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Key Points:

- Benthic algal production represents an underestimated dissolved organic carbon source in peatland reservoirs
- Phytoplankton dissolved organic carbon contributions may be more important in low productivity systems than expected
- Increased dissolved organic carbon loads of all fractions are predicted at drinking water treatment works in a future climate

Supporting Information:

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

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Effects of Climate Change on Peatland Reservoirs: A DOC Perspective

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Abstract Peatland reservoirs are global hotspots for drinking water provision and are likely to become more important as demand per capita rises and the climate changes. Dissolved organic carbon (DOC) is associated with harmful disinfection byproducts and reduced aesthetic quality, and its removal is the major treatment cost. Littoral zones are known to be disproportionately important for DOC production through macrophyte inputs, and such communities are predicted to expand with warming in northern regions. However, little is known about autochthonous DOC contributions and their response to climatic change. Here we exposed mesocosms to elevated CO₂ (eCO₂), warming and a combined treatment across a trophic gradient. Regression analysis indicated that while sediments, macrophytes, and phytoplankton are important DOC sources ($P < 0.05$), benthic algal biomass showed the strongest relationship with DOC ($P < 0.05$), suggesting it is an underestimated source. DOC removal indicators, namely phenol oxidase (depolymerization) and respiration (mineralization) were inversely related to DOC concentration in oligohumic ($P < 0.05$) and oligotrophic ($P < 0.1$) systems, suggesting heterotrophic processes are important in DOC removal. DOC concentrations increased across all systems ($P < 0.05$), irrespective of trophic status, due to increased photoautotrophic inputs (macrophyte, pelagic, and benthic algae) under eCO₂, warming, and combined scenarios, with inhibited depolymerization and mineralization under eCO₂, even when combined with warming ($P < 0.05$ and $P < 0.05$ excepting the oligo-mesotrophic reservoir $P < 0.1$ respectively). Increased DOC loads of all fractions, regardless of provenance, are predicted in a future climate and, thus, investment in techniques to remove a greater range of DOC fractions is proposed to help “future proof” drinking water supplies.

Plain Language Summary Peatlands form in wet areas and therefore are important sources of drinking water in many regions. The waterlogged conditions prevent decomposition of plant material and allow vast stores of carbon to accumulate as peat. Dissolved carbon leaches from these stores and into peatland reservoirs. This is a problem for the water treatment industry because the carbon interacts with chlorine used to disinfect our water, causing harmful byproducts. Algae and aquatic plants within reservoirs also produce dissolved carbon, while microbes consume it. However, little is known about how important these sources and sinks are, or how climate change might affect them, and therefore the treatability of our water. We used reservoir mesocosms exposed to elevated CO₂, warming, and combined climate change simulations to investigate this. Algal carbon sources were greater than expected, which is important because they can be associated with particularly toxic treatment byproducts. We also found that plant and algal production increased under all climate change scenarios, while microbial removal was inhibited, giving higher levels of dissolved carbon, but also a greater range of types and sizes. These results suggest that more efficient and varied treatment processes are needed to help future proof drinking water quality from peaty catchments.

1. Introduction

Dissolved organic carbon (DOC) has numerous effects on aquatic ecosystem properties (e.g., Evans et al., 2005) and therefore ecosystem goods and services (e.g., Lapierre et al., 2013; Winterdahl et al., 2014), including drinking water quality (Bull et al., 1995), feedbacks to climate change and mitigation strategies (Wallin et al., 2013). While trends are not necessarily universal (Winterdahl et al., 2014; Worrall et al., 2018), increased DOC concentrations across North America and Europe have been reported as a result of climatic changes (e.g., Fenner, Freeman, et al., 2007; Fenner, Ostle, et al., 2007; Freeman et al., 2004; Freeman, Evans, et al., 2001; Freeman, Ostle, & Kang, 2001; Larsen et al., 2011), increased solubility due to pH changes

(Monteith et al., 2007), or hydrological export (Forsberg, 1992 and references therein), and, peatland catchments have seen the greatest increase (Freeman, Evans, et al., 2001; Freeman, Ostle, & Kang, 2001). Understanding drivers of changes in DOC concentration is important, not least because terrestrial biomes where peatlands are abundant are global hotspots for drinking water provision (Xu et al., 2018) and DOC is becoming increasingly difficult to treat using conventional coagulation processes, due to changes in composition and increased concentration (Worrall & Burt, 2009). DOC removal represents the single largest treatment cost for the water treatment industry (Watts et al., 2001) and elevated concentrations in raw water increase costs by increasing coagulant and chlorine demand (Chow et al., 2005; Edzwald, 1993) and the frequency of filter backwashes (Eikebrokk et al., 2004). DOC in finished water reduces the aesthetic value (color, odor, and taste [WHO, 2011]), but also transports micro-pollutants (Gao et al., 1998; Rothwell et al., 2007) and leads to bacterial regrowth in distribution systems (Prévost et al., 1998). Moreover, DOC acts as a precursor during chlorination for harmful carbonaceous (C-), and nitrogenous (N-) disinfection byproducts (DBP) (WHO, 2011).

The majority of studies investigating trends in DOC concentrations and fluxes have focussed on the delivery to, and fate of, allochthonous DOC in freshwaters. This is probably due to the importance of catchment properties in dictating aquatic DOC concentrations (e.g., Freeman, Ostle, & Kang, 2001; Wetzel, 1992) and widespread CO₂ super saturation of inland waters, suggesting net heterotrophy fueled by such terrestrial subsidies (e.g., Raymond et al., 2013; Sobek et al., 2003). However, much less is known about potential changes to autochthonous DOC inputs, despite the fact that the littoral zone is an important source of DOC (Lauster et al., 2006; Stets & Cotner, 2008; Wetzel, 1992) and the vast majority of freshwater lakes are small (surface area <1 km²; Downing et al., 2006) meaning close proximity of pelagic and littoral zones (Stets & Cotner, 2008). Indeed, the concentration of biodegradable DOC (bDOC) in lakes has been found to be most closely related to the proportion of lake covered by littoral zone (Stets & Cotner, 2008).

The littoral zone of a lake can be defined as the area shallow enough to support rooted plant growth, including everything from emergent vascular macrophytes to submerged macroalgae, but not wetland areas adjacent to the lake basin (Stets & Cotner, 2008) that are less frequently inundated, and tends to exhibit favorable conditions for photoautotrophic colonization (They et al., 2013). Macrophytes are thought to be the major primary producers in lakes (Hempel et al., 2009), and are therefore particularly important contributors of organic carbon, often more so than algae (Lauster et al., 2006; They et al., 2013; Wetzel, 1992). Macrophyte organic carbon inputs are thought to be relatively recalcitrant compared with algal contributions, due to being predominantly poor quality (low in nitrogen and phosphorus; Lauster et al., 2006) high molecular weight, and rich in polymeric compounds (Bracchini et al., 2006). It is the recalcitrant, aromatic, and hydrophobic fraction of dissolved organic matter (DOM) that has been most strongly linked to DBP precursors, especially trihalomethanes (THM; Ritson et al., 2014, 2016), however, it is also the easiest to remove via coagulation (Bond et al., 2011; Ritson et al., 2016). It is also associated with lower bacterial respiration (They et al., 2013) and inhibited methanogenesis (e.g., Emilson et al., 2018; West et al., 2012). Stets and Cotner (2008) found relatively slow decomposition rates, even for bDOC in lake littoral zones in Minnesota. Some species of macrophyte have even been found to contain polyphenolic allelochemicals inhibitory to algae, cyanobacteria, and heterotrophs (Hempel et al., 2009).

Algal DOC, on the other hand, is thought to be labile and therefore preferentially metabolized (Bade et al., 2007; Romani et al., 2004), characterized by low molecular weight and hydrophilic fractions with more proteinaceous material, making it difficult to remove via conventional coagulation processes (Krasner, 2009; Ritson et al., 2014, 2016). The latter is also linked to formation of the potentially more harmful emerging DBPs (e.g., N-DBPs) either directly due to high inorganic nitrogen loads, or indirectly via increased algal biomass and consequently dissolved organic nitrogen in raw waters (Ritson et al., 2014). A substantial proportion of the DOC pool can be algal (e.g., 5% in a humic system, through 20% in lightly colored lakes, to 40% in a eutrophic lake) and this DOC becomes more refractory with time, with concentrations increasing proportionately to primary production (Bade et al., 2007). Both pelagic (phytoplankton) and benthic algal (biofilm) components are thought to play important roles in primary production, depending on the nutrient level (Vadeboncoeur et al., 2001), but little information apparently exists on whether the latter contributes appreciable levels of DOC. Conversely, benthic biofilm is known to be efficient in DOC and organic matter (OM) removal (Battin et al., 2003, 2008; Hynes et al., 1974; Pusch et al., 1998).

1.1. Elevated Atmospheric CO₂

Aquatic CO₂ fluxes can both affect and be affected by photoautotrophs (e.g., Maberly et al., 2015; Raven & Johnston, 1993; Stepien et al., 2016; Vogt et al., 2017). CO₂ has a high diffusion rate in air and in truly terrestrial systems, plants interact with inorganic carbon solely as CO₂ (Stepien et al., 2016). However, aquatic systems have low CO₂ diffusion rates and dissolved inorganic carbon occurs in several forms (Stepien et al., 2016).

Freshwater macrophytes require high CO₂ concentrations to saturate photosynthesis because of a high transport resistance across external boundary layers (Black et al., 1981; Maberly & Madsen, 1998). Intermittent depletion of CO₂ can further limit photosynthesis when rates of photosynthetic demand exceed those of supply and by the generation of high oxygen concentrations promoting photorespiration (Maberly & Madsen, 2002; Maberly et al., 2015). In order to reduce carbon limitation, aquatic photoautotrophs will employ avoidance, exploitation or amelioration strategies (Klavnsen et al., 2011). The first is based on living in a high CO₂ environment (e.g., a groundwater fed stream; Maberly et al., 2015), or where there are high levels of OM being decomposed by heterotrophs (Maberly, 1985a, 1985b). Exploitation strategies include accessing more consistent CO₂ sources, for example, the atmosphere (Maberly & Madsen, 2002), while amelioration strategies involve carbon concentrating mechanisms (CCMs) to minimize carbon limitation, whether biophysical or biochemical (Maberly & Madsen, 2002). Over 50% of freshwater macrophytes studied have CCMs (Maberly & Madsen, 2002), with the use of bicarbonate as an alternative source of carbon being most common (Maberly et al., 2015) where the pH exceeds 6.3 (Maberly et al., 2015). However, bicarbonate use is not universal, probably because the process requires adenosine triphosphate expenditure (Maberly et al., 2015), synthesis, and maintenance of proteins (Jones, 2005) and species that use this mechanism have a lower affinity for CO₂ than those using CO₂ alone (Maberly & Madsen, 1998).

While studies have investigated the effects of elevated atmospheric CO₂ (eCO₂), warming and even interactive effects of warming combined with eCO₂ on macrophyte carbon limitation (see Raven & Johnston, 1993), less is known about effects on DOC release. Elevated CO₂ has been found to increase vascular plant growth and DOC contributions from upland peatlands (Fenner, Ostle, et al., 2007; Freeman et al., 2004), despite CO₂ supersaturated porewaters in the rhizosphere (up to around 20,000 μ atm pCO₂; Whitfield et al., 2009), and also in lowland peatlands (Kang et al., 2001). This was attributed to increased inputs from emergent vascular macrophyte species such as *Juncus* and *Festuca*, through both root exudates and litter inputs, although bryophytes such as *Sphagnum* and *Polytrichum* were also present. These species are also common in the littoral zones of peatland reservoirs, lakes and ponds, and thus, could contribute increased DOC under eCO₂.

Many phytoplankton taxa also have CCMs (Raven et al., 2005) allowing them to overcome low CO₂ saturation of photosynthetic enzymes, which usually occurs at atmospheric equilibrium (Badger et al., 1998). However, there are taxa which lack such CCMs and these are predicted to benefit from higher CO₂ partial pressure (pCO₂; Maberly et al., 2009). Considerable evidence suggests freshwater algal carbon fixation can respond to eCO₂ levels across trophic levels (Schippers et al., 2004; Urabe et al., 2003), up to concentrations far higher (Urabe et al., 2003) than global average lake concentrations (1,036 μ atm; Cole et al., 1994) or 1,200 μ atm for nontropical lakes and established reservoirs (Raymond et al., 2013), humic lakes dominated by respiration (1,762 μ atm; Sobek et al., 2003) streams (average 3,100 μ atm; Raymond et al., 2013), and a range of supersaturated systems (Jansson et al., 2012). Recently, gross primary production (GPP) was found to be enhanced across a pCO₂ gradient represented by 69 boreal lakes (50–2,300 μ atm; Vogt et al., 2017), while Hamdan et al. (2018) found that CO₂ availability was an important driver of both pelagic and benthic GPP, by comparing ice removal treatments with ice free conditions in experimental ponds. However, the predominance of supersaturation particularly in organic-rich freshwaters (e.g., polyhumic systems; Sobek et al., 2003), suggests that algae will be unresponsive to increases in atmospheric CO₂ levels predicted because this will have little effect on actual water column pCO₂ levels (Vogt et al., 2017), though this has not been tested directly. Again, there is sparse information on the effects of such environmental changes on DOC production.

Elevated CO₂ could have a number of potential direct and indirect effects on aquatic heterotrophic processes. For example, increased dissolved CO₂ acidifies the water column (Hamdan et al., 2018), which may be

expected to directly inhibit a heterotrophic activity (Fenner & Freeman, 2013) where the water is at equilibrium with the atmosphere. While this may also reduce GPP in a theory, previous studies have attributed responses to CO₂ availability and not to pH (e.g., Jansson et al., 2012; Vogt et al., 2017) despite the carbonate system being inextricably linked to pH (see Hamdan et al., 2018). CO₂ fertilization effects on primary production may increase nutrient sequestration via direct uptake into plant tissues, making it unavailable to microbes, but also result in higher C:N ratios and polyphenolic structural materials, which can inhibit the heterotrophic activity indirectly (cf. Fenner, Freeman, et al., 2007; Fenner, Ostle, et al., 2007 in peatlands; Freeman et al., 1998 in soils); alternatively, increased supplies of labile carbon (as exudates and cell sloughing) may stimulate heterotrophic activity (Fenner, Ostle, et al., 2007 in peatlands; Fenner & Freeman, 2013 in a humic pool).

We hypothesized that DOC concentrations would increase under eCO₂ as a result of emergent macrophyte fertilization, coupled with inhibition of DOC consumption by heterotrophs, whilst algal primary production would not be significantly enhanced due to the predominance of CO₂ supersaturation (Hypothesis 1).

1.2. Warming

Macrophytes are expected to expand in Northern (temperate and boreal) lakes (Alahuhta et al., 2011; Jepsen et al., 2009) and wetlands (Fenner, Freeman, et al., 2007) as a result of global warming and were stimulated in model warmed ponds, representative of mid-latitude, shallow lakes (Yvon-Durocher et al., 2017). It follows that the quantity of DOC produced, as exudates and litter, could therefore increase (cf. Fenner, Freeman, et al., 2007 in peatlands).

Warming is likely to cause lower dissolved oxygen (DO) levels in the water column, reduced mixing, and increased nutrient concentration, creating conditions more favorable to algal blooms (e.g., George et al., 2007 in UK lakes and references therein; Paerl & Huisman, 2008; Ritson et al., 2014). Earlier spring blooms in lakes have been predicted but also earlier nutrient limitation in autumn, suggesting net production will remain similar (Elliott et al., 2005). Studies on the response of benthic communities to warming suggest that autotrophic biomass was stimulated in an Icelandic geothermally active stream/spring system (Williamson et al., 2016), and in a Portuguese stream (Ylla et al., 2014).

Mineralization of OM has been found to be accelerated in lake sediments under higher temperatures (Gudasz et al., 2010) and shifted to favor higher decomposition of polymeric compounds by stream benthos heterotrophs (Ylla et al., 2014). Yvon-Durocher et al. (2017) found that, although warming stimulated primary production, carbon sequestration capacity halved, due to increased CO₂ and CH₄ production in their 7-year experiment (where effects were amplified rather than dampening or adaptation occurring over time). However, little work appears to have been done on the effects of warming on respiration in organic-rich watersheds where high molecular weight, polyphenolic DOC, and low nutrient availability are likely to present very different physico-chemical environments, potentially being inhibitory to heterotrophs (Fenner & Freeman, 2013). Freeman, Evans, et al. (2001) found reduced DOC consumption due to increased inhibitory phenolic compounds under warming in waterlogged, anaerobic, nutrient-poor peat. Although, Fenner, Freeman, et al. (2007) found no significant change in microbial phenol oxidase activities in intact plant-peat mesocosms from flush (mesotrophic, aerobic) systems, suggesting hydrology (and inextricably linked factors such as nutrient availability) is important in modifying this response.

We hypothesized that warming would increase DOC concentrations via increased macrophyte and algal inputs coupled with reduced consumption due to increased inhibitory polyphenolic compounds (Hypothesis 2).

1.3. Elevated Atmospheric CO₂ and Warming Interactions

It is well documented that eCO₂ induces warming, but the combined effect of increased temperature and eCO₂ is poorly studied in freshwater ecosystems (Woodward & Perkins, 2015). Maberly (1985a, 1985b), studying *Fontinalis antipyretica* (C3 physiology; Bryophyta) in the English Lake District under natural conditions, report carbon limitation at high photon flux density and that CO₂ affinity at a given photon flux density was highest in August, when the environmental CO₂ concentration was lowest. The latter suggests

that DOM inputs may be affected by combined eCO₂ and warming. Fenner, Freeman, et al. (2007) found synergistic increases in peatland DOC under a combined eCO₂ and warming treatment and attributed this to increased vascular plant growth, coupled with impaired microbial degradation, induced by competition with the vegetation for nutrients and inhibitory phenolics.

Here we hypothesize that DOC concentrations will show a synergistic increase due to synergistic increases in inputs from emergent macrophytes coupled with a stimulation of algal inputs (via warming), and impaired heterotrophic consumption (Hypothesis 3).

2. Materials and Methods

In order to address these hypotheses, we focused on the littoral zones of Northern temperate freshwaters, where macrophytes are predicted to expand due to climatic warming (temperate and boreal zones: Alahuhta et al., 2011; Fenner, Freeman, et al., 2007; Fenner, Ostle, et al., 2007; Jeppesen et al., 2009) and where DOC concentrations have been rising (Fenner et al., 2001; Freeman, Evans, et al., 2001; Monteith et al., 2007), with the emphasis on natural site waters and DOC supplies for mesocosm maintenance, rather than artificially generated perfusion waters (cf. Stets & Cotner, 2008). Given the importance of peatlands for drinking water supply (Xu et al., 2018), we specifically selected reservoirs in peaty and organic-rich catchments across a trophic gradient, with an additional oligohumic upland pool representative of source waters (Table 1).

2.1. Field Sites

Field sites were located within the United Kingdom because peatlands here supply over 70% of drinking water (Watts et al., 2001) and focused on North Wales (Atlantic or hyper oceanic, temperate climatic zone) to avoid confounding effects of climatic zones and where long-term monitoring data and characterization in the UK Lake portal site existed (<https://eip.ceh.ac.uk/apps/lakes/> for waterbodies >1 km²).

2.1.1. In Situ Measurements and Sample Collection

Selected in situ measurements (DOC, NO₃⁻, O₂, pCO₂, pH, and PO₄³⁻) were carried out at field sites seasonally (every 3 months) and site water taken for system maintenance monthly. Mesocosms (8 L with an outer reservoir of water to allow lateral water circulation, 0.5 m depth, growing area 0.02 m², sampled at least monthly) maintained in solardomes (controlled environment geodesic glasshouses, growing area 15 m²) or growth cabinets (growing area 0.9 and 1.68 m²) were used to investigate warming, eCO₂ and the combined treatment. Mesocosm and treatment system specifications are given in Tables S1 and S2 respectively and the experimental approach and mesocosm design in Figures S1a and S1b respectively. Mesocosms were collected by hand using a large augur and PVC tubing from the littoral zone of lentic systems at 1 m water depth, where light penetrated to the bottom for all or most of the year. Mesocosms were taken from stands of the dominant species of macrophytes present to give at least 50% cover (Table 1a; 40 per site and 5 per treatment within solardomes or controlled environment cabinets) and included natural intact sediment/substratum, benthic and pelagic components, water column, and native biota (including microbial, algal, and meiofaunal components, but no fish). Flexible airlines (with air stones) were used to oxygenate the water, matching the mesocosms to the levels measured in the field. Light levels were ±10% of natural levels in the field (measured using a photosynthetically active radiation [PAR] meter).

2.2. Solardomes

Solardomes (Figure S1 at the Henfaes research site of the University of Wales Bangor; National Grid Ref. SH 654732) were used for the oligohumic pool, the oligotrophic reservoir, and the oligo-mesotrophic reservoir mesocosms. Eight solardomes were used with two CO₂ concentrations (ambient and +235 ppmv tracked above ambient), two temperatures (ambient and +3°C tracked above ambient), and a combined treatment (+235 ppmv + 3°C tracked above ambient). Solardomes were constructed from “Sanalux” glass that extends light transmission into the UV region, maintaining more realistic radiation conditions than conventional glass. Air is drawn into the domes through a particulate filter mounted behind a 120 × 120 cm duct inlet and then drawn over either an electrical heater for the elevated temperature domes, or a heat exchanger

Table 1
Summary of Peatland Waterbodies and Site Characteristics (a and b)

a										
System description	Location	Catchment	Sediment type	Dominant macrophyte	Mean depth (m)	Maximum depth (m)	Lake area (km ²)	Volume (m ³)	Catchment area (km ²)	Catchment: Lake area ratio
Oligohumic pool	Plynlimon, Mid-Wales	Upland, peatland/acidic heath	Organic peat/mudstone/shale	<i>Sphagnum</i>	2.0	2.8	0.0001	18	N/D	N/D
Oligotrophic reservoir	North Wales	Upland, peatland/Sphagnum blanket bog	Organic peat/mudstone/shale	<i>Juncus bulbosus/Sphagnum</i>	7.7	22	0.41	3138111	1.2	3.3
Oligo-Mesotrophic reservoir	North Wales	Upland, acidic wet & dry heath/peat at southern boundary	Stones/cobbles	<i>Juncus bulbosus/Sphagnum</i>	10.8	45	0.16	1776282	2.25	13.7
Meso-Eutrophic Lake*	North Wales	Mid-Altitude/sessile oak/grassland/slate shale	Organic-rich sediment/slate shale/stones & cobbles	<i>Juncus bulbosus/Litorella uniflora</i>	15.9	27	0.98	15509339	49.01	50.2
Eutrophic reservoir	Anglesey, North West Wales	Lowland/calcareous peatland/agricultural	Calcareous peat	<i>Typha latifolia/Juncus bulbosus</i>	2.2	4	0.68	1519590	40.68	60.1

b										
System description	Altitude (m ASL)	Precipitation (mm) ^a	Mean annual temperature (°C)	pH	pCO ₂ (μatm)	PO ₄ (mg L ⁻¹)	NO ₃ (mg L ⁻¹)	DOC (mg L ⁻¹)	Sediment organic matter (LOI %)	
Oligohumic pool	510	1074.7	9.0	5.18	1380.46	0.0029	0.389	4.01	91.2	
Oligotrophic reservoir	455	1099.7	9.0	5.38	N/D	0.0048	0.455	4.09	95.4	
Oligo-Mesotrophic reservoir	548	1263.4	9.3	7.11	1093.05	0.027	0.541	3.33	21.1	
Meso-Eutrophic Lake ^b	105	2612.2	10.6	7.21	676.80	0.018	4.86	9.01	25.3	
Eutrophic reservoir	32	841.1	13.0	8.12	409.25	0.047	5.997	15.80	28.9	

Note. N/D denotes not determined. ASL denotes above mean sea level. LOI denotes loss on ignition. Due to water company policies regarding data sensitivity, the names of these waterbodies have not been stated.

Abbreviation: DOC, dissolved organic carbon.

^aUK Met Office Climate Average data from the nearest weather station (1981–2010). ^bNot used for potable water supplies but heavily modified with a sewage outfall.

for the ambient temperature domes, by a variable speed fan. Elevated CO₂ domes had CO₂ injected into the air stream through an injection tube positioned in the ducting after the fan, constructed from a length of 6.3 mm tubing with 13 × 1.5 mm diameter holes at 50 mm intervals. A 6 metric tons bulk liquid CO₂ supply with an electrical vaporizer (MG Gas Products Ltd, Reigate, Surrey) was used as the CO₂ source to each eCO₂ dome and was measured by a computer operated 50 L min⁻¹ mass-flow controller (model AFC-202, ASM UK Sales, Wokingham, Berks). Temperature and relative humidity were recorded every 3 min (for a full system description see Rafeal et al., 1995). PAR was logged every 40 min at 1 m height from the ground throughout the growing season in the solardomes. An average of ca. 250 μmol photons m⁻² s⁻¹ was measured in the growing season (May–September) within the solardomes over 2 years (range ~2–1,900 μmol photons m⁻² s⁻¹). Limited seasonal PAR measurements suggest a level of ca. 110 μmol photons m⁻² s⁻¹ at macrophyte canopy height on average over the year.

2.3. Controlled Environment Cabinets

Controlled environment cabinets (Figure S1a) were used for the meso-eutrophic and eutrophic systems to allow these to be collected and treated simultaneously with the systems above, thus avoiding any confounding interannual effects on DOC and so on. Controlled environment cabinets (Sanyo Gallenkamp/Weiss technic Fitotron, 110 and 228, Table S2), which provided ambient air (at 350 ppmv) or eCO₂ controlled by a combined IRGA and controller (WMA-2, PP Systems Ltd., Stotfold, Herts., UK) with and without warming at 3°C. Cabinets were operated with 6 air changes h⁻¹ and a diurnal light regime approximately matched to the solardome PAR levels. This gave an average of ca. 230 μmol photons m⁻² s⁻¹ at 1 m height in the growing season and 100 μmol photons m⁻² s⁻¹ at macrophyte canopy height on average over the year.

2.4. Biogeochemical Measurements

Unless stated otherwise, routine measurements from mesocosms were taken every month for the pretreatment phase (2 months) and for the duration (12 months) of all experiments.

DOC (<0.45 μm pore size) concentrations were determined using a Shimadzu TOC analyzer (Tokyo, Japan). Polyphenolic compound concentrations (within the DOC fraction), indicating inhibitory high molecular weight material, were measured colorimetrically using a Folin-Ciocalteu reagent at 750 nm (Box, 1983). DOC absorbance at 440 m m⁻¹ was used as an index of colored terrestrial material (Bade et al., 2007), and SUVA (UV absorbance at 254 nm normalized to DOC concentration) as indicative of aromaticity, hydrophobicity, and molecular weight, which has been linked to DBP formation, particularly THMs (Ritson et al., 2014). Water samples were filtered immediately and refrigerated in the dark until analysis (<2 weeks of collection and usually within 4 days across all campaigns).

Above ground macrophyte biomass was harvested at the end of the experiment at the sediment level and dried to constant weight. Chlorophyll a was used to indicate algal biomass and extracted from subsamples taken from the water column (50 mL from mesocosms, 1 L from field sites) or benthic biofilm (e.g., 1 stone from each mesocosm) and standard colorimetric techniques employed, after concentration on a glass fiber filter (Whatman GF/F, 25 mm diameter, 0.7 μm pore size) and immediate freezing (Kasprzak et al., 2008) until an analysis (<1 month). Biofilm chlorophyll concentrations, expressed per unit surface area, were determined by first separating biofilm from the substratum using sonication (3 × 3 min).

Algal contributions to the DOC pool were estimated using the method of Bade et al. (2007), that is, using the color (absorbance at 440 nm and expressed as a wavelength-specific absorption coefficient [a₄₄₀; m⁻¹]) to chlorophyll a ratio, with the following equation (note extrapolation beyond empirical data):

$$\% \text{ Algal DOC} = 56.36 \times \exp\left(-3.73 \times \left[\text{absorbance at 440 nm} / \text{Chlorophyll } a \text{ concentration}\right]\right)$$

Indicators of heterotrophic DOC removal (extracellular phenol oxidase activity representing depolymerization and respirometry as a proxy for mineralization) were measured according to the routine methods described in Fenner and Freeman (2013) within 2 days of sample collection at field temperature (Fenner et al., 2005a). Briefly, phenol oxidase was assayed colorimetrically at 460 nm using L-DOPA as the substrate. Respirometry (CO₂ production) was carried out on 1 cm³ of sediment placed in amber glass vials. After 1 h incubation at field temperature, the trace gas concentration above background in the headspace was calculated.

Water samples for a pCO₂ analysis were collected seasonally from the field in glass bottles capped with rubber septa under the surface to ensure samples were devoid of atmospheric air, according to the method of Whitfield et al. (2009). Briefly, samples were analyzed immediately, according to Hope et al. (1995), establishing a headspace of ambient air by extracting water simultaneously with a double plastic syringe system. The sealed sample bottle was then shaken (1 min) to equilibrate the dissolved CO₂ with the headspace (Cole & Caraco, 2001) and the latter measured using a Gas Chromatograph (Varian model 450 gas chromatograph). Dissolved CO₂ was corrected (following Hope et al., 1995) using Henry's Law (Raymond et al., 2013) and the CO₂ fugacity-pressure relationship (Weiss, 1974). Limited measurements were taken from the mesocosms to check for artefacts induced by a changed hydrological regime, and a short (60 days)

experiment was also performed using 2 L of oligohumic pool and oligo-mesotrophic reservoir site water under the solardome treatments, to determine whether higher atmospheric pCO₂ would likely lead to higher aquatic CO₂ concentrations directly.

2.5. Statistical Considerations

Triplicate measurements of standard solutions were used to estimate analytical precision, which was within $\pm 5\%$ (Pierson-Wickmann et al., 2011). All statistics were performed using Minitab. The data were tested for normality and homogeneity of variance using the Anderson Darling and Levene's test for equal variance respectively, and transformed if necessary (Johnson Transformation, Minitab). Linear regression analysis was used to explore potential sources and sinks for water column DOC. ANOVA (General Linear Model) on true dome or cabinet replicates was employed (i.e., means of five mesocosms over time per dome [$n = 2$] or cabinet [$n = 2$]), incorporating CO₂, temperature, and their interaction effects, to analyze the data for synergistic (i.e., significantly more than additive) effects between factors (Fenner, Freeman, et al., 2007). Averages over time were used to summarize time series data. The associated error was included by retaining individual replicate values (averaged over time), rather than averaging means pooled at each time point (Fenner, Freeman, et al., 2007; Fenner, Ostle, et al., 2007).

3. Results

3.1. Trophic Level Patterns

Generally, both sediment (sDOC) and water column (wDOC) DOC and phenolics concentrations along with macrophyte, phytoplankton, and biofilm biomass increased with the trophic status, based on the control mesocosms (Figures 1a–1g). Benthic phenol oxidase activities and respiration also showed a general increase with the increasing trophic status (Figures 1h and 1i). Terrestrial DOC (indicated by color), was highest in the upland peatland oligohumic pool and reservoir and showed a general decrease with the trophic level (Figure 2), the exception being the eutrophic system, which is heavily peat influenced but lowland. SUVA followed a similar pattern, whilst algal DOC contributions increased with the increasing trophic status.

In situ littoral zone CO₂ partial pressures (pCO₂) were similar to those within the control mesocosms ($\pm 15\%$, $P > 0.05$) and increased with decreasing trophic level (Table 1b). Undersaturation (implying uptake from the atmosphere) was found in the summer for the eutrophic and meso-eutrophic systems, but supersaturation (implying evasion to the atmosphere) for all systems in the winter (Figure 3a). Using site water only (based on 50 days in the solardomes, following 10 days of equilibration), in the oligohumic pool the eCO₂ treatment led to a 25% rise in pCO₂ ($F = 7.59$, $P = 0.014$), warming induced a fall of 4% (nonsignificant [n.s]) and there was no significant interaction between these factors in the combined treatment (14%; Figure 3b). A similar pattern was found for the meso-oligotrophic site water in that both the eCO₂ treatments led to higher pCO₂ levels (eCO₂ 21%, $F = 3.97$, $P = 0.064$; combined 18%, n.s.). However, here the warming treatment led to a nonsignificant increase in pCO₂, although this was more variable (7%; Figure 3b).

3.2. Potential Littoral Zone DOC Sources and Sinks

Pooling all data (across treatments rather than trophic levels), in order to investigate DOC sources and heterotrophic sinks, suggests a strong significant correlation between sDOC concentrations and wDOC concentrations across all systems, with the strongest association ($R^2 = 92\%$, $P = 0.000$) for the meso-oligotrophic system. The lowest in terms of strength and significance was found at the extremes of the trophic system (Table 2).

Aboveground macrophyte biomass and sDOC showed significant relationships across all systems (highest under the oligohumic pool system $R^2 = 91\%$, $P = 0.000$) as did wDOC and above ground biomass (although highest in the eutrophic system $R^2 = 82\%$, $P = 0.002$; Table 2). Benthic algal biomass showed a significant relationship with wDOC across all trophic systems (Table 2), and, interestingly, had the strongest relationship with wDOC of any parameter across most systems; but this was most pronounced in the oligotrophic reservoir ($R^2 = 89\%$, $P = 0.000$) and oligohumic pool ($R^2 = 85\%$, $P = 0.001$). Relationships between phytoplankton

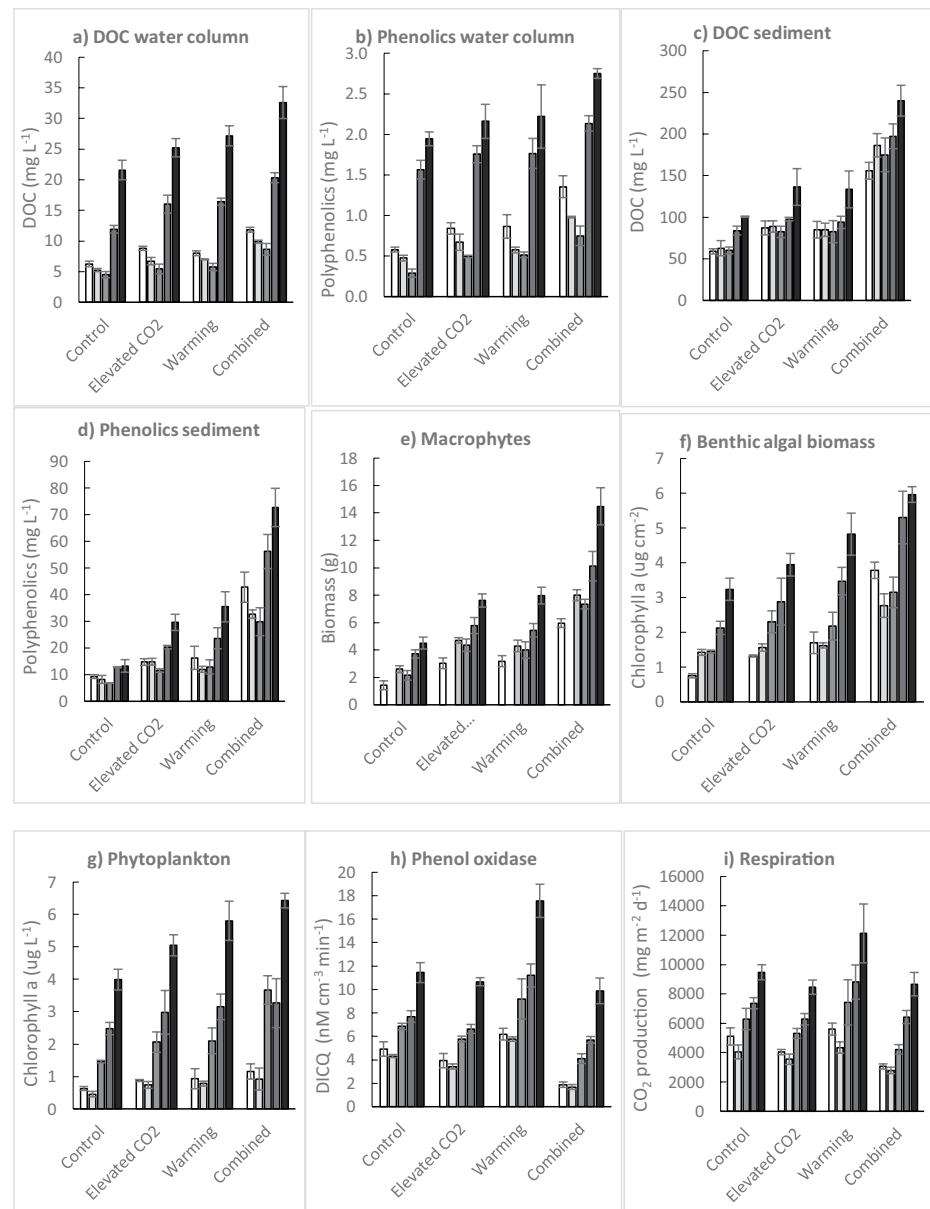


Figure 1. Effects of elevated CO₂, warming, and combined treatments on littoral zone (a) water column dissolved organic carbon (DOC), (b) water column polyphenolics, (c) sediment porewater DOC, (d) sediment porewater polyphenolics, (e) macrophyte above ground biomass, (f) benthic algal biomass, (g) phytoplankton biomass, (h) benthic phenol oxidase activity, (i) benthic respiration, across peatland water bodies (oligohumic no fill, oligotrophic light shade, meso-oligotrophic mid-shade, meso-eutrophic dark shade, and eutrophic black fill).

biomass and wDOC were also significant across nutrient-poor systems with the oligo-mesotrophic system showing the strongest linkage ($R^2 = 94\%$, $P = 0.000$), while the meso-eutrophic and eutrophic systems showed significance at $P < 0.1$ only (Table 2).

Benthic phenol oxidase activities (Table 2) were negatively related to wDOC in the oligohumic pool ($R^2 = 83\%$, $P = 0.002$), with the oligotrophic reservoir showing significance at the $P < 0.1$ only ($R^2 = 46\%$, $P = 0.067$). No significant relationships were found at higher trophic levels though. A similar negative pattern was found with respiration, the oligohumic pool showing a strong significant relationship ($R^2 = 67\%$, $P = 0.013$) and the oligotrophic system showing significance at the $P < 0.1$ only ($R^2 = 49\%$, $P = 0.053$).

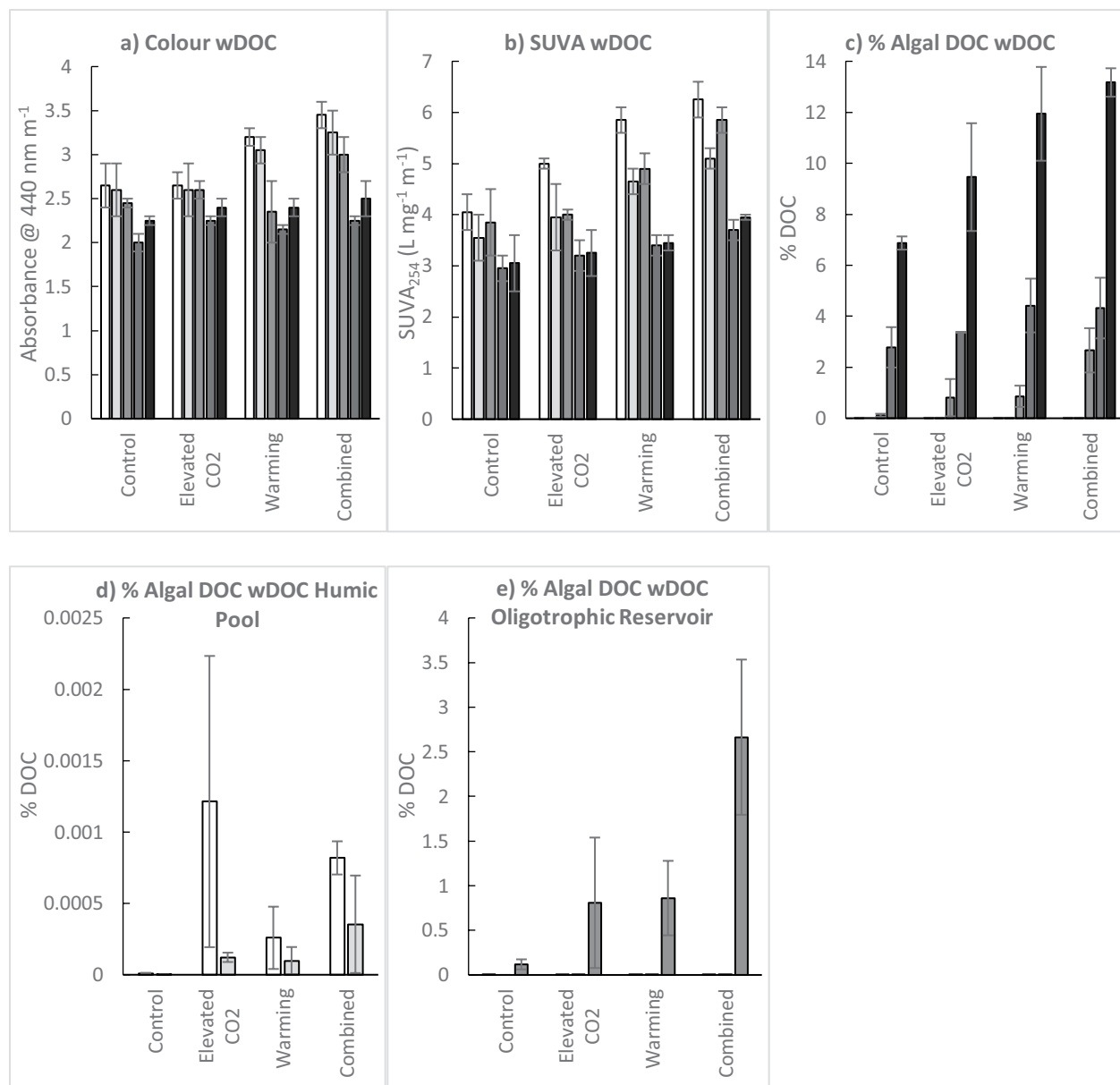


Figure 2. Effects of elevated CO₂, warming, and combined treatments on littoral zone water column dissolved organic carbon (DOC) (a) absorbance at 440 m⁻¹ indicative of colored terrestrial material, (b) specific UV absorbance at 254 nm (SUVA) indicative of aromaticity/molecular weight, (c–e), percentage of algal DOC (estimated using color and water column chlorophyll *a* concentrations) across peatland water bodies at different scales (oligohumic no fill, oligotrophic light shade, meso-oligotrophic mid-shade, meso-eutrophic dark shade, and eutrophic black fill).

3.3. Elevated Atmospheric CO₂

All systems showed higher wDOC concentrations under eCO₂ compared with their ambient controls, from 17% in the eutrophic lake to 41% in the oligohumic pool, significant at $P < 0.05$ or lower, except for the meso-oligotrophic ($P = 0.058$) and eutrophic ($P = 0.074$) systems (Figure 1a). Polyphenolics within the wDOC pool increased significantly ($P < 0.05$) across all systems under eCO₂, except the meso-eutrophic system ($P = 0.097$) and the eutrophic system (n.s.). Percentage increases ranged from 11% in the eutrophic to 71% in the meso-eutrophic system (Figure 1b).

Elevated CO₂ increased sDOC concentrations across all systems ($P < 0.05$ or below), from 16% in the meso-eutrophic site to 55% in the eutrophic site (Figure 1c). Polyphenolics showed a similar pattern, in that eCO₂ increased levels across all systems ($P < 0.05$ or lower; Figure 1d), but percentage changes were

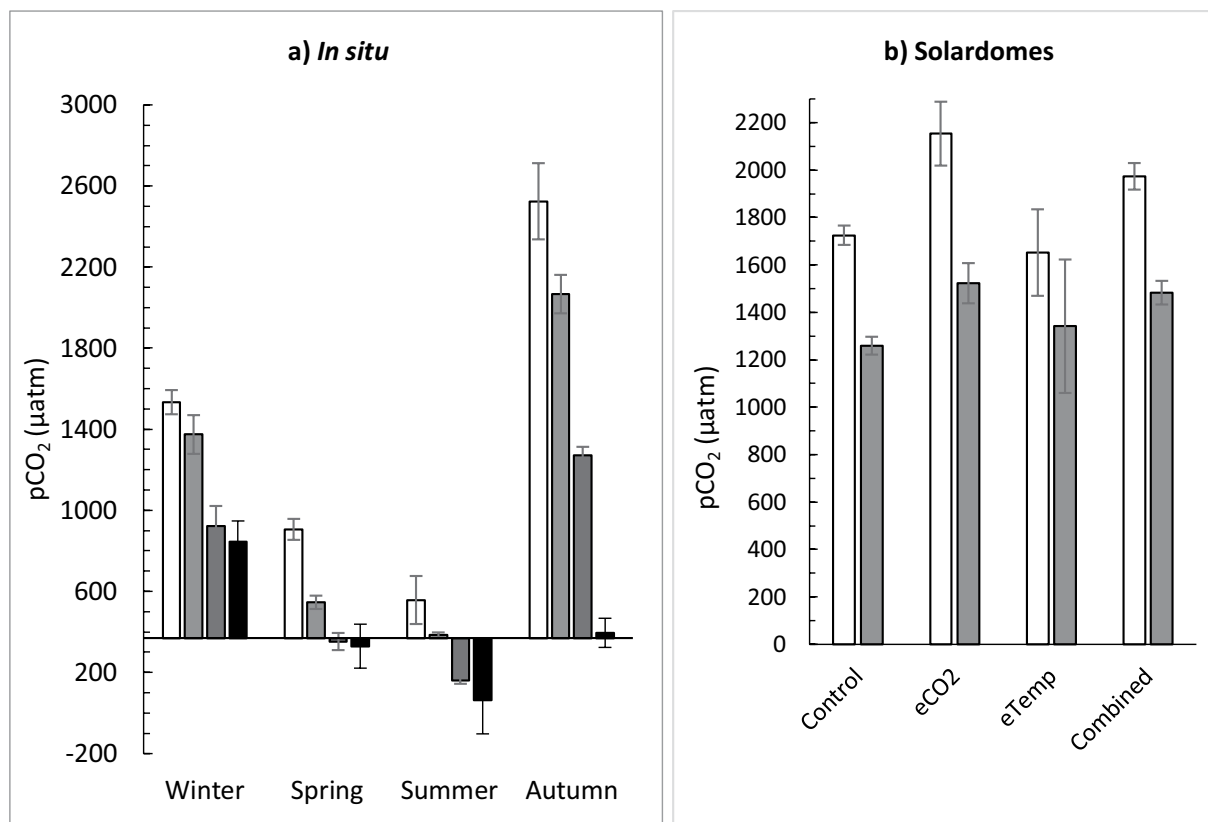


Figure 3. Littoral zone CO₂ partial pressures (a) in situ for oligohumic (no fill), meso-oligotrophic (mid-shade), meso-eutrophic (dark shade), and eutrophic (black fill) peatland water bodies, (b) for oligohumic pool (no fill) and meso-oligotrophic reservoir site water in the solar domes (mean across time for 50 days for water collected in Autumn following 10 days of equilibration).

higher (from 59% in the meso-eutrophic system to 123% in the eutrophic system), giving proportionately higher polyphenolics concentrations within the total sDOC pool in the lower nutrient systems as a result (Figure S2).

Macrophyte biomass increased across all systems under eCO₂ ($P < 0.01$ or below), ranging from 56% in the meso-eutrophic system to 112% in the oligohumic pool (Figure 1e). Benthic algal biomass was also increased across all systems at $P < 0.1$ or below (Figure 1f), with the oligohumic pool system showing significance at $P = 0.003$ (76%). Percentage increases ranged from 76% in the oligohumic pool system to 10% in the oligotrophic system. For the more nutrient-rich systems, this was 59%, 36%, and 22% in the oligo-meso, meso-eutrophic, and eutrophic systems respectively. For the phytoplankton component, only the oligohumic pool system showed a significant response ($P = 0.021$) and the oligo-mesotrophic system at $P < 0.1$ only ($P = 0.097$); although, the tendency was for increased biomass ranging from 20% in the meso-eutrophic to 63% in the oligotrophic system (i.e., higher response in the nutrient-poor systems; Figure 1g).

Benthic phenol oxidase activities were inhibited across all systems ($P < 0.05$ or below) under eCO₂, with suppression becoming less pronounced across trophic systems (from 21% in the oligotrophic system to 7% in the eutrophic system; Figure 1h). Respiration showed a somewhat similar pattern, in that the oligohumic pool was the most affected (−21%, $P = 0.009$), with the oligotrophic system also showing a significant response at $P < 0.05$; other systems were significant at $P < 0.1$ only and the suppression generally decreased with trophic status (−11% in the eutrophic system; Figure 1i).

The tendency was for modest increases in color under eCO₂, but this was not significant at $P < 0.05$ (Figure 2a); only the mesotrophic system came close (13%, $P = 0.057$). SUVA was increased to the greatest extent in the oligohumic pool (Figure 2b), but this was significant at $P < 0.1$ only (24%, $P = 0.075$). Algal DOC showed large and significant increases in the oligohumic pool (13,063%, $P = 0.046$) under eCO₂ (Figures 2c–2e).

Table 2
Linear Regression Analysis Investigating Potential Sources and Sinks for Littoral Zone DOC in Peatland Waterbodies

Trophic description	Continuous predictor	Response	F-value	P-value	R ² (%)	Slope
Oligohumic	Sediment porewater DOC	Water column DOC	10.75	0.017	64	0.06
Oligotrophic			16.16	0.007	73	0.03
Meso-oligotrophic			72.03	0.000	92	0.04
Meso-eutrophic			16.36	0.007	73	0.06
Eutrophic			8.40	0.027	58	0.06
Oligohumic	Macrophyte above ground biomass	Sediment porewater DOC	61.46	0.000	91	21.05
Oligotrophic			N/D	N/D	N/D	N/D
Meso-oligotrophic			4.22	0.006	75	20.75
Meso-eutrophic			4.16	0.006	74	16.87
Eutrophic			4.75	0.003	79	13.24
Oligohumic	Macrophyte above ground biomass	Water column DOC	2.50	0.046	51	1.16
Oligotrophic			N/D	N/D	N/D	N/D
Meso-oligotrophic			3.90	0.008	72	0.75
Meso-eutrophic			3.67	0.010	69	1.06
Eutrophic			5.22	0.002	82	1.07
Oligohumic	Benthic algal Biomass	Water column DOC	5.79	0.001	85	1.63
Oligotrophic			6.82	0.000	89	2.70
Meso-oligotrophic			3.76	0.009	70	2.07
Meso-eutrophic			4.4	0.005	77	2.11
Eutrophic			3.45	0.014	67	3.29
Oligohumic	Phytoplankton biomass	Water column DOC	5.1	0.002	81	9.40
Oligotrophic			3.81	0.009	71	7.36
Meso-oligotrophic			9.56	0.000	94	1.72
Meso-eutrophic			2.23	0.067	45	4.67
Eutrophic			2.07	0.083	42	2.50
Oligohumic	Benthic phenol oxidase	Water column DOC	-5.43	0.002	83	-0.99
Oligotrophic			-2.24	0.067	46	-0.78
Meso-oligotrophic			-1.86	0.112	37	-0.50
Meso-eutrophic			-0.52	0.623	4	-0.30
Eutrophic			0.05	0.964	0	0.03
Oligohumic	Benthic respiration	Water column DOC	-3.5	0.013	67	-0.002
Oligotrophic			-2.42	0.053	49	-0.002
Meso-oligotrophic			-1.2	0.276	19	-0.001
Meso-eutrophic			-0.67	0.526	7	-0.001
Eutrophic			-0.11	0.919	0	0.000

Note. Significant *P* values ($P < 0.05$) are shown in bold (black) and $P < 0.1$ in bold (green). Highest R^2 values are shown in bold. N/D denotes not determined.

Abbreviation: DOC, dissolved organic carbon.

3.4. Warming

The warming treatment increased wDOC concentrations in all systems ($P < 0.05$) from 26% in the eutrophic to 38% in the meso-eutrophic systems (Figure 1a). Warming induced significant increases in wDOC

polyphenolics again in all but the meso-eutrophic ($P = 0.089$) and eutrophic systems (n.s.). Percentage increases ranged from 13% in the meso-eutrophic to 78% in the oligo-mesotrophic systems (Figure 1b).

Warming increased sDOC concentrations (Figures 1c and 1d) across all systems ($P < 0.05$), except for the meso-eutrophic site ($P = 0.067$). Percentage increases ranged from 12% in the meso-eutrophic site, to 142% in the eutrophic site. Warming also increased polyphenolics concentrations across all systems ($P < 0.05$ or lower, from 46% in the oligotrophic system to 167% in the eutrophic system), again giving higher polyphenolics to sDOC ratios in the nutrient-poor systems (Figure S2).

Above ground macrophyte biomass increased across all systems under the warming treatment ($P < 0.01$ or below, from 47% meso-eutrophic to 124% in the oligohumic pool; Figure 1e). Biofilm showed significant increases in all systems ($P < 0.05$ level or below), ranging from 75% to 14% in the humic and oligotrophic systems respectively (Figure 1f). Phytoplankton responded at $P < 0.1$ or below in all but the meso-eutrophic system, with the oligohumic pool showing the greatest sensitivity ($P = 0.01$). Percentage increases were in the range 27% in the oligotrophic system to 71% in the meso-eutrophic system (Figure 1g).

Warming induced increased benthic phenol oxidase activities and the response became more pronounced (from 26% in the oligohumic pool to 54% in the eutrophic system) and significant ($P < 0.1$ only for meso-eutrophic and eutrophic systems, the latter $P = 0.056$) with an increasing nutrient status (Figure 1h). Respiration also increased across the trophic status, from 8% in the oligotrophic to 28% in the eutrophic system, but this was not significant (Figure 1i).

Color was increased under warming in the oligohumic pool (21%, $P = 0.017$; Figure 2a) and in the oligotrophic system there was a 17% increase ($P = 0.099$ only). SUVA was also increased in the oligohumic pool 44% ($P = 0.006$) and meso-oligotrophic system (27%, $P = 0.019$), with the oligotrophic system (31%, $P = 0.058$) being significant at $P < 0.1$ only (Figure 2b). Considerable increases in algal DOC across all systems were found (Figure 2c), and this was significant in the eutrophic system (74%, $P = 0.038$) and came close in the oligo-mesotrophic system (626%, $P = 0.099$).

3.5. Elevated Atmospheric CO₂ and Warming Interactions

Under the combined treatment, wDOC increases ranged from 51% in the eutrophic system to 92% in the meso-oligotrophic. Additive, rather than synergistic increases were found, but lower nutrient systems were generally more responsive (Figure 1a). Similarly, additive effects were found on wDOC polyphenolics, from a 36% increase in meso-eutrophic, to a 159% in the oligo-mesotrophic system (Figure 1b).

The combined treatment induced additive effects on sDOC mainly, with larger percentage changes being seen in the nutrient-poor systems (Figure 1c). A synergistic interaction was found in the meso-oligotrophic system ($P = 0.05$), with the oligohumic pool showing significance at $P = 0.064$ only. Percentage changes in polyphenolics were far higher than either of the separate treatments (from 298% in the oligotrophic site to 448% in the eutrophic system), however, this was additive (i.e., no significant interaction was found at $P < 0.05$; Figure 1d).

Macrophyte biomass under the combined treatment showed additive effects, with percentages ranging from 318% in the oligohumic pool to 173% in the meso-eutrophic (Figure 1e) and again tending to be higher in the nutrient-poor systems. Benthic algal biomass showed additive effects and percentage increases ranged from 84% in the eutrophic to 405% in the oligohumic pool system (Figure 1f). Phytoplankton biomass also responded additively from 32% in the meso-eutrophic system to 151% in the meso-oligotrophic system (Figure 1g).

Benthic phenol oxidase under the combined treatment showed a synergistic inhibition at $P < 0.05$ for all but the meso-oligotrophic system, which was significant at $P = 0.089$ only, and percentage suppression increased with decreasing trophic status, from 14% in the eutrophic system to 62% in the oligohumic pool (Figure 1h). Respiration was suppressed across trophic status, ranging from 40% in the humic system to 9% in the eutrophic system; however, this was additive (Figure 1i).

The combined treatment induced additive, rather than synergistic, effects on DOC character, with color increasing by 30% in the oligohumic pool and declining with the trophic status (Figure 2a). SUVA was in-

creased to the greatest extent in the lower trophic systems (54% in the oligohumic pool; Figure 2b). Increases in algal DOC were large in the oligotrophic reservoir and oligohumic pool in particular, generally declining with trophic level (Figure 2c).

4. Discussion

4.1. Limitations of the Experimental Approach

In situ littoral zone pCO₂ were not significantly to those within the control mesocosms and natural site waters were used to maintain mesocosms in order to preserve natural seasonal changes in allochthonous DOC inputs and so on. However, edge effects and limited environmental interaction (Ahn & Mitsch, 2002; Carpenter, 1996; Schindler, 1998), along with other inherent problems associated with mesocosm experiments cannot be precluded. Specific issues here may include processes related to a lack of mixing of source waters from upstream watersheds, the omission of fish and other animals, or enhanced biofilm growth on mesocosm surfaces, leading to an over-estimation of the benthic contributions to biogeochemical cycling. Similarly, while we were interested in relative changes in DOC between trophic systems and as a result of treatments, rather than absolute concentrations, differences in air circulation or a lack of natural light regime in the growth cabinets compared with the solardomes may have had an effect.

4.2. Trophic Level Patterns

DOC and polyphenolics concentrations in both the water column (Figures 1a and 1b) and the sediment porewaters (Figures 1c and 1d) of reservoir littoral zones increased with trophic status, in line with increased primary productivity in emergent, benthic, and pelagic compartments (Figures 1e–1g). Benthic phenol oxidase and respiration also increased (Figures 1h and 1i), as would be expected due to stimulation via increased pH, nutrient levels, and labile carbon (Fenner & Freeman, 2013). Colored DOC inputs were highest in the upland peatland oligohumic pool and reservoir, consistent with higher exports of terrestrial OM from peaty catchments (e.g., Freeman, Evans, et al., 2001; Freeman, Ostle, & Kang, 2001), and showed a general decrease with trophic level (Figure 2a). The exception being the eutrophic system, which is heavily peat influenced but lowland in character, with high nitrate inputs from surrounding agricultural land and high alkalinity (Tables 1a and 1b). SUVA followed a similar pattern (Figure 2b), suggesting high molecular weight, hydrophobic, aromatic inputs, whilst algal DOC contributions increased with increasing trophic status (Figure 2c). Such results are in line with the general assumption that drinking water treatment works (DWTW) in upland nutrient-poor peaty catchments are optimized for receiving high molecular weight, predominantly terrestrial DOC, while lowland systems are more prone to algal inputs due to higher inorganic nutrient levels (cf. Ritson et al., 2014).

4.3. Potential Littoral Zone DOC Sources and Sinks

Pooling the data suggests there was a strong correlation between sDOC concentrations and wDOC concentrations across all systems (Table 2), in line with Pierson-Wickmann et al. (2011), who suggest that sediment is an important autochthonous DOC source. Likely mechanisms include DOC solubilization from particulate organic carbon, as well as direct release from macrophyte roots in the form of exudates and litter (Fenner et al., 2004; Fenner, Freeman, et al., 2007; Fenner, Ostle, et al., 2007). The strongest association was found in the meso-oligotrophic system and this may relate to the substratum type, which was thin sediment, interspersed with loose cobbles and stones, meaning the water column and sediment was likely to be most homogenous. The weakest association was found at the extremes of trophic system (Table 2), that is, where either the terrestrial input was highest (oligohumic pool) or where the autochthonous input was highest (eutrophic system). This may be due to a greater stratification between sediments and water column processes physically and/or dominance of organic sediments, meaning different predominant carbon cycling processes (such as DOC preservation under more reduced conditions and therefore less direct coupling with the water column), however, this needs further work.

Both sDOC and wDOC were strongly related to aboveground macrophyte biomass across all systems (Table 2), suggesting that plant inputs are important in dictating DOC concentrations in the littoral zone, irre-

spective of species (Table 1a) and supporting work suggesting that macrophytes are the major DOC source to lakes (Lauster et al., 2006; They et al., 2013; Wetzel, 1992), although the overall importance of this will likely depend on the level of lateral terrestrial inputs. Interestingly, the relationship between macrophyte biomass and sDOC was strongest in the oligohumic pool, possibly due to the close linkage of macrophytes and sediment formation in these small systems, and/or the species involved, for example, a predominance of peat forming *Sphagnum* and preservation of DOC. Conversely, macrophyte-wDOC relationships appeared to be strongest in the eutrophic system, possibly explained by higher direct exudate and/or relatively labile litter inputs supported by higher nutrient levels (Table 1b).

Surprisingly, benthic algal biomass showed a strong relationship with wDOC across all trophic systems and interestingly had the strongest relationship with wDOC of any parameter across most systems (Table 2), suggesting it is an underappreciated source of DOC, in line with studies suggesting up to 80% of primary production in lakes is of a benthic origin (Vadeboncoeur et al., 2001). This pattern was most pronounced in the nutrient-poor systems (oligotrophic and oligohumic pool), possibly due to low N/P levels (Table 1b), favoring biofilm processes, due to their higher metabolic rates and linked functions (Pusch et al., 1998), and/or access to nutrients from the substratum; or the greater levels of phytoplankton in the higher trophic levels which would lead to shading of biofilm. Alternatively, there may be differences due to the species present, and their adaptations to the conditions (see later).

Relationships between phytoplankton biomass and wDOC were strong across nutrient-poor systems (Table 2), with the oligo-mesotrophic system showing the strongest linkage, while the meso-eutrophic and eutrophic systems showed significance at $P < 0.1$ only. The reason for the stronger apparent coupling for the nutrient-poor systems is not clear, but may relate to preservation of DOC under low nutrient and high polyphenolic conditions (Tables 1a and 1b; Figure 2b), rather than higher consumption and transformation in higher trophic level systems, a concept borne out by the indicators of microbial catabolism (below; Figures 1h and 1i). If, in eutrophic systems, algal DOC is utilized preferentially by heterotrophs (Bade et al., 2007; Romani et al., 2004), and therefore not preserved, it may explain the lack of significant contribution from algal blooms found by Pierson-Wickmann et al. (2011), in a eutrophic French reservoir, using natural abundance carbon isotopic signatures. However, to quantify the contributions of littoral zone DOC to whole lake carbon budgets, and determine its fate, would require a suite of pulse labeling experiments across trophic levels and seasons.

Benthic phenol oxidase activities were strongly and negatively related to wDOC in the oligohumic pool, with the oligotrophic reservoir showing significance at $P < 0.1$ (Table 2), suggesting that phenol oxidase is an important regulator of DOC concentrations, as has been found in peatlands (Freeman, Ostle, & Kang, 2001). No significant relationships were found in the higher trophic level reservoirs, perhaps suggesting that there are other drivers of DOC consumption due to differing polyphenolic compound sources and therefore character and/or a greater availability of low molecular weight carbon sources (Figures 2a–2c) and nutrients (Table 1b), despite higher total polyphenolic concentrations (Figures 1b and 1d). Certainly, the relationship between the phenol oxidase activity and phenolic compound concentration has been found to be complex with the former being associated not only with consuming the latter as a substrate, but also producing it via cleavage of longer chain polymers, dependent on factors such as oxygen saturation (Fenner & Freeman, 2013; Fenner et al., 2005a, 2005b). A similar pattern was found with respiration (Table 2), with the oligohumic pool and the oligotrophic system showing significance, but the latter at $P < 0.1$ only. This may indicate that phenol oxidase is an important driver of intracellular (as well as extracellular) metabolism and carbon effluxes in both aqueous and gaseous form in such systems, and where it is inhibited there is preservation of DOC.

4.4. Elevated Atmospheric CO₂

Water column DOC concentrations were increased across all systems under eCO₂ (Figure 1a), however, the oligohumic pool showed the highest response. Polyphenolics within this pool (Figure 1b) also increased across all systems ($P < 0.1$ only), except for the eutrophic system. Sediment DOC and polyphenolics concentrations were increased across all systems, which is likely to be a major driver of this effect, given the strong

relationship between these two variables (Table 2). However, the eutrophic site was most responsive, as well as showing the highest absolute values (Figures 1c and 1d), suggesting an increasing DOC store.

Macrophytes showed significantly increased above ground biomass across all systems studied under eCO₂ (Figure 1e) supporting hypothesis 1 and suggesting that macrophyte contributions to wDOC will increase in a future climate, both directly and via sediment inputs. Surprisingly, however, the lower nutrient systems showed a greater response, with increases up to 112% in the oligohumic pool, a figure broadly in line with a mesotrophic flush peatland and an oligotrophic site sampled by Fenner, Freeman, et al. (2007) and Fenner, Ostle, et al. (2007). The greater response may relate to the inherently higher pCO₂ levels (Table 1a, Figure 3a), low pH, low N levels (Table 1b) or high molecular weight polyphenolic substances (Figures 1b, 1d, 2a and 2b). Indeed, such factors are inextricably linked; field aquatic pCO₂ levels were the highest overall (Table 1a) in the oligohumic pool (as expected), and this may favor taxa lacking CCMs, meaning they are more responsive to eCO₂ (Maberly & Madsen, 1998, 2002). In the growing season, pCO₂ showed much lower levels (Figure 3a), corresponding to when photoautotrophs are at their most active (Maberly 1985a, 1985b), meaning carbon limitation is possible in these shallow, relatively warm and therefore highly productive zones. Thus, photoautotrophs are likely to drive aquatic pCO₂ levels (Maberly et al., 2015; Raven & Johnston, 1993; Stepien et al., 2016; Vogt et al., 2017). Based on site water effects, the oligohumic pool also showed a significant increase in aquatic pCO₂ (Figure 3b), which may suggest direct effects of eCO₂ on aquatic pCO₂ are possible, even in high pCO₂ systems, contrary to Vogt et al. (2017). However, this needs further research to disentangle direct physico-chemical and indirect biological effects, since raw site waters were used. Moreover, the effects of trophic level, season, and hydrology are likely to be complex, with interactions and feedbacks between the sediment and water column. Indeed, a further factor to consider is that supersaturated outflows from peaty catchments may be curtailed during the summer dry season. Lower pH (Table 1a) would also favor degassing of dissolved CO₂ in the water column, which may mean that emergent macrophyte growth is more dependent on atmospheric CO₂ levels in these systems, especially given that bicarbonate use is most common at higher pH (>6.3; Maberly et al., 2015). Furthermore, oligohumic pool nitrate levels were found to be the lowest of all the sites (Table 1b) and long chain aromatic polyphenolic compounds, characteristic of these systems (Figures 1b, 1d, 2a and 2b), are known to bind nitrogen compounds effectively (Wetzel, 1992), as well as other nutrients (Fenner & Freeman, 2020), which may mean CCMs are too costly to synthesize and maintain (Jones, 2005; Maberly et al., 2015). The potential role of rhizosphere heterotrophs in eliciting this response needs more research, but Fenner, Freeman, et al. (2007) and Fenner, Ostle, et al. (2007) found increased competition for nutrients and this may reduce respired CO₂ production in the root zone (cf. Fenner et al., 2004 who found recaptured CO₂ was likely to be an important carbon source for bryophytes).

Contrary to hypothesis 1, benthic algal biomass increased with eCO₂ across all systems (Figure 1f), with the oligohumic pool system again showing the highest sensitivity. As with the macrophytes, this suggests that such communities could be limited by current atmospheric CO₂ levels, and is in line with recent theoretical (Low-Decarie et al., 2013) and experimental (Jansson et al., 2012; Schippers et al., 2004; Urabe et al., 2003; Verspagen et al., 2014) studies on phytoplankton, suggesting increased photosynthetic efficiency (via enhanced diffusion) due to Rubisco often being unsaturated at equilibrium CO₂ concentrations (Jansson et al., 2012; Urabe et al., 2003). Undersaturated pCO₂ levels—particularly in the growing season (Figure 3a), suggest that drawdown by photoautotrophs can drive concentrations (rather than vice versa Vogt et al., 2017) in these littoral zones. The greater sensitivity of benthic algae in oligohumic systems may relate to the factors discussed above in relation to macrophytes.

Phytoplankton response to eCO₂ was again highest in the oligohumic pool system, with more response in the nutrient-poor waters (Figure 1g). This again may be explained by CCMs being too energetically costly (Engel et al., 2004; Schippers et al., 2004; Urabe et al., 2003) and/or higher ambient pCO₂ levels favoring taxa lacking CCMs (e.g., Maberly et al., 2009). Such results are supported by Vogt et al. (2017), who found that phytoplankton GPP increased across a pCO₂ gradient, but only for lakes already supersaturated. However, here we propose that eCO₂ could indeed affect aquatic productivity in littoral zones, even though the average condition is supersaturated, because temporally this is variable, with CO₂ being undersaturated in the growing season (Figure 3a). The lower level of statistical significance compared with other components may relate to the temporal and spatial patchiness of phytoplankton in relation to sessile benthic algae and

macrophytes. Alternatively, it may reflect the influence of different CO₂ sources, with benthic algae and macrophytes possibly having access to more stable CO₂ supplies due to larger communities of respiring heterotrophs in close proximity to autotrophs (cf. Fenner et al., 2004). Certainly, Raven and Johnston (1993) suggest there is a CO₂ concentration gradient between organic-rich sediments and the overlying water column, and that macrophytes close to this sediment-water interface can benefit from increases in CO₂ availability. Presumably, this would apply to benthic algae also.

Benthic phenol oxidase activities (Figure 1h) were significantly inhibited across all systems under eCO₂, with the suppression generally becoming less pronounced with the trophic status. This would provide a mechanism for selective enrichment of high molecular weight polyphenolics within the DOC fraction and preservation of terrestrial material (Figures 2a and 2b), and could be explained by nutrient sequestration by the photoautotrophs (in line with Fenner, Freeman, et al., 2007). The latter being less acute due to higher background nutrient levels in eutrophic systems. Phenol oxidase activities are known to be sensitive to pH and nutrient levels in aquatic systems (Fenner & Freeman, 2013) and negatively correlated with DOC concentrations (Freeman, Ostle, & Kang, 2001 in peatlands). Benthic biofilm respiration data (Figure 1i) suggest lower DOC mineralization under eCO₂, showing a somewhat similar pattern to phenol oxidase activities, with the nutrient-poor systems again being most sensitive. Where labile carbon is not limiting, that is, in those systems characterized by higher algal inputs (Figure 2c), respiration is likely to be less affected by increased polyphenolics, because the latter would be a less important source of carbon.

Modest, nonsignificant increases in color and SUVA support the reduced consumption of DOC with a terrestrial provenance and aromatic character respectively (Figures 2a and 2b) and SUVA was increased to the greatest extent in the oligohumic pool ($P < 0.1$ only), in line with enhanced DOC preservation. However, increased production of colored autochthonous material cannot be precluded. Algal DOC showed large and significant increases in the oligohumic pool only under eCO₂ (Figure 2c), in line with the increased pelagic and benthic algal biomass, and this material might be better preserved due to the high level of inhibitory polyphenolic compounds (Figures 1a, 1b and 1d) and low N levels (Table 1b). Certainly, Fenner and Freeman (2013) found that polyphenolic inhibition was relieved by the addition of nutrients. The large increase in proteinaceous DOC is likely to be a problem for DWTW, especially those in upland peaty systems optimized for high levels of terrestrial DOC that is more effectively removed by conventional coagulation (Ritson et al., 2014). Increased costs from filter backwashes are also probable (Eikebrokk et al., 2004).

4.5. Warming

Warming increased wDOC concentrations (Figure 1a) in all systems (with significant increases in polyphenolics in all but the meso-eutrophic and eutrophic systems (the former significant at $P < 0.1$ only)). Again, this could be driven, in part, by increased sDOC (Table 2) concentrations, since these increased across all systems with selectively enriched polyphenolics in the lower nutrient systems (Figures 1b and 1d, Figure S2). This may be related to accelerated sDOC release from long chain polymers or anaerobic fermentation releasing organic acids, which is known to be enhanced under warming, and would contribute to the DOC pool (Fenner et al., 2005a, 2005b). However, sDOC and polyphenolics response was most pronounced in the eutrophic system, suggesting that production is higher than consumption here, compared with the water column.

Above ground macrophyte biomass increased across all systems studied under the warming treatment suggesting an important driver for wDOC (Table 2) in a warmer climate, again both directly and through increased sediment inputs (Figure 1e and Table 2). This supports predictions that macrophyte cover will increase in Northern systems (Alahuhta et al., 2011; Fenner, Freeman, et al., 2007; Fenner, Ostle, et al., 2007; Jeppesen et al., 2009) and work done in experimental ponds (Yvon-Durocher et al., 2017). Again, the oligohumic pool was the most responsive, which could relate to the mechanisms discussed above in relation to hypothesis 1, with warming exacerbating degassing (Raven & Johnston, 1993) and competition for nutrients in these N limited systems; although, there may be a point where higher temperatures override this, via increased nutrient release (through accelerated sediment and OM decomposition) and concentration (via evaporation), potentially interacting with increased drought frequency. While autumn site water pCO₂ levels showed no significant difference compared with the control under the warming treatment, this is likely to be modified with trophic level and potentially enhance carbon limitation, since pCO₂ levels fell

in the meso-oligotrophic system (Figure 3b). Such effects are likely to be exacerbated in the summer when temperatures and carbon fixation are at their highest (Figure 3a).

Warming has been found to favor algal blooms (e.g., George et al., 2007; Paerl & Huisman, 2008) and here we found both benthic and pelagic algae were stimulated (Figures 1f and 1g). Benthic algal biomass showed significant increases in all systems, but particularly in the oligohumic pool, in line with work on a geothermally active system (Williamson et al., 2016), despite N limitation, and in a Portuguese stream (Ylla et al., 2014). Phytoplankton responded ($P < 0.1$ or below) in all but the meso-eutrophic system, with the oligohumic pool showing the greatest sensitivity.

Increased benthic phenol oxidase activities were found under the warming scenario (Figure 1h) in line with Ylla et al. (2014), who found higher decomposition of polymeric compounds and peptides, but lower decomposition of lipids, by stream benthos heterotrophs. In our study, the response became more pronounced and significant with increasing nutrient status, suggesting that activities are limited by a lack of nutrients in the nutrient-poor systems and that nutrient-rich systems will therefore be more susceptible to warming. The same general pattern was observed for respiration across trophic status, but this was not statistically significant (Figure 1i), contrary to Gudasz et al. (2010) who found accelerated mineralization of OM in lake sediments under higher temperatures and Yvon-Durocher et al. (2017) who found increased CO_2 production in experimental ponds. This may be due to the low N levels across all systems here (Table S1b) and/or due to relatively large variance in CO_2 fluxes (Figures 1i and 3b). Fenner and Freeman (2013) found both activity and de novo production of phenol oxidase was increased with added nutrients in the oligohumic pool, leading to increased respiration. Such results suggest that nutrient limitation may be preserving carbon stocks by preventing rapid decomposition from long chain polyphenolics to DOC and CO_2 , but that eutrophication is a threat to this (Fenner & Freeman, 2013). However, the links between microbial enzymatic processes and water quality need further research.

Warming increased color levels in the oligohumic pool (Figure 2a) and in the oligotrophic system ($P < 0.1$ only), and this may be explained by increased release from sediments and/or preferential utilization of algal DOC by the heterotrophic community (Bade et al., 2007; Romani et al., 2004). SUVA was significantly increased in lower trophic level systems under warming (Figure 2b), consistent with increased aromatic DOC, which supports the increased polyphenolic concentrations and may be due to increased macrophyte inputs and/or sediment release. Again, the oligohumic pool was most responsive, with the meso-oligotrophic system also showing substantial and significant increases. Such changes are likely to be associated with reduced treatability due to C-DBP formation. Given that warming induced considerable increases in algal DOC across all systems (Figure 2c), it would be prudent to assume that the low molecular weight proteinaceous DOC will also increase, and therefore, N-DBP formation potential, given this was significant in the eutrophic system, and a seven-fold increase in the oligo-mesotrophic system was found ($P < 0.1$ only). However, increased phytoplankton growth may have a direct effect on DWTW running costs in necessitating increased filter backwashes (Eikebrokk et al., 2004), regardless of low molecular weight DOC issues.

4.6. Elevated Atmospheric CO_2 and Warming Interactions

Under the combined treatment, wDOC and polyphenolics were found to increase additively (Figures 1a and 1b). No synergistic increases were found, but lower nutrient systems were generally more responsive. Similarly, the combined treatment showed mostly additive effects on sDOC, as a potential driver (Table 2), with larger effects being seen in the nutrient-poor systems and with pronounced selective enrichment of polyphenolics (Figures 1c and 1d). However, a synergistic interaction was found for sDOC in the meso-oligotrophic system, with the oligohumic pool significant at $P < 0.1$ also, which may suggest that nutrient sequestration via the photoautotrophs (cf. Fenner, Freeman, et al., 2007; Fenner, Ostle, et al., 2007; Freeman et al., 1998) is driving the higher response by promoting sediment carbon accumulation (i.e., reduced decomposition, see below) and an indirect source of wDOC. However, this requires direct testing.

Again, contrary to hypothesis 3, macrophyte biomass under the combined treatment showed additive, rather than interactive effects, although increases were substantial (Figure 1e), and again higher in the nutrient-poor systems. This may relate to reduced CO_2 solubility at higher temperatures (Raven & Johnston, 1993), counteracting the fertilizing effect of the higher atmospheric levels and/or inhibiting hetero-

trophic production (below). Site water $p\text{CO}_2$ levels support this, being consistently increased compared with the control under the combined treatment (Figure 3b), but lower than the $e\text{CO}_2$ treatment.

Surprisingly, benthic algal biomass, likely to be a large wDOC driver (Table 2), also showed large (additive) effects (Figure 1f), suggesting that $e\text{CO}_2$ in combination with warming can influence aquatic primary production and not just emergent species subject to atmospheric air. This was supported further by the additive responses of the phytoplankton biomass (Figure 1g). Field $p\text{CO}_2$ levels (Table 1a, Figure 3a) suggest that, even under ambient temperature, there can be periods of undersaturation with respect to the atmosphere and these results suggest that littoral zones could be disproportionately affected in a future climate (where warming accompanies $e\text{CO}_2$) and underestimated in terms of carbon flux models, in line with suggestions that wetlands could also behave differently to truly aquatic systems (Raymond et al., 2013).

Benthic phenol oxidase under the combined treatment showed a synergistic inhibition for all but the meso-oligotrophic system ($P < 0.1$ only), and suppression increased with decreasing trophic level (Figure 1h). The combined treatment also suppressed respiration across trophic status (Figure 1i). However, this was additive. This generally supports the findings of Fenner, Freeman, et al. (2007), who found large increases in peatland DOC under a combined treatment and attributed this to increased plant growth coupled with impaired microbial degradation, induced by inhibitory polyphenolics and competition with the vegetation for nutrients. The response of peaty reservoirs seems to differ from peatland wetlands in that the DOC response was not necessarily synergistic (excepting sDOC in the mesotrophic system), and this may be related to lower polyphenolic concentrations in the former. However, such results support the theory that nutrient limitation, mediated by photoautotrophic carbon fixation, is an important carbon sequestration mechanism, limiting phenol oxidase activity and therefore sediment and DOC decomposition, with the interaction between CO_2 and warming strengthening this.

The combined treatment also induced additive effects on DOC character, with color increasing significantly (in the oligohumic pool) and SUVA being increased to the greatest extent in the lower trophic systems (Figures 2a and 2b). Again, this is consistent with DOC preservation. Increases in algal DOC were large in the oligotrophic reservoir and oligohumic pool in particular (Figure 2c), and this is attributed to the CO_2 mechanisms described earlier, exacerbated by warming effects driving even greater photoautotrophic inputs, while suppressing heterotrophic DOC removal, that is, DOC of all fractions and origins. Such changes are likely to be associated with reduced treatability, due to both C-DBP and N-DBP formation, with increased costs due to filter backwashes (Eikebrokk et al., 2004) across systems, but with nutrient-poor systems being especially vulnerable.

5. Conclusions

Given the correlations found here, understanding the release of DOC from sediments and littoral zone macrophytes under changing environmental conditions, along with enzymatic generation, preservation, depolymerization or removal of DOC fractions, is important for future DWTW design and planning. However, benthic algal DOC production showed the strongest relationship with wDOC across most systems and was significant in all of them, suggesting this is an underestimated DOC source. Furthermore, relationships between phytoplankton biomass and wDOC were significant across nutrient-poor systems, suggesting that pelagic algae may be more important in these low productivity systems than expected. While algal inputs to littoral zone DOC were found to be modest under ambient conditions (ca. 7% in the eutrophic reservoir; Figures 2c–2e), whole lake algal DOC contributions can be substantial (e.g., 40% in a eutrophic lake), with concentrations increasing proportionately to primary production (Bade et al., 2007). Furthermore, this DOC could be disproportionately important from a water treatment perspective, given its hydrophilic nature and because it becomes more refractory with time (Bade et al., 2007).

DOC concentrations were found to increase across all systems, irrespective of trophic status, due to increased photoautotrophic inputs under $e\text{CO}_2$, warming and combined scenarios. This was accompanied by inhibited enzymic DOC processing and mineralization as a result of $e\text{CO}_2$, even when combined with warming. This suggests increased DBPs formation, micro-pollutant transport (Gao et al., 1998; Rothwell et al., 2007) and bacterial regrowth in distribution systems (Prévost et al., 1998) will occur, but also increased treatment costs (Chow et al., 2005; Edzwald, 1993; Eikebrokk et al., 2004) and reduced aesthetic

values (WHO, 2011). Algal (pelagic and benthic) contributions appear to be increased irrespective of the climate change scenario, suggesting that hydrophilic fractions associated with more toxic N-DBPs are likely to increase in a future climate. Increased phytoplankton growth may also increase DWTW running costs through direct filter blocking (Eikebrokk et al., 2004).

DWTW are generally optimized to treat DOM depending on a catchment type (Ritson et al., 2014), with upland sources being optimized for terrestrial DOC removal. But here we found autochthonous sources were highly responsive to climate change scenarios, even in upland systems and without increased nutrient loads, which are also predicted to become more of a problem in the future due to N deposition and concentration effects (Ritson et al., 2014). Given their transport through conventional treatment works and association with N-DBPs, research on removing low molecular weight hydrophilic fractions would seem a priority. However, macrophyte inputs and preserved terrestrial DOC, characterized by high molecular weight (hydrophobic) fractions that are more easily coagulated, but associated with C-DBP formation, are also likely to increase in all scenarios, but particularly those with eCO₂ levels due to inhibited heterotrophic removal of DOC. Furthermore, any increased terrestrial inputs (e.g., from catchment plant fertilization [Fenner, Freeman, et al., 2007; Fenner, Ostle, et al., 2007; Freeman et al., 2004; Larsen et al., 2011], a longer growing season [Holden & Adamson, 2002], and changes in pH [Monteith et al., 2007]) are likely to persist longer under such scenarios, suggesting increased DOC loads of all fractions, regardless of provenance, to all receiving waters, whether man-made or natural. However, further research is required to determine whether catchment processes under warming and eCO₂ (i.e., altered allochthonous DOC supply) would override or modify the impacts on autochthonous DOC production.

Peaty catchments are global potable water supply hotspots (Xu et al., 2018) and likely to increase in importance as demand and transport of waters rise (Fenner et al., 2001). While tropical peat systems require further research, the findings from this study suggest that in order to help “future proof” temperate drinking water supplies in a changing climate, removing a greater amount and range of DOC by (a) “enhanced coagulation,” that is, optimized for DOM removal, (b) switching to ferric coagulants and using coagulant aids, (c) using magnetic ion exchange pre-coagulation, and (d) activated carbon filtration after coagulation, in order to increase the buffer between finished waters and regulatory limits (Ritson et al., 2014) would seem prudent. Further research into novel source water mixing regimes and catchment management techniques (Fenner & Freeman, 2020; Fenner et al., 2001; Ritson et al., 2016) is also important in the light of recent findings, along with investment in rapid monitoring techniques, catchment and algal modeling, and coagulant and disinfection switching (Ritson et al., 2014).

Data Availability Statement

The data that support this research are available at <https://figshare.com/>, <https://doi.org/10.6084/m9.figshare.14184902>.

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