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Key Points:

- Ramped oxidation and isotopic analysis provide a framework for assessing organic matter transformation and fate across Arctic waters
- Supra-permafrost groundwater exhibits an aged but reactive mid-*E* component, indicative of biodegradable dissolved organic carbon
- River and lagoon carbon exhibits less reactive mid-*E* and high-*E* components, suggestive of oxidative age and stabilization

Supporting Information:

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

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Elucidating the Reactivity and Fate of Dissolved Organic Matter in Groundwater Entering the Alaska Beaufort Sea Coast Using ¹⁴C Ramped Oxidation

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Abstract Supra-permafrost groundwater (SPGW) is a significant but understudied source of dissolved organic matter (DOM) to Arctic coastal systems. We applied ramped pyrolysis/oxidation (RPO) with $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ isotopic analysis to assess DOM reactivity and origin in SPGW, river, and lagoon waters along the Alaska Beaufort Sea coast. Activation energy (*E*) profiles revealed shared low-*E* and mid-*E* components (~ 150 , 170 , 185 kJ mol^{-1}), underscoring compositional ubiquity across sites. However, SPGW exhibited a pronounced peak at 170 kJ mol^{-1} , indicative of biodegradable carbon, while lagoon DOM showed a high-*E* peak at 204 kJ mol^{-1} , suggesting oxidative aging and stabilization. Isotopic signatures signal SPGW (640–1,020 yBP) and lagoon DOM (745–995 yBP) were derived from older carbon pools, contrasting the modern signatures of riverine DOM. These results highlight SPGW as a dominant late-season source of reactive DOM to lagoons, demonstrating a novel framework for tracing DOM transformation and fate in Arctic coastal environments.

Plain Language Summary Groundwater flowing above permafrost carries large amounts of dissolved organic matter (DOM) from land to Arctic coasts. Studying the reactivity of this DOM helps clarify its role in coastal ecosystems and how climate change may affect carbon cycling. Using a new technique to examine patterns in activation energy associated with thermal oxidation (ramped pyrolysis/oxidation, RPO) alongside indicators of carbon source, composition, and biodegradability, we assessed the reactivity and origin of DOM in groundwater, river, and lagoon waters of Alaska's Beaufort Sea coast during the summer. Our results reveal that groundwater DOM comes from older soils but contains a distinct, moderately reactive fraction, making it more biodegradable than river or lagoon DOM. In contrast, river and lagoon DOM contains less reactive fractions, signaling that prior degradation and stabilization lower its biodegradability. Importantly, older carbon ages of groundwater overlapped with lagoon DOM, indicating that groundwater is a major source of reactive DOM to lagoons in late-summer.

1. Introduction

Arctic coastal environments and the watersheds they drain into are undergoing rapid and unprecedented change (Feng et al., 2021; Irrgang et al., 2022; Sejr et al., 2024). As rising temperatures and shifting hydrologic regimes reshape permafrost landscapes, the movement of water and water-borne materials is being altered by a suite of geomorphic and ecological responses, signaling a pervasive, systematic shift in biogeochemical connectivity throughout the land–ocean Arctic system (Tank et al., 2023). Studies on the transport and transformation of organic matter (OM) across the land–sea continuum are critical to broaden understanding of the impacts to carbon cycling in the Arctic. Among the key pathways that mobilize land-derived OM to the Arctic coast, supra-permafrost groundwater (SPGW) has emerged as a significant but understudied conduit for the transport of dissolved organic matter (DOM) to Arctic coastal waters, motivating recent efforts to further understand its influence on coastal biogeochemical cycling (Bristol et al., 2026; Connolly et al., 2020; Demir et al., 2024; Guimond et al., 2023).

SPGW is ubiquitous across Arctic permafrost landscapes during the thaw season, forming within a shallow, saturated active layer (Walvoord & Kurylyk, 2016). Coastal soils and permafrost contain large reservoirs of OM capable of rapidly leaching DOM, resulting in SPGW that is enriched in dissolved organic carbon and nitrogen (DOC and DON) as it enters Arctic coastlines (Connolly et al., 2020; Ping et al., 2011). Between the hydrologic spring and summer, northern high-latitude flowpaths transition from snowmelt-dominated surface runoff to rainfall-driven groundwater flow, during which time river export to the coastal ocean diminishes as SPGW

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contributions increase markedly (Frey & McClelland, 2009; Holmes et al., 2012; Rawlins et al., 2021). Notably, summer DOC and DON fluxes from SPGW rival those of smaller river export and coastal permafrost erosion along Arctic coastlines (Bristol et al., 2021; Connolly et al., 2020; Demir et al., 2024; Guimond et al., 2023).

The biogeochemical role of SPGW may be especially pronounced in Arctic lagoon systems, which encompass well over half of the Alaska Beaufort Sea coastline (Bullock et al., 2024; Dimova et al., 2015; Lecher, 2017). These productive, shallow, semi-enclosed estuaries support active microbial communities and sustain critical habitat for migratory birds, fish, and marine mammals (Pedersen & Linn, 2005; von Biela et al., 2011, 2022; Crump et al., 2023). Lagoon geomorphology, particularly the protection offered by barrier islands, limits ocean exchange and enhances the retention of terrestrial OM that subsidizes the diets of local fauna (Dunton et al., 2012; Harris et al., 2018; Stanek et al., 2024). As a result, lagoon water column processes and food web structure are strongly influenced by land-derived OM (Connolly et al., 2015; Dunton et al., 2006; Kellogg et al., 2019). Along coastlines without rivers and during the summer/fall when river flow is low, SPGW represents the principal source of terrestrial-freshwater DOM to lagoons.

With this increasing recognition, recent work has sought to understand the composition and biodegradability of SPGW DOM entering Arctic estuaries (Bristol et al., 2026). The DOM found in Arctic rivers during the summer is relatively young but recalcitrant (Behnke et al., 2021; Holmes et al., 2008; Mann et al., 2015; Vonk et al., 2015), whereas the DOM in coastal SPGW is older but more labile (Bristol et al., 2026; Connolly et al., 2020). The older age likely reflects movement of SPGW through deeper soil layers near the land-estuary interface (Connolly et al., 2020), whereas its greater lability may be related to protection from photodegradation and/or retention of a bioavailable DOM pool during the short and direct transit of SPGW from coastal tundra soils to the estuaries (Bristol et al., 2026). As climate change intensifies permafrost thaw and increases groundwater flow, SPGW is expected to become a more prominent source of land-derived carbon and nutrients to Arctic coastal waters (Frey & McClelland, 2009; St. Jacques & Sauchyn, 2009; Walvoord et al., 2012), reinforcing the need to further understand its fate in Arctic coastal environments.

Here we employed ramped pyrolysis/oxidation (RPO) coupled with stable carbon ($\delta^{13}\text{C}$) and radiocarbon ($\Delta^{14}\text{C}$) isotope analyses to assess DOM reactivity and origin across interconnected hydrologic systems. The RPO instrumentation was set to oxidation mode for this work. RPO-isotopic analysis is a relatively new technique, seldom used on DOM (Hemingway et al., 2019), with only one study known by the authors to date that has applied it to Arctic (river and permafrost) DOM (Rogers et al., 2021). As configured for this study, RPO coupled to a regularized inverse model yields continuous distributions of activation energy (E) associated with thermal oxidation, an intrinsic property of molecular structure and bond strength used as a proxy for DOM reactivity (Hemingway, Rothman, et al., 2017). When paired with isotopic analysis of RPO fractions, their results can provide unique insight into DOM provenance, composition, and degradation state. While traditional measures of DOM composition often rely on bulk elemental, optical, or isotopic properties (e.g., C:N, CDOM, $\delta^{13}\text{C}$), which may conflate inputs from multiple sources and obscure underlying signatures that govern DOM reactivity and origin, RPO provides insight into the compositional reactivity of complex mixtures (Hemingway et al., 2019). When combined with high-resolution molecular fingerprinting via Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) and biodegradation estimates (BDOC), we improve our ability to jointly assess DOM sources and mixtures, transformation history, and biolability (Rogers et al., 2021; Spencer et al., 2015; Textor et al., 2019).

We applied RPO-isotopic analysis paired with FT-ICR MS and BDOC experiments to SPGW, river, and lagoon DOM endmembers collected during late-summer along the Alaska Beaufort Sea coast. This study focuses on elucidating the reactivity profiles of SPGW DOM relative to river and lagoon DOM, drawing connections to origin partitioning from isotopic compositions of RPO-derived E components. Insights gained from FT-ICR MS and BDOC were used to strengthen RPO-isotopic linkages to their respective biodegradable compositions and transformation histories.

2. Methods

2.1. Study Site and Sample Collection

This study was conducted along the eastern Alaska Beaufort Sea coast, where numerous small streams and rivers enter Arctic lagoons that experience seasonal shifts in environmental conditions due to shallow water depths,

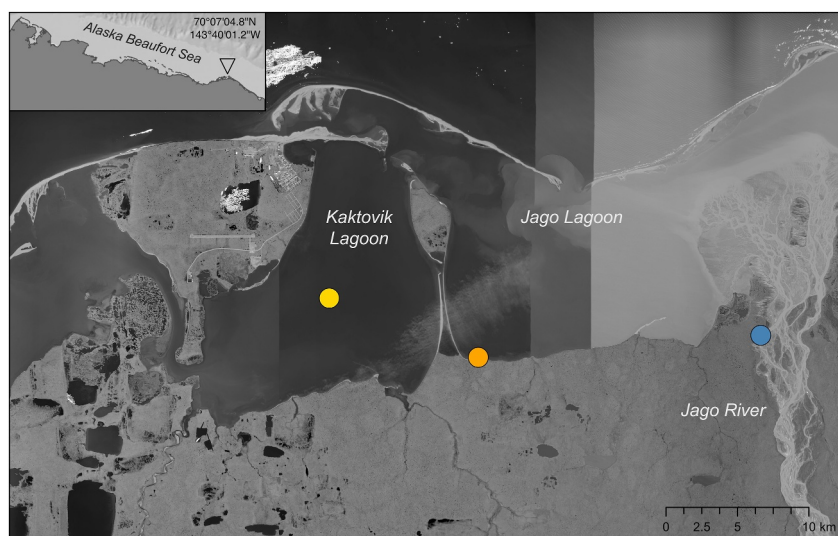


Figure 1. Study sites along the eastern Alaska Beaufort Sea coast where samples were collected for SPGW (orange circle), river water (blue circle), and lagoon water (yellow circle). The triangle point in the map inset marks the study site, with coordinates of Barter Island.

limited connectivity with the open ocean, and varying freshwater inflow (Harris et al., 2017). During the winter ice-covered period (November to May), inputs from land are minimal and lagoons largely contain marine water from the Beaufort Shelf, referred to herein as the Polar Mixed Layer (PML). Brine rejection during ice formation within the lagoons leads to the development of hyper-saline conditions over the winter (Harris et al., 2017). In late spring (mid-May to early-June), snowmelt facilitates an increase in runoff and accelerates sea-ice melt, freshening the lagoon water column, although hypersaline bottom waters (≥ 3 m) can persist in some areas (Harris et al., 2017; Macdonald et al., 1989). Riverine DOM inundates lagoons during the spring freshet, when rivers deliver over half of their annual supply of OM to the coast (Connolly et al., 2021; McClelland et al., 2014). During the summer open-water period (July to September), the lagoons experience greater water exchange with the open ocean, leading to estuarine conditions shaped by lagoon geomorphology and the degree of spring/summer runoff. Streams and rivers return to baseflow, while increases in SPGW inputs and coastal erosion provide new sources of DOM to the lagoons (Bristol et al., 2024; Connolly et al., 2020; Demir et al., 2024).

Water samples were collected on 17 August 2017 from SPGW, river water (Jago River), and lagoon water (Kaktovik Lagoon) near Barter Island, USA (Figure 1). SPGW was collected from ten shoreline locations along the beach of Jago Lagoon using piezometers that were installed to ~ 1 m depth. A composite SPGW sample was made using equal parts groundwater from each beach location. River water was sampled from the edge of the Jago River's main channel near its delta, above tidal influence. Kaktovik Lagoon water was collected at 2–3 m depth in the water column. All water samples were collected using a peristaltic-pump attached with acid washed and Milli-Q rinsed Master-Flex tubing. Sample water was dispensed unfiltered into 1 L acid-washed and Milli-Q rinsed low-density polyethylene (LDPE) containers and transported in a cooler to the U.S. Fish and Wildlife facilities in Kaktovik, AK.

Kaktovik Lagoon was selected for this study because it lacks direct connection to the Beaufort Sea, experiences limited exchange with neighboring lagoons, and does not receive major river inputs, offering a unique opportunity to trace SPGW DOM signals in the lagoon environment. At the time of sampling, the lagoon water column exhibited strong stratification, with freshwater in the upper 2 m and salinity of 17–18 at 2–3 m depth. This latter depth was selected for sampling to capture representative late-season lagoon conditions (Harris et al., 2017). Based on prior work, we expect that Kaktovik Lagoon bottom water contained a mixture of overwintering PML water, spring runoff, and new summer additions from direct SPGW and small SPGW-fed streams (Harris et al., 2017). Additional details on lagoon conditions can be found in Text S1 in Supporting Information S1.

2.2. Ramped Pyrolysis/Oxidation and Isotopic Analysis

Serial thermal oxidation using RPO involves heating a sample at a controlled rate of 5°C per minute to 800°C while continuously quantifying and collecting oxidized CO₂, which is binned over user-defined temperature windows (i.e., “fractions”). Each fraction is then analyzed for its $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ compositions (Rosenheim et al., 2008). Serial thermal oxidation was performed using DOM from background SPGW, river, and lagoon samples on the RPO instrument set to “oxidation mode” at the Woods Hole Oceanographic Institution, National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility (Hemingway, Galy, et al., 2017; Plante et al., 2013). To prepare samples for RPO, DOM was concentrated by solid phase extraction (SPE) using 100 mg Bond Elut PPL cartridges and methods described in Dittmar et al. (2008). Five or six fractions were collected during serial oxidation where rising and falling CO₂ peaks were observed, reflective of shifts in the sources of OM being oxidized (Williams et al., 2014). ^{14}C and ^{13}C measurements were made using standard NOSAMS procedures (McNichol et al., 1994). $\delta^{13}\text{C}$ values were determined separately using a VG Prism Stable Mass Spectrometer. $\Delta^{14}\text{C}$ and radiocarbon age (yBP) were determined from percent modern carbon using the year of sample analysis (Stuiver & Polach, 1977).

Thermal profiles of CO₂ were transformed into non-parametric E distributions using a regularized inverse method described by Hemingway, Rothman, et al. (2017) with the “rampedpyrox” package in Python (Hemingway, 2017a). This process involves smoothing noise in the RPO instrument measurements and applying the inverse model to generate a probability density function that quantifies the E required to oxidize carbon to CO₂ over the full thermal profile. The distribution of E , or $p(0, E)$, represents the fraction of total carbon for a given E value. E is a quantitative measure of carbon bond strength that can be used to assess OM reactivity, where individual E components, often defined by a range of E values corresponding to $p(0, E)$ peaks, reflect distinct pools of reactive OM (Hemingway, Rothman, et al., 2017). Distinct E components mix conservatively (i.e., they do not form a peak at their average E value), and so evaluation of their distribution and peaks across OM types allow for comparisons of composition and mixtures (Hemingway et al., 2019). Of importance are the E values associated with maximum peaks containing the highest $p(0, E)$, or the highest proportion of carbon associated with a unique set of activation energies, which is correlated to the presence of DOM molecular formulas linked to its bioavailability (Rogers et al., 2021). Additional information on SPE, RPO, and the regularized inverse methodology can be found in Text S2 in Supporting Information S1.

2.3. Biodegradable Dissolved Organic Carbon

Biodegradable DOC (BDOC) experiments were conducted using a standard procedure described by Vonk et al. (2015). Following field collection, water samples were filtered through pre-combusted (450°C for >5 hr) GF/F glass microfiber filters (0.7 μm) into 125 mL acid-washed and Milli-Q rinsed polycarbonate bottles. BDOC experiments were initiated by incubating triplicate sets of each sample type in the dark at 20°C for 0 and 28 days. Samples for the 0-day time point were frozen after filtration and thus represent background DOM. At each subsequent time point, samples were re-filtered through pre-combusted GF/F filters and frozen for preservation. Concentrations of DOC were quantified using a Shimadzu TOC analyzer at the University of Texas at Austin, Marine Science Institute.

2.4. Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

We measured DOM composition via FT-ICR MS to derive molecular formulas from background SPGW, river, and lagoon water samples and following biodegradation. SPE-DOM was extracted from BDOC 0-day and 28-day samples, then analyzed for their FT-ICR MS compositions. SPE-DOM extracts were stored at −20°C before analysis on a 9.4 T FT-ICR MS at the National High Magnetic Field Laboratory (Tallahassee, Florida, USA) with the instrument set to negative ion mode. Molecular formulas were categorized into the following compound classes based on their elemental stoichiometry and modified aromaticity indices: (a) highly unsaturated and phenolic high oxygen (HUP high O/C), (b) highly unsaturated and phenolic low oxygen (HUP low O/C), (c) polyphenolic, (d) condensed aromatic, (e) aliphatic, and (f) peptide-like (Koch & Dittmar, 2006; O'Donnell et al., 2016; Santi-Temkiv et al., 2013). Relative abundances (RA) were estimated from the number of molecular formulas assigned to each compound class using Python (Hemingway, 2017b). Further details on SPE and FT-ICR MS methodology can be found in Text S3 in Supporting Information S1.

3. Results and Discussion

3.1. DOM Reactivity and Isotopic Assessment

RPO analysis revealed similar CO₂ thermoprofiles between SPGW and river DOM, oxidizing between ~200 and 550°C, with peaks at 458°C and 510°C (Figure S1 in Supporting Information S1). Lagoon DOM oxidized over a broader temperature range between ~200 and 700°C, with two peaks at 524°C and 578°C. Activation energy (*E*) distributions overlapped across all endmembers between ~100 and 190 kJ mol⁻¹, with two reproducible peaks in *p*(0, *E*) centered at ~170 and 185 kJ mol⁻¹ (Figure 2). SPGW and river DOM were distinguished by more prominent peaks at 170 and 185 kJ mol⁻¹, while lagoon DOM exhibited much lower peaks at 170 and 185 kJ mol⁻¹ as well as a broader *E* distribution with a unique high-*E* peak at 204 kJ mol⁻¹ (Figure 2). *E*_{max} and *E*_{mean} values of the full *E* distribution increased from our SPGW to river to lagoon endmembers (Table S1 in Supporting Information S1) and were typically higher than those reported of other DOC types (Hemingway et al., 2019; Rogers et al., 2021).

Broadly speaking, these results show that summer DOM across SPGW, river, and lagoon sites share thermal reactivity characteristics. SPGW contains a more thermally reactive DOM component evident by a greater *p*(0, *E*) peak at 170 kJ mol⁻¹, suggesting the potential presence of bioavailable material that is absent in rivers and lagoons. SPGW flow paths deepen near the land-lagoon interface, and consequently, SPGW accesses deeper leachable carbon pools that circumvent degradation as it enters the lagoons (Connolly et al., 2020). The favorable OC bond strength of unprocessed, bioavailable DOM compounds found in SPGW is the likely basis of this reactivity component and may play a pivotal role in enhancing its utilization in the lagoon environment.

In contrast, river and lagoon DOM may contain similar SPGW-derived material but in a more altered/degraded state due to photo-oxidation and microbial processing (Cory et al., 2014). While SPGW and river DOM *E* distributions are similar, trends in the reduction of *p*(0, *E*) intensity at overlapping peaks and the shift toward higher *E*_{max} and *E*_{mean} values across our endmembers corroborate an increase in oxidation state and stabilization from SPGW to river to lagoon DOM (Table S1 in Supporting Information S1; Figure 2). Notably, the broad, high-*E* tail in lagoon DOM may reflect greater cumulative effects of photo/biodegradation, with the high-*E* peak at 204 kJ mol⁻¹ signaling the presence of a stable, highly transformed component that has not yet been oxidized in SPGW and riverine DOM. Among the few *E* distributions measured of DOC by other studies, most have one or two prominent peaks at <180 kJ mol⁻¹ (Hemingway et al., 2019; Rogers et al., 2021), but none have an *E*_{max} > 200 kJ mol⁻¹ that was observed in our lagoon endmember. Rather, this broad high-*E* tail and peak in lagoon DOM is more similar to that of stabilized OC (Hemingway et al., 2019).

All DOM types exhibited depleted δ¹³C values between -30‰ and -26.5‰ (Table 1), consistent with terrestrial signatures across Arctic Alaska rivers and coastal waters (Dunton et al., 2012; Raymond et al., 2007). Lagoon DOM is more enriched in δ¹³C, increasing with *E*, signaling a portion of highly oxidized terrestrial or marine-derived material from the PML (Druffel et al., 2017). While our δ¹³C results alone did not resolve SPGW and river DOM origin and contributions, radiocarbon signatures (Δ¹⁴C) from RPO fractions offered a more discriminating proxy. SPGW and lagoon DOM exhibited overlapping ¹⁴C-DOC ages, ranging from 640 to 1,020 yBP and 745 to 995 yBP, respectively (Table 1; Figure 2), signaling that SPGW DOM is a significant component of the summer lagoon environment. In contrast, riverine DOM displayed modern ¹⁴C-DOC signatures, with exception of a small, aged (440 yBP), low-*E* component (Table 1; Figure 2), indicating that river DOM is dominated by modern surface soil inputs and/or there are disproportionate losses of aged DOC during transport through the river network. The divergence between SPGW and river ¹⁴C-DOC is most likely due to differences in subsurface hydrology, which controls DOC production and its routing through the active layer (Neilson et al., 2018). While SPGW near the land-lagoon interface accesses older and deeper soil carbon (Connolly et al., 2020), SPGW is constrained to a shallower active layer farther inland. During saturated summer conditions, SPGW rapidly flows through a shallow organic mat (<10 cm) rich in recently formed, highly leachable soil OM, where hydraulic conductivity far exceeds that of underlying mineral horizons, making modern surface-derived carbon the dominant source of stream DOM (Khosh, 2015; Neilson et al., 2018; O'Connor et al., 2019, 2020).

To further resolve the presence of SPGW DOM in the lagoon environment, it is important to consider the possibility that our lagoon endmember contains a mixture of aged DOC from the PML and modern DOC from spring runoff, resulting in an isotopic signature that resembles our measured lagoon composition. To examine whether DOC contributions from the PML and spring runoff can account for our summer lagoon δ¹³C and Δ¹⁴C-DOC

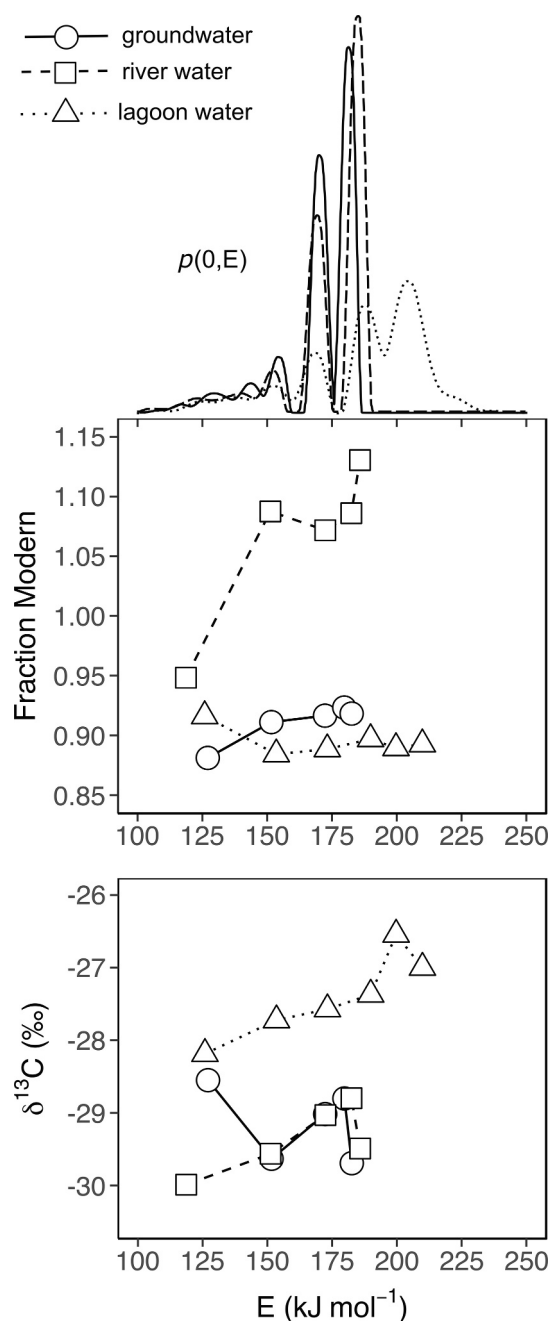


Figure 2. Top: regularized $p(0, E)$ distributions from SPE-DOM of SPGW (labeled as groundwater; solid line), river (dashed line), and lagoon (dotted line) endmembers. The area under each $p(0, E)$ curve integrates to 1. Only $p(0, E)$ between 100 and 250 kJ mol^{-1} is shown, $p(0, E)$ outside this range is at or near zero. Middle and bottom: plots of mean E values versus Fm and fractionation-corrected $\delta^{13}\text{C}$ of SPE-DOM RPO fractions.

lagoon DOM at similar or higher abundances, these common formulas showed little sign of biodegradation. Although phenolic and aromatic formulas are generally resistant to biodegradation (Freeman et al., 2001; Mann et al., 2014) and have been linked to low amounts of BDOC observed in Arctic streams and rivers (Mann et al., 2015), their degradation in SPGW but not river or lagoon DOM reveals that the OC bond strength and reactivity of this aromatic pool, rather than its mere presence, impacts its biodegradability.

signatures, we applied an endmember mixing model similar to Harris et al. (2017) (Text S4 in Supporting Information S1). Using the endmembers shown in Table S2 in Supporting Information S1, we estimate that 78.6% of lagoon DOC would be derived from spring runoff and 21.4% from the PML in this scenario, resulting in $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of -49.2‰ and -26.1‰ , respectively. While our bulk lagoon $\delta^{13}\text{C}$ composition (-27.4‰ , fraction total) may be achievable from a mixture of DOC from the PML and spring runoff, our lagoon $\Delta^{14}\text{C}$ signature (-115.4‰ , fraction total) is much lower than expected if it contained only these two sources. Although inputs of DOC via coastal erosion and submarine groundwater discharge may also contribute to an aged lagoon DOC pool, these simple model results reinforce that SPGW is the primary late-season source of terrestrial DOM to lagoons lacking major river inputs.

3.2. Biodegradable DOC and DOM Composition

Our findings build upon a seasonally comprehensive study conducted by Bristol et al. (2026), who characterized DOM composition and biodegradability across SPGW, river, and lagoon waters near Simpson Lagoon, AK. Their work demonstrated that DOM biodegradability varies markedly across seasons and water types, driven by shifts in hydrologic connectivity and degradation along the SPGW–river–lagoon continuum. Notably, SPGW DOM was both aromatic and biodegradable, with BDOC of 17.9% in spring and 7.6% in mid-summer over 28 days, whereas river and lagoon DOM exhibited lower spring-summer BDOC, consistent with a decline in SPGW inputs to rivers and an increase in photochemical and microbial processing that occurs between spring and summer.

Our BDOC results confirm that SPGW DOM remains moderately biodegradable (4.5% over 28 days) as the summer progresses, despite its highly aromatic composition (Table S3 in Supporting Information S1). Although its percentage of BDOC is modest, concentrations of summer SPGW DOC are very high (28 mg C L^{-1} in Table S3 in Supporting Information S1, median $\sim 49 \text{ mg C L}^{-1}$ from 7/21–8/17 data), resulting in considerable absolute losses of DOC (Bristol et al., 2026; Connolly et al., 2020; Demir et al., 2024). Its pronounced $p(0, E)$ peak at 170 kJ mol^{-1} aligns with this observation, reinforcing the presence of a reactive, biodegradable DOM component. FT-ICR MS characterization further corroborates these findings: we found higher pre-incubation, background relative abundances of polyphenolic and condensed aromatic compounds (14.6% RA) and observed a reduction of CHO-type compounds typical of lignin-rich material, features previously linked to SPGW DOC biodegradability (Figures S2 and S3 in Supporting Information S1; Bristol et al., 2026). By contrast, river and lagoon DOM exhibited substantially lower DOC concentrations (5.0 and 2.3 mg C L^{-1}) and BDOC content (1.8% and 0.6%), the latter is consistent with their higher E_{max} and E_{mean} values, and in the case of lagoon DOM, its broader high- E distribution. Both also contained lower abundances of polyphenolic and condensed aromatic compounds (10.5% and 10.6% RA), and while all formulas in SPGW that decreased by $\geq 2\%$ RA from biodegradation were also present in river and

Table 1*Temperature Range, Activation Energy (E), and Isotopic Data for Each RPO Fraction (f) Collected From SPE-DOM Endmembers*

Endmember	f	Temperature range (°C)	E (kJ mol ⁻¹)	¹⁴ C age (yr BP)	Fraction modern	δ ¹³ C (‰)	C trapped (μg C)
SPGW	1	103–295	127 ± 10	1,020	0.881	–28.5	305
	2	295–382	152 ± 11	750	0.911	–29.6	521
	3	382–458	172 ± 7	700	0.917	–29.0	1,824
	4	458–510	180 ± 4	640	0.923	–28.8	1,214
	5	510–539	183 ± 2	685	0.918	–29.7	162
River	1	102–243	119 ± 8	440	0.948	–30.0	155
	2	243–401	151 ± 15	>Modern	1.087	–29.6	647
	3	401–451	172 ± 7	>Modern	1.072	–29.0	708
	4	451–510	182 ± 6	>Modern	1.086	–28.8	1,089
	5	510–564	186 ± 2	>Modern	1.130	–29.5	450
Lagoon	1	110–283	126 ± 9	745	0.916	–28.2	70
	2	283–411	154 ± 12	995	0.884	–27.7	181
	3	411–460	173 ± 10	955	0.889	–27.6	123
	4	460–524	190 ± 8	875	0.897	–27.4	245
	5	524–577	200 ± 7	940	0.890	–26.5	299
	6	577–682	210 ± 7	915	0.893	–27.0	261

Note. Values for *E* are the mean ± 1 standard deviation calculated from the distribution of *E* values associated with each fraction. Analytical error for δ¹³C is ±0.15 (1 standard deviation). Analytical error in ¹⁴C measurements is very small so and was not included in the table.

Patterns in DOM formulae diversity and RPO-isotopic provenance further resolve the role of hydrologic connectivity and source contributions across our endmembers. Consistent with their overlapping *E* distributions and shared *p*(0,*E*) peaks, nearly all molecular formulas in SPGW (93.6%) were also present in river (63.1%) and lagoon DOM (55.1%), whereas the proportion of formulas unique to each endmember increased from SPGW (2.7%) to river (11.8%) to lagoon (22.8%) (Figure S4 in Supporting Information S1). These results confirm the ubiquity of SPGW-derived DOM across our endmembers, while also indicating that downstream processes or additional sources introduce new formulae diversity. The increase in unique formulas and *E*_{mean} values from river to lagoon DOM tracks with expectations of progressive photochemical and microbial transformation during the summer (Cory et al., 2014), with lagoon DOM experiencing greater expected processing. Lagoon DOM exhibited greater diversity of N- and S-containing formulas (Figure S4 in Supporting Information S1), likely also reflecting autochthonous inputs and cycled DOM from the PML and submarine groundwater discharge (Connolly et al., 2021; Sleighter and Hatcher, 2008). Although the increase in molecular diversity from our SPGW to river endmember can be attributed to an increase in degradation byproducts, their formulae totals more closely resemble that of the spring (Bristol et al., 2026), suggesting that rivers receive surface-derived SPGW inputs during the summer when hydrologic connectivity is high. This is supported by the modern Δ¹⁴C signatures of our river endmember and its compositional similarity to DOM leached from the surface organic mat (Figure S4 in Supporting Information S1; Ward & Cory, 2015).

3.3. A Mechanistic Framework for DOM Reactivity and Fate

Together, our findings support a conceptual model in which summer SPGW delivers a minimally transformed, aromatic, and moderately reactive DOM pool sourced from deeper soils to Arctic lagoons of the Alaska Beaufort Sea coast. Given that SPGW contains very high concentrations of DOC, even its modest percentage of biodegradable DOC is expected to yield significant losses of DOM that promote coastal biogeochemical cycling. River and lagoon DOM may contain similar SPGW-derived molecular and reactive chemical structures (river more so than lagoon DOM) but are increasingly stabilized or transformed through microbial processing and photo-degradation. For river DOM, photo- and bio-decomposition during transit through the river network likely contributes to its more limited biodegradability. In lagoon systems with little river influence and restricted ocean

exchange, SPGW may represent the dominant late-season source of DOM, adding to an OM pool that includes benthic-circulated, internally produced, and eroding coastal material. However, the window during which biodegradable DOC in groundwater entering river networks and lagoons remains accessible appears to be relatively short, resulting in a more stable DOM pool in river and lagoon environments. Our results imply that the fate of DOM across the land–lagoon interface depends on its composition, origin, hydrologic routing, and transformation history—factors that collectively govern the reactivity and cycling of DOM.

Conflict of Interest

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

Availability Statement

All data in this study are publicly available at Connolly (2025). The Environmental Data Initiative (EDI) Data Portal requires users to login to access data package summaries.

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