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Wildfires Impact the Thermal Stability and Molecular Composition but Not the Age of Dissolved Organic Carbon Exported by Northern Streams

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Abstract Understanding how wildfires impact the biogeochemistry of dissolved organic matter (DOM) in peatland catchments is important for predicting how they may respond to climate change. However, the net effects of wildfires on the composition of DOM are not yet well understood. We investigated how fire changes the age, thermal stability, and molecular composition of stream DOM in blanket peatlands in the Flow Country and the Isle of Lewis, North of Scotland. Radiocarbon measurements showed that stream DOC was predominantly modern in both bulk and ramped thermal fractions with no apparent change observed due to wildfires. Ramped thermal oxidation revealed higher thermal stability of stream DOM in wildfire impacted areas, as demonstrated by higher activation energies, a proxy for organic C bond strength. This was prominent between 350 and 470°C and was also associated with an increase in the content of thermally stable C and a reduction in bond diversity. Using ultra high-resolution mass spectrometry, we found an increase in the molecular diversity of DOM and in the relative abundance of highly unsaturated and phenolic class. There was also a higher relative abundance of highly oxygenated N- and S-containing formula, potentially from partially combusted plant and soil material, which could explain the shift in activation energy. Together, our results demonstrate ways that wildfires can impact the reactivity and composition of DOM, with implications for its stability and residence time along the terrestrial-aquatic continuum.

Plain Language Summary Increasing frequency and severity of wildfires across peatland catchments in the Northern hemisphere could impact the composition and export of dissolved organic matter. We investigated how the wildfires of 2019 in the Flow Country and 2022 in the Isle of Lewis in the North of Scotland impacted the age, thermal stability and molecular composition of dissolved organic matter in river catchments. Our results show that the wildfires had a minimal effect on the age of dissolved organic carbon. We observed, however, an increase in the content of more thermally stable organic carbon in wildfire impacted catchments. This shift in thermal stability could be related to the higher relative abundance of nitrogen- and sulfur-containing compounds. These changes in thermal stability and composition could modify processes and budgets downstream with implications for carbon and nutrient cycling, greenhouse gas emissions, and drinking water management.

Key Points:

- Stream DOC was mostly modern in age in both bulk and ramped thermal fractions
- Stream DOC in burnt catchments showed a higher thermal stability
- Stream DOM in burnt catchments presented higher relative abundance of N- and S-containing molecular formulas

Supporting Information:

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

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1. Introduction

Wildfires threaten the role of peatlands as global C stores. Peatlands are a natural C sink, accumulating >600 Pg of C in organic matter since the Last Glacial Maximum (Yu et al., 2010). They cover 2%–3% of the Earth's land surface and are most extensive in Northern high latitudes where low temperatures and waterlogged soils favor the slow decay of biomass (Turunen et al., 2016). In Northern peatlands, changes in hydro-meteorological conditions and land use practices increase their vulnerability to wildfires (Limpens et al., 2008; Turetsky et al., 2014). Wildfires generally affect the upper soil layers, particularly where soils are dry as a result of either antecedent drought or management impacts such as drainage. They produce changes in the composition of biomass and

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resulting greenhouse gas emissions (Andersen et al., 2024; Gray et al., 2020), which could offset the peatland C sink capacity in the long-term (Wilkinson et al., 2023). Wildfires also influence the processes that regulate the mobilization of organic C from across the soil profile and surface waters (Hudiburg et al., 2023; Nelson et al., 2021; Rein et al., 2008). Because peatlands are major sources of dissolved organic matter (DOM) and dissolved organic carbon (DOC) to aquatic ecosystems (Rosset et al., 2022), contributing to the global river DOC flux of 0.30 ± 0.14 Pg C yr^{-1} (Liu et al., 2024), ongoing and future changes in the frequency and severity of wildfires could impact the composition and export of DOM. These changes can then modify biogeochemical processes and budgets downstream of river catchments with wider impacts for upland drinking water management (Ritson et al., 2014).

The net effects of wildfires on the concentration of stream DOC and character of DOM in peatland catchments are still unclear (Brown et al., 2015; Wei et al., 2021). The concentrations of stream DOC have shown inconsistent trends following wildfires (Burd et al., 2018; Davidson et al., 2019; Evans et al., 2016; Granath et al., 2021), indicating that hydrological conditions, catchment characteristics, and soil biogeochemical processes likely offset fire severity in modulating DOC export. In contrast, changes in the composition of DOM appear more closely related to fire intensity, duration, and frequency (Rodriguez-Cardona et al., 2020). The combination of temperature, oxygen availability, and the nature of the parent organic material influences the chemical reactions and resulting products during burning (Gonzalez-Perez et al., 2004; Kennedy-Blundell et al., 2025; Wagner et al., 2018). Changes in the composition of DOM can result from the breakdown of macromolecular material (e.g., depolymerization) or the formation of new condensed aromatic and heterocyclic compounds (Brown et al., 2015). Therefore, the effects of wildfires on the composition of DOM are complex and there appears to be significant variability across catchments (Tshering et al., 2023). Moreover, in highly eroded catchment soils, wildfires can also favor the mobilization of stored C from deep soil layers that can be thousands of years old (Bowen et al., 2024; Evans et al., 2022). Together, these fire-induced modifications can impact the bioavailability, photoreactivity, and preservation of stream and river DOM which determine whether it contributes to greenhouse gas emissions during river transport or upon export to the coastal ocean (Cory et al., 2014; Evans et al., 2017).

A combination of analytical approaches is needed to better understand the effect of wildfires on the composition and character of DOM in peatlands, and thus the fate of C mobilized by rivers. Changes in composition are usually inferred from optical indexes that do not capture variations originating from non-chromophoric compounds (Olefeldt et al., 2013; Wagner et al., 2018). As an alternative, direct infusion-ultra high resolution mass spectrometry, which provides molecular-level information of the organic matter pool, could be used to help uncover the impacts of burning on the composition and cycling of DOM (Roebuck et al., 2025; Y. Xu et al., 2024; Z. Zhang et al., 2024). In parallel, thermal analysis can provide further insights into the reactivity of DOM. The susceptibility of organic matter to chemical oxidation over a temperature gradient is related to its chemical composition and bond-structure (Hemingway, Rothman, et al., 2017; Leifeld & von Lützow, 2013; Rogers et al., 2021). Quantifying thermal stability for the entire DOM sample can then provide detailed insights into its resistance to mineralization (Peltre et al., 2013). Although wildfire may lead to organic matter charring and alteration, thus causing shifts in thermal stability, there remain few measurements of the thermal stability of DOM from peatland catchments in response to wildfire. Recent developments in ramped thermal oxidation now allow for coupled C isotope analysis (^{13}C and ^{14}C), providing a unique opportunity to investigate relationships between the thermal stability, source, and age of organic matter (Garnett et al., 2023; Hemingway, Galy, et al., 2017; Rogers et al., 2021; Rosenheim & Galy, 2012). This approach can be particularly useful in streams and rivers draining peatland ecosystems where questions remain about the reactivity and age of DOM (Dean et al., 2019; Evans et al., 2022; Schwab et al., 2020).

Here we provide new insights into the impact of wildfires on the age, thermal stability, and molecular composition of DOM in two Scottish peatland dominated catchments. We collected stream samples from burnt and unburnt catchments in the Flow Country and the Isle of Lewis in the North of Scotland. The study areas were affected by wildfires in 2019 (Flow Country) and 2022 (Isle of Lewis). We use a combination of bulk C isotope analysis (^{13}C and ^{14}C), ramped thermal oxidation coupled to C isotope analysis, and Fourier Transform-Ion Cyclotron Resonance-Mass Spectrometry (FT-ICR MS) to assess changes in the age, thermal stability, and composition of stream DOM, respectively. We hypothesized that wildfires would increase the thermal stability of stream DOM, on the basis that burning would increase the aromaticity of surface organic matter stores in the peatland. Moreover, we explored whether ramped thermal oxidation could reveal a potentially "hidden" old C component of the bulk DOM pool (Dean et al., 2019) that may have been mobilized as a consequence of fires. We then

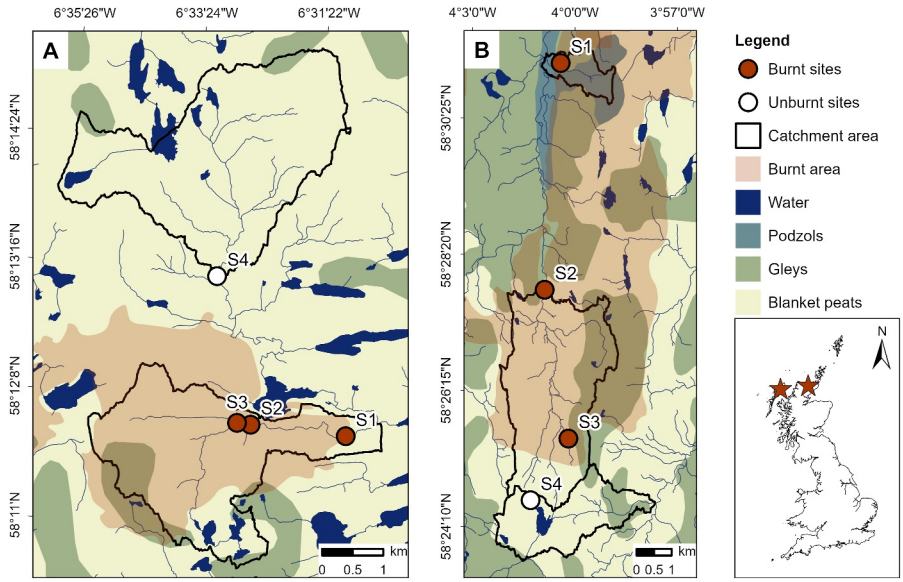

Figure 1. Study sites in the Isle of Lewis (a) and the Flow Country (b) in northern Scotland, with burnt areas from EFFIS (2025) and soil classification from NatureScot (2016). Catchments upstream are shown outlined in black for burnt (red) and unburnt (white) areas.

contextualize the age of stream DOM against the bulk age of soil organic C from these catchments. This study provides important insights into the biogeochemistry of stream DOM in peatland catchments under current climate change.

2. Materials and Methods

2.1. Site Description and Sampling

The Flow Country of Caithness and Sutherland, North of Scotland, covers 4,000 km^2 and is among the largest blanket bogs in Europe (Lindsay et al., 1988). As well as multiple conservation designations (Special Area for Conservation, RAMSAR site, and Special Protection Area), the Flow Country became the first and only peatland in the world to be inscribed as a UNESCO World Heritage Site in 2024. Vegetation includes *Sphagnum papillosum*, *S. capillifolium*, *Erica tetralix*, *Calluna vulgaris*, *Eriophorum angustifolium*, and *Narthecium ossifragum* (Lindsay & Andersen, 2016). The base flow index is 0.29 and average annual rainfall is 1,207 mm (NRFA, 2025b). The wildfire event occurred in May 2019 and covered ~65 km^2, making it the largest single wildfire event to be recorded in the UK at the time (Andersen et al., 2024). The Isle of Lewis in the Western Isles is mainly dominated by blanket peat that extends over 600 km^2. Vegetation is dominated by *Calluna vulgaris*, *Erica tetralix*, *Sphagnum rubellum*, *Cladonia uncialis* and *C. impexa* (Goode & Lindsay, 2011). The base flow index is 0.23 and average annual rainfall is 1,503 mm (NRFA, 2025a). Manual peat cutting for fuel is common across the Western Isle (Brown et al., 2007). A large fire event occurred in March 2022 and burnt an area of ~18 km^2 of peatlands which were predominantly not impacted by cutting. Sampling sites were selected with no active impacts of peat cutting in the catchment areas.

We sampled three burnt catchments and one unburnt catchment in each study area (Figure 1). We use "unburnt" to describe the catchments that were not directly impacted by the wildfires in 2019 and 2022. Sampling campaigns took place in September 2022 in the Flow Country (~3.5 years following the wildfire). On the Isle of Lewis, sampling was completed in April (~3 weeks after the wildfire) and September 2022 (~6 months following the wildfire). Stream water samples were collected using acid washed HDPE bottles, stored refrigerated in the dark, and filtered within 6 hr of collection using pre-combusted (3 hr, 450°C) GF/F filters (0.7 µm, Whatman). Soils were also sampled at three depths (~5.5, 35, and 55 cm) from one burnt and one unburnt site in September 2022. Cores were taken from three systematically randomized locations within the catchment, and the soil from the same depths at each of the three locations were combined into a single sample to capture the spatial variability.

Samples were collected using a Russian peat corer (4 cm diameter) and stored in pre-combusted (3 hr, 450°C) aluminum foil. Soil samples were refrigerated at 4°C until analysis.

2.2. DOC Concentrations and C Isotope Analysis

Concentrations of stream DOC were measured within a week of collection via a Shimadzu TOC-L analyser at the University of Bristol using the non-purgeable OC method. For isotopic analysis, filtered water samples (0.5 L) were freeze-dried, and the solid residue was acid fumigated to remove any inorganic carbonates (Ascough et al., 2024). Soil samples were homogenized, pre-treated with 1 M HCl overnight, and then freeze-dried (Ascough et al., 2024). Stream DOM and soil material were combusted to CO_2 using the sealed quartz tube method (Boutton et al., 1983). The CO_2 was then cryogenically purified in a vacuum line and split into two aliquots for stable C isotope and radiocarbon measurements. Stable C isotope ratios were determined using an Isotope Ratio Mass Spectrometry (Delta V, Thermo Fisher). To measure the ^{14}C activity of the samples, CO_2 was graphitized following the Fe-Zn reduction method and radiocarbon measurements were carried out at the Scottish Universities Environmental Research Center (SUERC) Accelerator Mass Spectrometry Facility in East Kilbride, UK (S. Xu et al., 2004). Stable C isotope ratios are reported in δ-notation, relative to the Vienna Pee Dee Belemnite standard, as per mille (‰), and have a precision and accuracy <0.2‰ based on external standards. The ^{14}C activities were normalized to a $\delta^{13}C$ value of −25‰ and expressed as fraction modern ($F^{14}C$) (Reimer et al., 2016).

2.3. Thermal Analysis

Thermal analysis was carried out using the ramped thermal oxidation system at the NEIF Radiocarbon Laboratory, East Kilbride, UK (Garnett et al., 2023). Freeze-dried DOM was heated under a constant stream of pure O_2 at 30 mL min^{-1} from 20 to 800°C at 5°C min^{-1}. The resultant gases were then passed through platinized wool at 950°C followed by a $Mg(ClO_4)_2$ water trap. Evolved CO_2 over time with increasing oxidation temperature (i.e., thermogram) was measured using a non-dispersive infrared analyser. After an initial inspection of the thermograms following combustion of a sample aliquot, samples were combusted again and CO_2 fractions were collected in cleaned foil gas bags at: 20–350°C (fraction A), 350–470°C (fraction B) and 470–750°C (fraction C) for the Flow Country, and 20–350°C (fraction A), 350–450°C (fraction B) and 450–700°C (fraction C) for the Isle of Lewis. The CO_2 in the foil bags was cryogenically purified in a vacuum line and split for stable C isotope and radiocarbon measurements as described in Section 2.2.

Thermograms were used to calculate a non-parametric distribution of activation energy (E) using the *ramped-pyrox* package in Python (Hemingway, Galy, et al., 2017; Hemingway, Rothman, et al., 2017). The Arrhenius pre-exponential factor (Ω) was 10^{10} s^{-1}. The weighting factor (λ) was automatically estimated or set at 0.5 if it could not be defined ($n = 2$) (Hemingway, Galy, et al., 2017). The mean of E (μ_E) and its standard deviation (σ_E) were calculated for each distribution. These metrics are interpreted as a proxy for organic C bonding strength and heterogeneity within a sample, respectively. σ_E does not represent the standard deviation of replicate measurements. Both parameters, μ_E and σ_E, were also calculated for each temperature interval (fractions). The package *rampedpyrox* was also used to correct the $\delta^{13}C$ values of CO_2 for isotopic fractionation during thermal oxidation ($\delta^{13}C_c$).

2.4. FT-ICR MS

The molecular composition of DOM was analysed using the 21 T FT-ICR MS at the National High Magnetic Field Laboratory in Tallahassee, Florida (Hendrickson et al., 2015; Smith et al., 2018). Filtered water samples (0.2 µm) were acidified to pH 2 (10 M HCl) and passed through pre-conditioned Bond-Elut PPL cartridges (3 mL, 100 mg, Agilent Technologies) (Dittmar et al., 2008). The volume of sample extracted was adjusted dependant on the sample concentration of DOC to achieve a target loading of 50 µg of C. An extraction efficiency 65% was assumed (Dittmar et al., 2008). Cartridges were rinsed twice with milli-Q water (2 mL, pH 2), dried with ultra-high purity nitrogen gas, and eluted with 1 mL of HPLC grade methanol. Extracts were stored in the dark at −20°C until analysis. Extracts were analysed by negative electrospray ionization. Each sample's spectra was formed from 75 scans, which were conditionally co-added, phase corrected and then internally calibrated in Predator software using the "walking calibration" and 10–15 abundant homologous series that spanned the entire molecular weight distribution (Blakney et al., 2011; Savory et al., 2011).

Table 1
Concentrations, Bulk C Isotopes, and Ramped Thermal Oxidation Results of Stream DOC From the Flow Country and the Isle of Lewis

Site	Type	Sampling date	DOC (mg L^{-1})	δ^{13}C-DOC (‰)	F^{14}C-DOC	^{14}C yBP	μ_E (kJ mol^{-1})	σ_E (kJ mol^{-1})	$p(E)_{max}$
Flow Country									
S1	Burnt	September 2022	11.11	−28.8	1.028(4)	Modern	158.11	20.47	0.03
S2	Burnt	September 2022	24.24	−28.4	1.048(5)	Modern	167.93	23.16	0.05
S3	Burnt	September 2022	26.10	−27.5	1.060(5)	Modern	167.93	24.85	0.04
S4	Unburnt	September 2022	29.95	−28.5	1.078(5)	Modern	152.34	23.83	0.07
Isle of Lewis									
S1	Burnt	April 2022	10.00	−28.4	0.991(5)	75(37)	158.01	18.97	0.04
S2	Burnt	April 2022	18.37	–	0.964(7)	291(61)	–	–	–
S3	Burnt	April 2022	7.26	−28.5	0.985(5)	119(61)	–	–	–
S4	Unburnt	April 2022	10.18	–	0.964(7)	297(61)	155.62	17.13	0.05
S1	Burnt	September 2022	20.32	−28.7	1.058(5)	Modern	163.60	21.67	0.08
S2	Burnt	September 2022	24.98	−28.4	1.048(5)	Modern	157.00	19.33	0.04
S3	Burnt	September 2022	18.13	−28.6	1.063(5)	Modern	157.46	22.57	0.04
S4	Unburnt	September 2022	21.31	−28.6	1.043(5)	Modern	154.69	22.25	0.04

Note. Values in parenthesis show 1σ. Dash lines indicate missing samples.

Elemental compositions were assigned between 170 and 1,200 Da to mass peaks with a signal intensity greater than six times the standard deviation of the root mean square baseline signal-to-noise. Formulas were assigned within the bounds $C_{1\text{-}100}H_{4\text{-}200}O_{1\text{-}30}N_{0\text{-}4}S_{0\text{-}2}$ using PetroOrg© and had an assignment mass accuracy of <0.3 ppm (Corilo, 2015). The modified aromaticity index (AI_{mod}) (Koch & Dittmar, 2006, 2015) and the Nominal Oxidation State of Carbon (NOSC) (Riedel et al., 2012) were calculated for each neutral elemental composition. Assigned formulas were categorized into six compound classes: polyphenolic ($0.5 < AI_{mod} < 0.67$) and condensed aromatics (CA; $AI_{mod} > 0.67$), highly unsaturated and phenolic (HUP; $AI_{mod} < 0.5$ and $H/C < 1.5$), aliphatic ($H/C \geq 1.5$–2.0, $O/C \leq 0.9$ and $N = 0$), peptide-like ($H/C \geq 1.5$–2, $O/C \leq 0.9$ and $N > 0$); and sugar-like ($H/C \geq 1.5$–2 and $O/C > 0.9$). Formulas were further categorized into four groups according to the presence of heteroatoms: CHO, CHON, CHOS, and CHONS. Because molecular structure cannot be determined by direct infusion FT-ICR MS, compound classes are operational, and thus each molecular formulas may contain multiple isomers (Hertkorn et al., 2007). The relative abundance of each assigned peak was calculated by dividing its peak intensity by the sum intensity of all assigned peaks within a sample, scaled to 10,000. The relative abundance of each compound and heteroatom class was calculated as the sum of the relative abundance of all the peaks belonging to that class.

2.5. Data Analysis

Changes in the properties of stream DOM between the burnt and unburnt sites were assessed using the relative change in % following $[(X_{burnt} - X_{unburnt})/X_{unburnt}] * 100$ or the fold change ratio. We used a Mann-Whitney U test and a permutation test to evaluate differences in the relative or fold changes and between thermal fractions, respectively. Analysis and visualizations were carried out in R version 4.4.1 (R Development Core Team, 2024).

3. Results and Discussion

3.1. Effect of Wildfire on Stream DOC

3.1.1. Impact on Source and Age

There were no systematic trends in the concentration of stream DOC and C isotope composition between burnt and unburnt sites (Table 1, Figure 2, Table S1 in Supporting Information S1). Concentrations of stream DOC ranged between 7.26 and 29.95 mg L^{-1} (Table 1). The bulk δ^{13}C values were typical of peatland vegetation (Granath et al., 2018; Loisel et al., 2009). In soils, the F^{14}C values of the upper layers indicated modern C fixation

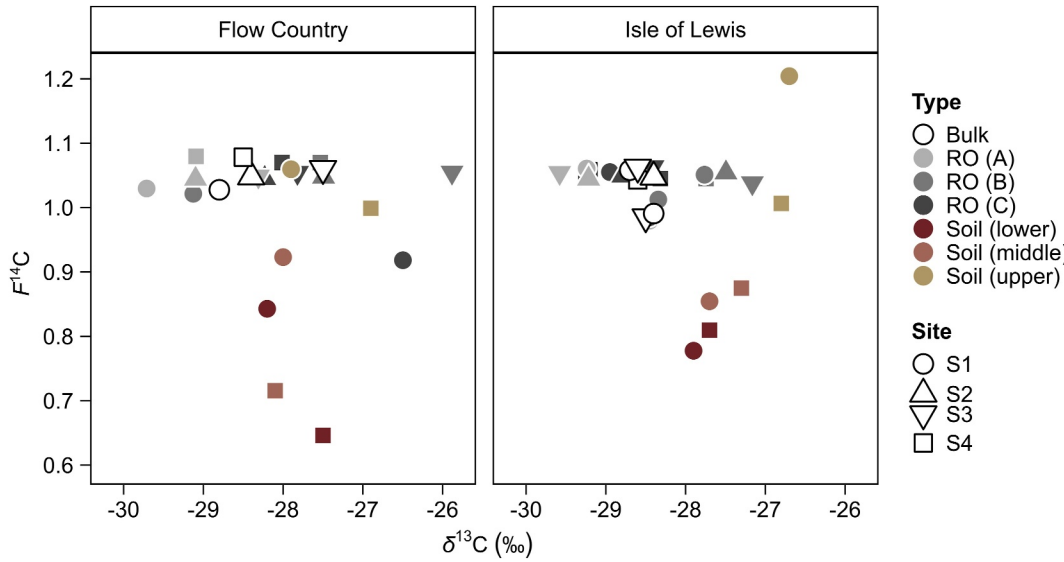

Figure 2. Radiocarbon activity (reported as fraction modern, $F^{14}C$) and stable C isotope composition ($\delta^{13}C$) of bulk stream DOC, ramped thermal oxidation fractions (RO) of stream DOC, and soils from burnt (S1–S3) and unburnt (S4) sites in the Flow Country and the Isle of Lewis. Fraction A 20–350°C, fraction B 350–470°C, fraction C 450–750°C (see Section 2.3).

(i.e., C fixed through photosynthesis since ~1955). $F^{14}C$ values then decreased with depth to 0.646 (3,508 ± 37 ^{14}C yBP) at a depth of 55.5 cm in the Flow Country and to 0.778 (2021 ± 35 ^{14}C yBP) at a depth of 57.5 cm in the Isle of Lewis. The $F^{14}C$ values of bulk stream DOC were modern, with a mean of 1.028 ± 0.041, and the majority of values fell within the range of the surface soils layers, indicating little evidence of aged organic C contributions.

During ramped thermal oxidation of stream DOM, the C isotope composition showed minimal differences across temperature interval ($\delta^{13}C_c < -3.8‰$ and $F^{14}C < 0.033$) (Figure 2, Table S2 in Supporting Information S1). One exception was a burnt site in the Flow Country (S1), where the $F^{14}C$ value decreased from 1.030 (modern) in fraction A (20–350°C) to 0.918 (691 ± 37 ^{14}C yBP) in fraction C (470–750°C). The latter is lower than that of bulk stream DOC ($F^{14}C = 1.028$, modern), suggesting the presence of an older and more thermally stable component within the stream DOM. This partially supports previous findings demonstrating an old C signal within the DOM pool, despite the bulk ^{14}C measurements indicating modern C (Dean et al., 2019). The origin of this signal is unclear, but it is attributed to degradation/desorption products of particulate organic C that is generally much older (Bowen et al., 2024; Coppola et al., 2019).

Despite the no systematic differences in the $F^{14}C$ values between burnt and unburnt sites at both locations, we noted that the unburnt site in the Flow Country had the highest $F^{14}C$ values of stream DOC between 1.070 and 1.079, and that these were homogeneous across temperature fractions (Figure 2, Table S2 in Supporting Information S1). During the wildfires in 2019, the $F^{14}C$ values of atmospheric CO_2 in the Northern Hemisphere were close to 1.00 (Hua et al., 2021). As such, higher $F^{14}C$ values of stream DOC reflect a higher proportion of modern C in the organic matter at this site. In contrast, the lower $F^{14}C$ values in the burnt sites could reflect the input of DOC from slightly deeper and older organic C layers in the soil profile, given the impact of wildfires on peatland hydrology and C mobilization (Evans et al., 2014). However, why the unburnt site in the Isle of Lewis had lower $F^{14}C$ compared to the burnt sites is unclear, but it suggests the input of aged organic C perhaps due to site specific differences in C mobilization linked to hydrological flow paths. Moreover, we found an apparent seasonal variability, where the $F^{14}C$ values of both bulk and temperature intervals of stream DOC were lower in April compared to September (Table 1, Table S2 in Supporting Information S1). These trends are further discussed in Section 3.1.4.

3.1.2. Effect on the Thermal Stability

The thermograms of stream DOM showed a bimodal distribution in all samples (Figure S1 in Supporting Information S1). Evolved concentrations of CO_2, during the combustion of stream DOM, increased from ~150°C to

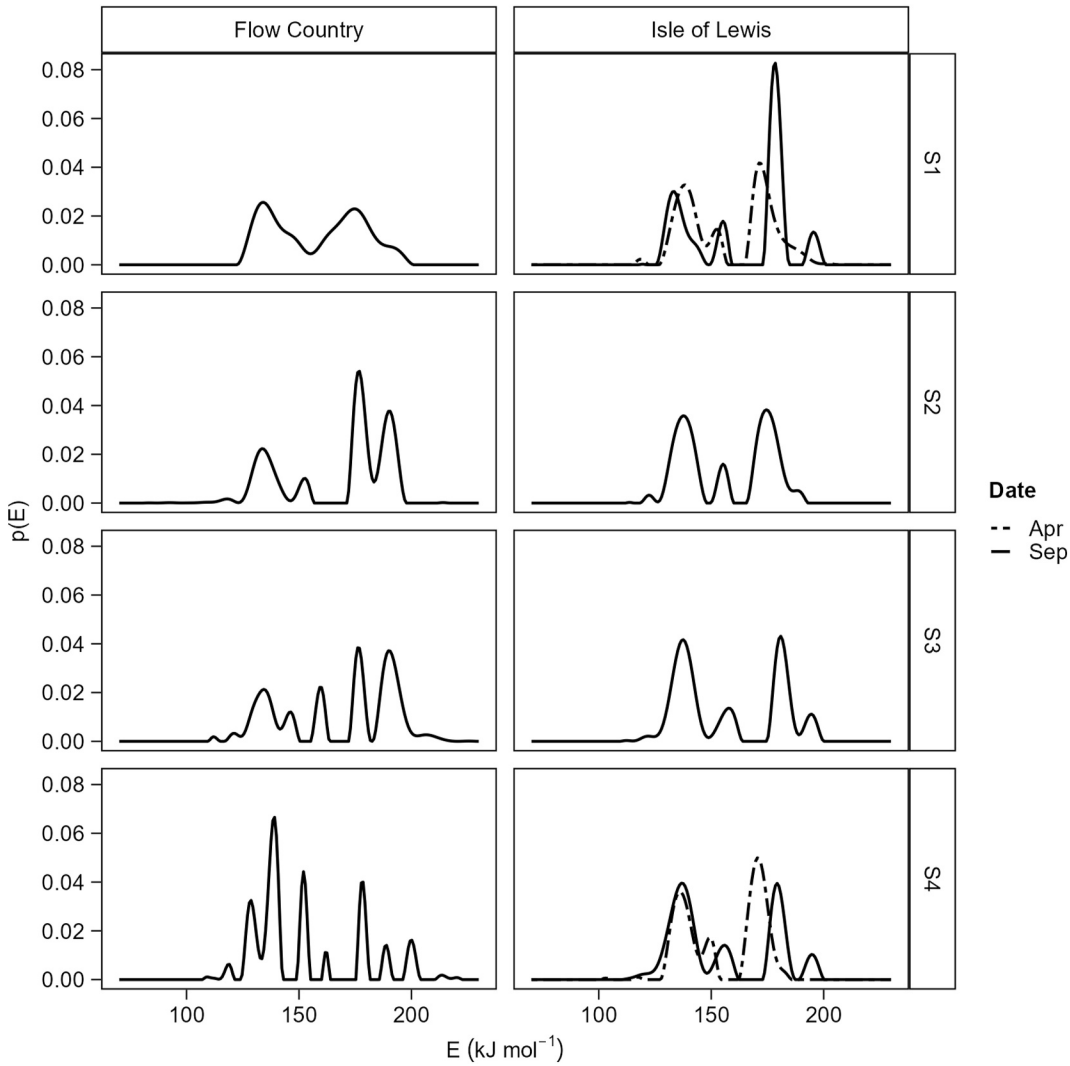

Figure 3. Probability distribution of activation energy (E, kJ mol^{-1}) for stream DOM in burnt (S1–S3) and unburnt (S4) sites in the Flow Country (left) and the Isle of Lewis (right).

a first maximum at 298 ± 7°C, followed by a slight decline. CO_2 increased again to a second peak at 470 ± 23°C and decreased to background levels after ~650°C. Thermograms were used to calculate E distributions that presented E values within the 100–200 kJ mol^{-1} range (Figure 3). The mean of μ_E and σ_E were 159.3 ± 5.4 kJ mol^{-1} and 21.4 ± 2.4 kJ mol^{-1} ($n = 10$), respectively. To the best of our knowledge, these are the first E estimates from stream DOM in blanket peatlands using the ramped thermal oxidation approach. The μ_E value is lower than that of river DOM (global mean 163.2 kJ mol^{-1}, $n = 6$) (Hemingway et al., 2019), but higher than that of a permafrost stream (151.8 kJ mol^{-1}) (Rogers et al., 2021). We do not compare the new analyses to these published data further due to the present lack of spatial and temporal information available ($n = 20$, including this study), and the variability of the methods used to extract DOM whose impact on thermograms has not been explored.

The thermal stability of stream DOM was higher in the burnt sites (Table 1). To assess the differences between sites and locations, we calculated the relative change in μ_E, and σ_E using the unburnt site as a reference. On average, the burnt sites showed an increase in μ_E of 5.0 ± 3.9% ($V = 28$, $p = 0.022$; ~7.7 kJ mol^{-1}) and a decrease in σ_E of −2.3 ± 9.0% ($V = 10$, $p = 0.578$; ~0.5 kJ mol^{-1}). These results suggest that the energy required to oxidize C increases upon thermal alteration whereas C bond diversity likely decreases. To explore this further, we separated the E distributions into the three fractions (using the temperature ranges for isotopic analysis) and

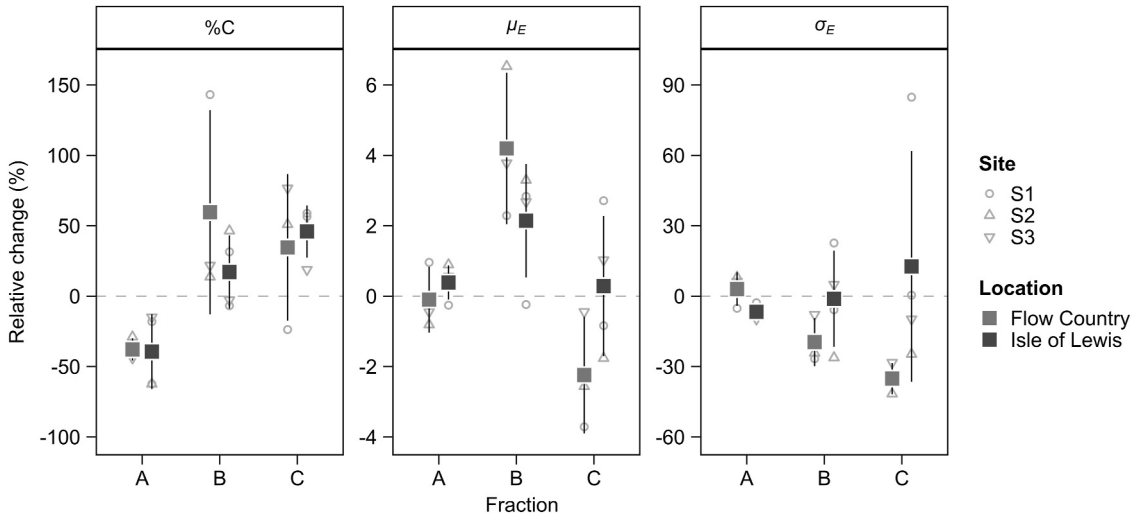

Figure 4. Change (%, relative to the unburnt site) in C content, mean activation energy (μ_E), and standard deviation of activation energy (σ_E) of different fractions during ramped thermal oxidation of stream DOM in the burnt sites in the Flow Country and the Isle of Lewis. Fraction A 20–350°C, fraction B 350–470°C, fraction C 450–750°C (see Section 2.3). Squares show the mean value and error lines show $\pm 1\sigma$. Dashed line highlights a zero reference.

calculated for each the relative change in C content, μ_E, and σ_E (Figure 4, Table S2 in Supporting Information S1). We found differences in the relative change in C content ($\chi^2 = 10.6$, $p = 0.005$) and μ_E ($\chi^2 = 10.0$, $p = 0.007$) across fractions. In the low temperature fraction (A, <350°C), stream DOC in the burnt sites showed a negative change in C content, but minimal changes in μ_E. In contrast, we observed positive changes in both C content and μ_E in fraction B (350–470°C). There were varying trends in σ_E ($\chi^2 = 0.243$, $p = 0.886$), but negative changes were predominant. Altogether, these results indicate that stream DOC in the burnt sites had lower content of labile C and higher content of thermally stable C (Plante et al., 2009).

We suggest that these changes in content of C and thermal stability of stream DOC in the burnt sites is due to wildfires. First, there were minimal changes in the sources of organic C between burnt and unburnt sites as indicated by the isotopic analysis. Second, the higher thermal stability (μ_E) and lower bond diversity (σ_E) at temperatures >350°C, which are both independent of the C content, are in agreement with the expected chemical transformation of organic matter during burning. Pyrogenic alteration of organic matter results in the loss of some functional groups (e.g., alkyl, *O*-alkyl) and the preferential formation of structures with aryl groups and condensed aromatic compounds (Chen et al., 2022; Wozniak et al., 2020; Q. Zhang et al., 2023). Although these changes are temperature-dependant, the resulting organic matter can exhibit higher thermal stability and lower C bond diversity. Thus, the decrease in σ_E in the burnt samples can likely indicate the loss of functional groups or the structural modifications of stream DOM. This is also supported by the higher mean thermal stability of the burnt sites compared to the unburnt sites and, in particular, its increase in the 350–470°C range.

3.1.3. Changes in Molecular-Level Composition

We evaluated compositional changes in stream DOM following wildfire using FT-ICR MS (Table 2). Of the 15,373 molecular formulas assigned, 21.5% and 2.2% were unique to the burnt and unburnt sites respectively, and 76.3% were common to both site types. The burnt sites showed consistently higher number of formulas compared to the respective unburnt site with additional formulas ranging from 169 to 2752. They also showed higher N/C ratios (V = 45, $p = 0.009$) and lower AI_{mod} (V = 5, $p = 0.039$). Trends in molecular weight, and the H/C and O/C ratios were less consistent across site types ($p > 0.05$). We found that burnt sites presented lower relative abundance of the CHO class (V = 0, $p = 0.009$) and higher relative abundance of CHON (V = 45, $p = 0.004$), and CHOS (V = 40, $p = 0.039$). Regarding compound classes, burnt sites were characterized by a higher relative abundance of HUP (V = 43, $p = 0.018$) and lower relative abundance of CA (V = 3, $p = 0.020$).

It is widely assumed that the combustion of organic material results in compounds with low H/C and O/C ratios and high aromaticity, which are more thermally stable (Collard & Blin, 2014; Knicker, 2007; Wagner et al., 2018). However, we observed a decrease in aromaticity (AI_{mod}) in stream DOM in the burnt sites. A similar

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Table 2
Molecular-Level Composition of Stream DOM as Determined by FT-ICR MS

Site	Type	Sampling date	Formulas (#)	Mass (Da)	H/C	O/C	N/C	AI_{mod}	NOSC	CHO (%)	CHON (%)	CHOS (%)	CHONS (%)	HUP (%)	Polyphenolic (%)	CA (%)	Aliphatic (%)
Flow Country																	
S1	Burnt	September 2022	10,758	534.8810	0.9856	0.5360	0.0059	0.3796	0.1104	83.2	10.1	6.5	0.2	74.0	19.0	5.1	2.0
S2	Burnt	September 2022	10,792	562.5885	0.9728	0.5455	0.0044	0.3832	0.1359	87.3	7.9	4.8	0.0	73.3	19.8	4.8	2.1
S3	Burnt	September 2022	11,234	566.6598	0.9731	0.5480	0.0044	0.3813	0.1406	87.3	7.9	4.8	0.0	73.3	19.5	5.0	2.2
S4	Unburnt	September 2022	10,589	568.7684	0.9583	0.5451	0.0037	0.3930	0.1465	89.5	6.7	3.7	0.1	70.8	21.1	6.0	2.1
Isle of Lewis																	
S1	Burnt	April 2022	12,713	526.7813	1.0179	0.5214	0.0070	0.3653	0.0533	80.9	11.4	7.4	0.3	73.2	17.8	4.8	4.1
S2	Burnt	April 2022	10,597	531.4936	0.9868	0.5239	0.0067	0.3835	0.0870	82.0	11.7	6.2	0.2	71.1	19.9	6.0	3.0
S3	Burnt	April 2022	11,088	536.9019	0.9984	0.5184	0.0063	0.3785	0.0638	82.5	10.7	6.7	0.1	71.4	19.5	5.7	3.5
S4	Unburnt	April 2022	9,961	529.7462	0.9881	0.5226	0.0050	0.3849	0.0786	84.6	8.6	6.8	0.1	70.3	20.2	6.0	3.5
S1	Burnt	September 2022	9,607	541.8757	0.9691	0.5418	0.0051	0.3887	0.1350	85.1	9.1	5.8	0.0	71.8	20.6	5.5	2.1
S2	Burnt	September 2022	9,392	554.1065	0.9610	0.5355	0.0046	0.3948	0.1285	86.1	8.8	5.2	0.0	70.4	21.3	6.2	2.1
S3	Burnt	September 2022	11,059	545.5808	0.9771	0.5374	0.0056	0.3845	0.1202	84.2	9.7	6.1	0.1	72.0	20.0	5.6	2.5
S4	Unburnt	September 2022	9,175	545.3873	0.9701	0.5406	0.0042	0.3884	0.1283	87.6	7.5	5.0	0.0	71.1	20.4	6.0	2.4

Note. FT-ICR MS results are reported as weighted average. Heteroatom and compound classes are reported as percentage of relative abundance. Peptide-like and sugars-like classes were <0.03%.

trend was reported by Y. Xu et al. (2024). This slightly less aromatic character can be related to the loss of highly oxygenated aromatic compounds, potentially from the CHO class (Wozniak et al., 2020). Stream DOM in the burnt sites not only had an overall lower relative abundance of the CHO class, but also a lower relative abundance of HUP, polyphenolic, and aliphatic compounds with a high O/C ratio (>0.5) within this class, leading to lower AI_{mod} and NOSC indexes (Table S3 in Supporting Information S1). Similarly, they presented lower relative abundance of CA. These results suggest that the variations in CHO compounds alone do not explain the higher thermal stability of stream DOM at the burnt sites. This is also supported by the decrease in the relative change of μ_E in the 470–750°C range, indicating that the incorporation of more stable pyrogenic compounds (e.g., condensed polycyclic aromatic hydrocarbons) into the stream DOM pool was perhaps unlikely.

The changes in the relative abundance of the CHON and CHOS heteroatom classes could explain the higher thermal stability of stream DOM. The relative abundance of these classes was higher in the burnt sites, increasing the AI_{mod} and NOSC indexes (Table S3 in Supporting Information S1). In the case of N-containing compounds, this observation agrees with those of heating experiments showing a positive relationship between combustion temperature and the degree of saturation and aromaticity (Z. Zhang et al., 2024). The CHON class was dominated by HUP and polyphenolic compounds in which those with high O/C (>0.5) showed the highest relative abundance. We found that these compounds primarily contained one or two N atoms with an O/N ratio >5. These characteristics are in line with the formation of heterocyclic aromatic structures during the burning of organic matter including the production of pyrrole-like or pyridine-like moieties, and Malliard reaction products, like melanoidins (Bahureksa et al., 2022; Knicker, 2007; Wagner et al., 2015).

Regarding the CHOS class, most compounds exhibited an O/S ratio >4, suggesting the presence of organic sulfates or sulfonates (Y. Xu et al., 2024). At the burnt sites, we also observed a predominance in the relative abundance of HUP compounds with high O/C (>0.5). The formation of S-containing structures during burning is also well known and their presence has been reported in atmospheric aerosols (Bao et al., 2017; Meade et al., 2016) and surface waters (Y. Xu et al., 2024). The contribution of the CHNOS class to the burnt sites was less significant ($V = 25$, $p = 0.075$) with individual compound classes accounting for a relative abundance of <0.3% (Table S3 in Supporting Information S1). In this case, HUP compounds with high O/C (>0.5) were also slightly dominant. Together, these results suggest that the higher contribution of N- and S-containing compounds to the stream DOM pool likely resulted in a higher thermal stability. These compounds tend to be more thermally stable due to aromaticity and resonance stabilization (Blake et al., 1961; Johns et al., 1962). Although the combined increase in the relative abundance of the CHON, CHOS, and CHONS heteroatom classes ranged only between 1.5% and 6.3%, the apparent high solubility of these compounds could have implications for the export of nutrients downstream.

3.1.4. Temporal Differences in the Isle of Lewis

An initial comparison of the FT-ICR MS data of stream DOM from the two sampling campaigns in the Isle of Lewis could suggest diminishing impacts following the wildfire. From April to September 2022, there was an increase in the percentage of common formulas between burnt and unburnt sites (from 72% to 77%). We also found an overall decrease in the relative abundance of organic N and a less aliphatic character (Table 2), which are likely indicators of vegetation recovery (Gustine et al., 2021; Rodriguez-Cardona et al., 2020). However, these changes in the composition of stream DOM shortly after the wildfire in the Isle of Lewis are consistent with those observed in the Flow Country nearly 3.5 years after the wildfire event. Alternatively, the temporal variations could be related to changes in the water table. During base-flow conditions (i.e., drier periods), stream DOM can contain a higher proportion of soil-derived organic matter, which can be demonstrated by more depleted $F^{14}C$ values (Evans et al., 2007). In this regard, our radiocarbon data, lower $F^{14}C$ values in April compared to September along with the declining trend in soil $F^{14}C$ values with depth, likely suggest underlying seasonal and hydrological effects. Unfortunately, the limited number of samples analysed for ramped thermal oxidation in April hinders an assessment in terms of thermal stability. The factors controlling the mobilization of stored C, including pyrogenic C, from peatlands are complex (Brown et al., 2015). Site specific characteristics (e.g., topographic, vegetation) and fire conditions (e.g., temperature and duration) would also regulate the response of stream DOM to the wildfire event (Lopez et al., 2024). Nevertheless, these are interesting shifts in the molecular composition and radiocarbon activity of stream DOM but require higher spatial and temporal sampling to resolve the ultimate drivers.

3.2. Environmental Implications

Increasing wildfire frequency and severity across Northern high latitudes (Wilkinson et al., 2023) could have impacts on aquatic biogeochemistry with implications for C cycling, nutrient fluxes, and drinking water supply. Our findings indicate that wildfires in peatland catchments can affect stream DOM by increasing the thermal stability and the relative content of N- and S-containing molecular formulas. This effect is possibly due to superficial burning of the upper soil layers, primarily litter, as indicated by $F^{14}C$ values ~1 of bulk stream DOC and across temperature intervals that match those of top soil. Because the nature of organic matter is an important factor in the metabolism of aquatic ecosystems (Battin et al., 2023), the wildfire-induced changes in composition can influence C mineralization processes. The higher thermal stability could suggest a slower DOM cycling pool. This is in line with previous research showing lower biodegradability of DOM in catchments impacted by wildfire (Burd et al., 2020). The mobilization of less bioavailable organic C can also potentially reduce stream greenhouse gas emissions (Hodgkins et al., 2018; Hu et al., 2024) and favor C transport to coastal areas. It is also possible that a proportion of the recalcitrant compounds become more susceptible to photodegradation, contributing to CO_2 emissions; in particular, those that are more aromatic (Gomez-Saez et al., 2017; Lian et al., 2021). Considering the limited number of catchments included in this study, further research is needed to better constrain the fate of pyrogenically modified stream DOM.

Wildfires in peatlands could be important sources of organic N and S to the stream DOM pool. Increasing concentration of organic N due to wildfires have been widely reported (Gustine et al., 2021; Paul et al., 2022; Rhoades et al., 2018). These compounds could enhance primary production, particularly in nutrient-limited streams (Brailsford et al., 2019; Mackay et al., 2020). The export of organic S requires further attention as peatlands are large S sinks (Novák et al., 2005). Organic S plays an important role in transport and bioavailability of Hg (Ravichandran, 2004). Structural information is necessary to better understand the reactivity of these compounds and their broader role as nutrient source or in the cycling of other elements. The frequency of wildfires in northern latitudes is expected to increase (Baker et al., 2025; Turetsky et al., 2014). Therefore, increased wildfire-modified DOM in streams could have several implications for water quality and drinking water management. For instance, the higher aromaticity and higher abundance of N- and S-containing molecular formulae could favor the formation of potentially harmful by-products during disinfection processes (Chen et al., 2023). This is particularly important in peatland dominated areas where the removal of high concentrations of DOC is required (Ferretto et al., 2021). In summary, this research showed how a combined assessment of thermal stability and molecular geochemistry offer complementary insights on the impacts of wildfire to stream DOM with modifications that are potentially preserved for years following the event.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Data supporting the findings of this manuscript is available at Zenodo, DOI: https://doi.org/10.5281/zenodo.16682506 (Mena-Rivera, 2025).

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