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Key Points:

- Glacier dissolved organic matter is diverse but with an underlying compositional uniformity suggesting universal controls on composition
- Composition appears driven by the relative balance of in situ production versus atmospheric deposition derived organic matter
- Glacier dissolved organic matter composition is predictable by region and linked to source

Supporting Information:

Supporting Information may be found in the online version of this article.

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Gradients of Deposition and In Situ Production Drive Global Glacier Organic Matter Composition

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Abstract Runoff from rapidly melting mountain glaciers is a dominant source of riverine organic carbon in many high-latitude and high-elevation regions. Glacier dissolved organic carbon is highly bioavailable, and its composition likely reflects internal (e.g., autotrophic production) and external (i.e., atmospheric deposition) sources. However, the balance of these sources across Earth's glaciers is poorly understood, despite implications for the mineralization and assimilation of glacier organic carbon within recipient ecosystems. We assessed the molecular-level composition of dissolved organic matter from 136 mountain glacier outflows from 11 regions covering six continents using ultrahigh resolution 21 T mass spectrometry. We found substantial diversity in organic matter composition with coherent and predictable (80% accuracy) regional patterns. Employing stable and radiocarbon isotopic analyses, we demonstrate that these patterns are inherently linked to atmospheric deposition and in situ production. In remote regions like Greenland and New Zealand, the glacier organic matter pool appears to be dominated by in situ production. However, downwind of industrial centers (e.g., Alaska and Nepal), fossil fuel combustion byproducts likely underpin organic matter composition, resulting in older and more aromatic material being exported downstream. These findings highlight that the glacier carbon cycle is spatially distinct, with ramifications for predicting the dynamics and fate of glacier organic carbon concurrent with continued retreat and anthropogenic perturbation.

Plain Language Summary The controls on glacier organic matter composition globally remain poorly constrained, despite the importance of this material for downstream carbon cycling, and freshwater and marine ecosystems. We present the first systematic global analysis of glacier dissolved organic matter and demonstrate that its composition is largely determined by the relative balance of organic material derived from in situ production versus atmospheric deposition. As a result, globally, glaciers can be considered a diverse organic matter pool, exporting regionally distinct material to recipient ecosystems. Glaciers relatively dominated by atmospheric-derived organics export older and more stable material with ramifications for the fate of glacier-derived carbon in recipient ecosystems. Ultimately, this work highlights glaciers globally as having a dynamic role in carbon cycling.

1. Introduction

Globally, mountain glaciers are disappearing at accelerated rates (Rounce et al., 2023) with cascading impacts on downstream ecosystems (Milner et al., 2017). Yet, our understanding of the carbon cycle in this vulnerable biome remains incomplete. Glacier runoff provides ancient, aliphatic-rich (i.e., energy-rich) and bioavailable dissolved organic matter (DOM) to downstream ecosystems (Hood et al., 2009; Kellerman et al., 2021; Lawson et al., 2014; Singer et al., 2012; Spencer, Guo, et al., 2014), which can be assimilated into proglacial food webs (Arimitsu et al., 2018; Fellman, Hood, Raymond, Hudson, et al., 2015; Hågvar & Ohlson, 2013). Thus, glacier-derived DOM may act as a carbon subsidy to freshwater and marine ecosystems, the respiration of which can also fuel carbon dioxide outgassing to the atmosphere (Hood et al., 2009; Singer et al., 2012). Despite the importance of DOM for aquatic food webs and its fundamental role in the global carbon cycle (Arimitsu et al., 2018; Battin et al., 2009; Fellman, Hood, Raymond, Hudson, et al., 2015; Hågvar & Ohlson, 2013; Hood et al., 2009), the sources of organic matter (OM) underpinning glacier carbon cycling and DOM export are uncertain (Bhatia et al., 2013; Hood et al., 2009; Lawson et al., 2014; Musilova et al., 2017; Singer et al., 2012; Stubbins

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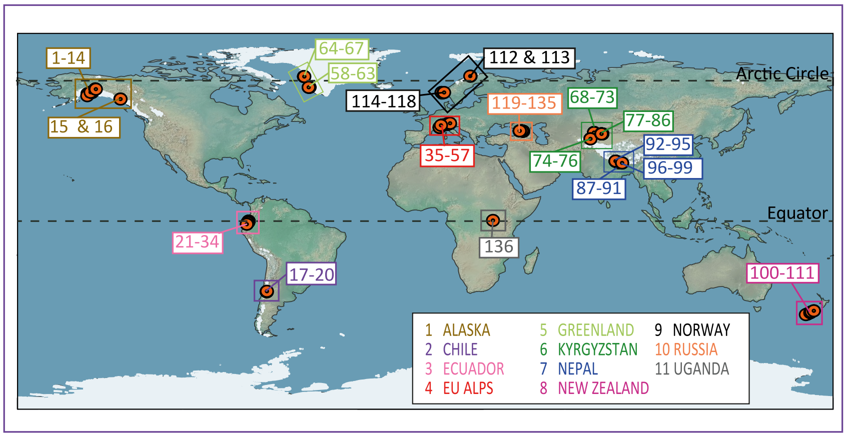

Figure 1. Location of glacier outflow sample sites. Boxes are colored to represent the sample regions. Regions are ordered alphabetically, and samples are numbered from 1 to 136.

et al., 2012). Specifically, it is unclear how the sources and composition of glacier DOM vary globally, and what the drivers of that spatial variability may be.

Glacier DOM has been postulated to be derived from external, allochthonous sources, namely anthropogenic aerosols (i.e., fossil fuel combustion byproducts) and the deposition of soil and plant-derived material (including biomass burning byproducts), as well as internal, autochthonous sources from microbial processes and leached subglacial OM (Antony et al., 2014; Bhatia et al., 2013; Hood et al., 2009; Lawson et al., 2014; Musilova et al., 2017; Singer et al., 2012; Stubbins et al., 2012). Variability in the relative contribution of these sources may impact the age of glacier dissolved organic carbon (DOC) as well as DOM composition and thus its fate in recipient ecosystems (Fellman, Hood, Raymond, Stubbins, & Spencer, 2015; Kellerman et al., 2020; Spencer, Vermilyea, et al., 2014). Furthermore, identifying the fraction of glacier OM derived from anthropogenic sources elucidates the extent of human impacts on carbon cycling in glacier ecosystems, with implications for the global carbon cycle (Spencer, Guo, et al., 2014; Stubbins et al., 2012).

In this study, we present the first systematic global assessment of glacier outflow DOM composition. We use ultrahigh resolution 21 T Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to characterize molecular-level DOM composition across 136 glacier outflow rivers spanning six continents (Figure 1). We draw on carbon isotopic analyses (δ^{13}C-DOC and Δ^{14}C-DOC) from a subset of outflows ($n = 16$) to constrain global relationships between molecular-level DOM composition and organic carbon (OC) source and processing. We characterize the global diversity in glacier DOM and explore the degree to which spatial variability in OM sources across glacierized regions produces distinct regional DOM compositions in glacier outflows. Ultimately, this study provides insights into the diversity of OM sources in glacier ecosystems as well as the extent to which carbon cycle processes are analogous across this biome.

2. Materials and Methods

2.1. Study Sites, Sample Collection and Processing

Water samples were collected from 136 glacier outflow rivers across 11 glacierized regions between 2019 and 2022 (Figure 1). Sampling of the high-latitude (winter accumulation type) glaciers was conducted between spring and fall, and typically during the months of peak melt (e.g., Alaskan catchments sampled in June–July, and New Zealand glaciers January–March; Table S1 in Supporting Information S1). Year-round ablation type glaciers in the tropics, which have a relatively stable seasonal hydrograph (Benn & Evans, 2014; Gualco et al., 2022; Taylor et al., 2006), were sampled in February (Ecuador) and March (Uganda). Summer accumulation type glaciers in Nepal, which experience monsoonal precipitation simultaneous with maximum ablation (Benn & Evans, 2014), were sampled during March and May. Each sampling campaign lasted a period of days to weeks, with each glacier sampled once (Table S1 in Supporting Information S1). Thus, the DOM composition observed reflects only the sample period and does not examine temporal variability that could occur at a site or within a region (e.g., Kellerman et al., 2020; Lawson et al., 2014; Spencer, Vermilyea, et al., 2014). At each glacier, samples were collected as close to the terminus as possible (median 73 m, range 0–3,300 m) to prevent instream processing of glacier-derived DOM and to avoid overprinting of glacier DOM by lateral inputs of OM (e.g., from soils or vegetation).

All glacier outflow streamwater samples were immediately filtered using ashed (5 hr, 450°C) GF/F filters (0.7 µm) or trace metal grade Geotech Polyethersulfone dispos-a-filter™ capsules (0.45 µm). Samples for FT-ICR MS were solid phase extracted (SPE; Dittmar et al., 2008). In brief, Bond Elut 100 mg (3 mL) PPL cartridges were conditioned sequentially with HPLC grade MeOH, Milli-Q, MeOH and pH 2 Milli-Q (10 M HCl; Dittmar et al., 2008). The PPL cartridges were stored capped until extraction. In the field, 500–1,000 mL of filtrate was acidified to pH 2 (10 M HCl) and extracted onto PPL cartridges. Following extraction, PPL cartridges were rinsed with two cartridge volumes of pH 2 Milli-Q (10 M HCl), and stored in the dark at 4°C (Dittmar et al., 2008). Samples for DOC and carbon isotopic analyses were stored frozen (−20°C) in either acid-washed (10% HCl v/v) and combusted glass vials (5 hr, 550°C) or acid-washed polycarbonate bottles.

2.2. Organic Carbon Quantification and Isotopic Analyses

For glacier outflows 15, 16, 21–34, 38 and 39 (Figure 1), DOC concentrations were measured on a Shimadzu TOC-$L_{CPH/CPN}$ analyzer following standard methods (Kellerman et al., 2021; Stubbins & Dittmar, 2012). All remaining samples were measured on a GE Sievers M9 TOC analyzer (Boix Canadell et al., 2021). Concentrations were calculated based on replicate measurements with a coefficient of variance <2%. For a subset of glacier outflows ($n = 16$; Table S1 in Supporting Information S1) 1 L of filtered and acidified (pH 2, 10 M HCl) sample was analyzed for δ^{13}C-DOC and Δ^{14}C-DOC. In brief, DOC was UV-oxidized and evolved CO_2 purified, trapped cryogenically, and analyzed for ^{14}C at the National Ocean Sciences Accelerator Mass Spectrometry Facility at Woods Hole Oceanographic Institution, USA (Roberts et al., 2010; Xu et al., 2021, 2022). A split of CO_2 was measured for ^{13}C on a stable isotope ratio mass spectrometer (Xu et al., 2021).

2.3. Ultrahigh Resolution Mass Spectrometry

Field extracted PPL cartridges were dried with a flow of ultrahigh purity nitrogen gas and then eluted with HPLC grade MeOH into 2 or 4 mL (5 hr, 550°C) combusted glass vials. The volume of MeOH used for each elution was adjusted dependent on extraction volume and the DOC concentration of the sample to achieve a target eluent concentration of 50 µg C mL^{-1}. The SPE extracts were stored at −20°C until analysis.

Extracts were analyzed in negative mode electrospray ionization (typical conditions for ion formation were emitter voltage: −2.8–3.2 kV; S-lens RF level: 45%; heated metal capillary temperature: 350°C) using a custom-built hybrid linear ion trap/FT-ICR MS equipped with a 21 T superconducting solenoid magnet (Hendrickson et al., 2015; Smith et al., 2018). Time-domain transients of 3.1 s were conditionally co-added (100 scans) within the Predator data station prior to phase-correction with absorption-mode time domain processing to improve resolving power up to 30% (Xian et al., 2010). Each mass spectra was internally calibrated with a "walking" calibration using 10–15 abundant homologous series that spanned the molecular weight distribution (Savory et al., 2011). Peaks with signals greater than the root mean square baseline noise plus 6σ were exported to a peak list, and elemental compositions assigned between 170 and 1,200 Da in PetroOrg© (Corilo, 2014) within the bounds $C_{1\text{-}100}H_{4\text{-}200}O_{1\text{-}30}N_{0\text{-}4}S_{0\text{-}2}$.

Each molecular formula was prescribed to compound and heteroatom classes according to their neutral elemental composition. Formulae that contained only carbon, hydrogen and oxygen were classed as CHO-only and where heteroatoms of nitrogen and/or sulfur were assigned, formulae were classed as CHON, CHOS or CHONS. For each neutral elemental composition, the nominal oxidation state of carbon (NOSC), double bond equivalents (DBE), and modified aromaticity index (AI_{mod}) were calculated (Koch & Dittmar, 2006, 2016; Riedel et al., 2012). Based on AI_{mod} and elemental ratios (H/C and O/C), formulae were categorized into five operational compound classes: polyphenolic and condensed aromatics (AI_{mod} values of 0.5–0.67 and >0.67, respectively), highly unsaturated and phenolic (HUP; AI_{mod} of <0.5 and $H/C < 1.5$), aliphatic ($H/C \geq 1.5$, $O/C \leq 0.9$; Spencer, Guo, et al., 2014) and N-containing aliphatic ($H/C \geq 1.5$, $O/C \leq 0.9$ and $N > 0$). The relative abundance (RA) of each assigned formula was calculated as the contribution of its peak as a fraction of the total intensity of all assigned peaks in a sample, scaled to 10,000. Additionally, the percent RA of formulae in each sample belonging to the island of stability (IOS) was calculated (based on the IOS peak list; Lechtenfeld et al., 2014). The Core Glacier Signature was determined as the formulae present in all 136 glacier outflow samples. Within this core, it

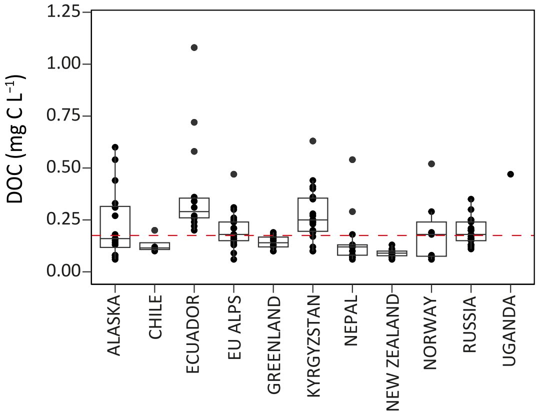

Figure 2. Concentrations of DOC separated by region. Black dots represent individual observations and red dashed line represents the global median.

was determined whether formulae overlapped with those in the IOS (based on peak list; Lechtenfeld et al., 2014) and Core Arctic Riverine Fingerprint (based on peak list; Behnke et al., 2021) or whether they were in the region of van Krevelen space attributed to carboxylic-rich alicyclic molecules (limits: DBE/C = 0.30–0.68; DBE/H = 0.20–0.95; and DBE/O = 0.77–1.75; Hertkorn et al., 2006).

2.4. Statistical Analysis

All data analysis was conducted in R (version 2022.12.0 + 353), and figures were made using base R and ggplot2 (Wickham, 2016). Rarefaction analysis was calculated using the Vegan R package and considered all assigned peaks across the data set (Dixon, 2003). Principal component (PC) analysis was conducted to assess variability in molecular-level glacier outflow DOM composition across glacierized regions. PC analysis was produced using the Factomine R package, and considered RA weighted FT-ICR MS metrics and DOC concentrations (Tables S1, S2 and S3 in Supporting Information S1; Lê et al., 2008). For the subset of samples where Δ^{14}C-DOC was available, Spearman's Rank correlations were calculated between radiocarbon age and the RA of individual molecular formulae using base R and the “cor.test” function. This was performed to assess the molecular assemblages of the DOM pool associated with contemporary and ancient OM sources. Only formulae that were significantly correlated (p-value <0.05) and present in ≥3 samples are discussed. A linear discriminant (LD) analysis was conducted to assess if variability in DOM composition across glacierized regions was sufficient to lead to distinct regional signatures. The LD analysis considered the same metrics as PC analysis and was conducted using the MASS R package (Table S4 in Supporting Information S1; Ripley et al., 2013). Both PC and LD analyses were conducted since the former maximizes variability explained within the data set and thus is most appropriate for assessing gradients in molecular-level composition, whereas the latter maximizes separation between groups, allowing for a robust assessment of the regional classification of outflow samples based on DOM composition.

3. Results and Discussion

3.1. The Diverse Composition of Glacier Outflow Organic Matter

Across the globe, glacier outflow DOC concentrations were consistently low (0.06–1.08 mg C L^{-1}; Table S1 in Supporting Information S1, Figure 2) and DOM was compositionally distinct compared to non-glacial riverine systems. At the molecular-level, glacier outflow DOM exhibited a high RA of aliphatic (median 28.8%), N-containing aliphatic (median 4.5%) and heteroatom-containing molecular formulae (combined CHON, CHOS, CHONS median 33.8%), compared to non-glacial rivers (e.g., aliphatics typically <10% RA; Table S2 in Supporting Information S1, Figure 3, Figure S1 in Supporting Information S1; Behnke et al., 2021; Kellerman et al., 2021). This is consistent with OM primarily derived from in situ microbial production either on or beneath the glacier and degraded atmospheric depositional sources (e.g., including OM from soils, and anthropogenic and biomass combustion; Antony et al., 2018; Bhatia et al., 2010; Holt et al., 2021; Kellerman et al., 2021; Lawson et al., 2014; Musilova et al., 2017; Stubbins et al., 2012). Furthermore, glacier outflow DOM had a low RA of polyphenolic and condensed aromatic compounds (combined median 3.0%), compared to non-glacial rivers (median 22.4% RA; Table S2 in Supporting Information S1, Figure 3; Kellerman et al., 2021). This suggests, at the time of sampling, there was limited direct inputs of unprocessed OM from vegetation and soils, which are typically rich in aromatic and polyphenolic moieties, for example, wind-blown proglacial soils, and leached subglacial or lateral inputs of OM, which have been shown to be elevated in low flow periods (Holt et al., 2021; Kellerman et al., 2020; Spencer, Vermilyea, et al., 2014; Stubbins et al., 2012). The pervasive low aromaticity and aliphatic-enriched properties of glacier outflow DOM are consistent with previous studies characterizing DOM across regional glacier ecosystems (Bhatia et al., 2010; Kellerman et al., 2021; Lawson et al., 2014; Singer et al., 2012; Stubbins et al., 2012) and may suggest broad similarity between glacier outflows in molecular-level composition.

Despite this ostensible homogeneity in character, we demonstrate that glacier outflow DOM is actually a highly diverse OM pool. For example, the RA of aliphatic, N-containing aliphatic, and heteroatom-containing compounds ranged between 8.6%–71.5%, 0%–23.5%, and 15.4%–82.1%, respectively (Table S2 in Supporting

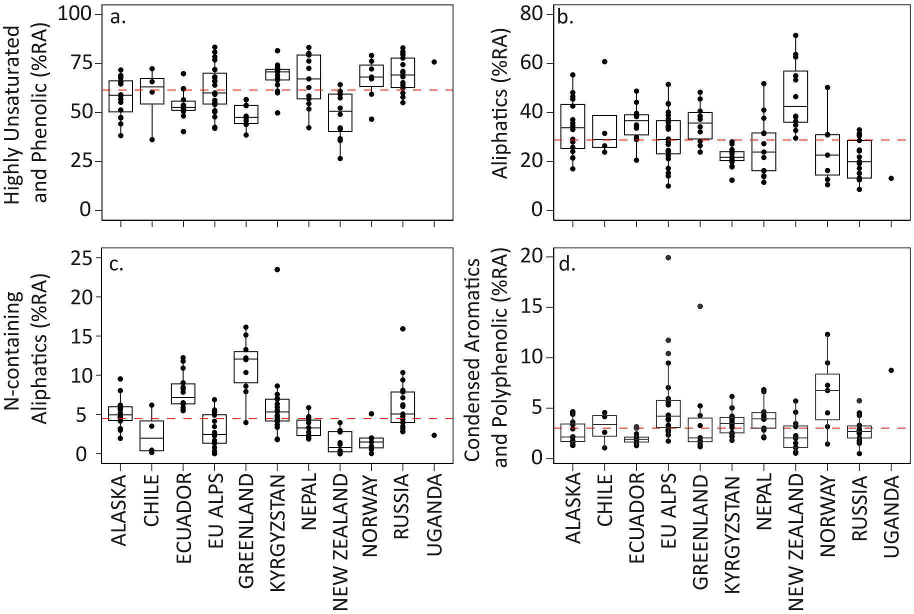

Figure 3. Global distribution of glacier outflow DOM composition. Boxplots show the percent relative abundance (% RA) of (a) highly unsaturated and phenolic, (b) aliphatic, (c) N-containing aliphatic, and (d) condensed aromatic and phenolic formulae, respectively, across study regions. Red dashed lines represent the global median value for each compound class and black dots represent individual observations.

Information S1, Figure 3, Figure S1 in Supporting Information S1). Furthermore, we document >35,000 unique molecular formulae globally, and rarefaction analysis showed that with each additional glacier outflow, new formulae were identified (Figure 4a). The remarkable molecular diversity of glacier DOM can be contrasted with molecular assessments of DOM from Swedish lakes using 15 T FT-ICR MS, which demonstrated saturation at 70 out of 120 lakes (~7,000 formulae), despite encompassing a comparatively broad environmental gradient in climate and hydrology as well as substantial variability in compositional drivers such as wetland, forest, and agricultural extent (Kellerman et al., 2014). Specifically, the higher molecular richness we observed for glacier DOM was partly due to the global nature of this study as well as potentially the increased molecular-level resolution of 21 T FT-ICR MS (Smith et al., 2018). Nevertheless, the high molecular diversity and richness highlights significant variability in the sources and processing of DOM across mountain glaciers, despite the extreme and relatively homogenous biophysical conditions of glacier ecosystems (Hodson et al., 2008).

Furthermore, globally, there was a narrow underlying compositional uniformity between outflows, demonstrating that glacier DOM is composed of a highly heterogenous pool of OC compounds. There were 341 molecular formulae shared across all glacier outflows globally (Figure 4b), and these core formulae made up 9.8%–42.9% of RA. Formulae within this Core Glacier Signature are generally pervasive and persistent across environments, since they overlap heavily with formulae found in either the six largest Arctic rivers (Core Arctic Riverine Fingerprint; CARF; Behnke et al., 2021), the oceanic Island of Stability (IOS; Lechtenfeld et al., 2014), or the region of van Krevelen space attributed to stable carboxylic-rich alicyclic molecules (CRAM; Figure 4b; Hertkorn et al., 2006). Similar to the bulk composition of glacier DOM, the Core Glacier Signature was also characterized as low in aromaticity as evidenced by a higher mean H/C ratio (1.35), and a lower mean modified aromaticity index (AI_{mod}; 0.21) than both IOS and CARF (H/C 1.17 and 1.14, and AI_{mod} 0.27 and 0.33, respectively; Behnke et al., 2021; Lechtenfeld et al., 2014). This Core Glacier Signature, linked to chemical stability, suggests underlying similarity in the sources and processes shaping molecular-level glacier outflow DOM composition globally, in spite of its apparent global diversity.

3.2. Deposition and Production Drive Organic Matter Composition

The global heterogeneity in molecular-level glacier outflow DOM composition was primarily (45% of DOM variance) associated with a gradient in relative aromatic and aliphatic content (Figure 5a; Table S3 in Supporting Information S1). This gradient was demonstrated in principal component (PC) space, where glacier outflows

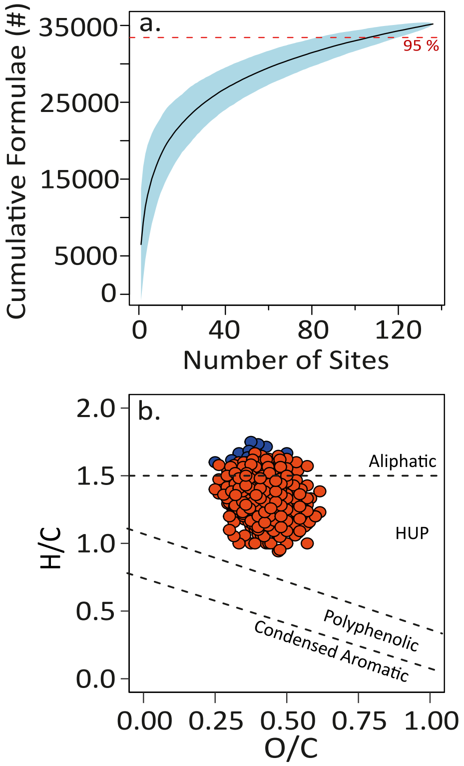

Figure 4. The molecular diversity and core signature of global glacier organic matter. (a) Cumulative number of assigned formulae with each added outflow. Blue shading represents the confidence interval calculated over 1,000 permutations. Red dashed line indicates 95% of the total number (35,191) of assigned formulae. (b) Formulae assigned in all glacier outflows (Core Glacier Signature) plotted in van Krevelen space. Formulae are colored according to whether they overlap with the Island of Stability or Core Arctic Riverine Fingerprint or fall within the region of van Krevelen space attributed to carboxylic-rich alicyclic molecules (red) or fall outside these previously described parameters (blue). Dashed lines represent approximate location of compound classes. HUP, Highly unsaturated and phenolic.

positioned at positive values of PC1 had relatively higher H/C ratios, aliphatic, and sulfur content; whereas those positioned at negative values contained relatively more aromatic DOM (i.e., higher AI$_{\text{mod}}$ values, and an increased RA of highly unsaturated and phenolic, and condensed aromatic and polyphenolic compounds) that was more stable (i.e., higher nominal oxidation state of carbon, O/C ratios, and % RA of IOS formulae; Figures 5a and 5b; Kellerman et al., 2018; McDonough et al., 2022). The global heterogeneity in glacier outflow DOM composition may be driven by shifts in the balance of OM sourced from in situ microbial production (e.g., in cryoconite holes, by ice algae or beneath the glacier) versus atmospheric deposition (a mix of OM, including that derived from soil, and biomass burning and fossil fuel combustion byproducts) across glacier catchments, or variability in the degree of processing (i.e., bio- or photodegradation) with respect to these source endmembers.

To evaluate whether shifts in DOM source versus degradation processes were the primary driver of composition, we investigated a subset of outflows where carbon isotopes (δ^{13}C-DOC and Δ^{14}C-DOC) were measured in addition to molecular-level DOM composition. Glacier outflow δ^{13}C-DOC and Δ^{14}C-DOC ranged from −28.0 to −20.5‰ and −896.9 to −114.5‰ (18,200–910 yBP), respectively (Table S1 in Supporting Information S1), consistent with previously reported isotopic signatures of glacier DOC (Andrews et al., 2018; Csank et al., 2019; Fellman, Hood, Raymond, Stubbins, & Spencer, 2015; Holding et al., 2017; Hood et al., 2009). Both δ^{13}C-DOC and Δ^{14}C-DOC were significantly positively correlated with the position of glacier outflows on PC1 (Figures 5c and 5d). As no change in Δ^{14}C-DOC is expected as a result of degradation of source endmembers, the variability in glacier outflow DOM composition was primarily driven by a shifting balance of DOC sourced from young and ^{13}C enriched versus aged and ^{13}C deplete OC. Specifically, in aliphatic-enriched glacier outflows there was likely greater relative contributions of OC from young, ^{13}C enriched and lower aromaticity OM sources, such as from in situ microbial production and atmospheric deposition of C4 plant material including combustion byproducts (Figures 5a–5d; Bird et al., 2015; Budhavant et al., 2023; Fan et al., 2016; Liu et al., 2020; Schmidt et al., 2022; Tang et al., 2020). Although the δ^{13}C signature of in situ production sources on glacier surfaces are currently unknown, our most ^{13}C enriched glacier outflows are comparable to the isotopic signature of sea ice algae (−21 to −16‰) and broadly cyanobacteria (−16 to −6‰; Figure 5c; Hobson & Welch, 1992; McMahon et al., 2006; Schmidt et al., 2022). Furthermore, cryoconite sediment OC concentrations are shown to increase with ^{13}C, leading to the suggestion that relatively greater inputs from autotrophy over deposition on the glacier surface result in ^{13}C enriched OC values (Schmidt et al., 2022). This is consistent with the most ^{13}C, ^{14}C and aliphatic-enriched glacier outflows studied here containing the highest relative contributions of OM from in situ production (e.g., via ice algae or cyanobacteria). Conversely, the more aromatic-enriched outflow DOM likely contained increasing contributions of OM from atmospheric deposition (e.g., including soil-derived OM, and biomass burning and fossil fuel combustion byproducts), with the most aged, ^{13}C depleted, and aromatic signatures likely derived from fossil fuel combustion sources (Figures 5a–5d; Budhavant et al., 2023; Liu et al., 2020; Tang et al., 2020). Nonetheless, photodegradation processes may still play a role in modulating the DOM composition observed across glacier outflows. Photodegradation is known to relatively increase the nitrogen content of DOM and significantly reduce DOM aromaticity (Antony et al., 2018; Holt et al., 2021). This gradient was observed along PC2 (23% of global DOM variability), which ranged from high aromaticity (positive PC2 position) to enrichment in N-containing aliphatics (negative PC2 position), and thus may reflect the extent of photodegradation in the intense ultraviolet radiation on glacier surfaces (Figures 5a and 5b).

The primary gradient in DOM composition and the dichotomy between DOM sourced from in situ production versus aged atmospheric deposition were reflected beyond bulk compositional metrics. The RA of individual

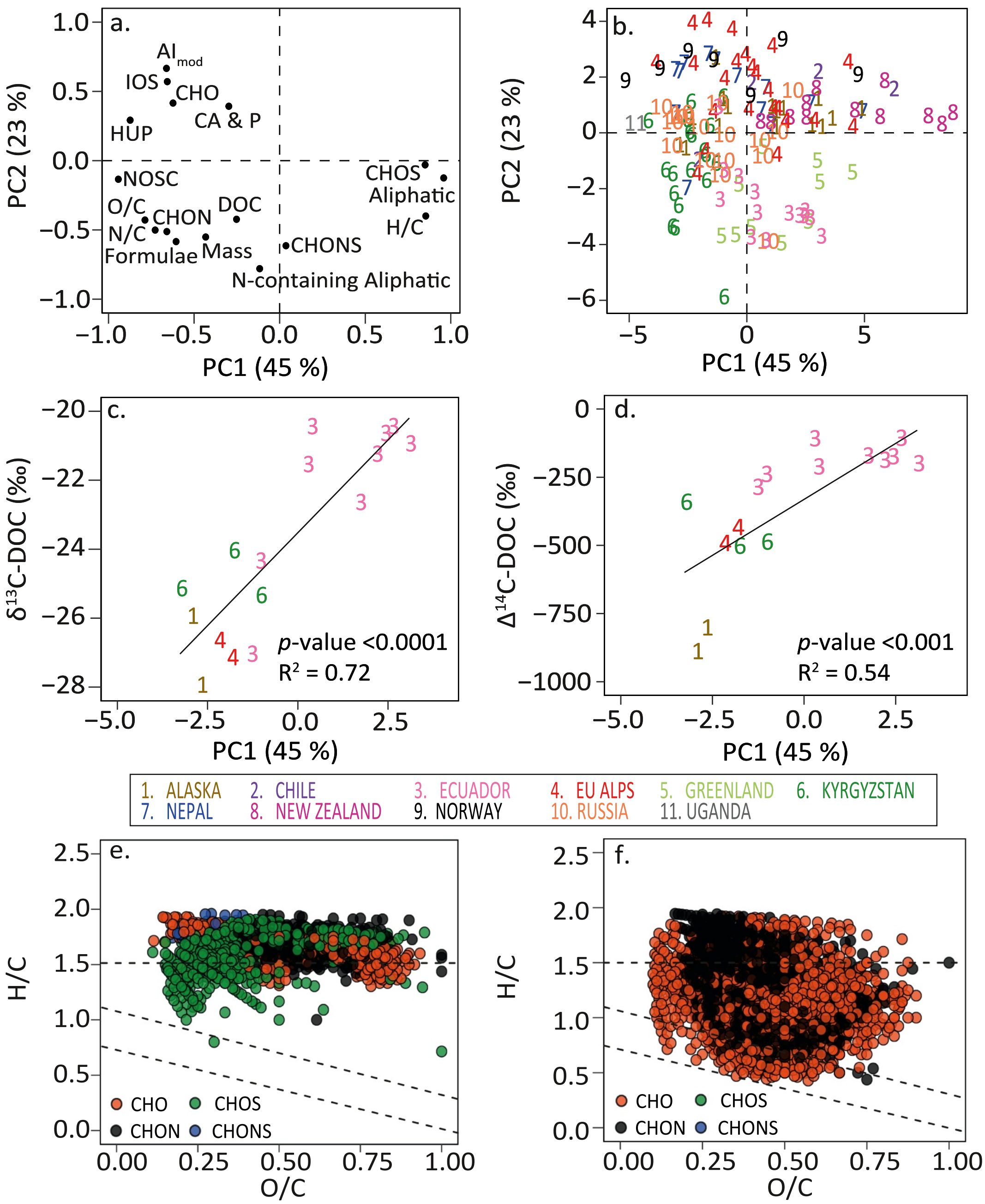

Figure 5. Drivers of global glacier DOM composition. Principal component (PC) analysis of glacier outflow molecular-level composition. (a) Loading plot and (b) scores plot of glacier outflows. (c and d) Linear regressions of PC1 position of samples against carbon isotopes of DOC. (b–d) Samples are numbered and colored by sample region. (e and f) Spearman's Rank correlation between the relative abundance of individual molecular formulae and Δ^{14}C-DOC. Formulae are plotted in van Krevelen space and separated by the direction of correlation: formulae (e) positively and (f) negatively correlated with Δ^{14}C-DOC. Individual formulae are colored by heteroatom class. Dashed lines represent approximate location of compound classes (see Figure 4b). HUP, Highly unsaturated and phenolic; CA and P, condensed aromatic and polyphenolic; NOSC, nominal oxidation state of carbon; AI_{mod} modified aromaticity index.

molecular formulae positively correlated with Δ^{14}C-DOC (i.e., younger) were aliphatic-enriched and heteroatom diverse, and thus likely biolabile (Figure 5e; D'Andrilli et al., 2015). However, the aged DOM pool was more aromatic (Figure 5f). These contemporary and aged molecular signatures have similar elemental ratios to in situ-derived DOM and photodegraded depositional sources (e.g., soil-derived OM, and biomass burning and anthropogenic combustion byproducts), respectively (Figures 5e and 5f; Holt et al., 2021; Liu et al., 2020).

Table 1
Confusion Matrix for Linear Discriminant Analysis, Showing Percentage of Observation Classified Into Each Region and Overall Accuracy of the Model

		Predicted group membership (%)										
Group	*n*	Alaska	Chile	Ecuador	EU alps	Greenland	Kyrgyzstan	Nepal	New Zealand	Norway	Russia	Uganda
Alaska	16	81	0	0	6	0	0	13	0	0	0	0
Chile	4	0	50	0	25	0	25	0	0	0	0	0
Ecuador	14	0	0	86	0	0	0	0	0	0	14	0
EU Alps	23	4	4	0	78	0	4	4	0	4	0	0
Greenland	10	0	0	0	0	80	0	0	20	0	0	0
Kyrgyzstan	19	0	0	0	5	0	84	11	0	0	0	0
Nepal	13	8	0	0	0	0	8	85	0	0	0	0
New Zealand	12	0	0	0	8	0	0	0	92	0	0	0
Norway	7	0	0	0	57	0	0	0	0	43	0	0
Russia	17	0	0	6	0	6	6	0	0	0	82	0
Uganda	1	0	0	0	0	0	0	0	0	0	0	100
Overall Accuracy: 80												

Overall, the relative contribution of atmospheric deposition versus in situ production across glacier outflows not only has a considerable effect on the age of DOC in glacier runoff, but also imparts a substantial and consistent effect on bulk DOM composition and the individual molecular formulae exported to downstream ecosystems. Thus, the dominant OM source may determine the age of DOC respired by aquatic microbial communities and the fate of glacier DOM in downstream ecosystems.

3.3. Global Variability in Glacier Organic Matter

Glacier DOM composition varied across regions, with glacier outflow DOM in Alaska, the European Alps, Kyrgyzstan, Nepal, and Norway more aromatic than that in Ecuador, Greenland, and New Zealand (Figure 5b). Although glacier outflow DOM composition is likely to have a temporal dimension (e.g., due to drainage evolution and mobilization of ancient subglacial sources, or shifts in the magnitude and source of production and deposition; Kellerman et al., 2020; Lawson et al., 2014; Li et al., 2018; Musilova et al., 2017; Spencer, Vermilyea, et al., 2014), the observed broad regional patterns suggested substantial geographic differences in the relative contributions of OM from atmospheric deposition versus in situ production across the globe. To assess if variability in DOM compositional metrics could be used to classify the DOM in glacier outflows by region, we employed a linear discriminant (LD) analysis (Table 1, Table S4 in Supporting Information S1, Figure 6). The regional origin of DOM was successfully predicted in 80% of glacier outflows (Table 1), demonstrating that DOM source and composition varied significantly between regions (Figure 6). Regions with a higher degree of molecular-level compositional similarity (e.g., Norway with European Alps, and Russia with Ecuador) or relatively broad regional gradients in composition (e.g., European Alps) were more difficult to correctly classify (range of correct predictions 43%–100%; Table 1, Figure 6). This highlighted some underlying regional variability in DOM composition as well as commonality in glacier DOM sources across geographically disparate regions.

The regionally distinct glacier outflow DOM compositions appear to in part reflect proximity to sources of anthropogenic emissions. Glacier outflows in Alaska, the European Alps, Kyrgyzstan, Nepal, and Norway are typically distinct from one another (Table 1, Figure 6). Nonetheless, they are all relatively aromatic, and thus likely have relatively higher contributions of OM derived from atmospheric deposition, particularly of fossil fuel combustion byproducts, over in situ production compared to glaciers in Ecuador, Greenland, New Zealand, and Russia (Figure 6). Glaciers in the European Alps, Kyrgyzstan, Nepal, and Norway lie in, or are close to, industrialized centers, while glaciers in Alaska receive anthropogenic pollution from local sources and via long range atmospheric transport from heavily industrialized Asia (Nagorski et al., 2014; Yu et al., 2012), consistent with the aromatic-enriched composition of DOM in these glacier outflows. In contrast, glaciers in Ecuador, Greenland, New Zealand, and Russia likely have a lower relative proportion of glacier DOM derived from anthropogenic sources (Figure 6). This is consistent with atmospheric deposition in Greenland, the tropical Andes, and New

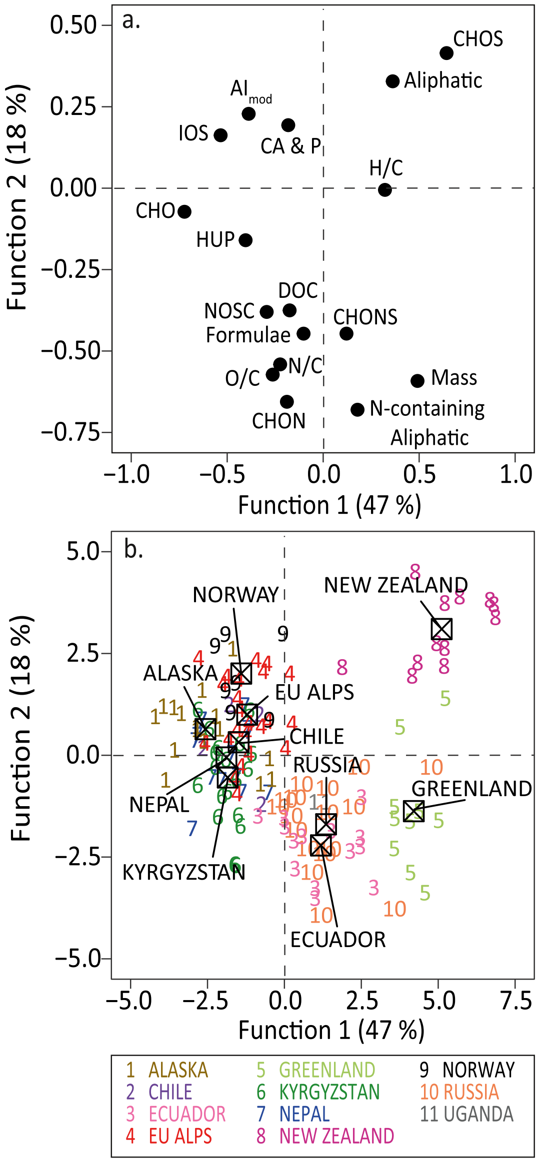

Figure 6. Regionally distinct glacier DOM. Linear discriminant (LD) analysis based on relative abundance weighted molecular-level DOM metrics and DOC concentration, (a) loading plot of function 1 and 2, (b) scores plot for LD analysis showing separation of glacier outflows. (b) Individual samples are numbered and colored according to their region, and labeled black squares represent group centroids (i.e., mean position of each region in function 1 and 2 space). HUP, Highly unsaturated and phenolic; CA and P, condensed aromatic and polyphenolic; NOSC, nominal oxidation state of carbon; AI_{mod} modified aromaticity index.

Zealand, having been linked to contemporary biomass combustion sources (Bonilla et al., 2023; Khan et al., 2017; Koch & Hansen, 2005; Pu et al., 2021). Additionally, the Greenland Ice Sheet has been shown to be darkening due to algal production on the ice surface (Halbach et al., 2023). Therefore, the aliphatic-enriched molecular properties of glacier outflow DOM in Greenland, Ecuador, New Zealand, and Russia are likely due to atmospheric deposition derived predominantly from biomass burning byproducts, and, importantly, reflect greater relative contributions of OM from in situ microbial production over atmospheric deposition. Past studies in different glacierized regions have proposed a singular or dominant source of glacier DOM (Bhatia et al., 2010, 2013; Lawson et al., 2014; Musilova et al., 2017; Singer et al., 2012; Spencer, Guo, et al., 2014; Stubbins et al., 2012). For example, studies in Greenland have suggested that glacier DOM is predominantly microbial in origin (Lawson et al., 2014; Musilova et al., 2017), whereas studies in Alaska have suggested that a substantial component of glacier DOM is derived from deposition, particularly of fossil fuel combustion byproducts (Stubbins et al., 2012). Our global data set demonstrates a clear gradient between in situ production and atmospheric depositional sources, resulting in regionally distinct glacier DOM exported to downstream and marine ecosystems. Therefore, this work reconciles past studies offering competing explanations of a singular dominant OM source in glacier environments.

Our findings show that glacier outflow DOM has an underlying compositional uniformity and is comprised of a high RA of aliphatic, and typically bioavailable compounds (D'Andrilli et al., 2015). Thus, glacier ecosystems represent a distinct, and highly reactive, OC pool in the global carbon cycle (Hood et al., 2009, 2015; Kellerman et al., 2021). Nonetheless, we report substantial global diversity in glacier outflow DOM, with discrete regional molecular-level compositions. We show that global variability in the relative contribution of OC from in situ production and aged atmospheric deposition has concomitant effects on both the age and composition of DOC exported to downstream ecosystems. Glacier DOC likely derived predominantly from atmospheric deposition, particularly of fossil fuel combustion byproducts (e.g., in Nepal and Alaska), is older and aromatic-enriched, and thus likely less biolabile, compared to that derived mainly from in situ production (e.g., in Greenland and New Zealand). Ultimately, this global variability in OC source and DOM composition has implications for predicting changes in the dynamics of glacier DOC fluxes with continued melt. Particularly, it highlights the age of OC respired and the fate of glacier DOC subsidies may vary across glacier-fed freshwater and marine ecosystems. Through this work, we have identified regions (i.e., Nepal and Alaska, vs. Greenland and New Zealand) that are dominated by either in situ production or atmospheric deposition and suggest them as useful for constraining the diversity of impacts to mountain glacier ecosystems and downstream carbon cycling with unabated glacier retreat. Fundamentally, the geographic and molecular-level diversity reported here for global glacier outflows underscores the dynamic role this biome, which until recent decades was merely thought to be a passive, abiotic component of the Earth system (Wadham et al., 2019), plays in the storage, cycling and release of OC.

Global Research Statement

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Data Availability Statement

Raw FT-ICR MS spectra files, calibrated peak lists, and assigned elemental compositions are publicly available through the Open Science Framework (OSF; Holt et al., 2023).

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