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Particulate organic matter composition and organic carbon flux in Arctic valley glaciers: examples from the Bayelva River and adjacent Kongsfjorden

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Abstract

In the face of ongoing global warming and glacier retreat, the composition and flux of organic matter in glacier–fjord systems are key variables for updating the carbon cycle and budget, whereas the role of Arctic valley glaciers seems unimportant when compared with the huge Greenland Ice Sheet. Our field observations of the glacier-fed Bayelva River, Svalbard, and the adjacent Kongsfjorden allowed us to determine the compositions of particulate organic matter from glacier to fjord and also to estimate the flux of organic carbon, both for the river and for Svalbard in general.

Particulate organic carbon (POC) and dissolved organic carbon (DOC) in the Bayelva River averaged 56 and 73 µM, respectively, in August 2012. Amino acids (AAs) and phytoplankton pigments accounted for ~ 10 % of the particulate organic matter (POM) in the Bayelva River, while AAs represented > 90 % of particulate nitrogen in fjord surface water, suggesting the strong in situ assimilation of organic matter. Bacteria accounts for 13 and 19 % of the POC in the Bayelva River and the Kongsfjorden, respectively, while values for particulate nitrogen (PN) are much higher (i.e., 36 % in Kongsfjorden).

The total discharge from the Bayelva River in 2012 was 29×10^6 m^3. Furthermore, we calculated the annual POC, DOC, and PN fluxes for the river as 20 ± 1.6, 25 ± 5.6, and 4.7 ± 0.75 t, respectively. Using the POC content and DOC concentration data, we then estimated the annual POC and DOC fluxes for Svalbard glaciers. Although the estimated POC ($0.056 \pm 0.02 \times 10^6$ t yr^{-1}) and DOC ($0.02 \pm 0.01 \times 10^6$ t yr^{-1}) fluxes of Svalbard glaciers are small compared with those of the Greenland Ice Sheet, the area-weighted POC flux of Svalbard glaciers is twice that of the Greenland Ice Sheet, while the flux of DOC can be 4 to 7 times higher. Therefore, we propose that valley glaciers are efficient high-latitude sources of organic carbon.

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1 Introduction

The composition and flux of organic carbon are two key factors in the study of global climate change and material cycling. Current retreat of Arctic glaciers, as a consequence of global warming, not only contributes to sea-level rise but also serves to increase the input of terrigenous material to the ocean. This in turn impacts the composition of oceanic organic carbon and modifies the carbon flux, with potential ramifications for global climate variability and material cycles.

Terrigenous dissolved organic matter (DOM) in the Arctic Ocean exhibits a considerably shorter lifespan than that in the Pacific and Atlantic oceans (Opsahl et al., 1999). Furthermore, despite the relative depleted nature of ^{14}C values of glacial DOM, which results in old apparent ^{14}C ages, significant proteinaceous signals (Dubnick et al., 2010) and a high labile proportion (23–66 %; Hood et al., 2009) were identified in the glacier meltwater DOM. This decoupling of age and stability in glacial DOM is probably due to the contribution of subglacial microbial communities (Sharp et al., 1999). In contrast, the flux of particulate organic carbon (POC) in glacial meltwater is typically higher than that of DOC (e.g., Bhatia et al., 2013), while the labile proportion is relatively low (9 %) (Lawson et al., 2014). Owing to the efficiency of erosion and transport within Arctic drainage basins and the high productivity of adjacent sea water, Arctic fjords contribute 11 % of the global burial of marine organic carbon, yet comprise less than 0.1 % of the global ocean surface (Smith et al., 2015). Therefore, particulate organic matter (POM) in Arctic glacial meltwater and adjacent fjords is an important component of the global carbon cycle and budget.

To date, most studies of organic matter in Arctic glacial meltwater have focused on the Greenland Ice Sheet (e.g., Bhatia et al., 2013; Lawson et al., 2014), with little attention paid to smaller valley glaciers, such as those on Svalbard (Kuliński et al., 2014; Tye and Heaton, 2007). However, a comparison of Alaskan glaciers (Hood et al., 2009) and the Greenland Ice Sheet (Bhatia et al., 2013) reveals that valley glaciers exhibit higher area-weighted fluxes of organic carbon. Although regional fluxes of POC have

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been estimated for glaciers on Svalbard (Kuliński et al., 2014), the area-weighted flux of organic carbon for the entire archipelago has yet to be determined. Furthermore, to our knowledge, little or no information exists on potential labile proportions in Svalbard glacial meltwater POM, or on the POM composition of glacier meltwater that enters adjacent fjords.

We carried out field observations of the Bayelva River and Kongsfjorden in summer of 2012. Using amino acid enantiomers and phytoplankton pigments as biomarkers, we first focused on variations in POM composition between glacial meltwater and the fjord. Subsequently, we employed 2012 discharge data for the Bayelva River to estimate the riverine flux of organic matter, and up-scaled this flux to cover the whole of Svalbard. Finally, we compared the organic carbon flux in Svalbard with that of other Arctic glaciers, including the Greenland Ice Sheet.

2 Materials and methods

The Bayelva River in Ny-Ålesund, Svalbard, is the principal meltwater channel draining the Austre Brøggerbreen valley glacier into Kongsfjorden (also known as Kings Bay). Downstream of the glacier terminus, a hydrologic station collects river discharge data during the freshet. The physical and biological characteristics of Kongsfjorden have been summarized by Hop et al. (2006). Nitrogen limitation of primary production occurs during summer months (Rokkan Iversen and Seuthe, 2011), when stratification of the water column and input of nutrient-depleted glacial meltwater results in oligotrophic surface water in the inner fjord (e.g., increase proportion of cyanobacteria and cryptophytes in surface phytoplankton communities; Hop et al., 2002). Moreover, where turbid meltwater has yet to mix with clear sea water, phytoplankton growth is limited by reduced illumination (Svendsen et al., 2002). In the outer fjord, the high abundance of zooplankton exerts considerable grazing pressure on algae, resulting in a relatively low standing stock in surface water (Hop et al., 2002).

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The study area is shown in Fig. 1a. The Bayelva River is ∼ 4 km long and occupies a basin underlain by Permian and Carboniferous lithologies (Hjelle, 1993). In normal years, river flow begins in early–mid June, while the riverbed and banks are still frozen, and for approximately 10 days the water flows clear. Subsequently, the river flow becomes turbid and remains so until the river refreezes in autumn (usually in September/October). In Kongsfjorden, which lacks a sill at its mouth, the exchange of intermediate and deep fjord water with Arctic Water and Atlantic Water is facilitated by a prominent trench that decreases in depth towards the shallow continental shelf (Svendsen et al., 2002).

2.1 Monitoring discharge of the Bayelva River

Approximately 700 m upstream from where the river enters the fjord, a monitoring station (NVE; Fig. 1b) is operated by the Norwegian Water Resources and Energy Directorate, and includes an artificial concrete flume with a so-called crump weir. Water level is measured using a system comprising a float, counterweight, and encoder, and the data are stored in a logger. Ultimately, water discharge is determined using a rating curve. In 2012, discharge data were collected between 15 June and 1 October. For the remainder of the year, data collection was not possible due to freezing.

2.2 Field observations and biogeochemical sampling

We conducted our field investigation between 6 and 19 August 2012. The area sampled covers both the Bayelva River basin and Kongsfjorden (Fig. 1b). For the terrestrial stations, we carried out our investigation on foot, collecting samples with a pre-cleaned bucket. Using a portable water quality meter (WTW®, multi 350i, Germany), which was calibrated daily, we measured salinity/conductivity, temperature, pH, and dissolved oxygen. For the marine/estuarine stations, sampling was carried out from the R/V *Tiesten* or a rubber boat, and samples were collected using Niskin samplers. When on the R/V *Tiesten*, we obtained salinity, temperature, fluorescence, and turbidity profiles us-

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ing a CTD (SD204, SAIV A/S, Norway). For comparison, discrete water samples were also measured with a portable water quality meter. Both terrestrial and marine samples were returned immediately to the marine laboratory for processing. Additionally, clean floating ice, without visible soil or sediment, was collected from the fjord for analysis of dissolved nutrients.

In the laboratory, suspended particles were concentrated onto pre-combusted glass fiber membranes (Whatman®, GF/F, pore size 0.7 µM) under a mild vacuum, before being analyzed for total hydrolysable particulate amino acids (THPAA), particulate nitrogen (PN), phytoplankton pigments, and particulate organic carbon and its stable isotopes (POC and $\delta^{13}C$). Filtration volume ranged from 0.09 to 5.4 L, depending on the concentration of suspended particles. During filtration, visible swimmers (Calanoida and other zooplankton) were observed in fjord samples, especially those from open western areas. Whenever possible, all swimmers were removed from the membrane prior to storage, using clean tweezers. Water samples for dissolved nutrients were filtered through acid-cleaned acetate cellulose filters (pore size 0.45 µM), whereas samples for DOC were cleaned using nylon filters (pore size 0.45 µM) and a syringe. Nutrient samples were poisoned with $HgCl_2$ and stored at 4 °C in the dark. All other samples were kept frozen (−20 °C) until laboratory analysis.

2.3 Instrumental measurements

Our measurement of AA enantiomers followed the protocol of Fitznar et al. (1999), a detailed description of which is provided by Zhu et al. (2014). Briefly, GF/F filters were first freeze-dried and then hydrolyzed with HCl at 110 °C for 24 h. Following pre-column derivatization with *o*-Phthaldialdehyde and *N*-Isobutyryl-L/D cysteine (IBLC/IBDC), AA enantiomers were measured in hydrolyzates using a High Performance Liquid Chromatography (HPLC) system (1200 series, Agilent, USA). Asx and Glx were used for aspartic acid + asparagine and for glutamic acid + glutamine, respectively, due to the corresponding acids being formed through deamination during hydrolysis. In addition to Asx and Glx, we measured alanine (Ala), arginine (Arg), isoleucine (Ile), leucine (Leu),

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lysine (Lys), methionine (Met), phenylalanine (Phe), serine (Ser), threonine (Thr), tryptophan (Try), tyrosine (Tyr), and valine (Val). The non-chiral AAs, γ–aminobutyric acid (GABA) and glycine (Gly), were also measured. The D forms of AAs (D-AAs) generated by acid hydrolysis were calibrated according to Kaiser and Benner (2005). The degradation index (DI) was derived from the AA data set using the calculations of Dauwe and Middelburg (1998) with minor modifications (Zhu et al., 2014).

Phytoplankton pigments were extracted with *N*,*N*-dimethylformamide and analyzed using an HPLC system (1100 series: Agilent, USA), following a modified version of the method of Mantoura and Llewellyn, (1983) and Van Heukelem and Thomas (2001). Solvent A was methanol and 1 mol L^{-1} ammonium acetate (80 : 20, v/v), and solvent B was pure methanol. A detailed description of the gradient elution procedure is given by Huang et al. (2010). We identified pigments by their retention times and absorption spectra, using a set of 21 pigment standards (chlorophyll c3, chorophyllide a, chlorophyll c1 + c2, peridinin, 19'-butanoyloxyfucoxanthin, fucoxanthin, neoxanthin, prasinoxanthin, 19'-hexanoyloxyfucoxanthin, violaxanthin, diadinoxanthin, alloxanthin, diatoxanthin, zeaxanthin, lutein, chlorophyll *b*, chlorophyll *a*, β,ε-carotene, β,β-carotene, pheophorbide a, and pheophytine a) obtained from DHI (Denmark).

Following the removal of inorganic carbon with HCl, POC and PN were measured with an elemental analyzer (Vario EL *III*: Germany). The detection limits for carbon and nitrogen were 7.5 and 8.0 µg, respectively, with a precision better than 6 %. We measured $\delta^{13}C$ samples using an isotope-ratio mass spectrometer (Deltaplus XP: *Thermo Finnigan*, USA) connected to a Flash EA 1112 analyzer. The $^{13}C/^{12}C$ is expressed in ‰ relative to the V-PDB standard using the conventional δ notation. DOC samples were measured with a TOC analyzer (TOC-L_{CPH}: Shimadzu, Japan), whereas ammonium was measured manually using the sodium hypobromite oxidation method, with an analytical precision of 0.04 µM. The other four nutrients were measured using an autoanalyzer (AA3: SEAL Analytical, USA), with the precisions of nitrate, nitrite, dissolved inorganic phosphorus (DIP, PO_4^{3-}), and silicate (H_4SiO_4) being 0.01, 0.003, 0.005, and

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0.02 µM, respectively. The concentration of total suspended matter (TSM) was determined from POC samples (i.e., GF/F filters).

2.4 CHEMTAX and DI calibration

We applied CHEMTAX to the phytoplankton pigment data set to estimate the structure of phytoplankton communities (Mackey et al., 1996). To avoid apparent changes in diagnostic pigment ratios, we avoided riverine samples and focused solely on samples from the fjord surface (Mackey et al., 1997). Based on our observations and those of previous workers (Not et al., 2005; Piquet et al., 2014; Schulz et al., 2013), the phytoplankton groups analyzed in this study include diatoms, cryptophytes, prasinophytes, dinoflagellates, haptophytes (e.g., *Emiliania* Hay and Mohler, *Phaeocystis* Lagerheim), chlorophytes, cyanobacteria (e.g., *Synechococcus*), and chrysophytes. Initial ratios are similar to the values reported by Not et al. (2005) for a neighboring study area. Finally, we present ratio data from a single CHEMTAX run, as our attempt at ratio-iteration (Latasa, 2007) produced anomalous results.

We note that the taxonomic terms are operationally defined based on the composition of the diagnostic pigments. Therefore, "chlorophytes" includes both chlorophytes and prasinophytes lacking prasinoxanthin. Similarly, "diatoms" may include both diatoms and some haptophytes and chrysophytes with a similar pigment composition. "Haptophytes" refers to the specific type of algae with both 19'hexanoyloxyfucoxanthin and fucoxanthin; e.g., *Emiliania* and *Phaeocystis*, which have been found in previous studies of Kongsfjorden (Piquet et al., 2014).

DI was calculated using the THPAA data set developed by Dauwe et al. (1998) and later modified by Vandewiele et al. (2009):

$$\mathrm{DI} = \sum_i \left(\frac{\mathrm{var}_i - \mathrm{AVG\,var}_i}{\mathrm{SD\,var}_i} \right) \cdot \mathrm{fac.coef.}_i$$

where var_i, $\mathrm{AVG\,var}_i$, $\mathrm{SD\,var}_i$, and $\mathrm{fac.coef.}_i$ are the mol%, mean, standard deviation, and factor score coefficient of amino acid i, respectively. Factor score coefficients were

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calculated using principal component analysis. The index ranges from +1 for phytoplankton/bacteria to −1.5 for highly degraded oxic sediments.

3 Results

Reflecting the considerable turbidity of the Bayelva River, we recorded TSM concentrations of up to 345 mg L^{-1} at the NVE station (Table 1) and as high as 740 mg L^{-1} at the BC station (Fig. 1b). Riverine POC was 56 µM, while the POC content in TSM (i.e., POC%) averaged 0.35 % (Table 1). Particulate AAs at the NVE station were low, with an average value of 1 µM (Table 1). Also at the NVE station, D-AAs averaged 42 nM (Table 1) and the proportion of D-AAs in THPAA was 4.0 %. While trace amounts of several pigments were measured in the river, chlorophyll *a* (Chl *a*) was the dominant pigment, with a mean concentration at NVE of 257 ng L^{-1} (Table 1). In contrast, the principal diagnostic riverine pigment, fucoxanthin, gave a mean value at NVE station of 54 ng L^{-1}. Over the course of our observation, DOC concentrations at NVE station ranged from 20.8 to 97.8 µM, with a mean value of 73 µM (Table 1). In 2012, the annual water discharge of the Bayelva River was 29×10^6 m^3 according to the hourly-averaged instrumental record.

In Kongsfjorden, surface concentrations of TSM, POC, and THPAA generally decreased from the eastern end, where tidewater glaciers enter the sea, to the open western end. We identified an additional area of high concentration close to the Bayelva River mouth (Fig. 2a–c). The POC% of surface water averaged 1.3 % in the marine sectors (i.e., $S > 30$) of the fjord, but fell to 0.6 % in near-bottom water. In comparison, the mean POC% of Bayelva River water was 0.3 %. $\Delta\delta^{13}C$ values of samples from the Bayelva River, the fjord surface, and near-bottom fjord water averaged −23.4, −24.6, and −24.5 ‰, respectively. The distribution of PN was similar to that of POC, with the PN content in TSM (PN%) in near-bottom water and Bayelva River water being comparable. The mean PN% of samples from the fjord surface, near-bottom, and Bayelva River was 0.17, 0.06, and 0.07 %, respectively. Not only was the DI of fjord surface wa-

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ter (0.54) higher than that of river water (−0.13), we also observed elevated DI values (e.g., 0.75 at station 6#) in the western part of the fjord, where high concentrations of Chl *a* and chlorophyllide a occur (Fig. 2d and e). The DI value of near-bottom water was 0.4. The proportion of D-AAs in the fjord surface water (1.6 %) was lower than that of the Bayelva River (4.7 %) and of near-bottom water (1.8 %), whereas levels of the non-protein AA, GABA, averaged 0.92 nM in fjord surface water and 2.6 nM in the Bayelva River. GABA was most depleted in the near-bottom water (mean value of 0.49 nM).

A clear difference exists in the concentration of dissolved nutrients among respective regions/sources. For example, both the river water and floating glacier-derived ice are depleted in nutrients, whereas high concentrations of nutrients occur in the near-bottom water of Kongsfjorden, beneath the pycnocline (Table 2). Despite this disparity in concentration, nitrate is the main form of dissolved inorganic nitrogen (DIN) in both the river water and the fjord near-bottom water (Table 2).

Cyanobacteria, chrysophytes, and dinoflagellates occur only in trace amounts in the fjord surface water, where diatoms are the primary contributor to the total fjord phytoplankton biomass (i.e., Chl *a*), followed by cryptophytes. On average, diatoms contributed half of the total phytoplankton biomass, with cryptophytes contributing another 28 % (Table 3). In western and middle parts of the fjord, diatoms are dominant, whereas in other regions there is a greater contribution from tiny cryptophytes. For example, at stations 14# and 15# (Fig. 1a), cryptophytes accounted for 40 and 48 % of the total Chl *a*, respectively.

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4 Discussion

4.1 POM composition and implications

4.1.1 In situ POM assimilation in Kongsfjorden

The contribution of AAs to the total carbon and nitrogen budgets reflects the freshness of POM (Davis et al., 2009). Using our measurements of THPAA, we calculated AA carbon and nitrogen amounts, and normalized the results against bulk POC and PN, respectively (i.e., POC_{AAs}/POC and PN_{AAs}/PN, in %). For the turbid glacier meltwater, phytoplankton pigments are depleted (Table 1) and AAs account for only 10–20 % of the riverine POC and PN (Fig. 3a). In contrast, the PN_{AAs}/PN of Kongsfjorden is as high as 90 %, with an average of 78 % (Fig. 3a). With the exception of one outlier, Chl *a*/POC values rise gradually from glacier meltwater to the fjord surface water (Fig. 3a), suggesting an increasing contribution from in situ POM production.

In the case that other obvious sources of protein and AAs are negligible, we attribute the increasing PN_{AAs}/PN in the fjord (i.e., samples with $S > 0$) to the in situ assimilation of ambient nitrogen via autotrophs (e.g., phytoplankton) and further transfer within the food web (PN_{AAs}/PN vs. Chl *a*: $r = 0.49$, $p = 0.01$, $n = 25$; Fig. 3b). As glacier meltwater is rich in TSM (Fig. 2a; Table 1), the observed distribution of POM composition suggests that light is a limiting factor for organic matter (OM) assimilation in the fjord surface water (i.e., PN_{AAs}/PN vs. TSM: $r = -0.79$, $p < 0.001$, $n = 25$; figure not shown). However, since the fjord is also characterized by a very low N/P ratio (Bazzano et al., 2014), as confirmed by our data (the mean N/P ratio in fjord surface water is 7.7), nitrogen could be another limiting factor for primary production (Rokkan Iversen and Seuthe, 2011). This effect is suggested by the distribution of POM composition when plotted against nitrate (PN_{AAs}/PN vs. nitrate: $r = -0.72$, $p < 0.001$, $n = 25$; Fig. 3b). However, PN_{AAs}/PN is not related to ammonium or nitrite (figure not shown).

Although ammonium is typically the preferred nitrogen nutrient for phytoplankton, we found nitrate, rather than ammonium, to be coupled with POM assimilation in Kongs-

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fjorden (Fig. 3b). As glacier meltwater is depleted in nutrients relative to fjord water (Table 2), the seaward dilution effect on nitrate is expected to play a minor role in the coupling between nitrate and POM assimilation (Fig. 3b). Instead, surface-water ammonium originates primarily from zooplankton, which exerts grazing pressure on phytoplankton and also leads to increased PN_{AAs}/PN (Fig. 3b). Also, as estimated by CHEMTAX (Table 3), diatoms are the principal phytoplankton group, particularly in open-fjord environments such as western Kongsfjorden. Previous work, using cultured diatoms preconditioned for nitrate, has shown that ammonium uptake in diatoms can be inhibited by nitrate (Dortch and Conway, 1984). In Kongsfjorden, inflowing Atlantic water masses are the main source of nutrients for phytoplankton (Hegseth and Tverberg, 2013). Therefore, since nitrate is the main form of DIN in Atlantic water (Table 2), it is possible that the presence of diatoms in the fjord induces (or enhances) the nitrate limitation during OM assimilation (Fig. 3b).

Although the proportion of proteins and AAs in total-cell nitrogen can vary (due to algae physiological status and inter-group phytoplankton differences), proteins, together with AAs, constitute the primary form of phytoplankton nitrogen and on average account for 70 % of total algal cellular nitrogen (Dortch et al., 1984). In bacteria cells, however, the ratio of bacterial carbon to protein/AA nitrogen has been calculated as 7.46 on the basis of bacteria protein : cell dry weight ratios, carbon : cell dry weight ratios, and AA compositions of bacterial proteins (Simon and Azam, 1989). Furthermore, by employing a phytoplankton POC : Chl *a* ratio of 50 (Hop et al., 2002) and a Redfield ratio of 6.6 (Redfield et al., 1963), and considering that bacteria, on average, account for 20 % of fjord POC (Rokkan Iversen and Seuthe, 2011), it is possible to estimate the contribution of phytoplankton and bacteria THPAA nitrogen to PN. For Kongsfjorden, we estimate this total contribution as 38 %.

On average, THPAA nitrogen accounted for 78 % of the fjord PN (Fig. 3a), leaving 40 % of the THPAA nitrogen contribution unaccounted for. We suggest that this inconsistency results from uncertainty in the above estimate, particularly concerning the bacteria. The samples with $PN_{AAs}/PN > 70$ %, however, were all obtained from the

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open western end of the fjord, where zooplankton are abundant (Hop et al., 2006), and we also observed abundant zooplankton during filtration. Due to their similar compositional distribution among different lives, amino acid composition can rarely be used to distinguish the respective contributions of phytoplankton, bacteria, and zooplankton (Cowie and Hedges, 1992). Degraded chlorophylls (e.g., chlorophyllide a), however, showed elevated concentrations at the western end of the fjord (Fig. 2e), suggesting the grazing pressure was heavier there (Hop et al., 2002). Therefore, for samples with extremely high (> 70 %) PN_{AAs}/PN value, it is likely that the zooplankton played an important role in modifying the composition of POM. In doing so, the zooplankton contribution to PN is comparable to that of phytoplankton and bacteria (i.e., 40 % vs. 38 %).

4.1.2 Bacterial influence on amino acid enantiomers and its contribution to POM

In a study at two other two marine sites (BATS and HOTS) at lower latitudes, Kaiser and Benner (2008) suggested that 12–32 % of the POC and 20–64 % of the PN were derived from bacteria. In Kongsfjorden, bacterial contributions to POC and PN can also be estimated. Here, we exploited the universal distribution of D-Ala in bacteria to calculate the amounts of bacterial organic carbon and nitrogen. Additionally, considering the potential differences between riverine and marine bacterial community structures, we estimated bacterial contributions for both riverine and marine samples (Table 4). For riverine samples (i.e., $S = 0$), we used only freshwater culture data from Table 2 of Kaiser and Benner (2008) for the D-Ala converting factor, whereas for marine samples (i.e., $S > 30$) the D-Ala converting factor is based solely on marine bacteria (Kaiser and Benner, 2008). Note that we did not estimate the contribution of bacteria in brackish water (i.e., $0 < S < 30$).

In Kongsfjorden, the bacterial contribution to POC (19 %; Table 4) is well within the value reported by Rokkan Iversen and Seuthe (2011) based on the cell density and conversion factor approach, and is similar to values reported for other marine regions

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at lower latitudes (Kaiser and Benner, 2008). The bacterial contribution to POC was slightly lower (13 %) in the Bayelva River. With respect to nitrogen, the bacterial contribution accounted for 36 % of POC in fjord water (Table 4).

Given that D-Ala occurs widely in biopolymers, whereas D-Glx is present in relatively few bacterial compounds, the overall D-Ala/D-Glx ratio would become > 1 (Kaiser and Benner, 2008 and ref. therein). Both the riverine ($r = 0.83$, $p = 0.006$, $n = 9$) and fjord ($r = 0.95$, $p < 0.001$, $n = 31$) D-Ala levels are strongly related to their respective D-Glx levels, exhibiting almost identical slopes (river: 1.26, fjord: 1.21; Fig. 4). The D-Ala/D-Glx slopes in both the river and the fjord (i.e., 1.26 and 1.21, respectively; Fig. 4) are comparable to the reported D-Ala/D-Glx value of 1.3 ± 0.4 (Kaiser and Benner, 2008), which was derived from a pure bacteria culture that included both marine/fresh and heterotrophic/autotrophic bacteria. Also, riverine D-Ala and D-Glx levels are coupled in an almost identical manner to fjord samples (Fig. 4). Given that Glx has a higher abiotic racemization rate than Ala (Wehmiller et al., 2012), the slightly higher D-Ala/D-Glx slope for river samples relative to fjord samples (i.e., 1.26 vs. 1.21; Fig. 4) indicates that D-AAs in riverine suspended particles likely originate from a modern contribution (e.g., bacteria) rather than abiotic racemization in the river basin. The presence of bacteria and their modification of OM in the underlying rock/paleosols of glaciers has been confirmed in previous study (Sharp et al., 1999).

4.2 Organic carbon flux on Svalbard

The annual water discharge of the Bayelva River in 2012 (29×10^6 m^3) was relatively low compared with levels recorded between 1990 and 2001 ($\sim 27 \times 10^6$ to more than 40×10^6 m^3) (Bogen and Bønsnes, 2003). Although some studies of glacier meltwater flux reported no clear temporal variability in the concentration of suspended particles over the course of the melt season (Bhatia et al., 2013), sediment flux in the Bayelva River did show large inter-annual variation, ranging from 5126 to 22 797 t year^{-1} (Bogen and Bønsnes, 2003). Based on the discharge data and results from the NVE station (Table 1), Bayelva River fluxes of TSM, POC, DOC, and PN in 2012 are estimated to be

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6400 ± 1300, 20 ± 1.6, 25 ± 5.6, and 4.7 ± 0.75 t, respectively. Therefore, our estimated POC flux for the Bayelva River is very close to a previous estimate (22 ± 3 $t\,yr^{-1}$) for the 2011 season (Kuliński et al., 2014).

Given that the POC% in TSM is 0.35 % (Table 1) and that the TSM flux for Svalbard is 16×10^6 $t\,yr^{-1}$ (Hasholt et al., 2006), we estimate that the POC flux for all of Svalbard is $0.056 \pm 0.02 \times 10^6$ $t\,yr^{-1}$ (Table 5). Moreover, by incorporating the total surface runoff from Svalbard's glaciers due to melting of snow and ice (25 $km^3\,yr^{-1}$; (Hagen et al., 2003) and the DOC content of glacier meltwater (Table 1), we estimate the DOC flux for Svalbard to be $0.02 \pm 0.01 \times 10^6$ $t\,yr^{-1}$. The POC flux of Svalbard is equivalent to only 6 % of that from the Greenland Ice Sheet ($0.9–0.94 \times 10^6$ $t\,yr^{-1}$) (Bhatia et al., 2013; Lawson et al., 2014), and is significantly smaller than the POC flux of the Mackenzie River ($1.8–2.1 \times 10^6$ $t\,yr^{-1}$) (Dittmar and Kattner, 2003). However, in terms of DOC flux, the value from Svalbard is 13 %–25 % that of the Greenland Ice Sheet ($0.08–0.15 \times 10^6$ $t\,yr^{-1}$) (Bhatia et al., 2013; Lawson et al., 2014). In comparison, DOC fluxes from glaciers in the Gulf of Alaska and from the small Arctic Yana River and the Mackenzie River are 0.13×10^6, 0.09×10^6, and 1.4×10^6 $t\,yr^{-1}$, respectively (Dittmar and Kattner, 2003; Holmes et al., 2012).

The glacier area on Svalbard is ~ 36 600 km^2 (Hagen et al., 2003), resulting in area-weighted fluxes of POC and DOC of 1.5 and 0.55 $t\,km^{-2}\,yr^{-1}$, respectively. Therefore, the Svalbard DOC area-weighted flux is ~ 40 % that of glaciers in the Gulf of Alaska (1.3 $t\,km^{-2}\,yr^{-1}$) (Hood et al., 2009) and is comparable to that of the Mackenzie River (i.e., 0.82 $t\,km^{-2}\,yr^{-1}$) (Holmes et al., 2012). It can be, however, 4 to 7 times higher than that of the Greenland Ice Sheet, considering its area of 1 200 000 km^2 (Rignot and Kanagaratnam, 2006) (i.e., 0.55 vs. 0.07 or 0.12; Table 5). Similarly, POC flux from Svalbard is only 6 % of that from the Greenland Ice Sheet, but the corresponding area-weighted flux is two times higher in Svalbard than in Greenland (Table 5). The singular Greenland Ice Sheet is considerably greater in both area and thickness (> 2000 m) than the glaciers on Svalbard, which comprise small, relatively thin alpine glaciers. Therefore, potential reasons for the offset in area-weighted flux include differences in

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glacier mass balance, as well as various organic carbon processes and content at both the supraglacial and subglacial interfaces. Furthermore, the influence of different ocean currents means that most of the DOC exported from the Greenland Ice Sheet is expected to be transported southwards to the Atlantic, whereas DOC from Svalbard is expected to travel northward. Therefore, among the glaciers, Svalbard glaciers play a more important role than the Greenland Ice Sheet in terms of contributing terrestrial material to the Arctic.

As reported by Bhatia et al. (2013) DOC showed temporal variability throughout the melt season, yet DOC concentration in glacier meltwater typically remains depleted (~ 27 µM) during the peak melt season. In the turbid Bayelva River, however, although DOC measured at the NVE station exhibited variability (Table 1), it was maintained at a much higher level compared with values from the Greenland Ice Sheets. DOC concentration was as much as 167 µM at the glacier terminus and remained elevated (73 µM) even as far as the NVE station (Table 1). Although we cannot assess monthly variability in DOC in this study, previous work in neighboring drainage basins suggests that DOC concentration in Svalbard glacial meltwater is maintained at high levels (250–426 µM in glaciated basins and 165–204 µM in non-glaciated basins) between mid June and early September (Tye and Heaton, 2007). Such high concentrations of organic matter in glacier meltwater are an important reason for the observed differences in area-weighted DOC flux between Svalbard and the Greenland Ice Sheet. And the area-weighted DOC flux would be even greater had we used the previous monthly DOC concentration (Tye and Heaton, 2007).

With respect to POM in the Bayelva River, AA and phytoplankton carbon together accounted for 9.5 % of the POC flux, and nitrogen accounted for 11 % of the PN flux. Assuming that AA and phytoplankton carbon represent the labile POM pool, the labile proportion in the total POM flux will be ~ 10 % of the total POM flux (i.e., for POC flux, 9.5 %; for PN flux, 11 %). This proportion is comparable to that of the Greenland Ice Sheet POM, in which the labile component is estimated at 9 % using a carbohydrates approach (Lawson et al., 2014), and is considerably lower than the labile proportion of

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glacier meltwater DOM, which ranges from 23 to 66 % (Hood et al., 2009). Considering the greater flux (Table 5) and lower labile proportion, POM in glacier meltwater plays a more significant role in glacier terrigenous carbon sequestration than DOM (Smith et al., 2015).

Due to both the asymmetry of the organic carbon flux in a single glacier meltwater river and the heterogeneity among different meltwater drainages, we consider our provisional estimates of Svalbard POC and DOC to be tentative. Moreover, the precision of these values is dependent on the organic carbon content and on approximations of TSM/runoff. Therefore, more work is needed to improve our estimates. Furthermore, the fluxes reported here are based solely on glacier meltwater runoff data and thus exclude iceberg calving, which accounts for one-sixth of the runoff flux in Svalbard (Hagen et al., 2003). Consequently, the organic carbon flux will need to be updated when further data become available.

5 Conclusions

Using AAs and phytoplankton pigments as biomarkers, we elucidated the POM composition in the glacier-fed Bayelva River and adjacent Kongsfjorden. In the glacier meltwater, AAs and pigments represent ~ 10 % of the bulk POM, whereas in the fjord, PN_{AAs}/PN can exceed 90 %, suggesting strong in situ assimilation. Furthermore, AAs in POM indicate that bacteria accounts for 13 and 19 % of the POC in the Bayelva River and Kongsfjorden, respectively. This proportion is even greater for PN, with values of 36 % being determined for the fjord.

The annual flux of terrigenous material in the Bayelva River is estimated at 6400 ± 1300 t for TSM, 20 ± 1.6 t for POC, 25 ± 5.6 t for DOC, and 4.7 ± 0.75 t for PN. Furthermore, annual POC and DOC fluxes for all of Svalbard are estimated to be 0.056×10^6 and $0.02 \times 10^6\,t\,yr^{-1}$, respectively. Though lower in bulk value, the area-weighted organic carbon flux for Svalbard is much higher than that for the Greenland Ice Sheet. Furthermore, given the opposite terrigenous DOC transport direction between the

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Greenland Ice Sheet (to the Atlantic in the south) and Svalbard (to the Arctic Ocean in the north), which results from the respective surrounding ocean currents, we propose that the Svalbard glaciers are an important source of terrigenous material for the Arctic Ocean relative to the massive Greenland Ice Sheet.

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Table 1. Basic parameters for the Bayelva River at NVE station in August 2012.

date	TSM	POC		δ^{13}C	PN	THPAA	D-AA*	DI	Chl *a*	DOC
	mg L^{-1}	µM	%	‰	µM	µM	nM		ng L^{-1}	µM
8th	159	49	0.37	−23.8	13	0.8	29	−0.38	223	75
12th	115	46	0.48	−24.1	8.3	0.6	18	0.69	213	98
13rd	169	58	0.41	−24.3	6.9	1.1	50	−0.51	209	80
16th	281	55	0.23	−23.5	16	1.2	54	−0.44	264	21
19th	345	70	0.25	−23.8	12	1.3	58	−0.06	377	92
average	214	56	0.35	−23.9	11	1.0	42	−0.14	257	73

TSM: total suspended matter.
POC: particulate organic carbon.
PN: particulate nitrogen.
THPAA: total hydrolysable particulate amino acids.
D-AA: D-forms of amino acids.
DI: degradation index.
Chl *a*: chlorophyll *a*.
DOC: dissolved organic carbon.
*: all D-amino acids combined together.

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Table 2. Dissolved inorganic nutrients (mean, min – max) in this study.

unit: μM	NH_4^+	NO_2^-	NO_3^-	SiO_3^{2-}	PO_4^{3-}
Bayelva River	0.28 (0.18–0.42)	0.05 (0.02–0.1)	2.87 (0.62–5.65)	5.68 (3.73–6.88)	0.06 (0.04–0.13)
Floating ices	0.33 (0.23–0.44)	0.003 (bdl* –0.01)	0.20 (0.03–0.43)	0.08 (bdl* –0.13)	0.02 (0.01–0.03)
Fjord waters (surface)	0.76 (0.18–2.2)	0.059 (bdl* –0.17)	0.6 (0.01–2.32)	1.74 (0.56–6.07)	0.05 (0.01–0.26)
Fjord waters (near-bottom)	1.65 (1.07–2.45)	0.3 (0.2–0.43)	7.88 (4.95–9.44)	3.85 (1.95–5.51)	0.66 (0.49–0.76)

*: below detection limit.

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Table 3. Phytoplankton groups contributions to total Chl *a* estimated via CHEMTAX.

Group	Average	Min.	Max.
Diatoms	50	6.6	78
Cryptophytes	28	5.9	48
Prasinophytes	11	4.5	17
Chlorophytes	4.3	0	17
Haptophytes	3.8	0	9.5
Dinoflagellates	3.1	0	7.3
Chrysophytes	0.5	0	2
Cyanobacteria	0.2	0	2.2

Unit: %.

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Table 4. Bacteria-contributed POC and PN proportion relative to bulk POC and PN (in %) derived from D-Ala concentrations[a].

Region [b]	bacterial POC%	bacterial PN%
Bayelva R.	13 ± 3.5	
Marine	19 ± 9.5	36 ± 18

[a] Terrestrial bacteria D-Ala content: 108 nmol mg^{-1} C, marine bacteria D-Ala content: 50.3 nmol mg^{-1} C, 215 nmol mg^{-1} N. The value is derived/cited from literature (Kaiser and Benner, 2008).
[b] Bayelva River used all the samples with $S = 0$ and marine samples only used samples in the Kongsfjorden with $S > 30$.
POC: particulate organic carbon.
PN: particulate nitrogen.

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Table 5. Estimated organic carbon flux from Svalbard and its comparison with Greenland ice sheet.

	POC flux $10^6\,t\,yr^{-1}$	DOC flux $10^6\,t\,yr^{-1}$	Area-weighted POC flux[a] $t\,km^{-2}\,yr^{-1}$	Area-weighted DOC flux[a] $t\,km^{-2}\,yr^{-1}$
Svalbard archipelago	0.056 ± 0.02	0.02 ± 0.01	1.5 ± 0.5	0.55 ± 0.3
Greenland ice sheet	0.9[b]–0.94[c]	0.08[b]–0.15[c]	0.7–0.8	0.07–0.12
Gulf of Alaska[c]		0.10 ± 0.01 [d]		1.3 ± 0.11 [d]

POC: particulate organic carbon.
DOC: dissolved organic carbon.
[a] Organic flux divided by glacier area.
[b] Data cited from Bhatia et al. (2013).
[c] Data cited from Lawson et al. (2014).
[d] Data cited from Hood et al. (2009).

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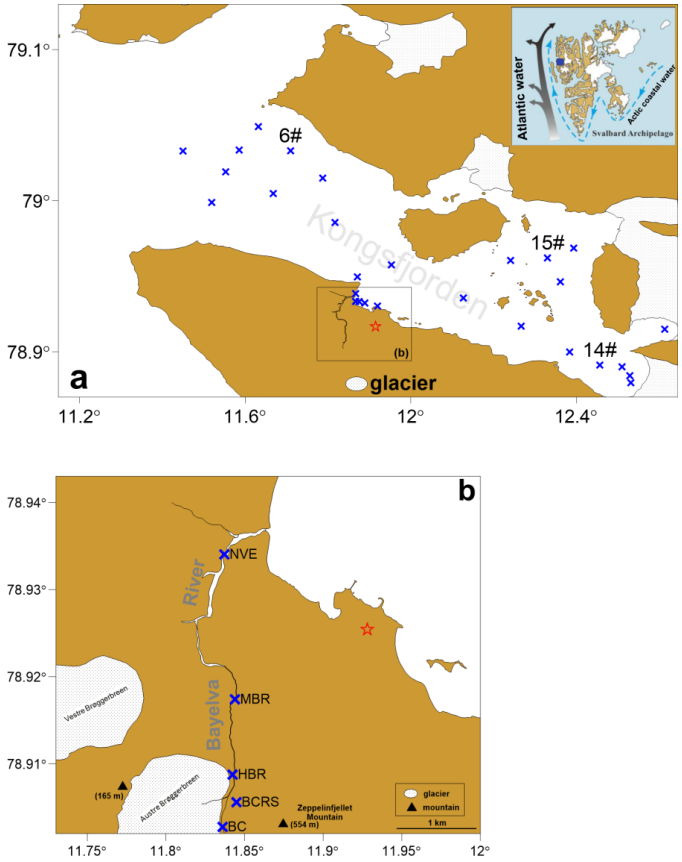

Figure 1. Study area and sampling stations in the Kongsfjorden **(a)** and the Bayelva River **(b)** in August 2012 (red star indicates the location of Ny-Ålesund; note that only tidewater glaciers are shown in plot **a**).

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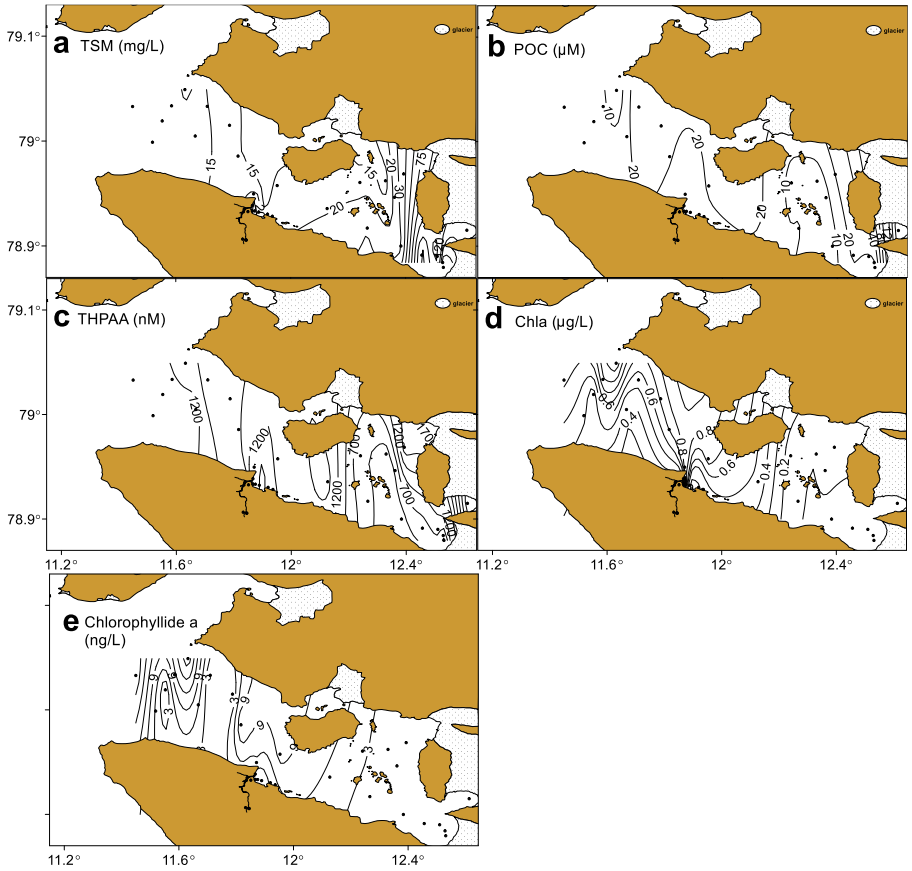

Figure 2. Surface **(a)** total suspended matter (TSM), **(b)** particulate organic carbon (POC), **(c)** total hydrolysable particulate amino acids (THPAA), **(d)** chlorophyll *a* (Chl *a*) and **(e)** chlorophyllide a distribution in the Kongsfjorden.

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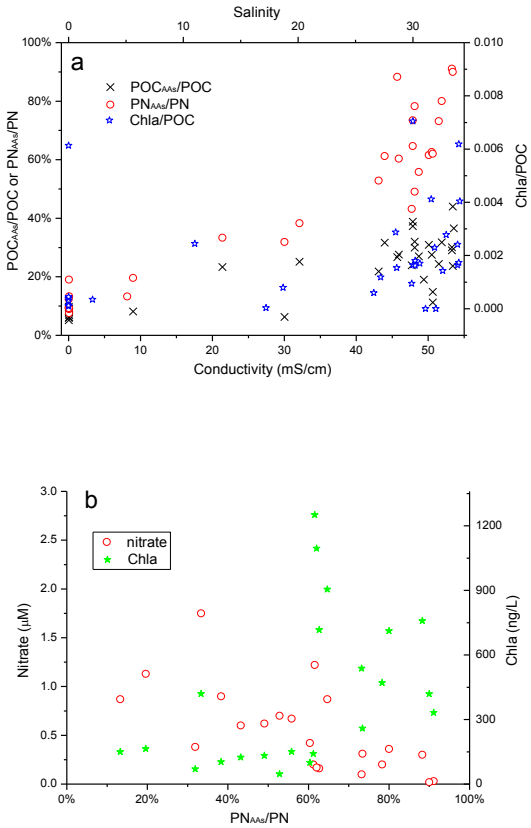

Figure 3. THPAA contribution to carbon and nitrogen: **(a)** along with salinity in the surface waters from glacier melt water to the Kongsfjorden; **(b)** its relations with nitrate and Chl *a* for fjord samples only (i.e., $S > 0$). (THPAA: total hydrolysable particulate amino acids, Chl *a*: chlorophyll *a*, PN: particulate nitrogen, POC_{AAs}/POC or PN_{AAs}/PN: amino acids carbon or nitrogen divided by POC or PN, respectively.)

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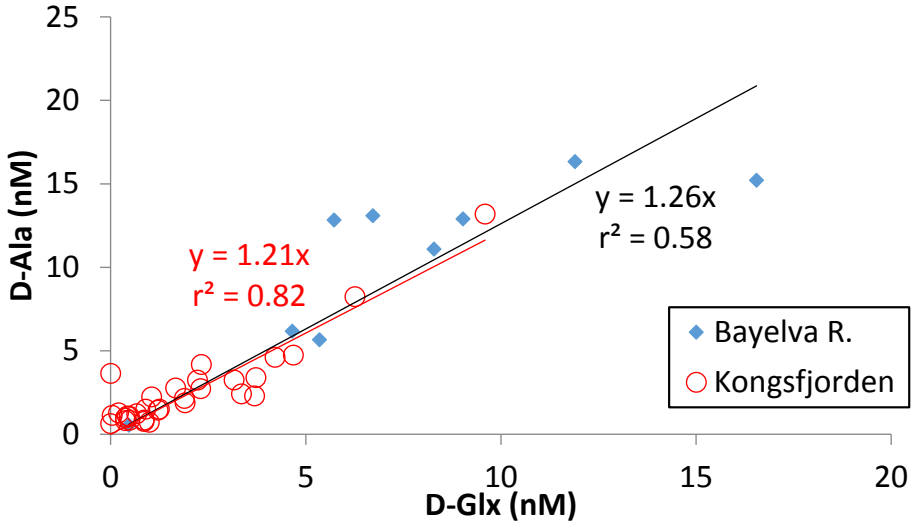

Figure 4. D-Ala plotted against D-Glx for both river ($S = 0$) and fjord ($S > 0$) particulate samples. (D-Ala: D-form of alanine, D-Glx: D-forms of glutamic acid and glutamine.)

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