Greenland Ice Sheet exports labile organic carbon to the Arctic oceans

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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 (1200 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 for the “bioavailable” (free carbohydrates) 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 (30–58 %) 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 ~2 fold difference in runoff fluxes, suggesting production-limited DOC sources. POC fluxes were also insensitive to an increase in seasonal runoff volumes, indicating supply-limitation of suspended sediment in runoff. Scaled to the GrIS, the combined DOC and POC fluxes (0.13–0.17 Tg C yr$^{-1}$ DOC, 0.36–1.52 Tg C yr$^{-1}$ mean POC) are of a similar order of magnitude to a large Arctic river system, and hence represent an important OC source to the 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). These drive subglacial chemical weathering (Montross et al., 2012; Sharp et al., 1999).
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, 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, ~10–60 µMC (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 km³ 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. Further, little data exists on par-
Particulate OC (POC) exports from glacial environments (Bhatia et al., 2013a), although this is recognised as important for some nutrients such as phosphorus (Hodson et al., 2008). The high erosive capacity of ice sheets (Cowton et al., 2012) further suggests potential for significant downstream sediment transport and the export of bioreactive particulate material. 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 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 from the ice sheet. We focused on a subset of low molecular weight (LMW) DOC compounds (free carbohydrates and amino acids), in addition to the presence of protein-like compounds in fluorescence 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 at the catchment and ice sheet scale, 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 export from a large ice sheet system aims to enhance understanding of how future changes in glacier export dynamics, caused by a changing climate, could affect the cycling of DOC in Arctic coastal ecosystems.
2 Methods

2.1 Field site 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, West Greenland (∼ 67.10° N, 50.20° W, Fig. 1, from Hawkings et al., 2013). Leverett Glacier is representative of many land-terminating Greenland outlet glaciers, draining a large catchment area (> 1200 km²) 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). Supraglacial meltwater, snow and cryoconite hole water samples were collected in 2009–2011 (see Supplement Sect. 1.1 and Table S1). Discharge and suspended sediment concentration (SSC) were calculated following the methods in (Bartholomew et al., 2011; Cowton et al., 2012).

2.2 Analytical protocols

2.2.1 Glacial sediment

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 (Supplement Sect. 2.1). SS POC minimum, mean and maximum values in 2009 were 0.040,
Glacial meltwater, basal ice and snow

DOC, measured as non-purgeable organic carbon, was determined by high temperature combustion (680 °C) using a Shimadzu TOC-VCSN/TNM-1 Analyzer equipped with a high sensitivity catalyst. Free carbohydrate and free amino acid determinations were performed by an ICS-3000 dual-analysis Reagent-Free Ion Chromatography system (Dionex, Sunnyvale, USA). Full details of the analytical procedures are given in Supplement Sects. 2.2 and 2.3. 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\(_{3}^{-}\) calculated by charge deficit. Dissolved Si was determined using a continuous segmented-flow Bran and Luebbe AutoAnalyser. 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-Black, 2001; Chen et al., 2003). Synchronous fluorescence spectra were determined on a HORIBA Jobin Yvon Fluorolog-3 spectrofluorometer.

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 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. 2.4). Sample water was extracted after 1, 2 and 22 days (hereafter referred to as T(time)1, T2 and T22) and used in determinations of DOC and bacterial cell abundance.

2.4 Flux calculations

OC fluxes were calculated for the Leverett Glacier catchment and the GrIS using chemical data and discharge data (see Supplement Sect. 1.2 for full details). Briefly, seasonal DOC and free carbohydrate fluxes from the catchment were calculated from the product of measured analyte concentrations and discharge measurements. Fluxes were calculated separately for the main monitoring period when chemical samples were collected, and the start (37 days in 2009, 13 in 2010) and end of each season (17 days in 2009, 42 in 2010) when only discharge data was available (Supplement Sect. 1.2.1).

Seasonal POC fluxes from Leverett Glacier for each year were derived from the product of the total SSC flux (4.7 ± 0.7 × 10⁶ t in 2009 (Bartholomew et al., 2011), 2.75 × 10⁶ t in 2010, Cowton et al., 2012) and the % POC content of SS measured in 2009 and 2010. Due to the limited number of SS samples analysed for POC and the variability in POC % contents, we employed a minimum, mean and maximum % POC in order to generate minimum, mean and maximum seasonal POC fluxes.

DOC and free carbohydrate fluxes from the Greenland Ice Sheet were calculated from the product of the annual runoff from the GrIS (347.9 km³ yr⁻¹ in 2009 and 558.9 km³ yr⁻¹ in 2010) (Fettweis et al., 2011) and seasonal discharge weighted mean (DWM) DOC and free carbohydrate concentrations from Leverett Glacier. We calculated an envelope of POC fluxes from the GrIS. Briefly, the GrIS SSC flux in 2009 and 2010 (in grams) was derived from the product of the discharge weighted mean SSC (gL⁻¹) measured in Leverett runoff in 2009 and 2010 and the seasonal GrIS runoff fluxes (L) for these years. These SSC fluxes were then multiplied by the minimum, mean and maximum Leverett Glacier POC contents in each year (%) to generate minimum, mean and maximum POC fluxes from the ice sheet.
3 Results

3.1 Hydrological and hydrochemical context

The subglacial drainage system beneath Leverett Glacier evolves seasonally from slow-inefficient distributed drainage to a fast-efficient channelized system (Chandler et al., 2013). Melting was initiated earlier in 2010 and the seasonal water flux \((1.98 \times 10^9 \text{ m}^3)\) was almost double that observed in 2009 \((1.07 \times 10^9 \text{ m}^3)\). 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, \(\text{SO}_4^{2-}\), \(\text{Na}^+ \) + \(\text{K}^+\) and SSC measured in outflow during all 2009 periods (Table S4). P-events re-occurred throughout the 2010 melt season prior to the season’s peak discharge as the subglacial channelized system expanded headwards in response to inputs of surface meltwater progressively further 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 were observed (Fig. S1). Early season runoff differed from runoff during P-events and the rest of the season (detailed in Tables S4 and 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), and progressively declined with increasing ionic strength during both years (Fig. S2). \((\text{Ca}^{2+} + \text{Mg}^{2+}) : (\text{Na}^+ + \text{K}^+)\) 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 Greenland basal sediment (0.44 % POC, \( n = 5 \)) and Leverett Glacier SS (0.010–0.151 % POC, \( n = 26 \)). However, on average, 9 % of the SS POC comprised extractable carbohydrates (Table S2), which are potentially bioavailable. Estimates of POC export from Leverett Glacier in 2009 ranged from 1.76–6.64 \( \times 10^6 \) mg L\(^{-1} \) and averaged 4.05 \( \times 10^6 \) mg L\(^{-1} \) (Table 2). This exceeded the range in 2010 (0.14–1.57 \( \times 10^6 \) mg L\(^{-1} \), mean = 5.98 \( \times 10^5 \) mg L\(^{-1} \)), despite double the water flux in 2010. These differences in POC export characteristics between 2009 and 2010 are thought to be influenced by meltwater supply and basal hydrological routing.

Mean DOC concentrations in bulk runoff were low (17.7–41.4 \( \mu \)MC, Table 1) and comparable to concentrations from other glacier systems (Barker et al., 2006; Bhatia et al., 2010). DOC and free carbohydrate concentrations in 2010 runoff were significantly lower than 2009 (independent-samples \( t \) tests, 95 % significance level, \( p < 0.001 \)), likely due to dilution caused by elevated discharge during the 2010 season (Table 1, Fig. 3b). The highest mean concentrations of DOC (285 \( \mu \)MC), free carbohydrate (1240 nMC) and amino acids (5.85 \( \mu \)MC) were observed in cryoconite hole meltwaters (Tables 1 and 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. 3a), 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 nMC) and amino acid (566 ± 50 nMC) concentrations were also observed in snowmelt (Fig. 3c). Moulin and surface stream meltwaters generally exhibited low DOC concentrations (12.1–15.4 \( \mu \)MC) compared with runoff, but had a similar mean free carbohydrate fraction (47.1–49.3 nMC). No significant temporal or spatial trends in free carbohydrate fraction (47.1–49.3 nMC). No significant temporal or spatial trends in free carbohydrate fraction (47.1–49.3 nMC).
low mean free carbohydrate and amino acid concentrations (7.84 nMC and 0.11 µMC, respectively). Free carbohydrate fractions in runoff were low (< 0.6 %), yet 30–58 % of the DOC exported from Leverett Glacier was found to be bioavailable during the 22 day bioavailability incubations (Fig. 4). The DOC decline between T1–T22 averaged 25.8 ± 20.4 µMC and ranged from 5.0–51.6 µMC, and was concurrent with a mean increase in bacterial abundance of 15.1 ± 6.4 × 10^8 cellsL^{-1} (mean for all experiments). Protein-like fluorophores accounted for 11.9 ± 3.1 % and 6.7 ± 2.8 % of the net fluorescence in the proglacial and glacial incubations, respectively, and did not change significantly over the course of the bioavailability experiment.

3.3 Investigating solute provenance via fluorescence spectra

Protein-like fluorescence (c. 280 nm) (Yamashita and Tanoue, 2003) was enhanced in cryoconite hole waters (26 ± 6 % of the total fluorescence, Table 1), as indicated by peaks at 279 and 314 nm (Fig. 5a), 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. In contrast, the average synchronous fluorescence spectra in basal ice, snow and supraglacial meltwaters were dominated by several key fluorophores at c. 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 (~ 280 nm) were also observed in supraglacial meltwaters and snow. Basal ice demonstrated the greatest fluorescence intensity at all levels of excitation (Fig. 5b) yet had no strong protein-like peak. Protein-like fluorescence only accounted for 2.6 ± 0.4 % of the total fluorescence in basal ice (Table 1), which was comparable to mean protein-like fluorescence in runoff (2.5–2.7 %) but lower than mean values in supraglacial samples (4.2–26 %).
4 Discussion

4.1 Hydrological and hydrochemical context 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 channelized flow during peak discharge, 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 absence of an inverse association between solute concentrations in bulk runoff and bulk meltwater discharge (Fig. S1), normally effected by dilution of a concentrated baseflow component by a dilute channelized component, contrasts with observations from temperate and smaller polythermal systems (Wadham et al., 1998). This suggests that additional solute acquisition takes place when bulk meltwater discharge is high, countering dilution effects. The channelized 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 channelized 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, 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, \((\ast Ca^{2+} + \ast Mg^{2+}) : (\ast Na^+ + \ast K^+)\) during peak discharge after DY 194 in 2009 ranged from 2–3 (Fig. S2), 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 at the glacier bed.

4.2 Bioavailable DOC abundance, composition and provenance

The enhancement in both mean amino acids and mean carbohydrates in runoff compared to the mean composition of input waters via supraglacial streams (Table S3) suggests that both the subglacial and supraglacial environments are important sources for LMW-DOC compounds. We analyse the DOC and LMW-DOC compositions of several major pools (snowpack, icemelt, surface lakes and cryoconite holes and basal ice) in order to better distinguish different sources for 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 promotes abiotic leaching of DOC from the ancient soil. The characteristics of basal ice derived DOC are relatively high DOC concentrations but consistently low mean 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 important to note that basal ice represents only part of the subglacial environment, and hence, there may be potential for LMW-DOC production in other subglacial settings, e.g. subglacial porewaters. Our results suggest that some LMW-DOC may be derived from these other non-frozen subglacial environments, as mean free carbohydrate and amino acid concentrations in runoff exceeded mean concentrations in inputs of supraglacial waters via moulins.

The identification of trace levels of monosaccharides in basal ice indicated either the presence of allochthonous terrestrial carbohydrates from plant material (arabi-
nose and xylose) and/or microbial metabolites (galactose and mannose) produced in situ (Stibal et al., 2010; Turchenek and Oades, 1979). The latter is consistent with microbial abundance in subglacial sediment beneath the Leverett Glacier catchment ($8.7 \times 10^5$ 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). It is likely that most of the basal ice DOC is sourced from terrestrial pools because of the predominance of fulvic acid fluorophores in basal ice, which are indicative of soil or plant organic matter precursor material (Coble, 1996; McKnight et al., 2001). Fulvic acid fluorophores represent a major constituent of DOM in natural waters (Thurman, 1985) and typically form by abiotic condensation of reduced organic matter, and were incorporated into the GrIS basal ice. Terrestrially-derived, humic-like fulvic acid compounds also dominated the supraglacial meltwater spectra, as protein-like compounds derived from local hotspots of microbial activity were less prevalent (Fig. 5, Table 2). This suggests that allochthonous OC inputs, e.g. the deposition of airborne terrestrial particles, are a significant source of OC to the surface of the GrIS, particularly at the margin (Stibal et al., 2012a).

In 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. 3) and percentage of protein-like fluorophores (Fig. 5, Table 2). These are attributable to the photosynthetic activity of algae and cyanobacteria widely observed on glacier surfaces (Foreman et al., 2007; Grannas et al., 2004). 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). Cryoconite holes are the most dynamically active habitat within glacial ecosystems (Sawström et al., 2002) and are known to support viable biotic communities and high primary production rates (Stibal et al., 2012a).
Data presented in this study suggest that a significant proportion of the bioavailable LMW-DOC (e.g. free carbohydrates and protein-like fluorescing compounds) in glacial systems may be sourced from snow and cryoconite ecosystems in the supraglacial environment, and hence, supraglacially-derived DOC may display high concentrations of LMW-DOC. This study 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), but strongly points towards an in situ microbial production source for at least a fraction of the bioavailable DOC.

Recent studies investigating the bioavailability of glacially-derived DOC have reported an increase in BDOC with % 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 directly assess the impact of glacial DOC upon near-coastal marine microbial populations via bioavailability experiments on the GrIS. Subglacial runoff collected near the glacier terminus (glacial) and ∼30 km downstream (proglacial) provided the DOC substrate for marine microorganisms. We assume that glacial runoff derives entirely from ice melt as no terrestrial stream inputs were evident at either site. BDOC (30–58 %) in GrIS bioavailability experiments were at the low end of BDOC estimates in glacial runoff and ice with high percentages of glacial catchment coverage (52–64 %, compared with 100 % for Leverett glacial incubations and c. 60 % for proglacial incubations) (Hood et al., 2009; Singer et al., 2012). This may be due to much lower mean proportions of protein-like, and hence, highly bioavailable, compounds in GrIS subglacial runoff (2.5–2.7 %) compared with that measured in runoff exported from the Gulf of Alaska (41–77 %, watersheds with >50 % glacial coverage) (Hood et al., 2009). The observed increase in bacterial abundance concurrent with the net DOC decline during the 22-day bioavailability experiment demonstrates heterotrophic microbial activity and utilisation of the glacially-derived DOC. This includes mineralisation of DOC (as an energy source) and incorporation of DOC into microbial biomass. Importantly, this provides evidence that the potentially bioavailable
compounds exported from GrIS glacial outflows may be successfully utilised by coastal heterotrophs.

### 4.3 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. 4) shows that only ~30% of all DOC and free carbohydrate peaks were synchronous (Tables S6 and S7), and that there was no significant association between the timings of DOC and free carbohydrate peaks. A combination of synchronous and asynchronous timing in DOC and free carbohydrate pulses in runoff supports the assertion that the bioavailable carbohydrate fraction has multiple sources. Peaks in carbohydrates which do not concur with those in DOC may reflect the export of DOC largely derived from the glacier surface, which is distinct from the dominant bulk DOC fraction (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, most likely associated with supraglacial lake drainage. The pulses of free carbohydrates well into the late melt season, e.g. ~DY 212–14 in 2009, may be explained by the progressive mobilisation of surface DOC pools situated further into the GrIS interior as the snowline retreats (Fig. S3, method described in Supplement Sect. 5). It is likely that some variability in free carbohydrate export in runoff is associated with microbial utilisation en route to the terminus. Accumulation and export of LMW-DOC to the subglacial environment is extremely probable given the high rates of primary production on the GrIS surface (Stibal et al., 2012a).
Episodic pulses of high SSCs in runoff, coinciding with high rates of sediment evacuation (Cowton et al., 2012), reflect 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. 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, and hence POC in subglacial runoff largely derives from the ice sheet bed via erosion of bedrock and overridden paleosols (Cowton et al., 2012).

4.4 OC fluxes from Leverett Glacier, 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. We calculated both DOC and POC fluxes from the Leverett Glacier catchment (Supplement Sect. 1.2). DOC fluxes were similar in both 2009 (0.56 GgDOCyr$^{-1}$) and 2010 (0.52 GgDOCyr$^{-1}$), equal to ~ 0.9 gDOCm$^{-2}$ yr$^{-1}$. DOC fluxes from Leverett Glacier are similar to those from an Arctic river of comparable catchment area (Lobbes et al., 2000). Approximately 7% (0.041 GgCyr$^{-1}$, 2009) and 13% (0.069 GgCyr$^{-1}$, 2010) of the DOC comprised free carbohydrates, which 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 high SSC that frequently exceed 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 $4.7 \pm 0.7 \times 10^6$ t in 2009 (Bartholomew et al., 2011) was much larger than the $2.75 \times 10^6$ t 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 drainage system config-
uration, 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) suggests that it is a source of carbon to downstream environments. POC, on average, accounted for 70–89% of OC export, which is comparable to 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 non-glacial 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 was underlain by overridden paleosols than at Leverett Glacier. We contend that a greater proportion of SS exported from Leverett Glacier was derived from the erosion of minerogenic material from further into 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 gCm$^{-3}$ was exported from Leverett Glacier ($n = 26$, 2009 and 2010), which is similar to POC exported from “N” Glacier (3.5 ± 1.1 gCm$^{-3}$, $n = 28$, from 2008) (Bhatia et al., 2013a). The 9% bioreactive carbohydrate fraction present in Leverett SS is likely sourced from overridden soil organic matter. This is consistent with earlier work that showed subglacial sediments from the Russell Glacier catchment to display a high OC content (∼0.4%), thought to be derived from overridden paleosols (Stibal et al., 2012b).

It is notable that in both study years the snowline reached a comparable position by the end of the monitoring period (Fig. S3), suggesting similar 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$_2$ fixa-
tion 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. Higher SSC fluxes in 2009 also suggest an insensitivity to runoff volumes, believed to reflect supply limitation of suspended sediment in runoff and evolution of basal hydrology (Cowton et al., 2012).

4.5 Present and future 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 datasets are sparse due to the difficulty of making measurements (Bhatia et al., 2013a, b; 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) is representative of the wider GrIS. This is discussed in Supplement Sect. 6. To summarise, 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.

To date, there are few studies of GrIS OC export (Bhatia et al., 2010, 2013a) and none from large Greenlandic catchments. DOC concentrations in Leverett Glacier
runoff (Table 1) are within the range of those (22–341 µMC) reported in runoff from the smaller (∼5 km²) “N” Glacier, West GrIS (Bhatia et al., 2013a). Extrapolation of fluxes from Leverett Glacier to the GrIS generates similar DOC fluxes of 0.17 TgOC yr⁻¹ (2009) and 0.13 Tg OC yr⁻¹ (2010), which are higher than recent estimates of GrIS DOC export (0.08 ± 0.02 TgOC yr⁻¹) using geochemical data from a much smaller catchment (∼5 km²) (Bhatia et al., 2013a). These fluxes are comparable to glacial DOC fluxes to the Gulf of Alaska and small Arctic rivers (Hood et al., 2009; Lobbes et al., 2000).

Similar OC export dynamics were also displayed at Leverett Glacier and “N” Glacier; the majority of the derived OC is released over the summer months (captured in this study in both 2009 and 2010) and the POC fraction typically dominates (>70% of the total OC mass flux, based on mean values). In addition, the average POC export from the GrIS is estimated here to range from 0.36–1.52 Tg C yr⁻¹, which brackets the 0.9 Tg yr⁻¹ estimated by Bhatia et al. (2013). Our GrIS flux estimates are equal to 9.7–44.7% of the riverine POC flux to the Arctic Ocean (3.4–3.7 Tg yr⁻¹), which is dominated by the MacKenzie River (1.8–2.1 Tg yr⁻¹) (Dittmar and Kattner, 2003). While the POC from the GrIS may be rapidly removed in the near-coastal zone, it may be locally important in stimulating heterotrophic activity considering the 9% bioreactive component. In contrast, DOC may travel further and have significant downstream effects at greater distance from the glacier terminus (Bhatia et al., 2013a). It is notable that the GrIS OC flux largely supplies the North Atlantic, Greenland and Labrador Seas, whereas the major Arctic rivers enter the central Arctic Ocean. Indeed, the combined POC and DOC flux to these ocean masses from the GrIS is of a similar order of magnitude to DOC supplied via major currents from the central Arctic Ocean to the North Atlantic (e.g. East Greenland current = 4.4–6.6 Tg C yr⁻¹) (Benner et al., 2005). Unlike these currents, however, ice sheet inputs supply POC and DOC to coastal regions. These findings are significant owing to the identified OC limitation of marine bacteria in some Arctic regions (Cuevas et al., 2011; Middelboe and Lundsgaard, 2003).
It is difficult to speculate on the combined impact of increased meltwater fluxes and an expanded melt zone upon OC export from the ice sheet, 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 hypothesize 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 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 the North Atlantic, Greenland and Labrador Seas, and its inclusion in biogeochemical models could 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, 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 “labile” 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 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 ~ 2 fold difference in runoff fluxes, suggesting production-limited DOC sources. Significant proportions of the exported DOC (30–58 %) were found to be bioavailable to downstream marine microorganisms and stimulated bacterial activity in bioavailability experiments. Scaled to the GrIS, the combined DOC and POC fluxes (0.13–0.17 Tg C yr$^{-1}$ DOC, 0.36–1.52 Tg C yr$^{-1}$ mean POC), are of a similar order of magnitude to other large Arctic river systems and may represent an important bioavailable OC source 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.

Supplementary material related to this article is available online at http://www.biogeosciences-discuss.net/10/19311/2013/bgd-10-19311-2013-supplement.pdf.

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References


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**Table 1.** POC, DOC, free carbohydrate (FCHO) abundance, and percentage protein-like fluorescence in bulk runoff, subglacial and supraglacial samples collected in 2009–2011. Standard deviation is given in parentheses. Outliers (≥ mean ±3 × standard deviation) have been excluded. Protein-like fluorescence is the relative contribution of compounds fluorescing between 260–285 nm to the total fluorescence (adapted from Hood et al., 2009), calculated as a mean % (± standard deviation) for the sample subset.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean POC (mg L(^{-1}))</th>
<th>Mean DOC (µMC)</th>
<th>DOC range (µMC)</th>
<th>Mean FCHO (nMC)</th>
<th>FCHO range (nMC)</th>
<th>% FCHO in DOC</th>
<th>% FCHO in DOC range</th>
<th>Protein-like fluorescence (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk runoff 2009</td>
<td>4.05 × 10(^8)</td>
<td>41.4 (23.2)</td>
<td>12.3–124</td>
<td>121 (171)</td>
<td>1.50–1220</td>
<td>0.22 (0.27)</td>
<td>0.0–1.83</td>
<td>2.7 ± 0.8</td>
</tr>
<tr>
<td>Bulk runoff 2010</td>
<td>5.98 × 10(^5)</td>
<td>17.7 (10.2)</td>
<td>0.62–70.3</td>
<td>77.2 (93.6)</td>
<td>3.86–704</td>
<td>0.52 (1.01)</td>
<td>0.0–9.90</td>
<td>2.5 ± 1.0</td>
</tr>
<tr>
<td>Supraglacial (2 and 4 km)</td>
<td>N.D</td>
<td>12.1 (8.76)</td>
<td>1.57–39.9</td>
<td>47.1 (56.9)</td>
<td>1.74–174</td>
<td>0.41 (0.42)</td>
<td>0.0–1.49</td>
<td>5.1 ± 2.6</td>
</tr>
<tr>
<td>Supraglacial (7–50 km)</td>
<td>N.D</td>
<td>15.4 (4.28)</td>
<td>10.4–24.3</td>
<td>49.3 (41.7)</td>
<td>0.00–138</td>
<td>0.30 (0.18)</td>
<td>0.0–0.57</td>
<td>4.2 ± 1.4</td>
</tr>
<tr>
<td>Snow</td>
<td>N.D</td>
<td>15.8 (12.0)</td>
<td>2.29–32.8</td>
<td>230 (241)</td>
<td>6.44–637</td>
<td>1.36 (1.26)</td>
<td>0.13–3.48</td>
<td>5.6 ± 4.6</td>
</tr>
<tr>
<td>Basal ice</td>
<td>N.D</td>
<td>51.3 (38.1)</td>
<td>3.79–155</td>
<td>7.84 (9.11)</td>
<td>0.00–34.9</td>
<td>0.06 (0.19)</td>
<td>0.0–0.92</td>
<td>2.6 ± 0.4</td>
</tr>
<tr>
<td>Cryoconite waters (2 km)</td>
<td>N.D</td>
<td>285 (194)</td>
<td>63.6–559</td>
<td>1240 (1020)</td>
<td>272–2680</td>
<td>0.43 (0.17)</td>
<td>0.23–0.73</td>
<td>25.7 ± 6.2</td>
</tr>
</tbody>
</table>

N.D: not determined.
### Table 2. Summary of the dominant fluorophores (denoted by *) in each glacial environment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fluorophore (peak wavelength, nm)</th>
<th>Dominant fluorophore identification</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basal ice</td>
<td>336, 385*, 440, 483, 551</td>
<td>Fulvic acid, marine humic-like</td>
<td>7</td>
</tr>
<tr>
<td>Snow</td>
<td>276, 352*, 398,</td>
<td>Fulvic acid, marine humic-like</td>
<td>3</td>
</tr>
<tr>
<td>NSupra (2–4 km)</td>
<td>279, 353*, 385, 447, 559</td>
<td>Fulvic acid, marine humic-like</td>
<td>7</td>
</tr>
<tr>
<td>FSupra (7–50 km)</td>
<td>280, 352*, 439</td>
<td>Fulvic acid, marine humic-like</td>
<td>7</td>
</tr>
<tr>
<td>Cryoconite hole waters</td>
<td>278*, 319, 386, 438, 555</td>
<td>Protein-like (tryptophan)</td>
<td>10</td>
</tr>
</tbody>
</table>
Fig. 1. Map of the terminus of Leverett Glacier (sampling location starred) and context within the wider Greenland Ice Sheet. Contour elevations are shown in meters and landuse type is denoted (white corresponds to ice sheet). From Hawkings et al. (2013).
Fig. 2. Export of major inorganic (total ions and dissolved silica) and organic (DOC and free carbohydrates) compounds in Leverett Glacier bulk runoff in (a) the 2009 melt season, and (b) the 2010 melt season. Total discharge and suspended sediment concentration (SSC) are also plotted. The approximate timing of water pulses that punctuate the discharge hydrograph (P) and are associated with a rise in solutes are 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.
Fig. 3. Comparisons of low molecular weight 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.
Fig. 4. 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.
Fig. 5. 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 ($n = 7$). All spectra have been normalized to the highest fluorescence peak spectral maximum in the entire dataset. Note the difference in scale on the y-axis.