Continuous summer export of nitrogen-rich organic matter from the Greenland Ice Sheet inferred by ultrahigh resolution mass spectrometry

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ABSTRACT

Runoff from glaciers and ice sheets has been acknowledged as a potential source of bioavailable dissolved organic matter (DOM) to downstream ecosystems. This source may become increasingly significant as glacial melt rates increase in response to future climate change. Recent work has identified significant concentrations of bioavailable carbon and iron in Greenland Ice Sheet (GrIS) runoff. The flux characteristics and export of N-rich DOM are poorly understood. Here, we employed electrospray ionization (ESI) coupled to Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to determine the elemental compositions of DOM molecules in supraglacial water and subglacial runoff from a large GrIS outlet glacier. We provide the first detailed temporal analysis of the molecular composition of DOM exported over a full melt season. We find that DOM pools in supraglacial and subglacial runoff are compositionally diverse and that N-rich material is continuously exported throughout the melt season as the snowline retreats further inland. Identification of protein-like compounds and a high proportion of N-rich DOM, accounting for 27-41% of the DOM molecules identified by ESI FT-ICR MS, may suggest a microbial provenance and high bioavailability of glacially-exported DOM to downstream microbial communities.

INTRODUCTION AND RATIONALE

Glacial runoff has recently been acknowledged as an important source of nutrients to downstream coastal and marine ecosystems[1-4]. Total nutrient fluxes from glaciers are predominantly controlled by freshwater fluxes and the physico-chemical and microbiological cycling of nutrients at the glacier surface[5, 6] and bed[7, 8]. Here we focus on the Greenland Ice Sheet (GrIS), where outlet glaciers discharge *c.* 1000 Gt yr^{-1} freshwater runoff to the neighboring oceans[9]. Freshwater fluxes from the GrIS into the North Atlantic are increasing at a rate of 16.9 ± 1.8 km^3 yr^{-1} [9], which may enhance the net terrestrial export of nutrients from the ice sheet. This has the potential to impact primary productivity at local[10] and regional scales[11] and may affect fjord and marine microbial food webs[12]. Recent work suggests that meltwater discharged from the GrIS may export significant quantities of potentially bioavailable dissolved organic matter (DOM)[2, 4] and iron[3, 13] to the coastal oceans. Glacially-exported DOM contains a high proportion of protein-like compounds[1, 14, 15], suggesting the potential export of bioavailable dissolved organic nitrogen (DON). Several studies have estimated the annual DON yield in glacial runoff[16-18] and suggested a microbial[19, 20] or aerosol provenance [21] for DON compounds. However, the abundance and character of the nitrogen-rich compounds in the DOM are still not well known. High N:C elemental ratios (≥0.27; determined by electrospray ionization (ESI) coupled to Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) following C_{18} DOM extraction) in supraglacial samples from a small (5 km^2) western GrIS outlet glacier suggest that nitrogen-containing compounds are an important component of DOM[20]. However, this research has yet to be extended over an entire melt season and to large GrIS catchments.

DOM exported from glaciers reflects OM provenance (allochthonous or autochthonous), age and source location (glacier surface or bed), as well as any abiotic or biotic processing as

meltwater transits the glacial system. At the glacier surface, allochthonous DOM may derive from the deposition of aerosols comprising fossil fuel combustion by-products[15, 21-24] and wind-blown organic material[25]. Allochthonous DOM at the bed likely originates from overridden material (ancient terrestrial origin)[1] or via inputs of DOM from the surface where hydrological connections exist. Autochthonous DOM, arising from in situ microbial production, is generated largely via photoautotrophic activity on the glacier surface[5, 6] and via chemoautotrophic metabolism at the glacier bed[2]. The molecular composition of the DOM of meltwaters may allow us to "fingerprint" surface-derived and subglacially-derived compounds, and thus, would yield insight into the controls on the type and reactivity of DOM exported from the GrIS[4].

DOM export from glaciers and ice sheets may drive heterotrophic production in nearby coastal and marine ecosystems[1]. It may also influence primary production in these ecosystems, via the uptake of amino acids and urea by some phytoplankton[26, 27] or via the remineralisation of DON to dissolved inorganic nitrogen (DIN)[26-28]. It is notable that nitrogen is a primary limiting nutrient for phytoplankton productivity in many of the world's oceans[29], including basins surrounding the GrIS, e.g. the Labrador Sea[30], and the West Greenland[31] and NE Greenland coasts[29]. Reduced levels of DIN are commonly observed in marine surface waters in summer, causing a decline in primary productivity after the seasonal maxima in spring[29, 32]. Primary production also plays a critical role in the net biologically-mediated exchange of CO_2 between the atmosphere and ocean[33], which exerts an important regulatory effect on the global climate system[34]. Summer nutrient limitation of phytoplankton in the Arctic may be enhanced in the future as ocean temperatures increase and marine growing seasons lengthen[35]. Since nitrogen is a limiting nutrient in the Greenland fjords[29] and near

coastal oceans[30, 36], DON and DIN inputs from external sources such as glaciers and ice sheets, are of key importance.

Here, we investigate the abundance and composition of DOM exported from Leverett Glacier, a large (>600 km^2) land-terminating GrIS glacier, during the 2010 melt season. We focus on the presence and proportion of DOM formulas with an N-rich component and low aromatic carbon content. Aliphatic DOM with low C:N ratios may be considered highly bioavailable for microbial metabolism[37], and thus may have the potential to support downstream primary productivity. ESI FT-ICR MS was used to determine the elemental compositions of specific molecules within the DOM and identify compositional differences among DOM pools[20]. We assign elemental formulas solely from the mass measurement, owing to the high mass accuracy (<1 ppm) of this technique[38, 39]. We extend previous work using ESI FT-ICR MS to investigate glacial systems[20, 22] to provide the first detailed temporal analysis of the molecular composition of DOM exported in GrIS runoff, and identify the key controls on the export of N-rich DOM.

METHODS

Field Site and Sample Collection. Glacial samples were collected during the 2010 melt season from Leverett Glacier, West Greenland (~67.10º N, 50.20° W). Leverett Glacier drains a large catchment area (>600 km^2), with an altitudinal range of 100 to >1200 m a.s.l, and is representative of many large land-terminating Greenland outlet glaciers along the western margin. Several re-advances over Quaternary deposits containing fresh organic matter (e.g. paleosols) during the late Holocene[40] suggest a highly dynamic regional ice margin. Runoff is exported through a primary subglacial channel which drains into a large

proglacial river system. This river system joins the Watson River, which discharges into Kangerlussuaq Fjord, eventually emptying into the Davis Strait and the northern arm of the Labrador Sea. Supraglacial meltwater samples were collected on July 20th (day of year (DY) 201) and August 11th (DY 223). A total of 12 subglacial runoff samples were collected from the main outflow channel, ~2.2 km from the Leverett Glacier portal, between May and August (Table S1). Water stage in the subglacial outflow channel was logged at 5 minute intervals and converted to discharge using a rating curve ($r = 0.92$) with an uncertainty of ± 14% (as detailed in[41, 42]). Snowline migration at Leverett Glacier was delineated from Moderate-resolution Imaging Spectrometer (MODIS)[43] imagery (detailed in the Supplementary Methods).

Sample Filtration and Preparation in the Field. Glacial samples for DOC and major ion analyses were collected in pre-furnaced (400 °C for 6 hrs) borosilicate glass bottles and filtered <2 hrs after collection using either plastic apparatus with 0.45 µm cellulose-nitrate membrane filters (major ion determination) or pre-furnaced glass filtration apparatus with pre-furnaced GF/F filters (0.70 µm nominal pore size; DOC determination). Filtered water samples were stored in the dark at -12 ºC (in-field freezer) prior to storage in the University of Bristol LOWTEX facility (≤ -20 ºC). Glacial samples for mass spectrometry analysis were collected in acid-cleaned polycarbonate bottles. Approximately 5 L of meltwater was collected for the supraglacial samples. For the subglacial samples, 2 L was collected due to higher anticipated DOC concentrations in these meltwaters. Due to the high suspended sediment load, subglacial samples were first pre-filtered through 0.7 µm GF/F filters. The subglacial filtrate and the supraglacial samples were then filtered through pre-furnaced 0.2 µm Anodisc membrane filters and acidified to pH 3 with 12 M HCl (Trace-Metal grade, Thermo Fisher Scientific). Filtered water samples for mass spectrometry analysis were stored

in a cold, dark field environment and were refrigerated (~4 ºC) < 7 days after collection and frozen (-20 ºC) on return to Woods Hole Oceanographic Institution (WHOI).

DOC Determination. DOC, measured as non-purgeable organic carbon, was determined by high temperature combustion (680ºC) using a Shimadzu TOC-V_{CSN} Analyzer equipped with a high sensitivity catalyst. Daily precision and accuracy determined via repeat analysis of a DOC standard solution containing potassium hydrogen phthalate ($C_8H_5KO_4$) (Merck, DE) were < ± 6%. The limit of detection was 5 µM C.

Major Ion Determination. Major anions (Cl^-, NO^{3-}, SO_4^{2-}) and cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) were measured on a DX-500 Ion Chromatograph (Dionex, Sunnyvale, CA, USA). HCO_3^- was calculated by charge deficit. Measurement precision and accuracy was *c.* ± 4% and *c.* ± 7%, respectively, although this increased near the instrument detection limit (*c.* 0.5 µeq L^{-1}). SO_4^{2-}, K^+, Na^+, Mg^{2+} and Ca^{2+} concentrations in basal ice and subglacial runoff samples were corrected for snowpack contributions[44], and the residual crustal-derived component is denoted with an asterisk (*).

Solvent Extraction. DOM was extracted with 6 mL PPL cartridges (1 g resin, Varian). The solvent extraction protocol was modified from[45]. Briefly, the cartridges were pre-cleaned according to the manufacturer's instructions (2 volumes of 100% MeOH, Optima grade). The acidified samples were then passed through the cleaned cartridges and the cartridges rinsed with 0.01 M HCl. The cartridges were dried (under a vacuum) for 5 min then the DOM was eluted (by gravity) with MeOH into a pre-furnaced amber vial with PTFE-lined cap. Samples were frozen and later evaporated to dryness under vacuum at 30 ºC. A procedural blank (MeOH) was also evaporated to dryness under vacuum. The samples and solvent blank were

142 stored dry at -20 ºC until further analysis. The DOM extraction efficiency was likely between
143 40 and 60%[45].
144
145 **FT-MS Data Acquisition.** All samples and the solvent blank were analysed on a 7-T ESI
146 FT-ICR mass spectrometer (LTQ-FT-MS, Thermo Fischer Scientific, Waltham, MA) at the
147 WHOI mass spectrometry facility. Samples were reconstituted in 70% MeOH, and analysed
148 in negative ion mode. The solvent used to dilute the samples (70% MeOH) was also analysed
149 as an instrument blank. Samples were infused into the ESI interface at 5 μL min^{-1}, and
150 instrument parameters were optimized for each sample. Samples were diluted to optimize
151 spray conditions; dilutions ranged from 1:2 to 1:8. The capillary temperature was set at 250
152 ºC, and the spray voltage varied between 3.60 and 4.10 kV. As in[20], ~200 scans were
153 collected for each sample. The mass range for full-scan negative ion mode collection was 100
154 < *m/z* < 1000. Weekly mass calibrations were performed with an external standard (Thermo
155 Calibration Mix), and resulted in mass accuracy errors of <1 ppm. The target average
156 resolving power was 400,000 at *m/z* 400.
157
158 **FT MS Data Analysis.** Peak detection, solvent blank correction, peak calibration and
159 elemental formula assignments followed the protocol described in[20]. Negative ion mode
160 spectra were internally re-calibrated using the *m/z* values provided in Table S2. After internal
161 re-calibration, the root mean square (RMS) errors for the calibrants ranged from 0.08 to 0.20
162 (mean value: 0.11). As in previous work[20], elemental formulas of our samples were compared
163 to those assigned to Suwannee River Fulvic Acid (SRFA) Standard I (Suwannee River –
164 International Humic Substances Society, Stock #1S101F), previously analysed with negative
165 ion mode ESI FT-ICR MS, to identify terrestrially-derived components. Similarly, Pony Lake
166 Fulvic Acid (PLFA) Reference (International Humic Substances Society, Lot #1R109F),

167 analysed in negative ion mode, was used to identify microbially-derived components of our
168 Greenland samples. Magnitude-averaged elemental ratios and double bond equivalencies
169 (DBE), a proxy for the amount of double-bonds and rings in a molecule, were also
170 calculated[46] (Table S3).
171
172 **Multivariate Statistics.** Differences among all samples in our dataset were assessed using
173 cluster analysis and non-metric multidimensional (NMS) scaling based on a Bray-Curtis
174 distance measure. For this analysis we limited our interpretation solely to peak diversity by
175 transforming all relative peak heights to presence (peak height = 1) or absence (peak height =
176 0). This was done in order to circumvent known issues associated with using peak height[20]. In
177 the cluster analysis, Ward's linkage was used to group the samples, and p-values for each
178 cluster were calculated via multiple bootstrap resampling (see Supplementary Methods). No
179 additional information was gained from the NMS ordinations so we focus here only on the
180 cluster analysis (Figure 1). The cluster analysis separated the samples into four significantly
181 different groups: Sub1, Sub2, Sub3 and Supra. We then reduced the complexity of our dataset
182 by focusing on the peaks that appear more than once in each group. Thus, we derived what
183 we refer to as 'consolidated sample groups'. For instance, peaks present in Sub1 had to be
184 present in >1 of the samples that are included in the Sub1 group defined by the cluster
185 analysis. This increased our confidence in our observations because they are based on
186 repeatable *m/z* values, rather than on the full dataset, which may contain spurious noise peaks
187 and/or peaks near the signal-to-noise threshold. We also defined 'unique sample groups' for
188 subglacial and supraglacial samples, which required peaks to be present in either only
189 supraglacial sample groups or only subglacial sample groups (labelled 'unique supra' and
190 'unique sub' respectively). Wilcoxon rank-sum tests were conducted to assess the
191 significance of differences in magnitude-averaged N:C, H:C, DBE, and the percentages of

condensed hydrocarbons and terrestrial-like compounds in Supra, Sub1, Sub2 and Sub3 groups (see Supplementary Methods, Table S4).

RESULTS

Formulas were assigned for >90% of the resolved peaks (4999-8747 peaks) in all samples in this dataset (Table S3). Between 29-45% of the peaks identified by ESI FT-ICR MS were assigned to formulas containing CHO (Table 1), with small but significant contributions (18-29%) from other heteroatoms such as S and P. The relative contribution of N is very high, with 27-41% of formulas containing CHON. This is consistent throughout this dataset and contrasts with other published freshwater and marine datasets[46-48]. In comparison to other glacial datasets, the N-containing compounds in this study are within the range previously reported from the European Alps (5-58% as determined by FT-ICR MS)[15]. Interestingly, this N-rich component is present regardless of the glacial source, appearing in both supraglacial and subglacial samples. We analyzed a SRFA standard during these sample runs to monitor instrument performance and ascertained that the instrument was not biased toward N-containing formulas. Therefore, we conclude that these samples are particularly N-rich in the ESI-amenable component of glacial-derived DOM.

We ran a hierarchical cluster analysis and identified four clusters that are distinct at the 90% significance level (based on approximately unbiased (AU) p-values). The two supraglacial samples clustered together (supra, AU p-value = 94%) and are statistically different from the subglacial samples (Figure 1), which clustered into three statistically distinct groups (Sub1, Sub2 and Sub3). Sub1 and Sub2 are the most similar and differentiated by small changes in carbohydrate and lignin percentages (Table 2). Sub3 contains lower

proportions of condensed hydrocarbons than Sub1 and Sub2 but higher contributions in most other compound classes. Notably, many of the N-rich elemental formulas in each group appear in the region associated with protein-like formulas in a van Krevelen diagram (Table 2, Figure S1). The proportion of protein-like elemental formulas in the consolidated sample groups (19.0 – 21.6%) is similar to those from a PLFA standard (23%).

The formula assignments were found to differ between the supraglacial and subglacial samples. Approximately 20% of supraglacial DOM compounds are not found in subglacial runoff (based on total number of formulas assigned, Table S3), and ~50% are unique to the subglacial runoff. The magnitude-averaged elemental ratios suggest that the supraglacial samples are also generally more aliphatic, indicated by the higher H:C and the lower DBE magnitude-averaged values (significant at the 80% and 96% confidence levels, respectively, Tables S3, S4). The elemental formulas in the van Krevelen diagram regions support this hypothesis with higher protein- and lipid-like compounds and lower condensed hydrocarbon contributions[39] (Tables 2, S5) in the consolidated and unique supraglacial groups. The difference in condensed hydrocarbon contributions in consolidated subglacial and supraglacial samples was significant at the 96% confidence level (Table S4). In contrast, the subglacial samples have relatively low H:C and higher DBE magnitude-averaged values, likely from increased condensed hydrocarbon and terrestrial contributions[49], including compounds present in SRFA, the terrestrial end-member[37]. While the differences between subglacial and supraglacial samples outlined above were statistically significant, there may be some bias in the dataset created by the larger number of subglacial samples analysed relative to supraglacial samples. This was unavoidable due to the time-consuming nature of sampling and the logistical complexity of sampling waters far into the GrIS interior. We acknowledge

241 this potential bias when discussing differences between the DOM compositions of subglacial
242 and supraglacial waters.
243
244 There is no apparent temporal trend in the composition of the subglacial samples analysed
245 by ESI FT-ICR MS. This compares well with previous work on DOC export from the
246 catchment[4]. Bulk DOC concentrations (7-32 μM C) were comparable to concentrations in
247 other glacial systems[19, 20] and were not significantly associated with discharge (Table S1). We
248 compared the timing of subglacial sample acquisition with their DOM cluster patterns (Figure
249 2) to ascertain if there were specific hydrological or hydrochemical processes driving these
250 distinctions. We found no clear pattern in the timing of the three clusters in relation to the
251 trends in bulk discharge and major hydrological events (e.g. subglacial "outburst events"
252 denoted by shading in Figure 2).
253
254 We further compared DOM subglacial cluster patterns to geochemical proxies to determine
255 the extent to which subglacial water routing influenced these sample groups. The ratio of
256 divalent to monovalent (di:mono) cations is a proxy for rock:water residence time[50, 51], with
257 higher proportions of monovalent ions believed to reflect enhanced silicate dissolution in
258 long residence time subglacial waters (Figure S3). The di:mono cation ratio appeared to
259 correlate directly with the percent of protein-like formulas in Sub2 (R^2 = 0.86). No
260 correlations were observed in Sub1 and geochemical associations were not determined for
261 Sub3 due to the small sample size (n=3).
262
263 DISCUSSION
264

Molecular character of GrIS DOM. The detailed characterisation of DOM compounds by ESI FT-ICR MS illustrates the unique character of glacial DOM. The wide distribution of assigned formulas within the van Krevelen diagram, including condensed hydrocarbons, lipids, lignins, proteins, carbohydrates and terrestrial groups, and the large diversity in compound formulas within the groupings shows that a chemically diverse range of DOM compounds is exported in runoff from the GrIS. We attribute this to the existence of multiple surface and basal sources for DOM within this large ice sheet catchment, which mix to form the meltwaters exported via the glacier portal at the margin. Glacially-derived DOM also differs markedly to that from marine and other freshwater systems due to higher proportions of N-rich elemental formulas and protein-like formulas (Tables 1, 2, S3). Our characterisation of GrIS DOM is consistent with recent FT-ICR MS analyses of glacial DOM in Alaska[21], the Alps[15] and Greenland[20], and hence, we support the notion that DOM exported from glaciers and ice sheets has a unique molecular signature, albeit influenced by the degree of supraglacial vs. subglacial inputs, which we consider below.

Different compounds from the glacier surface and bed. We performed an inter-comparison of subglacial and supraglacial spectra and found some distinct contrasts in DOM composition which may indicate different pathways of DOM production and transformation in surface and basal environments. However, some differences may arise from the very different number of samples analysed from subglacial and supraglacial environments. The latter may particularly explain the significantly higher (at the 96% confidence level) proportion of condensed hydrocarbons in the subglacial samples compared with the supraglacial samples (Table S4). Condensed hydrocarbons are associated with the combustion products found in anthropogenic aerosols[21] and likely originate from the atmospheric deposition of soot particles[52] containing black carbon-like molecules[53]. The

290 condensed hydrocarbons in the subglacial samples are thought to derive from the deposition
291 of anthropogenic aerosols on the glacier surface and their subsequent transport to the glacier
292 bed via moulins and surface lake drainage[4, 41]. Supraglacial meltwater sampled in this study
293 was collected only 2 km from the GrIS margin, and contained low proportions of condensed
294 hydrocarbons (8.7%), similar to a previous study on the GrIS which reported 6.8%[20]. Here,
295 high levels of erosion on steep ice surfaces is common and may preclude accumulation of
296 condensed hydrocarbons[54]. Earlier research reports higher condensed hydrocarbon percentage
297 contributions in GrIS snow and supraglacial samples located further inland (12.6% and
298 16.0%, respectively)[20]. The reduced physical erosion of surface particulate material in flatter,
299 inland areas of ice and snow permits the accumulation of organic matter, including condensed
300 hydrocarbons, over successive melt seasons[54]. Runoff exported from Leverett Glacier is
301 predominantly sourced from such inland areas, where condensed hydrocarbon contributions
302 are known to be higher[20]. These findings imply some degree of sample bias introduced by the
303 collection of our supraglacial samples close to the ice margin, when runoff is sourced from a
304 much wider area.
305
306 The high N:C ratios identified by ESI FT-ICR MS in the supraglacial (Table S3, mean =
307 1.47 ± 0.13) and subglacial samples (mean = 1.35 ± 0.07) suggest that nitrogen-containing
308 molecules may be a major contributor to glacial DOM[55]. While supraglacial samples were
309 shown to have significantly higher N:C ratios compared with subglacial samples, we do not
310 discuss this difference due to the lower confidence levels (87%) and the potential bias
311 towards the more numerous subglacial samples. Our overall observations concur with those
312 reported in glacial systems elsewhere, which show a high proportion of N-rich formulas in
313 ice cores[22], supraglacial meltwater[20], and runoff from an Arctic Glacier (based on high
314 percentage of protein-like fluorescence)[1]. There are two possible sources of the N-rich

315 aliphatics observed in supraglacial DOM; the water-soluble organic carbon fraction in
316 aerosols[21, 56] or *in situ* microbial activity[15, 20]. Similarly, the provenance of the high proportion
317 of lipid-like compounds found in the supraglacial samples (mean = 1.85 ± 0.07%, compared
318 with a mean of 0.81 ± 0.21% in the subglacial samples, Table S4) may also be microbial[20, 57,
319 58] or aerosol[59]. The high proportion of protein-like formulas in the supra group (21.6%) may
320 also reflect a microbial origin for the N-rich DOM. Protein-like compounds have previously
321 been interpreted as evidence for in situ microbial activity[13, 36, 53] and likely derive from the
322 highly productive photosynthetic microbial communities on the GrIS surface[54]. Based on the
323 large proportion of protein-like compounds, we believe that in situ microbial production is
324 the most likely source of the N-rich DOM on the GrIS surface. This is a pertinent observation
325 since it implies high bioavailability of DOM to downstream microbial communities[1, 4], which
326 may include communities in the glacier subsurface[13].
327
328 Our data also suggest that physico-chemical processes in the subglacial environment may
329 generate new DOM compounds of a distinct character that are not observed on the glacier
330 surface. The presence of unique subglacial formulas is consistent with the addition of new
331 DOM compounds as meltwaters transit the subglacial environment. Unique subglacial
332 compounds typically have high aromaticity which likely reflects the leaching of more
333 recalcitrant, terrestrial material from paleosols known to be present in the catchment[7]. The
334 significantly higher DBE values in subglacial samples compared with supraglacial samples
335 also suggests that allochthonous sources, such as overridden terrestrial material, may be a
336 major contributor to subglacial DOM beneath the GrIS. A terrestrial origin for DOM
337 produced in subglacial environments has been reported elsewhere[19, 60]. Contact with
338 particulate organic matter on the GrIS surface is limited to windblown debris from both local
339 proglacial terrain and more distant sources, explaining the lower proportion of terrestrial-like

compounds in the supraglacial DOM. It is notable that only 14% of the uniquely supraglacial formulas was categorized as terrestrial (Table 2) compared with 31% of the uniquely subglacial formulas. We also find evidence of microbial production of DOM compounds in the subglacial environment based on 18% of the protein-like compounds identified by ESI FT-ICR MS being classified as unique-subglacial (Table 2). Thus a key finding is that N-rich DOM may also derive from the glacier bed. These N-rich compounds may be generated by a range of microbial processes such as in situ chemoautotrophic production[2, 61], chemoheterotrophic oxidation of OM substrates to lower molecular weight compounds[20] and/or the release of DOM from decaying cells. Glacially-overridden material can thus act as a direct or indirect (via microbial cycling) source of DOM.

N-rich export from Leverett Glacier throughout the melt season. We provide the first detailed temporal analysis of the molecular composition of DOM exported in glacial runoff and show that N-rich DOM emerges throughout the melt season[16-18] as the snow line retreats up glacier, with no association with discharge. Mean DON concentrations (~2.3 μM) in Leverett Glacier runoff sampled in 2012 accounted for >50% of the total dissolved nitrogen flux[18], supporting recent work that proposes glacial systems as a source of bioavailable material to downstream ecosystems[1, 2, 4]. We assert that the intermittent tapping of new subglacial and surface DOM sources, including the flushing out of stored subglacial water by rapid supraglacial inputs, or "outburst events", creates the unique DOM signature in GrIS runoff and provides the continuous export of N-rich DOM. This suggests that DOM export from Leverett Glacier comprises inputs from multiple sources, which contribute to the net export throughout the melt season. Supraglacial meltwater, containing DOM sourced from snow and from supraglacial microbial activity, may be transferred rapidly through the glacier system (channelized drainage). Meltwater contributions from the distributed drainage system

365 also contribute to the net DOM export. Meltwater transport rates are typically slow in this
366 latter drainage system and may include DOM derived from in situ microbial metabolism of
367 subglacial organic substrates during over winter storage[62]. The concentration and
368 composition of DOM in meltwater illustrate little change as the slow, inefficient distributed
369 drainage component is diluted by the fast, efficient channelized drainage system. This implies
370 that there is no exhaustion of specific DOM types as the melt season at Leverett Glacier
371 progresses.
372
373 The lack of seasonal exhaustion of DOM types may be explained by the large ablation zone
374 (> 600 km^2 during peak melt) and the potential for meltwaters to access new DOM sources at
375 the ice surface and bed in response to retreat of the snowline further inland[4]. We compare the
376 distribution of compound classes in subglacial samples from a small ('N' Glacier, ~5 km^2)[20]
377 and large (Leverett Glacier) GrIS outlet glacier to investigate whether glaciers with different
378 catchment sizes influence the DOM composition in Greenland. Key differences observable
379 between individual subglacial samples from these two glaciers for samples collected in June-
380 August are a) a higher proportion of terrestrial-like compounds in 'N' Glacier subglacial
381 runoff (56%[20], compared with 26-34% for Leverett Glacier, Table S5), and b) a higher
382 proportion of CHON formulas and protein-like compounds in Leverett Glacier subglacial
383 runoff (27-41% and 16-22%, respectively) compared with 'N' Glacier (8-10% for both, Table
384 1). Ice sheet surfaces can be divided into three 'ecological zones'; the marginal zone, the bare
385 ice zone and the slush zone[54, 63]. Runoff at Leverett Glacier is dominated by melt sourced
386 from the bare ice zone, which may extend ~100 km into the GrIS interior (Figure S2). This
387 contrasts with 'N' Glacier where most of the runoff is derived from the marginal zone.
388 However, contrasts in melt zone proportional contributions to runoff may not fully explain
389 the differences in the DOM compound classes in subglacial runoff between the two glaciers.

Glacier margin supraglacial samples presented here and in [20] show a higher % CHON and protein-like content, and a lower % terrestrial contribution than those sampled from further inland (presented in [20]). This is the reverse of what would be required to explain differences in subglacial runoff from the two systems based upon contrasting runoff contributing areas. This tentatively suggests that the differences in compounds classes in runoff from the two glacier systems arise from processes at the GrIS bed. The GrIS margin has fluctuated considerably over the last few 1000 years, resulting in the sequestration of soil carbon beneath the ice sheet[64]. It is likely that 'N' Glacier overrode a larger area of soil relative to the total catchment size, compared with Leverett Glacier, as it is confined to the marginal zone of the GrIS. This would explain the larger percentages of terrestrial-like compounds at 'N' Glacier and the lower percentages of CHON and protein-like formulas (when excluding the 'N' Glacier May sample), which may arise from modification of the DOM composition as meltwaters leach DOM from a subglacial soil layer or as N-rich glacial DOM is utilized for microbial activity in this soil layer. This suggests that contrasts in DOM character between glaciers in Greenland may be due to contrasts in the overridden substrate material.

At large GrIS outlet glaciers, additional solute acquisition during periods of high bulk meltwater are expected to counter dilution effects normally occurring when a solute-rich baseflow component is diluted by a solute-poor channelized component[4]. Here, this is illustrated by the absence of an inverse association between DOM concentrations and bulk meltwater discharge. The geochemical proxy employed (ratio of di:mono cations) also shows that meltwater residence time in the subglacial drainage system, and the resultant character of DOM in subglacial export, is more complex than the typical relationship between geochemical species and residence time as applied to smaller glacier systems[44]. Monovalent ion concentrations are thought to increase in longer residence time waters due to enhanced

silicate, relative to carbonate, dissolution[51], resulting in a lower di:mono ratio. Higher ratios are indicative of carbonate weathering and rapid meltwater transport through the subglacial system[50]. In Sub2, there is evidence that the percentage of protein-like compounds increases with the di:mono ratio (Figure S3), which may be indicative of a supraglacial origin and rapid, conservative transport through the glacial system with limited subglacial storage at times when subglacial residence time are low. However, no trends were observed in Sub1 and we were unable to conduct a robust regression analysis on Sub3 due to the small sample number (n=3). The lack of significant associations between these geochemical indices may support earlier assertions that meltwater from a range of sources is constantly being flushed through the subglacial drainage system. This is strengthened by the lack of a temporal trend in the export of the subglacial groups and evidence that the net meltwater export comprises runoff that is delivered through several hydrological pathways

In summary, our results indicate that the molecular composition of DOM exported from large, GrIS outlet glaciers is compositionally diverse and exhibits a high proportion of N-rich and protein-like formulas compared with marine and other freshwater systems. The source for the protein-like compounds is likely to be microbial activity at the surface and bed of the ice sheet, but we cannot rule out the possibility that there is also an aerosol source for N-containing formulas. The continuous supply of this potentially highly bioavailable DOM to runoff throughout the melt season implies a lack of any seasonal exhaustion trend in the study year. It suggests that new sources of DOM are tapped at the surface and bed with progressive retreat of the snowline. As such, the GrIS may be providing an important nitrogen subsidy to proglacial, fjord and coastal marine environments, where such bioavailable DOM may be particularly important in sustaining microbial production at the height of the summer melt season.

440 Table 1 General parameters from negative ion mode formula assignments. Elemental ratios
441 were calculated as magnitude-averaged values from m/z values with assigned elemental
442 formulas. Previously published general parameters from other environments are also shown
443 for comparison. The consolidated group name is given in parentheses for samples reported in
444 this study. 'n.r.' means the data was not reported. [§]proglacial tarn sampled at the margins of
445 the Greenland Ice Sheet. †Antarctica. [1]recalculated from raw data published in reference.
446 [2]mean, n=4. [3]CHONS only. SRFA = Suwannee River Fulvic Acid. WSOC = Water Soluble
447 Organic Carbon. DY = day of year.

448

Sample – Group	**% formula with CHO**	**% formula with CHON**	**% formula with CHONS, CHONP, CHONSP**	**Reference**
		Greenland Supraglacial		
DY 201 (Supra)	31.5	31.5	26.1	This study
DY 223 (Supra)	35.2	27.0	28.6	This study
Snow	17.4	23.4	42.5	Bhatia et al., (2010)
Supra inland	1.7	32.0	50.1	Bhatia et al., (2010)
Supra margin	23.3	34.7	23.0	Bhatia et al., (2010)
		Greenland Subglacial		
DY 178 (Sub1)	32.1	36.4	22.4	This study
DY 181 (Sub1)	32.2	35.6	23.1	This study
DY 207 (Sub1)	29.8	40.9	20.5	This study
DY 220 (Sub1)	34.7	38.9	18.6	This study
DY 151 (Sub2)	34.1	33.7	23.3	This study
DY 164 (Sub2)	38.2	33.3	21.3	This study
DY 212 (Sub2)	36.2	34.7	20.8	This study
DY 218 (Sub2)	40.1	31.7	21.5	This study

DY 224 (Sub2)	37.5	36.3	18.2	This study
DY 161 (Sub3)	29.4	39.8	23.6	This study
DY 204 (Sub3)	36.3	32.1	23.5	This study
DY 210 (Sub3)	44.5	27.4	21.6	This study
May Sub	55.6	26.1	11.3	Bhatia et al., (2010)
July Sub 1	69.2	8.1	18.9	Bhatia et al., (2010)
July Sub 2	58.9	10.8	26.2	Bhatia et al., (2010)
		Terrestrial End-Members		
Proglacial tarn[§]	65.7	12.3	17.5	Bhatia et al., (2010)
SRFA	91.3	2.0	4.5	Bhatia et al., (2010)
		Microbial End-Member		
Pony Lake[†]	31.2	58.4	5.1	This study
		Fresh Water		
Delaware River[1]	91.6	0.6	0.8	Kujawinski et al., (2009)
Chesapeake Bay[2*]	90.5	Sum: 9.5%[*]	n.r.	Sleighter and Hatcher (2008)
		Surface Water		
Sargasso Sea[1]	78.8	6.6	2.0	Kujawinski et al., (2009)
		Deep Ocean		
Sargasso Sea[1]	72.2	2.4	5.4	Kujawinski et al., (2009)
		Aerosol-derived WSOC		
Virginia[3]	77.0	12.0	<1.0	Wozniak et al., (2008)
New York[3]	75.0	6.0	<1.0	Wozniak et al., (2008)

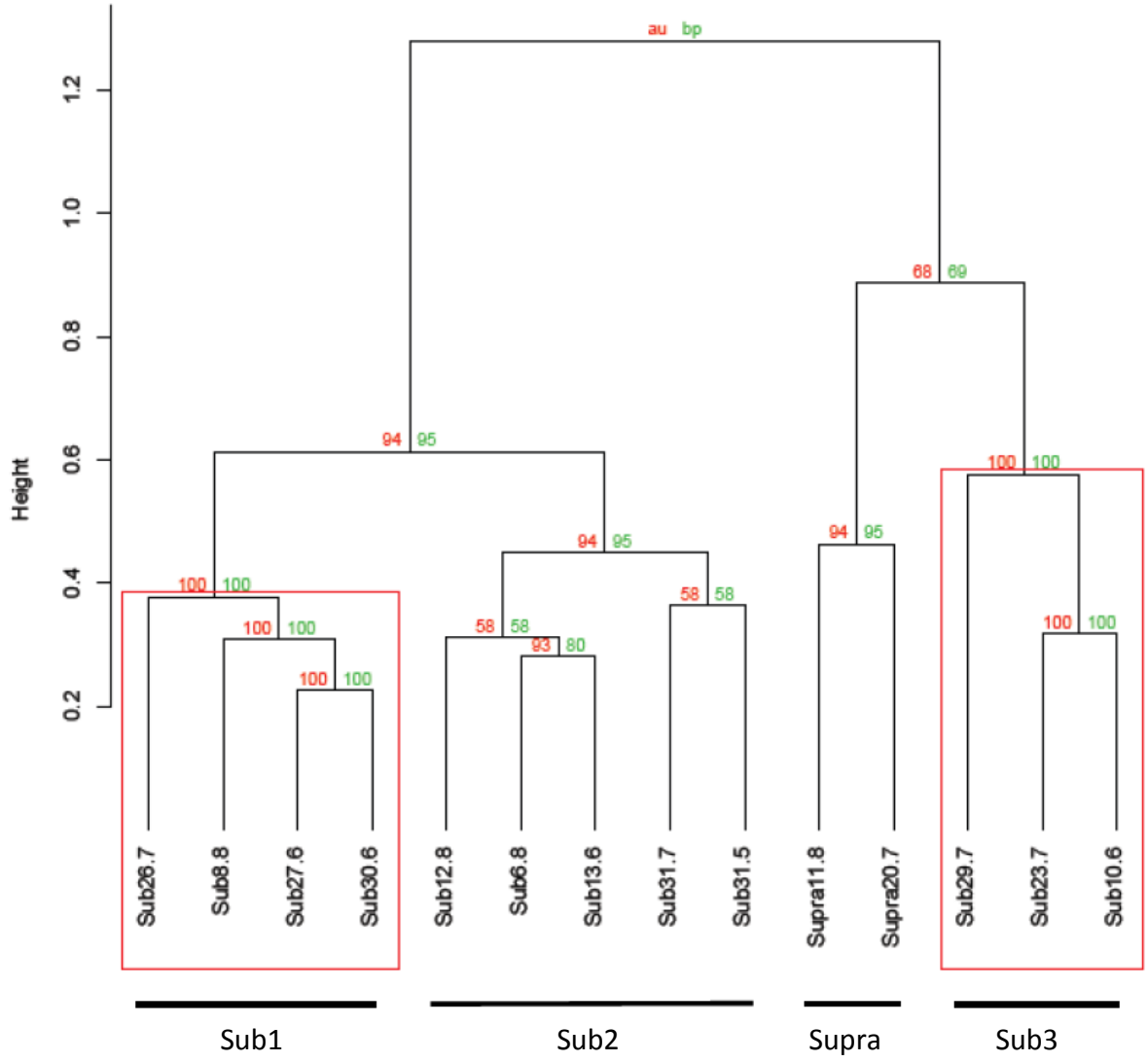
[*]Values from Chesapeake Bay Bridge were not reported as individual formula classes and are shown here as the sum of non-CHO formulas (as in reference).

452 Table 2. Percentage of negative ion mode formula assignments located in different regions of the van Krevelen diagram for each consolidated
453 group, and the percentage unique to the subglacial and supraglacial groups. Data that was not reported is denoted by "n.r". † = Antarctica. * =
454 recalculated from raw data in Kujawinski et al., (2009). SRFA = Suwannee River Fulvic Acid. The terrestrial compound class refers to formula
455 assignments that exactly matched the SRFA samples.

456

Sample	Condensed hydrocarbons	Lipids	Lignin	Protein	Carbohydrate	Terrestrial	Reference
Supra	8.7	1.81	5.5	21.6	0.40	21.9	This study
Sub1	11.1	0.67	6.3	20.6	0.55	29.3	This study
Sub2	11.5	0.72	5.8	19.6	0.31	30.6	This study
Sub3	9.5	0.88	6.8	19.0	0.41	30.2	This study
Unique supra	6.0	4.10	1.5	13.6	0.00	14.0	This study
Unique Sub	12.4	0.54	5.4	18.0	0.53	31.4	This study
SWFA	2.0	0.00	4.5	1.9	0.00	85.6	Bhatia et al., (2010)
Pony Lake†	3.0	0.30	10.0	23.0	0.90	45.0	This study
Fresh Water*	1.9	0.40	25.5	11.9	0.00	54.9	Kujawinski et al., (2009)
Surface Water*	9.0	0.30	21.9	12.4	0.00	57.6	Kujawinski et al., (2009)
Deep Ocean*	13.1	0.10	21.6	6.2	0.00	65.4	Kujawinski et al., (2009)

457 Figure 1 Cluster dendrogram of the negative ion mode samples, based on presence/absence data
458 and Bray-Curtis distance measure, using Ward's linkage method, and illustrating au/bp
459 confidence levels (%). DY refers to day of year. au = approximately unbiased p-value (given in
460 red in the figure) and bp = bootstrap probability value (given in blue in the figure, see
461 Supplementary Methods). Boxes are drawn around the clusters with au ≥ 95%.

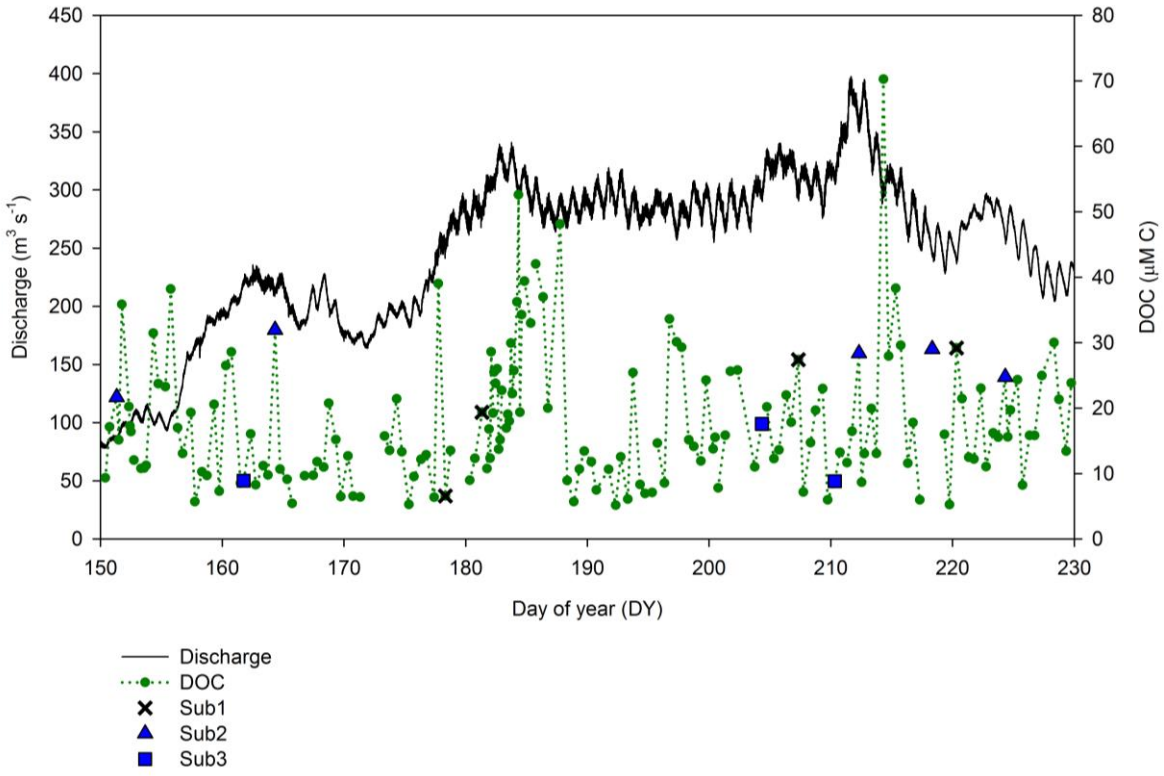


462

463 Figure 2 Time series of DOC export and discharge from Leverett Glacier including markings of
464 when subglacial samples were collected for FT-ICR MS analysis (black crosses, blue triangles
465 and squares) and outburst events (shaded).

466

467



ASSOCIATED CONTENT

Methods (delineation of the snowline and associated figure, statistical analyses (hierarchical cluster analysis with p-values and Wilcoxon rank-sum test)), results tables with information on sample collection, ESI FT-ICR MS and statistical analyses, a figure illustrating van Krevelen diagrams for two of the samples, and a figure comparing geochemical parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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