Biogeosciences, 11, 4015–4028, 2014
www.biogeosciences.net/11/4015/2014/
doi:10.5194/bg-11-4015-2014

Biogeosciences Open Access

Greenland Ice Sheet exports labile organic carbon to the Arctic oceans

E. C. Lawson[1,2], J. L. Wadham[2], M. Tranter[2], M. Stibal[3], G. P. Lis[2], C. E. H. Butler[2], J. Laybourn-Parry[2], P. Nienow[4], D. Chandler[2], and P. Dewsbury[5]

[1]School of Geography, University of Nottingham, University Park, Nottingham, NG7 2RD, UK
[2]Bristol Glaciology Centre, School of Geographical Sciences, University Road, Bristol, BS8 1SS, UK
[3]Department of Geochemistry, Geological Survey of Denmark and Greenland, Øster Voldgade 10, 1350 Copenhagen K, Denmark
[4]School of Geosciences, University of Edinburgh, Geography Building, Drummond Street, Edinburgh, EH8 9XP, UK
[5]Thermo Fisher Scientific, 4, Albany Court, Camberley, GU16 7QL, Surrey, UK

Correspondence to: E. C. Lawson (emily.lawson@nottingham.ac.uk)

Received: 15 November 2013 – Published in Biogeosciences Discuss.: 10 December 2013
Revised: 25 April 2014 – Accepted: 18 June 2014 – Published: 31 July 2014

Abstract. Runoff from small glacier systems contains dissolved organic carbon (DOC) rich in protein-like, low molecular weight (LMW) compounds, designating glaciers as an important source of bioavailable carbon for downstream heterotrophic activity. Fluxes of DOC and particulate organic carbon (POC) exported from large Greenland catchments, however, remain unquantified, despite the Greenland Ice Sheet (GrIS) being the largest source of global glacial runoff (ca. 400 $km^3\,yr^{-1}$). We report high and episodic fluxes of POC and DOC from a large (> 600 km^2) GrIS catchment during contrasting melt seasons. POC dominates organic carbon (OC) export (70–89 % on average), is sourced from the ice sheet bed, and contains a significant bioreactive component (9 % carbohydrates). A major source of the "bioavailable" (free carbohydrate) LMW–DOC fraction is microbial activity on the ice sheet surface, with some further addition of LMW–DOC to meltwaters by biogeochemical processes at the ice sheet bed. The bioavailability of the exported DOC (26–53%) to downstream marine microorganisms is similar to that reported from other glacial watersheds. Annual fluxes of DOC and free carbohydrates during two melt seasons were similar, despite the approximately two-fold difference in runoff fluxes, suggesting production-limited DOC sources. POC fluxes were also insensitive to an increase in seasonal runoff volumes, indicating a supply limitation in suspended sediment in runoff. Scaled to the GrIS, the combined DOC (0.13–0.17 Tg C yr^{-1} (±13 %)) and POC fluxes (mean = 0.36–1.52 Tg C yr^{-1} (±14 %)) are of a similar order of magnitude to a large Arctic river system, and hence may represent an important OC source to the near-coastal North Atlantic, Greenland and Labrador seas.

1 Introduction

Glaciers and ice sheets are known to harbour diverse and active populations of microorganisms (Anesio et al., 2009; Cheng and Foght, 2007; Lanoil et al., 2009; Sharp et al., 1999; Stibal et al., 2012a). These drive subglacial chemical weathering (Montross et al., 2012; Sharp et al., 1999) and are responsible for nutrient export in glacial runoff (Barker et al., 2006). Glacial ecosystems thus act as potential "fertilisers" of downstream ecosystems, including coastal waters (Bhatia et al., 2013a; Hood et al., 2009). On the glacier surface, supraglacial ecosystems fix atmospheric carbon and generate bioavailable dissolved organic carbon (DOC) (Anesio et al., 2009; Anesio et al., 2010; Stibal and Tranter, 2007), which in turn can be transported into the subglacial drainage system via the network of moulins and crevasses (Das et al., 2008; Nienow et al., 1998). At the glacier bed, microorganisms may fix inorganic carbon via chemolithoautotrophy, and can metabolise organic carbon (OC) present in overridden soils and vegetation (Bhatia et al., 2010; Skidmore et al., 2000). Recent evidence of viable microbial communities

(Cheng and Foght, 2007; Christner et al., 2009; Lanoil et al., 2009; Sharp et al., 1999) that can actively degrade OC in sediment beneath glaciers challenges traditional views of a subglacial environment dominated by abiotic processes (Chillrud et al., 1994; Raiswell, 1984). Instead, a mounting body of evidence documents active carbon cycling in small glacier systems (Barker et al., 2009; Hood et al., 2009; Singer et al., 2012; Stubbins et al., 2012). In particular, the balance between supraglacial phototrophy and heterotrophy and the resultant provision of bioavailable DOC for downstream utilisation has been studied extensively in both Alpine glacier systems (Anesio et al., 2009; Stibal et al., 2008) and on the surface of large ice sheets (Hodson et al., 2010; Stibal et al., 2012a). DOC concentrations in glacial runoff are typically low, $\sim$ 10–60 µM C (Barker et al., 2006; Bhatia et al., 2010; Lafrenière and Sharp, 2004), yet the high content of protein-like compounds and low C : N ratios (Barker et al., 2009; Hood et al., 2009; Singer et al., 2012) suggests that glacial DOC is highly labile and that the source is microbial (Hood et al., 2009). Bioavailable DOC yields from ice sheets may be considerable due to the high meltwater fluxes. Approximately 350 meltwater outlets around the periphery of the Greenland Ice Sheet (GrIS) terminate in the ocean (Lewis and Smith, 2009), and discharge ca. 351–397 $km^3\,yr^{-1}$ of freshwater runoff (Hanna et al., 2008; Mernild et al., 2010). However, the bioavailable DOC export from large ice sheet catchments and their response to changing melt conditions are unknown. Furthermore, few data exist on particulate OC (POC) exports from glacial environments (Bhatia et al., 2013a), although particulate export is recognised as important for some nutrients such as phosphorus (Hodson et al., 2008). The high erosive capacity of the GrIS (Cowton et al., 2012) furthermore suggests the potential for significant downstream sediment transport and the export of bioreactive particulate material. An understanding of the controls upon the type and reactivity of OC exported from large glacial outlets of the GrIS is currently lacking.

Here, we report on both DOC and POC concentrations in runoff from a large Greenland outlet glacier during two contrasting melt seasons to determine the quality, quantity and temporal variation of OC fluxes. We focused on a subset of low molecular weight DOC (LMW–DOC) compounds (free carbohydrates and free amino acids), in addition to the presence of protein-like compounds in florescence spectra (Fellman et al., 2009; Hood et al., 2009), in order to assess the magnitude and possible origins of the bioavailable fractions. Free carbohydrates and amino acids have been used as markers for labile DOC in natural waters (Kirchman et al., 2001) and are associated with recent production, e.g. by photosynthesis or chemosynthesis (Biersmith and Benner, 1998; Jansen et al., 1982). They have high turnover rates (hours to days) and are the preferred substrate for bacterial growth (Rich et al., 1997). We also investigated the lability of DOC exported from the GrIS to downstream near-coastal marine microorganisms via a suite of incubation experiments, and determined changes in bacteria concentrations that were likely associated with the utilisation of the glacially derived bioavailable DOC. Finally, we calculated DOC and POC fluxes on the catchment and ice sheet scales, and explored the potential change in these fluxes in response to predicted future increases in runoff (Hanna et al., 2008). The evaluation of the bioavailability and magnitude of OC exports from a large ice sheet system aims to enhance the understanding of how future changes in glacier export dynamics, caused by a changing climate, could affect the cycling of DOC in Arctic coastal ecosystems.

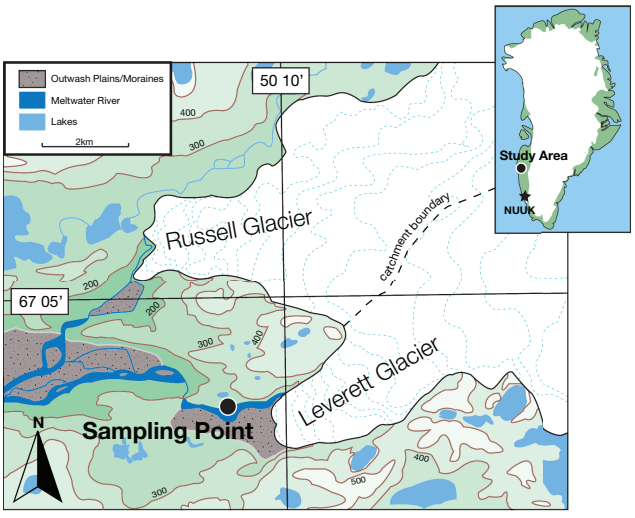

Figure 1. Map of the terminus of Leverett Glacier (sampling location is noted) and context within the wider Greenland Ice Sheet. Contour elevations are shown in metres and land-use type is denoted (white corresponds to the ice sheet); from Hawkings et al. (2014).

2 Methods

2.1 Field site description and sampling

Runoff samples were collected during the 2009 and 2010 melt seasons from the primary subglacial channel draining Leverett Glacier, the southern lobe in the Russell Glacier catchment, western Greenland ($\sim$ 67.10° N, 50.20° W; Fig. 1 from Hawkings et al., 2014). Leverett Glacier is representative of many land-terminating Greenland outlet glaciers, draining a large catchment area (> 600 km^2) with an altitudinal range of 100 to > 1000 m a.s.l. (Bartholomew et al., 2011). The bedrock consists of amphibolites and granulite facies gneisses reworked in the early Proterozoic (Escher and Watt, 1976). The regional ice margin re-advanced over Quaternary deposits containing fresh organic matter (e.g. paleosols) during the late Holocene (Ten Brink and Weidick, 1974). Runoff from Leverett Glacier feeds a large river system which flows into Kangerlussuaq Fjord and then into the Davis Strait.

Runoff samples were collected at times of approximate daily discharge maxima and minima for a 53-day period in 2009 (23 June–18 August) and an 81-day period in 2010 (25 May–21 August). Discharge ($m^3\,s^{-1}$) and suspended sediment concentration (SSC, $g\,L^{-1}$) were calculated following the methods in Bartholomew et al. (2011) and Cowton et al. (2012). Supraglacial meltwater, snow and cryoconite hole water samples were collected in 2009–2011 (Supplement Sect. 1.1 and Table S1). Samples were transported frozen ($\leq -20\,°C$) to the University of Bristol LOWTEX facility and subsequently prepared for analytical processing following the protocol detailed in Supplement Sect. 2 and 3.

2.2 Analytical protocols

2.2.1 POC and particulate carbohydrates

POC was calculated as the difference between total sediment carbon (TC) and sediment inorganic carbon (IC) for 26 suspended sediment (SS) samples (7 from 2009 and 19 from 2010) collected from the Leverett Glacier outflow channel. TC and IC were measured on a EuroVector EA1108 elemental analyser (EuroVector, Milan, Italy) and a modified Coulomat 702 analyser (Strohlein Instruments, Kaarst, Germany), respectively (Supplement Sect. 3.1). We multiplied the concentration of OC (in mg per gram of sediment) by the SSC ($g\,L^{-1}$) to give the POC value in $mg\,L^{-1}$, and then converted it to µM C. Approximately 9 % of the POC is assumed to be reactive, based on conservative estimates of extractable carbohydrates in basal sediment (mean $= 9.04 \pm 7.55$, $n = 11$; Table S2), as quantified by ion chromatography following an acid-extraction protocol to convert any polysaccharides to lower molecular weight components (Jensen et al., 1995; Stibal et al., 2010) (Supplement Sect. 3.2). The particulate carbohydrate measurements that we refer to represent monosaccharides and disaccharides present in the sediment that were not destroyed by the hydrolysis procedure, plus the hydrolysis product of polysaccharides present in the subglacial sediment.

2.2.2 DOC

DOC concentrations in the glacial samples, measured as non-purgeable organic carbon, were determined by high-temperature combustion (680 °C) using a Shimadzu TOC-V_{CSN}/TNM-1 analyser equipped with a high-sensitivity catalyst (detailed in Supplement Sect. 3.3).

2.2.3 Free carbohydrates and amino acids

Free carbohydrate and free amino acid determinations were performed by an ICS-3000 dual-analysis Reagent-Free Ion Chromatography system (Dionex, Sunnyvale, USA). Polysaccharides and larger DOC compounds, e.g. combined carbohydrates and amino acids, were not resolved by ion chromatography in this study, as we focused on free carbohydrates and amino acids owing to their bioavailability to microorganisms (Biersmith and Benner, 1998; Kirchman et al., 2001). Hence, we likely underestimate the total carbohydrate and amino acid concentrations in the glacial samples. Nine carbohydrates (fucose, rhamnose, arabinose, galactose, glucose, xylose/mannose, fructose/sucrose, ribose and lactose) were separated isocratically on a CarboPac PA20 column (3×150 mm) at a flow rate of $0.35\,mL\,min^{-1}$. Fourteen free amino acids (lysine, alanine, threonine, glycine, valine, serine/proline, isoleucine, leucine, methionine, phenylalanine, cysteine, aspartic acid, glutamic acid and tyrosine) were separated on an AminoPac PA10 column (2×250 mm) using a gradient mix of 0.25 M NaOH, 1.0 M Na–acetate (NaOAC) and deionised water, at a flow rate of $0.25\,mL\,min^{-1}$. Full details are given in Supplement Sect. 3.4.

2.2.4 Major ions and dissolved Si

Major anions (Cl^-, NO^{3-}, SO_4^{2-}) and cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) were measured on a DX-500 Ion Chromatography system (Dionex, Sunnyvale, USA), and HCO_3^- was calculated by charge deficit. Dissolved Si was determined using a continuous segmented-flow Bran and Luebbe AutoAnalyser. Full details are given in Supplement Sect. 3.5.

2.2.5 Spectrofluorescence

Spectrofluorometric analyses provided a qualitative overview of the relative proportions of protein-like and humic-like fluorophores based on the complexity of DOC in the fulvic acid fraction (Baker and Lamont-BIack, 2001; Chen et al., 2003). Synchronous fluorescence spectra were determined on a HORIBA Jobin Yvon Fluorolog-3 spectrofluorometer. A 10 nm bandwidth and an 18 nm offset between excitation and emission monochromators were employed. This followed the protocol of previous investigations into the synchronous fluorescence spectra of glacial samples, for example by Barker et al. (2006). All scans were corrected for Ramen and Rayleigh scattering (detailed in Supplement Sect. 3.6).

2.3 Bioavailability experiments

The bioavailability of DOC (BDOC) in glacial runoff was determined as the difference in DOC at the start and end of laboratory incubations (22-day duration) (Fellman et al., 2008; Fellman et al., 2010). 18 live BDOC incubations were set up (9 containing glacial runoff and 9 containing proglacial runoff, inoculated with near-coastal marine water) and incubated at 1 °C in the dark (full details are given in Supplement Sect. 3.7). 21 control incubations (9 containing 100 mL proglacial runoff, 9 containing 100 mL glacial runoff, and 3 containing marine 100 mL water) were also set up and sampled according to the live incubations. Sample water was extracted after 1, 2 and 22 days (hereafter referred to as

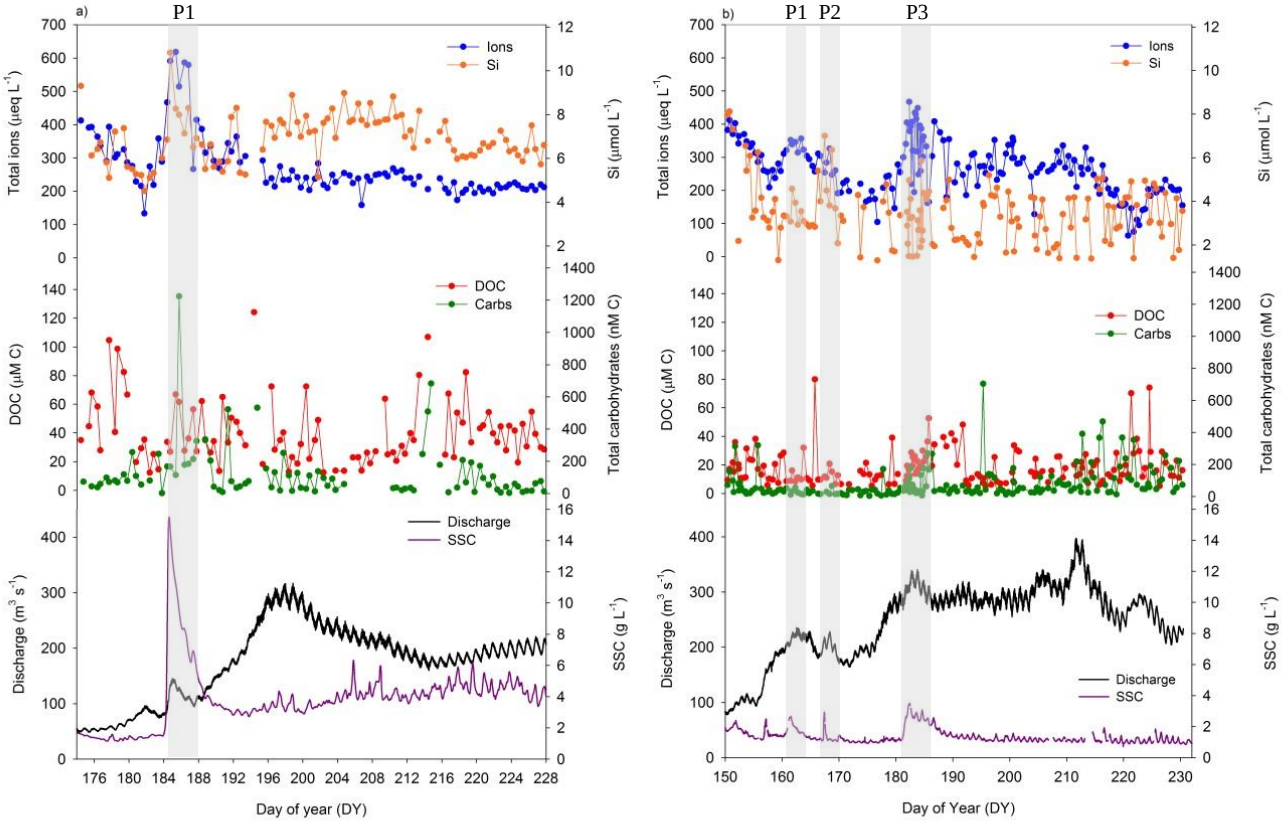

Figure 2. Export of major inorganic (total ions and dissolved silica) and organic (DOC and free carbohydrates) compounds in Leverett Glacier bulk runoff in the 2009 melt season **(a)** and the 2010 melt season **(b)**. Total discharge and suspended sediment concentration (SSC) are also plotted. The approximate timing of water pulses that punctuate the discharge hydrograph (P) and which are associated with a rise in solutes is denoted by shading. P1(2010) is synonymous with P4 in Bartholomew et al. (2011). Outliers ($\geq$ mean $\pm$ 3 $\times$ standard deviation) have been excluded from the time series and DOC concentrations on DY 166.33 and 217.75 excluded from mean calculations.

T(time)1, T2 and T22) and used in determinations of DOC and bacterial cell abundance.

2.4 Flux calculations

Seasonal DOC and free carbohydrate fluxes from the Leverett Glacier catchment were calculated using a linear interpolation approach. A discharge-weighted mean approach was employed outside of the chemical monitoring period (full details are provided in Supplement Sect. 4.1.1). Seasonal POC fluxes from the catchment were derived from the product of the total SSC flux and the % POC content in the suspended sediment. Due to the limited number of SS samples analysed for POC and the variability in POC % content, we employed a minimum, mean and maximum % POC in order to generate minimum, mean and maximum seasonal POC fluxes (described in Supplement Sect. 4.1.3). Annual DOC, free carbohydrate, and POC fluxes from the GrIS were calculated using a discharge-weighted mean approach (described in Supplement Sect. 4.2). Estimates of the uncertainties have been calculated and are also detailed in Supplement Sect. 4.1 and 4.2.

3 Results

3.1 Hydrological and hydrochemical contexts

The subglacial drainage system beneath Leverett Glacier evolves seasonally from slow, inefficient distributed drainage to a fast, efficient channelised system (Chandler et al., 2013). Melting was initiated earlier in 2010 and the seasonal water flux (1.98×10^9 m^3) was almost double that observed in 2009 (1.03×10^9 m^3) (Cowton et al., 2012). The seasonal discharge hydrograph in both years was punctuated by distinct water and SSC pulses (P events) (Fig. 2). P events were generally associated with elevated ion and dissolved Si concentrations and high SSC. We might also expect elevated POC fluxes when SSC fluxes are high. For instance, P1(2009) (referred to as P4 in Bartholomew et al. (2011)) began on DY 184 and was associated with the highest dissolved silica, $*SO_4^{2-}$, $*Na^+ + *K^+$ and SSC measured in outflow during all the 2009 periods (Table S4). P events re-occurred throughout the 2010 melt season prior to the season's peak discharge as the subglacial channelised

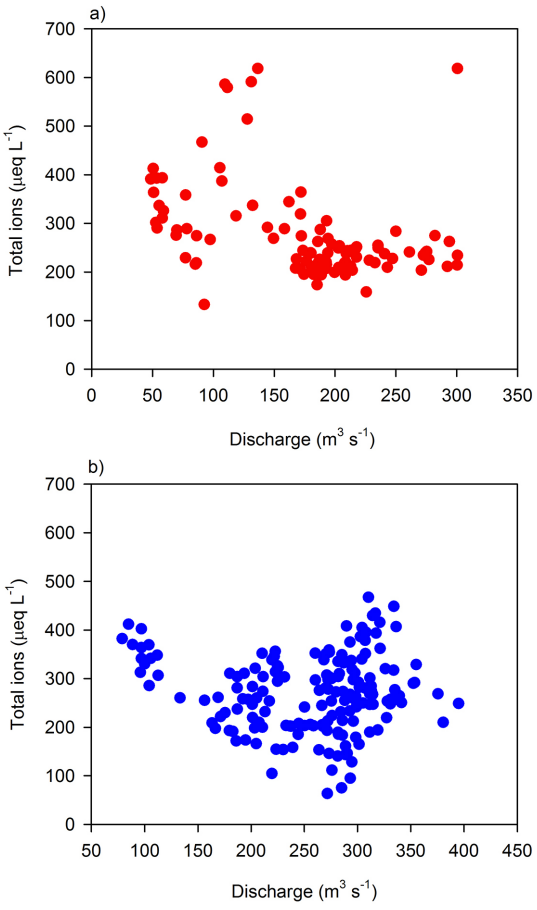

Figure 3. Comparing discharge with total ion concentration (snowpack corrected) in **(a)** 2009 and **(b)** 2010 subglacial runoff. Note the lack of linear correlation between the two variables in both years ($R^2 = 0.0239$ and 0.0031 in 2009 and 2010, respectively).

system expanded headwards in response to inputs of surface meltwater progressively farther upglacier (Bartholomew et al., 2011). Major ion and DOC concentrations fluctuated throughout the 2009 and 2010 summer melt periods, yet no significant linear correlation between dissolved analyte concentration and discharge was observed (Fig. 3). Early season runoff differed from runoff during P events and the rest of the season (detailed in Tables S4–S5), having higher DOC and ionic strength. The ratio of divalent to monovalent crustal cations was calculated to assess the relative contributions of carbonate and silicate dissolution to bulk runoff chemistry (Wadham et al., 2010) to help investigate the mobilisation of discrete subglacial OC pools and to reconcile source contributions to the net OC flux. ($*Ca^{2+} + *Mg^{2+}$):($*Na^{+} + *K^{+}$) progressively declined with increasing ionic strength during both years (Fig. 4), and were particularly low at high ionic strengths during the P events, which, in 2009, are clearly separated from the rest of the season.

3.2 POC and DOC abundance, composition, and bioavailability

Low OC content was observed in Leverett Glacier basal sediment (0.44 % POC, $n = 5$) and suspended sediment. SS POC minimum, mean and maximum values in 2009 were 0.040, 0.092 and 0.151 % ($n = 7$), and 0.010, 0.043 and 0.113 % in 2010 ($n = 19$). However, on average, 9 % of the SS POC comprised extractable carbohydrates (Table S2), which are potentially bioavailable. POC concentrations in 2009 bulk runoff from 2009 averaged 345.6 ± 135.1 µM C (Table 1), and were an order of magnitude higher than mean POC concentrations in the 2010 runoff (42.9 ± 30.2 µM C).

Mean DOC concentrations in bulk runoff were low (17.7–41.4 µM C; Table 1) and comparable with concentrations from other glacier systems (Barker et al., 2006; Bhatia et al., 2010). DOC and free carbohydrate concentrations in the 2010 runoff were significantly lower than in 2009 (independent-sample t tests, $p < 0.001$), likely due to dilution caused by elevated discharge during the 2010 season (Table 1, Fig. 5b). The highest mean concentrations of DOC (285 µM C), free carbohydrates (1240 nM C) and amino acids (5.85 µM C) were observed in cryoconite hole meltwaters (Table 1, Table S3). Free amino acid concentrations in a range of glacial samples correlated significantly ($R^2 = 0.89$, $p = 0.05$) with those of free carbohydrates (Fig. 5a), indicating a common origin. Glucose dominated the carbohydrate signal, with trace concentrations of arabinose, xylose, galactose and mannose observed in most samples. The amino acid pools were compositionally diverse and predominantly comprised of alanine, valine, glycine, isoleucine, and leucine. Relatively high free carbohydrate (230 ± 241 nM C) and amino acid (566 ± 50 nM C) concentrations were also observed in snowmelt (Fig. 5c). Moulin and surface stream meltwaters generally exhibited low DOC concentrations (12.1–15.4 µM C) compared with runoff, but had a similar mean free carbohydrate fraction (47.1–49.3 nM C). No significant temporal or spatial trends in free carbohydrate or amino acid abundance were evident in the DOC pools. Basal ice contained relatively high DOC concentrations (51.3 µM C) but consistently low mean free carbohydrate and amino acid concentrations (7.84 nM C and 0.11 µM C, respectively).

Free carbohydrate fractions in runoff were low (< 0.6 %), yet 26–53 % of the DOC exported from Leverett Glacier (glacial samples only) was found to be bioavailable during the 22-day bioavailability incubations (Fig. 6). We observed a 46–64 % decline in DOC between T1 and T22 in the glacial incubations. This exceeded the average DOC decline (19 ± 10 %) in the glacial controls over the same time period. DOC declined by 9–41 % between T1 and T22 in the proglacial incubations, and by 17 ± 11 % (average) in the proglacial controls. We thus exclude the proglacial incubations from the BDOC determinations, owing to the larger DOC decline in the proglacial controls than in two of the

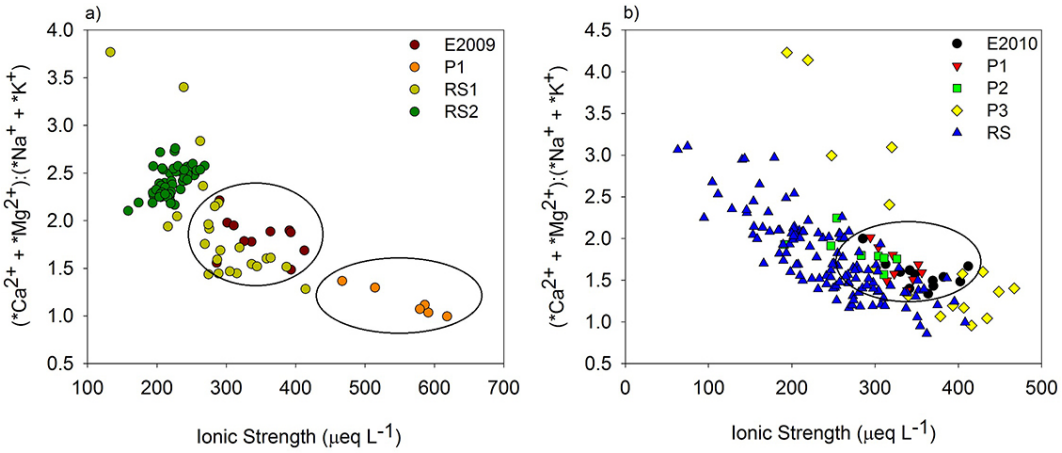

Figure 4. Associations between ionic strength and $(*Ca^{2+}+*Mg^{2+}):(*Na^{+}+*K^{+})$ in subglacial runoff from 2009 **(a)** and 2010 **(b)**. P-event (P) waters have been highlighted. RS refers to water exported throughout the remainder of the melt season, subdivided into RS1 and RS2 in 2009 due to contrasting geochemistry.

Table 1. POC, DOC and free carbohydrate (FCHO) abundance in bulk runoff, subglacial and supraglacial samples collected in 2009–2011. Standard deviation is given in parentheses. Outliers ($\geq$ mean $\pm 3 \times$ standard deviation) have been excluded. N.D. = has not been determined.

Sample	Mean POC (μM C)	Mean DOC (μM C)	DOC range (μM C)	Mean FCHO (nM C)	FCHO range (nM C)	% FCHO in DOC	% FCHO in DOC range
Bulk runoff 2009	345.6 (135.1)	41.4 (23.2)	12.3–124 ($n = 96$)	121 (171)	1.50–1220 ($n = 91$)	0.22 (0.27)	0.0–1.83
Bulk runoff 2010	42.9 (30.2)	17.7 (10.2)	0.62–70.3 ($n = 176$)	77.2 (93.6)	3.86–704 ($n = 175$)	0.52 (1.01)	0.0–9.90
Supraglacial (2 and 4 km)	N.D.	12.1 (8.76)	1.57–39.9 ($n = 26$)	47.1 (56.9)	1.74–174 ($n = 26$)	0.41 (0.42)	0.0–1.49
Supraglacial (7–50 km)	N.D.	15.4 (4.26)	10.4–24.3 ($n = 9$)	49.3 (41.7)	0.00–138 ($n = 9$)	0.30 (0.18)	0.0–0.57
Snow	N.D.	15.8 (12.0)	2.29–32.8 ($n = 6$)	230 (241)	6.44–637 ($n = 6$)	1.36 (1.26)	0.13–3.48
Basal ice	N.D.	51.3 (38.1)	3.79–155 ($n = 23$)	7.84 (9.11)	0.00–34.9 ($n = 22$)	0.06 (0.19)	0.0–0.92
Cryoconite waters (2 km)	N.D.	285 (194)	63.6–559 ($n = 10$)	1240 (1020)	272–2680 ($n = 10$)	0.43 (0.17)	0.23–0.73

live proglacial incubations. DOC was found to increase, on average, by 6 % in the marine control incubations. We also observed large increases in bacterial abundance in all live incubations: between T1 and T22 the number of bacterial cells increased from $< 1 \times 10^8$ cells L^{-1} to 9–26 $\times 10^8$ cells L^{-1}, representing a significant change (Fig. 6). By contrast, between T1 and T22, average bacterial abundance declined by 99 % in the glacial and proglacial controls, and by 100 % in the marine controls.

3.3 Investigating solute provenance via fluorescence spectra

Protein-like fluorescence (ca. 280 nm excitation) (Yamashita and Tanoue, 2003) was enhanced in cryoconite hole waters, as indicated by excitation peaks at 278 and 319 nm (Fig. 7a, Table 2). By contrast, the average synchronous fluorescence spectra in basal ice, snow and supraglacial meltwaters were dominated by several key fluorophores at ca. 335–440 nm, indicative of humic-like fulvic acid and humic compounds (Coble, 1996; Ferrari and Mingazzini, 1995; Miano and Senesi, 1992; Yamashita and Tanoue, 2003). Small, albeit ill-defined, peaks associated with protein-like compounds

Table 2. Summary of the dominant fluorophores (denoted by *) in different glacial environments ($\lambda em = \lambda ex + 18$ nm).

Sample	Fluorophore (peak excitation wavelength, nm)	Fluorophore (peak emission wavelength, nm)	Dominant fluorophore identification	*n*
Basal ice	336, 385*, 440, 483, 551	364, 403*, 458, 501, 569	Fulvic acid, marine humic-like	7
Snow	276, 352*, 398	294, 370*, 416	Fulvic acid, marine humic-like	3
Supra (2–4 km)	279, 353*, 385, 447, 559	297, 371*, 403, 465, 577	Fulvic acid, marine humic-like	7
Supra (7–50 km)	280, 352*, 439	298, 370*, 457	Fulvic acid, marine humic-like	7
Cryoconite hole waters	278*, 319, 386, 438, 555	296*, 337, 404, 453, 573	Protein-like (tryptophan)	10

(~ 280 nm) were also observed in supraglacial meltwaters and snow. Basal ice demonstrated the greatest fluorescence intensity at all levels of excitation (Fig. 7b), yet had no strong protein-like peak.

3.4 DOC and POC export from Leverett Glacier

DOC fluxes from the Leverett Glacier catchment were similar in both 2009 ($0.56 \pm 16\%$ Gg DOC yr^{-1}) and 2010 ($0.52 \pm 16\%$ Gg DOC yr^{-1}), equal to ~ 0.9 g DOC m^{-2} yr^{-1}. Estimates of POC export from Leverett Glacier in 2009 ranged from 1.88 to $7.10 \pm 8\%$ Gg yr^{-1} and averaged $4.32 \pm 8\%$ Gg yr^{-1}. This exceeded the range in 2010 (0.28–$3.11 \pm 12\%$ Gg yr^{-1}, mean $= 1.18 \pm 12\%$ Gg yr^{-1}), despite double the water flux in 2010.

4 Discussion

4.1 Hydrological and hydrochemical contexts for export

2009 and 2010 present contrasting years hydrologically (Cowton et al., 2012), and hence a comparison of DOC and POC export between the two years offers an opportunity to assess OC flux characteristics under contrasting discharge regimes. The conceptual model of subglacial drainage from Leverett Glacier advocates a migration from predominantly slow, inefficient distributed drainage at the start of the melt season to fast, efficient channelised flow during peak discharge. This is driven by the episodic drainage of surface lakes to the bed and pulsed water release at the margin (Bartholomew et al., 2011). Drainage then returns to slower distributed flow in early winter. The lack of an inverse association between solute concentrations in bulk runoff and bulk meltwater discharge (Fig. 3) suggests that additional solute acquisition takes place when bulk meltwater discharge is high, countering dilution effects. The channelised drainage system expands headwards and laterally with increased melt volumes, and additional solute sources could include both chemical dissolution of SS during transit through the drainage system and/or the expulsion of both subglacial and supraglacial stored waters (Bartholomew et al., 2011). Subglacial water stores include porewaters in channel-marginal sediments and subglacial water pockets/lakes. These recharge the channelised system when higher flow rates in the distributed system reverse the hydraulic gradient, as observed in similar glacial environments (Barker et al., 2006). Meltwater transit through the subglacial system and displacement of longer residence time subglacial water stores is consistent with the progressive decrease in the ratio of divalent to monovalent ions, with increasing ionic strength in bulk subglacial runoff. This is thought to reflect enhanced silicate dissolution in longer residence time waters (Tranter et al., 2002; Wadham et al., 2010). The variable ratio of divalent to monovalent ions throughout both melt seasons suggests that meltwaters drain distinct chemical weathering environments at different points in the season. For example, (*Ca^{2+} + *Mg^{2+}):(*Na^{+} + *K^{+}) during peak discharge after DY 194 in 2009 ranged from 2 to 3 (Fig. 4), suggesting that relatively rapid carbonate dissolution occurred in the major channels. Ratios were lower during P1(2009), when Si concentrations and ionic strength also peaked, suggesting larger inputs of stored water from the glacier bed.

4.2 Bioavailable DOC abundance, composition and provenance

The enhancement in both mean amino acids and mean carbohydrates in runoff compared with the mean composition of input waters via supraglacial streams (Table 1, Table S3) suggests that both the subglacial and supraglacial ecosystems may be important sources of LMW–DOC compounds. We analysed the DOC and LMW–DOC compositions of several major pools (snowpack, icemelt, surface lakes and cryoconite holes and basal ice) in order to distinguish different sources of these compounds.

Basal ice forms when pore-waters freeze onto the glacier sole following upward flow through water-saturated subglacial sediments (Souchez et al., 2004). This enriches the basal ice with organic matter from overridden paleosols and

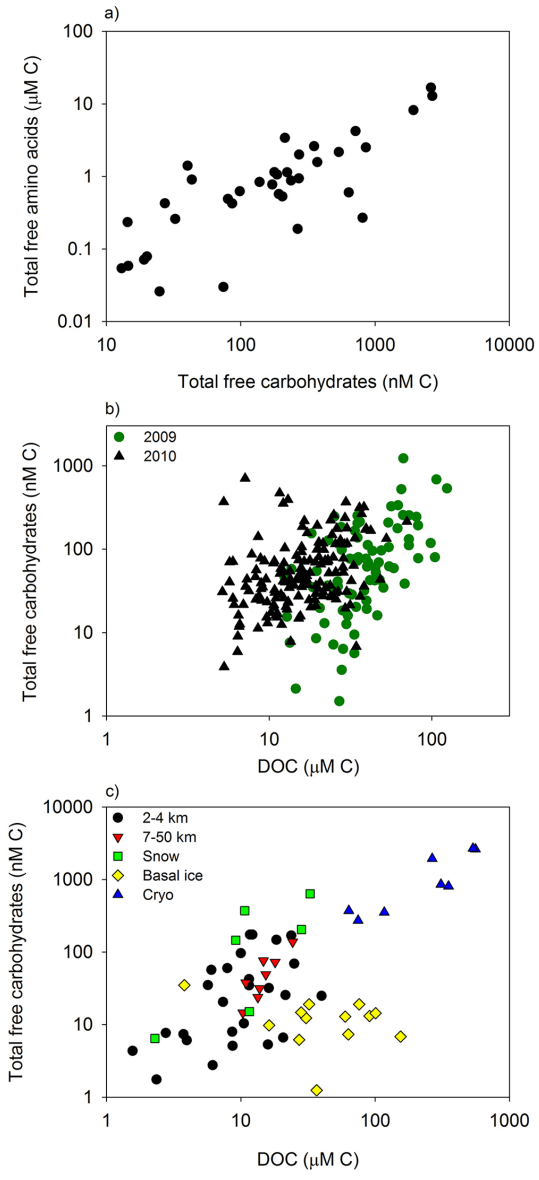

Figure 5. Comparisons of LMW-DOC compounds. **(a)** Free carbohydrates vs. free amino acids for a sample subset collected in 2010, **(b)** DOC vs. free carbohydrates in bulk runoff from 2009 and 2010, **(c)** DOC vs. free carbohydrates in basal ice and supraglacial melt samples (2009–2011). All data have been plotted on a logarithmic scale.

promotes abiotic leaching of DOC from the ancient soil. The characteristics of basal ice-derived DOC are relatively high DOC concentrations but consistently low free carbohydrate and amino acid concentrations, and little protein-like fluorescence. This suggests either tight cycling of LMW–DOC species in the subglacial environment (Bhatia et al., 2010) or limited LMW–DOC production within the basal ice. It is likely that most of the basal ice DOC is sourced from terrestrial pools because of the predominance of fulvic acid fluorophores, which are indicative of soil or plant organic matter precursor material (Coble, 1996; McKnight et al., 2001). Despite the predominance of terrestrially derived material, some compounds in basal ice reflect a potential microbial provenance, e.g. galactose and mannose (Stibal et al., 2010; Turchenek and Oades, 1979). The latter is consistent with microbial abundance in subglacial sediment beneath the Leverett Glacier catchment (8.7×10^5 cells g^{-1}; Stibal et al., 2012b), which is of a similar magnitude to that beneath a range of glaciers where large active microbial communities exist (Lanoil et al., 2009; Mikucki et al., 2009; Sharp et al., 1999).

By contrast, DOC in snow and cryoconite hole waters has been shown to possess a distinct microbial character and the highest free carbohydrate and amino acid concentrations (Fig. 5). These are attributable to the photosynthetic activity of algae and cyanobacteria widely observed on glacier surfaces (Anesio et al., 2009; Foreman et al., 2007; Stibal et al., 2012a). For instance, neutral aldose carbohydrates such as glucose and galactose are typical exudates of recent photosynthesis (Biersmith and Benner, 1998; Kirchman et al., 2001) and chemoautotrophic microbial production (Jansen et al., 1982), and free amino acids (Table S3) are a major product of microbial metabolic pathways and indicate recent biosynthesis (Barker et al., 2009; McKnight et al., 2001; Yamashita and Tanoue, 2003). The fluorescence excitation peaks at 278 and 319 nm (Fig. 7a) are consistent with the presence of tryptophan/tyrosine-like compounds and microbial precursor material (Table 2). The peak at 555 nm in cryoconite hole waters is likely associated with the accessory photosynthetic pigment phycoerythrin (Lombardi and Jardim, 1999) and, hence, a microbial provenance. Cryoconite holes are the most dynamically active habitat within glacial ecosystems (Säwström et al., 2002) and are known to support viable biotic communities and high primary production rates (Stibal et al., 2012a). Our data suggest that a significant proportion of the bioavailable LMW–DOC in glacial systems may be sourced from snow and cryoconite ecosystems in the supraglacial environment. We show that supraglacially derived DOC may display high concentrations of LMW–DOC, which supports recent work in the Gulf of Alaska suggesting that the labile DOC fraction in glacial runoff originates on the glacier surface (Stubbins et al., 2012).

4.3 Bioavailability and active bacterial growth

Recent studies investigating the bioavailability of glacially derived DOC have reported an increase in BDOC with percentage glacial coverage and DOC radiocarbon age (Hood et al., 2009; Singer et al., 2012). We built on this by investigating BDOC and active bacterial growth in bioavailability experiments using Greenland marine and glacial water. This is the first study to assess directly the impact of glacial DOC upon near-coastal marine microbial populations via bioavailability experiments on the GrIS. Subglacial runoff

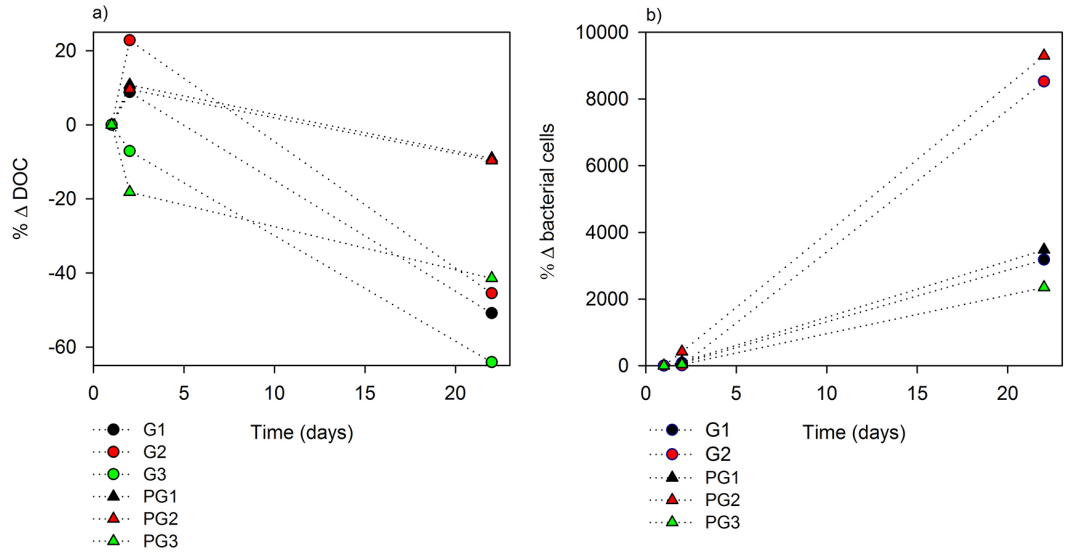

Figure 6. Mean % changes in **(a)** DOC and **(b)** bacterial abundance in bioavailability experiments containing proglacial (PG) or glacial (G) water and marine inoculum (filtered to 2.7 µM). Each replicate is plotted separately.

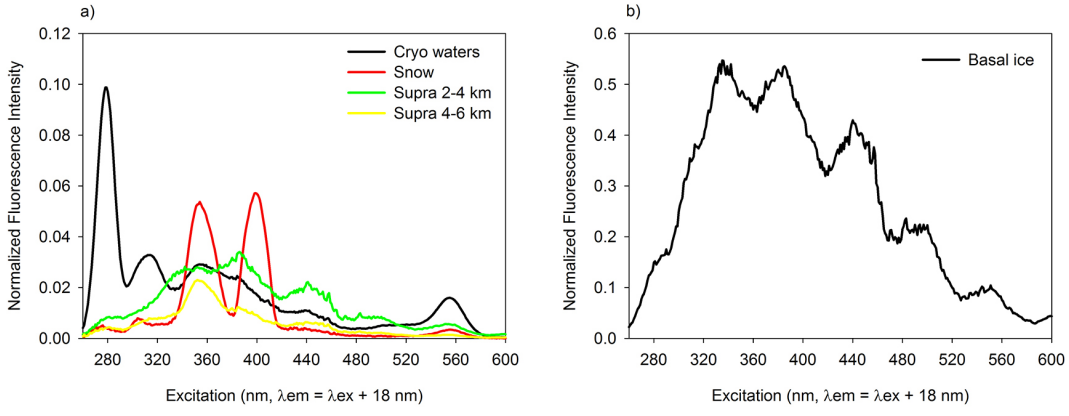

Figure 7. Synchronous fluorescence spectra for averaged **(a)** supraglacial water samples ($n = 7$, 7, 3 and 10 for the supra 2–4 km, supra 7–50 km, snow and cryoconite waters (2011 samples only), respectively) and **(b)** basal ice ($n = 7$). $\lambda em = \lambda ex + 18$ nm. All spectra have been normalised to the highest fluorescence peak spectral maximum in the entire data set. Note the difference in scale on the y axis.

collected near the glacier terminus (glacial) and ∼ 30 km downstream (proglacial) provided the DOC substrate for marine microorganisms. We assume that runoff derives entirely from ice melt, as no terrestrial stream inputs were evident at either site. We report estimates of BDOC based on the glacial incubations only, as the average decline in DOC in the proglacial controls exceeded the DOC decline in two of the three proglacial incubations. The decline in DOC in the glacial incubations, at levels exceeding the controls, supports our assertion that the DOC decline is due to biotic processes when marine inoculum is added to glacial export. The fact that this trend is only illustrated in one of the proglacial incubations may reflect compositional changes in DOC in the proglacial zone, and requires continued investigation. BDOC (26–53 %) in GrIS bioavailability experiments were at the low end of BDOC estimates in glacial runoff and ice from Alaska and the Alps (Hood et al., 2009; Singer et al., 2012), possibly due to lower proportions of LMW–DOC and protein-like compounds in GrIS subglacial runoff compared with the other sites. The observed increase in bacterial abundance concurrent with the net DOC decline during the 22-day bioavailability experiment demonstrates heterotrophic microbial activity and the utilisation of the glacially derived DOC. We approximate that it would take glacial export from Leverett Glacier a maximum of 7 h (in the peak melt season) to travel from the portal to the coastal waters. Our incubation times were 22 days. This tentatively suggests that a relatively large proportion of the potentially bioavailable DOC may be transported to the near-coastal regions. It is possible that a fraction of the bioavailable DOC might be removed prior to

it reaching the near-coastal zone, yet it was beyond the scope of this study to determine how DOC would change compositionally during transit from the portal to coastal waters. However, our incubation experiments suggest that degradation of the total DOC is slow relative to proglacial river transit times. Importantly, this provides evidence that the potentially bioavailable compounds exported from GrIS glacial outflows may be utilised successfully by heterotrophs in the downstream fjord systems and near-coastal zones.

4.4 DOC and POC export dynamics

The episodic release of DOC throughout the melt season may be explained by the intermittent tapping of new subglacial and surface sources, including the flushing out of stored basal waters by rapid supraglacial inputs. Virtually all subglacial runoff is derived from the ice sheet surface and transported through the subglacial drainage system, resulting in the runoff having DOC with characteristics of both surface and basal sources (Barker et al., 2009). The strength of each contribution is shown by the abundance and character of DOC in the runoff. Attribute agreement analysis (Kappa statistics, 95 % significance level; Supplement Sect. 6) shows that only ~ 30 % of all DOC and free carbohydrate peaks were synchronous (Tables S6–S7) and that there was no significant association between the timing of DOC and free carbohydrate peaks. Peaks in carbohydrates which do not concur with those in DOC may reflect the export of LMW-DOC largely derived from the glacier surface, which is distinct from the dominant bulk DOC fraction sourced from subglacial sediments. Some of the free carbohydrate pulses in runoff, e.g. P1(2009) and P3(2010), represent significant rapid inputs of supraglacial waters to the drainage system, which are most likely associated with supraglacial lake drainage. The pulses of free carbohydrates well into the late melt season, e.g. $\sim$ DY 212–14 in 2009, may be explained by the progressive mobilisation of surface LMW-DOC pools situated farther in the GrIS interior as the snowline retreats (Fig. S1, Supplement Sect. 7). It is likely that some variability in free carbohydrate export in runoff is associated with microbial utilisation en route to the terminus.

Supraglacial SS input to the glacial system was assumed to be negligible, given the very low sediment loads found when filtering the surface melt samples. We thus infer that POC in subglacial runoff largely derives from the ice sheet bed via the erosion of bedrock and overridden paleosols. Episodic pulses of high SSCs in runoff, coinciding with high rates of sediment evacuation (Cowton et al., 2012), reflect the access of surface meltwaters to basal sediment stores and the release of subglacial meltwaters from slow, inefficient drainage systems with elevated rock : water ratios and contact times.

4.5 OC fluxes from Leverett Glacier, an outlet of the GrIS

The impact of glacially derived DOC or POC on heterotrophic (secondary) production in downstream ecosystems is dependent on the magnitude of the glacial flux and the contribution of labile compounds (Hood et al., 2009), including free carbohydrates. Comparable DOC fluxes in 2009 and 2010 (0.56 ± 16% and 0.52 ± 16 % Gg DOC yr^{-1}, respectively) are similar to those from an Arctic river of comparable catchment area (Lobbes et al., 2000). Approximately 7 % (0.041 Gg C yr^{-1}, 2009) and 13 % (0.069 Gg C yr^{-1}, 2010) of the DOC comprised free carbohydrates (with an uncertainty of ± 17 %). This is large compared with Arctic rivers, where total free and combined carbohydrates comprise < 6 % of DOC (Dittmar and Kattner, 2003).

POC fluxes were derived from SSC data for the Leverett Glacier catchment. Meltwater draining glacier basins typically has a high SSC that frequently exceeds global averages (Gurnell et al., 1996). Sediment entrainment by turbulent incidental contact is typically amplified by the large volumes of water transported through the system and the abundance of glacially comminuted rock flour. The SSC seasonal flux of $4.7 \pm 0.7 \times 10^6$ tonnes in 2009 (Bartholomew et al., 2011) was much larger than the 2.75×10^6 tonne flux calculated for 2010 (Cowton et al., 2012). It is suggested that the simultaneous drainage of several supraglacial lakes in 2009 altered the hydraulic gradient and the drainage system configuration, diverting the main melt channels through an area of comparatively abundant sediment storage that was not tapped in 2010 (Cowton et al., 2012). The finding that this suspended sediment also contained, on average, 0.043–0.092 % POC (2009 and 2010 values, respectively), and a 9 % bioreactive carbohydrate fraction, suggests that it is a source of bioavailable carbon to downstream environments. POC, on average, accounted for 70–89 % of OC export, which is comparable with POC fractions (84–93 %) in net OC export from a much smaller (~ 5 km^2) GrIS outlet glacier catchment, "N" Glacier (Bhatia et al., 2013a). These data contrast markedly with those from most nonglacial Arctic rivers, where over 90 % of exported OC is in the dissolved phase (Lobbes et al., 2000), and reflects the highly erosive capacity of ice sheets (Cowton et al., 2012). This identifies POC as a previously neglected component of ice sheet OC fluxes.

We infer that the much higher mean POC content (1 ± 0.5 %) in "N" Glacier SS reflects the small size of this catchment and the likelihood that a larger proportion of the catchment, compared with Leverett Glacier, was underlain by paleosols. We contend that a greater proportion of SS exported from Leverett Glacier was derived from the erosion of minerogenic material from farther in the GrIS interior, resulting in the smaller percentage mass contribution of paleosols to POC. However, the higher SSC fluxes from Leverett Glacier meant that similar mean POC fluxes were observed at both Leverett Glacier and "N" Glacier.

On average, 0.60–4.05 g C m^{-3} were exported from Leverett Glacier ($n = 26$, 2009 and 2010, ± 8–12 %), which is similar to POC exported from "N" Glacier (3.5 ± 1.1 g C m^{-3}, $n = 28$, from 2008) (Bhatia et al., 2013a).

It is notable that in both study years the snowline reached a comparable position by the end of the monitoring period, suggesting similarly sized contributing areas for runoff. Hence, similar DOC fluxes, despite large annual variation in runoff, suggest that glacial DOC production may be restricted by other environmental factors. CO_2 fixation and phototrophic production of labile DOC on the glacier surface is limited by nutrients, light and hydrological disturbance (Stibal et al., 2012a). Increasing melt rates and water fluxes through the system may only alter the total exportable DOC if melt areas expand significantly and new microbial communities contribute DOC to runoff. In the basal environment, comparable arguments may apply. If the area of DOC production at the bed remains static (i.e. there is no expansion of the zone of meltwater penetration on inter-annual timescales), the subglacial (largely allochthonous) DOC pool may not increase. The similar aerial extent of melting in 2009 and 2010 and a production-limited DOC supply may explain why DOC export between these years was so similar despite the contrasting runoff fluxes.

4.6 OC fluxes from the GrIS

We scale up our total OC flux estimates to the entire ice sheet in 2009 and 2010 using modelled annual runoff from the GrIS (Fettweis et al., 2011) and discharge-weighted mean DOC and POC concentrations from Leverett Glacier (Sect. 2.4). Such an approach is widely employed for calculating solute fluxes from large glacial systems, where data sets are sparse due to the difficulty in making measurements (Bhatia et al., 2013a; Bhatia et al., 2013b; Hood et al., 2009; Wadham et al., 2013). The validity of such an exercise in this instance depends upon the degree to which the Leverett Glacier catchment and fluxes of OC are representative of the wider GrIS (discussed in Supplement Sect. 8). In summary, we have no reason to believe that surface organic carbon cycling and export at Leverett Glacier would be substantially different to any other melting glacial ice surface in Greenland, and contend that the drivers for OC export at Leverett Glacier are widely applicable. Hence, our GrIS flux estimates derived from scaling up Leverett Glacier OC fluxes should provide robust order of magnitude estimates.

Extrapolation of fluxes from Leverett Glacier to the GrIS generates similar DOC fluxes of $0.17\,\mathrm{Tg} \pm 13\,\%$ OC yr^{-1} (2009) and $0.13 \pm 13\,\%\,\mathrm{Tg\,OC\,yr}^{-1}$ (2010), which are higher than recent estimates of GrIS DOC exports ($0.08 \pm 0.02\,\mathrm{Tg\,OC\,yr}^{-1}$) using geochemical data from a much smaller catchment ($\sim 5\,\mathrm{km}^2$; Bhatia et al., 2013a). These fluxes are comparable with glacial DOC fluxes to the Gulf of Alaska and small Arctic rivers (Dittmar and Kattner, 2003; Hood et al., 2009; Lobbes et al., 2000). The average POC export from the GrIS is estimated here to range from 0.36 to $1.52\,\mathrm{Tg\,C\,yr}^{-1}$ (±14 %), which brackets the $0.9\,\mathrm{Tg\,yr}^{-1}$ estimated by Bhatia et al. (2013). POC export from the GrIS may be locally important in stimulating heterotrophic activity, considering the 9 % bioreactive component, and may also be removed rapidly in the near-coastal zone. By contrast, DOC may travel farther and have significant downstream effects at greater distances from the glacier terminus (Bhatia et al., 2013a). There is potential for the GrIS OC fluxes to supply the North Atlantic, Greenland and Labrador seas, depending on the amount of bioavailable OC to leave the fjord systems and/or near-coastal zones that surround the GrIS. Recent estimates of DOC from the six largest Arctic watersheds indicate that between 25 and $36\,\mathrm{Tg\,yr}^{-1}$ may be delivered to the Arctic Ocean (Holmes et al., 2012; Raymond et al., 2007). However, these major Arctic rivers enter the central Arctic Ocean, and hence potentially limit the input of bioavailable OC to the more marginal North Atlantic, Greenland and Labrador seas. If substantial proportions of bioavailable OC are exported in glacial runoff to the ocean masses surrounding the GrIS, these findings may be significant, owing to the identified OC limitation of marine bacteria in some Arctic regions (Cuevas et al., 2011; Middelboe and Lundsgaard, 2003).

4.7 Future trends

It is difficult to speculate on the combined impact of increased meltwater fluxes and an expanded melt zone upon OC export from the GrIS, as predicted in future climate warming scenarios (Hanna et al., 2008). This could create new source areas for DOC and POC at both the ice sheet surface and bed. However, hydrological processes and, in the case of POC, sediment supply, are also important controls (Cowton et al., 2012). The abundance and composition of DOC in subglacial runoff from the GrIS may undergo significant changes if climate warming significantly alters the timing and magnitude of hydrological events that determine the mobilisation of OC pools and runoff export dynamics. We hypothesise that increasing the size of the supraglacial melt zone may potentially increase the DOC export. The POC flux, which is highly dependent on access to fresh areas of sediment at the glacier bed and efficient evacuation in subglacial runoff, will not necessarily show a concurrent increase in response to greater supraglacial melt input. POC flux characteristics from 2009 and 2010 suggest that synchronous, rapid drainage of large supraglacial lakes in close proximity to each other can alter the subglacial drainage system configuration and enhance sediment entrainment and export (Cowton et al., 2012). This, in combination with the expected upglacier expansion of the subglacial drainage system in response to climate warming, may incorporate new areas of potentially reactive, stored sediment and meltwater, and could increase the net POC export. The GrIS is thus a quantitatively important source of OC to near-coastal and fjord

ecosystems surrounding the GrIS, and potentially a key OC source to the North Atlantic, Greenland and Labrador seas. Inclusion of the GrIS in biogeochemical models may be important for understanding regional carbon cycling under future change scenarios.

5 Conclusions

The biogeochemical signature of subglacial runoff from large ice sheet catchments results from the mixing of multiple meltwater sources, with solute export characterised by episodic pulses of highly concentrated waters that punctuate the seasonal discharge hydrograph. Potential glacial sources of LMW and bioavailable DOC were identified and quantified, and organic fingerprints for supraglacial (high LMW–DOC, variable DOC) and basal ice (low LMW–DOC, high DOC) inputs to bulk subglacial runoff were derived. The bioavailable, free carbohydrate fraction derives largely from microbial activity on the ice sheet surface, thought to be concentrated in cryoconite hole ecosystems and snow. Basal OC stores contained larger humic-like DOC fractions derived from overridden basal material and a substantial bioreactive POC component (9 %). Higher LMW–DOC concentrations in runoff, compared with supraglacial input waters, however, show some potential for LMW–DOC production at the glacier bed. POC accounted for the majority of OC runoff in both melt seasons, was insensitive to runoff volumes, and was likely influenced by basal hydrology and supply limitation of runoff-suspended sediment. Annual fluxes of DOC and free carbohydrates during two melt seasons were similar, despite the approximately two-fold difference in runoff fluxes, suggesting production-limited DOC sources. Significant proportions of the exported DOC (26–53 %) were found to be bioavailable to downstream marine microorganisms and stimulated bacterial activity in bioavailability experiments. This highlights the potential for glacial runoff to impact downstream ecosystems and heterotrophic activity, which may become increasingly significant in a warmer future climate. Scaled to the GrIS, the combined DOC ($0.13–0.17 \pm 13\,\%\,\mathrm{Tg\,C\,yr^{-1}}$) and POC fluxes (mean $= 0.36–1.52 \pm 14\,\%\,\mathrm{Tg\,C\,yr^{-1}}$) are of a similar order of magnitude to a large Arctic river system, and may represent a bioavailable OC source to near-coastal oceans and fjord systems, and potentially to the North Atlantic, Greenland and Labrador seas. The inclusion of the GrIS in biogeochemical models could be important for understanding regional carbon cycling under future change scenarios.

The Supplement related to this article is available online at doi:10.5194/bg-11-4015-2014-supplement.

Acknowledgements. This research was funded by the Natural Environment Research Council (UK – NERC grants NE/E004016/1 (to J. L. Wadham) and NE/F0213991 (to P. Nienow)) and a NERC CASE studentship to E. C. Lawson (NERC DTG/GEOG SN1316.6525) co-sponsored by the Dionex Corporation (part of Thermo Fisher Scientific). Support to J. L. Wadham was also provided by the Leverhulme Trust via a Phillip Leverhulme award and a Leverhulme Trust Research Fellowship. We thank K. Jones for assistance with the statistical analysis and all who helped in the field and the lab, particularly W. Rosser. We acknowledge the use of imagery from the Land Atmosphere Near-real time Capability for EOS (LANCE) system operated by the NASA/GSFC/Earth Science Data and Information System (ESDIS), with funding provided by NASA/HQ. We also thank three anonymous reviewers, whose comments improved the manuscript.

Edited by: B. A. Bergamaschi

References

Anesio, A. M., Hodson, A. J., Fritz, A., Psenner, R., and Sattler, B.: High microbial activity on glaciers: importance to the global carbon cycle, Glob. Change Biol., 15, 955–960, 2009.

Anesio, A. M., Sattler, B., Foreman, C., Telling, J., Hodson, A., Tranter, M., and Psenner, R.: Carbon fluxes through bacterial communities on glacier surfaces, Ann. Glaciol., 51, 32–40, doi:10.3189/172756411795932092, 2010.

Baker, A. and Lamont-BIack, J.: Fluorescence of dissolved organic matter as a natural tracer of ground water, Ground Water, 39, 745–750, 2001.

Barker, J. D., Sharp, M. J., Fitzsimons, S. J., and Turner, R. J.: Abundance and dynamics of dissolved organic carbon in glacier systems, Arct. Antarct. Alp. Res., 38, 163–172, 2006.

Barker, J. D., Sharp, M., and Turner, R. J.: Using synchronous fluorescence spectroscopy and principal component analysis to monitor dissolved organic matter dynamics in a glacier system, Hydrol. Process., 23, 1487–1500, 2009.

Bartholomew, I., Nienow, P., Sole, A., Mair, D., Cowton, T., Palmer, S., and Wadham, J.: Supraglacial forcing of subglacial drainage in the ablation zone of the Greenland ice sheet, Geophys. Res. Lett., 38, L08502, doi:10.1029/2011GL047063, 2011.

Bhatia, M., Das, S., Longnecker, K., Charette, M., and Kujawinski, E.: Molecular characterization of dissolved organic matter associated with the Greenland ice sheet, Geochim. Cosmochim. Ac., 74, 3768–3784, doi:10.1016/j.gca.2010.03.035, 2010.

Bhatia, M. P., Das, S. B., Xu, L., Charette, M. A., Wadham, J. L., and Kujawinski, E. B.: Organic carbon export from the Greenland ice sheet, Geochim. Cosmochim. Ac., 109, 329–344, doi:10.1016/j.gca.2013.02.006, 2013a.

Bhatia, M. P., Kujawinski, E. B., Das, S. B., Breier, C. F., Henderson, P. B., and Charette, M. A.: Greenland meltwater as a significant and potentially bioavailable source of iron to the ocean, Nat. Geosci., 6, 274–278, doi:10.1038/ngeo1746, 2013b.

Biersmith, A. and Benner, R.: Carbohydrates in phytoplankton and freshly produced dissolved organic matter, Mar. Chem., 63, 131–144, 1998.

Chandler, D., Wadham, J., Lis, G., Cowton, T., Sole, A., Bartholomew, I., Telling, J., Nienow, P., Bagshaw, E., and

Mair, D.: Evolution of the subglacial drainage system beneath the Greenland Ice Sheet revealed by tracers, Nat. Geosci., 6, 195–198, 2013.

Chen, J., LeBoef, E. J., Dai, S. and Gu, B. H.: Fluorescence spectroscopic studies of natural organic matter fractions, Chemosphere 50, 639–647, 2003.

Cheng, S. M. and Foght, J. M.: Cultivation-independent and -dependent characterization of Bacteria resident beneath John Evans Glacier, FEMS Microbiol. Ecol., 59, 318–330, 2007.

Chillrud, S. N., Pedrozo, F. L., Temporetti, P. F., Planas, H. F., and Froelich, P. N.: Chemical-weathering of phosphate and germanium in glacial meltwater streams – effects of subglacial pyrite oxidation, Limnol. Oceanogr., 39, 1130–1140, 1994.

Christner, B., Skidmore, M., Priscu, J., Tranter, M., and Foreman, C.: Bacteria in subglacial environments, in: Psychrophiles: From Biodiversity to Biotechnology, edited by: Margesin, R., Schinner, F., Marx, J. C., and Gerday, C., Springer, Berlin, 51–71, 2009.

Coble, P. G.: Characterization of marine and terrestrial DOM in seawater using excitation emission matrix spectroscopy, Mar. Chem., 51, 325–346, 1996.

Cowton, T., Nienow, P., Bartholomew, I., Sole, A., and Mair, D.: Rapid erosion beneath the Greenland ice sheet, Geology 40, 343–346, 2012.

Cuevas, L. A., Egge, J. K., Thingstad, T. F., and Topper, B.: Organic carbon and mineral nutrient limitation of oxygen consumption, bacterial growth and efficiency in the Norwegian Sea, Polar Biol., 34, 871–882, 2011.

Das, S. B., Joughin, I., Behn, M. D., Howat, I. M., King, M. A., Lizarralde, D., and Bhatia, M. P.: Fracture propagation to the base of the Greenland Ice Sheet during supraglacial lake drainage, Science, 320, 778–781, 2008.

Dittmar, T. and Kattner, G.: The biogeochemistry of the river and shelf ecosystem of the Arctic Ocean: a review, Mar. Chem., 83, 103–120, 2003.

Escher, A. and Watt, W. S.: Geology of Greenland, Grønlands Geologiske undersøgelse, 1976.

Fellman, J., D'Amore, D., Hood, E., and Boone, R.: Fluorescence characteristics and biodegradability of dissolved organic matter in forest and wetland soils from coastal temperate watersheds in southeast Alaska, Biogeochemistry, 88, 169–184, 2008.

Fellman, J. B., Hood, E., Edwards, R. T., and D'Amore, D. V.: Changes in the concentration, biodegradability, and fluorescent properties of dissolved organic matter during stormflows in coastal temperate watersheds, J. Geophys. Res., 114, G01021, doi:10.1029/2008JG000790, 2009.

Fellman, J. B., Spencer, R. G. M., Hernes, P. J., Edwards, R. T., D'Amore, D. V., and Hood, E.: The impact of glacier runoff on the biodegradability and biochemical composition of terrigenous dissolved organic matter in near-shore marine ecosystems, Mar. Chem., 121, 112–122, 2010.

Ferrari, G. M. and Mingazzini, M.: Synchronous fluorescence-spectra of Dissolved organic-matter (Dom) of algal origin in marine coastal waters, Mar. Ecol.-Prog. Ser., 125, 305–315, 1995.

Fettweis, X., Tedesco, M., van den Broeke, M., and Ettema, J.: Melting trends over the Greenland ice sheet (1958–2009) from spaceborne microwave data and regional climate models, The Cryosphere, 5, 359–375, doi:10.5194/tc-5-359-2011, 2011.

Foreman, C., Sattler, B., Mikucki, J., Poranzinska, D., and Priscu, J.: Metabolic activity and diversity of cryoconites in the Taylor valley, Antarctica, J. Geophys. Res., 112, G04S32, doi:10.1029/2006JG000358, 2007.

Gurnell, A., Hannah, D., and Lawler, D.: Suspended sediment yield from glacier basins, IAHS-AISH P., 236, 97–104, 1996.

Hanna, E., Huybrechts, P., Steffen, K., Cappelen, J., Huff, R., Shuman, C., Irvine-Fynn, T., Wise, S., and Griffiths, M.: Increased runoff from melt from the Greenland Ice Sheet: a response to global warming, J. Climate, 21, 331–341, 2008.

Hawkings, J. R., Wadham, J. L., Tranter, M., Raiswell, R., Benning, L. G., Statham, P. J., Tedstone, A., Nienow, P., Lee, K., and Telling, J.: Ice sheets as a significant source of highly reactive nanoparticulate iron to the oceans, Nature Commun., 5, 3929, doi:10.1038/ncomms4929, 2014.

Hodson, A., Anesio, A.M., Tranter, M., Fountain, A., Osborn, M., Priscu, J., Laybourn-Parry, J., Sattler, B.: Glacial ecosystems. Ecol. Monogr., 78, 41-67, 2008.

Hodson, A., Boggild, C., Hanna, E., Huybrechts, P., Langford, H., Cameron, K., and Houldsworth, A.: The cryoconite ecosystem on the Greenland ice sheet, Ann. Glaciol., 51, 123–129, 2010.

Holmes, R. M., McClelland, J. W., Peterson, B. J., Tank, S. E., Bulygina, E., Eglinton, T. I., Gordeev, V. V., Gurtovaya, T. Y., Raymond, P. A., and Repeta, D. J.: Seasonal and annual fluxes of nutrients and organic matter from large rivers to the Arctic Ocean and surrounding seas: Estuaries and Coasts, 35, 369–382, doi:10.1007/s12237-011-9386-6, 2012.

Hood, E., Fellman, J., Spencer, R., Hernes, P., Edwards, R., D'Amore, D., and Scott, D.: Glaciers as a source of ancient and labile organic matter to the marine environment, Nature, 462, 1044–1047, 2009.

Jansen, K., Stupperich, E., and Fuchs, G.: Carbohydrate synthesis from acetyl CoA in the autotroph Methanobacterium thermoautotrophicum, Arch. Microbiol., 132, 355–364, 1982.

Kirchman, D. L., Meon, B., Ducklow, H. W., Carlson, C. A., Hansell, D. A., and Steward, G. F.: Glucose fluxes and concentrations of dissolved combined neutral sugars (polysaccharides) in the Ross Sea and Polar Front Zone, Antarctica, Deep-Sea Res. Pt. II, 48, 4179–4197, 2001.

Lafrenière, M. and Sharp, M.: The concentration and fluorescence of Dissolved Organic Carbon (DOC) in glacial and nonglacial catchments; interpreting hydrological flow routing and DOC sources, Arct. Antarct. Alp. Res., 36, 156–165, doi:10.1657/1523-0430(2004)036[0156:TCAFOD]2.0.CO;2, 2004.

Lanoil, B., Skidmore, M., Priscu, J. C., Han, S., Foo, W., Vogel, S. W., Tulaczyk, S., and Engelhardt, H.: Bacteria beneath the West Antarctic Ice Sheet, Environ, Microbiol., 11, 609–615, 2009.

Lewis, S. and Smith, L.: Hydrologic drainage of the Greenland Ice Sheet, Hydrol. Process., 23, 2004–2011, doi:10.1002/hyp.7343, 2009.

Lobbes, J. M., Fitznar, H. P., and Kattner, G.: Biogeochemical characteristics of dissolved and particulate organic matter in Russian rivers entering the Arctic Ocean, Geochim. Cosmochim. Ac., 64, 2973–2983, 2000.

Lombardi, A. T. and Jardim, W. F.: Fluorescence spectroscopy of high performance liquid chromatography fractionated marine and terrestrial organic materials, Water Res., 33, 512–520, 1999.

McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T., and Andersen, D. T.: Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity, Limnol. Oceanogr., 46, 38–48, 2001.

Mernild, S. H., Liston, G. E., Hiemstra, C. A., and Christensen, J. H.: Greenland Ice Sheet surface mass-balance modeling in a 131-yr perspective, 1950–2080, J. Hydrometeorol., 11, 3–25, 2010.

Miano, T. M. and Senesi, N.: Synchronous excitation fluorescence spectroscopy applied to soil humic substances chemistry, Sci. Total. Environ., 118, 41–51, 1992.

Middelboe, M. and Lundsgaard, C.: Microbial activity in the Greenland Sea: role of DOC lability, mineral nutrients and temperature, Aquat. Microb. Ecol., 32, 151–163, 2003.

Mikucki, J. A., Pearson, A., Johnston, D. T., Turchyn, A. V., Farquhar, J., Schrag, D. P., Anbar, A. D., Priscu, J. C., and Lee, P. A.: A contemporary microbially maintained subglacial ferrous "Ocean", Science, 324, 397–400, 2009.

Montross, S. N., Skidmore, M., Tranter, M., Kivimäki, A. L., and Parkes, R. J.: A microbial driver of chemical weathering in glaciated systems, Geology, 41, 215–218, doi:10.1130/G33572.1, 2012.

Nienow, P., Sharp, M., and Willis, I.: Seasonal changes in the morphology of the subglacial drainage system, Haut Glacier d'Arolla, Switzerland, Earth Surf. Proc. Land., 23, 825–843, 1998.

Raiswell, R.: Chemical-models of solute acquisition in glacial melt waters, J. Glaciol., 30, 49–57, 1984.

Raymond, P. A., McClelland, J. W., Holmes, R. M., Zhulidov, A. V., Mull, K., Peterson, B. J., Striegl, R. G., Aiken, G. R., and Gurtovaya, T. Y.: Flux and age of dissolved organic carbon exported to the Arctic Ocean: A carbon isotopic study of the five largest arctic rivers. Global Biogeochem. Cy., 21, GB4011, doi:10.1029/2007GB002934, 2007.

Rich, J., Gosselin, M., Sherr, E., Sherr, B., and Kirchman, D. L.: High bacterial production, uptake and concentrations of dissolved organic matter in the Central Arctic Ocean, Deep-Sea Res Pt II, 44, 1645–1663, 1997.

Säwström, C., Mumford, P., Marshall, W., Hodson, A., and Laybourn-Parry, J.: The microbial communities and primary productivity of cryoconite holes in an Arctic glacier (Svalbard 79° N), Polar Biol., 25, 591–596, 2002.

Sharp, M., Parkes, J., Cragg, B., Fairchild, I. J., Lamb, H., and Tranter, M.: Widespread bacterial populations at glacier beds and their relationship to rock weathering and carbon cycling, Geology, 27, 107–110, 1999.

Singer, G. A., Fasching, C., Wilhelm, L., Niggemann, J., Steier, P., Dittmar, T., and Battin, T. J.: Biogeochemically diverse organic matter in Alpine glaciers and its downstream fate, Nat. Geosci., 5, 710–714, doi:10.1038/ngeo1581, 2012.

Skidmore, M. L., Foght, J. M., and Sharp, M. J.: Microbial life beneath a high Arctic glacier, Appl. Environ. Microb., 66, 3214–3220, 2000.

Souchez, R., Samyn, D., Lorrain, R., Pattyn, F., and Fitzsimons, S.: An isotopic model for basal freeze-on associated with subglacial upward flow of pore water, Geophys. Res. Lett., 31, L02401, doi:10.1029/2003GL01886, 2004.

Stibal, M. and Tranter, M.: Laboratory investigation of inorganic carbon uptake by cryoconite debris from Werenskioldbreen, Svalbard, J. Geophys. Res.-Biogeo., 112, G04S33, doi:10.1029/2007JG000429, 2007.

Stibal, M., Tranter, M., Benning, L. G., and Rehak, J.: Microbial primary production on an Arctic glacier is insignificant in comparison with allochthonous organic carbon input, Environ. Microbiol., 10, 2172–2178, 2008.

Stibal, M., Lawson, E., Lis, G., Mak, K., Wadham, J., and Anesio, A.: Organic matter content and quality in supraglacial debris across the ablation zone of the Greenland ice sheet, Ann. Glaciol., 51, 1–8, 2010.

Stibal, M., Telling, J., Cook, J., Mak, K., Hodson, A., and Anesio, A.: Environmental controls on microbial abundance and activity on the Greenland Ice Sheet: a multivariate analysis approach, Microb. Ecol., 63, 74–84, 2012a.

Stibal, M., Wadham, J. L., Lis, G. P., Telling, J., Pancost, R. D., Dubnick, A., Sharp, M. J., Lawson, E. C., Butler, C. E. H., and Hasan, F.: Methanogenic potential of Arctic and Antarctic subglacial environments with contrasting organic carbon sources, Glob. Change Biol., 18, 3332–3345, doi:10.1111/j.1365-2486.2012.02763.x, 2012b.

Stubbins, A., Hood, E., Raymond, P. A., Aiken, G. R., Sleighter, R. L., Hernes, P. J., Butman, D., Hatcher, P. G., Striegl, R. G., and Schuster, P.: Anthropogenic aerosols as a source of ancient dissolved organic matter in glaciers, Nat. Geosci., 5, 198–201, doi:10.1038/ngeo1403, 2012.

Ten Brink, N. W. and Weidick, A.: Greenland ice sheet history since the last glaciation, Quaternary Res., 4, 429–440, 1974.

Tranter, M., Sharp, M. J., Lamb, H. R., Brown, G. H., Hubbard, B. P., and Willis, I. C.: Geochemical weathering at the bed of Haut Glacier d'Arolla, Switzerland – a new model, Hydrol. Process., 16, 959–993, 2002.

Turchenek, L. and Oades, J.: Fractionation of organo-mineral complexes by sedimentation and density techniques, Geoderma, 21, 311–343, 1979.

Wadham, J. L., Hodson, A. J., Tranter, M., and Dowdeswell, J. A.: The hydrochemistry of meltwaters draining a polythermal-based, high Arctic glacier, south Svalbard: I. The ablation season, Hydrol. Process., 12, 1825–1849, 1998.

Wadham, J. L., Tranter, M., Skidmore, M., Hodson, A. J., Priscu, J., Lyons, W. B., Sharp, M., Wynn, P., and Jackson, M.: Biogeochemical weathering under ice: size matters, Global Biogeochem. Cy., 24, GB3025, doi:10.1029/2009GB003688, 2010.

Wadham, J. L., Death, R., Monteiro, F., Tranter, M., Ridgwell, A., Raiswell, R., and Tulaczyk, S.: The potential role of the Antarctic Ice Sheet in global biogeochemical cycles, Earth Env. Sci. T. R. So., 104, 1–13, 2013.

Yamashita, Y. and Tanoue, E.: Chemical characterization of protein-like fluorophores in DOM in relation to aromatic amino acids, Mar. Chem., 82, 255–271, 2003.