability by mid-summer, when the glacial nitrogen flux to coastal waters is highest. TDN
457 yields from Leverett Glacier are an order of magnitude higher than those reported for Arctic
458 rivers, a reflection of the high surface melt rates (and hence water fluxes) and continuous
459 nitrogen supply from several sources within the ice sheet. Estimated fluxes of nitrogen from the
460 ice sheet are similar in magnitude to those of a large Arctic river. Our findings suggest that a
461 melting GrIS may be an important source of nitrogen to downstream coastal ecosystems, and that
462 these nitrogen fluxes are likely to increase in a warming climate.

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7 Tables

Table 1 Mean concentrations of nitrogen species reported in LG runoff (including discharge weighted mean, DWM for TDN species), in comparison to those in moulin waters, surface ice (pre-melt and post-melt "Summer ice", where the latter samples were at the melting temperature and contained dispersed debris), snow, cryoconite water and basal ice (a-(Telling et al., 2012), b-(Wolff, 2013))

	NO_3^- (μM)			NH_4^+ (μM)			DIN (μM)			DON (μM)			TDN (μM)		
	mean	SD	n	mean	SD	n	mean	SD	n	mean	SD	n	mean	SD	n
Bulk runoff-dissolved	1.8	1.2	62	0.4	0.6	62	2.2	1.4	62	2.3	1.5	62	4.5	2.3	62
Bulk runoff-dissolved, DWM	1.1	-	-	0.3	-	-	1.4	-	-	1.7	-	-	3.2	-	-
Bulk runoff-sediment bound	n.d.	n.d.	-	1.2	0.6	39	1.2	n.d.	-	n.d.	n.d.	-	1.2	n.d.	-
Bulk runoff-sediment bound DWM	n.d.	n.d.	-	1.4	-	39	n.d.	n.d.	-	n.d.	n.d.	-	n.d.	n.d.	-
Moulins (same time period)	0.7	1.4	28	0.6	0.5	28	2.0	1.2	28	1.1	1.3	28	2.2	1.4	28
SURFACE															
Pre-melt ice[a]	0.59	0.14	6	0.3	0.1	6	0.9	0.3	6	0.0	0.0	6	0.6	0.1	6
Snow[a]	1.03	0.17	3	0.45	0.0	3	1.1	0.2	3	0.0	0.0	3	1.02	0.14	3
GrIS ice cores[b]	0.97	n.d.	-	0.45	n.d.	-	1.4	n.d.	-	n.d.	n.d.	-	n.d.	n.d.	-
Summer ice	0.64	0.42	7	0.6	0.6	7	1.3	0.9	7	3.0	2.6	7	2.9	2.1	7
Cryoconite meltwater	1.4	0.4	6	1.1	1.3	6	1.7	0.9	6	0.7	0.4	6	2.4	1.1	6
SUBGLACIAL															
Basal ice	1.5	0.0	6	2.7	0.1	6	3.7	0.1	6	12	1.3	6	15	1.3	6
Incubations (aerobic)	1.4	2.1	7	2.5	2.2	7	3.9	2.5	7	3.36	2	7	7.1	1.7	7
Incubations (anaerobic)	1.03	1.4	6	0.76	0.2	6	1.8	1.3	6	1.79	1	6	5.3	1.4	6

692 **Table 2** Estimates of seasonal fluxes of total dissolved (TDN) and particulate nitrogen (SS-
693 NH_4^+) species (total nitrogen=TN) from Leverett Glacier and the Greenland Ice Sheet in 2000-
694 2010 and 2012 (values marked with an asterisk were below the analytical limit of detection but
695 and hence, are purely indicative)

Glacial Runoff: Leverett Glacier (LG)							
[b]LG Water Flux ($km^3\ a^{-1}$) (2012)	2.2						
Concentration LG (μM)	**TDN**	**DIN**	**DON**	**NO_3^--N**	**NH_4^+-N**	**SS-NH_4^+-N**	**TN+SS-NH4+**
min	0.9*	0.5	0.1	0.1	0.4*	*0.31	1.2
DWM	3.2	1.5	1.7	1.1	0.3	1.4	4.6
max	11	7.5	6.3	5.1	2.4	3.7	15
Flux LG ($t\ a^{-1}$): 2012	**TDN**	**DIN**	**DON**	**NO_3^--N**	**NH_4^+-N**	**SS-NH_4^+-N**	**TN+SS-NH4+**
min	28	15	3	3	12	10	37
DWM	99	46	52	34	9	43	142
max	339	231	194	157	74	114	453
Yield, using DWM ($kg\ N\ km^2\ a^{-1}$)	164	77	87	56	15	72	236

[b]-measured water flux from Leverett Glacier (this manuscript)

696
697 **Table 3** Estimates of seasonal fluxes of total dissolved (TDN) and particulate nitrogen (SS-NH_4^+)
698 species (total nitrogen=TN) from the Greenland Ice Sheet in 2000-2010 and 2012

Glacial Runoff: Greenland Ice Sheet							
[a] GrIS Water Flux ($km^3\ a^{-1}$) (2000-2011)	418						
[a] GrIS Water Flux ($km^3\ a^{-1}$) (2012)	665						
	TDN	**DIN**	**DON**	**NO_3^--N**	**NH_4^+-N**	**SS-NH_4^+-N**	**TN+SS-NH4+**
Flux GrIS ($Gg\ a^{-1}$): 2000-2010							
Min	5.3	3	1	1	2	2	7.1
DWM	19	9	10	6	2	8	27
Max	64	44	37	30	14	22	86
Flux GrIS ($Gg\ a^{-1}$): 2012							
Min	8.4	4.7	0.9	0.9	3.7	2.9	11
DWM	30	14	16	10	2.8	13	43
Max	102	70	59	47	22	34	137
Ice Discharge Greenland Ice Sheet							
[a]GrIS Iceberg Discharge ($km^3\ a^{-1}$)	~600						
	TDN	**DIN**	**DON**	**NO_3^--N**	**NH_4^+-N**	**SS-NH_4^+-N**	**TN+SS-NH4+**
	1.4	1.4	0	0.97	0.45	n/a	1.4
	12	12	0.0	8	4	n/a	12
Arctic River Discharge							
[c]Arctic River mean summer water flux ($km^3\ a^{-1}$)	169						
	TDN	**DIN**	**DON**	**NO_3^--N**	**NH_4^+-N**	**SS-NH_4^+-N**	**TN+SS-NH4+**
[c]Concentration Arctic Rivers (μM)	14	2.7	12	2.0	0.7	n/a	n.d.
[d]Mean summer flux Arctic Rivers ($Gg\ a^{-1}$)	41	8.8	33	7.7	<0.5	n.d.	n.d.

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8 Figure Captions

Figure 1 Map showing the study area, including the location of Leverett Glacier runoff sampling station (white dot), surface sampling site (red dot) and the basal ice sampling location (brown dot), together with Søndre Strømfjord and the Watson River, into which runoff from Leverett Glacier drains.

Figure 2 Times series of nitrogen species in LG runoff from the 2012 melt season depicting concentrations of a) bulk meltwater suspended sediment and sediment-bound ammonium (SS-NH_4^+) b) TDN and DON, c) dissolved nitrate and ammonium, and instantaneous fluxes of, d) SS-NH_4^+ (bulk meltwater discharge, Q, is also shown), e) TDN and DON and f) dissolved nitrate and ammonium. Vertical dotted lines (left to right) indicate 1st May, 1st June and 1st July, 2012. The grey shaded bars reflect inferred subglacial outburst events (Hawkings et al., 2014)

Figure 3 Associations between TDN and DIN in a) runoff, moulin waters, snow and pre-melt ice, where data on snow and pre-melt ice are from (Wolff, 2013;Telling et al., 2012) and b) runoff and glacier surface ecosystems (cryoconite holes, summer ice including dispersed debris) and subglacial ecosystems (basal ice and meltwaters sampled from anaerobic/aerobic long-term subglacial (SG) incubation experiments). A line indicates ratios of 1 for TDN/DIN where the TDN content of samples is entirely comprised of DIN. Samples that plot below this line have a dissolved organic nitrogen component. All samples have been blank corrected and error bars reflect the uncertainty of nutrient analyses given known precision and accuracy.

Figure 4 Association between the TDN concentrations measured simultaneously at the moulin and runoff monitoring sites (the correlation is significant at the 99% confidence level). Insets show the same data (excluding runoff samples) at low concentrations (< 6 μM).

Figure 5 Time series of dissolved nitrogen concentrations measured in a) Live aerobic, b) Live anaerobic c) Sediment-free aerobic and d) Sediment-free anaerobic incubation experiments (note the difference in scale for the y axis between a) and b)-d).

Figure 6 Times series of a) bulk discharge, b) concentrations of sediment-bound NH_4^+ ($P\text{-}NH_4^+$) and dissolved sulphate and c) concentrations of DON and dissolved NH_4^+ in runoff measured during the first (and main) subglacial outburst event during the 2012 season.

Figure 1

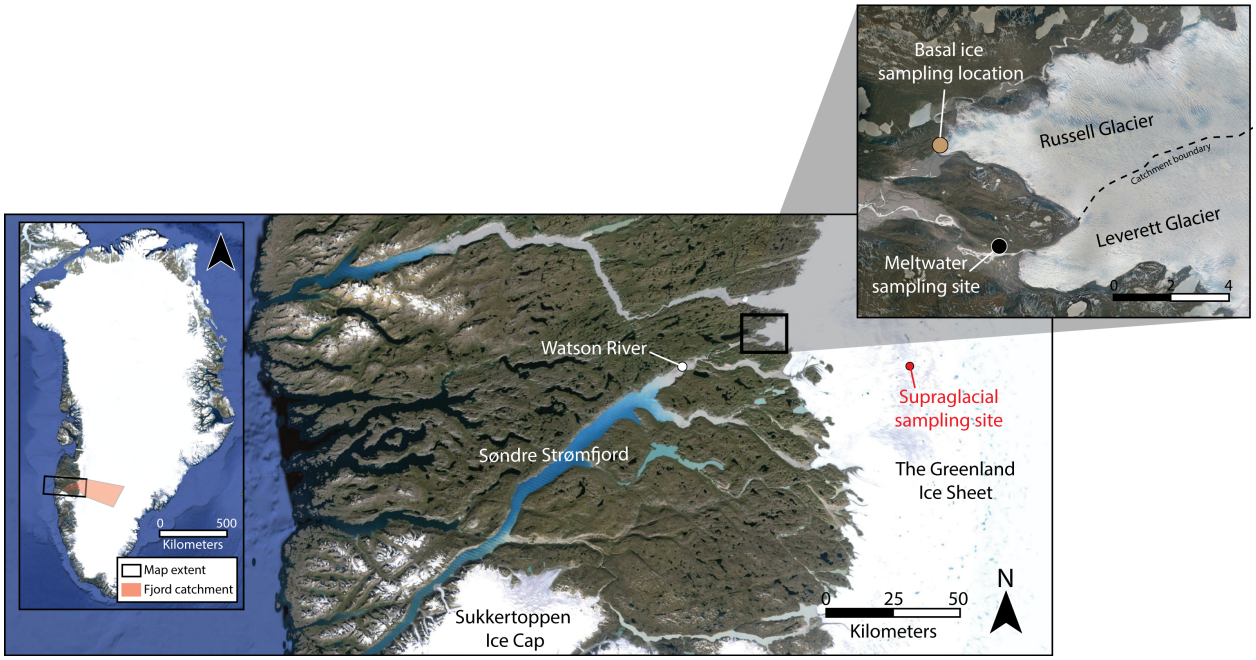


Figure 2

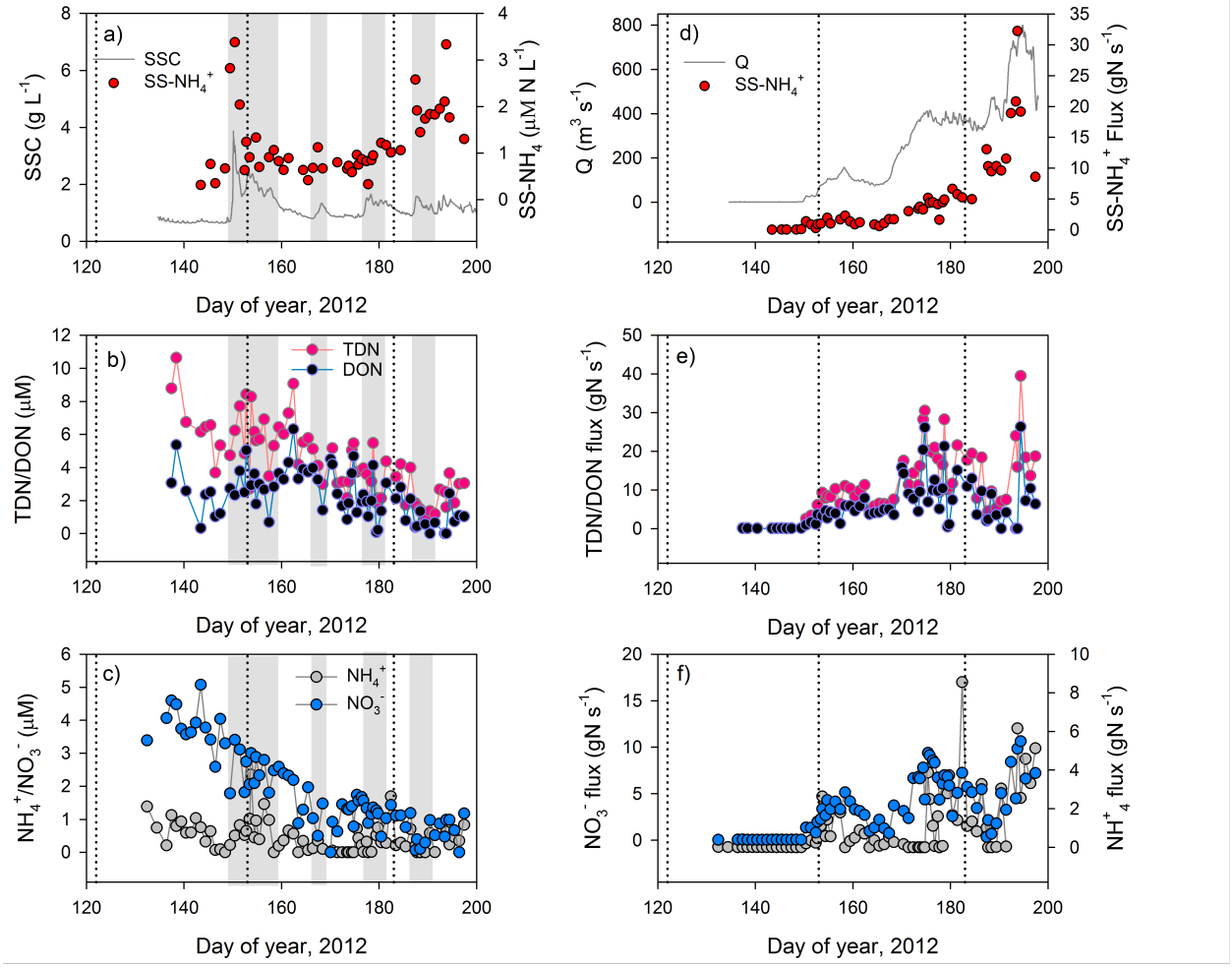

a)
SSC
SS-NH4+
SSC (g L-1)
SS-NH4 (µM N L-1)
d)
Q
SS-NH4+
Q (m3 s-1)
SS-NH4+ Flux (gN s-1)
b)
TDN
DON
TDN/DON (µM)
e)
TDN/DON flux (gN s-1)
c)
NH4+
NO3-
NH4+/NO3- (µM)
f)
NO3- flux (gN s-1)
NH+4 flux (gN s-1)
Day of year, 2012

Figure 3

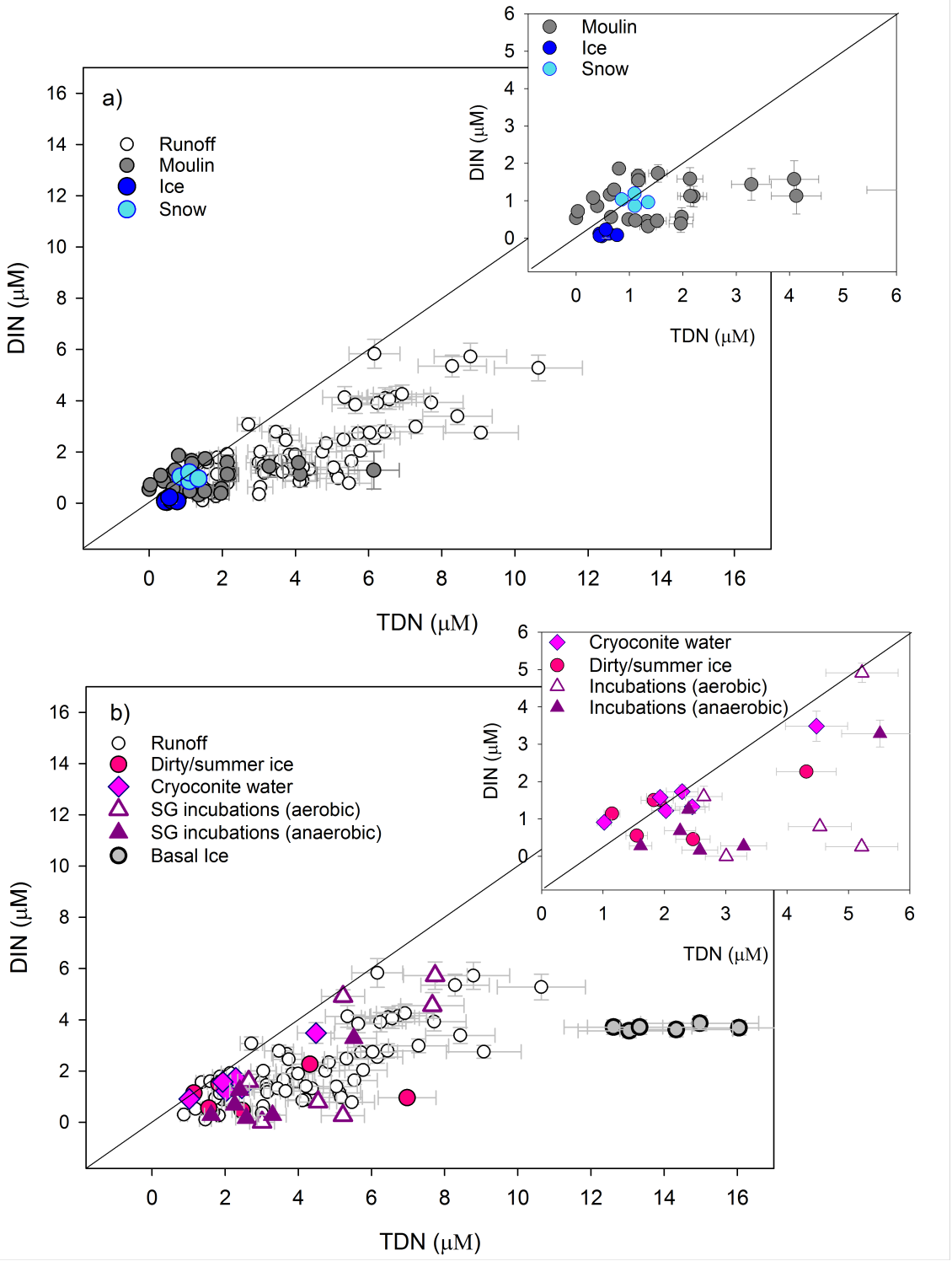

a)
Runoff
Moulin
Ice
Snow
DIN (µM)
TDN (µM)
b)
Runoff
Dirty/summer ice
Cryoconite water
SG incubations (aerobic)
SG incubations (anaerobic)
Basal Ice
Cryoconite water
Dirty/summer ice
Incubations (aerobic)
Incubations (anaerobic)

Figure 4

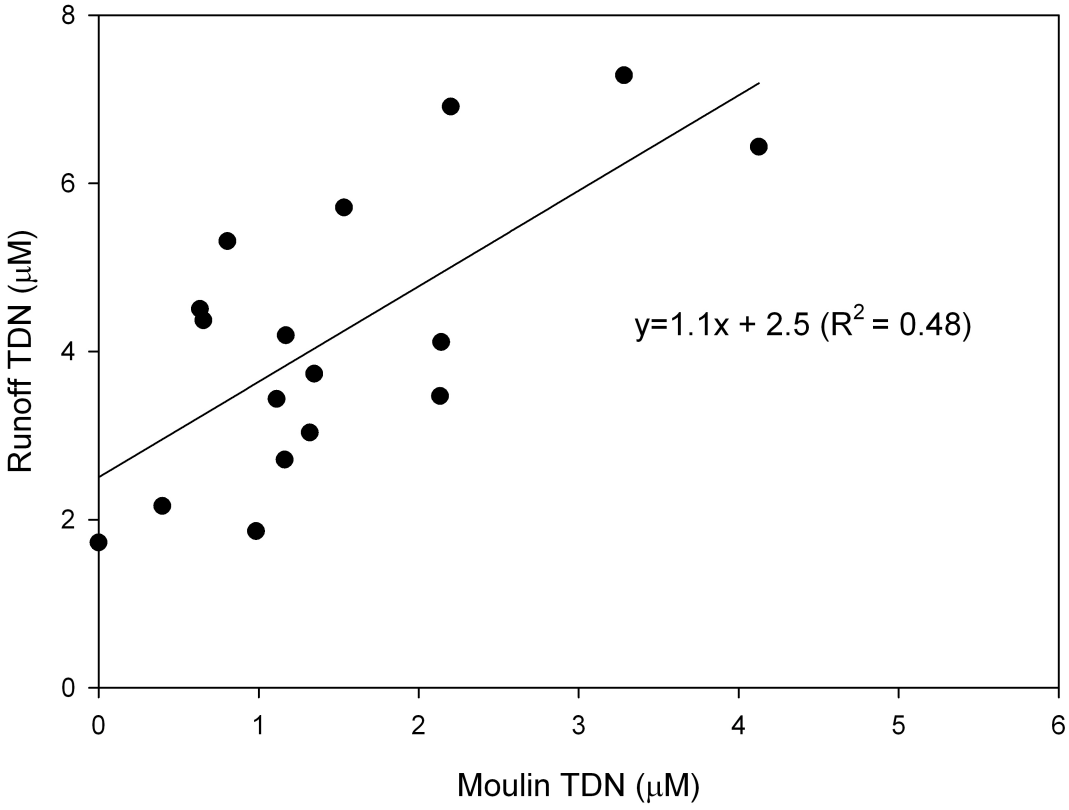
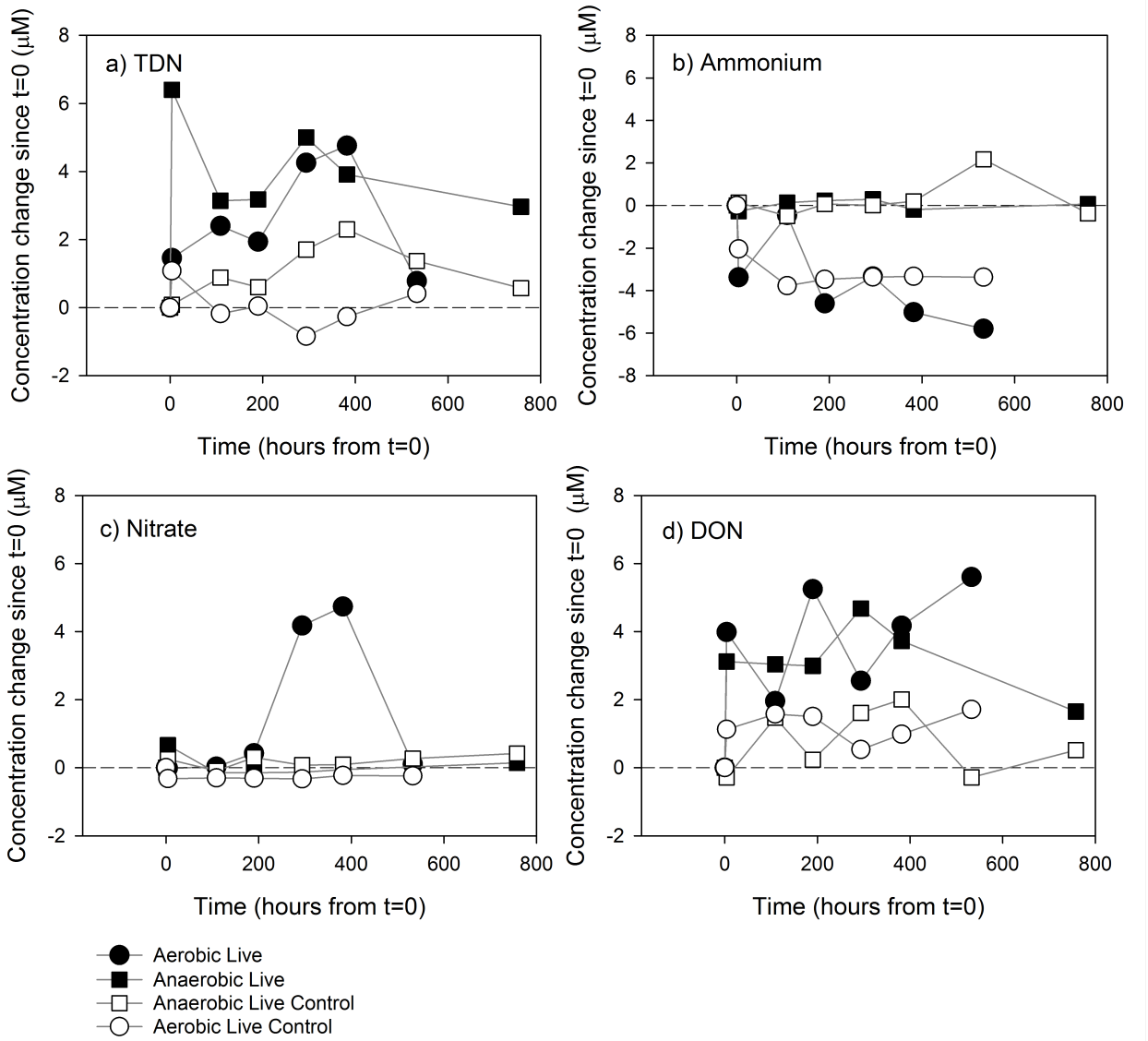


Figure 5


a) TDN
b) Ammonium
c) Nitrate
d) DON
Concentration change since t=0 (μM)
Time (hours from t=0)
Aerobic Live
Anaerobic Live
Anaerobic Live Control
Aerobic Live Control

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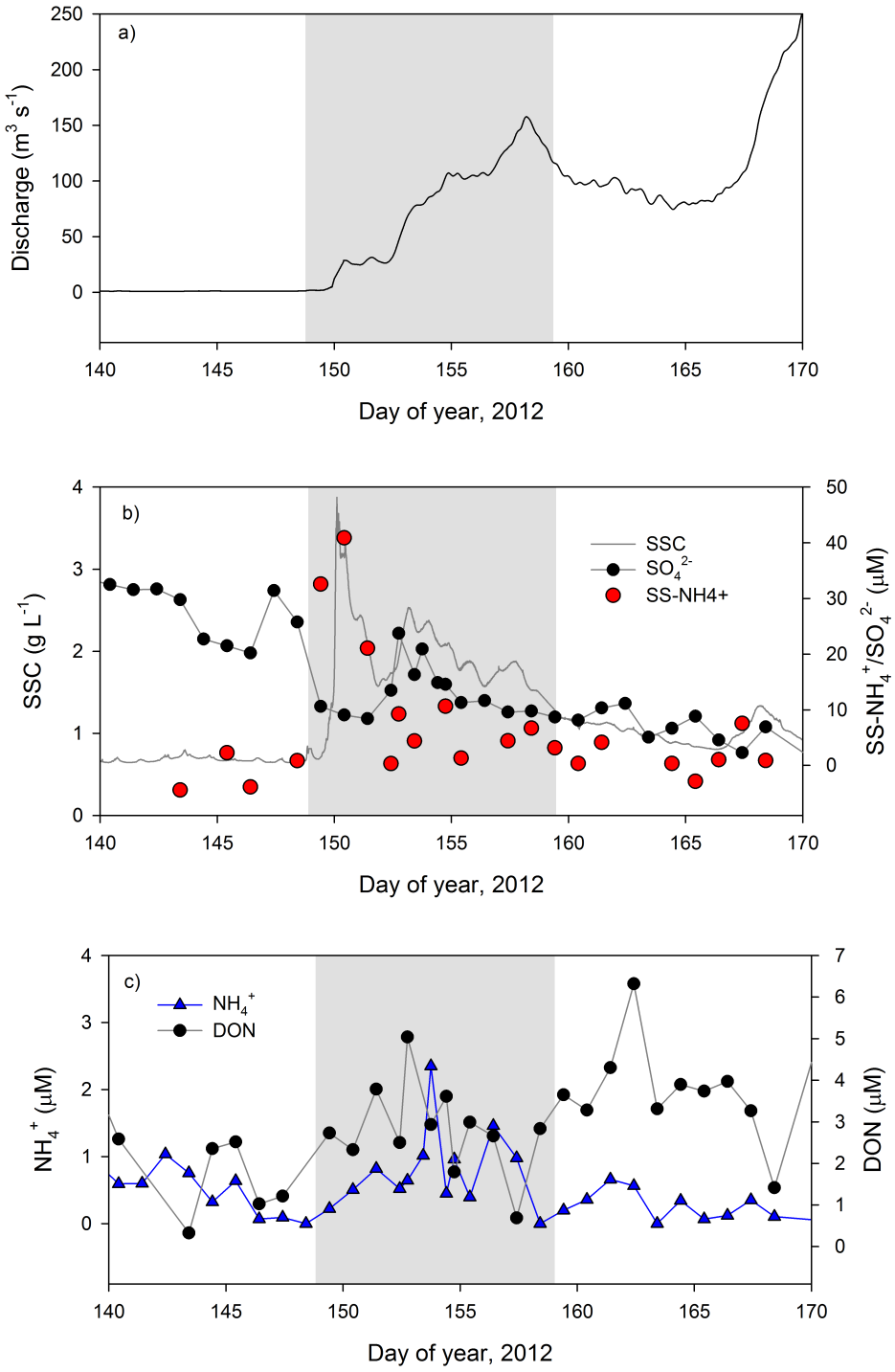
788 **Figure 6**



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