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Changes in dissolved organic carbon quality in soils and discharge 10 years after peatland restoration



HYDROLOGY

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SUMMARY

Peatlands are large sources of dissolved organic carbon (DOC) to downstream ecosystems and DOC losses account for an important portion of peatland carbon balance. Disturbance and restoration of peatland ecosystems alters ecohydrological conditions that are likely to affect DOC chemistry in both soil water and discharge, although the direction of change and controls on DOC chemistry post-restoration remain unclear. We investigated DOC chemistry (concentration, SUVA254, E2:E3, E4:E6, pentose and hexose concentration) during the growing season (May to October) in soil and discharge of a peatland restored for 10 years and compared the results to those measured at neighboring unrestored and natural peatland sites. Controls on the spatial and temporal variability of DOC chemistry, including pH, water table, temperature, plant cover and type, and carbon dioxide and methane flux were also investigated. After 10 years, restoration increased DOC concentration in soils compared to both natural and unrestored sites. This high DOC concentration likely resulted from high plant productivity post-restoration and a mean water table position deeper than the natural site. Ecohydrological conditions were also correlated to DOC chemistry. High vascular plant cover and photosynthesis rates were correlated to lower SUVA254 and higher pentose concentration, while deeper water table position was correlated to higher E2:E3 and E4:E6. DOC concentration in discharge was lower, and E2:E3 higher, at the restored compared to the unrestored site. Differences in DOC chemistry in discharge water were minimal between the sites except when water was likely sourced from the near surface layer at the restored site, which represents new peat accumulated post-restoration. These results suggest that DOC dynamics 10 years post-restoration remain intermediate between natural and unrestored peatland.

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1. Introduction

Dissolved organic matter (DOM) is operationally defined as any organic matter that passes through a 0.45 μ m filter. In aquatic ecosystems DOM acts as a carbon substrate for microbial communities (e.g. Franke et al., 2013), affects metal mobility and availability (Porasso et al., 2002; Brooks et al., 2007), colours water, and results in the production of potentially carcinogenic compounds when drinking water is chlorinated (e.g., Hsu et al., 2001). Peatlands are large sources of DOM, and export of dissolved organic carbon (DOC) can account for an important portion of the peatland carbon balance (e.g. Roulet et al., 2007; Nilsson et al., 2008) and the majority of this exported DOC is likely eventually

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released to the atmosphere as CO_2 (Wallin et al., 2013). Export of DOC from peatlands is dependent on net DOC production and local hydrology with greater runoff resulting in greater DOC export (Moore, 2009). This study investigates the impact of peat extraction and restoration on peatland DOC concentration and quality.

Peatlands are disturbed for a variety of land-uses, including agriculture, forestry, and resource extraction. In Canada, 25,000 ha have been cleared and drained for horticultural peat extraction with ~14,000 ha actively under extraction (Environment Canada, 2013). Drainage and extraction of peat increases DOC export from peatlands (Waddington et al., 2008; Worrall et al., 2007). Peatland restoration may reduce DOC export (Strack and Zuback, 2013; Waddington et al., 2008; Wilson et al., 2011) although this has not been observed at all locations (Armstrong et al., 2010). While reduced export may be largely due to reduction in discharge due to blocked drainage ditches (Worrall et al., 2007; Gibson et al., 2009; Strack and Zuback, 2013; Turner et al., 2013), shallower water table and changes in



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plant productivity may also affect rates of DOC production (e.g. Wickland et al., 2007). Anoxic soil conditions promote incomplete decomposition of organic matter such that DOC accounts for a larger proportion of total released carbon (Moore and Dalva, 2001), although anoxia will also slow the decomposition rate. Although rewetting during restoration will re-establish anoxic soil conditions, Strack et al. (2011) report 1.2-1.4 times higher DOC production rates in laboratory incubations under oxic compared to anoxic conditions, and several studies report lower DOC concentration following drain blocking (Wallage et al., 2006; Armstrong et al., 2010; Höll et al., 2009). In contrast, higher DOC concentration has been associated with higher plant productivity (e.g. Freeman et al., 2004), suggesting that establishment of vegetation cover during restoration could increase DOC concentration (Waddington et al., 2008). In fact, recent photosynthates were found to make a substantial contribution to DOC in a recolonized cutover peatland (Trinder et al., 2008) and may also increase decomposition of residual peat through priming (Basiliko et al., 2012).

These changing ecohydrological conditions should also alter DOC chemistry. Peatland DOC chemistry can be investigated using spectrophotometric properties of the DOC including specific absorbance of ultraviolet wavelengths (SUVA), and ratios of absorbance at 250 and 365 nm (E2:E3) and 465 and 665 nm (E4:E6) (e.g. Höll et al., 2009; Austnes et al., 2010; Grayson and Holden, 2012; Peacock et al., 2014). SUVA has been shown to be positively correlated with aromaticity of DOC (Weishaar et al., 2003) and also to decrease in value as the proportion of low molecular weight compounds in colored DOC was increased by irradiation (Helms et al., 2008). E4:E6 may indicate molecular size with Summers et al. (1987) reporting a negative log-log correlation between these variables. Grayson and Holden (2012) used E4:E6 ratios in discharge to evaluate relative contributions of fulvic and humic acids in peatland discharge suggesting that ratios of 2-5 indicate greater humification than higher E4:E6 values (see also Thurman (1985)); however, although E4:E6 has been linked to humification, Peuravuori and Pihlaia (1997) found no correlation between the ratio and aromaticity of DOC from Finnish lakes. Finally, E2:E3 is negatively correlated to aromaticity and molecular weight (Peuravuori and Pihlaja, 1997; Helms et al., 2008).

A few studies have investigated changes in DOC quality following peatland rewetting or restoration. Rewetting of a drained fen resulted in a reduction in SUVA and humification indices of soil water DOC, which the authors attribute to reduced rates of decomposition (Höll et al., 2009). Fenner et al. (2011) report a shift toward the high molecular weight fraction of DOC following rewetting, possibly due to release of DOC at higher pH (Grybos et al., 2009) and/or biologically mediated DOC release related to increased phenol oxidase activity. However, Glatzel et al. (2003) report no difference in similar humification parameters between undisturbed, extracted and restored peatlands. Similarly, although Strack et al. (2011) report higher proportions of humic acid production from plant materials present on a restored bog, chemistry of exported DOC was similar between unrestored and restored sites. This was likely due to the strong hydrological control on DOC export and the short time (2 years) since restoration.

Therefore, the effect of peatland restoration, as well as the relative role of rewetting and revegetation, on DOC production, chemistry and export remains unclear. Thus, the objectives of this study were to: (1) determine changes in soil water DOC concentration and chemistry 10 years after restoration by comparing results to unrestored and natural peatland sites, (2) investigate ecohydrological (carbon exchange, plant community, water table, etc.) controls on spatial variability of DOC chemistry in situ, and (3) investigate ecohydrological controls (water table, discharge, new peat layer thickness, etc.) on chemistry of exported DOC.

2. Methods

2.1. Study site

The study was conducted at the Bois-des-Bel (BDB) peatland (47.9671°N, 69.4285°W) located approximately 11 km northeast of Rivière-du-Loup, Quebec, Canada. The 11.5 ha cutover section of peatland is in the northeast section of a 200 ha open and treed bog complex. Horticultural peat extraction began in 1972 and continued until 1980. The cutover peatland was divided into two sections (Fig. 1) and in 1999 restoration activities took place on 7.5 ha (restored site). This restored site was subdivided into four sections with the construction of dykes to hold back snowmelt water. Most of the site was restored in autumn 1999, while the most western section was restored in autumn 2000. Prior to restoration. the restored site was cleared of all vegetation. Restoration was carried out using methods described by Quinty and Rochefort (2003) and involved levelling the peat fields, spreading donor material from a nearby Sphagnum bog in a ratio of 1:10, covering the donor material with straw mulch, applying phosphate rock fertilizer and blocking drainage ditches. In addition, eight open water pools were created (Fig. 1). A 1.8 ha section was left untouched and will be referred to as the unrestored site. A buffer strip separated the restored and unrestored sites (Fig. 1). Measurements were also made within the open section (un-treed) in the undisturbed area of the same peatland ~ 2 km to the northwest of the extracted section. This is referred to as the natural site.

Since only one restored, one unrestored and one natural site were used in the study, the overall design is pseudoreplicated (Hurlbert, 1984), but it was not feasible to replicate the study at the site scale given the limited number of long term peatland restoration projects in Canada and material requirements. This should be kept in mind when evaluating statistical results, particularly differences between restoration treatments.

Determination of in situ DOC concentration and CO₂ and CH₄ flux was carried out at plots distributed across the sites (Fig. 1). At least one plot was installed in each of the former peat fields at the restored site with additional plots chosen to represent the diversity of vegetation cover and microtopography that was observed. Triplicate plots were also placed on the open water pools and ditches. In total, 14 plots were installed on the restored peat fields with an additional three on pools and three on ditches for a total of 20 restored site plots. At the unrestored site, a vegetation gradient was observed, with very little spontaneous recolonization in the northwest portion of the site, much higher vegetation cover at the southeast portion and intermediate coverage between these areas. In each of the two unrestored fields, one plot was randomly placed in each of these three vegetation areas for a total of six unrestored plots. At the natural site, six plots were installed to capture the microtopographic gradient with triplicate plots at each of hummocks and hollows. Boardwalks were installed next to each plot to reduce disturbance during measurements.

2.2. Dissolved organic carbon concentration and water chemistry

Soil water samples were collected from wells adjacent to each sampling plot. Wells were constructed of 2.5 cm diameter PVC pipe and extended at least 1 m into the peat. At least five samples were collected from each well between May and September 2010. The day before sampling, wells were flushed and allowed to refill. The following day a foot-pump was used to collect water from the well into a 1 L Nalgene bottle that was first rinsed with a small volume of sample water. The sample was shaken vigorous to mix and a 100 mL subsample was collected. Water samples of discharge were also collected weekly at weirs installed at the outlet



Fig. 1. Study site showing restored and unrestored area. The natural site is in the same peatland, approximately 2 km to the northwest.

of both restored and unrestored sites (Fig. 1). More frequent sampling was conducted during several rainfall events over the sampling period (5–10 samples per event) to better understand effects of discharge and event flow on chemistry of DOC export.

Water samples were stored in the dark, on ice and were filtered within 48 h through 0.4 µm borosilicate glass fiber filters (Macherey–Nagel, GF-5). For samples with high particulate load, water was first pre-filtered using 1.5 µm borosilicate glass fiber filters and then passed through the 0.4 µm filter. Absorbance at 400 nm was measured using a UV–Vis Spectrophotometer (Perkin Elmer 3B Lambda) compared to a blank of Ultrapure Water. A subset of 10% of samples were acidified for preservation and shipped to University of Calgary for analysis of DOC concentration using a total carbon analyzer (Shimadzu 680). DOC concentration in remaining samples was determined based on the regression between absorbance at 400 nm and DOC concentration (DOC = 2.956 * ln(absorbance at 400 nm) + 77.74, R^2 = 0.93, p = 0.002). Unfiltered samples were used to determine pH (HANNA HI98130).

2.3. Dissolved organic carbon chemistry

Water samples collected for determination of DOC concentration were further characterized using spectrophotometric ratios. Specific ultraviolet absorbance (SUVA₂₅₄) was determined by dividing absorbance at 254 nm by estimated DOC concentration; E4:E6 was determined as the ratio between absorbance at 465 and 665 nm; E2:E3 was determined as the ratio of absorbance at 250 and 365 nm.

Three times during the growing season (May, June, July) water samples were also analyzed for pentose and hexose concentrations. 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 (Chantigny et al., 2008). Kawahigashi et al. (2003) used pentose and hexose concentrations to evaluate land use change effects on soil organic carbon. Pentose concentration was determined using Bial's orcinol test (Chantigny et al., 2008). Pentose concentration was determined by reacting 1 mL of DOC sample with an iron chloride reagent to form furfural from pentose sugars present in the sample. This was then reacted with an orcinol reagent creating a blue color that was quantified based on absorbance at 660 nm and comparing against a standard curve prepared from ribose solutions of 2.5, 5, 10, 20, 30, 50 and 100 mg L⁻¹. Thus, concentrations are expressed as ribose equivalents. Hexose concentration was determined using the anthrone reaction (Chantigny et al., 2008). Briefly, 1 mL of DOC sample was reacted for 15 min with an anthrone reagent to produce furfuraldehyde derivatives from all sugars present. This solution was then heated in a water bath at 95 °C for 20 min in order to react any pentose present and create furfuraldehyde-anthrone complexes which are vellow to colorless. Absorbance was determined at 625 nm and hexose concentration determined by comparison to a calibration curve using D-glucose and thus concentration is expressed as glucose equivalents.

2.4. Discharge

Discharge from the restored and unrestored sites was determined at V-notch weirs installed at the outlet ditches (Fig. 1). Stage was recorded continuously behind the weir (Solinst Levelogger) and corrected for barometric pressure. Manual discharge measurements were made at least weekly at each weir and regressed against stage to allow continuous estimation of discharge. Due to the shift from very low discharge in summer (June– August) to high discharge in autumn (September–October), separate stage-discharge relationships were fitted for each time period. Discharge was not determined from the natural site as it lacked a distinct outlet.

2.5. Carbon gas fluxes

Carbon dioxide exchange was determined using the closed chamber method. The net ecosystem exchange (NEE) of CO₂ was determined with a clear acrylic chamber ($60 \times 60 \times 30$ cm) placed on a stainless steel collar (60×60 cm) permanently installed at each sampling plot. A groove in the collar held the chamber and was filled with water to create a seal. A battery-operated fan installed inside the chamber circulated the headspace air throughout the measurement period and the chamber was lifted from the collar between each measurement and allowed to equilibrate to ambient CO₂ concentration and temperature. The concentration of CO₂ was determined inside the chamber at 15-s intervals for a maximum of 105 s using a portable infrared gas analyzer (EGM-4, PPSystems, Massachusetts, USA). The linear change in CO₂ concentration over time was used to calculate NEE. Ecosystem respiration (ER) was determined by darkening the chamber with an opaque shroud. Gross ecosystem photosynthesis (GEP) was calculated as the difference between NEE and ER. Maximum rate of GEP and NEE (GEP_{max} , NEE_{max}) was determined at each plot when photon flux density of photosynthetically active radiation was greater than 1000 μ mol m⁻² s⁻¹ and photosynthesis should not be limited by available radiation (Bubier et al., 2003). We use the sign convention that positive values indicate a release of CO_2 from the ecosystem to the atmosphere.

Methane flux was determined with opaque closed chambers $(60 \times 60 \times 30 \text{ cm})$ equipped with a battery-operated fan to circulate headspace. Chambers were placed on the collars described above and gas samples were collected 7, 15, 25 and 35 min after closure and stored in pre-evacuated vials. The concentration of CH₄ in the samples was determined on a Varian 3800 gas chromatograph equipped with a flame ionization detector. CH₄ flux was determined from the linear change in concentration over time.

2.6. Ecohydrological characteristics

Water table position was measured in a 2.5 cm diameter standpipe inserted into the peat to a depth of 1 m adjacent to each sample plot and was determined during each CO_2 and CH_4 flux measurement. In July, a vegetation survey was conducted for each plot. All species present were identified and their spatial cover estimated visually. Results were further summarized by grouping species to estimate moss, shrub, sedge and total vascular plant cover.

2.7. Data analysis

Variation between sites (natural, restored, unrestored) was evaluated using a general linear model with Tukey's pairwise comparisons. Prior to analysis, growing season averages were

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Ecohydrological characteristics and carbon gas fluxes^a of the study sites.

determined for each plot and these were compared in the model. Residuals of the model were examined to ensure that they met assumptions of normally and homogeneity and in some cases data was transformed and reanalyzed to meet these assumptions (e.g. log transformation of CH₄ flux). Controls on the spatial distribution of mean seasonal DOC concentration and chemistry were determined using Pearson correlation to investigate correlation between CO₂ flux, water table position and vegetation cover, and DOC characteristics. When significant correlation to multiple predictors was found stepwise regression was used to evaluate relative importance of each predictor with α = 0.15 used as criterion for a predictor to enter the model. Differences in DOC concentration and chemistry in discharge from restored and unrestored sites were investigated using *t*-tests. In all cases α of 0.05 was used to determine if results were statistically significant. All analyses were performed in Minitab 14.1.

3. Results

3.1. Ecohydrological characteristics

Vegetation cover varied among sites and among sample plots within a site (Table 1). Moss cover was significantly higher at natural and restored than unrestored plots while total vascular plant cover was not significantly different between sites. Variation in vascular plant cover was highest at the unrestored site where some plots were almost bare while others had up to 45% coverage.

Mean growing season (May to October) water table also varied among plots and sites (Table 1; GLM, $F_{4,29} = 101.5$, p < 0.001). The unrestored site was significantly drier than all other sites with mean water table -47.7 cm. Restored ditches had a similar water table position to the natural site but were significantly drier than restored pools (which were consistently flooded) and wetter than restored fields. The restored fields remained significantly drier than the natural bog with mean water table positions of -26.5and -12.0 cm, respectively.

Between May 22 and October 25, 2010 total precipitation measured on site was 526 mm. Discharge was greater from the unrestored site that from the restored site. Both sites had stage continuously monitored between June 30 and October 25, 2010 resulting in estimated discharge of 262 and 49 mm from the unrestored and restored sites, respectively. Stage was monitored at the restored site starting on May 22, 2010 and only an additional 1.2 mm of discharge was recorded between this date and the time that monitoring began at the unrestored site. Close to 99 mm of precipitation fell during this period and thus some additional discharge would have occurred at the unrestored site that was not recorded. See McCarter and Price (2013) for more details on site hydrology.

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	Natural	Unrestored	Restored	Restored		
			Field	Ditch	Pool	
Water table (cm)	-12.0 (1.1)	-47.7 (5.4)	-26.5 (8.7)	-6.8 (3.2)	48.4 (6.0)	
Moss cover (%)	91.9 (12.0)	0.1 (0.2)	88.4 (27.0)	46.7 (15.3)	53.5 (47.3)	
Sedge cover (%)	2.2 (2.7)	0	7.5 (8.4)	0	1.2 (1.6)	
Shrub cover (%)	10.9 (10.3)	24.8 (23.3)	10.8 (9.3)	1.0 (1.7)	0	
Total vascular plant cover (%)	19.6 (10.3)	30.1 (28.6)	20.2 (9.6)	10.8 (5.8)	5.0 (5.0)	
GEP_{max}^{b} (g CO ₂ m ⁻² d ⁻¹)	-8.8 (1.8)	-11.2 (12.1)	-13.3 (4.2)	-8.2 (1.2)	-11.3 (3.8)	
NEE_{max}^{b} (g CO ₂ m ⁻² d ⁻¹)	-1.1(1.4)	2.7 (7.0)	-4.3 (3.2)	6.0 (3.2)	-5.0 (0.8)	
ER (g CO ₂ m ^{-2} d ^{-1})	7.6 (2.4)	13.8 (8.1)	8.3 (2.2)	12.4 (2.8)	5.2 (2.4)	
$CH_4 \text{ flux } (mg CH_4 m^{-2} d^{-1})$	15.0 (17.6)	-1.3 (3.2)	1.8 (4.1)	38.6 (48.6)	(145.6)	

^a All values are the mean (standard deviation) of the seasonal means calculated at each sampling plot at each site (natural: *n* = 6, unrestored: *n* = 6, restored field: *n* = 14, restored ditch: *n* = 3, restored pool: *n* = 3).

^b GEP_{max} and NEE_{max} are gross ecosystem productivity and net ecosystem exchange, respectively and represent fluxes measured when the photon flux density of photosynthetically active radiation was greater than 1000 μ mol m⁻² s⁻¹. Negative values indicate CO₂ uptake by the ecosystem.

Details of CO₂ and CH₄ flux are given in Strack and Zuback (2013) and summarized in Table 1. Briefly, mean growing season GEP_{max} was -10.0 to -6.2 g CO₂ m⁻² d⁻¹ at natural site plots, -34.1 to -1.2 g CO₂ m⁻² d⁻¹ at unrestored site plots, and -19.6 to -7.7, -9.6 to -7.3, and -15.0 to -7.4 g CO₂ m⁻² d⁻¹ at restored field, ditch and pool plots, respectively. The broad range at the unrestored site resulted from the variation in vegetation cover. Mean ER remained high at the unrestored site (4.4-26.4 g CO₂ m⁻² d⁻¹) compared to the natural site (4.9-10.7 g CO₂ m⁻² d⁻¹) and restored peat fields (5.5-13.1 g CO₂ m⁻² d⁻¹). This resulted in unrestored sites acting as, on average, a net source of CO₂ even under full light conditions (NEE_{max}) while natural and restored fields were sinks (Table 1). Restored pools also acted as sinks while ditches were sources of CO₂.

Mean growing season CH₄ flux was $5.8-41.4 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ at the natural site. Both unrestored and restored sites had much lower fluxes except at ditches and pools on the restored site where CH₄ fluxes were high (Table 1). Water table position was significantly positively correlated to CH₄ flux (see Strack and Zuback, 2013).

3.3. In situ DOC concentration and chemistry

DOC concentration, E2:E3 and E4:E6 all varied significantly among sites (Table 2, DOC: *F*_{4.29} = 8.87, *p* < 0.001, E2:E3: $F_{4,29} = 8.99$, p < 0.001, E4:E6: $F_{4,29} = 10.11$, p < 0.001). Restored fields and ditches had the highest DOC concentration, being significantly higher than the natural site plots. Restored pools and the unrestored site had intermediate DOC concentrations. Both the unrestored and restored fields had E2:E3 values significantly lower than the natural site. E4:E6 of DOC at the unrestored and restored fields was also lower than the natural site although the difference was not significant. The restored pools had significantly higher E4:E6 values than all other sampling sites. Although not significantly different between sites, SUVA₂₅₄ of DOC was highest at the natural plots followed by restored pools, unrestored fields, and restored ditches, with lowest values at restored fields. Hexose and pentose concentrations were highly variable in space and time with hexose concentrations highest at the restored fields and pentose concentrations highest at unrestored plots (Table 2).

Controls on spatial variability of DOC concentration and chemistry were investigated using Pearson correlation (Table 3). DOC concentration was significantly negatively correlated to GEP_{max} and positively correlated to ER. Thus, more productive sites (i.e., large negative GEP_{max}) and sites with high ER had higher DOC concentration. These effects are likely related given that GEP_{max} and ER are correlated due to the large contribution of plant respiration to

Table 2	
Mean (standard deviation) soil water chemistry [*] .	

ER (Strack and Zuback, 2013). DOC concentration was also negatively correlated with water table and CH₄ flux. Again, the correlation with CH₄ flux is likely driven by water table given that this is the dominant control on CH₄ flux from peatlands in general (e.g. Couwenberg and Fritz, 2012) and this site (Strack and Zuback, 2013). Water table position may also control GEP_{max} and ER; however, stepwise linear regression considering these three predictors indicated that both water table and GEP_{max} were important for explaining the variation in DOC concentration across the sites with water table explaining 19.9% of the variation while GEP_{max} explained an additional 13.9%. Thus, high DOC concentration would be expected at dry, productive sites.

SUVA₂₅₄ of DOC was positively correlated with GEP_{max} (Fig. 2) and negatively correlated with shrub cover and total vascular plant cover (Table 3). Both E2:E3 and E4:E6 were negatively correlated to water table position (Fig. 2). Hexose concentration was negatively correlated to NEE_{max}. Pentose concentration and the ratio of pentose to hexose sugars were both significantly negatively correlated to GEP_{max} and positively correlated to shrub cover and total vascular plant cover (Table 3). Therefore, sites with more plant cover and thus higher rates of photosynthesis had higher pentose concentrations and more pentose relative to hexose sugars in DOC. Pentose concentration and pentose:hexose were also negatively correlated to CH₄ flux; however, this again is likely due to co-linearity with water table and CH₄ flux. Stepwise regression relating pentose concentration with a combination of these variables indicates that only water table and vascular plant cover enter the model.

3.4. DOC concentration and chemistry in discharge

DOC export from the restored and unrestored sites has been previously reported (Waddington et al., 2008; Strack and Zuback, 2013). Briefly, prior to restoration, growing season (May– October) DOC export was 10.3 g C m^{-2} from the unrestored site and 4.8 g C m^{-2} from the restored site (Waddington et al., 2008). In the first and second year post-restoration, respectively values were 8.5 and 6.2 g C m^{-2} from the unrestored site and 3.4 and 3.5 g C m^{-2} from the restored site (Waddington et al., 2008). In the same year as the present study, 10 years post-restoration, growing season DOC export was 28.8 and 5.5 g C m $^{-2}$ at unrestored and restored sites, respectively (Strack and Zuback, 2013). This accounted for 5.3% of the carbon balance at the unrestored site and 3.3%, at the restored site, where both sites were net carbon sources in the study year.

Mean (standard deviation) pH of discharge was not significantly different between sites (*t*-test, $T_{47} = 1.67$, p = 0.101) being 6.2 (0.4) at the restored site and 5.9 (0.6) at the unrestored site. Mean DOC concentration in sampled discharge was 86.3 (20.9) and 102.0 (15.4) mg L⁻¹ at restored and unrestored sites, with sites being

	Natural	Unrestored	Restored		
			Field	Ditch	Pool
рН	4.13 (0.39) ^a	6.06 (0.22) ^b	5.86 (0.52) ^b	5.67 (0.80) ^b	5.92 (0.46) ^b
$[DOC] (mg L^{-1})$	44.6 (3.2) ^a	62.0 (15.5) ^{bc}	69.2 (4.9) ^c	64.9 (8.4) ^{bc}	47.0 (9.6) ^{ab}
E2:E3	4.03 (0.03) ^c	3.00 (0.50) ^a	2.96 (0.37) ^a	3.15 (0.40) ^{ab}	3.79 (0.18) ^{bc}
E4:E6	6.35 (1.47) ^a	5.54 (0.79) ^a	5.56 (0.42) ^a	5.47 (0.32) ^a	9.07 (2.08) ^b
$SUVA_{254}$ (L mg ⁻¹ m ⁻¹)	5.52 (0.19)	5.24 (1.06)	5.02 (0.36)	5.21 (0.04)	5.34 (0.12)
Hexose (mg L^{-1})	19.0 (2.8)	16.1 (1.9)	23.0 (10.5)	19.3 (3.5)	16.5 (1.1)
Pentose (mg L^{-1})	13.5 (3.7)	24.3 (15.0)	22.1(7.1)	15.1 (4.0)	14.6 (8.8)
Pentose:Hexose	0.68 (0.16)	1.43 (0.82)	1.09 (0.33)	0.77 (0.12)	0.82 (0.46)

* Bold indicates statistically significant differences between sites (GLM, p < 0.05) and letters in these row indicate significant differences if sites have no letters in common. Letters should be compared only within a row. All values are the mean (standard deviation) of the seasonal means calculated at each sampling plot at each site (natural: n = 4, unrestored: n = 6, restored field: n = 14, restored ditch: n = 3, restored pool: n = 3).

Table 3

Pearson correlations between DOC properties and site conditions.

	[DOC]	SUVA ₂₅₄	E2:E3	E4:E6	Pentose	Hexose	Pentose:Hexose
рН	0.31	-0.11	-0.33	-0.07	0.11	0.01	0.19
WT	-0.45^{*}	0.11	0.49**	0.74***	-0.36	-0.13	-0.34
GEPmax	-0.40^{*}	0.40*	0.28	0.05	-0.49^{**}	-0.30	-0.41^{*}
NEEmax	-0.06	0.19	-0.01	-0.15	-0.29	-0.38*	-0.20
ER	0.39*	-0.27	-0.34	-0.26	0.29	-0.02	0.29
$\log (CH_4 flux + 5)$	-0.37^{*}	0.17	0.39	0.33	-0.49^{**}	-0.04	-0.51**
Vascular cover	0.33	-0.41^{*}	-0.34	-0.26	0.60***	-0.06	0.62***
Moss cover	0.14	-0.14	0.01	-0.11	-0.08	0.33	-0.25
Sedge cover	0.27	-0.07	-0.13	-0.12	0.12	0.04	0.11
Shrub cover	0.21	-0.40^{*}	-0.33	-0.26	0.56**	-0.08	0.58**

* p < 0.05.

p < 0.01.

**** p < 0.001.



Fig. 2. (A) SUVA₂₅₄ versus GEP_{max}, (B) E2:E3 versus water table, and (C) E4:E6 versus water table. Water table position is measured relative to the surface with negative values indicating a depth below the surface. GEP_{max} is gross ecosystem photosynthesis when photon flux density of photosynthetically active radiation is greater than 1000 µmol m⁻² s⁻¹, where negative values indicate uptake of CO₂ by the ecosystem. Each point represents the mean of the plotted value over the study period measured at one study plot.

significantly different from each other (*t*-test, $T_{95} = -4.40$, p < 0.001). E4:E6 was 6.4 (1.5) and 6.7 (1.5), while SUVA₂₅₄ was 0.41 (0.11) and 0.37 (0.12) at the restored and unrestored site,

respectively. Neither parameter was significantly different between sites. E2:E3 was significantly different between sites (*t*-test, T_{67} = 2.90, p = 0.005), with a value of 2.8 (0.9) at the restored site and 2.3 (0.7) at the unrestored site. Pentose and hexose concentrations were only measured twice at the restored site and six times at the unrestored site. Based on this minimal data set, mean pentose and hexose concentrations in discharge were 23.7 and 19.2 mg L⁻¹ at the restored site and 16.3 and 15.8 mg L⁻¹ at the unrestored site.

Dissolved organic carbon concentration in discharge showed a general pattern of increasing into July and August followed by a decrease in late September and early October at both restored and unrestored sites (Figs. 3 and 4). Precipitation events also resulted in lower DOC concentrations in discharge (Figs. 3 and 4). E2:E3, E4:E6, and SUVA₂₅₄ followed an inverse pattern, having lower values in midsummer and higher values early in the season and again in early autumn. The greatest difference in E2:E3 values between restored and unrestored sites occurred in early May and again in September and October when water tables were shallower and discharge was higher compared to midsummer (Figs. 3 and 4). SUVA₂₅₄ values appear to diverge between sites most in spring when restored site had higher values that unrestored (data not shown). Precipitation events tended to result in an increase in E2:E3. E4:E6 appeared to decrease during events at the restored site, but at the unrestored site it increased slightly during events in the autumn (Fig. 4).

4. Discussion

Mean soil water DOC concentration reported in this study of 44–69 mg L⁻¹ is similar to that reported elsewhere. For example, Moore (2009) reports values in the upper 1 m depth of peat in an undisturbed Canadian bog of 50–68 mg L^{-1} , Höll et al. (2009) report ranges of 82–92 and 52–64 mg L⁻¹ in drained and rewetted German fens, and Urbanova et al. (2011) found DOC concentration in the upper 30 cm of $17-54 \text{ mg L}^{-1}$ across a range of intact and drained peatlands in the Czech Republic. SUVA254 values were near the upper end of the range reported for peat (e.g. Austnes et al., 2010; Clark et al., 2012; Weishaar et al., 2003). As Fe³⁺ ions can increase UV absorbance (Weishaar et al., 2003) this may be partially responsible for their higher values (Austnes et al., 2010). although Fe³⁺ concentrations were not determined in the present study. E2:E3 and E4:E6 are also similar to previously reported values for peat soil water DOC (e.g. Austnes et al., 2010; Grayson and Holden, 2012).

Restoration has altered both soil DOC concentration and chemistry during the growing season in a cutover peatland compared to a neighboring unrestored site, although the changes in chemistry were not statistically significant in some cases. This is likely at least



Fig. 3. Precipitation, discharge, DOC concentration, E2:E3 and E4:E6 of DOC measured in discharge water collected at the outlet of unrestored and restored sites in spring and summer. Bars give daily precipitation.

partially due to the fact that the water table resided within the residual peat layer at the restored site for most of the growing season (see also McCarter and Price, 2013) reducing the impact of new peat accumulation and plant productivity on pore water DOC characteristics. In most cases, DOC chemistry of the restored site is intermediate between the unrestored peatland and the natural plots (Table 2). In contrast, while the unrestored site had higher soil DOC concentration than the natural peatland, DOC concentrations were higher still at the restored site 10 years post-restoration. Several studies report declining soil water DOC concentration following rewetting and/or restoration (Wallage et al., 2006; Höll et al., 2009). Glatzel et al. (2003) found higher DOC concentration following restoration but predicted that this effect would be short-lived. High DOC concentration at the restored site in this study likely arose from the fact that, unlike the natural site, the water table at the restored site remained deeper and unconnected to the surface (McCarter and Price, 2015) and that plant productivity was high (Table 1), both factors that were significantly correlated to DOC concentrations (Table 3).

The specific ecohydrological conditions at the restored site also affected soil DOC chemistry. Although not significantly different, restored peat fields had lower pH, E2:E3 and SUVA₂₅₄, and slightly

higher E4:E6 than unrestored fields. Pentose concentration was lower at restored fields while hexose concentration was higher, resulting in lower pentose to hexose ratio at the restored fields compared to the unrestored fields. Most of these changes were linked to shallower water table position and changes in vegetation composition and productivity following restoration. Together these DOC proxies indicate that DOC at the restored site consists of smaller, less aromatic molecules, likely sourced from inputs of fresh litter from the growing vegetation.

Plant establishment also alters pore water chemistry that could alter mobility of organic molecules and impact DOC chemistry. For example, the colonization of the restored site with mosses, particularly *Sphagnum* moss, resulted in lower pH (moss cover-pH correlation, R = -0.394, p = 0.031). Lower pH has been linked with lower SUVA values (e.g. Clark et al., 2012) and thus this could be partially responsible for lower SUVA following restoration. On the other hand, we found no significant correlation between pH and SUVA₂₅₄, possibly due to the wide range of plots (natural, restored, unrestored) included in the analysis, suggesting that pH would be only one of many controls on SUVA₂₅₄ in this case and that the input of fresh organic material is likely the main driver of these changes.



Fig. 4. Precipitation, discharge, DOC concentration, E2:E3 and E4:E6 of DOC measured in discharge water collected at the outlet of unrestored and restored sites in autumn. Bars give daily precipitation.

Water table position was positively correlated to both E2:E3 and E4:E6 suggesting that wetter sites would result in pore water with smaller, less aromatic DOC that would likely be more labile and mobile. While these parameters changed little in restored field plots, pools on the restored site had elevated values for these ratios relative to both restored and unrestored fields. In contrast, Wallage et al. (2006) observed an increase in E4:E6 following drain blocking. Peacock et al. (2014) noted that E4:E6 ratios had greater temporal variation compared to E2:E3 and SUVA and suggest that this may make E4:E6 a good proxy for temporal change, but limit its utility for assessing treatment effects. GEP_{max} was positively related to SUVA₂₅₄ indicating that more productive plots (large negative GEP) resulted in less aromatic DOC. This is consistent with the results of Wickland et al. (2007) who observed lower SUVA in DOC samples derived from fresh plant material compared to soil water extracts. Peacock et al. (2014) suggest that E2:E3 and SUVA may be good indicators of between site differences in DOC quality; however, despite higher productivity at the restored site, there were no significant difference between soil water E2:E3 and SUVA between restored and unrestored peat fields (Table 2). This was likely due to dry conditions during the study period and limited hydrologic connectivity between residual peat layers and the newly deposited peat (McCarter and Price, 2015) that limited contact between soil pore water and the new litter.

Pentose concentrations were also correlated to GEP_{max} and vascular plant cover, as was pentose:hexose. Given that pentose sugars in soils are largely derived from plants (Chantigny et al., 2008), the correlation is not surprising. The higher pentose concentrations in restored field soil DOC supports the hypothesis that carbon recently fixed by the recovering plant community makes an important contribution to the DOC pool (see also Trinder et al., 2008) and likely leads to the observed increase in DOC concentration post-restoration.

Dissolved organic carbon concentration, E2:E3 and pentose concentration were also correlated to CH₄ flux (Table 3). While this correlation likely arises due to the link between these DOC parameters with water table and plant productivity, both of which are also know to be predictors of CH₄ flux (this study, Lai, 2009; Couwenberg and Fritz, 2012), it may also indicate biochemical interactions between DOC and CH₄ production. DOC can act as an electron acceptor in peat soils, possibly reducing rates of methanogenesis (Heitmann et al., 2007); thus, the negative correlation between DOC concentration and CH₄ flux observed in this study is not unexpected. Despite shallower water tables and increasing plant productivity, CH₄ flux from the restored fields remain low and this could be explained, at least partially, by the high DOC concentration. Further study is required to evaluate the importance of DOC dynamics for CH₄ production post-restoration. Moreover, high CH₄ flux indicates slow, anaerobic decomposition of organic matter and therefore likely less production and mobilization of DOC.

Waddington et al. (2008) reported similar DOC concentrations pre-restoration at unrestored and restored areas, and higher DOC concentration in discharge from the restored site at Bois-des-Bel than the unrestored site in the first two years post-restoration. Despite higher soil DOC concentration at the restored site, DOC concentration in discharge was significantly lower from the restored site compared to the unrestored site 10 years after restoration. Similarity between the sites prior to restoration, suggests that changes observed 10-years post-restoration are related to site development post-restoration and not inherent differences between the sites. During restoration straw mulch was applied to the peat surface to protect donor plant material and Waddington et al. (2008) hypothesized that this was the source of the higher DOC concentration immediately following restoration. Given that the mulch decomposes within approximately three years (Waddington et al., 2003), it is no longer contributing to DOC production on site. The reduction in DOC concentration in discharge following restoration or rewetting is consistent with several other studies (Glatzel et al., 2003; Armstrong et al., 2010; Höll et al., 2009), although it has not been observed in all cases (Armstrong et al., 2010; Turner et al., 2013).

Dissolved organic carbon concentration measured in discharge was higher at both restored and unrestored sites than that measured in soils during mid-summer, although in autumn the reverse was true. This suggests either an additional source of DOC contributing to discharge or evapo-concentration (Waiser, 2006) of DOC prior to export. Although blocked at their outlets at the restored site, water in ditches remains open to the atmosphere and subject to evaporative losses. Armstrong et al. (2010) report higher concentrations in standing water in blocked peatland ditches; however, concentration data from our measured ditches have values below those measured in export. As all our ditch plots were over 150 m from the outlet, within ditch production and evapoconcentration closer to the outlet could still increase DOC concentration.

The summer of 2010 was extremely dry receiving only 54% and 10% of normal rainfall in July and August, respectively (Strack and Zuback, 2013). Therefore, it is also possible that decomposition in the unsaturated peat produced mobile organic compounds that were flushed during precipitation events, but not captured in our well measurements in which source water would have been only the saturated zone. Hydrological studies on site (McCarter and Price, 2015) determined that hydrologic connectivity between the cutover peat and new moss layer at the restored site was extremely limited except during large precipitation events, suggesting that this DOC flushing mechanism is likely to occur. Moreover, Clark et al. (2012) report a rapid increase in DOC concentrations upon rewetting in peat soil columns coincident with an increase in acid neutralizing capacity, again suggesting that precipitation events could result in a rapid increase in DOC mobilization that was subsequently flushed to the outlet. In September and October when water tables were shallow and discharge was high, DOC concentration in discharge was lower than soil DOC concentration suggesting dilution of soil pools with rainwater.

Temporal patterns in chemistry and concentration of exported DOC indicate both hydrological and biological controls. Higher DOC concentration midsummer is associated with the period of highest plant productivity. Low flows during this time period also allow longer contact time resulting in higher concentration. During precipitation events and high flow periods in spring and autumn, DOC concentration decreased, probably due to shorter contact times and dilution (Fraser et al., 2001). Higher values of E2:E3 and E4:E6 during these high flow periods suggest that smaller, less aromatic compounds were exported, again consistent with rapid flushing and export of more mobile DOC components. During the

high flow period in the autumn, differences in chemistry of exported DOC between restored and unrestored sites were clear (Fig. 4) with the restored site having higher E2:E3 values. This result contrasts that of Strack et al. (2011) who report no significant difference between the sites two years post-restoration.

The highly porous new peat layer that has developed at the restored site has very poor soil water retention (McCarter and Price, 2015), such that when water table is deeper than this layer (e.g., during midsummer) precipitation percolates rapidly through the new peat to the water table in the old residual cutover peat. Low hydraulic conductivity of this layer limits lateral flow and thus stormflow from the restored site is limited (McCarter and Price, 2013). In contrast, during the autumn period water table was at or above the surface of the restored site, resulting in greater stormflow. Although this could result in saturated overland flow in some sections of the restored site, it also enables mixing of precipitation with soil pore water that is in direct contact with the newly formed peat layer. Given that the newly formed post-restoration peat layer is 15-20 cm thick in most locations (McCarter and Price, 2013), during this time water flows predominantly through the newly deposited peat likely mobilizing fresh DOC that is less aromatic. In fact, continuous water table measurement on the restored peat fields (data not shown) indicate that water table resides within the new peat layer only 6% of the time between June and late September, but 100% of the time after September 24 (day 267). As this new peat layer continues to thicken and water table fluctuations remain in this zone throughout the growing season, differences in DOC export chemistry between the restored and unrestored sites are likely to become more distinct and present throughout the majority of the growing season. Since new peat accumulation and plant productivity following restoration are the likely causes of the difference in DOC chemistry in discharge during the growing season between restored and unrestored sites, it is unclear how annual patterns would change and whether processing of DOC overwinter would mask these differences. More research characterizing both the export and chemistry of DOC with snowmelt and the effect of restoration on these patterns is required to address this question.

5. Conclusions

After 10 years, restoration increased DOC concentration in soils compared to both natural and unrestored sites. The natural site, and restored site pools and ditches had DOC with higher E2:E3 and E4:E6 indicating that shallow water table results in a higher proportion of small size compounds and with more fulvic nature in DOC. There was no difference in E2:E3 or E4:E6 between restored and unrestored field plots suggesting that the water table at the restored site is still deep enough to prevent significant changes in these aspects of DOC quality. In contrast, both hexose and pentose concentrations were intermediate at the restored field plots between natural and unrestored plots. Given that concentrations of these sugars were both significantly correlated to measures of plant productivity, these changes at the restored site suggest a link to the plant cover established post-restoration.

Export of DOC was lower from the restored site compared to the unrestored site (Strack and Zuback, 2013) with concentration in discharge significantly lower at the restored site 10 years post-restoration. Similar to results of Strack et al. (2011), differences in the quality of the exported DOC between restored and unrestored sites remained minimal except at times of year where water table is close to the surface at the restored site and the newly accumulated peat layer can impact discharge chemistry. Restoration activities that increase hydrological connectivity between new litter layers and the underlying peat are likely to result in more significant changes in DOC quality post-restoration. Given that the restored site has DOC chemistry intermediate between natural and unrestored sites, this suggests that 10 years post-restoration DOC dynamics are still recovering toward patterns in an undisturbed system.

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