

Source and biolability of ancient dissolved organic matter in glacier and lake ecosystems on the Tibetan Plateau

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Abstract

The Tibetan Plateau is the world's largest and highest plateau and holds the largest mass of ice on Earth outside the ice-sheets of Greenland and Antarctica, as well as abundant lakes. This study examined the molecular and isotopic signatures of dissolved organic matter (DOM) along with its biolability in glacier ice, glacier-fed streams, and alpine lakes on the Tibetan Plateau. The aim was to assess the sources of DOM and the potential of DOM to provide a carbon subsidy to downstream ecosystems. Tibetan glaciers and glacier streams exhibited low dissolved organic carbon (DOC) concentrations (17.7–27.9 μM) and ancient DOC radiocarbon ages (749–2350 ybp). The optical properties, stable carbon isotope ratios ($\delta^{13}\text{C}$ -DOC) and the molecular composition (Fourier transform ion cyclotron resonance mass spectrometry) of Tibetan glacier DOM are consistent with data from other glacier systems around the world. The geochemical signatures and the ancient apparent ages of Tibetan glacier DOM suggest a significant fraction is derived from the atmospheric deposition of pre-aged, possibly fossil fuel derived organics. Within the Tibetan alpine lakes, DOC was also ancient (525–675 ybp), due to either inputs of pre-aged organics from glacier runoff, direct deposition, or due to the aging of organics in situ (i.e. a radiocarbon reservoir effect). The glacier ice and glacier stream sites exhibited high biolability of DOC and so provide a carbon subsidy to downstream environments that will change as glaciers on the Tibetan Plateau recede.

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1. INTRODUCTION

Glacier and alpine lake ecosystems represent two extremely sensitive environments to climate change and anthropogenic impacts such as inputs of dust and atmospheric

pollutants (Hodson et al., 2008; Mladenov et al., 2011; Stubbins et al., 2012). Alpine lakes are typically not directly impacted by anthropogenic processes, but receive atmospheric pollutants, dust and organic matter (OM) from aeolian deposition (Neff et al., 2008; Mladenov et al., 2009, 2011). Similarly, glaciers are often viewed as pristine environments but receive significant OM inputs from terrestrial and anthropogenic sources (Xu et al., 2009; Singer et al., 2012; Stubbins et al., 2012; Spencer et al., 2014). Autotrophic production of OM has also been reported in

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both glacier and alpine lake environments (Anesio et al., 2009; Miller et al., 2009; Stibal et al., 2012), and so these ecosystems can contain DOM from diverse sources. Recent studies have highlighted that DOM exported from glacial environments in Alaska, Svalbard and the European Alps can be extremely bioavailable and fuel subglacial (Hodson et al., 2005; Wynn et al., 2007) and pro-glacial food webs (Hood et al., 2009; Singer et al., 2012). Understanding the sources and biolability of DOM in glacial environments worldwide is critical for understanding how exported DOM impacts downstream ecosystems.

The Tibetan Plateau is the world's highest (average elevation > 4000 m) and largest plateau (~2,500,000 km²) and is relatively pristine due to limited direct anthropogenic impacts (Cong et al., 2013). However, regions around the Tibetan Plateau are growing sources of atmospheric pollution and black soot, leading to increased deposition on the Plateau (Xu et al., 2009; Cong et al., 2013). The Tibetan Plateau also holds the largest mass of ice on Earth outside the ice-sheets of Greenland and Antarctica (Yao et al., 2012). Tibetan glaciers have exhibited dramatic shrinkage in recent decades with models predicting many of the glaciers could be lost by 2050, increasing glacier runoff in the short-term, but reducing runoff in the long-term (Kehrwald et al., 2008; Li et al., 2008; Yao et al., 2012). The Tibetan Plateau also has an abundance of lakes covering an area of ~51,000 km² (Liu et al., 2009).

Previous studies have examined the sources and bulk DOM composition in both glacier and alpine lake ecosystems utilizing stable and radiocarbon isotope measurements ($\delta^{13}\text{C}$ -DOC, $\Delta^{14}\text{C}$ -DOC), and optical techniques such as fluorescence spectroscopy (Barker et al., 2009; Hood et al., 2009; Mladenov et al., 2009). In recent studies, ultrahigh-resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) has been used to examine DOM molecular composition in glacier ecosystems (Bhatia et al., 2010; Singer et al., 2012; Stubbins et al., 2012). The extreme mass accuracy and precision of FTICR-MS allows the determination of molecular formulae for thousands of DOM compounds, which is a major advance for the characterization of DOM and its molecular messages (Kujawinski, 2002; Mopper et al., 2007). This study examines the biolability, geochemical and isotopic signatures of DOM in glacier ice, glacier-fed stream, and alpine lake samples from the Tibetan Plateau to evaluate the sources of DOM and the potential for DOM to provide a carbon subsidy to receiving ecosystems downstream of glaciers and alpine lakes.

2. MATERIALS AND METHODS

2.1. Sample sites, collection, processing and bioincubations

Six sites were sampled on the Tibetan Plateau (Fig. 1; Table 1). These included, two glaciers, and their respective glacier-fed streams, plus two of the major lakes on the Tibetan Plateau. With a surface area of 1920 km² and a surface elevation of 4720 m, Namtso (Nam Co) Lake is the highest

lake on Earth with a surface area exceeding 500 km². Yamdrok (Yamzhog Yumco) Lake has a surface area of 638 km² at a surface elevation of 4440 m. Surface glacier ice samples were collected from the ablation zone about 100 m above the terminus of each glacier using a stainless-steel ice axe. All samples were collected in precleaned (acid and Milli-Q rinsed) high-density polyethylene plasticware and kept on ice and in the dark until return to the laboratory (<6 h), where they were thawed in the refrigerator (glacier ice). In the laboratory, all samples were filtered through precombusted (GF/F 0.7 μm) glass fiber filters to remove particulates. Samples for DOC concentration, absorbance at 254 nm, $\delta^{13}\text{C}$ -DOC, $\Delta^{14}\text{C}$ -DOC and FTICR-MS analyses were frozen and returned to the U.S.A. and Germany for analysis. To determine the bio-availability of DOC (BDOC), dark laboratory incubations in triplicate at 20 °C were started within 12 h of sample collection on the 0.7 μm filtered waters. These incubations lasted 28 days, at which point samples were acidified and subsequently analyzed for DOC (Hood et al., 2009; Fellman et al., 2010).

2.2. Dissolved organic carbon concentration and absorbance analyses

DOC concentrations were measured using a Shimadzu TOC-VCPH analyzer as described in Stubbins and Dittmar (2012). Aliquots of deep seawater reference material, Batch 10, Lot# 05-10, from the Consensus Reference Material Project (CRM) were analyzed to check the precision and accuracy of the DOC analyses. Analyses of the CRM deviated by less than 5% from the reported value for these standards (41–44 μM -DOC; <http://yyy.rsmas.miami.edu/groups/biogeochem/Table1.htm>). Routine minimum detection limits in the investigators laboratory are $2.8 \pm 0.3 \mu\text{M}$ -C and standard errors are typically 1.7 ± 0.5 of the DOC concentration (Stubbins and Dittmar, 2012). Absorbance at 254 nm was measured on a Shimadzu dual beam UV-1800 spectrophotometer and carbon-normalized specific ultraviolet absorbance at 254 nm (SUVA_{254}) values were derived by dividing the decadic absorption coefficient (a , m^{-1}) at $\lambda = 254 \text{ nm}$ by the DOC concentration (mg-C L^{-1}) and are reported in the units of liter per milligram carbon per meter (Weishaar et al., 2003).

2.3. Dissolved organic carbon stable and radiocarbon isotopic analyses

$\delta^{13}\text{C}$ -DOC samples were analyzed using an O.I. Analytical Model 1010 TOC analyzer interfaced to a PDZ Europa 20–20 IRMS (Sercon Ltd.) as described in previous studies (Spencer et al., 2009, 2012). Similarly, $\Delta^{14}\text{C}$ -DOC was measured as described previously (Raymond et al., 2007), in which, post inorganic carbon removal and UV-oxidation of DOC, the resultant CO_2 is transferred to a vacuum line and cryogenically purified. The purified CO_2 was analyzed for $\Delta^{14}\text{C}$ at the National Ocean Sciences Accelerator Mass Spectrometry Facility at the Woods Hole Oceanographic Institution (U.S.A.).

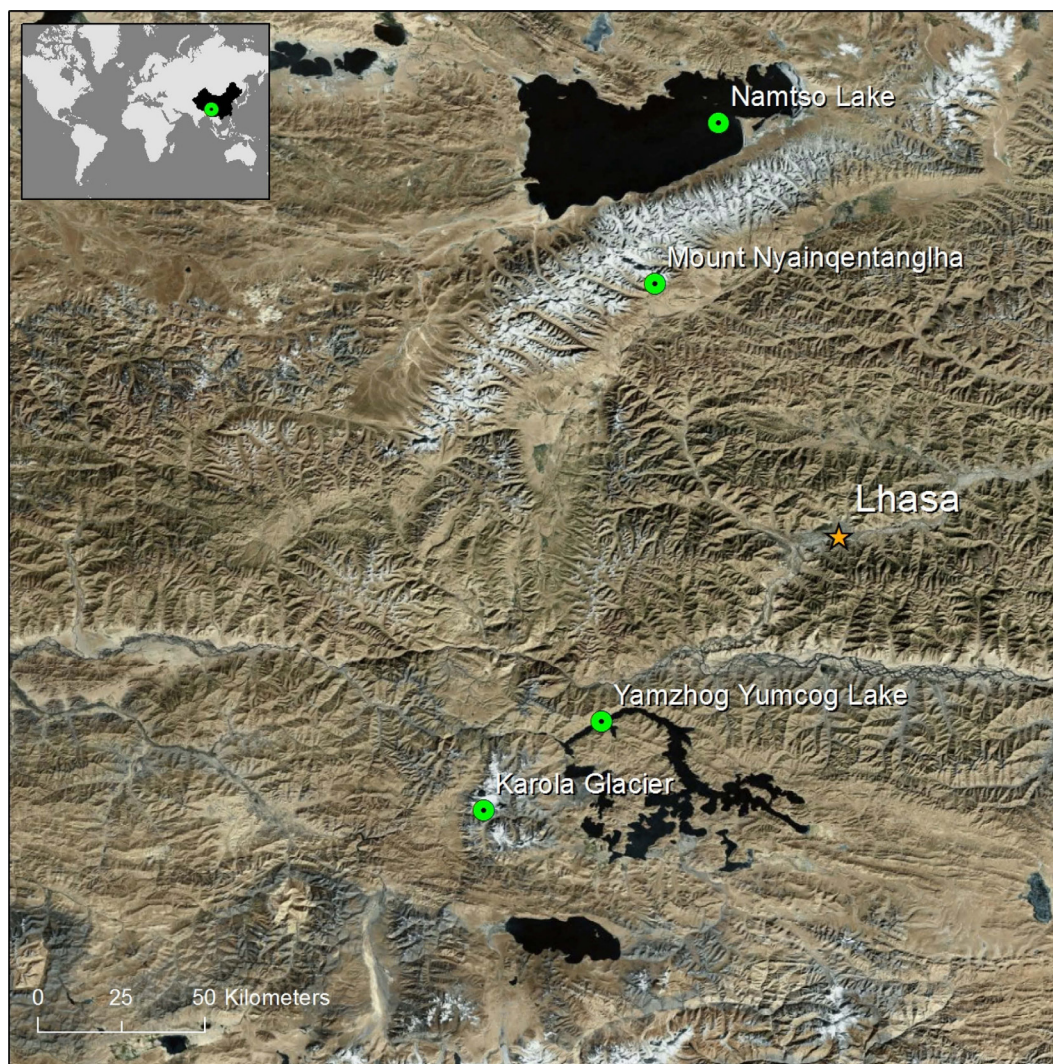


Fig. 1. Map of the study sites on the Tibetan Plateau. See [Table 1](#) for site names and details.

2.4. Fourier transform ion cyclotron resonance mass spectrometry and data analysis

Samples were solid phase extracted using PPL Bond Elut (Agilent) resins ([Dittmar et al., 2008](#)) before analysis by electrospray ionization FTICR-MS in negative ion mode. In brief, 40 mL samples were defrosted and acidified to pH 2 using reagent grade HCl (Carl Roth Germany, p.a. quality). 100 mg PPL columns were precleaned by passing 3 mL methanol (ULC-MS grade, Biosolve, The Netherlands), 3 mL of laboratory ultrapure water, and then 3 mL methanol through the columns, before sealing and soaking overnight full of methanol, and finally rinsing with 3 mL 0.01 M HCl, 3 mL methanol, and 3 mL 0.01 M HCl. In order to ensure a similar load of DOC was added to each PPL column, the volumes of sample loaded onto the columns were adjusted based upon initial DOC concentrations. Calculated volumes of acidified samples were passed through the cleaned PPL columns at a flow rate of $\sim 0.5 \text{ mL min}^{-1}$. Two 3 mL rinses with 0.01 M HCl washed away any inorganics before the PPL columns were dried under carbon free Argon gas (Air

Liquide Germany, 5.0 quality). Once dry, DOM was eluted from the columns with 3 mL of methanol. Due to low initial sample concentration and small available volume, the extraction efficiency of the procedure could not be determined. However, the extraction efficiency for DOM routinely obtained with this procedure is 60% (on a carbon basis; [Dittmar et al., 2008](#); [Green et al., 2014](#)). An ultrapure water sample was also loaded onto PPL, eluted and used as a procedural blank for extraction and FTICR-MS. The methanol extracts were diluted 1:1 with ultrapure water and analyzed in negative mode electrospray ionization using a 15 Tesla FTICR-MS (Bruker Solarix) at the University of Oldenburg, Germany. 500 broadband scans were accumulated for the mass spectra. After internal calibration, mass accuracies were within an error of $<0.2 \text{ ppm}$. Molecular formulae were assigned to peaks with signal to noise ratios greater than five based on published rules ([Koch et al., 2007](#); [Stubbins et al., 2010](#); [Singer et al., 2012](#)). Peaks detected in the procedural blank (PPL extracted ultrapure water) were removed. The full, non-standardized dataset is included to allow those interested in utilizing the data for comparison with their

Table 1

Glacier ice, glacier stream and alpine lake study site locations, DOC concentration, SUVA₂₅₄, $\delta^{13}\text{C}$ -DOC, $\Delta^{14}\text{C}$ -DOC and bioavailable DOC data.

Sample site	Altitude (m)	DOC (μM)	SUVA ₂₅₄ ($\text{L mg C}^{-1} \text{m}^{-1}$)	$\delta^{13}\text{C}$ -DOC (‰)	$\Delta^{14}\text{C}$ -DOC (‰)	^{14}C Age (ybp)	BDOC (%)
Mount Nyainqentanglha Glacier	5530	17.7	0.62	−23.9	−100.5	791	50
Karola Glacier	5370	27.9	0.57	−23.3	−95.7	749	46
Mount Nyainqentanglha Stream	5300	21.8	0.56	−23.3	−158.3	1325	61
Karola Glacier Stream	5250	22.6	0.59	−23.6	−259.2	2350	69
Namtso Lake	4720	260.2	0.67	−22.9	−70.2	525	23
Yamdruk Lake	4440	380.5	0.69	−22.4	−87.4	675	26

own results, using their own data work flow (Supplemental Table S1). Peak detection limits were standardized between samples by adjusting the dynamic range of each sample to that of the sample with the lowest dynamic range (dynamic range = average of the largest 20% of peaks divided by the signal to noise threshold intensity; standardized detection limit = average of largest 20% of peaks within a sample divided by the lowest dynamic range within the sample set). Peaks below the standardized detection limit were removed to prevent false negatives for the occurrence of a peak within samples with low dynamic range. Standardized peak intensities (z) within a sample were calculated following:

$$z = \frac{x - \mu}{\sigma} \quad (1)$$

where x is the measured peak intensity, μ is mean peak intensity within the sample, and σ is the standard deviation in peak intensity within the sample.

Assigned formulas were categorized by compound class based upon elemental stoichiometries (Santl-Temkiv et al., 2013). Modified aromaticity index (AI_{mod} ; Koch and Dittmar, 2006) values were calculated:

$$\text{AI}_{\text{mod}} = (1 + \text{C} - 0.5\text{O} - \text{S} - 0.5\text{H}) / (\text{C} - 0.5\text{O} - \text{S} - \text{N} - \text{P}) \quad (2)$$

AI_{mod} values 0.5–0.67 and >0.67 were assigned as aromatic and condensed aromatic structures, respectively (Koch and Dittmar, 2006). Further compound classes were defined as follows: Highly Unsaturated, Low Oxygen = $\text{AI}_{\text{mod}} < 0.5$, $\text{H/C} < 1.5$, $\text{O/C} < 0.5$; Highly Unsaturated, High Oxygen = $\text{AI}_{\text{mod}} < 0.5$, $\text{H/C} < 1.5$, $\text{O/C} 0.5\text{--}0.9$; Aliphatics = $\text{H/C} 1.5\text{--}2.0$, $\text{O/C} < 0.9$, $\text{N} = 0$; and; Peptide molecular formulae = $\text{H/C} 1.5\text{--}2.0$, $\text{O/C} < 0.9$ and $\text{N} > 0$. It should be noted that compounds identified as “peptides” have the molecular formulae of peptides, but their actual structure may differ.

3. RESULTS AND DISCUSSION

3.1. Tibetan Plateau glacier and alpine lake organic carbon concentration, age and biolability

Concentrations of DOC in the glacier ice and glacier-fed streams ranged from 17.7 to 27.9 μM (mean = 22.5 μM , $n = 4$; Table 1) which is comparable to values reported

from other glaciers and meltwater fed streams worldwide (Priscu et al., 1999; Barker et al., 2009; Hood et al., 2009; Bhatia et al., 2010; Singer et al., 2012). The radiocarbon ages of DOC for the Tibetan Plateau glacier sites (749–2350 ybp; Table 1) are comparable to the age of DOC reported in glacier ice and meltwaters from Alaska, Greenland and the European Alps (Hood et al., 2009; Singer et al., 2012; Stubbins et al., 2012; Bhatia et al., 2013; Spencer et al., 2014). The dominant source of DOM to glacier environments remains unclear, with in situ autotrophic production and atmospheric deposition being discussed as the main potential sources (Anesio et al., 2009; Singer et al., 2012; Stibal et al., 2012; Stubbins et al., 2012), and to a lesser extent subglacial organic matter stores (Zeng, 2003; Bhatia et al., 2013).

Concentrations of DOC in the two samples from lakes on the Tibetan Plateau are much higher than observed in the glacier samples (260.2 and 380.5 μM ; Table 1). The DOC from the two Tibetan alpine lakes was radiocarbon depleted (525 and 675 ybp), but was younger than for the glacier samples. As in glacier systems, DOM in alpine lakes can be produced in situ by autotrophs or derive from allochthonous sources such as deposition and terrestrial runoff (Mladenov et al., 2009, 2011). Furthermore, lakes on the Tibetan Plateau have been shown to have lake reservoir effects with respect to ^{14}C of dissolved inorganic carbon (DIC), typically ranging from a couple of hundreds years to a few thousands of years (Hou et al., 2012; Mischke et al., 2013). When radiocarbon depleted DIC in lake water is fixed during photosynthesis, the autochthonous organic matter formed entrains this ^{14}C signature and appears ancient, despite its contemporary source. Thus the apparent ages of lake DOC are difficult to interpret as they are potentially derived from a mixture of radiocarbon depleted DOM from contemporary primary production within the lake, from glacier runoff or direct deposition, plus radiocarbon replete DOM from autotrophs on land or at the lake surface that fix atmospheric CO_2 instead of lake DIC. Furthermore, the water residence times and turnover times of DOM within Tibetan lakes are poorly defined, thus it cannot be ruled out that a pool of refractory, autochthonous DOM has accumulated over time further complicating the use of DOC apparent age as a source indicator in these lakes.

All the Tibetan glacier and alpine lake samples contained relatively biolabile DOC in comparison to previous

studies of systems dominated by terrigenous inputs (typically <20% in comparable bioincubations; [Fellman et al., 2009](#); [Mann et al., 2012](#)). Glacier and glacier stream DOC (46–69% biolabile) was more biolabile than alpine lake DOC (23–26%; [Table 1](#)). The high biolability of glacier and glacier stream DOC is consistent with reports for glacier samples from Alaska and the European Alps ([Hood et al., 2009](#); [Singer et al., 2012](#)). The oldest (most ^{14}C depleted) Tibetan samples were also the most biolabile ([Fig. 2](#)) supporting findings in glacier environments from Alaska and the European Alps that also reported increasing DOC biolability with increasing radiocarbon age ([Hood et al., 2009](#); [Singer et al., 2012](#)). These results are interesting as they contradict the intuitive perception that young, freshly produced DOC will be the most biolabile fraction in fluvial networks. The biolability of lake DOC also suggests that its relatively old ages are not the result of long half-lives within the lakes, but are instead due to inputs of pre-aged DOC.

3.2. Tibetan Plateau glacier and alpine lake organic matter composition

SUVA₂₅₄ and $\delta^{13}\text{C}$ -DOC are routinely used to assess DOM sources in aquatic ecosystems. SUVA₂₅₄ values are often positively correlated to the percentage of aromatic compounds in DOM as measured by ^{13}C NMR ([Weishaar et al., 2003](#); [Stubbins et al., 2008](#)). Consistently, more depleted $\delta^{13}\text{C}$ -DOC values are typical of freshwaters dominated by inputs from vascular plants (ca. -27‰) versus autochthonously dominated waters (ca. -21‰ ; [Weishaar et al., 2003](#); [Fellman et al., 2010](#); [Spencer et al., 2012](#)). The low SUVA₂₅₄ and enriched $\delta^{13}\text{C}$ -DOC values of Tibetan glacier and glacier stream samples ([Table 1](#)) indicate limited terrestrial inputs, in agreement with data for DOM from Alaskan glacier environments ([Stubbins et al., 2012](#)), and/or the loss of terrestrial optical and isotopic sig-

natures during extensive sunlight-driven photo-degradation ([Spencer et al., 2009](#); [Osburn et al., 2011](#)). The limited difference between the SUVA₂₅₄ and $\delta^{13}\text{C}$ -DOC values of two glacier sites and their downstream glacier-fed streams ([Table 1](#)) suggest that similar processes control DOM composition in both glacier sites and that the glacier stream DOM can be accounted for simply by export from the glacier.

The SUVA₂₅₄ values for both lake samples are low and the $\delta^{13}\text{C}$ -DOC values are comparable to those reported for autochthonous DOC in lake ecosystems ([Table 1](#); [Osburn et al., 2011](#)), suggesting there is limited terrigenous DOM within the lakes. A further driver of the DOM signature in these alpine lakes is likely coupled evapoconcentration and photo-degradation ([Anderson and Stedmon, 2007](#); [Spencer et al., 2009](#); [Osburn et al., 2011](#)). Elevated DOC concentrations in lakes have been attributed to evapoconcentration, which would be expected to be extreme in the arid environment of the Tibetan Plateau. Exposure to high ultraviolet radiation doses at altitude is expected to photo-degrade DOM, bleaching out the colored fraction of the DOM pool, leading to near-colorless lakes (i.e. low SUVA₂₅₄). Photodegradation of DOM has also been shown to enrich $\delta^{13}\text{C}$ -DOC values ([Anderson and Stedmon, 2007](#); [Spencer et al., 2009](#); [Osburn et al., 2011](#)).

The molecular composition of Tibetan Plateau glacier and alpine lake DOM were determined on a molecular formula-level by FTICR-MS. Solid phase extracted samples for glacier and glacier stream DOM contained between 4351 and 4520 resolved molecular masses to which elemental formulas were assigned. Between 2301 and 2399 formulas were assigned to peaks detected within extracts of alpine lake DOM ([Table 2](#)). Cluster analysis of the standardized peak intensities of assigned formulas (Ward clustering in JMP®) allowing three clusters, indicated that the two alpine lake samples had the greatest molecular similarity (distance between clusters, $d = 57$; [Fig. 3](#)). The samples from Mount

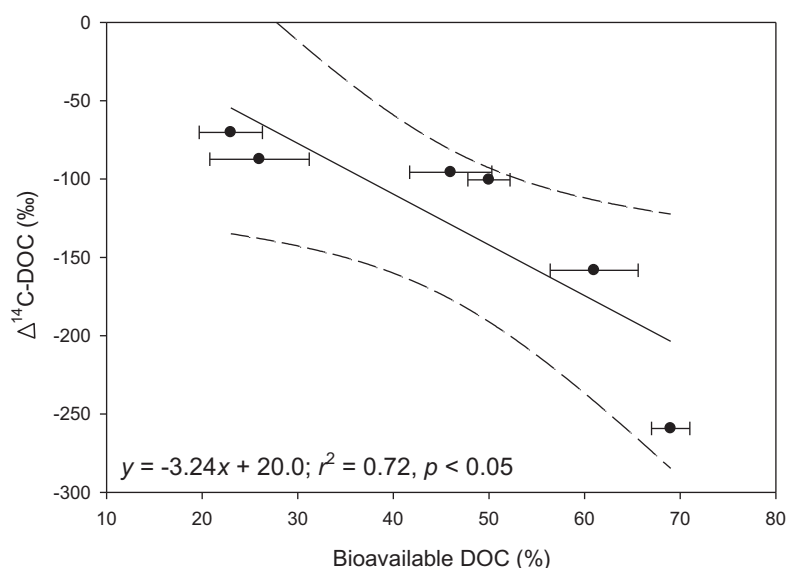


Fig. 2. Relationship between $\Delta^{14}\text{C}$ -DOC and bioavailable DOC for the glacier and alpine lake study sites. Whiskers on bioavailable DOC represent the range observed in triplicate bioincubations (black dot is the mean).

Table 2

The number of molecular formulas identified, the % containing the heteroatoms N, P, and S, and their average molecular weight as revealed by FTICR-MS for DOM samples isolated from the waters of the Tibetan Plateau.

Sample site	Formulas assigned	CHO-only (%)	Contains N (%)	Contains S (%)	Contains P (%)	Mean mass
Mount Nyainqentanglha Glacier	4399	1848 (42%)	2035 (46%)	371 (8%)	195 (4%)	390
Karola Glacier	4351	1761 (40%)	2078 (48%)	279 (6%)	289 (7%)	404
Mount Nyainqentanglha Stream	4416	1739 (39%)	2158 (49%)	363 (8%)	229 (5%)	398
Karola Glacier Stream	4520	1758 (39%)	2189 (48%)	402 (9%)	261 (6%)	395
Namtso Lake	2301	953 (41%)	997 (43%)	355 (15%)	40 (2%)	402
Yamdruk Lake	2399	972 (41%)	1032 (43%)	409 (17%)	42 (2%)	413

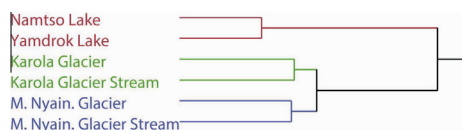


Fig. 3. Hierarchical cluster analysis of the standardized peak intensities of assigned formulas (Ward clustering in JMP®).

Nyainqentanglha Glacier and its runoff stream formed a second cluster ($d = 78$), with samples from Karola Glacier and the Karola Glacier stream forming the third cluster ($d = 80$; Fig. 3). If only two clusters were allowed for, then the lake samples were clustered separately from all the glacier and glacier stream samples ($d = 116$; Fig. 3). These results reveal that DOM within Namtso and Yamdruk Lake has similar molecular characteristics, and that these characteristics are distinct from DOM within glacier and glacier-fed stream samples. Such differences could arise from greater processing or additional inputs of DOM within the lake systems. Secondly, DOM within glacier streams bears the greatest similarity to the DOM within the ice of the glacier feeding the stream, suggesting minimal extra-glacial inputs and minimal processing or production of DOM within supra- or sub-glacial flow paths.

To visualize the qualitative differences between the samples, FTICR-MS data was plotted in van Krevelen space (H/C versus O/C) with points colored based upon relative peak intensity (Fig. 4a–f). Marked differences between the samples are evident. Most notably, alpine lake DOM peak intensities are elevated at high O/C (O/C 0.6–1.0; Fig. 4e and f), possibly indicating greater microbial and/or photochemical oxidation of lake DOM relative to glacier DOM. Peaks within Mount Nyainqentanglha Glacier and stream DOM spectra had low intensities at high H/C and high O/C (H/C > 1; O/C > 0.5) and higher intensities throughout the rest of van Krevelen space (Fig. 4a and c). Finally, peaks within DOM samples from Karola Glacier and stream had a few higher intensity peaks at low H/C, low O/C, as well as at higher H/C (Fig. 4b and d).

Examination of the elemental compositions and stoichiometries of peaks revealed further trends (Table 2). All samples contained similar percentages of CHO-only formulas (39–42%), were of similar average molecular mass (390–413 Da), and had similar percentages of highly unsaturated, low oxygen (32–34%) and aliphatic formulas (10–13%; Table 3; Fig. 5). Compared with marine and terrestrial DOM samples isolated using PPL (Dittmar and Paeng,

2009; Rossel et al., 2013; Osterholz et al., 2014), these Tibetan samples are low in CHO-only peaks, and consequently high in compounds containing N, P and/or S. Compared to the glacier samples analyzed here, the lakes contained lower percentages of N and P, and higher percentages of S containing formulas (Table 2). The lakes also contained lower percentages of peptide-molecular formulae DOM (Table 3). A lower number of N and P containing formulas, along with lower number of peptide-molecular formulae within the lakes is consistent with lake DOM being more biodegraded and less biolabile than glacier and glacier stream DOM. However, in terms of N and P content, the lake samples were still heavily enriched in N and P containing formulas compared to terrigenous and marine DOM (Dittmar and Paeng, 2009; Rossel et al., 2013; Osterholz et al., 2014).

Lake samples were enriched (42–44%) in highly unsaturated, high oxygen formulas, while glacier samples were modestly enriched in condensed aromatics relative to lake samples (Table 3; Fig. 5). These condensed aromatics are indicative of combustion derived DOM (dissolved black carbon, Koch and Dittmar, 2006) and have been identified in glacier samples from Alaska and the European Alps (Singer et al., 2012; Stubbins et al., 2012). As local fires are an unlikely source of black carbon to glaciers, the occurrence of dissolved and particulate black carbon within glacier waters and ice has been attributed to the atmospheric transport and subsequent deposition of charred organics from remote processes such as natural forest fires, anthropogenic biomass burning, and fossil fuel combustion (Xu et al., 2009; Stubbins et al., 2012). In addition to condensed aromatics, other aromatics are also more prevalent in Tibetan glacier and glacier stream DOM than in alpine lake DOM (Table 3; Fig. 5). Due to the ambiguities in assigning structure based upon molecular formulas, these formulas could be functionalized condensed aromatics, and therefore of a similar, combustion-derived source as the condensed aromatic/black carbon molecules (Singer et al., 2012; Stubbins et al., 2012). Alternatively, they could derive from depositional inputs of terrigenous organic matter and/or in situ production of aromatics. Low levels of both condensed aromatics and aromatics in lake DOM is consistent with the low carbon normalized color of these waters (SUVA₂₅₄; Table 3; Fig. 5) and is likely due to the limited inputs of terrigenous organics coupled with high rates of photochemical degradation in these UV-bathed, optically thin waters.

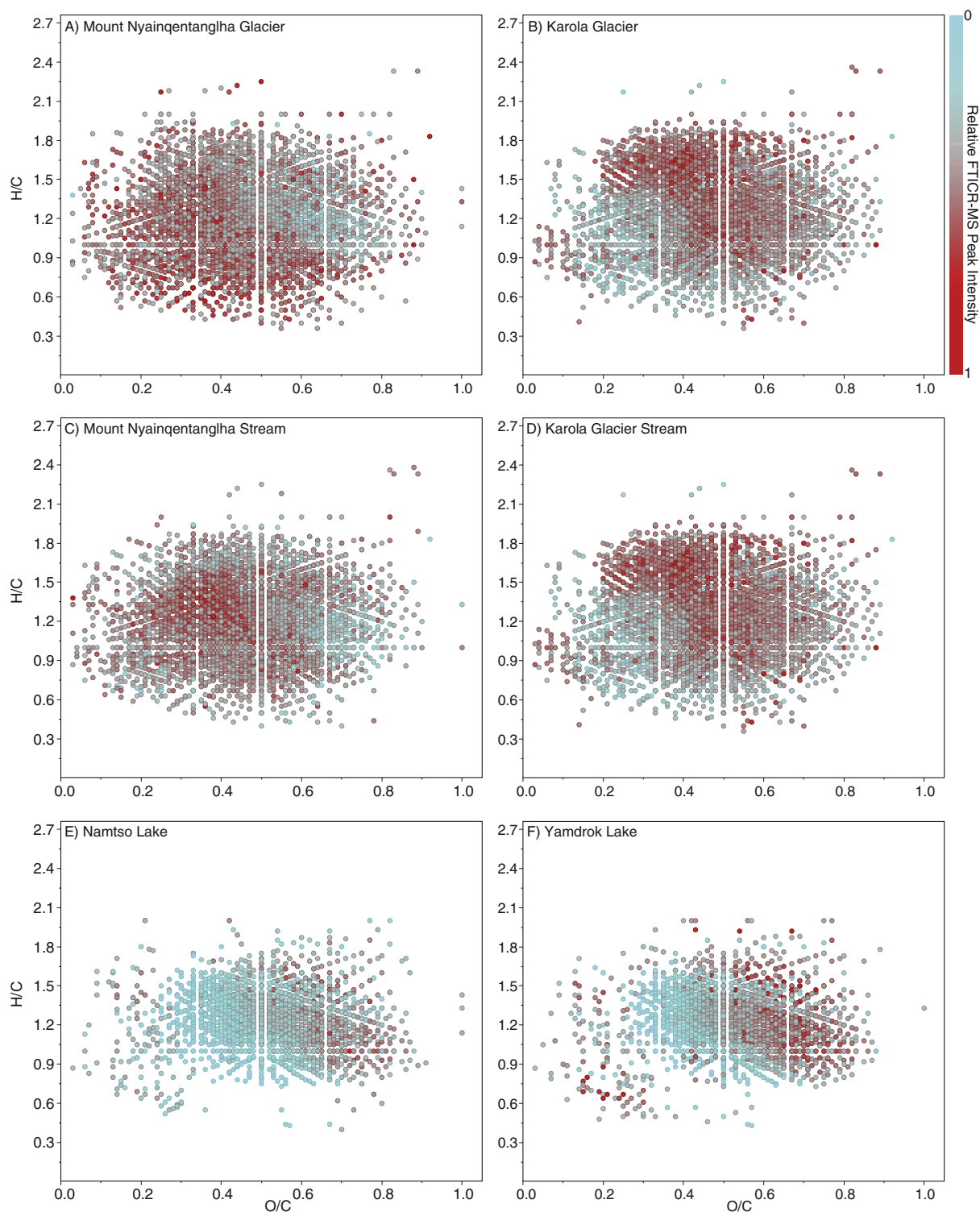


Fig. 4. van Krevelen diagrams of the distribution of DOM in samples from the Tibetan Plateau. See titles of each panel for sample ID and the legend for the color scaling. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.3. Evidence for a depositional source of organic matter on the Tibetan Plateau

In broad agreement with previous studies of glacier DOM from around the world (Hood et al., 2009; Singer

et al., 2012; Stubbins et al., 2012; Bhatia et al., 2013; Spencer et al., 2014), the Tibetan glacier and glacier stream DOM samples analyzed here were of similarly low DOC concentration, ancient age, low absorbance, high biolability, and similar molecular composition. In concert, these

Table 3

The number and % of molecular formulas assigned to each defined compound class as revealed by FTICR-MS for DOM samples isolated from the waters of the Tibetan Plateau.

Sample site	Condensed aromatics (%)	Polyphenols (%)	Highly unsaturated O/C < 0.5 (%)	Highly unsaturated O/C > 0.5 (%)	Aliphatics (%)	Peptides (%)
Mount Nyainqentanglha Glacier	158 (4%)	840 (19%)	1481 (34%)	991 (23%)	564 (13%)	348 (8%)
Karola Glacier	105 (2%)	680 (16%)	1414 (32%)	1035 (24%)	688 (16%)	420 (10%)
Mount Nyainqentanglha Stream	120 (3%)	799 (18%)	1560 (35%)	1023 (23%)	548 (12%)	353 (8%)
Karola Glacier Stream	122 (3%)	787 (17%)	1480 (33%)	1047 (23%)	639 (14%)	429 (9%)
Namtso Lake	27 (1%)	187 (8%)	790 (34%)	968 (42%)	243 (11%)	82 (4%)
Yamdruk Lake	34 (1%)	186 (8%)	809 (34%)	1049 (44%)	247 (10%)	73 (3%)

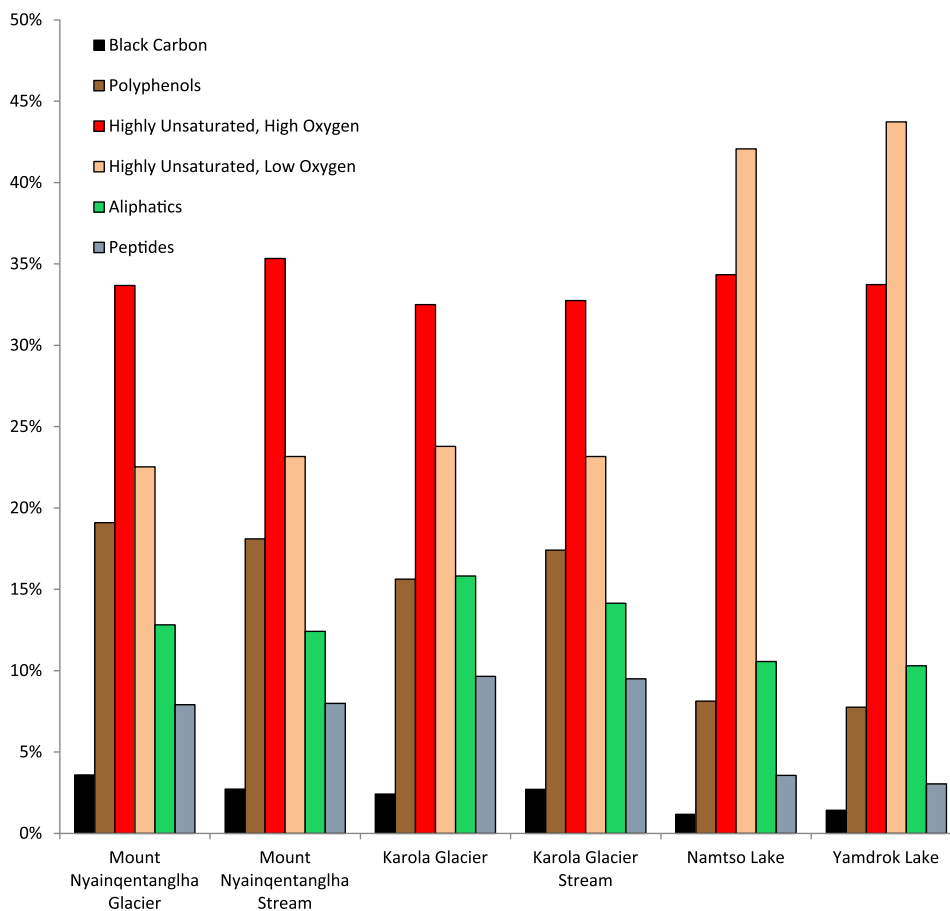


Fig. 5. Bar chart depicting the % of molecular formulas assigned to each defined compound class as revealed by FTICR-MS for DOM samples isolated from the waters of the Tibetan Plateau.

geochemical signatures are consistent with a depositional source of organics originally derived from combustion or possibly aged soil derived organics.

The measured radiocarbon ages in glacier DOC provide the strongest evidence as to the DOM source. The DOC ages equate to the average radiocarbon age of all carbon atoms comprising the DOM pool. Although this average age could represent the median sample age, this is not the case for aerosol organics, which are primarily derived from a mixture of modern biomass and fossil fuels (Gelencser et al., 2007; Jurado et al., 2008; Hodzic et al., 2010), the latter of which will be ^{14}C -dead (i.e. free of ^{14}C) due to the radioactive

decay of all ^{14}C during the millions of years that have elapsed since fossil fuel formation. Tibetan glacier DOM presumably derives from deposition and/or in situ production. Assuming DOM derives solely from pools of ^{14}C -dead (e.g. atmospheric fossil fuel derived) and modern (atmospheric biomass derived and in situ autochthony) carbon, the youngest DOM sample we analyzed from the glaciers and glacier streams (749 ybp) would comprise 91% modern carbon and 9% ^{14}C -dead carbon. For the oldest glacier sample (2350 ybp), 25% of the carbon atoms in the DOM sample would be ^{14}C -dead. Globally, much of the organic matter in aerosols is derived from anthropogenic activities,

with approximately 33% coming directly from industrial sources, 30% coming from biomass combustion and 37% from natural sources (Jurado et al., 2008). Assuming the industrial aerosol components are derived from fossil fuels and that all other organic aerosols are modern, then aerosol organic matter has an average apparent age of 3217 ybp (Stubbins et al., 2012). Direct measurements of the apparent age of rainwater DOM indicate that fossil fuels can contribute up to 66% of the DOM in rainwater, resulting in an apparent age of up to 8567 ybp (Raymond, 2005). Finally, average DOC concentrations in rainwater from marine and terrestrial environments are 21.5 μM and 151 μM , respectively (Willey et al., 2000). These examples demonstrate that both the concentrations and apparent ages of DOM in Tibetan glacier surface ice (Table 1) are compatible with a depositional organic matter source.

Further lines of evidence point to an anthropogenic source of the deposited, radiocarbon depleted glacier DOC. First, two alpine ice core studies report that organic carbon in modern (i.e. near surface) glacier ice is radiocarbon depleted due to fossil fuel inputs, whereas organic carbon in preindustrial ice appeared younger (radiocarbon enriched) as preindustrial DOC was derived from biogenic carbon (e.g. vegetation) fixed and then deposited to glacier surfaces at the time the ice was formed (Jenk et al., 2006; Steier et al., 2006). Secondly, previous studies analyzing ice cores from Tibetan mountain glaciers similar to those glaciers studied here, report that the concentrations of elemental carbon (i.e. combustion-derived graphitic carbon) and total organic carbon correlate with one another (Xu et al., 2009). In turn, both black and organic carbon correlate with decadal patterns in anthropogenic combustion emissions (Xu et al., 2009), providing further evidence that deposited anthropogenic aerosols are the main source of organics to these remote glacier environments.

Although there are multiple lines of evidence suggesting anthropogenic, fossil fuel derived organics are deposited in both glacier and alpine lake ecosystems, the percentage of DOM derived from autochthony versus atmospheric inputs cannot be determined based upon the data available. The most radiocarbon depleted sample analyzed in this study could contain $\sim 25\%$ radiocarbon-dead, fossil carbon. Thus, up to 25% of this sample could have come from fossil fuel combustion. If deposited organics were $\sim 33\%$ fossil fuel derived C, with the rest from anthropogenic combustion of biomass, natural forest fires and other natural sources (Jurado et al., 2008), then $\sim 76\%$ of the total organics on the glacier would be deposition derived with the remainder being made up by in situ production. This value should be regarded as highly uncertain because without knowing the radiocarbon age of organics in wet and dry deposition to the Tibetan plateau it is impossible to determine what percentage of total organics are likely derived from deposition based upon DOM radiocarbon signatures in glacier, glacier stream, and alpine lake DOM. Additionally it is unknown whether subglacial organic matter stores could be contributing fossil DOC (Zeng, 2003; Bhatia et al., 2013) at these sites. Therefore, future work is needed to better constrain the relative importance of depositional, in situ and subglacial DOM sources.

What is apparent is that glacier environments appear to be receiving a windfall of biolabile, anthropogenic organics that are having an unknown influence upon the biogeochemical cycles of glaciers, alpine lakes, and downstream environments. Furthermore, the deposition of pre-aged DOC to the glacier surface provides an insight into anthropogenic perturbation of the carbon cycle as it shows the influence of fossil fuel combustion products in what is typically viewed as an extremely pristine environment. The impact of these anthropogenic combustion products seems unlikely to be restricted solely to glacier environments and wet deposition of DOC originating from fossil fuels has been suggested to be a significant flux globally (Jurado et al., 2008; Yan and Kim, 2012). As DOC exported from Tibetan glaciers as well as other glacier environments has been shown to be highly biologically labile (Hood et al., 2009; Singer et al., 2012) this deposited DOM of anthropogenic origin may have ramifications for perturbation of the base of the food web in a wide range of environments.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.gca.2014.08.006>.

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