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Key Points:

- Water level variations strongly modulate the climate warming impact on dissolved organic carbon (DOC) composition in peatland mesocosms
- The climatic and hydrological impacts on the aromaticity of peatland DOC are weak in laboratory settings

Supporting Information:

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

Correspondence to:

M. Berggren,
martin.berggren@nateko.lu.se

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Author Contributions:

Conceptualization: Martin Berggren
Data curation: Miklas Scholz
Formal analysis: Martin Berggren, Shokoufeh Salimi, Bradley Sparkes
Funding acquisition: Martin Berggren, Miklas Scholz
Investigation: Martin Berggren, Shokoufeh Salimi, Bradley Sparkes
Methodology: Martin Berggren
Project administration: Miklas Scholz
Resources: Miklas Scholz
Visualization: Martin Berggren
Writing – original draft: Martin Berggren
Writing – review & editing: Martin Berggren, Shokoufeh Salimi, Bradley Sparkes, Miklas Scholz

Climate Impact on Dissolved Organic Carbon Composition in a North-Temperate Peatland and Recipient Surface Water

Martin Berggren¹ , Shokoufeh Salimi^{2,3}, Bradley Sparkes^{1,4} , and Miklas Scholz^{2,5,6,7}

¹Department of Physical Geography and Ecosystem Science, Lund University, Lund, Sweden, ²Division of Water Resources Engineering, Faculty of Engineering, Lund University, Lund, Sweden, ³Now at Department of Forest Ecology and Management, Swedish University of Agricultural Sciences, Umeå, Sweden, ⁴Now at Department of Soil and Environment, Swedish University of Agricultural Sciences, Uppsala, Sweden, ⁵Department of Civil Engineering Science, School of Civil Engineering, and the Built Environment, Faculty of Engineering and the Built Environment, University of Johannesburg, Johannesburg, South Africa, ⁶Directorate of Engineering, School of Science, Engineering and Environment, The University of Salford, Greater Manchester, UK, ⁷Now at Nexus by Sweden, Västerås, Sweden

Abstract Climate may regulate dissolved organic carbon (DOC) composition across the peat-water interface, but experimental evidence is scarce. We manipulated the climate in peatland and recipient surface water mesocosms to reflect four different climate warming scenarios. In half of the mesocosms, the water level was managed to avoid drought, after which responses were recorded during two annual cycles. It was hypothesized that warming and drought increase the aromaticity and humic-like fluorescence character of DOC, and that this change propagate to recipient waters. Pore water DOC concentrations increased with temperature and peaked in hydrologically unmanaged mesocosms. Aromaticity increased as expected after drought in the warmest scenario (+3.2°C), but the overall evidence for hypothesized changes in DOC aromaticity and fluorescence composition (%) was limited. In managed warming scenarios, one aromatic humic component expectedly increased together with microbially derived humic fluorescence, whereas two other humic-like components decreased. In the unmanaged mesocosms which were exposed to drought, water level exerted an overriding control of humic DOC; for example, as the microbially derived humic fluorescence diminished after drought in all climate scenarios. In the surface water recipients, warming had nearly no impact on humic-like fluorescence, but there were decreases in protein-like fluorescence. Overall, this experiment revealed no conclusive support for the hypothesized aromatization and humification of peatland-derived DOC in response to drought or warming. Nonetheless, both factors increase the quantity of DOC in peatland pore waters and affect composition in complex ways, calling for further investigation of chemical and functional traits of peatland DOC in a changing environment.

Plain Language Summary It is well known that peatlands leach organic carbon into recipient freshwaters, affecting their water quality. We hypothesized that warming and drying of peatlands make the material that leaches out from the peat more aromatic and brownish-colored. Such a browning would, chemically, be comparable to what happens in a fruit or vegetable that becomes brown faster due to air exposure or being taken out from the fridge. This hypothesis was tested in a laboratory experiment with peatland and receiving surface water ecosystems in glass tanks, in which the climate and water level were manipulated. Warming increased the concentrations and fluxes of dissolved organic carbon, but the “brownness” of the leached material generally did not change. Nonetheless, we found that different groups of fluorescent organic compounds either increased or decreased because of the combined influence of climate and water level. Thus, despite lacking support for our overall hypothesis, peatland leachate responses to climate change and water level clearly exist but are more complex than what could be expected. Our study underscores the importance of further characterization of the organic matter that leaches from peatlands in a changing environment, and how the freshwater network is affected.

1. Introduction

Northern hemisphere peatlands are hot spots in the global carbon cycle, storing more than 400 Pg of carbon in as little as ~2% of earth's land surface (Hugelius et al., 2020). Much attention has been drawn to peatland response to a changing environment (Gallego-Sala et al., 2018; Qiu et al., 2020; Salimi et al., 2021), especially in the context of warming and alterations in hydrology, frost conditions and wildfire dynamics (Loisel et al., 2021). These

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pressures not only affect the biogeochemical cycles within peatlands, but also the lateral export of solutes including dissolved organic carbon (DOC), to recipient freshwaters (Burd et al., 2020; Rosset et al., 2022). Thus, climate-related factors shape the role played by peatlands in the carbon cycle across land and water.

Over the last three decades, increased leakage of DOC from land into water has been widely reported in Europe and North America, related to changes in factors that include soil acidity (Evans et al., 2012), hydrology (de Wit et al., 2016) and temperature (Wauthy et al., 2018; Weyhenmeyer & Karlsson, 2009). For peatlands, there is empirical and experimental evidence of increasing DOC fluxes in a moderately warmer climate (Lou et al., 2014; Rosset et al., 2022). The hydrological impact is complex and partly indirect, for example, as drought may induce increased sulfur oxidation that lowers pH, hence limiting DOC solubility and export (Clark et al., 2012). Nonetheless, DOC production and accumulation in pore waters generally increase with boosted microbial activity in response to a lowered water table, whereas downstream DOC export increases with rising discharge during high water table conditions (Lou et al., 2014; Strack et al., 2008). Thus, DOC export from peatlands is controlled by the complex hydrological and biogeochemical dynamics of interchangeable dry and wet periods.

The concentrations and fluxes of DOC are relatively well-studied in peatland warming experiments (Pastor et al., 2003) and field studies (Rosset et al., 2022), but less is known about the warming effects on composition and characteristics of the DOC (Fenner et al., 2007). A long-standing hypothesis has been that warming increases the aromaticity of peatland DOC, due to temperature-dependent oxidation of plant phenolics into aromatic compounds (Freeman et al., 2001, 2004). This is the same mechanism as that which causes browning of fruit and vegetables, that is, phenol oxidase transforms phenols into brown-pigmented aromatic compounds upon exposure to oxygen, at rates that are speeded up by higher temperatures (Queiroz et al., 2008). However, peatland warming experiments have provided inconclusive evidence for the expected effect on DOC aromaticity, with responses ranging from positive (Lou et al., 2014) to absent (Luan et al., 2019) and even negative (Kane et al., 2014). To advance the understanding of climate change effects on peatland DOC, there is need to address the combined impact of warming and other major aspects of the environment, such as water table dynamics.

Most aromatic DOC is hydrophobic and generally referred to as “humic” if alkali-extracted (Olk et al., 2019) or “humic-like” (Murphy et al., 2013) if measured using fluorescence excitation-emission matrix (EEM) analysis. Humic DOC causes a dark, acidic and carbon-rich environment in freshwaters, which constrains biodiversity and changes food web structures (Creed et al., 2018; Jansson et al., 2007). However, in spite of this pivotal key role of humic DOC, the general hypothesis that climate change causes a relatively more humic character of the DOC largely remains poorly tested (Creed et al., 2018). Studies have found support for increasing DOC aromaticity with dropping peatland water level (Hribljan et al., 2014) and vice versa (Kane et al., 2021), as indicated patterns in Specific UV absorbance (SUVA) (specific ultraviolet absorbance; a proxy variable for aromaticity). However, no experimental study has analyzed the combined effects of warming and hydrological conditions on DOC composition in both peatlands and their recipient freshwaters.

Based on the idea of temperature-dependent oxidative aromatization of organic matter, we here hypothesized that well-aerated and warm environments transform peatland DOC into a more aromatic state. We predicted that both warming and drought (low water level) cause elevated SUVA and increased relative abundance of humic-like fluorescence, while other components such as protein-like fluorescence decrease. It was further predicted that these changes propagate to recipient waters. The hypotheses were tested in a laboratory study which involved manipulation of climate and water levels in peatland and recipient surface water mesocosms. Water levels were managed in half of the mesocosms to avoid drought, and the DOC composition response at different simulated future climates was recorded using EEM analysis. Besides allowing for the predictions to be tested, the setup provided a basis for discussion of possible interactions between warming, water table dynamics and other environmental factors on DOC composition.

2. Methods

2.1. Study Site and Experimental Design

The experiment was based on peatland samples from the ombrotrophic bog Fäjemyr in southern Sweden (56° 15'N, 13°33'E), dominated by dwarf shrubs (*Calluna vulgaris* and *Erica tetralix*), sedges (*Eriophorum vaginatum*) and Sphagnum mosses like *S. magellanicum* and *S. rubellum* (Lund et al., 2012). Fäjemyr is a raised (eccentric) bog, with the mean annual temperature of 6°C and precipitation (mainly rain) of 700 mm (Lund

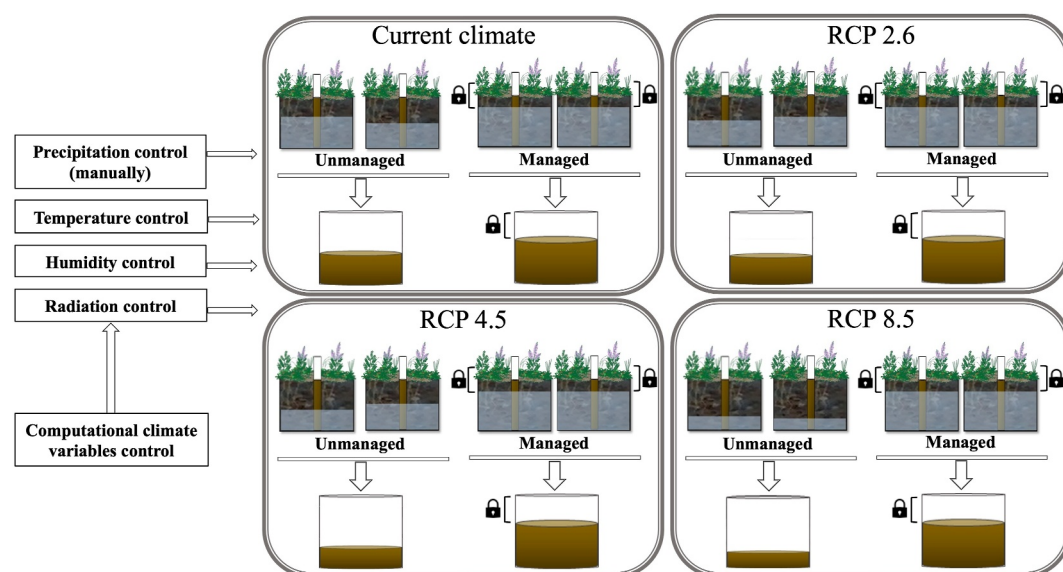


Figure 1. Schematic representation of how peat and recipient surface water mesocosms were distributed in four climate chambers. Each climate chamber simulated a specific computed climate scenario by controlling temperature, humidity and radiation automatically. Precipitation was added manually, and runoff was transferred manually from each pair of replicate peat mesocosms to one recipient surface water mesocosm. Water levels varied freely from top to bottom in the unmanaged mesocosms, while being adjusted toward a fixed depth, indicated by lock symbol, in managed mesocosms.

et al., 2007). Most of the area is naturally saturated in fall and winter, with a water table a couple of cm above ground level, while during and spring and summer the water table depth typically varies from 0 to 20 cm (Lund et al., 2007). The bog is drained by multiple streams that discharge into nearby small lakes and open water wetlands.

The samples were dug up on 15 June 2017, from the top 20 cm of the bog and placed directly in 16 glass tanks (30 × 22 cm inner surface, 24 cm height; one sample per tank). Each tank had a representative abundance of sedges and dwarf shrubs, underlain by living moss at the top, decaying moss and plant material in the middle and young peat at the bottom. A vertical 3 cm wide pipe was inserted in the middle of each peat mesocosm tank, with an inlet at the tank bottom, from which water samples and outflow water was collected throughout the experiment. The peatland mesocosms were directly and randomly placed in four different climate chambers (model KK 750 Pol-Eko-Aparatura Wodziszaw Slski, Poland) and incubated for more than three years in total, during which temperature, relative humidity and light (using 840 fluorescent lamps) were regulated at 3-hr interval. Sampling and monitoring of the mesocosms were initiated on first of October 2017.

Each of the climate chambers represented one climate scenario and contained four peatland mesocosms plus two additional recipient surface water mesocosms that received the peatland mesocosm outflow (see schematic in Figure 1 and climate scenario data in Figure 2). Conceptually, these recipients represent shallow lakes or open water wetlands. The recipient surface water mesocosms were initially filled by 5 cm depth sediment and 18 cm depth stormwater with 5 mg L⁻¹ of DOC from an urban stormwater pond at Lund University campus (Sjön Sjön, located at the Faculty of Engineering). Due to the shallow depth of these mesocosms, they were always well mixed and oxygenated even if no stirring occurred (dissolved oxygen saturation >50%). No outflow pipes were installed in the recipient water mesocosms, as sampling and removal of runoff could be done directly from the middle of the open water.

The simulated climates scenarios involved drought periods with different degrees of severity. To disentangle the effects of hydrology and temperature, respectively, we managed the water table in half of the mesocosms, whereas the other half were allowed to flood or dry out. Hence, each climate chamber contained one managed and one unmanaged set of duplicate peatland mesocosms, each associated with a recipient surface water mesocosm (Figure 1). The water table dynamics of the unmanaged mesocosms roughly followed the water table dynamics of the field site Fäjemyr (Lund et al., 2007). However, drought probably hit harder in the mesocosms than in the

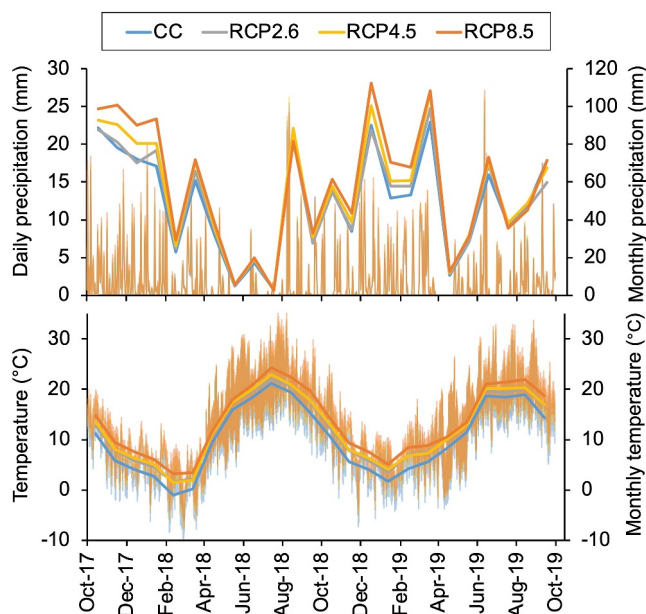


Figure 2. Simulated climate scenarios. Precipitation and temperature raw data are shown as thin semi-transparent lines read on the left-side y axes. To make the differences between the scenarios more visible, monthly values (plotted in the middle of each month range) for precipitation and mean temperature are shown as thick lines read on the right-side y axes.

identified as appropriate management thresholds. Water level management was performed by either adding water from the pond Sjön Sjön to the mesocosms when the water level declined to less than 10 cm due to evapotranspiration, or by removing excess water from the mesocosms as runoff when the water level exceeded 18 cm (Figure 3). All the outflow from the managed peatland mesocosms was transferred to the managed recipient surface water mesocosm and the outflow from the unmanaged peatland mesocosms was transferred to the unmanaged recipient mesocosm (Figure 1). The managed surface water recipient mesocosms went through the same management protocol as the peatland mesocosms, that is, confining the water level to a 10–18 cm range.

For the unmanaged mesocosms, the water level management procedures were skipped, and rainwater was simulated using climate scenario precipitation values. Runoff from the unmanaged mesocosms was based on overflow only: when water approached the top of the glass tanks it was siphoned through a tube from which it was collected. This siphon was inserted in the outflow pipes of the peatland mesocosms and in the middle of the water in the recipient surface water mesocosms. Unmanaged peatland and their recipient mesocosms experienced drought in 2018, with little or no water in the tanks (Figure 3), hence there was insufficient water for any sampling of unmanaged peat mesocosms during the simulated dry months of May–July 2018. Overall, the water level showed more than three times greater fluctuations in unmanaged than in hydrologically managed peat mesocosms (Figure 3).

2.3. Climate Scenarios

Current climate (CC) simulations were based on measurements from the Swedish Meteorological and Hydrological Institute, with a time lag of 1 year. Thus, when the measurements for this study started in October 2018, the simulated climate represented October 2017. The procedure for defining climate scenarios is explained in detail by Salimi et al. (2021) and Salimi and Scholz (2022). In short, future climate warming scenarios (Figure 2) were calculated with the delta change approach, using the differences and ratios between historical climate data and regional climate models data based on future representative concentration pathway (RCP) climate scenarios. Besides temperature and precipitation, relative humidity and photosynthetically active radiation were controlled for each scenario as explained by Salimi et al. (2021). The four different climate conditions included a CC (2017–2019) and the three future RCP climate scenarios RCP 2.6 (low), RCP 4.5 (moderate), and RCP 8.5 (extreme). Compared with the CC, simulated climate warming scenarios elevated the average temperatures by 1.7°C (RCP

field, especially at elevated experimental temperatures, because the mesocosm glass bottom prevented capillary rise of water from deeper peat layers. In this study, the management treatment provided a stable hydrological baseline for evaluation these droughts. More generally, we chose to include hydrological management in the experiment as a response to the social demand for knowledge on carbon dynamics in managed wetlands, for example, given the increased interest in peatland rewetting projects (Salimi & Scholz, 2022; Salimi et al., 2021).

No measurements of DOC composition were carried out during the first year of the incubation. Thus, from the perspective of this study, the experiment started in year two and covered years two and three, whereas year one was an initial stabilization and climate acclimatization period.

2.2. Precipitation, Runoff, and Water Level Management

Precipitation and runoff simulation was conducted discretely, once per week, by sprinkling rainwater that was collected from neighboring greenhouse glass roofs to the top of peatland and recipient surface water mesocosms, and by manually transferring runoff water from the peatland outflow pipes to the recipient surface water mesocosms using a syringe and tube. Thus, there was no continuous flow through the system, but a manual weekly simulation of water fluxes.

Water levels were managed in half of the replicates directly after the weekly rainwater addition, while the other half remained unmanaged. Water levels between above 10 and below 18 cm (from the bottom of the mesocosm) were

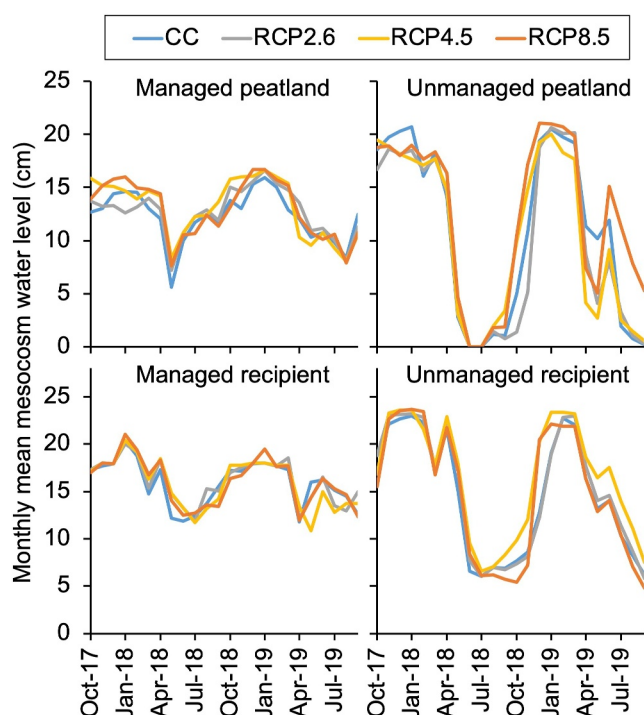


Figure 3. Water levels in the different experiment mesocosms, in four simulated climate scenarios. In the managed mesocosms (panels to the left), the water level was adjusted by stormwater additions and water removal, to avoid drought and flooding. The unmanaged mesocosms (panels to the right) were allowed to dry out or flood without restrictions.

2.6), 2.0°C (RCP 4.5) and 3.2°C (RCP 8.5), and winter precipitation increased gradually in the warming scenarios by up to ~20 mm per month (Figure 3).

2.4. Sampling and Analyses

Samples for DOC concentration and optical composition analyses (absorbance and fluorescence) were collected monthly from the peatland mesocosm outlet pipes and from the center point of the recipient surface water mesocosms, using a syringe. However, in 12% of the cases it was not possible to extract sufficient water for analysis due to either drought (10%) or frost (2%). Ice and soil frost were generally absent and did not affect the sampling, with the exception of the simulated month February 2018 when the surface water mesocosms and one of the CC peatland mesocosms were frozen on the sampling day. The samples for optical analyses were filtered through glass fiber filters (Whatman GF/F) and stored cold until analysis. DOC samples were filtered through syringe filters (0.45 μm Filtropur S, Sarstedt, Nümbrecht, Germany), stored cold and analyzed through oxidative combustion-infrared analysis using a TOC analyzer (model TOC-V CPH-TNM-1, Shimadzu, Japan).

Absorbance scans and excitation-emission fluorescence matrices (EEMs) were collected on an Aqualog (Horiba Scientific) in a 1-cm quartz cuvette (2 s integration time) over 5 nm excitation wavelength increments from 230 to 800 and ~2 nm emission increments from 250 to 800 nm. The EEMs were blank-subtracted (Milli-Q water), corrected for inner filter effects (Kothawala et al., 2013), normalized to the Raman area of deionized (Milli-Q) water (Lawaetz & Stedmon, 2009) and cropped to excitation range 250–450 nm and emission range 300–600 nm. Fluorescent components were identified with parallel factor analysis (PARAFAC) of the corrected EEMs using the sixth release of the drEEM toolbox (Murphy et al., 2013) in MATLAB® release

2022a. To get a strong unified PARAFAC model for the whole project, we did not limit the data input to the time frame and mesocosms used in this study ($n = 496$) but used all available EEMs from the entire experiment ($n = 1,505$; Berggren et al., 2024), including those from constructed wetland mesocosms described by Salimi and Scholz (2021). After removing outliers (3% of the cases), where the inner filter correction failed because of too high absorbance, a six-component model was validated using split-half analysis (Figure S1 in Supporting Information S1) and cross-referenced against openFLUOR (Murphy et al., 2014). All components represented different known humic- and protein-like DOM fractions (Table 1).

Specific UV absorbance was used as an indicator of DOC aromaticity, where higher values mean increasing percentage of carbon in aromatic rings (Weishaar et al., 2003). We calculated the SUVA values at a wavelength of 254 nm ($SUVA_{254}$) by dividing the decadic absorbance coefficient at 254 nm (m^{-1}) by DOC concentration ($mg L^{-1}$).

2.5. Statistics

Hydrological management and climate scenario effects on DOC composition variables (% contribution from each PARAFAC component) were tested using paired *t*-tests in combination with Bonferroni corrections to maintain the overall alpha at 0.05. However, as we found that the scenarios often had different impact on managed and unmanaged mesocosms, respectively, we needed to do an additional test to confirm that there was an interaction between scenario and management. Therefore, we performed mixed linear effects modeling in Minitab® 19, with time as random factor, while climate scenario and management were fixed factors (not shown). This test showed that all six PARAFAC components were affected by significant ($p < 0.05$) interactions between scenario and management in the peatland mesocosms, confirming that any diverging *t*-test results between unmanaged and managed mesocosms accurately reflected underlying interactions. Finally, seasonal relationships and links between peatland source and recipient surface water mesocosms were explored using Pearson *r* correlations.

Table 1

Component Peak Positions, Peak Names and Descriptions Cross Referenced (Similarity 95% <) Using the OpenFluor Database (Murphy et al., 2014)

#	Excitation max (nm)	Emission max (nm)	Peak type	Cross reference examples	Description
1	<250 (310)	440	A & C	C1 in Hassan et al. (2023); C1 in Lambert et al. (2016b); C3 in Yamashita et al. (2010)	Humic-like
2	<250 (340)	519	D	C2 in Hassan et al. (2023); C2 in Lambert et al. (2016b); C5 in Yamashita et al. (2010)	Soil fulvic acid
3	<250 (305)	383	M	C4 in Zhou et al. (2019); C3 in Lambert et al. (2016b); C4 in Yamashita et al. (2010)	Microbially derived
4	<250 (385)	466	No name (upper em of A & C)	C4 in Shakil et al. (2020); C3 in Harjung et al. (2018); C4 in Cohen et al. (2014)	Humic-like
5	330	463	No name (upper em range of C)	C6 in Wheeler et al. (2017); C1 in Søndergaard et al. (2003); C3 in Lambert et al. (2016a)	Humic-like
6	280	330	B	C5 in Lambert et al. (2016b); C1 in Cohen et al. (2014); C7 in Yamashita et al. (2010)	Protein-like

Note. Peak type and description follow terminology of P. G. Coble (1996) and P. G. Coble et al. (2014).

3. Results

On average, DOC concentrations were significantly higher in hydrologically unmanaged (drought-exposed) than in the corresponding managed (water level-controlled) mesocosms, but in recipient surface waters this difference was only significant for CC and RCP 2.6 (Figure 4). The peat pore water DOC concentration was higher at RCP 8.5 than at CC in both managed and unmanaged mesocosms, but in contrast the managed RCP 2.6 scenario saw a slight drop in peat DOC. An overview of mean annual DOC fluxes through the mesocosms is presented in Figure S2 in Supporting Information S1. In disagreement with our prediction, $SUVA_{254}$ values did not change significantly in response to climate scenario. However, as an expected drought effect, $SUVA_{254}$ was higher in unmanaged than in managed peat mesocosms at RCP 8.5 (Figure 4).

Total fluorescence intensity showed a pattern that mirrored the DOC variations, with relatively high values in unmanaged systems and in warming scenarios, especially in peat pore waters at RCP 8.5 (Figure 5a). Seen over time, total fluorescence was similar in all mesocosm types until the simulated 2018 drought, after which the values increased strongly in unmanaged peat mesocosms and their recipients (Figure 5b). Seasonally, the absolute intensities of all individual fluorescence components correlated positively with temperature, with a few non-significant exceptions, like C5 in recipient mesocosms (Table 2). These increases in fluorescence intensities varied in strength between components, resulting in compositional changes. In the case of relative (%) fluorescence contributions, the two most abundant humic-like components C1 and C2 showed the predicted positive temperature relationships, and protein-like fluorescence (C6) decreased as expected (Table 2). The contributions (%) from remaining humic-like components unexpectedly showed absent (C4), mixed positive/negative (C3) or negative (C5) temperature responses. It is important to point out that these correlations were mainly driven by seasonality and not by (experimental) warming scenario, which had relatively minor impact on the temperature variations over time (Figure 3).

The experimental warming scenarios showed fluorescence composition (%) responses that were complex and often deviating from predictions. In most of the warming scenarios, humic-like components C1 and C3 increased as expected in managed peat mesocosms, but the remaining humic-like components showed unexpected decreases (C2 and C4) or mixed positive/negative (C5) responses (Figure 6). Moreover, no general pattern of changing humic-like fluorescence contributions across climate scenarios could be found in unmanaged mesocosms (Figure 6) or in any recipient surface water mesocosms (Figure S3 in Supporting Information S1). The protein-like component C6 (%) decreased as predicted in response to RCP 2.6 and RCP 8.5 in unmanaged peat mesocosms and in their recipients (Figure 6 and Figure S3 in Supporting Information S1). However, climate scenario had no impact on C6 in managed mesocosms (Figure 6 and Figure S3 in Supporting Information S1) except for in RCP 8.5 recipient mesocosms, where there expectedly was a slight yet significant decrease (Figure S3 in Supporting Information S1).

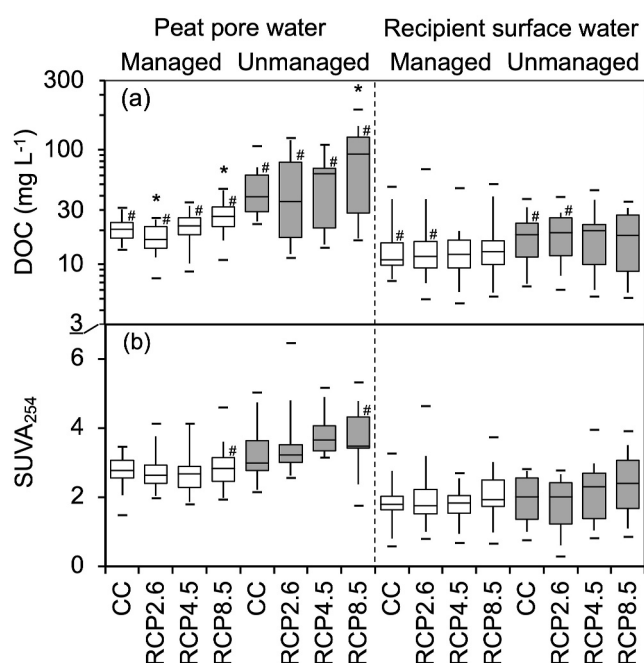


Figure 4. (a) Concentration of dissolved organic carbon and (b) specific ultraviolet absorbance at 254 nm in water from managed (controlled water level) and unmanaged (allowed to dry or flood) peatland and recipient mesocosms under different simulated climates. Boxes present quartiles 1, 2 (median) and 3. Lower and upper whiskers reach toward the 5th and 95th percentiles, respectively, and caps show mean/max values. Asterisk represents significant difference from the current climate and hash symbols denote significant difference between matching managed and unmanaged mesocosms, based on 2-tailed paired *t*-tests. The *t*-tests are Bonferroni-corrected for a total of 40 comparisons made in the figure (scaled alpha: $0.05/40 = 0.00125$).

The impact of drought itself on humic-like fluorescence contributions (%) was inconsistent, with effects ranging from strongly increased (C2) to strongly decreased (C3) values in the unmanaged compared to managed peat mesocosms (Figure 6). Contributions from C1 at RCP 2.6 and 4.5 were relatively lower in unmanaged than in managed peat mesocosms, while C4 at RCP 4.5 showed the opposite response and C5 was unchanged (Figure 6). Protein-like fluorescence (C6) partly responded as predicted, with decreased abundance in response to drought, but this effect was only statistically significant in the RCP 8.5 peat mesocosms (Figure 6). Interestingly, fluorescence composition in all recipient mesocosms was irresponsive to hydrological manipulation (Figure S3 in Supporting Information S1).

The slopes of the recipient versus peat mesocosm fluorescence intensity relationships (Figure 7) were at least twice as steep for managed compared with unmanaged mesocosms, in the case of C1–3 and C6 (but C4 and C5 showed no corresponding difference). Components C1 and C3 showed the largest degree of transfer from peat to recipient, whereas C5 was most lost in the recipient mesocosms.

4. Discussion

Warming and hydrological intensification change the DOC dynamics across the land-water interface, with a wide range of aquatic ecosystem effects (Blanchet et al., 2022; Jane et al., 2021; Solomon et al., 2015). The humic character of DOC, especially aromaticity, is a central feature for recipient ecosystem responses, but the idea that ongoing climate processes increase the humic content of terrestrially exported DOC remains a poorly tested hypothesis (Creed et al., 2018). Based on the manipulation of the climate in peat-based wetlands—a global hot spot for DOC export especially in northern landscapes (Rosset et al., 2022)—we discuss here that warming impacts both the quality and composition of peat DOC in ways that are sensitive to hydrology. However, our findings add to a growing number of studies with lacking support for the hypothesis of a generically increasing aromatic and

humic-like character of peat-derived DOC with warming, and in our experiment the DOC composition changes were mainly detected in the peatland pore waters but to a lesser extent in recipient surface waters.

Freeman et al. (2001) showed that warming can lead to selective accumulation of dissolved aromatics in peat wetlands, explained by temperature-limited oxidation of simple plant phenols into highly pigmented complex aromatic molecules (Freeman et al., 2001; Pinsonneault et al., 2016). However, this study found no support for the prediction that DOC aromaticity increases with warming, as SUVA₂₅₄ was roughly constant across climate scenarios. This contrasts experimental findings from the Tibetan Plateau, where peatland SUVA increased with warming (Lou et al., 2014), but agrees with some boreal peatland heating experiments with irresponsive SUVA (Luan et al., 2019; Sun et al., 2023). Interestingly, one temperate peat study found lowered SUVA with warming, linked to increasing bio-labile DOC at sites with more primary productivity (Kane et al., 2014), probably due to fresh plant-derived DOC (Strack et al., 2015). This suggests that plant productivity can dampen or reverse the negative impact of warming on SUVA, possibly explaining the lack of SUVA response at the Fäjemyr site, which is relatively productive as long as water is supplied (Salimi et al., 2021).

Nonetheless, hydrological management did increase SUVA (aromaticity) as expected in the warmest scenario, where the mesocosms that were exposed to drought cycles had relatively more aromatic DOC. The drought in the hydrologically unmanaged RCP 8.5 scenario was associated with strongly decreased net ecosystem productivity in our experiment, as reported by Salimi et al. (2021). Decreasing net ecosystem productivity in Fäjemyr has also been observed during drought through on-site field observations (Lund et al., 2012). In association with such productivity-limiting droughts, peatlands are expected to release relatively old and processed DOC with high aromaticity, especially upon subsequent rewetting (Clark et al., 2012; Tiwari et al., 2022). Thus, whereas climate per se appeared unimportant for total DOC aromaticity in this specific study, severe drought (RCP 8.5 climate)

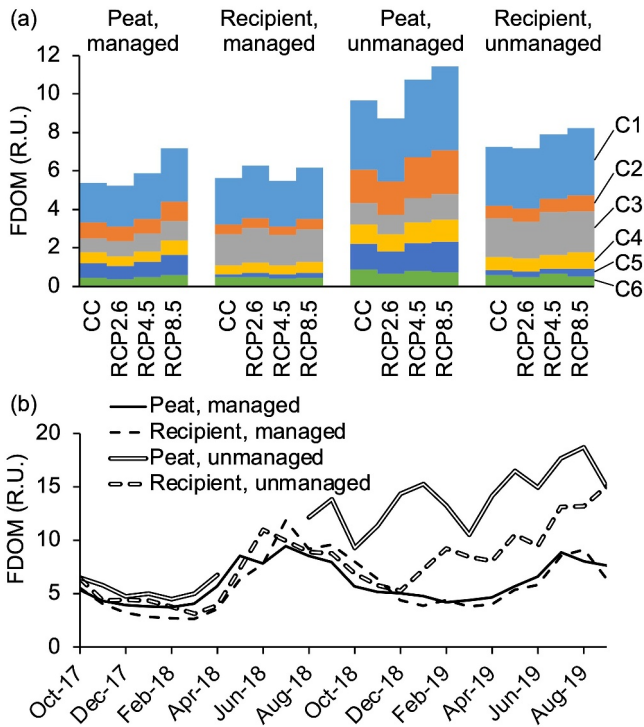


Figure 5. (a) Average contributions in Raman units (R.U.) to the fluorescent dissolved organic matter (FDOM) in peat mesocosms with managed and unmanaged water level, and their respective surface water recipient mesocosms, under four simulated climate scenarios. The contributions to the fluorescence intensities are stacked for six PARAFAC components, shown in different colors (C1–C6). (b) Average total FDOM across climate scenarios plotted over time for managed and unmanaged peat and recipient mesocosms.

had the predicted positive impact on $SUVA_{254}$. These results add to the broad range of previously reported $SUVA_{254}$ responses to peatland environment change, influenced by local differences between studies in factors including peatland productivity and hydrological functioning.

This study expands existing knowledge from peat warming experiments as DOC composition changes were measured using PARAFAC analysis of fluorescence EEMs, revealing complex and hydrology-dependent response patterns. For example, the protein-like fluorescence (C6, %) decreased as predicted in some peat warming scenarios (Figure 6) and was negatively related to seasonal temperature variations in peat (Table 2). However, the experimental warming effect on C6 was seen mainly in hydrologically unmanaged mesocosms, suggesting that it may not be primarily caused by climate scenario, but rather by the hydrology which caused severe drought and decreasing net primary productivity in our unmanaged warmed mesocosms (Salimi et al., 2021). This agrees with past findings of lower percentage protein-like fluorescence in DOC from relatively less productive peat wetlands (Fellman et al., 2008).

Two of the humic-like PARAFAC components, C1 and C3, followed the hypothesized pattern of increasing relative abundance with warming, but the effect was limited to peat mesocosms with managed water level. Component C1 fluoresces in a region that correlates with the highest-weight and most aromatic molecular fractions of natural DOC, while C3 is the classical M peak of presumed microbial origin representing relatively more nitrogen-rich and aliphatic molecules (Stubbins et al., 2014). Given that the managed mesocosms were designed to provide continuously optimal supply of water, warming likely stimulated microbial processes and increased the oxidative degradation of peat (Jassey et al., 2012; Pinsonneault et al., 2016), expected to boost C3 but also produce partly oxidized phenolics of aromatic C1-like character. However, in the hydrologically unmanaged mesocosms, C1 and C3 made up consistently low shares of the fluorescence, with no difference between climate scenarios. This observation disagrees with our prediction but

Table 2

Pearson r Correlations Between Monthly Mean Temperatures and the Absolute (Raman Units) or Relative (% of Total) Contributions to Fluorescent Dissolved Organic Matter Fluorescence by Six PARAFAC Components (C1–C6)

Variable	Peat, managed (<i>n</i> = 183)	Recipient, managed (<i>n</i> = 89)	Peat, unmanaged (<i>n</i> = 131)	Recipient, unmanaged (<i>n</i> = 80)
C1 (R.U.)	0.81 ^a	0.80 ^a	0.42 ^a	0.70 ^a
C2 (R.U.)	0.79 ^a	0.76 ^a	0.52 ^a	0.35
C3 (R.U.)	0.78 ^a	0.81 ^a	0.37 ^a	0.82 ^a
C4 (R.U.)	0.77 ^a	0.65 ^a	0.48 ^a	0.31
C5 (R.U.)	0.72 ^a	0.08	0.39 ^a	0.21
C6 (R.U.)	0.53 ^a	0.76 ^a	0.18	0.76 ^a
C1 (%)	0.25 ^b	0.35 ^b	0.12	0.29
C2 (%)	0.40 ^a	−0.29	0.58 ^a	−0.19
C3 (%)	−0.27 ^b	0.57 ^a	−0.36 ^a	0.18
C4 (%)	0.09	−0.34	0.15	−0.24
C5 (%)	−0.24 ^b	−0.48 ^a	−0.35 ^c	−0.13
C6 (%)	−0.34 ^a	−0.20	−0.43 ^a	−0.09

Note. The significance levels are Bonferroni-corrected for 48 tests made in this table. ^a2-tail $p < 0.001/48$ (<0.0000208). ^b2-tail $p < 0.05/48$ (<0.00104). ^c2-tail $p < 0.01/48$ (<0.000208).

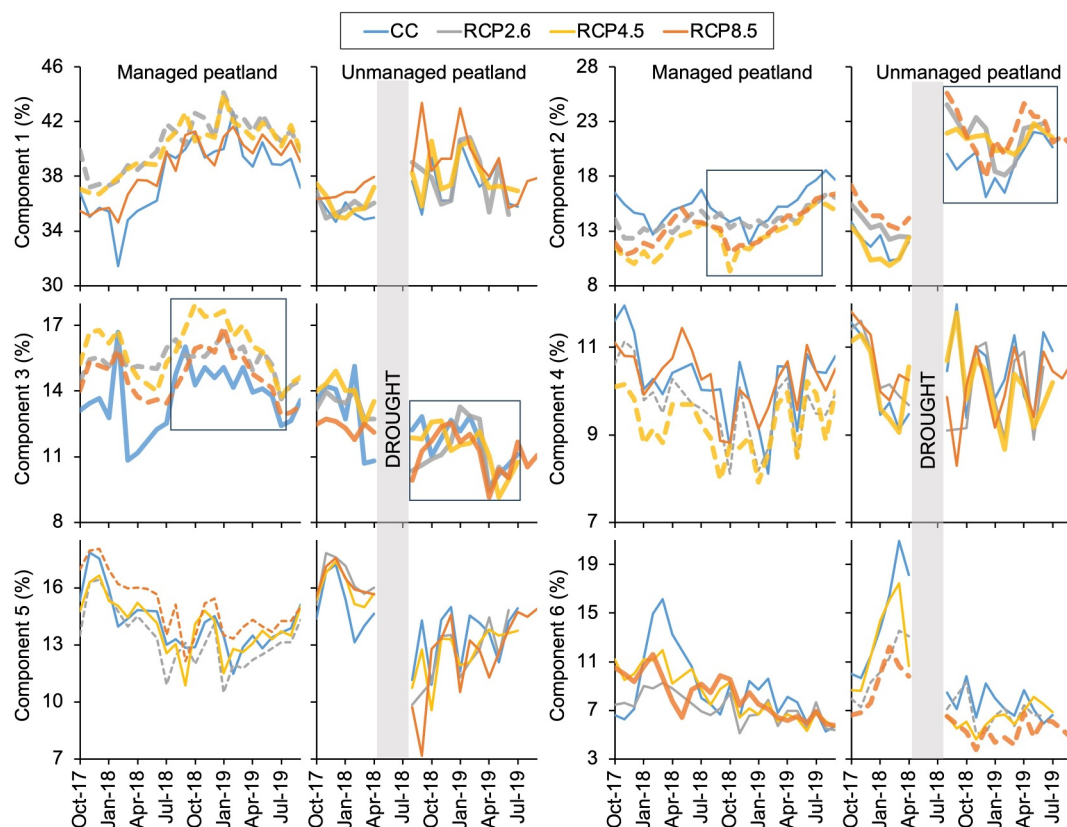


Figure 6. Contributions (%) to the fluorescence by six PARAFAC components, to the fluorescent dissolved organic matter in pore waters from managed (controlled water level) and unmanaged (allowed to dry or flood) peatland mesocosms under different simulated climates. Each line shows the average of two replicate mesocosms exposed to a specific climate simulation. Dashed line represents significant difference from the current climate and thick line denote significant difference between matching managed and unmanaged mesocosms, based on 2-tailed paired *t*-tests. The *t*-tests are Bonferroni-corrected for a total of 60 comparisons made across the panels (scaled alpha: $0.05/60 = 0.000833$). The squares highlight sustained periods without any overlap between curves for managed and unmanaged mesocosms, respectively.

supports the view that hydrology is the master factor of overriding importance and a limiting factor for peatland microbial processes (Gorecki et al., 2021).

The fact that C2 and C4 showed the complete opposite response patterns (compared to that of C1 and C3; see Figure 6), while C5 was not coherently affected by either climate scenario or hydrological management, demonstrates that humic DOC response to climate change is complex. Component C2 overlaps with peak “D,” possibly representing fulvic acids (P. G. Coble et al., 2014) or conjugated humics in general (Moona et al., 2021). Regarding C4, the OpenFluor cross-references (Cohen et al., 2014; Harjung et al., 2018; Shakil et al., 2020) propose an origin in the fluorophores “A + C,” but this is questionable because C4 had slightly higher emission maximum (466 nm) than the ranges of both “A” (400–460 nm) and “C” (420–460 nm) (P. G. Coble, 2007). It is similarly difficult to interpret C5, since the cross-references (Table 1) define this component as either “unknown” or as poor match with “C.” Nonetheless, in spite of these limitations in the interpretability of C2, C4 and C5, our analysis shows that the combined EEM-PARAFAC approach can detect response patterns among sub-components of humic DOC, even where SUVA fails to identify the impact of both warming and the hydrological regime. This calls for further, more detailed, characterizations of the DOC response to peatland change, for example, using high resolution mass spectroscopy or nuclear mass resonance approaches (McCallister et al., 2018). Given that northern peatlands are highly vulnerable to climate change while being one of the Earth’s largest sources of DOC export (Rosset et al., 2022), such analyses can shed light on globally significant changes in the chemical properties of exported DOC, and thus the anticipated ecosystem impacts including those on greenhouse gas emissions (Lapierre et al., 2013) and aquatic food webs (Creed et al., 2018).

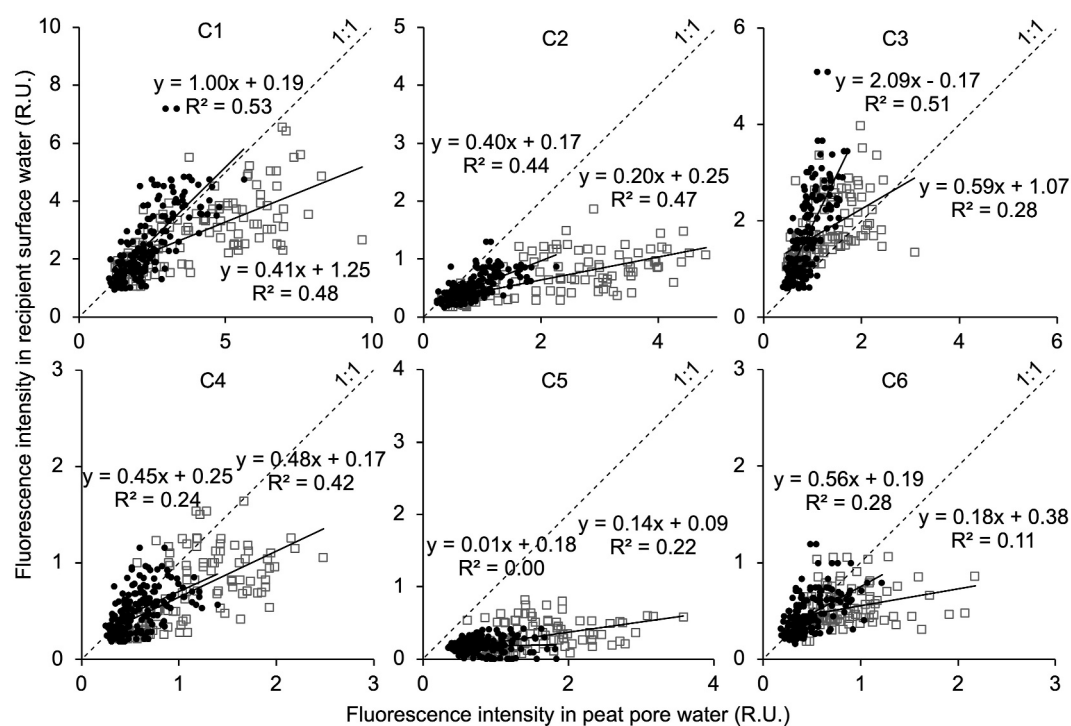


Figure 7. Relationships between fluorescence intensities of six PARAFAC components (C1–C6) in surface water recipient mesocosms and in peat source mesocosms, respectively. The data is split into managed mesocosms (filled circles, $n = 171$) with controlled water level and unmanaged mesocosms (open squares, $n = 119$) allowed to dry out or flood. The points show results across a range of simulated climate variations during a 2-year experiment, in which the runoff from peat mesocosms was transferred to matching recipient surface water mesocosms.

The experimental treatments mattered surprisingly little for DOC composition in recipient surface water mesocosms, and our prediction that hypothesized impacts from warming and drought propagate to recipient waters was poorly supported. Nonetheless, the transfer rates from peat to recipient provide important insights into the persistence of peat-derived DOC in receiving surface waters. Out of the six PARAFAC components, C1 and C3 in the managed mesocosms showed the highest transfer, with slopes of the recipient versus peat mesocosm concentrations of 1:1 (C1) or 2:1 (C3; see Figure 7), indicating either recalcitrance to degradation and/or additional production in the water at rates that compensated the consumption. These components are not only known to be persistent to biological degradation (Cory & Kaplan, 2012) but can also be net produced by bacterioplankton (Berggren et al., 2020). At the same time, they are susceptible to photo-degradation (Stubbins et al., 2014). On long time-scales, humic-like components tend to be lost from the water (Kellerman et al., 2015). However, since the lamps of the climate chambers simulated photosynthetically active radiation only (not ultraviolet light), the possibility of photodegradation was limited, and components C1 and C3 could accumulate in the water.

Remaining components were lost to various degrees in the water, presumably from a combination of degradation and rainwater dilution, especially C5 which was nearly completely degraded in recipient water mesocosms. However, there was no general pattern of protein-like and non-aromatic DOC being more persistent than humic-like DOC, as found by others (Kellerman et al., 2015; Weyhenmeyer et al., 2012), possibly because the residence time was too short and the photo-decay too limited in the experiment for such patterns to be realized. It should be noted that the low recipient versus peat slopes in unmanaged mesocosms (Figure 7) was caused by the delayed effect from the 2018 drought, as it took several months until total fluorescence intensities in recipient mesocosms balanced with the remarkably high post-drought fluorescence intensities of the unmanaged peat source mesocosms (Figure 5). This effect was a result of our experimental design, but also reflects the hydrological disconnection between surface waters and upland carbon sources induced by drought (Szkokan-Emilson et al., 2017). A similar disconnection and delay in DOC export from the Fåjemyr peatland its recipients could be expected, based on what is known about the hydrology (Lund et al., 2007) and sensitivity to drought (Lund et al., 2012) of this site.

The degree to which this experimental study is representative to the Fäjemyr site and its recipient surface waters is an open question, given that we simulated only the upper 20 cm of the peatland system. In situ measurements have shown that Fäjemyr switches from being a carbon sink during normal years to a carbon source during years with drought (Lund et al., 2012), confirming that the site is highly sensitive to hydrological variations. Climate warming has experimentally been shown to exacerbate the difference in the Fäjemyr carbon balance between dry and wet conditions, respectively (Salimi et al., 2021), but the overall picture from these past studies is that hydrology is the master regulator of carbon biogeochemistry. In this regard, it is unsurprising that this study found a relatively greater importance of water level dynamics, than of temperature, for the quantity and composition of DOC across the peat-surface water interface.

5. Conclusion and Outlook

In the face of ongoing climate change, the fate of peat-derived carbon in surface waters is getting increased attention. This study adds to growing evidence for increased peatland DOC concentrations and export in response to climate warming and intensified drought cycle dynamics. However, in disagreement with our hypothesis, none of the tested IPCC scenarios increased the overall aromaticity or the humic-like character of peatland DOC. Drought did increase pore water aromaticity of DOC as predicted, but only when combined with extreme warming. Moreover, we found weak support for climate warming impacts on DOC composition in recipient surface waters. Thus, no coherent support was received for the predictions that warming and drought conditions result in aromatic and humic-like DOC in peatlands as well as recipient waters. Nonetheless, EEM-PARAFAC revealed that some sub-components of the DOC pool in the peatland pore water increased with warming whereas other decreased, with especially clear patterns if drought was absent, calling for further studies to characterize these fractions with greater chemical detail (Tfaily et al., 2015). Interestingly, the two humic-like fluorescence components that showed coherent positive responses to climate warming were also the same two components that were most persistent in the recipient surface water mesocosms. Most importantly, our study highlights the role of hydrology, as drought can cancel or reverse the controls on DOC composition otherwise exerted by climate.

Data Availability Statement

A summary of PARAFAC component scores, DOC concentrations, SUVA and other data used in the analyses (monthly mean mesocosm temperature and water level) can be found in the supporting data file “Supplementary fluorescence data.xlsx.” This data is also deposited at figshare (<https://www.doi.org/10.6084/m9.figshare.25827340>), together with original and processed EEMs, and the MATLAB® code used in the PARAFAC modeling.

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