




## RESEARCH ARTICLE

# Peatland ditch blocking has no effect on dissolved organic matter (DOM) quality

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## Abstract

The globally widespread drainage of peatlands has often been shown to lead to increased concentrations and fluxes of dissolved organic carbon (DOC) in streams and rivers. Elevated DOC concentrations have implications for carbon cycling, ecosystem functioning, and potable water treatment. Peatland rewetting, principally through ditch blocking, is often carried out with the expectation that this will reduce DOC concentrations. Uncertainty still remains as to whether drainage, or its reversal via ditch blocking, will also lead to changes in the molecular composition of DOC/dissolved organic matter (DOM), which have the potential to affect downstream processing and treatability of U.K. drinking water supplies. To investigate this question, we used a replicated experiment consisting of 12 parallel ditches on an upland bog and took samples of ditch water, pore water, and overland flow water for 4 years. After a brief preblocking baseline period, eight ditches were blocked using two methods. A complementary suite of optical metrics, chemical measurements, and analytical techniques revealed that ditch blocking had no consistent effect on DOM quality, up to 4 years after blocking. Where significant differences were found, effect size calculations demonstrated that these differences were small and would therefore have minimal impact upon water treatability. Furthermore, some differences between ditches were evident before blocking took place, highlighting the need for robust baseline monitoring before intervention. Based on our results from a hillslope-scale experiment, we were unable to identify clear evidence that peatland ditch blocking will deliver benefits in terms of DOM treatability in potable water supplies, although we also did not find any evidence of short-term deterioration in water quality during the restoration period. We conclude that, although peatland restoration can be expected to deliver other benefits such as reduced carbon loss and enhanced biodiversity, it is doubtful whether it will lead to improvements in drinking water treatability.

## KEYWORDS

blanket bog, carbon cycling, dissolved organic carbon, peatland restoration, rewetting, trihalomethanes, water quality, water treatment

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## 1 | INTRODUCTION

On a global scale, vast areas of peat have been drained in an attempt to convert them to use for agriculture, forestry, and peat extraction. This drainage often results in the establishment of lower water tables (Haapalehto, Kotiaho, Matilainen, & Tahvanainen, 2014; Holden, Wallage, Lane, & McDonald, 2011), leading to soil subsidence (Schothorst, 1977; Williamson et al., 2017) and increased gaseous losses of carbon dioxide (CO<sub>2</sub>; Bussell, Jones, Healey, & Pullin, 2010), alongside negative effects on biodiversity due to increased sediment loads (Carroll, Dennis, Pearce-Higgins, & Thomas, 2011; Ramchunder, Brown, & Holden, 2009). In addition, there are concerns that drainage leads to increased concentrations and fluxes of dissolved organic carbon (DOC) in streams and rivers. This effect has been observed in tropical (Moore et al., 2013), temperate (Moore & Clarkson, 2007; Strack et al., 2008), boreal (Menberu et al., 2017), and subarctic peatlands (Lou, Zhai, Kang, Hu, & Hu, 2014) and has been recognised in the U.K. uplands for several decades (Mitchell, 1991; Naden & McDonald, 1989).

Increased exports of DOC are problematic for multiple reasons. DOC in fluvial systems can be mineralized to CO<sub>2</sub>, thereby contributing to atmospheric CO<sub>2</sub> concentrations (Cole et al., 2007; Jones, Evans,

Jones, Hill, & Freeman, 2016). Additionally, DOC affects light attenuation and can therefore affect the functioning of aquatic ecosystems (Karlsson, Byström, Ask, Persson, & Jansson, 2009), and DOC can bind with trace metals, some toxic (Lawlor & Tipping, 2003; Rothwell, Evans, Daniels, & Allott, 2007). Furthermore, DOC adds colour and odour to potable water which must be removed due to aesthetic concerns (Mitchell, 1991). Finally, when chlorinated during potable water treatment, high concentrations of DOC can lead to the formation of harmful disinfection by-products, including trihalomethanes (THMs; Chow, Kanji, & Gao, 2003). THM concentrations in potable water are strictly regulated; for example, the European Union limit is 100 µg L<sup>-1</sup> for total THMs, whereas the World Health Organisation recommends concentration limits for individual THMs of between 60 and 300 µg L<sup>-1</sup> (Werner, Valdivia-Garcia, Weir, & Haffey, 2016). Increased DOC concentrations therefore present a problem to water companies due to the cost associated with its removal and penalties for exceeding regulatory limits (Brooks, Freeman, Gough, & Holliman, 2015).

One potential method that has been proposed to reduce DOC concentrations in freshwaters is the rewetting of drained peatlands (Wilson et al., 2011). A recent synthesis by Evans, Renou-Wilson, and Strack (2016) suggests that drainage increases DOC in concentrations and

**TABLE 1** Summary of peatland rewetting studies measuring DOM quality

Disturbance	DOM measurement	Time (years) <sup>a</sup>	Water type	Conclusion	Reference
Peat extraction, drainage	Absorbance, fluorescence	5	Pore water	No difference in DOM following rewetting	Glatzel, Kalbitz, Dalva, and Moore (2003)
Peat extraction, drainage	Absorbance, pentose, hexose <sup>b</sup>	10	Pore water	Higher E2:E3 in undrained peat when compared to drained or rewetted peat, but no difference in E4:E6, SUVA, pentose or hexose	Strack, Zuback, McCarter, and Price (2015)
Peat extraction, drainage	Absorbance	10	Discharge water	Higher E2:E3 at the restored site when compared to unrestored, no difference in E4:E6 or SUVA	Strack et al. (2015)
Peat extraction, drainage	Absorbance	10	Pore water	Lower SUVA at rewetted and undrained sites compared to drained site	Frank, Tiemeyer, Gelbrecht, and Freibauer (2014)
Peat extraction, drainage	Absorbance, fluorescence	20	Pore water	Lower SUVA at rewetted site compared to drained site	Höll et al. (2009)
Peat extraction, drainage	Water colour	15	Discharge water	No change in water colour after rewetting	Lundin, Nilsson, Jordan, Lode, and Strömberg (2017)
Peat extraction, drainage, afforestation	FT-ICR-MS <sup>c</sup>	9	Pore water	DOM in drained sites more humified, and more variable both spatially and seasonally, when compared to natural peatlands	Herzprung et al. (2017)
Peat drainage	Absorbance	6	Pore water, overland flow	E4:E6 difference between peat, intact > drained > rewetted. Specific absorbance at 400 nm higher at rewetted site when compared to drained or intact	Wallage et al. (2006)
Peat drainage	Absorbance	3	Ditch water, stream water	Rewetting increased E4:E6 and decreased specific absorbance at 400 nm	Wilson et al. (2011)
Peat drainage	Absorbance, phenolics, HPSEC <sup>d</sup>	1	Pore water (mesocosms)	Rewetting had no effect on DOM quality or THMs	Gough, Holliman, Fenner, Peacock, and Freeman (2016)
Peat drainage, afforestation	Absorbance	6	Pore water	Rewetting increased SUVA	Menberu et al. (2017)

<sup>a</sup>This is the maximum time after rewetting that measurements were taken.

<sup>b</sup>From Strack et al. (2015): "Soil pentoses are largely derived from plants whereas hexoses are derived from microbes and thus the ratio of pentose to hexose sugars in soils may represent the relative importance of plant productivity to decomposition."

<sup>c</sup>Fourier-transform ion cyclotron resonance mass spectrometry.

<sup>d</sup>High performance size-exclusion chromatography.

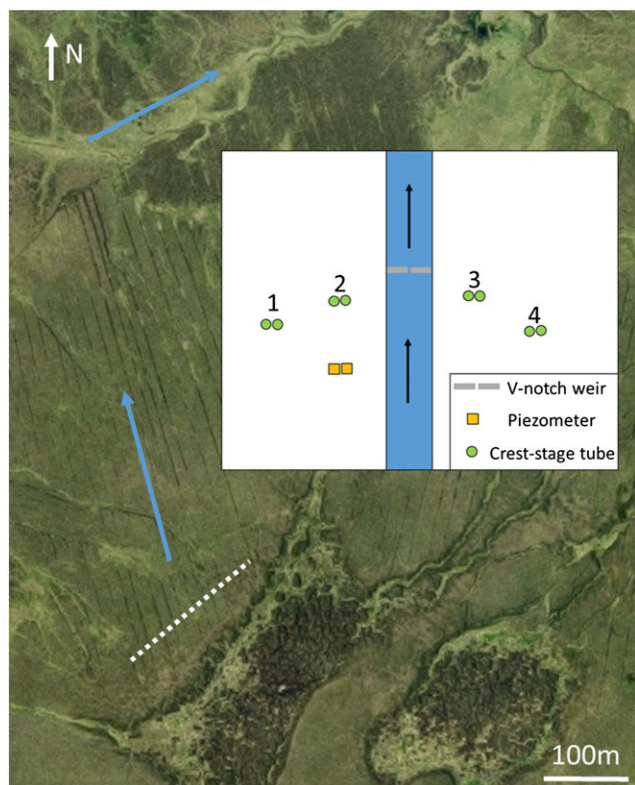
fluxes in most boreal and temperate peatlands and that rewetting appears to reverse this effect in a number of cases. In the United Kingdom, numerous water companies have invested in ditch blocking on upland blanket bog to pursue this goal. However, to date, there is little robust evidence to show resultant reductions in catchment-scale DOC concentrations in these systems. Sometimes this is because studies lack preblocking baseline data, making it impossible to confirm that observed differences in DOC concentration between control and intervention sites are actually due to rewetting (e.g., Wallage, Holden, & McDonald, 2006). Armstrong et al. (2010) conducted a snapshot survey across a number of sites and found that DOC concentrations were lower in blocked ditches with flowing water compared to unblocked ditches with flowing water, but this difference was not significant at the conventional  $p < 0.05$  significance threshold. Some studies have found significant effects of rewetting on DOC concentrations but of such small magnitude that they will have no meaningful impact on water treatment (e.g.,  $0.3 \text{ mg L}^{-1}$  by Gibson, Worrall, Burt, and Adamson (2009);  $2.5\%$  by Turner, Worrall, and Burt (2013), both of which had preblocking data), especially considering that the annual range in DOC in such systems can be  $\sim 25 \text{ mg L}^{-1}$  (Evans et al., 2018), and that individual storm events can increase DOC by  $\sim 10 \text{ mg L}^{-1}$  (Austnes, Evans, Eliot-Laize, Naden, & Old, 2009). It is worth noting that the majority of blanket bog rewetting studies compare drained and rewetted treatments,

due to the fact that most U.K. blanket bog has been managed by drainage, grazing, or burning, leaving little undisturbed bog left (Ramchunder et al., 2009).

As well as uncertainty regarding the effectiveness of ditch blocking at reducing DOC concentrations, it is still largely unclear whether rewetting has the capacity to alter the chemical composition of dissolved organic matter (DOM), which might be expected due to hydrological changes (Thacker, Tipping, Gondar, & Baker, 2008). Numerous methods can be used to investigate DOM character in relation to drinking water quality. These include fluorescence and absorbance measurements, which are relatively fast and accessible techniques and provide information on DOM character; for example, the degree of aromaticity, humification, or autochthonous DOM. Alongside these, there are analytical approaches such as nuclear magnetic resonance spectroscopy, high-performance size-exclusion chromatography (HPSEC), and Fourier-transform infrared spectroscopy (Matilainen et al., 2011). These analytical methods provide increased detail on DOM composition, even down to the molecular level, but they require specialised and expensive equipment. Specific UV absorbance (SUVA), whereby DOC concentration is normalised to light absorbance, usually measured at 254 nm, is used as a proxy for DOM aromaticity (Weishaar et al., 2003) and is perhaps the commonest absorbance metric used within the water industry, having been in use for several decades (Edzwald, 1993). Ratios of absorbance at different wavelengths are also used, such as E2:E3, E2:E4, and E4:E6, which relate to DOM composition and molecular weight (Peuravuori & Pihlaja, 1997; Summers, Cornel, & Roberts, 1987). In addition to ratios, there are absorbance metrics that require measurements at multiple wavelengths, such as spectral slopes, whereby the slope of the absorbance spectrum is a function of DOM molecular weight (Helms et al., 2008). Although absorbance measurements are unable to provide fine-scale resolution on DOM structure, they can be used to reliably detect differences or changes in composition (Erlandsson, Futter, Kothawala, & Köhler, 2012).

Various studies have used some of the above techniques to investigate the effects of rewetting on DOM quality, although only a handful have been on blanket bogs (Table 1). Most studies use only a few metrics, however, and contrasting results are common. For example, Wallage et al. (2006) noted lower E4:E6 ratios in pore water of ditch-blocked peat when compared with drained peat. They also recorded higher specific absorbance at 400 nm in rewetted peat. Conflictingly, Wilson et al. (2011) suggested that ditch blocking decreased specific absorbance at 400 nm and increased E4:E6. By using a broader suite of DOM metrics, it might be possible to reduce uncertainty regarding the effects of rewetting.

The lack of more detailed knowledge from field studies is important, as DOM quality directly affects the treatability of potable water and the formation of THMs (Alarcon-Herrera, Bewtra, & Biswas, 1994; Ritson et al., 2014). For example, if postblocking hydrological changes result in increased concentrations of phenolics (Fenner et al., 2011), then this would negatively affect DOC removal (Gough, Holliman, Willis, & Freeman, 2014), leading to increased treatment costs in combination with increased associated greenhouse gas emissions from treatment processes (Jones, Evans, & Freeman, 2016). On the other hand, if DOC becomes easier to treat, then ditch blocking could become an economically viable method of lowering water treatment costs (Martin-Ortega,



**FIGURE 1** Aerial photograph of the experimental hillslope. The dashed line marks the 12 parallel ditches. Blue arrows represent the direction of water flow down the ditches then into a stream at the bottom of the slope. Imagery ©2017 Getmapping plc, map data ©2017 Google. The schematic inset shows a ditch with arrows indicating flow, alongside sampling equipment. Overland flow water from crest stage tubes numbered 1 and 2 would be bulked to give one sample for the ditch, whereas water from crest stage tubes numbered 3 and 4 would be bulked to give the second sample

**TABLE 2** Numbers of months before and after rewetting that different analyses were conducted, for ditch water, pore water, and overland flow water

	Pre-rewetting			Post-rewetting		
	Ditch	Pore	Overland	Ditch	Pore	Overland <sup>a</sup>
DOC <sup>b</sup>	3	1	0	48	48	48
E ratios	3	1	0	44	44	44
SUVA	3	1	0	44	44	44
Spectral slopes	3	1	0	20	20	20
Phenolics	3	1	0	9	9	0
HPSEC <sup>c</sup>	0	0	0	17	17	17
THM <sup>c</sup>	0	0	0	17	0	0

<sup>a</sup>DOC analysis of overland flow started in July 2011, whereas DOM analysis of overland flow water sampling started in January 2012.

<sup>b</sup>Note that DOC was measured until February 2015, whereas E ratios and SUVA measurements ended in Oct 2014.

<sup>c</sup>HPSEC and THM analyses were performed on one batch of post-rewetting samples only, from July 2012.

Allott, Glenk, & Schaafsma, 2014), with the added benefit of providing other ecosystem services (Grand-Clement et al., 2013).

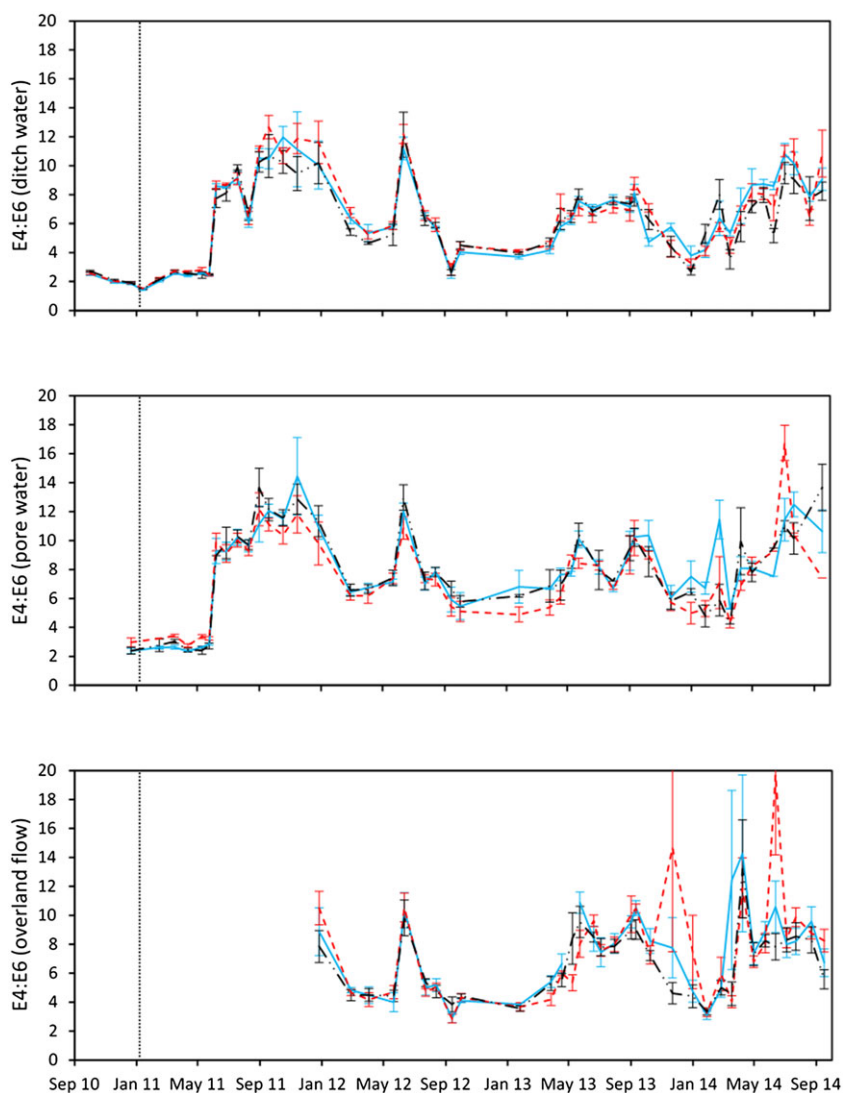
The aim of our study was therefore to test whether blanket bog rewetting would lead to alterations in DOM quality, which could

result in associated changes in the treatability of drinking water. To do this, we took pore water, ditch water, and overland flow water samples from an upland bog where a series of parallel ditches had either been blocked or left open as controls. Samples were collected on an approximate monthly basis for 4 years. We used optical metrics, chemical measurements, and analytical techniques to investigate the chemical composition of DOM. The main part of our analysis was a post-rewetting comparison of DOM from blocked and unblocked ditches, although we also had some limited pre-rewetting data which allowed us to test whether any differences in DOM between ditches existed before ditch blocking.

## 2 | MATERIALS AND METHODS

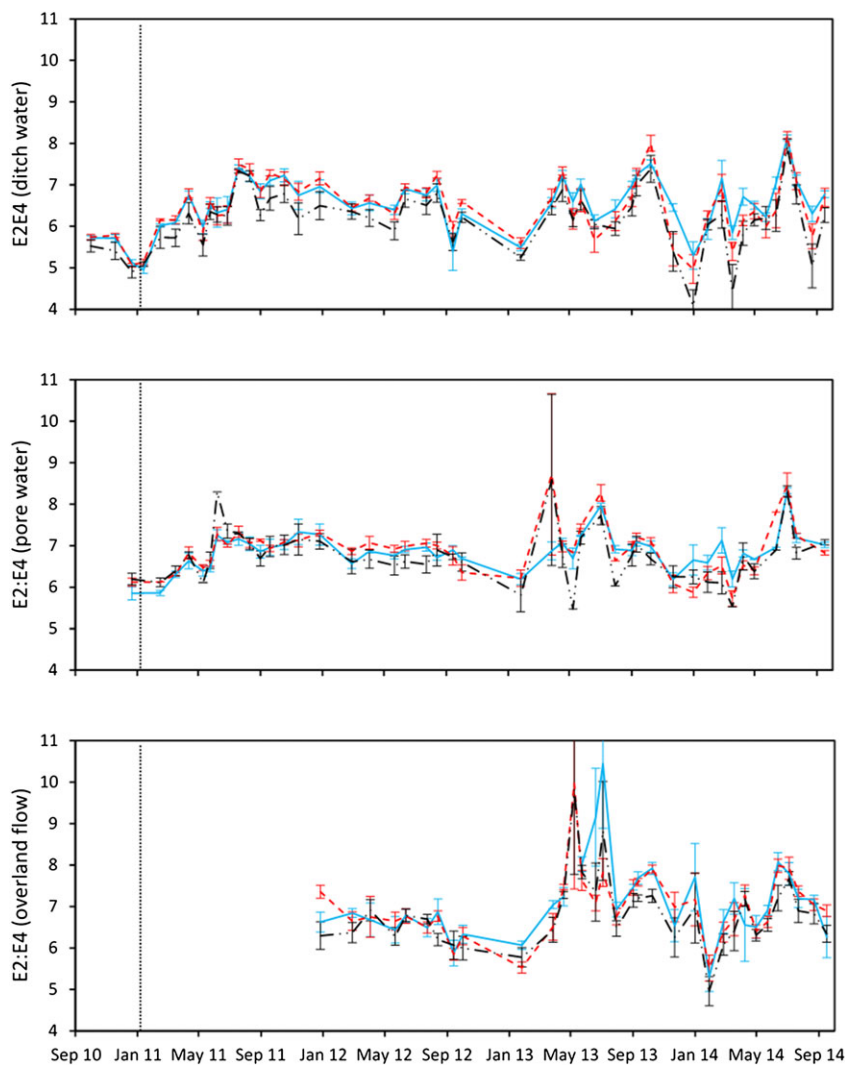
### 2.1 | Field site

The study was carried out on a hillslope on the Migneint blanket bog, North Wales, United Kingdom (latitude 52.97°N, longitude 3.84°W, ~500 m above sea level). Vegetation consisted of *Calluna vulgaris*, *Eriophorum vaginatum*, and *Sphagnum* species, with *Sphagnum capillifolium* being the most abundant of the latter (Green et al.,



**FIGURE 2** Mean E4:E6 for ditch water, pore water, and overland flow water in open ditches (blue continuous line), dammed ditches (black dot/dashed lines), and reprofiled ditches (red dashed lines). Vertical black dotted lines denote when ditch blocking took place. Error bars show standard error of the mean. Truncated error bars for reprofiled overland flow are 21.9 for December 2013 and 25.3 for July 2014





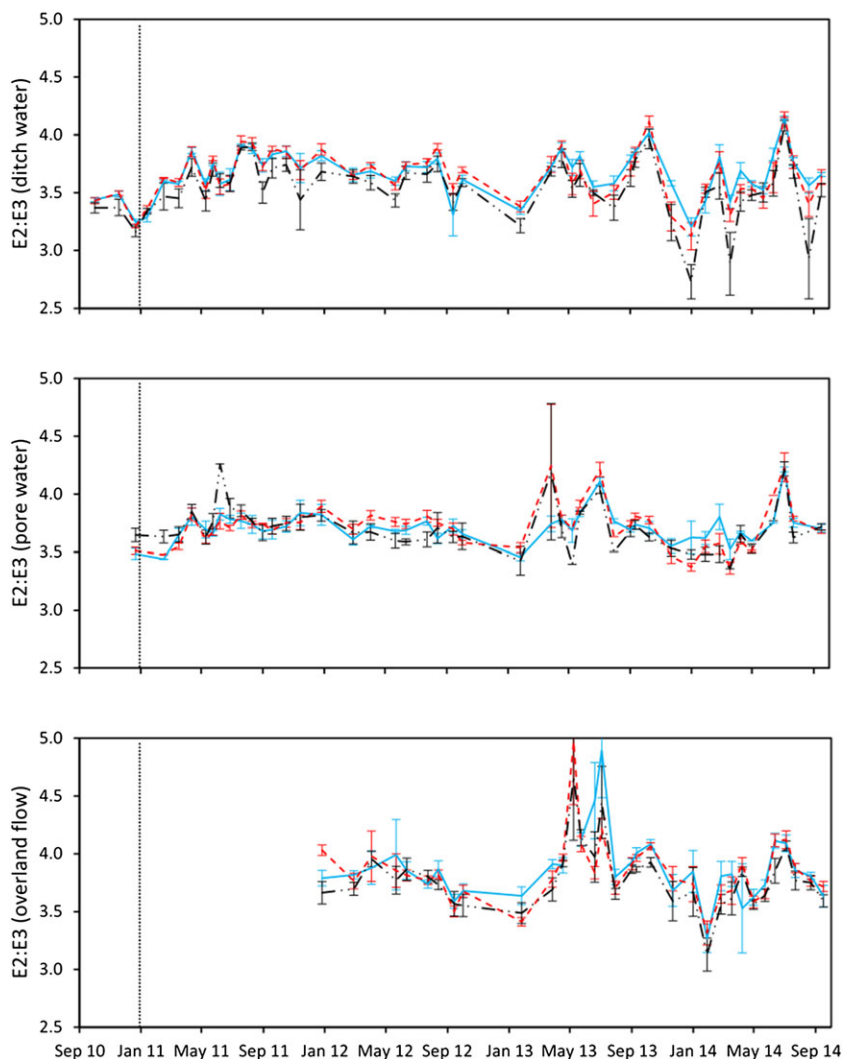
**FIGURE 3** Mean E2:E4 for ditch water, pore water, and overland flow in open ditches (blue continuous line), dammed ditches (black dot/dashed lines), and reprofiled ditches (red dashed lines). Vertical black dotted lines denote when ditch blocking took place. Error bars show standard error of the mean. Truncated error bars for dammed ditch water are 3.7 and 3.8 for January and April 2014, and for overland flow water are 12.5 and 11.9 for reprofiled and dammed ditches in June 2013, and 12.0 for open ditches in July 2013

2017). Mean annual air temperature for the period March 2011–March 2015 was 7.8°C, whereas mean annual rainfall for this period varied between 1,786 and 2,409 mm (Green et al., 2018). The entire hillslope was ditch drained in the 1970s and 1980s. A replicated experiment was established in August 2010 focusing on 12 parallel ditches running in an approximate downslope direction (Figure 1). After a 3-month period of baseline measurement, ditches were blocked in February 2011. Each ditch was assigned a treatment using a statistical approach that considered preblocking ditch flow rate; ditches with similar flows were grouped, then treatment was randomly allocated within each group. Four ditches were left unblocked as open controls, and four were blocked with peat dams at ~10 m intervals (“dammed”), creating a series of fairly deep pools. The other four were blocked by removing ditch vegetation, compressing the base and partially infilling it using peat from ditch sides, and replacing the vegetation (“reprofiled”). Peat dams are also placed along the reprofiled ditches, creating shallow pools. The experimental site was used to investigate the effects of peatland rewetting on numerous ecological responses such as greenhouse gas emissions (Green et al., 2018), DOC fluxes (Evans et al., 2018), hydrology (Holden et al., 2017), vegetation (Green et al., 2017), extracellular enzyme activity (Peacock et al., 2015), and testate amoeba (Swindles et al., 2016). Further

information concerning the study site can be found in Green et al. (2016) and includes soil physical and chemical properties, detailed meteorological data, and ditch topographical details.

## 2.2 | Water sampling

Sampling of ditch water started in October 2010. Samples were collected from water flowing over v-notch weirs (Holden et al., 2017) or from pools behind weirs if there was no flow. Pore water sampling started in January 2011 (giving 1 month of baseline data) from piezometers placed 2–3 m west of each ditch. Piezometers were made of polyvinyl chloride with intakes at 10–15 cm depth, and pore water was collected using plastic tubing attached to a syringe. On each sampling visit, piezometers were emptied of water and allowed to recharge overnight, before samples were collected the next day. Overland flow water sampling started after rewetting in January 2012. Overland flow water was collected using polyvinyl chloride crest-stage tubes (Holden & Burt, 2003). These comprised tubes that were sealed at both ends but with holes just above ground level to collect surface flow. For each ditch, two crest-stage tubes were sited 2 m west of the ditch, with another two 4 m west of the ditch. The water from these was bulked to give one sample, representing a



**FIGURE 4** Mean E2:E3 for ditch water, pore water, and overland flow in open ditches (blue continuous line), dammed ditches (black dot/dashed lines), and reprofiled ditches (red dashed lines). Vertical black dotted lines denote when ditch blocking took place. Error bars show standard error of the mean. Truncated error bars for overland flow are 5.5 and 5.2 for reprofiled and dammed ditches in June 2013, and 5.3 for open ditches in July 2013

mean value of overland flow associated with each ditch. The same set-up was established to the east of each ditch; therefore, each ditch had two overland flow water samples associated with it. Due to samplers sometimes being empty, it was not always possible to collect a full set of pore water and overland flow water samples on every occasion. For all the three water types (ditch, pore, and overland flow), sampling proceeded on an approximate monthly basis, though with a higher frequency in summer and lower frequency in winter. The final sampling date was in October 2014. Samples were collected in 125 ml polyethylene bottles, were filtered at 0.45  $\mu\text{m}$  using Whatman cellulose nitrate filters within 24 hr, and thereafter stored in the dark at 4°C before analysis. Mean pH was 4.2, 4.1, and 5.1, and mean EC was 49.3, 60.6, and 53.8  $\mu\text{S cm}^{-1}$  for ditch water ( $n = 624$ ), pore water ( $n = 480$ ), and overland flow water ( $n = 1,065$ ), respectively. Full water chemistry data are presented in Evans et al. (2018) and comprise DOC, POC, dissolved  $\text{CH}_4$  and  $\text{CO}_2$ , pH, EC, and alkalinity.

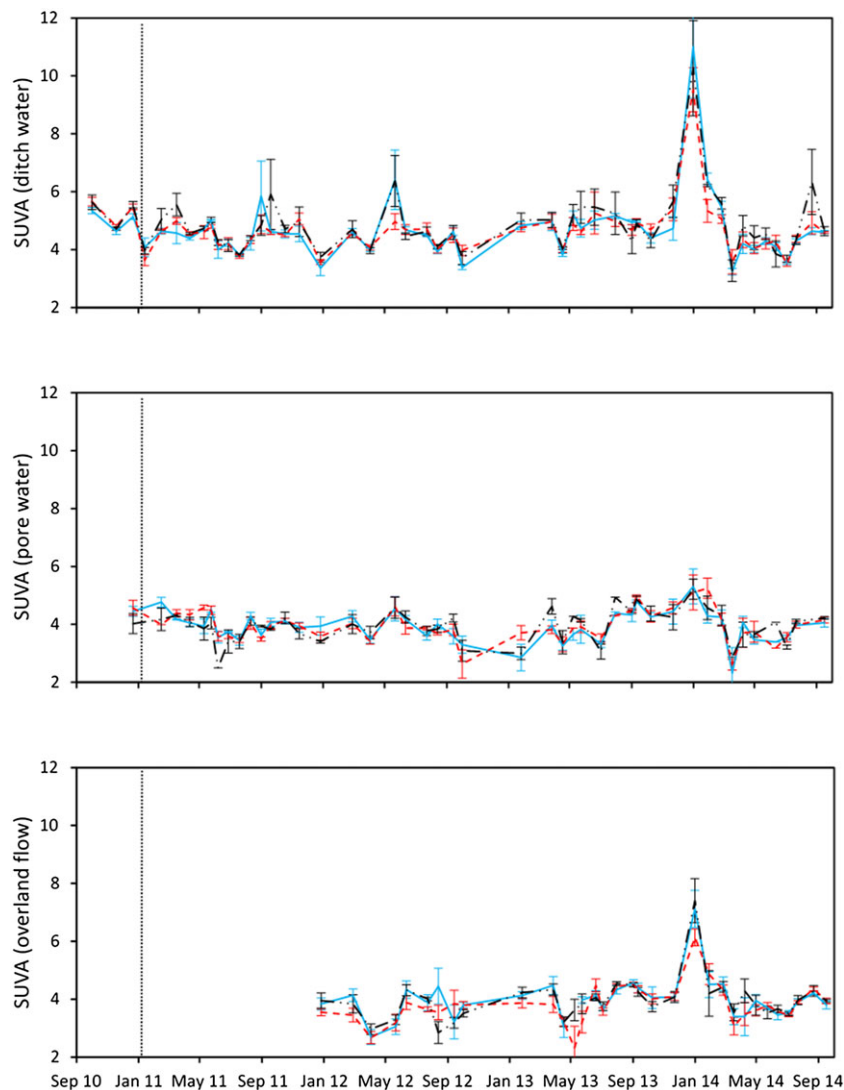
### 2.3 | Laboratory analysis

DOC was measured as nonpurgeable organic carbon using an Analytical Sciences Thermalox Total Carbon analyser (Peacock et al., 2014).

Samples were acidified ( $\text{pH} < 3$ ), sparged with oxygen to remove inorganic carbon, and DOC concentrations calculated using a seven-point calibration ( $0\text{--}60 \text{ mg L}^{-1}$ ) curve with additional standards to check for drift, plus a quality control sample. Between one and three samples per run were duplicated to check for reproducibility. Each individual sample was injected five times, and the result accepted if the coefficient of variation of the five injections was less than 3%.

UV-vis was measured with a Molecular Devices M2e Spectramax plate-reader and converted to cuvette values as in Peacock et al. (2014). Up until October 2012 (i.e., the first 2 years), full spectral scans were performed at 1 nm increments between 230 and 800 nm. From then on, samples were analysed at specific wavelengths to allow the following to be calculated: SUVA (at 254 nm), E2:E3 (250:365 nm), E2:E4 (250:400 nm), and E4:E6 (465:665 nm). Where full scans were available the spectral slopes at intervals of 275–295 nm ( $S_{275-295}$ ) and 350–400 nm ( $S_{350-400}$ ) were calculated by taking the slope of the log-transformed spectra, as in Helms et al. (2008).

Phenolic concentrations were measured for the first year using a method adopted from Box (1983). A total of 0.25 ml of sample was pipetted into a clear microplate well to which 12.5  $\mu\text{l}$  of Folin-Ciocalteu reagent was added, followed by 37.5  $\mu\text{l}$  of  $\text{Na}_2\text{CO}_3$



**FIGURE 5** Mean SUVA for ditch water, pore water, and overland flow water in open ditches (blue continuous line), dammed ditches (black dot/dashed lines), and reprofiled ditches (red dashed lines). Vertical black dotted lines denote when ditch blocking took place. Error bars show standard error of the mean. Truncated error bars are 12.8 for open ditch water in January 2014, 1.4 for dammed pore water in April 2014, and 1.6 for reprofiled overland flow water in June 2013

( $200 \text{ g L}^{-1}$ ). After 1.5 hr, the absorbance was measured at 750 nm on a Molecular Devices M2e Spectramax plate-reader and phenolic concentrations derived from a nine point phenol standard curve ( $0\text{--}20 \text{ mg L}^{-1}$ ). The ratio phenolic: DOC was then calculated.

One set of ditch water samples from July 2012 was analysed for THM formation potential (THMFP), using the method of Gough, Holliman, Willis, Jones, and Freeman (2012). Samples were diluted to  $1 \text{ mg L}^{-1}$  DOC to provide standardised values. A total of 2.0 ml of  $0.5 \text{ M KH}_2\text{PO}_4$  was added to 97.5 ml of diluted sample to buffer the solution to a pH of 6.8. Then, 0.5 ml of NaOCl was added to provide 5 mg of free Cl per mg of DOC. After a 7-day darkened incubation period at  $25^\circ\text{C}$ , 0.4 ml of  $0.8 \text{ M Na}_2\text{SO}_3$  was used to quench the reaction. Extraction of the four main THMs (chloroform— $\text{CHCl}_3$ ,  $\text{CHBrCl}_2$ —bromodichloromethane,  $\text{CHBr}_2\text{Cl}$ —dibromochloromethane and  $\text{CHBr}_3$ —bromoform) was performed using direct immersion solid-phase microextraction and quantified on a Varian 450 gas chromatograph coupled with an electron capture detector.

DOC apparent molecular weight distributions were measured on a subset of samples from July 2012 by HPSEC. The subset comprised one ditch water sample from each treatment (open, dammed, and reprofiled), one pore water sample from each treatment, and two overland flow water samples from each treatment. A Varian PL-GPC-50

DataStream unit detecting at 254 nm with a Bio Sep 2000 column was used for the analysis. Sodium polystyrene sulfonate polymers were used as calibration standards. Their molecular weights were 150,000, 77,000, 32,000, 13,000, and 4,300 Da, and cyanocobalamin (1,340 Da). The mobile phase was milli-q water buffered with phosphate ( $2 \text{ mM KH}_2\text{PO}_4 + 2 \text{ mM K}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$ ) to pH 6.8.

## 2.4 | Statistics

The amount of pre- and post-rewetting data for the various DOM metrics are summarised in Table 2. Statistical analysis was performed using IBM SPSS Statistics 24. Linear mixed models were used to test for differences between treatments (open, dammed, and reprofiled) for all determinands, using time as a repeated measure, and with Bonferroni corrections for pairwise comparisons. For ditch and pore water samples, some data were available from before ditches were blocked, and so separate analyses were performed on preblocking and postblocking datasets. This allowed us to determine if there were pre-existing differences in DOM quality before ditch blocking, which could be due to natural variation between the ditches. Direct comparisons of preblocking and postblocking data could not be made, due to the short duration of preblocking data. Significant results were

accepted if  $p \leq 0.05$ . We also report effect sizes for significant results, calculated as follows:

$$\text{Effect size} = \text{ABS}(\text{mean of treatment A} - \text{mean of treatment B}) / \text{standard deviation},$$

where treatment A and B are taken from the relevant open, dammed, or reprofiled treatments, and the standard deviation is taken as the mean of the standard deviations from the two treatments. Effect sizes were taken from Cohen (1988) and Sawilowsky (2009) as: 0.1–0.19 = very small, 0.2–0.49 = small, 0.5–0.79 = medium, and >0.8 = large.

### 3 | RESULTS

#### 3.1 | Variation in DOM quality

When considering the three E ratios, the temporal variation was greatest for E4:E6 (Figure 2), with individual values ranging from 1.4 to 48.8. This was in contrast to E2:E4 (Figure 3; range 1.4–18.6) and E2:E3 (Figure 4; range 1.2–7.0). SUVA generally displayed small fluctuations (Figure 5) although, in January 2014, a spike in ditch water of 10 and a lesser spike of 7 in overland flow water were observed. This was due to particularly low DOC concentrations (mean =  $2.5 \text{ mg L}^{-1}$ ) associated with winter storms and low pH (mean = 3.44) and low absorbance at 254 nm (mean = 0.243, which is low but nevertheless far greater than the limit of detection of 0.004 reported in Peacock et al., 2014). These spikes could be an artefact induced by low concentrations rather than being true values of SUVA, although we note that unusually high values of SUVA have been reported for other natural waters (e.g., Jaffé et al., 2008).  $S_{275-295}$  and  $S_{350-400}$  were both of the same magnitude and fluctuated but with no obvious seasonal pattern.

#### 3.2 | Effect of ditch blocking on DOM quality

There was no significant difference in DOC concentrations between open, dammed, or reprofiled ditches for ditch water, pore water, or overland flow water (Table 3). Additionally, there was no evidence of a consistent effect of ditch blocking on DOM quality as measured by UV-vis (summarised in Table 4). For ditch water, nine statistically significant differences were detected after ditch blocking in E4:E6, E2:E3, E2:E4, SUVA,  $S_{275-295}$ , and  $S_{350-400}$ . These differences were found between open and dammed ditches and reprofiled and dammed ditches but never between open and reprofiled ditches. However,

**TABLE 3** Mean DOC concentrations for the three treatments in ditch water, pore water, and overland flow water, with standard error of the means in parentheses, for the postblocking period from July 2011 to February 2015

DOC ( $\text{mg L}^{-1}$ )	Ditch	Pore water	Overland flow water
Open	22.4 (0.9)	39.3 (1.3)	24.6 (0.6)
Reprofiled	25.3 (1.0)	37.8 (1.3)	23.9 (0.7)
Dammed	23.0 (0.9)	39.5 (1.5)	24.4 (0.6)

Note. Repeated measures ANOVA showed no significant treatment effect for any water type. Full data and details of statistical analysis are detailed in Evans et al. (2018).

for all statistically significant results, the effect sizes were small, very small, or <very small. Furthermore, for E2:E3 and E2:E4, significant results were identified both before and after ditch blocking, and in the same direction (i.e., means were lowest in dammed ditches). Significant differences were found after ditch blocking in pore water for E4:E6 (open > reprofiled) and for  $S_{350-400}$  (reprofiled > open, reprofiled > dammed), but effect sizes were small or very small. Significant differences in postblocking overland flow waters were also small and were detected for E4:E6 (reprofiled > dammed), E2:E3 (open > dammed), and E2:E4 (open > dammed). Visual inspections of all UV-vis metrics showed that temporal fluctuations were larger than any differences between treatments (Figures 2–8). Although a significant difference was present in ditch water phenolic:DOC before blocking, no significant difference was found for ditch water or pore water after blocking (Figure 8, Table 4).

Two THMs were detected in ditch water samples from July 2012:  $\text{CHCl}_3$  and  $\text{CHBrCl}_2$ . Concentrations of  $\text{CHCl}_3$  were two orders of magnitude larger than those of  $\text{CHBrCl}_2$ . There was no significant difference in THM concentrations between open, dammed, and reprofiled ditches (Table 5). HPSEC showed that there was no difference in molecular weight of DOC in ditch water, pore water, or overland flow water after ditch blocking (Figure 9). Chromatograms showed a minor high molecular weight peak at ~4 min, followed by a dominant high molecular weight peak at ~7.5 min, with a lesser peak at ~9 min. In the pore water and overland flow water samples, there was a minor low molecular weight peak at ~14 minutes. The height difference between chromatograms is due to differences in DOC quantity (i.e., concentration) rather than quality.

### 4 | DISCUSSION

#### 4.1 | Effect of ditch blocking on DOM quality

Our results indicate that peatland ditch blocking had no effect on DOC concentrations or on the composition of DOM in pore water, ditch water, or overland flow water, after nearly 4 years of rewetting, when measured by various metrics of organic matter quality. Although some significant differences were observed in UV-vis, the size of these effects was statistically shown to be small, very small, or <very small (Table 4) and would therefore have no substantive effect (detrimental or beneficial) on the treatability of potable water. Furthermore, some significant differences between ditches were observed both before and after ditch blocking took place. This finding emphasises the importance of collecting prerestoration baseline data, if only for a short period, due to the fact that small but significant differences in organic matter quality can occur over relatively small spatial scales, and in a visually homogeneous ecosystem. We argue that it is thus inadvisable to conclude that ditch blocking has resulted in reductions in DOC concentrations when no baseline data are available (e.g., Wallage et al., 2006) because differences in DOC quality and quantity could instead be driven by microscale variation in DOC processing. When considering all the UV-vis metrics measured here, temporal variation was larger than between-treatment variation, with seasonal variations in E4:E6 being particularly pronounced (Figure 2). Wilson et al. (2011) reported



**TABLE 4** Mean UV-vis and phenolic data for ditch water, pore water, and overland flow water, both before and after ditch blocking

Ditch water	Preblocking					Postblocking				
	Open	Dam	Reprofile	<i>p</i>	Effect size	Open	Dam	Reprofile	<i>p</i>	Effect size
E4:E6	2.11	2.24	2.16	-	-	6.66	6.38 <sup>a</sup>	6.79 <sup>b</sup>	<sup>b</sup>	<Very small
E2:E3	3.39 <sup>c</sup>	3.30 <sup>d</sup>	3.38 <sup>c</sup>	<sup>a</sup>	Small	3.68 <sup>e</sup>	3.55 <sup>f</sup>	3.66 <sup>e</sup>	<sup>c</sup>	Small
E2:E4	5.52 <sup>g</sup>	5.28 <sup>h</sup>	5.54 <sup>g</sup>	<sup>a</sup>	Small	6.59 <sup>i</sup>	6.20 <sup>j</sup>	6.52 <sup>i</sup>	<sup>c</sup>	Small
SUVA	5.04 <sup>k</sup>	5.31 <sup>l</sup>	5.31 <sup>l</sup>	<sup>a</sup>	Small	4.68	4.84 <sup>m</sup>	4.62 <sup>n</sup>	<sup>a</sup>	Very small
S <sub>275-295</sub>	0.0100	0.0098	0.0100	-	-	0.0105	0.0103 <sup>o</sup>	0.0106 <sup>p</sup>	<sup>b</sup>	Small
S <sub>350-400</sub>	0.0138	0.0134	0.0140	-	-	0.0158 <sup>q</sup>	0.0153 <sup>r</sup>	0.0160 <sup>q</sup>	<sup>c</sup>	Small
Phenolics:DOC	0.19	0.17 <sup>s</sup>	0.21 <sup>t</sup>	<sup>a</sup>	Medium	0.18	0.17	0.18	-	-
<b>Pore water</b>										
E4:E6	2.37	2.39	2.97	-	-	8.17 <sup>u</sup>	8.00	7.60 <sup>v</sup>	<sup>a</sup>	Very small
E2:E3	3.48	3.65	3.52	-	-	3.72	3.70	3.73	-	-
E2:E4	5.85	6.20	6.12	-	-	6.88	6.78	6.92	-	-
SUVA	4.45	4.03	4.57	-	-	3.94	3.94	3.96	-	-
S <sub>275-295</sub>	0.0103	0.0108	0.0101	-	-	0.0104	0.0105	0.0105	-	-
S <sub>350-400</sub>	0.0148	0.0152	0.0158	-	-	0.0167 <sup>w</sup>	0.0166 <sup>w</sup>	0.0170 <sup>x</sup>	C v R <sup>a</sup> D v R <sup>c</sup>	C v R Very small D v R Small
Phenolics:DOC	0.16	0.14	0.16	-	-	0.15	0.14	0.15	-	-
<b>Overland flow</b>										
E4:E6	-	-	-	-	-	7.30	6.74 <sup>y</sup>	7.59 <sup>z</sup>	<sup>a</sup>	Very small
E2:E3	-	-	-	-	-	3.89 <sup>A</sup>	3.78 <sup>B</sup>	3.84	<sup>b</sup>	Very small
E2:E4	-	-	-	-	-	7.15 <sup>C</sup>	6.79 <sup>D</sup>	7.00	<sup>b</sup>	Very small
SUVA	-	-	-	-	-	3.97	3.95	3.83	-	-
S <sub>275-295</sub>	-	-	-	-	-	0.0108	0.0106	0.0107	-	-
S <sub>350-400</sub>	-	-	-	-	-	0.0151	0.0148	0.0153	-	-
Phenolics:DOC	-	-	-	-	-	-	-	-	-	-

Note. Nonidentical letters mark significant differences for pairwise comparisons between treatments; comparisons were made only for each metric between treatments, that is, not between water types, metrics, or preblocking and postblocking periods. Dashed lines show either where no significant difference was detected or, for overland flow water, where no preblocking data were available. For most tests where significant differences occurred between all treatments both *p* and effect size were identical. The exception was S<sub>350-400</sub> postblocking pore water, hence two treatment statistics are reported there.

<sup>a</sup>*p* ≤ 0.05,

<sup>b</sup>*p* < 0.01,

<sup>c</sup>*p* < 0.001.

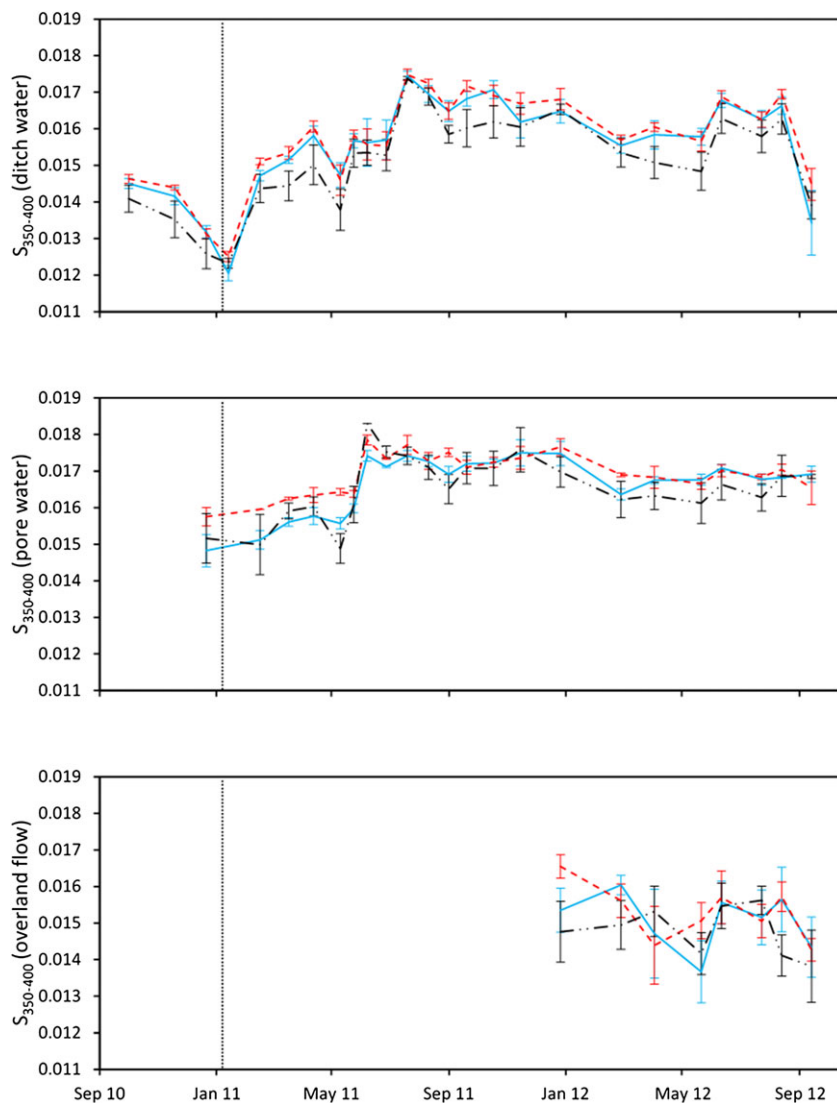
a change in mean E4:E6 from 2.7 to 5.8 in drains and streams after ditch blocking but did not report an associated E4:E6 for unblocked ditches. It is therefore impossible to confidently ascribe such a change to a rewetting effect, considering that temporal changes in our study for both blocked and open ditches ranged between 2 and 14 in ditch water.

We found no difference in the ratio of phenolics to DOC concentration in ditch water or pore water (Figure 8). If phenolic concentrations increased following hydrological changes (e.g., Freeman, Lock, & Reynolds, 1993) then this would have detrimental impacts on potable water, as phenolics are particularly difficult to remove by coagulation methods (Gough et al., 2014; Tomaszewska, Mozia, & Morawski, 2004). Likewise, the lack of difference in apparent molecular weight distributions that we observed using HPSEC between blocked and unblocked ditches (Figure 9) is important, as changes to molecular weight can affect water treatment processes (Collins, Amy, & Steelink, 1986). The HPSEC chromatograms presented here are similar to others measured on high-DOC natural waters and show that the DOC comprised predominantly high molecular weight compounds (Gough et al., 2014, 2016; Valencia, Marín, Velásquez, Restrepo, &

Frimmel, 2012.). To our knowledge, ours is the first study to report field measurements of THMFP following ditch blocking (Table 5). THMFP concentrations were in the same range as other field measurements from blanket peat (Delpla et al., 2015; Gough et al., 2012; Valdivia-Garcia, Weir, Frogbrook, Graham, & Werner, 2016) and did not differ between blocked and unblocked ditches. THM concentrations have been found to co-vary with molecular weight (Gang, Clevenger, & Banerji, 2003), and the lack of significant difference in THMs is expected due to the near identical chromatograms generated by HPSEC. Additionally, SUVA has been shown to relate to THM formation (Weishaar et al., 2003), and no strong effects of rewetting were detected for SUVA (Figure 5).

## 4.2 | Reasons for lack of a rewetting effect on DOM quality

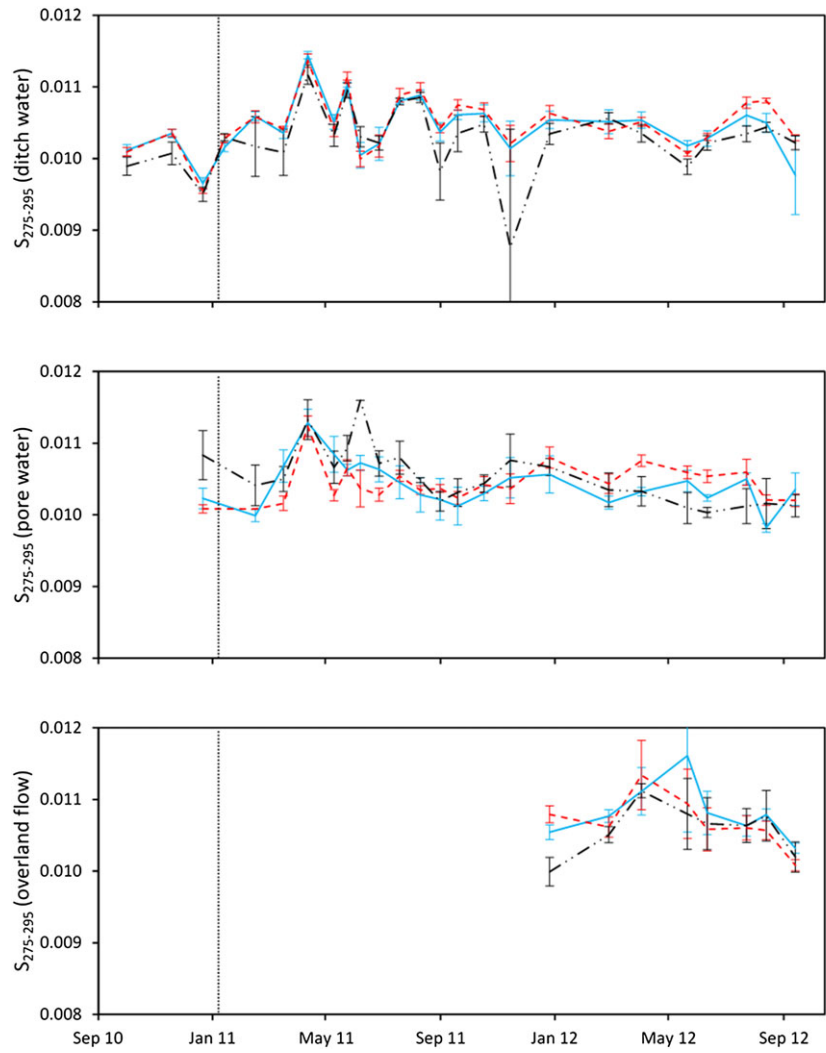
Detailed data concerning the dynamics of DOC quantity at this site are presented by Evans et al. (2018) but in summary (Table 3) show



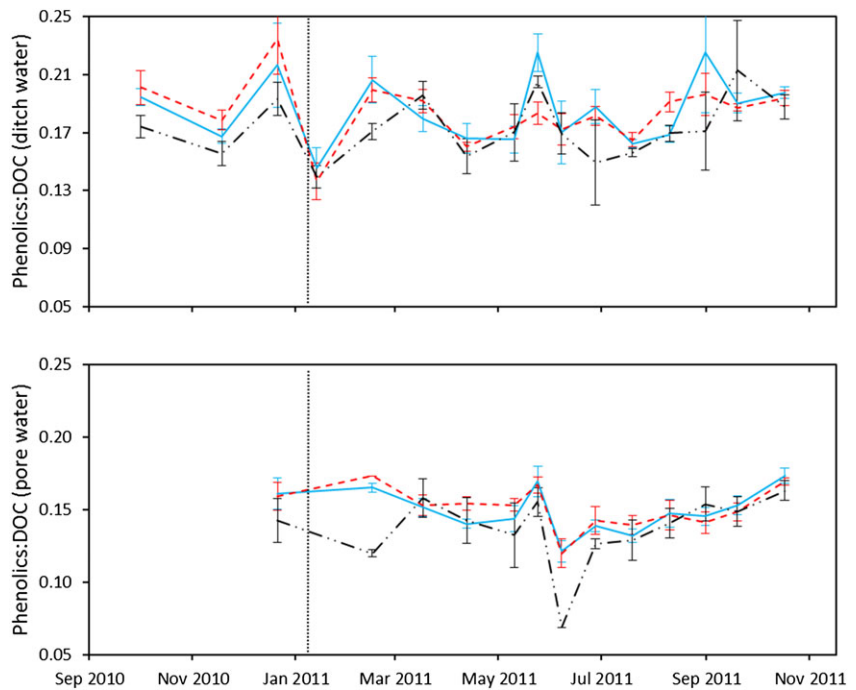
**FIGURE 6** Mean  $S_{350-400}$  for ditch water, pore water, and overland flow water in open ditches (blue continuous line), dammed ditches (black dot/dashed lines), and reprofiled ditches (red dashed lines). Vertical black dotted lines denote when ditch blocking took place. Error bars show standard error of the mean

no effect of rewetting on concentrations or fluxes of DOC. Changes in water table following blocking were variable but very small (<2 cm; Holden et al., 2017), but rewetting did lead to increases in wet-indicator testate amoeba suggesting the creation of wetter conditions across the site (Swindles et al., 2016). However, there was no difference in extracellular enzyme activity in the year following ditch blocking (Peacock et al., 2015), and Francez, Gogo, and Josselin (2000) noted a lag time in changes to microbial communities following restoration of a harvested raised bog. The lack of strong microbial or hydrological changes could be one reason for the associated lack of effect on DOM composition, as the water table was close to the bog surface despite the presence of open ditches (Holden et al., 2017). Recent experimental work at this site, and in the wider peatland surrounding it, has led to the hypothesis of “self-rewetting” (Williamson et al., 2017). Briefly, the digging of a ditch leads to a lowering of the water table, which results in peat oxidation/compaction lowering the peat surface, and thus, the peat surface becomes wetter again (Williamson et al., 2017; Young, Baird, Morris, & Holden, 2017); in more actively drained and cultivated peatlands, this “self-rewetting” is avoided by repeated lowering of the drainage ditches (Kuntze, 1986). Such a process would explain the modest increases in water-

table levels sometimes observed after ditch blocking (e.g., Holden et al., 2017). However, regardless of whether changes in water table occur, it might be expected that the physical interventions of damming or reprofiling would lead to the exposure of previously buried peat, along with soil disturbance and localised inundation of peat and vegetation along former ditch lines. For instance, a short-term study by Worrall, Armstrong, and Holden (2007) recorded increases in ditch DOC and specific absorbance at 400 nm in the 10 months after ditch blocking. Conflictingly, a study of a Finnish peatland found little difference in DOM quality between a control and forest harvested area (Kiikkilä, Smolander, & Ukonmaanaho, 2014). Similarly, although Glatzel et al. (2003) found that ecosystem disturbance in the form of vacuum-harvesting of peat from a Canadian bog resulted in elevated DOC concentrations, they observed no change in DOM composition following restoration or harvesting. For our site, pore water DOC concentrations reached their highest in the summer after rewetting (year 2011), and then declined to early 2014 possibly suggesting a disturbance event (see Evans et al., 2018), but this was not reflected in the DOM quality data. It therefore seems that ecosystem disturbance of peat does not always cause observable changes in DOM composition.



**FIGURE 7** Mean  $S_{275-295}$  for ditch water, pore water, and overland flow in open ditches (blue continuous line), dammed ditches (black dot/dashed lines) and reprofiled ditches (red dashed lines). Vertical black dotted lines denote when ditch blocking took place. Error bars show standard error of the mean. Truncated error bars are 0.0071 for dammed ditch water in December 2012, and 0.0127 for open overland flow water in June 2012



**FIGURE 8** Mean phenolic: DOC for ditch water and pore water in open ditches (blue continuous line), dammed ditches (black dot/dashed lines), and reprofiled ditches (red dashed lines). Vertical black dotted lines denote when ditch blocking took place. Error bars show standard error of the mean. Note truncated error bars for ditch water are 0.259 for reprofiled ditches in January 2011 and 0.267 for open ditches in September 2011

**TABLE 5** Mean standardised trihalomethane formation potentials for  $\text{CHCl}_3$  and  $\text{CHBrCl}_2$  ( $\mu\text{g THM}/\text{mg DOC}$ ), with standard errors of the mean

	$\text{CHCl}_3$	$\text{CHBrCl}_2$
Open	145	0.83
SE	11.5	0.06
Dam	150	0.89
SE	15.7	0.03
Reprofiled	146	0.87
SE	11.9	0.05

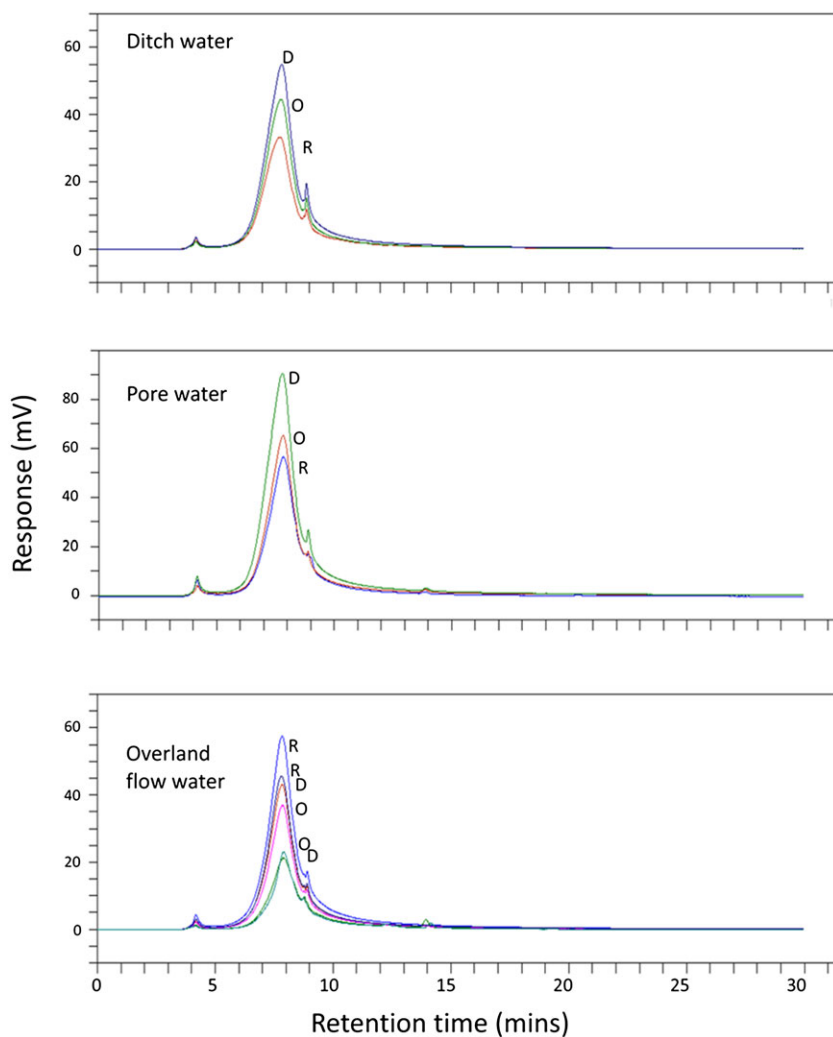
### 4.3 | Assessment of methods

The majority of previous studies on blanket bog ditch blocking have reported only a few metrics of DOM quality alongside DOC concentrations and/or fluxes; for example, E4:E6 and/or specific absorbance at 400 nm (Wallage et al., 2006; Wilson et al., 2011; Worrall et al., 2007). Although UV-vis measurements are undoubtedly useful, this technique has been described as a “black box,” with little understanding of exactly how DOM composition affects light absorbance (Stedmon & Álvarez-Salgado, 2011). The expanded number of metrics that we used, which included additional optical and chemical measurements, has facilitated a more robust investigation of the effects of blocking on DOM quality.

It is perhaps noteworthy that the mesocosm study by Gough et al. (2016) that also measured optical and chemical metrics similarly found no evidence that ditch blocking improves water treatability. By complementing both basic (E ratios) and advanced (spectral slopes) UV-vis metrics with measurements of phenolics, THMFP, and molecular weight distributions (derived by HPSEC), a more complete picture of whether differences in water chemistry are significant and/or meaningful can be obtained.

### 4.4 | Wider implications

Analyses of peat chemistry from our site suggest that it is representative of other U.K. blanket bogs (Green & Baird, 2017) and the type of ditching is also commonly found elsewhere (Evans et al., 2016). It can therefore be hypothesised that ditch blocking will not cause catchment-scale improvements or reductions in water quality at other upland sites, with no real-world effects for water treatment operations in the years immediately following rewetting especially when the local hydrological change (e.g., water table position) after rewetting is minimal. The caveat must be stated that such a lack of response will be noted at sites where ditches are relatively shallow or the blanket bog still relatively wet (due to the aforementioned self-rewetting effect). However, effects on DOM quality may be observed if ditch



**FIGURE 9** HPSEC chromatograms for ditch water, pore water and overland flow water from July 2012. Letters indicate treatments (O = open ditch, D = dammed ditch, R = reprofiled ditch) and are aligned alongside the top of the relevant peak. Note different y axis scales



blocking results in larger rises in water tables than those that we observed (e.g., 2.6 cm noted by Holden et al. (2011) for blanket peat). Alternatively, results from studies on fens and raised bogs elsewhere in Europe have found changes in DOM composition after 10–20 years of rewetting (Frank et al., 2014; Höll et al., 2009), and it could be that such differences will eventually manifest themselves at our site. The difficulty then arises of untangling restoration effects on DOM from the effects of long-term environmental perturbations such as climate change and recovery from acidification that will also exert controls on DOM composition (Ekström et al., 2011; Ritson et al., 2014).

## 5 | CONCLUSIONS

We found no difference in the quality of DOM in the first 4 years following ditch blocking on an upland blanket bog, using a suite of both optical and chemical measurements. Ditch blocking is thus unlikely to lead to either positive or negative changes in the treatability of potable water at our site. Although the lack of improved treatability may prove disappointing to water utilities, the null result can also be perceived as a “no regrets” outcome if other benefits can be obtained from ditch-blocking, for example, reducing peak flows (Ballard, McIntyre, & Wheeler, 2012), reducing sediment loss (Holden, Gascoign, & Bosanko, 2007), improving biodiversity (Carroll et al., 2011; Hannigan, Mangan, & Kelly-Quinn, 2011), restoring bog vegetation (Bellamy, Stephen, Maclean, & Grant, 2012), and improving landscape aesthetics (Bonn et al., 2014), without concern that these aims will interfere with potable water supplies.

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