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Direct and Indirect Effects of Water-Table Levels on Redox-Active Organic Matter Reduction in an Alaskan Rich Fen

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Key Points:

- Ecosystem-level, indirect effects of water-table levels on redox-active organic matter (RAOM) reduction are captured during a common substrate peat experiment
- RAOM was the most reduced at the Raised experimental plot and this pattern persisted even when all plots were flooded
- Laboratory incubation results suggest that greater RAOM reduction in the Raised plot was due to differences in microbial processing

Supporting Information:

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

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Abstract Redox-active organic matter (RAOM) reduction is an important control on methane production in northern peatlands, but it is unclear how global climate change will affect RAOM reduction. We investigated the effects of water-table levels on RAOM reduction by leveraging a long-term water-table manipulation experiment in an Alaskan fen, which includes Lowered and Raised treatment plots relative to a Control. Common substrate peat was incubated in each plot during one summer of experimental manipulation and another summer of site-wide flooding. During experimental manipulation, common substrate RAOM was more reduced in the Raised plot than the Lowered plot at both 10–20 cm (19.1 ± 0.8 vs. 0.7 ± 0.3 μmol e^{-} g^{-1} dw peat, $p = 0.003$) and 30–40 cm (18.0 ± 0.5 vs. 3.6 ± 1.2 μmol e^{-} g^{-1} dw peat, $p = 0.011$). During site-wide flooding, differences in common substrate RAOM persisted with greater RAOM reduction in the Raised plot than both Control and Lowered plots ($p < 0.05$) and greater methane production from Raised plot common substrate. A comparison of the chemical composition of Raised and Control peat during an anaerobic laboratory incubation showed that the compounds removed during microbial processing differed between plots with a higher double bond equivalence to carbon ratio for the Raised plot (0.54 ± 0.13) compared to the Control plot (0.44 ± 0.17). Together, these field and laboratory results suggest that long-term increases in water-table levels can have complex effects on RAOM beyond oxygen availability with the potential to impact methane production from northern peatlands.

Plain Language Summary Global climate change is expected to affect peatland processes that control the production of greenhouse gases including methane. One key, understudied process is the microbial use of organic molecules as electron acceptors during respiration (called organic matter reduction) in these oxygen-limited environments. To better understand peatland response to global climate change, we studied how long-term differences in water-table levels in an Alaskan fen would affect organic matter reduction. We incubated a well-mixed peat sample in three different water-table manipulation plots and found that organic matter reduction closely followed water-table level, but that legacy water-table levels still had an effect on these organic molecules even when all plots were completely flooded. Plots that had experienced higher water-table levels and higher organic matter reduction also had higher rates of methane production. Our results from in situ porewater chemistry and laboratory incubations of peat suggest that the differences in organic matter reduction observed at the peat surface may be due to a change in how microbes process carbon following long-term water-table changes. Taken together, these findings show that long-term changes to peatland water-table levels can have lasting effects on processes controlling peatland carbon cycling.

1. Introduction

Northern peatlands above 45°N latitude are large, natural sources of methane (CH_4), a potent greenhouse gas, to the atmosphere (Abdalla et al., 2016; Frolking et al., 2006). The water-logged, anaerobic conditions of northern peatlands enable methanogenesis, but CH_4 production rates vary widely across northern peatland ecosystems in part because of differences in the abundance of alternative, inorganic terminal electron acceptors (TEAs; nitrate, oxidized iron, sulfate etc.) within the soil (Bridgham et al., 2013; Lai, 2009). When these TEAs are reduced by microbes during anaerobic respiration, carbon dioxide (CO_2) is produced as a byproduct, and CH_4 production is suppressed because of the energetic favorability of inorganic TEA reduction over methanogenesis (Bridgham et al., 2013). There is now a large body of work demonstrating that the redox-active organic matter within peat (RAOM; defined by Valenzuela & Cervantes, 2021) is an underrecognized and important organic TEA for anaerobic microbial respiration in peatland ecosystems (Keller et al., 2009; Klüpfel et al., 2014; Rush et al., 2021; Walpen et al., 2018). The electron-accepting components of RAOM include both quinone moieties, which act as reversible TEAs, and double-bonded carbon molecules, which serve as a permanent electron sink via hydrogenation (Wilson et al., 2017). Regardless of the redox-active component, the reduction of RAOM within the peat suppresses CH_4 production in peatlands mainly via its energetic favorability over methanogenesis (Gao et al., 2019; Keller & Takagi, 2013; Wilson et al., 2017). Obradović et al. (2024) estimated that competitive suppression of CH_4 by RAOM could explain lower CH_4 production in peatland ecosystems by $\sim 33 \times 10^5$ mol CH_4 km^{-2} per year, playing a key role in regulating peatland carbon (C) cycling. Despite its importance, the effects of a changing climate on RAOM reduction in northern peatlands are unknown.

One global change driver currently affecting northern regions is changing precipitation patterns with predictions of more intense rainfall events followed by increased periods of drought on the landscape (Barel et al., 2021; Lehmann et al., 2015). The changes in hydrology mean northern peatlands are experiencing more extreme fluctuations in water-table levels both within growing seasons and from year-to-year (Zhong et al., 2020). Changes in water-table levels relative to peat surface can have direct effects on RAOM reduction because the water-table directly regulates oxygen availability, and redox states, along the peat profile (Niedermeier & Robinson, 2007; Urquhart & Gore, 1973). The direct effects of oxygen availability on RAOM redox state have been explored previously in laboratory studies (Gabriel et al., 2017; Klüpfel et al., 2014) but only recently have studies moved from the laboratory to explore direct effects in field environments. Rush et al. (2021) was one of the first in situ studies to show progressive reduction of RAOM within the peat relative to different water-table levels in a peatland ecosystem. Obradović et al. (2024) took this approach a step further and showed that an oxidized, reference RAOM material was reduced when incubated below the water-table in a series of ombrotrophic bogs. These studies demonstrate the potential for in situ RAOM reduction, but whether this holds across different water-table levels and different peatland types needs to be explored.

Additionally, while these field-based in situ studies of RAOM reduction have been crucial to our growing understanding of the direct effects (Rush et al., 2021), the indirect effects of long-term water-table level shifts on RAOM reduction remain largely unknown (see Zhang & Furman, 2021). Changes in water-table levels may indirectly alter RAOM reduction by affecting peat plant communities, which will impact peat composition, microbial activity, and dissolved organic matter (DOM) composition (Rober et al., 2023; Wyatt et al., 2024). For example, a sustained drop in water-table levels over multiple growing seasons can increase ericaceous shrub community abundance (Breeuwer et al., 2009; Potvin et al., 2015) leading to a change in peat composition by introducing inputs of decaying organic matter with higher levels of aromaticity, conjugated moieties, and phenolic moieties compared to inputs from mosses or sedges (Wu & Roulet, 2014). Given that these compounds are expected to be constituents of RAOM (Klavins & Purmalis, 2013), this shift in peat composition via indirect water-table level effects could lead to changes in RAOM reduction. Conversely, higher water-table levels may lead to greater sedge abundance, and subsequent increases in microbial colonization around the rooting zone as sedges support more oxidized rhizospheres (Rupp et al., 2021). Both increased sedge abundance and microbial colonization may change rates of RAOM reduction by adding more simple C substrates for respiration (Yan et al., 2022) and stimulating microbes to utilize more complex compounds, like RAOM, as a TEA (Kuzyakov & Blagodatskaya, 2015; Yin et al., 2013). These interactions between changes in vegetation and microbial communities can also affect the composition of DOM available for anaerobic respiration (Reiche et al., 2010). Many studies have focused on water-table induced changes to peatland C quality in the DOM pool (Haapalehto et al., 2014; Hribljan et al., 2014; Strack et al., 2008) but few have looked at the solid-phase C pool. Taken together, the current literature demonstrates the complex, indirect effects of water-table levels on anaerobic C cycling, emphasizing the need for more in situ studies to understand how climate-induced changes to peatland water-table levels affect processes such as RAOM reduction and subsequent CH_4 production.

Considering this knowledge gap, we investigated the effects of water-table level on the reduction of RAOM within peat (herein referred to as "RAOM reduction") via two research questions: (a) What are the *direct* effects (i.e., oxygen availability) of water-table levels on RAOM reduction? and (b) What are the long-term, *indirect* effects of water-table levels on RAOM reduction? We approached these questions by leveraging a long-term

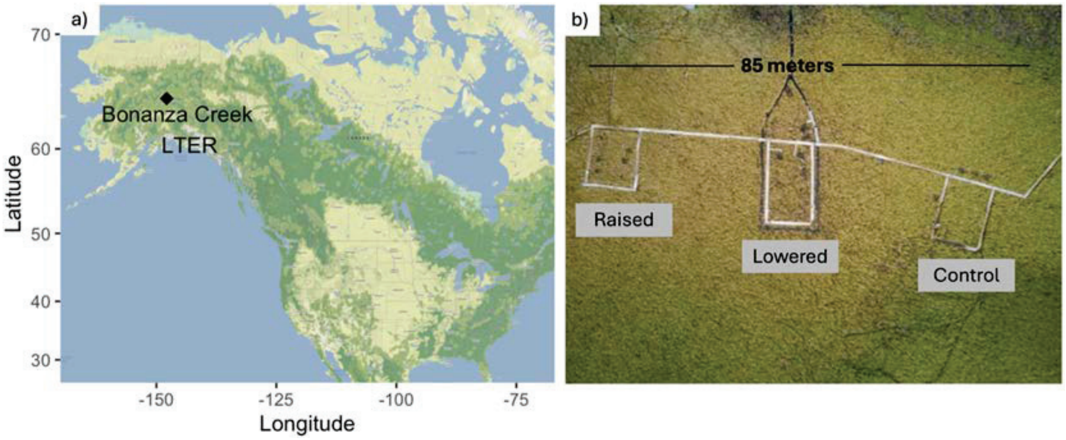

Figure 1. Depictions of the study site. (a) Location of the Bonanza Creek Long-Term Ecological Research Site in interior Alaska (made using ggmap; Kahle & Wickham, 2013). (b) Aerial view of the Alaskan Peatland Experiment site with Raised, Lowered, and Control plots from left to right. Photo credit: Evan Schijns.

(15 years) water-table manipulation experiment in a rich fen in Alaska. Fens are one of the most common peatland types in boreal regions of North America, and the C storage in these systems is more sensitive to the effects of global climate change than in other peatland types, experiencing prolonged periods of both drought and flooding (Vitt, 2006; Wu & Roulet, 2014). Our study site, the Alaskan Peatland Experiment (APEX), has been undergoing water-table level manipulation since 2005, providing unique insights into the long-term cumulative effects of water-table level fluctuations on peatland C stores; a key knowledge gap outlined in reviews of peatland climate research (Loisel & Gallego-Sala, 2022; Page & Baird, 2016). The APEX site includes three, 120-m^2 experimental plots: Raised and Lowered water-table plots that are relative to a Control plot (Turetsky et al., 2008). On average, the water-table level is 9 cm lower in Lowered and 10 cm higher in Raised relative to the Control (Olefeldt et al., 2017). This water-table manipulation was maintained during each growing season for ∼7 years until the site underwent flooding in the summers of 2012, 2013, 2014, 2017, 2018, 2020, and 2022 (Euskirchen et al., 2020; Kane et al., 2021; Olefeldt et al., 2017). During these flooded years, all experimental plots, regardless of assigned water-table treatment, were completely submerged. The long-term water-table manipulation, combined with sporadic flooding years, offers an opportunity to investigate the effects of water-table level changes on RAOM reduction over time.

We designed a series of experiments to investigate direct and indirect effects of water-table levels on RAOM reduction at the APEX site in a series of experiments. We investigated (a) the direct effects of water-table level on RAOM reduction and indirect effects of ∼15 years of water-table level manipulation mediated by changes in (b) DOM composition and (c) changes in solid-phase C composition. We hypothesized that water-table level would be a strong control on RAOM reduction with RAOM being the most reduced in the Raised plot during a non-flooded year. However, during a flooded year—when all plots were fully submerged—we hypothesized that RAOM reduction would be similar among plots as oxygen availability would be a stronger control on reduction than differences in DOM composition. Finally, we hypothesized that ∼15 years of water-table level manipulation would lead to changes in peat composition among the plots and that these changes would impact RAOM reduction and C greenhouse gas production. By using a combination of in situ field and laboratory techniques to determine multiple consequences of water-table level changes on RAOM reduction, we provide greater insight into how RAOM reduction, CH_4 production, and, more broadly, how peatlands may respond to global climate change.

2. Materials and Methods

2.1. Study Area

The APEX site (Figure 1) is in the Tanana River floodplain just outside the boundary of the Bonanza Creek Experimental Forest near Fairbanks, Alaska (64.70°N, 148.31°W). Interior Alaska is classified as a boreal region with a mean annual air temperature of −2.9°C and mean annual precipitation of ∼269 mm (Hinzman et al., 2006). The site is characterized as a moderate to rich fen (surface water pH 6.0–6.5) and is comprised of vascular species

(*Carex*, *Comarum*, and *Equisetum*), brown moss, and *Sphagnum* (Chivers et al., 2009; Kane et al., 2010; Turetsky et al., 2008). In situ water-table manipulation has led to a decrease in sedge abundance in the Lowered plot relative to the Control and Raised plots (Churchill et al., 2015; Rupp et al., 2021). The peat depth is ∼1 m and has no distinct microtopography (Turetsky et al., 2008).

2.2. Peat Peeper Design and Peat Core Collection

To investigate in situ differences in RAOM reduction between the water-table manipulation plots, we employed "peat peepers", a design inspired by the peepers typically used in sampling aquatic ecosystems (see Risacher et al., 2023). Peat peepers were constructed from ∼2.5 cm diameter PVC pipes with 16, ∼0.6 cm holes drilled along 10 cm increment sections along the sides, allowing for equilibration between the inside of the pipe and the surrounding soil environment. Peepers were 60 cm long and capped on the top and bottom to prevent water flowing in from either end. The depth increments used for this study were 0–10, 10–20, and 30–40 cm below the peat surface.

Three replicate peat peepers were installed in each plot. Peepers were installed by first sampling to 40 cm below the peat surface using a sharpened, stainless-steel corer (∼2.5 cm diameter) with a drill bit attachment (Nalder & Wein, 1998). Peat was removed and peepers were immediately installed in its place. Peat core samples were shipped overnight, on ice, to Chapman University (Orange, CA) and frozen (−20°C) until analysis (described below in Section 2.5). Within each peat peeper, we inserted mesh packets of homogenized commercial peat (Premier 0128P peat moss; referred to herein as "common substrate peat") at the three depth increments in the peeper. The depth increments used for this study were 0–10, 10–20, and 30–40 cm below the peat surface. We used a common substrate to remove confounding effects of peat heterogeneity (solid-phase peat composition) when measuring RAOM reduction, thereby isolating effects of water-table levels. Approximately 5 g of dry, sieved (≤20 mm) homogenized peat was wrapped inside a 15 × 15 cm square of 35 μm nylon mesh, rolled, and secured with hot glue. Mesh packets were attached to a rod and placed inside the peat peeper at their corresponding depths for equilibration with the in situ soil environment.

2.3. Direct Effects: RAOM Reduction in Common Substrate Peat

In Summer 2021, common substrate peat was deployed in the peat peepers once water-table manipulation began in each plot (early July). Water-table levels were measured at 5 locations within each plot four times during the field incubation (see Figure 2a for water-table levels). Packets were collected after ∼1 month of water-table manipulation and at peak water-table separation among the plots (Figure 2a). Porewater was collected from corresponding depth increments next to each peat peeper using a stainless-steel sipper (∼100 cm in length with a 2 cm slotted region wrapped in 35 μm nylon mesh) and syringe. We filled 50 mL centrifuge tubes with porewater and quickly pulled the peat packets from the peepers and submerged them in the porewater. Tubes did not have headspace and were capped immediately to preserve in situ redox conditions. If peat packets were collected from above the water-table, they were placed in tubes with no added porewater. Samples were kept on ice and shipped overnight to Chapman University (Orange, CA). Upon arrival, the tubes were immediately centrifuged at 4,000 rpm for 5 min and stored at 4°C to allow for settling of particulates.

Less than 24 hr after arrival, samples were brought into an anaerobic chamber filled with <2% H_2 and a balance of N_2 (Coy Laboratory Products, Grass Lake, Michigan, USA). The peat packets were removed from the porewater in the centrifuge tubes, cut open, and peat was homogenized in a plastic weigh boat. Approximately 3 g of field-moist peat was added to a preweighed 50 mL centrifuge tube and used to measure electron shuttling capacity (ESC) following the methods by Keller and Takagi (2013). This assay allowed us to measure the approximate redox state of RAOM via electron shuttling from reduced RAOM to an oxidized iron solution (further details in Text S1 in Supporting Information S1). Solid-phase ESC is reported as μmol e^- g^{-1} dry weight peat with higher values indicating more reduction of the RAOM.

2.4. Indirect Effects: RAOM Reduction in Common Substrate Peat and DOM Composition

2.4.1. Common Substrate Collection During a Flooded Year

Following collection of the initial common substrate peat in August 2021, we deployed a second set of packets in the peepers with the intention of recovering them at the start of the subsequent field season. However, in Summer

2022, there was a site-wide flooding event that precluded establishment of the water-table manipulations. We opted to take advantage of these flooded conditions—when all common substrate peat in the peepers was fully submerged, regardless of experimental plot—and collected the second round of peat packets in late July of 2022 using the same methods described above. Water-table level measurements occurred 11 times throughout the field incubation at 3 different locations within each plot (Figure 3). Common substrate peat was collected as described above and shipped to Chapman University for ESC analysis. Only 1 replicate is reported for Control at the 10–20 cm depth due to sample loss during shipment. Because of the difference in equilibration time between the two rounds of peeper deployment, that is, ∼1 month for samples collected in the non-flooded Summer 2021 and ∼12 months for samples collected in flooded Summer 2022, we do not directly compare the ESC of the substrate between each year.

2.4.2. Methane Production From Common Substrate Peat

In addition to ESC, a subsample of the common substrate peat from each packet was incubated for 2 days to quantify potential CH_4 and CO_2 production. A subset of wet weight peat (∼5 g) and 10 mL of unfiltered porewater from each tube containing the peat packets were added to a 72 mL serum bottle in the anaerobic chamber. Bottles were mixed to create a slurry, and bottles were capped with gray butyl septa in the anaerobic chamber. Finally, samples were flushed with N_2 for 15 min to ensure anaerobic conditions.

Greenhouse gas concentrations, CH_4 and CO_2, were collected after 2 days of anaerobic incubation at 15°C and were measured using a gas chromatograph equipped with a flame ionization detector and methanizer to convert CO_2 to CH_4 (SRI 8610C, SRI Instruments, Torrance, CA). Values were corrected for headspace pressure, solubility, and sample pH (Clesceri et al., 1989; Drever, 1997) and are reported as μmol gas g^{-1} dry weight peat. Because RAOM reduction is a key control on methanogenesis, we only report CH_4 values in the main text (see Figure S1 in Supporting Information S1 for CO_2 values).

2.4.3. Porewater DOM Composition

To investigate potential differences in DOM composition of each plot during a flooded year, we sampled porewater at the three depth increments next to the peat peepers. Porewater was collected using a stainless-steel sipper and syringe. Prior to each porewater collection, the syringes were rinsed with deionized water three times followed by a pre-sample rinse. Porewater was filtered through a 0.45 μm syringe filter into a 20 mL glass amber bottle, filled to overflowing, and immediately capped with no headspace to preserve in situ conditions. Samples were kept on ice and shipped overnight to Michigan Technological University (Houghton, MI) and stored at 4°C until analysis.

Ultraviolet-visible fluorescence and absorbance spectra were collected simultaneously using a Horiba Aqualog fluorometer (Horiba-Jobin-Yvon Aqualog C; Horiba Co., Edison, NJ). Run parameters and processing were as described previously by Kane et al. (2019) and Text S2 in Supporting Information S1. In this study, we compared three measures of DOM chemistry: fluorescence index (FI), a proxy for DOM freshness and aromaticity (Johnson et al., 2011; McKnight et al., 2001); spectral slope ratio (S_R), a proxy for DOM average molecular weight (Helms et al., 2008); and humification index (HIX), a proxy for degree of microbial processing (Ohno, 2002).

2.5. Indirect Effects: Changes to Solid-Phase Peat Composition

To evaluate changes in solid-phase peat composition after ∼15 years of water-table manipulation (see Euskirchen et al. (2024) for average water-table levels of the fen immediately adjacent to the APEX experimental plots), we incubated peat from the cores collected during peeper installation. Peat samples were thawed and spread out in a thin layer on trays for 24 hr at 4°C to allow for oxidation before the first measurement. Due to limited material, all peat samples from the shallow depths at each plot (0–10 and 10–20 cm depths x 3 peat cores) were composited and homogenized, and all samples from the deeper depths at each experimental plot (20–30 and 30–40 cm x 3 peat cores) were composited and homogenized.

Following thawing and oxidation, ∼6 g of wet weight peat was added with 20 mL of deionized water in a 72 mL serum bottle to create a peat slurry. Slurries were mixed and allowed to equilibrate for 20 min before measuring pH. Bottles were subsequently sealed with gray butyl septa and flushed with N_2 for 15 min. An initial set of samples was immediately analyzed for ESC. The remaining samples were incubated for 50 days at 15°C. Previous experiments have shown that 50 days is enough time to observe relative differences in RAOM reduction in different sample types (Rush et al., 2021). Greenhouse gas measurements were taken on days 5, 25, and 50. After greenhouse gas measurements, corresponding bottles were destructively sampled for pH and solid-phase ESC measurements. Due to limited material, there were two replicates for each plot (Raised, Control, and Lowered) and depth (2 depths = shallow and deep) combination at each time point (3 time points). Any incubated peat remaining from the shallow depth after the day 0 and day 50 time points was frozen for further analysis via liquid chromatography (LC) tandem mass spectrometry (MS/MS; see below). Due to similarities between day 25 and day 50 results, we only report the ESC and CH_4 values on days 5 and 50 in the main text (see Figure S2 in Supporting Information S1 for day 25 results and Figure S3 in Supporting Information S1 for CO_2 results).

To evaluate whether differences in RAOM reduction could be due to differences in initial peat composition or differences in microbial processing of solid-phase peat during the incubation, we extracted organic matter from shallow depths at the Raised and Control plots from day 0 and day 50 (organic matter from the Lowered plot not measured due to budget contraints). We analyzed these samples for their chemical composition using a nontargeted metabolomics approach via LC MS/MS (see full protocol in Text S3 in Supporting Information S1). The molecular formulas assigned for each initial peat sample were compared as the mean oxygen to carbon (O/C) ratio, hydrogen to carbon (H/C) ratio, the double bond equivalence normalized to C (DBE/C), and the modified aromaticity index (AI_{mod}; Koch & Dittmar, 2006). The molecular formulas removed during the 50 days incubation were defined as those that decreased in relative abundance by more than 25% in both replicates with a 95% confidence interval that did not overlap with zero. The chemical characteristics of molecular formulas removed during the 50 days were compared between the surface peat from the Raised plot and Control plot.

2.6. Statistical Analyses

We used *R* statistical software (v4.2.3; R Core Team, 2021) to compare the ESC, CH_4 and CO_2 production, and porewater DOM composition using an analysis of variance (ANOVA). To identify which specific groups differed significantly after a significant ANOVA result, we conducted a post-hoc Tukey test (Tukey's Honestly Significant Difference test). Statistical significance was accepted at $p < 0.05$.

For the field incubations of common substrate peat, all ESC, CH_4, and CO_2 production values are reported as the mean of samples collected from the three peepers at the same experimental plot and depth interval. The only exception was the common substrate peat incubated at the 10–20 cm depth interval at the control plot during the 1 year field incubation, which had one replicate because the other two peat packets recovered from this depth interval were broken during transit. For the lab incubations of solid-phase peat at each plot, all ESC, CH_4, and CO_2 production values are reported as the mean of duplicate samples incubated in serum vials for each experimental plot and depth interval. Statistically significant differences were analyzed via ANOVA as described above.

The chemical characteristics of molecular formulas for each initial peat sample and the formulas removed during the 50 days incubation are reported as the mean ± 1 standard deviation of O/C ratio, H/C ratio, DBE/C, or AI_{mod} across formula.

3. Results

3.1. Direct Effects of Water-Table Levels on RAOM Reduction

Differences in water-table levels among the plots was achieved in mid-July of Summer 2021 with the most extreme differences among mean water-table levels observed at the time of substrate collection (Figure 2a): -34.2 ± 0.9 cm for Lowered, -10.7 ± 0.6 cm for Control, and -0.6 ± 0.3 cm for Raised.

Along the depth profile, changes in ESC closely matched changes in water-table levels (Figure 2). For example, the mean ESC of common substrate peat at the 0–10 cm depth increment was lower than 1.5 $\mu mol\ e^{-}\ g^{-1}$ dry weight peat for all plots, indicating a more oxidized environment due to the lower (Control and Lowered) or near-surface water-table levels (Raised; Figure 2). In the two deeper depths, the common substrate peat in the Raised plot was significantly more reduced ($p < 0.05$, see Figure 2b) than the common substrate in the Lowered plot at

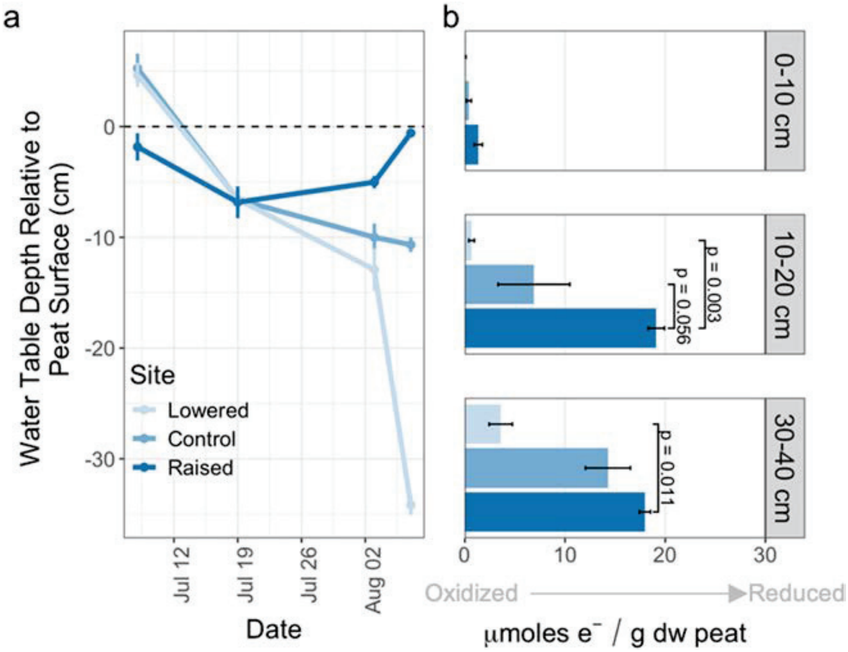

Figure 2. Reduction of redox-active organic matter (RAOM) within common substrate peat during water-table manipulation. (a) Mean (±SE) water-table level relative to peat surface of each plot over the incubation period. The dotted black line at 0 cm represents peat surface. (b) Mean electron shuttling capacity (ESC) (±SE, *x*-axis) of the common substrate peat ($n = 3$) after ~1 month of field incubation along the depth profile. Higher ESC values indicate more reduced RAOM.

both 10–20 cm (19.1 ± 0.8 vs. 0.7 ± 0.3 μmol e^- g^{-1} dry weight peat) and 30–40 cm (18.0 ±- 0.5 vs. 3.6 ± 1.2 μmol e^- g^{-1} dry weight peat). The common substrate in Raised was also more reduced than the common substrate in Control at both depths and almost statistically significant ($p = 0.056$) at 10–20 cm (19.1 ± 0.8 vs. 6.9 ± 3.6 μmol e^- g^{-1} dry weight peat; Figure 2b).

3.2. Indirect Effects of Water-Table on RAOM Reduction: Field Incubation

During the flooded year, the ESC of the common substrate differed across the water-table treatments even during a period of similar water-table levels. All plots had comparable water-table levels-well above peat surface-for the duration of the field season (averaging 40 ± 1.5 cm for all plots, Figure 3a). At 0–10 cm, the Raised common substrate ESC (44.1 ± 5.8 μmol e^- g^{-1} dry weight peat) was significantly higher than both the Control common substrate (20.6 ± 2.2 μmol e^- g^{-1} dry weight peat) and Lowered common substrate (22 ± 0.8 μmol e^- g^{-1} dry weight peat, $p < 0.05$; Figure 3b). The common substrate ESC was also higher in Raised than the other two plots at 10–20 cm but only statistically significant when compared to the Lowered common substrate ($p = 0.009$). All common substrate ESC values were similar (~20 μmol e^- g^{-1} dry weight peat) across the plots at 30–40 cm (Figure 3b). Similar to the ESC of the common substrate, CH_4 values trended higher (although not significantly) in the Raised common substrate than in the substrate of the other two plots in the top two depths (Figure 3c). Across all depths and treatment plots, common substrate ESC was a significantly strong predictor of CH_4 production ($R^2 = 0.62$, $p = 0.007$, see Figure S4 in Supporting Information S1).

The composition of the DOM collected next to each peeper was similar in all experimental plots during the flooded year. The mean S_R, FI, and HIX of porewater DOM were not significantly different among plots ($p > 0.05$). Spectral slope averaged 0.76 ± 0.01, FI averaged 1.26 ± 0.01 and HIX averaged 17.1 ± 0.7 across all depths and plots (see Table S1 for full results).

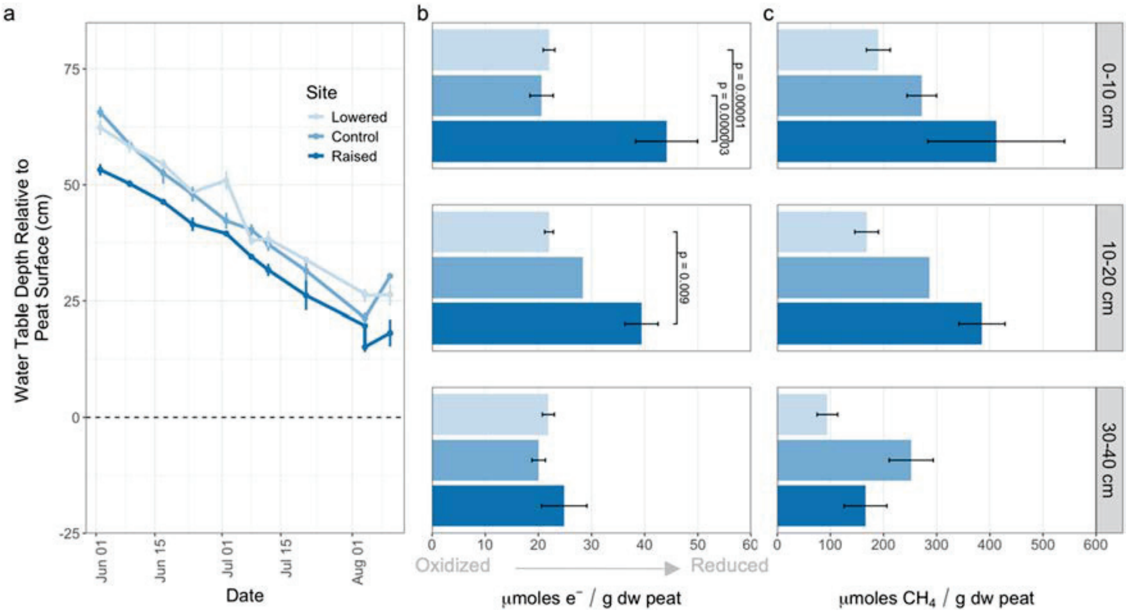

Figure 3. Reduction of redox-active organic matter (RAOM) and production of CH_4 from common substrate peat during a flooded year. (a) Mean (±SE) water-table level relative to peat surface of each experimental plot over the incubation period when water-table levels were being monitored. The dotted black line at 0 cm represents peat surface. (b) Mean (±SE; *x*-axis) electron shuttling capacity (ESC) of the common substrate packets ($n = 3$, except Control 10–20 cm where $n = 1$) after ~12 months of field incubation along the depth profile. Higher ESC values indicate more reduced RAOM. (c) Mean (±SE) CH_4 production (*x*-axis) of common substrate packets after a 2-day anaerobic incubation.

3.3. Indirect Effects of Water-Table on RAOM Reduction: Laboratory Incubation

To further assess the indirect effects of water-table levels on RAOM reduction, peat from each experimental plot was oxidized and incubated anaerobically for 50 days. The initial peat from the experimental plots had negligible ESC values, demonstrating that the peat started off oxidized at the start of the incubation (low ESC on Day 0 (D0); Figure 4a). Within 5 days of the anaerobic incubation, the peat became reduced with ESC values that increased up to ~50 and ~30 μmol e^- g^{-1} dry weight peat in the shallow and deep depths, respectively (Figure 4a). Between 5 and 50 days, the ESC of shallow peat increased by an additional ~10 μmol e^- g^{-1} dry weight peat, whereas deeper peat increased by an additional ~20 μmol e^- g^{-1} dry weight peat (Figure 4a). The ESC of shallow peat from Raised trended higher than that of Lowered and Control and was only significantly higher on day 50 ($p = 0.035$). Methane production also increased over the course of the incubation with CH_4 values in the shallow depth an order of magnitude higher than at the deeper depth (Figure 4b). Methane production in the Raised plot peat trended higher than Control peat at the shallow depth although not significantly ($p = 0.54$). For the deep depth, average CH_4 values within Raised and Control peat were comparable (~14 μmol CH_4 g^{-1} dry weight peat) and about three-times higher than CH_4 production in Lowered peat at that depth.

The initial composition of peat organic matter from the Raised plot was similar to the composition of peat organic matter from the Control with only 5% of molecular formulas identified unique to the Control plot and 2% of formulas identified unique to the Raised plot (<150 molecular formulas; Figure 5a). There were minimal differences in the average O/C ratio, H/C ratio, DBE/C, or AI_{mod} across the formulas identified for peat from the Raised versus Control plot (see Table S2).

Despite similarities in the initial peat composition detected, differences were observed in the number and composition of molecular formulas that were removed from that pool during the 50 days anaerobic incubation (Figure 5a). The analysis of organic matter from the surface peat of each plot at the start of the incubation identified a total of 3,186 unique molecular formulas (see Table S3 for C extractions). Of the 3,186 total, 217 molecular formulas were removed from Control peat and 1,710 were removed from Raised peat over the 50 days laboratory incubation. The DBE/C, which estimates the degree of conjugation within a molecular structure, for

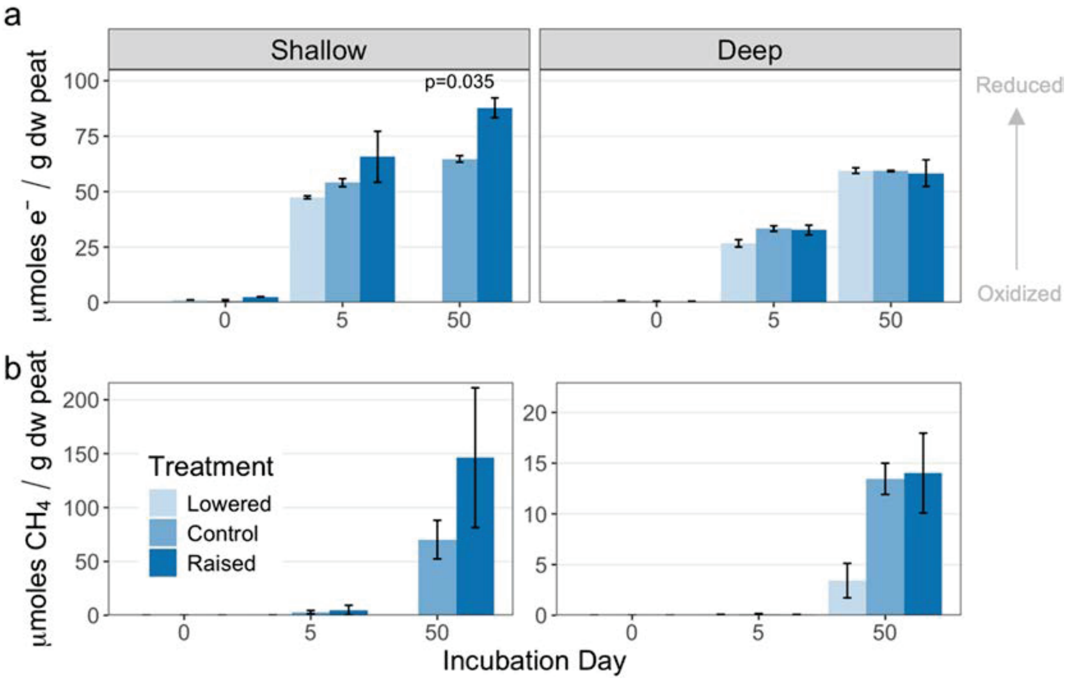

Figure 4. Reduction of redox-active organic matter (RAOM) and CH_4 production of peat collected from each experimental plot. (a) Mean (±SE) electron shuttling capacity (ESC) of plots on days 0, 5, and 50 of the anaerobic incubation in the shallow and deep depth. Higher ESC values indicate more reduced RAOM. (b) Mean (±SE) CH_4 production over time. Note the difference in y-axis scale between shallow and deep. Day 0 CH_4 values were not measured. For the shallow depth, Day 50 does not have samples from the Lowered plot due to low peat volume during sample collection.

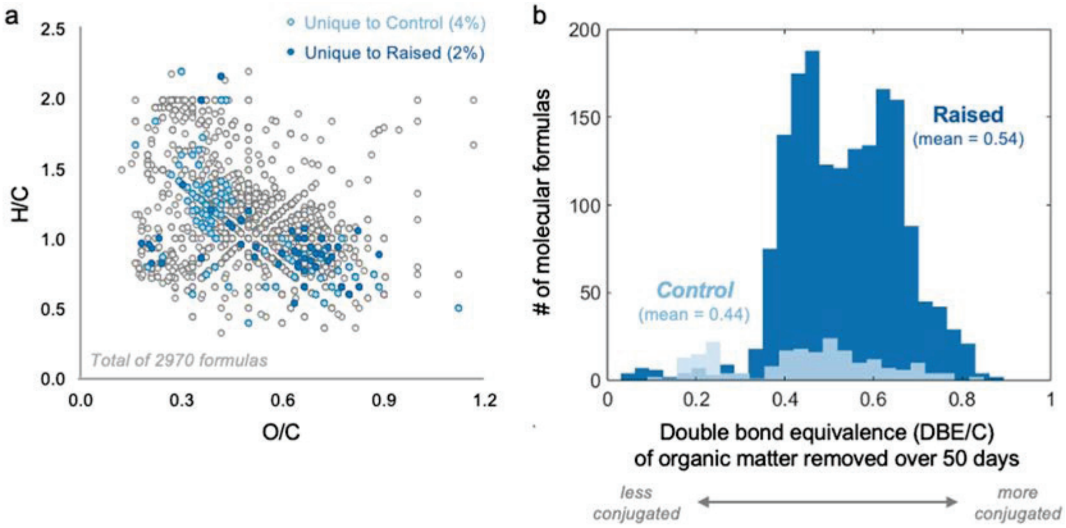

Figure 5. Peat composition of the shallow depth from Raised and Control experimental plots. (a) Van Krevelen diagram of the molecular formulas identified within initial peat organic matter from the Control and Raised plots (i.e., prior to incubation) using nontargeted metabolomics. Open gray circles show all molecular formulas present in the initial Control and Raised peat, whereas the light and dark blue circles show those unique to the Control peat and the Raised peat, respectively. (b) Double bond equivalence normalized to carbon (DBE/C) of the molecular formulas uniquely removed from the shallow Control peat versus the shallow Raised peat during the 50 days anaerobic incubation. Additional characteristics of the molecular formulas shown in (a) and (b) can be found in Table S2.

the formulas removed from surface peat at the Raised plot was also higher than that for the molecular formula removed from peat at the Control plot (0.54 vs. 0.44, respectively; Figure 5b), indicating that more conjugated C compounds were removed in the Raised peat. Additionally, the AI_{mod}, a measure of aromaticity, for molecular formulas removed from peat at the Raised plot, was higher relative to the Control (0.37 vs. 0.16, respectively; Table S2). The average O/C ratio of formula removed from peat was slightly lower and the average H/C slightly higher at the Raised plot compared to the Control plot (Table S2).

4. Discussion

By using the peat peeper design in combination with a decadal-scale water-table manipulation experiment, this is among the first studies to demonstrate the direct effect of water-table levels on in situ RAOM reduction in northern peatlands. The in situ incubation of a common peat substrate during water-table manipulation of APEX plots demonstrates that RAOM reduction closely tracks the water-table level with more oxidized RAOM when peat is aerated above the water table and more reduced RAOM when peat is submerged below the water table (Figure 3). These findings are aligned with the results of past laboratory (Gabriel et al., 2017; Klüpfel et al., 2014) and field-based studies (Obradović et al., 2023; Rush et al., 2021) where RAOM is shown to be reduced below the water table. Additionally, we build on the work of Obradović et al. (2024) which is the only other study, to our knowledge, to show how a common substrate can be used to differentiate environmental impacts on RAOM reduction.

Because we used a homogenized, common peat substrate across the water-table treatments, we assume that the differences in RAOM reduction among plots and depths were largely due to the direct water-table effects on oxygen availability throughout the peat profile with oxygen availability directly impacting the RAOM oxidation state (Gunina & Kuzyakov, 2022; Yang et al., 2024). This finding is consistent with the current paradigm that water table is a strong, if not the strongest, driver on C cycling in peatlands (Munir & Strack, 2014; Zhong et al., 2020).

However, if water-table level was the main control on RAOM reduction, we would have expected the common substrate peat to have similar levels of reduction (higher ESC values) during a flooded year when all of the treatment plots at APEX were fully submerged (Figure 4; also see Boonman et al., 2024). Instead, there was significantly higher RAOM reduction of the common substrate incubated in the Raised plot compared to the common substrate incubated in the Control and Lowered plots (Figures 3 and 4). The higher RAOM reduction of the common substrate in the Raised plot was also strongest at the 0–10 cm depth (Figure 4), the depth increment where treatments have experienced the greatest amount of variation in water-table levels over the ∼15 years of manipulation at APEX (Olefeldt et al., 2017). Given this sustained difference in RAOM reduction, we suggest that factors other than immediate oxygen availability, mediated by water-table levels, must be impacting RAOM reduction of the common substrate peat.

Work by Hribljan et al. (2014), also done in a fen ecosystem, showed that although DOM concentrations increased in both lowered and raised water-table sites, the composition of the DOM differed with Raised having less humified DOM. We therefore hypothesized that one explanation for differences in RAOM reduction of the common substrate during a flooded year could be altered DOM composition among plots due to past water-table level differences. Although DOM is a small portion of the total organic matter pool, it is often the most reactive (Li et al., 2022), and DOM is thought to be a major source of smaller molecular weight C substrates acting as electron donors for anaerobic respiration in peatlands (Chanton et al., 2008; Hopple et al., 2019). Indeed, other studies have provided evidence that the DOM pool can donate electrons to the solid-phase RAOM pool (Huang et al., 2021; Rush et al., 2021). Given that lower average molecular weights for DOM have been reported for the Raised plot compared to Lowered and Control plots at our site (Kane et al., 2021), we thought it possible that there were more substrates in the DOM pool available for the anaerobic respiration of common substrate RAOM in the Raised plot relative to the other two plots.

However, our measures of porewater DOM composition in this study did not support DOM as an explanation for differences in common substrate RAOM reduction during a flooded year. If the greater RAOM reduction measured in the common substrate at the surface of the Raised plot was due to a higher abundance of lower molecular weight DOM compounds, then we would expect higher S_R values at the surface that decrease with depth (Table S1). Instead, changes in S_R with depth were not observed and in fact, there were no significant changes in any metric of DOM quality with depth (Table S1). Although we did not observe a significant difference in S_R between the experimental plots as observed by Kane et al. (2021), the average values of FI, S_R, and HIX in this study were comparable to average values of these same indices reported by Kane et al. (2021) during a flooded year at the site. The lack of significant differences in DOM composition in our study could be attributed to sampling at just one time point, whereas Kane et al. (2021) analyzed DOM compositon multiple times over the growing season. Still, similar DOM composition measured combined with differences seen in the RAOM of common substrate peat does suggest there are other factors, such as microbial C processing, that may play a larger role in the continued, significant differences in RAOM reduction of common substrate peat during a flooded year that are worth exploring especially as the site experiences more frequent flooding events (Euskirchen et al., 2020).

To see if shifts in solid-phase peat composition with long-term water-table manipulation could also affect RAOM reduction, we incubated peat from each experimental plot at a common temperature in the laboratory. Other studies have shown that composition of the solid-phase peat in the top layers of peatlands is altered by water-table level leading to subsequent changes in anaerobic C respiration (Abbott et al., 2013; Hribljan et al., 2017; Weiss et al., 2006). We therefore hypothesized that sustained water-table manipulation would lead to differences in RAOM reduction within peat from each treatment plot when incubated at a common temperature. Indeed, we saw significantly more reduced RAOM in peat from the Raised plot compared to peat from the Control plot but only in the shallow depth (0–20 cm; Figure 4a). These findings support our current understanding that peat composition will be most affected at depths with the greatest variation in water-table level (Abbott et al., 2013), which was 0–10 cm in our study (Olefeldt et al., 2017). However, the more reduced RAOM in peat from the Raised plot could be a result of changing peat composition or changes in microbial C processing compared to the Control plot.

Our results from the nontargeted metabolomic analysis of peat composition suggest one explanation for the higher RAOM reduction of peat from the Raised plot compared to the Control plot could be a shift in microbial C processing. Although our characterization method only captures a fraction of the entire organic matter pool, we found that of the pool that was characterized (Figure 5a), molecular formulas with relatively more conjugated bonds were removed in peat from the Raised plot than peat from the Control plot (as shown by a higher DBE/C ratio, Figure 5b). Although quinone moieties are recognized as the primary reversible electron acceptor in RAOM reduction, recent research showed that conjugated compounds of RAOM may also serve as a nonreversible electron sink via hydrogenation (Guth et al., 2023; Wilson et al., 2017, 2022). Although we cannot determine which of these pathways led to RAOM reduction from our nontargeted approach, our result is consistent with previous work showing that hydrogenation occurred more frequently in a fen ecosystem compared to other peatland types (Wilson et al., 2022). Alternatively, the greater removal of conjugated compounds during anaerobic respiration of the Raised peat could be due to other processes, such as fermentation, which lead to the breakdown of organic matter to substrates, such as acetate, typically used in RAOM reduction (Rush et al., 2021). Regardless of the cause, these findings suggest that microbes associated with the Raised plot processed peat C differently than those in the Control plot.

The difference in microbial processing of peat C between experimental plots makes sense in that long-term, raised water-table levels would give microbes at peat surface time to adapt to reducing the available RAOM compounds (i.e., higher amounts of RAOM reduction as they are accustomed to leveraging RAOM as a TEA under prolonged anoxic conditions). This potential explanation for our results agrees with findings from He et al. (2015), which showed that microbial functioning shifted to genes associated with anaerobic respiration, such as sulfate reduction, under prolonged, high water-table levels in a California wetland. Although it is difficult to disentangle the effects of water-table manipulation on microbial function, peat composition, and DOM composition, these are among the first results showing that changes to microbial processing induced by water-table levels extends to RAOM reduction in northern peatlands. Our findings demonstrate that future work aimed at understanding peat C cycling should aim to understand how microbes may be processing peat differently under different water-table levels (Wyatt et al., 2024). These results also highlight the potential for both quinone reduction and hydrogenation to contribute to changes in microbial processing of RAOM under different water-table levels.

Finally, our study adds to the growing body of literature that RAOM reduction is a main control on CH_4 production in northern peatlands (Obradović et al., 2024; Rush et al., 2021). We provide both field-based (Figure 4c) and laboratory evidence (Figure 5b) that when the RAOM pool progressively becomes more reduced, there is increased CH_4 production. Also, when introducing common substrate peat and, therefore, removing peat heterogeneity, we can more accurately predict the relationship between RAOM reduction and CH_4 (Figure S4 in Supporting Information S1). Taken together, our results suggest that long-term flooding of the peat surface can lead to a more reduced RAOM pool and higher rates of CH_4 production. As such, to better understand peatland CH_4 response to global change, including changes in both temperature and precipitation regimes, we must consider climate change effects on RAOM reduction of solid-phase peat.

5. Conclusions

The results of our study demonstrate that water-table levels have both direct and indirect effects on RAOM reduction in northern peatlands moving beyond the assumption that oxygen availability is the sole consequence of water-table level fluctuation. We show that differences in RAOM redox-state, driven by legacy water-table level effects, persist even during flooding events and are possibly driven by changes to microbial C processing. Future studies should leverage common substrate peat and in situ field designs to better capture the complex interactions among water-table levels, dissolved and solid-phase peat C composition, and microbial communities that lead to changes in RAOM reduction. Redox-active organic matter reduction also remains a key area of study in peatland research, as our results show it correlates strongly to CH_4 production and is an important TEA in these ecosystems. In this study, we demonstrate the need for a better understanding of whole-ecosystem effects driven by water-table as well as a shift to in situ methods and more advanced C characterization as it becomes widely available.

Abbreviations

AI_{mod}	modified aromaticity index
ANOVA	analysis of variance
APEX	Alaskan Peatland Experiment
C	carbon
CH_4	methane
CO_2	carbon dioxide
DBE/C	double bond equivalence normalized to C
DOM	dissolved organic matter
FI	fluorescence index
HIX	humification Index
LC	liquid chromatography
MS/MS	tandem mass spectrometry
RAOM	redox-active organic matter
S_R	Spectral slope ratio
TEA	terminal electron acceptor

Conflict of Interest

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

Data Availability Statement

The data sets used in this study are openly available through the Environmental Data Initiative at Rush et al., 2025.

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References

Abbott, G. D., Swain, E. Y., Muhammad, A. B., Allton, K., Belyea, L. R., Laing, C. G., & Cowie, G. L. (2013). Effect of water-table fluctuations on the degradation of *Sphagnum* phenols in surficial peats. *Geochimica et Cosmochimica Acta*, *106*, 177–191. https://doi.org/10.1016/j.gca.2012.12.013

Abdalla, M., Hastings, A., Truu, J., Espenberg, M., Mander, Ü., & Smith, P. (2016). Emissions of methane from northern peatlands: A review of management impacts and implications for future management options. *Ecology and Evolution*, *6*(19), 7080–7102. https://doi.org/10.1002/ece3.2469

Barel, J. M., Moulia, V., Hamard, S., Sytiuk, A., & Jassey, V. E. J. (2021). Come rain, come shine: Peatland carbon dynamics shift under extreme precipitation. *Frontiers in Environmental Science*, *9*, 659953. https://doi.org/10.3389/fenvs.2021.659953

Boonman, J., Harpenslager, S. F., van Dijk, G., Smolders, A. J. P., Hefting, M. M., van de Riet, B., & van der Velde, Y. (2024). Redox potential is a robust indicator for decomposition processes in drained agricultural peat soils: A valuable tool in monitoring peatland wetting efforts. *Geoderma*, *441*, 116728. https://doi.org/10.1016/j.geoderma.2023.116728

Breeuwer, A., Robroek, B. J. M., Limpens, J., Heijmans, M. M. P. D., Schouten, M. G. C., & Berendse, F. (2009). Decreased summer water table depth affects peatland vegetation. *Basic and Applied Ecology*, *10*(4), 330–339. https://doi.org/10.1016/j.baae.2008.05.005

Bridgham, S. D., Cadillo-Quiroz, H., Keller, J. K., & Zhuang, Q. (2013). Methane emissions from wetlands: Biogeochemical, microbial, and modeling perspectives from local to global scales. *Global Change Biology*, *19*(5), 1325–1346. https://doi.org/10.1111/gcb.12131

Chanton, J. P., Glaser, P. H., Chasar, L. S., Burdige, D. J., Hines, M. E., Siegel, D. I., et al. (2008). Radiocarbon evidence for the importance of surface vegetation on fermentation and methanogenesis in contrasting types of boreal peatlands. *Global Biogeochemical Cycles*, *22*(4), GB4022. https://doi.org/10.1029/2008GB003274

Chivers, M. R., Turetsky, M. R., Waddington, J. M., Harden, J. W., & McGuire, A. D. (2009). Effects of experimental water table and temperature manipulations on ecosystem CO2 fluxes in an Alaskan rich fen. *Ecosystems*, *12*(8), 1329–1342. https://doi.org/10.1007/s10021-009-9292-y

Churchill, A. C., Turetsky, M. R., McGuire, A. D., & Hollingsworth, T. N. (2015). Response of plant community structure and primary productivity to experimental drought and flooding in an Alaskan fen. *Canadian Journal of Forest Research*, *45*(2), 185–193. https://doi.org/10.1139/cjfr-2014-0100

Clesceri, L. S., Greenberg, A. E., & Eaton, A. D. (1989). *Standard methods for the examination of water and wastewater* (17th ed.). American Public Health Association.

Drever, J. I. (1997). *The geochemistry of natural waters surface and groundwater environments* (3rd ed.). Prentice Hall.

Euskirchen, E. S., Edgar, C. W., Kane, E. S., Waldrop, M. P., Neumann, R. B., Manies, K. L., et al. (2024). Persistent net release of carbon dioxide and methane from an Alaskan lowland boreal peatland complex. *Global Change Biology*, *30*(1), e17139. https://doi.org/10.1111/gcb.17139

Euskirchen, E. S., Kane, E. S., Edgar, C. W., & Turetsky, M. R. (2020). When the source of flooding matters: Divergent responses in carbon fluxes in an Alaskan rich fen to two types of inundation. *Ecosystems*, *23*(6), 1138–1153. https://doi.org/10.1007/s10021-019-00460-z

Frolking, S., Roulet, N., & Fuglestvedt, J. (2006). How northern peatlands influence the Earth's radiative budget: Sustained methane emission versus sustained carbon sequestration. *Journal of Geophysical Research*, *111*(G1), G01008. https://doi.org/10.1029/2005JG000091

Gabriel, K. N., Medvedeff, C. A., & Keller, J. K. (2017). Research article: Microbial organic matter reduction in a peatland soil: The importance of water-table level. *BIOS*, *88*(1), 39–45. https://doi.org/10.1893/BIOS-D-16-00002.1

Gao, C., Sander, M., Agethen, S., & Knorr, K.-H. (2019). Electron accepting capacity of dissolved and particulate organic matter control CO2 and CH4 formation in peat soils. *Geochimica et Cosmochimica Acta*, *245*, 266–277. https://doi.org/10.1016/j.gca.2018.11.004

Gunina, A., & Kuzyakov, Y. (2022). From energy to (soil organic) matter. *Global Change Biology*, *28*(7), 2169–2182. https://doi.org/10.1111/gcb.16071

Guth, P., Gao, C., & Knorr, K.-H. (2023). Electron accepting capacities of a wide variety of peat materials from around the globe similarly explain CO2 and CH4 formation. *Global Biogeochemical Cycles*, *37*(1), e2022GB007459. https://doi.org/10.1029/2022GB007459

Haapalehto, T., Kotiaho, J. S., Matilainen, R., & Tahvanainen, T. (2014). The effects of long-term drainage and subsequent restoration on water table level and pore water chemistry in boreal peatlands. *Journal of Hydrology*, *519*, 1493–1505. https://doi.org/10.1016/j.jhydrol.2014.09.013

He, S., Malfatti, S. A., McFarland, J. W., Anderson, F. E., Pati, A., Huntemann, M., et al. (2015). Patterns in wetland microbial community composition and functional gene repertoire associated with methane emissions. *MBio*, *6*(3), 10–1128. https://doi.org/10.1128/mbio.00066-15

Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., & Mopper, K. (2008). Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnology & Oceanography*, *53*(3), 955–969. https://doi.org/10.4319/lo.2008.53.3.0955

Hinzman, L. D., Viereck, L. A., Adams, P. C., Romanovsky, V. E., & Yoshikawa, K. (2006). *Climate and permafrost dynamics of the Alaskan boreal forest* (pp. 39–61). Alaska's changing boreal forest.

Hopple, A. M., Pfeifer-Meister, L., Zalman, C. A., Keller, J. K., Tfaily, M. M., Wilson, R. M., et al. (2019). Does dissolved organic matter or solid peat fuel anaerobic respiration in peatlands? *Geoderma*, *349*, 79–87. https://doi.org/10.1016/j.geoderma.2019.04.040

Hribljan, J. A., Kane, E. S., & Chimner, R. A. (2017). Implications of altered hydrology for substrate quality and trace gas production in a poor fen peatland. *Soil Science Society of America Journal*, *81*(3), 633–646. https://doi.org/10.2136/sssaj2016.10.0322

Hribljan, J. A., Kane, E. S., Pypker, T. G., & Chimner, R. A. (2014). The effect of long-term water table manipulations on dissolved organic carbon dynamics in a poor fen peatland. *Journal of Geophysical Research: Biogeosciences*, *119*(4), 577–595. https://doi.org/10.1002/2013JG002527

Huang, W., Li, Y., Liu, X., Wang, W., Wen, P., Yu, Z., & Zhou, S. (2021). Linking the electron transfer capacity with the compositional characteristics of dissolved organic matter during hyperthermophilic composting. *The Science of the Total Environment*, *755*, 142687. https://doi.org/10.1016/j.scitotenv.2020.142687

Johnson, M. S., Couto, E. G., Abdo, M., & Lehmann, J. (2011). Fluorescence index as an indicator of dissolved organic carbon quality in hydrologic flowpaths of forested tropical watersheds. *Biogeochemistry*, *105*(1), 149–157. https://doi.org/10.1007/s10533-011-9595-x

Kahle, D., & Wickham, H. (2013). Ggmap: Spatial visualization with ggplot2. *The R Journal*, *5*(1), 144. https://doi.org/10.32614/rj-2013-014

Kane, E. S., Dieleman, C. M., Rupp, D., Wyatt, K. H., Rober, A. R., & Turetsky, M. R. (2021). Consequences of increased variation in Peatland hydrology for carbon storage: Legacy effects of drought and flood in a boreal fen ecosystem. *Frontiers in Earth Science*, *8*, 577746. https://doi.org/10.3389/feart.2020.577746

Kane, E. S., Turetsky, M. R., Harden, J. W., McGuire, A. D., & Waddington, J. M. (2010). Seasonal ice and hydrologic controls on dissolved organic carbon and nitrogen concentrations in a boreal-rich fen. *Journal of Geophysical Research*, *115*(G4), G04012. https://doi.org/10.1029/2010JG001366

Kane, E. S., Veverica, T. J., Tfaily, M. M., Lilleskov, E. A., Meingast, K. M., Kolka, R. K., et al. (2019). Reduction-oxidation potential and dissolved organic matter composition in northern peat soil: Interactive controls of water table position and plant functional groups. *Journal of Geophysical Research: Biogeosciences*, *124*(11), 3600–3617. https://doi.org/10.1029/2019JG005339

Keller, J. K., & Takagi, K. K. (2013). Solid-phase organic matter reduction regulates anaerobic decomposition in bog soil. *Ecosphere*, *4*(5), 1–12. https://doi.org/10.1890/ES12-00382.1

Keller, J. K., Weisenhorn, P. B., & Megonigal, J. P. (2009). Humic acids as electron acceptors in wetland decomposition. *Soil Biology and Biochemistry*, *41*(7), 1518–1522. https://doi.org/10.1016/j.soilbio.2009.04.008

Klavins, M., & Purmalis, O. (2013). Properties and structure of raised bog peat humicacids. *Journal of Molecular Structure*, *1050*, 103–113. https://doi.org/10.1016/j.molstruc.2013.07.021

Klüpfel, L., Piepenbrock, A., Kappler, A., & Sander, M. (2014). Humic substances as fully regenerable electron acceptors in recurrently anoxic environments. *Nature Geoscience*, *7*(3), 195–200. https://doi.org/10.1038/ngeo2084

Koch, B. P., & Dittmar, T. (2006). From mass to structure: An aromaticity index for high-resolution mass data of natural organic matter. *Rapid Communications in Mass Spectrometry*, *20*(5), 926–932. https://doi.org/10.1002/rcm.2386

Kuzyakov, Y., & Blagodatskaya, E. (2015). Microbial hotspots and hot moments in soil: Concept and review. *Soil Biology and Biochemistry*, *83*, 184–199. https://doi.org/10.1016/j.soilbio.2015.01.025

Lai, D. Y. F. (2009). Methane dynamics in Northern peatlands: A review. *Pedosphere*, *19*(4), 409–421. https://doi.org/10.1016/S1002-0160(09)00003-4

Lehmann, J., Coumou, D., & Frieler, K. (2015). Increased record-breaking precipitation events under global warming. *Climatic Change*, *132*(4), 501–515. https://doi.org/10.1007/s10584-015-1434-y

Li, J., Zhao, L., Li, M., Min, Y., Zhan, F., Wang, Y., et al. (2022). Changes in soil dissolved organic matter optical properties during peatland succession. *Ecological Indicators*, *143*, 109386. https://doi.org/10.1016/j.ecolind.2022.109386

Loisel, J., & Gallego-Sala, A. (2022). Ecological resilience of restored peatlands to climate change. *Communications Earth and Environment*, *3*(1), 1–8. https://doi.org/10.1038/s43247-022-00547-x

McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T., & Andersen, D. T. (2001). Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology & Oceanography*, *46*(1), 38–48. https://doi.org/10.4319/lo.2001.46.1.0038

Munir, T. M., & Strack, M. (2014). Methane flux influenced by experimental water table drawdown and soil warming in a dry boreal Continental bog. *Ecosystems*, *17*(7), 1271–1285. https://doi.org/10.1007/s10021-014-9795-z

Nalder, I., & Wein, R. (1998). A new forest floor corer for rapid sampling, minimal disturbance and adequate precision. *Silva Fennica*, *32*(4), 678. https://doi.org/10.14214/sf.678

Niedermeier, A., & Robinson, J. S. (2007). Hydrological controls on soil redox dynamics in a peat-based, restored wetland. *Geoderma*, *137*(3), 318–326. https://doi.org/10.1016/j.geoderma.2006.08.027

Obradović, N., Joshi, P., Arn, S., Aeppli, M., Schroth, M. H., & Sander, M. (2023). Reoxidation of reduced peat organic matter by dissolved oxygen: Combined laboratory column-breakthrough experiments and In-Field push-pull tests. *Journal of Geophysical Research: Biogeosciences*, *128*(11), e2023JG007640. https://doi.org/10.1029/2023JG007640

Obradović, N., Schmitz, R. A., Haffter, F., Meier, D. V., Lever, M. A., Schroth, M. H., & Sander, M. (2024). Peat particulate organic matter accepts electrons during in situ incubation in the anoxic subsurface of ombrotrophic bogs. *Journal of Geophysical Research: Biogeosciences*, *129*(9), e2024JG008223. https://doi.org/10.1029/2024JG008223

Ohno, T. (2002). Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter. *Environmental Science & Technology*, *36*(4), 742–746. https://doi.org/10.1021/es0155276

Olefeldt, D., Euskirchen, E. S., Harden, J., Kane, E., McGuire, A. D., Waldrop, M. P., & Turetsky, M. R. (2017). A decade of boreal rich fen greenhouse gas fluxes in response to natural and experimental water table variability. *Global Change Biology*, *23*(6), 2428–2440. https://doi.org/10.1111/gcb.13612

Page, S. E., & Baird, A. J. (2016). Peatlands and global change: Response and resilience. *Annual Review of Environment and Resources*, *41*(1), 35–57. https://doi.org/10.1146/annurev-environ-110615-085520

Potvin, L. R., Kane, E. S., Chimner, R. A., Kolka, R. K., & Lilleskov, E. A. (2015). Effects of water table position and plant functional group on plant community, aboveground production, and peat properties in a peatland mesocosm experiment (PEATcosm). *Plant and Soil*, *387*(1), 277–294. https://doi.org/10.1007/s11104-014-2301-8

R Core Team. (2021). *R: A language and environment for statistical computing*. R Foundation for Statistical Computing. Retrieved from https://www.R-project.org/

Reiche, M., Gleixner, G., & Küsel, K. (2010). Effect of peat quality on microbial greenhouse gas formation in an acidic fen. *Biogeosciences*, *7*(1), 187–198. https://doi.org/10.5194/bg-7-187-2010

Risacher, F. F., Schneider, H., Drygiannaki, I., Conder, J., Pautler, B. G., & Jackson, A. W. (2023). A review of peeper passive sampling approaches to measure the availability of inorganics in sediment porewater. *Environmental Pollution*, *328*, 121581. https://doi.org/10.1016/j.envpol.2023.121581

Rober, A. R., Lankford, A. J., Kane, E. S., Turetsky, M. R., & Wyatt, K. H. (2023). Structuring life after death: Plant leachates promote CO2 uptake by regulating microbial biofilm interactions in a Northern peatland ecosystem. *Ecosystems*, *26*(5), 1108–1124. https://doi.org/10.1007/s10021-023-00820-w

Rupp, D. L., Lamit, L. J., Techtmann, S. M., Kane, E. S., Lilleskov, E. A., & Turetsky, M. R. (2021). The rhizosphere responds: Rich fen peat and root microbial ecology after long-term water table manipulation. *Applied and Environmental Microbiology*, *87*(12), e0024121. https://doi.org/10.1128/AEM.00241-21

Rush, J. E., Kane, E., & Keller, J. K., & Bonanza Creek LTER. (2025). *Redox-Active Organic Matter measurements at the APEX fen in the Bonanza Creek Experimental Forest near Fairbanks, Alaska (2021-2022) ver 2*. Environmental Data Initiative. https://doi.org/10.6073/pasta/14ef83b1f4c4ebd771bb68b9dc238cf3

Rush, J. E., Zalman, C. A., Woerndle, G., Hanna, E. L., Bridgham, S. D., & Keller, J. K. (2021). Warming promotes the use of organic matter as an electron acceptor in a peatland. *Geoderma*, *401*, 115303. https://doi.org/10.1016/j.geoderma.2021.115303

Strack, M., Waddington, J. M., Bourbonniere, R. A., Buckton, E. L., Shaw, K., Whittington, P., & Price, J. S. (2008). Effect of water table drawdown on peatland dissolved organic carbon export and dynamics. *Hydrological Processes*, *22*(17), 3373–3385. https://doi.org/10.1002/hyp.6931

Turetsky, M. R., Treat, C. C., Waldrop, M. P., Waddington, J. M., Harden, J. W., & McGuire, A. D. (2008). Short-term response of methane fluxes and methanogen activity to water table and soil warming manipulations in an Alaskan peatland. *Journal of Geophysical Research*, *113*(G3), 2007JG000496. https://doi.org/10.1029/2007JG000496

Urquhart, C., & Gore, A. J. P. (1973). The redox characteristics of four peat profiles. *Soil Biology and Biochemistry*, *5*(5), 659–672. https://doi.org/10.1016/0038-0717(73)90056-4

Valenzuela, E. I., & Cervantes, F. J. (2021). The role of humic substances in mitigating greenhouse gases emissions: Current knowledge and research gaps. *The Science of the Total Environment*, *750*, 141677. https://doi.org/10.1016/j.scitotenv.2020.141677

Vitt, D. H. (2006). Functional characteristics and indicators of boreal peatlands. In R. K. Wieder & D. H. Vitt (Eds.), *Boreal peatland ecosystems* (Vol. 188, pp. 9–24). Springer Berlin Heidelberg. https://doi.org/10.1007/978-3-540-31913-9_2

Walpen, N., Getzinger, G. J., Schroth, M. H., & Sander, M. (2018). Electron-Donating phenolic and electron-accepting quinone moieties in peat dissolved organic matter: Quantities and redox transformations in the context of peat biogeochemistry. *Environmental Science & Technology*, *52*(9), 5236–5245. https://doi.org/10.1021/acs.est.8b00594

Weiss, R., Shurpali, N. J., Sallantaus, T., Laiho, R., Laine, J., & Alm, J. (2006). Simulation of water table level and peat temperatures in boreal peatlands. *Ecological Modelling*, *192*(3), 441–456. https://doi.org/10.1016/j.ecolmodel.2005.07.016

Wilson, R. M., Hough, M. A., Verbeke, B. A., Hodgkins, S. B., Tyson, G., Sullivan, M. B., et al. (2022). Plant organic matter inputs exert a strong control on soil organic matter decomposition in a thawing permafrost peatland. *The Science of the Total Environment*, *820*, 152757. https://doi.org/10.1016/j.scitotenv.2021.152757

Wilson, R. M., Tfaily, M. M., Rich, V. I., Keller, J. K., Bridgham, S. D., Zalman, C. M., et al. (2017). Hydrogenation of organic matter as a terminal electron sink sustains high CO2:CH4 production ratios during anaerobic decomposition. *Organic Geochemistry*, *112*, 22–32. https://doi.org/10.1016/j.orggeochem.2017.06.011

Wu, J., & Roulet, N. T. (2014). Climate change reduces the capacity of northern peatlands to absorb the atmospheric carbon dioxide: The different responses of bogs and fens. *Global Biogeochemical Cycles*, *28*(10), 1005–1024. https://doi.org/10.1002/2014GB004845

Wyatt, K. H., Cieslik, J., Dieleman, C. M., Kane, E. S., Rober, A. R., Sullivan, B., & Turetsky, M. R. (2024). Legacy effects of plant community structure are manifested in microbial biofilm development with consequences for ecosystem CO emissions. *Global Change Biology*, *30*(12), e17603. https://doi.org/10.1111/gcb.17603

Yan, W., Wang, Y., Ju, P., Huang, X., & Chen, H. (2022). Water level regulates the rhizosphere priming effect on SOM decomposition of peatland soil. *Rhizosphere*, *21*, 100455. https://doi.org/10.1016/j.rhisph.2021.100455

Yang, S., Wang, K., Yu, X., Xu, Y., Ye, H., Bai, M., et al. (2024). Fulvic acid more facilitated the soil electron transfer than humic acid. *Journal of Hazardous Materials*, *469*, 134080. https://doi.org/10.1016/j.jhazmat.2024.134080

Yin, H., Li, Y., Xiao, J., Xu, Z., Cheng, X., & Liu, Q. (2013). Enhanced root exudation stimulates soil nitrogen transformations in a subalpine coniferous forest under experimental warming. *Global Change Biology*, *19*(7), 2158–2167. https://doi.org/10.1111/gcb.12161

Zhang, Z., & Furman, A. (2021). Soil redox dynamics under dynamic hydrologic regimes - A review. *The Science of the Total Environment*, *763*, 143026. https://doi.org/10.1016/j.scitotenv.2020.143026

Zhong, Y., Jiang, M., & Middleton, B. A. (2020). Effects of water level alteration on carbon cycling in peatlands. *Ecosystem Health and Sustainability*, *6*(1), 1806113. https://doi.org/10.1080/20964129.2020.1806113

References From the Supporting Information

Bowen, J. C., Hoyt, A. M., Xu, X., Nuriman, M., Anshari, G. Z., Wahyudio, P. J., & Aluwihare, L. I. (2024). The loss of aged carbon from drained and burned peatlands. *Global Change Biology*, *30*(7), e17394. https://doi.org/10.1111/gcb.17394

Dührkop, K., Fleischauer, M., Ludwig, M., Aksenov, A. A., Melnik, A. V., Meusel, M., et al. (2019). Sirius 4: A rapid tool for turning tandem mass spectra into metabolite structure information. *Nature Methods*, *16*(4), 299–302. https://doi.org/10.1038/s41592-019-0344-8

Kane, E. S., Chivers, M. R., Turetsky, M. R., Treat, C. C., Petersen, D. G., Waldrop, M., et al. (2013). Response of anaerobic carbon cycling to water table manipulation in an Alaskan rich fen. *Soil Biology and Biochemistry*, *58*, 50–60. https://doi.org/10.1016/j.soilbio.2012.10.032

Koester, I., Quinlan, Z. A., Nothias, L.-F., White, M. E., Rabines, A., Petras, D., et al. (2022). Illuminating the dark metabolome of pseudo-nitzschia–microbiome associations. *Environmental Microbiology*, *24*(11), 5408–5424. https://doi.org/10.1111/1462-2920.16242

Ludwig, M., Nothias, L.-F., Dührkop, K., Koester, I., Fleischauer, M., Hoffmann, M. A., et al. (2020). Database-independent molecular formula annotation using Gibbs sampling through ZODIAC. *Nature Machine Intelligence*, *2*(10), 629–641. https://doi.org/10.1038/s42256-020-00234-6

Schmid, R., Heuckeroth, S., Korf, A., Smirnov, A., Myers, O., Dyrlund, T. S., et al. (2023). Integrative analysis of multimodal mass spectrometry data in MZmine 3. *Nature Biotechnology*, *41*(4), 447–449. https://doi.org/10.1038/s41587-023-01690-2

Stubbins, A., Spencer, R. G. M., Chen, H., Hatcher, P. G., Mopper, K., Hernes, P. J., et al. (2010). Illuminated darkness: Molecular signatures of Congo River dissolved organic matter and its photochemical alteration as revealed by ultrahigh precision mass spectrometry. *Limnology & Oceanography*, *55*(4), 1467–1477. https://doi.org/10.4319/lo.2010.55.4.1467

Tfaily, M. M., Cooper, W. T., Kostka, J. E., Chanton, P. R., Schadt, C. W., Hanson, P. J., et al. (2014). Organic matter transformation in the peat column at Marcell Experimental Forest: Humification and vertical stratification. *Journal of Geophysical Research: Biogeosciences*, *119*(4), 661–675. https://doi.org/10.1002/2013JG002492

Tfaily, M. M., Wilson, R. M., Brewer, H. M., Chu, R. K., Heyman, H. M., Hoyt, D. W., et al. (2019). Single-throughput complementary high-resolution analytical techniques for characterizing complex natural organic matter mixtures. *Journal of Visualized Experiments*(143). https://doi.org/10.3791/59035

Veverica, T. J., Kane, E. S., Marcarelli, A. M., & Green, S. A. (2016). Ionic liquid extraction unveils previously occluded humic-bound iron in peat soil pore water. *Soil Science Society of America Journal*, *80*(3), 771–782. https://doi.org/10.2136/sssaj2015.10.0377