

Anthropogenic aerosols as a source of ancient dissolved organic matter in glaciers

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Glacier-derived dissolved organic matter represents a quantitatively significant source of ancient, yet highly bioavailable carbon to downstream ecosystems¹. This finding runs counter to logical perceptions of age-reactivity relationships, in which the least reactive material withstands degradation the longest and is therefore the oldest². The remnants of ancient peatlands and forests overrun by glaciers have been invoked as the source of this organic matter^{1,3,4}. Here, we examine the radiocarbon age and chemical composition of dissolved organic matter in snow, glacier surface water, ice and glacier outflow samples from Alaska to determine the origin of the organic matter. Low levels of compounds derived from vascular plants indicate that the organic matter does not originate from forests or peatlands. Instead, we show that the organic matter on the surface of the glaciers is radiocarbon depleted, consistent with an anthropogenic aerosol source. Fluorescence spectrophotometry measurements reveal the presence of protein-like compounds of microbial or aerosol origin. In addition, ultrahigh-resolution mass spectrometry measurements document the presence of combustion products found in anthropogenic aerosols. Based on the presence of these compounds, we suggest that aerosols derived from fossil fuel burning are a source of pre-aged organic matter to glacier surfaces. Furthermore, we show that the molecular signature of the organic matter is conserved in snow, glacier water and outflow, suggesting that the anthropogenic carbon is exported relatively unchanged in glacier outflows.

Glaciers and ice sheets combined represent the second largest reservoir of water in the global hydrologic system and glacier ecosystems cover 10% of the Earth, yet the carbon dynamics underpinning these ecosystems remain poorly understood⁵. Increased understanding of glacier biogeochemistry is a priority, as glacier environments are among the most sensitive to climate warming and industrial forcing.

Anthropogenic combustion products are the main sources of the aerosol organic carbon deposited on glacier surfaces and a driver of glacier recession⁶. However, the biogeochemical role and fate of this aerosol carbon once deposited to glacier ecosystems has not been addressed. Here we demonstrate that anthropogenic aerosol organic matter (OM) is the main source of fossil dissolved organic matter (DOM) in glacier waters and

runoff. As such, anthropogenic activities are amplifying the export of DOM from glaciers by increasing glacier water discharge through global warming and the load of fossil OM delivered to glaciers through deposition.

In this study, we characterized DOM in samples from the recently deposited snowpack (<1 year since deposition; one sample 25 May 2010), supra-glacial aquatic environments (one sample 10 Aug 2009; six samples 25 May 2010), and the outflow of Mendenhall Glacier (two samples 10 Aug 2009; one sample 25 May 2010) in southeast Alaska, USA. A further sample was collected from the outflow of Herbert Glacier, southeast Alaska (10 Aug 2009). Peterson Creek, a nearby temperate rainforest watershed that exports DOM derived predominantly from forest and wetland soils, was sampled as a non-glacier endmember (10 Aug 2009). As well as measuring bulk dissolved organic carbon (DOC), ultraviolet-visible absorbance, fluorescence, and the vascular plant biomarker lignin, we employed Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) on non-fractionated samples to develop molecular fingerprints for the different DOM samples. Finally, radiocarbon ($\Delta^{14}\text{C}$) measurements were used to constrain the fossil contributions to DOM collected from three geographically diverse glaciers, ranging from Wyoming to central Alaska. The resultant optical, molecular and radiocarbon signatures were used to determine the source of glacier DOM.

Concentrations of DOC were 0.19 mg-C l^{-1} in the Mendenhall Glacier snowpack (one sample), $0.32 \pm 0.01 \text{ mg-C l}^{-1}$ in Mendenhall supra-glacial waters (seven locations), $0.38 \pm 0.02 \text{ mg-C l}^{-1}$ in the Mendenhall Glacier outflow (two samples), and 0.28 mg-C l^{-1} in the outflow of Herbert Glacier (one sample; Table 1; see Supplementary Table S1 for the complete dataset). These values are consistent with DOC concentrations reported for glacier waters globally^{1,4,7,8}. It is informative to consider that although supra-glacial samples were collected from cryoconite holes, small supra-glacial streams (<1 m wide) and large supra-glacial streams (>1 m wide), DOC concentrations did not vary significantly (Table 1; data for each sample site are presented in Supplementary Table S1). Similar DOC concentrations for supra-glacial and glacier outflow waters indicate that the entire exported DOC load from Mendenhall Glacier could be accounted for by transport of DOC from supra-glacial environments, although future work is required to determine if this is indeed the case.

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Table 1 | Concentrations and quality indicators for dissolved organic matter samples from Mendenhall Glacier, Herbert Glacier and the forested Peterson Creek.

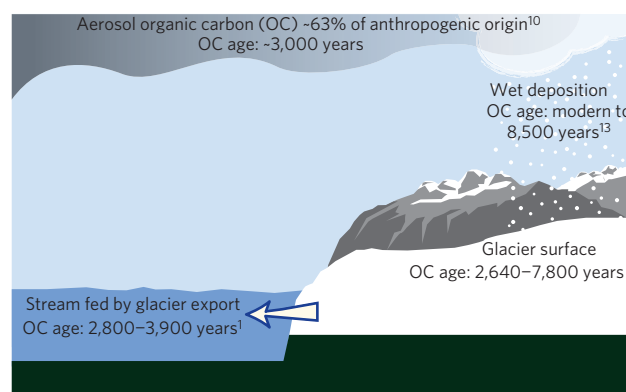
Sample (number of samples)	DOC (mg L ⁻¹)	Protein-like fluorescence (%)	SUVA ₂₅₄ (L mg C ⁻¹ m ⁻¹)	Λ ₈ (mg (100 mg-C) ⁻¹)
Mendenhall snowpack (1)	0.19	84	1.01	No data
Mendenhall supra-glacial (7)	0.32 ± 0.01	88 ± 1	0.57 ± 0.02	0.09 (n = 1)
Mendenhall outflow (2)	0.38 ± 0.02	88 ± 0	0.64 ± 0.16	0.10 (n = 1)
Herbert outflow (1)	0.28	90	0.76	0.09
Peterson creek (1)	3.37	2	4.62	0.67

Standard deviations are provided when multiple samples were analysed for the same environment and represent sample variation rather than analytical error.

Two indicators related to terrestrial DOM inputs—carbon-normalized lignin (Λ₈) and specific ultraviolet absorbance (SUVA₂₅₄)—revealed glacier samples to be uniformly low in vascular plant-derived DOM (Table 1). In contrast, Peterson Creek DOM was enriched in these indicators of terrestrial inputs (Table 1), consistent with organic-rich rivers receiving their DOM inputs from higher plant and soil sources^{8,9}. The lack of terrestrial signatures (Table 1) in glacier waters precludes the possibility that glacier DOM is formed from ancient vascular plant material at the base of the glacier.

The radiocarbon ages and concentrations of DOC in a cryoconite pool on Mendenhall Glacier (7,800 yr BP; 0.32 mg-C l⁻¹), in surface ice from Gulkana Glacier in Alaska (5,570 yr BP; 0.38 mg-C l⁻¹) and in surface ice from Fremont Glacier in Wyoming (2,640 yr BP; 1.02 mg-C l⁻¹) indicated that isotopically old DOM is being added to the upper surfaces of glaciers across a range of latitudes (43° N–63° N) that encompass the vast majority of glacier ice in western North America. These measured 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 OM, which is primarily derived from a mixture of modern biomass and fossil fuels^{10–12}, the latter of which will be ‘¹⁴C-dead’ owing to the radioactive decay of all ¹⁴C during the millions of years that have elapsed since fossil fuel formation. Assuming glacier DOM also derives solely from pools of ¹⁴C-dead and modern carbon, the youngest DOM sample we analysed from the glacier surfaces (2,640 yr BP) would comprise 72% modern carbon and 28% fossil carbon; whereas, 62% of the carbon atoms in the cryoconite DOM sample (7,800 yr BP) would be derived from fossil fuels. Globally, much of the OM in aerosols is derived from anthropogenic activities, with approximately 33% coming directly from industrial sources, 30% coming from biomass combustion and 37% from natural sources¹⁰. Assuming the industrial aerosol components are derived from fossil fuels and that all other organic aerosols are modern, then aerosol OM would have an average apparent age of 3,217 yr BP. 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 8,567 yr BP (ref. 13). Finally, average DOC concentrations in rainwater from marine and terrestrial environments are 0.26 mg-C l⁻¹ and 1.83 mg-C l⁻¹, respectively¹⁴. These examples demonstrate that both the concentrations and apparent ages of DOC on glacier surfaces (0.32–1.02 mg-C l⁻¹; 2,640–7,800 yr BP) and in glacier runoff (0.28–0.38 mg-C l⁻¹ (Table 1); 2800–3900 yr BP; ref. 1) are compatible with a depositional OM source (Fig. 1).

To further characterize glacier ecosystem DOM, samples were analysed by means of fluorescence spectrophotometry and electrospray ionization coupled to FTICR-MS. The high contribution of protein-like fluorescence to the fluorescence spectra of snowpack and glacier DOM (Table 1) was indicative of a labile fluorescent DOM pool dominated by protein-like compounds of microbial¹⁵ or aerosol¹⁶ origin. Annual ice velocity on Mendenhall Glacier averages ~70 m yr⁻¹ (ref. 17), thus the ice residence time

**Figure 1 | The glacier organic carbon cycle, including apparent radiocarbon ages associated with the organic carbon fluxes.**

over the 22 km glacier is approximately 300 years. This timeframe is too short for exported fossil DOC (2,800–3,900 yr BP; ref. 1) to have originated from past microbial production on the surface of the glacier, leaving deposition as the more likely source.

The ultra-high resolution and mass accuracy of FTICR-MS allowed the assignment of exact molecular weights and formulae to thousands of individual organic molecules¹⁸, providing a fingerprint that contains information concerning the source and history of the glacier DOM. DOM from the supra-glacial snowpack and glacier outflow at Mendenhall had similar molecular signatures, on the basis of the distribution of peaks identified in van Krevelen space (Fig. 2a,b), as did the eight additional DOM samples from glacier waters (van Krevelen diagrams not shown). In contrast, the van Krevelen diagram for Peterson Creek (Fig. 2c) exhibits a dense population of peaks in a region that includes lignin-like compounds¹⁹ and carboxylic-rich alicyclic molecules (CRAM; ref. 20). These lignin/CRAM-like peaks dominate the FTICR mass spectra for DOM from most aquatic environments, including other rivers^{19,21} and the ocean²⁰. The fact that these peaks are poorly represented in all glacier samples indicates that glacial DOM has a unique molecular fingerprint, suggestive of a singular source that is substantially different from the dominant sources supplying DOM to other aquatic environments.

Previously identified relationships between FTICR-MS-derived elemental formulae and molecular structure were used to further probe the character of glacier DOM. The aromaticity index²² showed that snowpack and all glacier DOM contained substantially higher numbers of condensed aromatics peaks than Peterson Creek DOM (Fig. 2d provides a subset of data and Supplementary Fig. S1 includes data for all samples). As condensed aromatics can only be formed through heating of OM (ref. 22), their presence is an indicator that the glacier samples, from snowpack to outflow, contain previously combusted OM, such as found in soot aerosols²³. Glacially derived DOM also contained higher abundances of aliphatic compounds (Fig. 2d; Supplementary Fig. S1), particularly

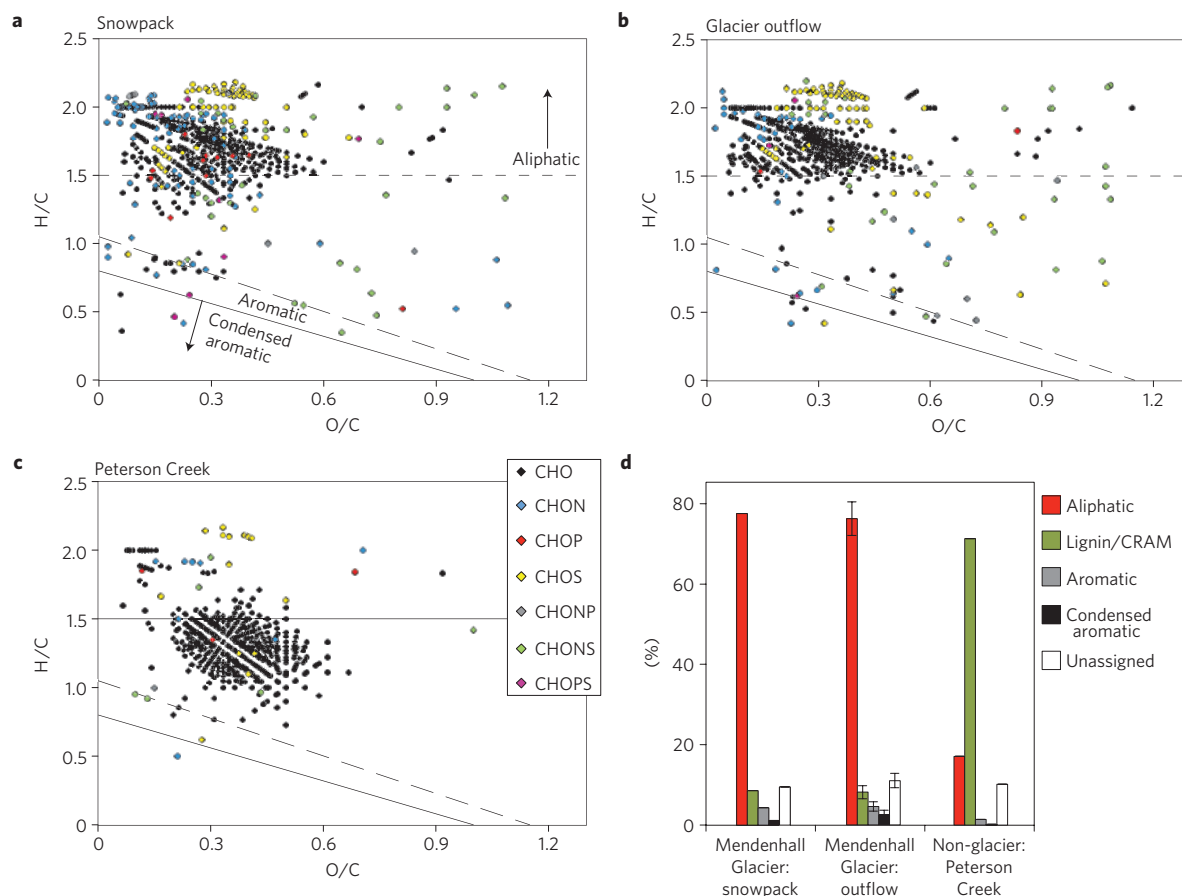


Figure 2 | Molecular signatures for glacier and non-glacier (Peterson Creek) dissolved organic matter as revealed by Fourier transform ion cyclotron mass spectrometry. a–c, van Krevelen distributions of dissolved organic molecular formulae identified in Mendenhall Glacier snowpack (**a**), Mendenhall Glacier outflow (**b**), and Peterson Creek (**c**). **d,** Bar chart detailing the structural classes assigned to the dissolved organic molecular formulae identified in Mendenhall Glacier snowpack (one sample), Mendenhall Glacier outflow (error bars represent variability between three samples taken on different dates) and Peterson Creek (one sample).

fatty acids with chain lengths reaching 30+ carbons, as have previously been found to be associated with soot²⁴ and are recognized to be highly biodegradable²⁵. Finally, snowpack and glacier DOM samples were enriched in organics containing sulphur and nitrogen, particularly sulphuric aliphatics (yellow data points $>1.5\text{H/C}$ in Fig. 2a–c). Although sulphur-rich and nitrogen-rich aliphatics are not usually represented in high abundance in the FTICR mass spectra for DOM (refs 18–22), they are prevalent in the water-soluble organic carbon fraction of aerosols, where they probably originate from the incomplete combustion of fossil fuels²⁶.

The molecular fingerprints we identified for DOM throughout the Mendenhall Glacier ecosystem are similar to those for anthropogenic OM deposited on other remote glaciers. For example, the post-industrial, upper section of an ice core (1950 AD) in Franz Josef Land, Russia, was heavily enriched in sulphur- and nitrogen-containing DOM when compared with deeper, pre-industrial sections of the core²⁷. Similarly, the concentrations of soot and organic combustion products in the glaciers of the remote Tibetan plateau correlate with decadal trends in anthropogenic combustion emissions⁶. Taken together with our results, these findings lead to the conclusion that deposition of anthropogenic combustion products is the primary driver of glacier DOM export and carbon-cycling in glacier ecosystems.

The finding that DOM in glacier runoff has an anthropogenic origin indicates that the quantitatively important supply of labile carbon from Gulf of Alaska glaciers to coastal margins¹ is largely a modern, post-industrial phenomenon. The microbes underpinning

marine foodwebs are particularly sensitive to alterations in the quantity and quality of DOM entering marine systems²⁸. Therefore, inputs of labile, anthropogenic DOM from either glaciers or from the quantitatively significant, direct deposition of anthropogenic organic aerosols to the ocean surface¹⁰ could have altered the marine foodwebs we study today. The impacts of increasing deposition are likely to be felt across the globe, with some of the greatest perturbations likely to occur along glacially dominated coastal margins, such as those off the Gulf of Alaska and Greenland, which are experiencing the highest levels of glacier ice loss and attendant shifts in material fluxes^{29,30}. Although it is not known to what extent OM deposition has perturbed and will continue to alter glacially dominated coastal ecosystems or the open ocean, it is clear that glaciers provide a unique window through which to discern the role anthropogenic deposition plays in our changing environment.

Methods

Samples were collected in pre-cleaned (acid and MilliQ rinsed) high-density polyethylene plasticware and kept on ice until back in the laboratory ($<6\text{ h}$), where they were then passed through precombusted 47 mm 0.7 μm glass fibre filters followed by 0.3 μm filters to remove particulates¹. Sample DOC concentrations (OI Analytical 700 TOC analyser), ultraviolet–visible absorbance spectra (Hewlett-Packard 8453), lignin phenols and $\Delta^{14}\text{C}$ -DOC were measured following routine methods^{2,8,9}. The analytical errors for individual samples are typically less than 2% for DOC and coloured DOM absorbance at 254 nm, the latter was used to calculate the SUVA values reported in Table 1. Fluorescence excitation–emission matrix spectra (EEMS; Jobin Yvon FluoroMax-3) were measured and protein fluorescence components were quantified using multivariate modelling technique parallel factor analysis (PARAFAC; ref. 1). Samples for FTICR-MS were processed

and spectra acquired in negative-ion mode, as described in ref. 19, but with the following modifications. Samples were amended with methanol and ammonium hydroxide to produce a final sample composition of 75/25 (v/v) water/methanol, plus 0.1% ammonium hydroxide. The electrospray shield voltage was optimized to 3,600 V (shield current 130–150 nA) and the capillary voltage was 4,300 V (capillary current of 15–20 nA). Ions were accumulated in the hexapole for 3.0 s before being transferred to the ICR cell, except for the snowpack sample, for which the accumulation time was 5.0 s. A molecular formula calculator (MolecularFormulaCalc-© NHMFL) generated formula matches, using carbon (5–50), hydrogen (5–100), oxygen (1–30), nitrogen (0–7), sulphur (0–2) and phosphorus (0–2), that agreed with measured masses within an error value of less than ± 0.5 ppm. All other data treatment was as described in ref. 21. Further details of the sampling locations and the methodology employed are presented in the Supplementary Information.

Received 20 September 2011; accepted 18 January 2012;
published online 19 February 2012

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Acknowledgements

K. Butler is thanked for help with measurements of DOC concentrations and DOM optical properties, R. Dyda for help with lignin analyses, A. Wozniak for discussions regarding aerosol OM, A. Boyette for assistance with design and production of figures, and the College of Sciences Major Instrumentation Cluster (COSMIC) at ODU for FTICR-MS instrument time. NorthStar Trekkers and the US Forest Service are thanked for providing transport and access to Mendenhall Glacier. This work was funded by the US National Science Foundation (DEB-1146161/-1145313/-1145932/-11455885, OCE-0728634, EAR-0943599/-0838587), the Climate Effects Network of the US Geological Survey, and a Fellowship from the Hanse Institute for Advanced Studies (HWK, Delmenhorst, Germany) granted to A. Stubbins. The use of brand names is for identification purposes only and does not imply endorsement. Any opinions, findings, conclusions or recommendations expressed are those of the authors and do not necessarily reflect the views of the funding bodies.

Author contributions

A.S., E.H., R.G.M.S. and G.R.A. designed the research. E.H. led the fieldwork at Mendenhall and Herbert glaciers with assistance from R.G.M.S., A.W.V. and D.T.S., and G.R.A., P.S. and R.G.S. led the fieldwork at Gulkana and Fremont glaciers. P.A.R. and D.B. analysed samples for radiocarbon ages. P.J.H. and R.G.M.S. ran lignin analyses. G.R.A. and A.W.V. ran DOC, absorbance and fluorescence analyses. FTICR-MS data acquisition and analysis were conducted by R.L.S., H.A.N.A., P.G.H. and A.S. Writing and data integration were done by A.S. with significant contributions from E.H., R.G.M.S. and P.A.R. All authors commented on the manuscript.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturegeoscience. Reprints and permissions information is available online at <http://www.nature.com/reprints>. Correspondence and requests for materials should be addressed to A.S.