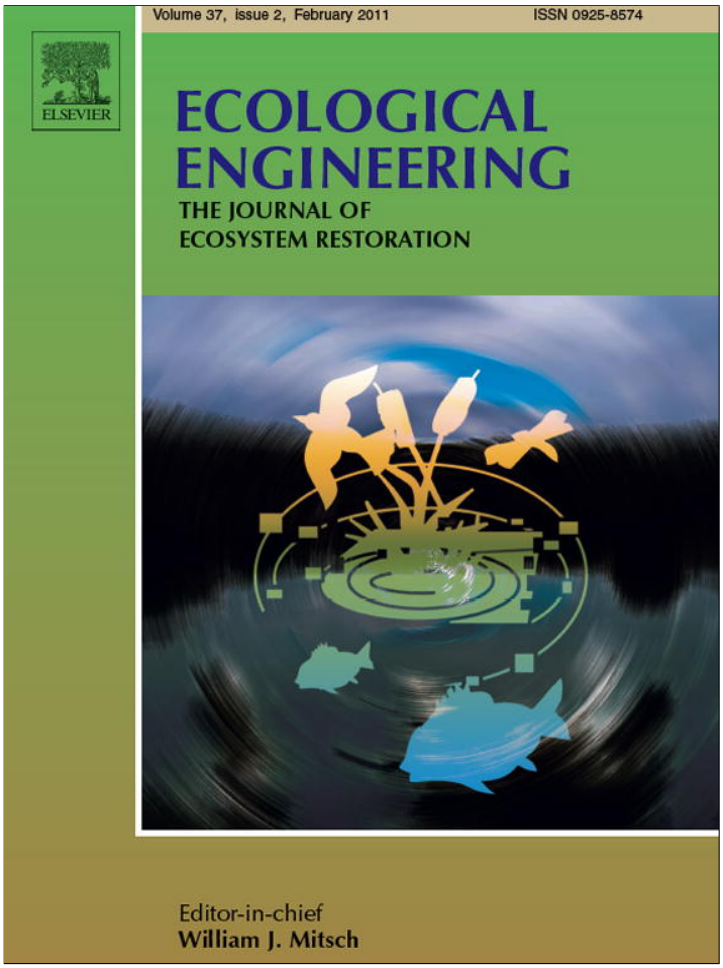

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Ecological Engineering 37 (2011) 1998–2008

Contents lists available at ScienceDirect

Ecological Engineering

journal homepage: www.elsevier.com/locate/ecoleng

Dissolved organic carbon production and runoff quality following peatland extraction and restoration

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ARTICLE INFO

Article history:
Received 8 June 2011
Received in revised form 28 July 2011
Accepted 7 August 2011

Keywords:
Decomposition
Dissolved organic carbon
Dissolved organic matter
Peatland
Peat extraction
Restoration
Wetland

ABSTRACT

We examined dissolved organic carbon (DOC) production and quality in a cutover (extracted) and restored peatland in eastern Québec through a combined laboratory DOC production study and an accompanying field DOC runoff quality study. Both temperature and substrate were significant for explaining variability in net DOC production rate in both short (5 days) and longer term (25 day) laboratory incubations. Moss (*Sphagnum* spp. and *Polytricum* spp.) produced the least amount of DOC, with initial release rates of 0.02–0.35 mg DOC g^{-1} d^{-1}. Shrubs, and to a lesser extent herbaceous vegetation, showed an initial high release of DOC followed by a decrease. Peat from the restored site had significantly higher longer-term DOC production rates than the cutover site. Humic acid (HA) was more likely to be produced by shrub and herbaceous plant material than by peat, mosses and straw. The hydrophilic (HPI) fraction of the DOC increased at higher temperatures. Despite differences in the surface cover of available substrate (e.g. vascular vegetation, moss, and straw), there was no difference in the quality of DOC exported from the cutover and restored sites. However, hydrological and biogeochemical controls were apparent in temporal variability of DOC quality in discharge. DOC exported during snowmelt and most storm events was high in HPI with little contribution from HA. Since contact time between water and soil is limited during these high flow periods, larger more hydrophobic HA molecules are less likely to be mobilized. Higher export of HA in summer compared to spring and autumn suggests that polycondensation and increased vascular plant productivity are important for controlling seasonal patterns of DOC export quality. As various substrates produced different amounts and quality of DOC, it is likely that the DOC quality exported from the restored site will continue to change as the new vegetation community develops. DOC production rates and DOC quality should be considered when developing a plan to control DOC runoff/export from managed peatlands.

1. Introduction

Peat is extracted from northern peatlands for use as fuel in countries such as Finland, Sweden and Ireland (Schilstra, 2001), while in Canada most peat is extracted for horticultural purposes. Canadian peat extraction is concentrated in the provinces of Québec and New Brunswick, where in some regions more than 70% of the peatlands have been impacted by peat extraction activities (Lavoie and Rochefort, 1996). The most common extraction method is vacuum extraction which involves drainage of the peat and successive removal of the dry surface layer over approximately two decades. Following vacuum extraction, the remnant peat deposits often remain devoid of vegetation for decades (Poulin et al., 2005). These sites, hereafter referred to as cutover peatlands, are often colonized by ericaceous shrubs and cotton grass (*Eriophorum* spp.) with limited to or no recolonization by *Sphagnum* mosses (Campeau and Rochefort, 1996). This, coupled with a deeper and more variable water table position (e.g. Van Seters and Price, 2001), switches these ecosystems from a net long-term atmospheric carbon dioxide (CO_2) sink to a large and persistent source of CO_2 (Waddington et al., 2002). Moreover, the drainage (to allow extraction) of these ecosystems not only increases runoff but also enhances net dissolved organic carbon (DOC) production (Glatzel et al., 2003) resulting in a large increase in DOC export (Waddington et al., 2008). Because DOC plays a role in nutrient cycling, acidification (Marin et al., 1990; Thurman, 1985; Urban et al., 1986), light penetration (Schindler and Curtis, 1997) and metal complexation (e.g. Porasso et al., 2002) in freshwaters, the downstream aquatic impacts of peat extraction can be far reaching. The overwhelming majority of studies examining DOC production

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doi:10.1016/j.ecoleng.2011.08.015

and fluxes from peatlands do not assess DOC quality (Bourbonniere, 1989). However, it is of utmost importance to measure DOC quality as it controls its long-term fate and hence effect on many biogeochemical processes.

In order to alleviate cutover peatland carbon losses (aquatic and atmospheric) and potentially decrease the impact on downstream water quality, many peatland ecological engineering, re-wetting and/or restoration programs have been initiated (e.g. Price et al., 1998; Rochefort et al., 2003 for details). While several studies suggest that enhanced CO_2 sequestration and the net CO_2 sink function can be achieved in a short to medium-term (e.g. Tuittila et al., 1999; Waddington and Warner, 2001; Lucchese et al., 2010; Waddington et al., 2010), recent research suggests that DOC pore water concentrations actually increase following restoration (Worrall et al., 2007), and re-wetting likely enhances respiration (Fenner et al., 2001; Glatzel et al., 2003; Waddington et al., 2003, 2010) and CH_4 emissions (e.g. Waddington and Day, 2007). These studies suggest that higher effluxes of CO_2 and CH_4 following re-wetting or restoration are due to an increase in net DOC production and/or to a more labile DOC quality. For example, Höll et al. (2009) observed a decrease in the humification index of DOC in a peatland following rewetting suggesting an increase in the proportion of labile compounds. However, despite the importance of DOC to within peatland biogeochemistry and downstream water quality, very few studies have investigated DOC production and quality in cutover and restored peatlands. Consequently, the aim of this paper is to examine DOC production and quality in a cutover and restored peatland in eastern Québec through a combined laboratory DOC production study and an accompanying field DOC runoff quality study.

In order to investigate DOC quality, we utilized DOC fractionation. The fractionation technique used derives three DOC fractions: humic acid (HA), hydrophobic acid (HPO) and hydrophilic acid (HPI). Details of the fractionation are described in Section 2. These three fractions have been shown to vary in mobility and lability and may be related to the age/extent of processing of the DOC and thus should be useful to distinguish sources of DOC within the peatland and suggest differences in its fate downstream.

The formation of humic matter is thought to involve both processes of polycondensation of small molecules as well as the stepwise biological degradation of natural biopolymers (Bourbonniere, 1979). Bourbonniere (1989) found HA to be prominent in porewaters of deeper bog layers as well as samples where the processes of oxidative polycondensation can readily occur. HPO has been observed to account for the major portion of DOC in natural waters, is responsible for most of the colour in DOC and is an intermediate in humic matter formation that can be degraded to smaller components or produced through polycondensation (Bourbonniere, 1989). The HPO fraction also contains compounds that are non-polar, and rich in moieties that closely resemble plant sources (Guggenberger et al., 1994). Bourbonniere (1989) concludes that some of these HPO compounds are highly unreactive and therefore can accumulate in integrated systems such as limnic sediments. Bourbonniere (1989), studying natural systems, found strong seasonal effects on the hydrophilic (HPI) component of DOC, with higher concentrations observed in the summer months compared to winter and spring. The HPI fraction was less coloured and contained soluble acidic components that were related to decomposition of biomass. Thus, he concluded that microbial activity has a strong influence on this component. Guggenberger et al. (1994) further confirmed this finding and added that this fraction contains both plant derived compounds as well as those directly produced by microbes. In addition, Wickland et al. (2007) reported a significant relationship between the biodegradability of DOC in leachates from a variety of vegetation types and the initial HPI content of the DOC.

In order to improve our understanding of the effect of peatland restoration on DOC quality, the objectives of this study were to: (1) determine the concentration and quality (DOC fractions) or DOC released by various substrates available at the cutover and restored sites, (2) compare quality of exported DOC between the cutover and restored sites and (3) investigate hydrological and biogeochemical controls on the observed patterns of DOC quality.

1.1. Study area

This study was carried out at the cutover and restored portions of the 210 ha Bois-des-Bel (BDB) peatland, located 14 km east of Rivière-du-Loup, Québec (47°53′N, 69°27′W) (Fig. 1). An 11.5 ha portion of the bog was drained in 1972, separated into 11 peat fields, approximately 30 m × 300 m, and cutover using the vacuum extraction technique from 1973 to 1980. The 30-year (1971–2000) mean annual temperature was 3 °C and the mean January and July temperatures were −13 °C and 18 °C, respectively (Environment Canada, 2010). Restoration, as described by Rochefort et al. (2003), began in the autumn of 1999, separating the cutover portion of the peatland into two catchments; a 7.2 ha restored section (peat fields 1–8) and a 1.8 ha cutover section (peat fields 10–11) (Fig. 1). Peat dykes were constructed on the restored site to increase water storage during high flow periods and they divided the restored area into four zones (Fig. 1). During restoration all spontaneously recolonizing vegetation from the restored site was cut and the surface of the peatland was milled to create a fresh surface for vegetation establishment. The cut vegetation, in many circumstances, was used as fill for the drainage ditches. *Sphagnum* fragments were added to the surface and covered by a layer of straw mulch. By 2001 the surface cover of moss and herbaceous vegetation on the restored site was 23% and 10%, respectively.

2. Methods

2.1. DOC production laboratory experiment

For the DOC production experiment triplicate samples of ericaceous shrubs (*Ledum groenlandicum* and *Kalmia angustifolia*), herbaceous species (*Eriophorum vaginatum* and *Typha latifolia*), moss (*Sphagnum* sp. and *Polytricum* sp.) and surface (0–20 cm) and subsurface (50–80 cm) peat were collected on September 7, 2001 from both the cutover and restored peatland. In addition triplicate samples of straw mulch were taken from the restored site. All of these substrate samples were stored in plastic bags at 4 °C until analysis.

From two of the field samples, ∼10 g of material was placed in clear 250 mL glass containers with 175 mL of distilled water, with ∼40 g from the third sample placed in a 1 L mason jar with 700 mL of distilled water. The large jars were used for the incubation of one-third of the samples to obtain sufficient volume of water for fractionation analysis (see below). An additional glass jar, only containing distilled water, was used as a blank. All samples were capped, stored in the dark, and incubated under oxic conditions at 7 and 22 °C for 25 days with the exception of the deep (50–80 cm) peat samples that were incubated under anoxic conditions. For the anoxic treatments the jars were flushed with nitrogen gas and sealed with a lid containing Tygon® tubing and a three-way valve in the lid for sampling.

Using a plastic syringe, 10 mL of water was withdrawn from the 250 mL jars immediately following distilled water addition and then twice a week for the entire incubation period. DOC concentrations were corrected to account for the removal of water during

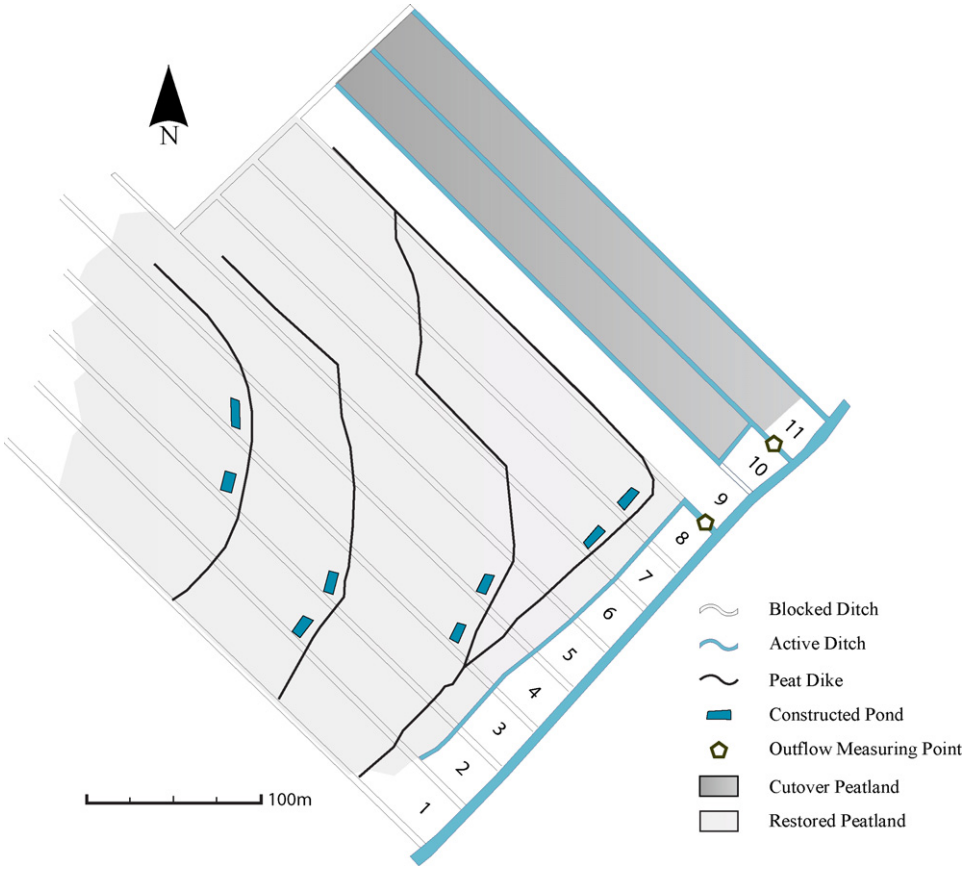

Fig. 1. Bois-des-Bel peatland study area. Pentagons indicate the outflow from the restored (light grey) and cutover (dark grey) catchments.

sampling. Water samples were filtered using Whatman® GF/F filters and stored at 4 °C until analyzed for DOC concentration. On a weekly basis, 60 mL of water was withdrawn from the 1 L containers, filtered through Whatman® GF/F filters, the pH measured and stored in covered plastic bottles at 4 °C until fractionation.

The total DOC net production rate (μg DOC g^{-1} dry weight d^{-1}) for the entire 25-day incubation period and initial 5-day net production rate (μg DOC g^{-1} dry weight d^{-1}) were then calculated by comparing the concentration of DOC on the noted sampling day to that of sample collected immediately following water addition to the substrate (time zero).

2.2. Peatland hydrology and DOC water sampling

Stage was recorded continuously at the outflow ditches (Fig. 1) in 2000 using a potentiometric water level recorder attached to a Campbell Scientific CR10X datalogger and in 2001 using a Remote Data System (RDS) water level recorder. Stage recorders were either placed in a V-notch bucket below the outflow or behind a V-notch weir. Discharge was determined by developing a stage-discharge rating curve at each outflow ditch during each study season. Precipitation was measured using both a tipping bucket and a manual rain gauge at a meteorological station located in the restored site.

Water samples from the catchment outflows were collected, primarily during baseflow, three times a week from May to October in 2000. Snowmelt was sampled from late March to the end of April (day of year, DOY = 87–120) in 2001. Given that a substantial proportion of total catchment DOC export can occur during storm events (Hinton et al., 1997), three summer storms in 2001 were also sampled: a medium-intensity storm with wet (a few weeks following snowmelt) antecedent conditions in May (DOY = 132–133), a high-intensity storm with dry antecedent conditions during a period of low water table position in July (DOY = 205) and a medium-intensity storm with dry antecedent conditions in August (DOY = 238–239). Rainfall samples were collected after each rain event in all field seasons.

All samples were filtered using 0.7 μm Whatman® GF/F filters within several hours of collection and a 7 mL aliquot was placed in a glass vial and transported at ~4 °C to the National Water Research Institute in Burlington, Canada, for total DOC analysis. The remainder of the sample was stored in plastic bottles at 4 °C until further analysis. The definition of dissolved is generally made using 0.45 μm, thus the use of GF/F filters with a nominal pore size of 0.7 μm will slightly overestimate DOC concentrations. This overestimate is likely small and filtered samples from this study held for archival purposes at 4 °C remained stable with no flocculation of colloidal material for up to three years.

2.3. DOC analysis

DOC concentrations were measured using high temperature catalytic oxidation on a Shimadzu TOC 5000A. Filtered water samples were acidified with 20% phosphoric acid and purged for 5 min with the instrument's carrier gas, zero air or oxygen, to remove dissolved inorganic carbon prior to injection for DOC determination (also called NPOC for non-purgeable organic carbon). All determinations were corrected for system blank, estimated daily by regressing the results of low concentration standards (0, 2, 5 mg C L^{-1}) analyzed as samples, against their "true" value. The system blank corrects for a combination of blank sources internal to the instrument and also residual carbon in the reagent water used

Table 1
Results of two-way analysis of variance for initial (5 days) and final (25 days) aerobic net DOC production rates.

	Initial net production rate $R^2 = 0.896$			Final net production rate[a] $R^2 = 0.756$		
	df	*F*	*p*	df	*F*	*p*
Substrate	7	28.27	<0.001	6	8.36	<0.001
Temperature	1	64.51	<0.001	1	33.92	<0.001
Substrate × temperature	7	1.70	0.145	6	0.49	0.807
Error	32			28		

[a] Ericaeous shrub data was not included in analysis due to negative values.

to make the standards. All the dissolved fractions described below were analyzed using the same method.

2.4. DOC fractionation

The fractionation method that splits DOC into HPI and HPO components was first developed by Leenheer and Huffman (1979). The operational definitions of these fractions depend on the ability of the compounds to adsorb onto amberlite XAD-8 resin. The point at which the HPO–HPI break occurs is arbitrary and depends on both polarity of the solute and the ratio of the resin quantity to the volume of water passed through it (Leenheer, 1981). HPO solutes, therefore, are defined as those solutes that are greater than 50% retained on XAD-8 resin at a given ratio of resin to water volume, and hydrophilic solutes are those that are greater than 50% eluted at the same ratio of resin to eluent (Leenheer, 1981). While Leenheer and Huffman (1979) fractionated the samples further into acids, bases and neutrals we chose to use a modification of the Leenheer (1981) fractionation technique for the high DOC water characteristic of peatlands (Bourbonniere, 1989). This technique involves the isolation of humic acid (HA) prior to application of the sample on the XAD-8 resin column (Bourbonniere, 1989) since Bourbonniere and van Halderen (1989) determined that HA, the most hydrophobic component, can be precipitated over a range of pH values. Thus, isolation of HA early in the analytical scheme as a separate fraction allows for three fractions to be isolated in a series of decreasing hydrophobicity: HA > HPO > HPI. Some of the common characteristics of these fractions have been established (Bourbonniere, 1989; Guggenberger et al., 1994) using a combination of analytical techniques and these are described below.

Filtered extract-samples were acidified to a pH of 2 using concentrated phosphoric acid (H_3PO_4), stored at 4 °C, and filtered using GF/F filters within 24 h of acidification. This process separated humic acid (HA), which remained on the filter, from fulvic acid (FA). A sub-sample of FA was analyzed for DOC concentration. The HA DOC concentration was calculated by subtracting the un-acidified extract DOC concentration from that of the FA such that: [HA] = [DOC] – [FA]. FA was further fractioned into HPO and HPI fractions by passing FA samples, diluted 10 times with distilled water (total volume of 132 mL), through a 2 mL XAD-8 resin column (Thurman and Malcolm, 1979; Leenheer, 1981). Prior to dilution DOC concentration of samples was between 50 and 150 mg L^{-1}. The HPI/HPO break ($k'_{0.5r}$) was equal to 50 (Leenheer, 1981). A 10 mL burette equipped with a Teflon valve was used to contain the column and a small plug of glass wool helped to keep the resin in place. A 250 mL separatory funnel was attached to the burette using silicone tubing to contain the sample. Flow-rate through the column was controlled by adjusting the valve of the burette and was set to be drop-wise. Once the HPI fraction passed through the column it was analyzed for DOC concentration using the method described above. The HPO fraction adsorbed to the column and its DOC content were calculated by difference such that: [HPO] = [FA] – [HPI]. Wickland et al. (2007) report a standard deviation of ±2% for DOC fractions estimated using a similar resin-based fractionation and precision in the present study is likely in a similar range.

2.5. Data analysis

Differences in net DOC production rate from the oxic experiment were investigated with a two-way analysis of variance with substrate and temperature as factors. For deep peat incubations, a general linear model was used to investigate the role of temperature, restoration and anoxia on net DOC production rate. Data for initial and final net DOC production rates were analyzed separately. In all cases data were tested for normality and *p* values of <0.05 were considered statistically significant. Initial oxic net DOC production rates were non-normal so a box-cox power transformation was applied. All analyses were completed in Minitab 14.

Differences between the cutover and restored sites for field measured discharge and DOC export were assessed using Student's *t*-tests in Microsoft Excel.

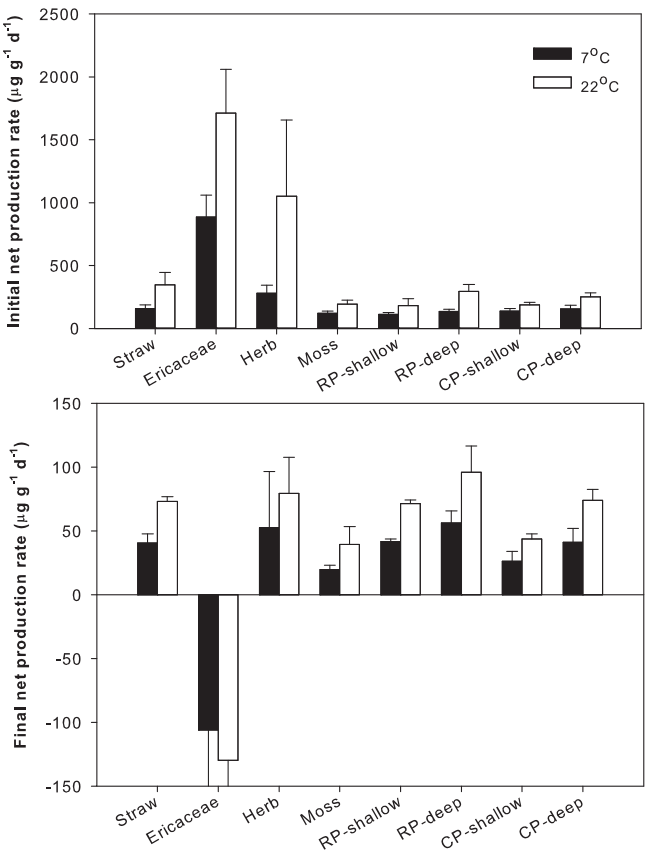

Fig. 2. Average 5-day (initial, top panel) and 25-day (final, lower panel) DOC production rates for various substrates incubated under oxic conditions. Error bars give standard deviations. RP and CP refer to restored peat and cutover peat, respectively. Details of statistical analyses can be found in Table 1.

Table 2
Q_{10}[a] for net DOC production rate determined from substrate incubation.

Substrate type		Initial 5-day net DOC production rate	Final 25-day net DOC production rate
Peat	Cutover shallow	1.2	1.4
	Cutover deep, oxic	1.3	1.3
	Cutover deep, anoxic	1.3	1.7
	Restored shallow	1.4	1.4
	Restored deep, oxic	1.6	1.4
	Restored deep, anoxic	1.7	1.4
Amendment	Straw	1.7	1.5
Vegetation	Moss	1.4	1.6
	Herb	2.4	1.3
	Shrub	1.6	1.1[b]

[a] Q_{10} was calculated at $(R_2/R_1)^{10/(T2-T1)}$ where R_1 and R_2 were the rates of net DOC production at the temperatures T_1 and T_2 which were 7 and 22 °C, respectively.
[b] Net DOC production rate over 25 days was negative for shrub material under both temperatures, with a higher negative rate at 22 °C.

3. Results

3.1. Net production of DOC from peat and restored vegetation

Initial aerobic net production rates varied between 110.4 ± 16.0 and $1713.0 \pm 347.0\ \mu g\ g^{-1}\ d^{-1}$. Both substrate type and temperature were significant factors in explaining differences in net production rate (Table 1), with higher initial net production rates at 22 °C compared with 7 °C and from shrub and herbaceous vegetation compared with peat, straw and moss (Fig. 2). Q_{10} for initial net production rates was between 1.2 for shallow cutover peat and 2.4 for herbs (Table 2).

Final aerobic net production rates followed a similar pattern to initial rates; however, negative values were determined for shrubs. Despite light rinsing of vegetation samples prior to incubation, the DOC concentration of water samples collected immediately following addition to shrubs indicated that up to $20\ mg\ g^{-1}$ was leached. As DOC concentration after 25 days was lower than these initial concentrations, DOC degradation in these samples was greater than production over this period. As these data greatly skewed the data set, they were eliminated from the ANOVA, but are included in Fig. 2. As with initial net production rates, both temperature and substrate were significant factors for explaining differences in final net production rates with higher rates at 22 °C and in general higher rates restored deep peat and herbs (Table 1). There was no significant interaction between temperature and substrate for either initial or final net production rates. Q_{10} for final net production rate was in the range from 1.1 for shrubs to 1.6 for moss (Table 2). Overall, final net production rates calculated over the 25 day incubation were lower than initial 5 day net production rates (Fig. 2).

The GLM indicated that the only significant factor explaining variability in initial net production of DOC from deep peat was temperature with a nearly significant interaction between temperature and restoration (Table 3). Final net production rate was significantly described by restoration status, temperature and anoxia with no significant first order interactions between factors (Table 3). Higher net production rates were observed from the restored site, at the higher temperature, and under oxic conditions. The ratio of final DOC production rate between oxic and anoxic conditions was 1.0 and 1.4 for cutover peat and 1.2 and 1.2 for restored peat at 7 and 22 °C, respectively.

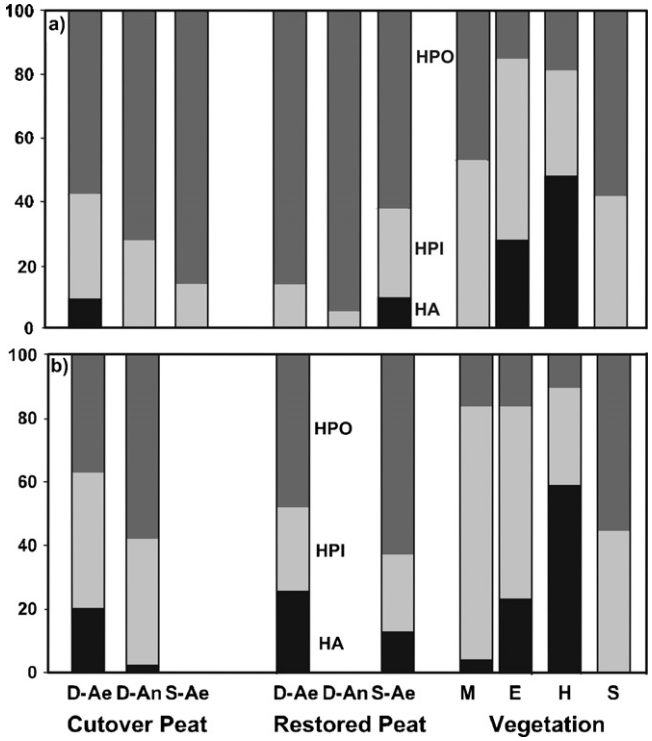

Fig. 3. DOC fractions produced from peatland samples after 21 days of incubation at (a) 7 and (b) 22 °C. The fractions have been normalized to DOC concentration so the *y*-axis refers to percentage (%) of total DOC. D-Ae, D-An, and S-Ae refer to deep aerobic, deep anaerobic, and shallow aerobic peat, respectively. M, E, H, and S refer to moss, ericaceous shrubs, herbaceous plants and straw, respectively. Black, light grey, and dark grey bars refer to the HA, HPI, and HPO fractions, respectively.

3.2. Quality of DOC released from peat and restored vegetation

The proportions of HA, HPO and HPI varied substantially between different substrates. Moss and straw produced high proportions of HPI (~80%), some HPO and little HA during the lab experiment (Fig. 3). The largest component in the DOC produced by herbaceous vegetation was HA representing 47–58% of DOC while HPI ranged from 30 to 33% and HPO between 9 and 11% (Fig. 3). For shrubs the HA fraction was also important accounting for 27–32%

Table 3
Results of general linear model for deep peat incubation for initial (5 days) and final (25 days) net DOC production rates.

	Initial net production rate $R^2 = 0.818$			Final net production rate $R^2 = 0.808$		
	df	*F*	*p*	df	*F*	*p*
Restoration	1	0.64	0.434	1	13.62	0.002
Temperature	1	70.37	<0.001	1	51.81	<0.001
Anoxia	1	0.01	0.919	1	5.11	0.037
Restoration × temperature	1	4.32	0.053	1	0.49	0.495
Restoration × anoxia	1	0.07	0.793	1	0.47	0.501
Temperature × anoxia	1	0.81	0.379	1	0.09	0.770
Error	17			17		

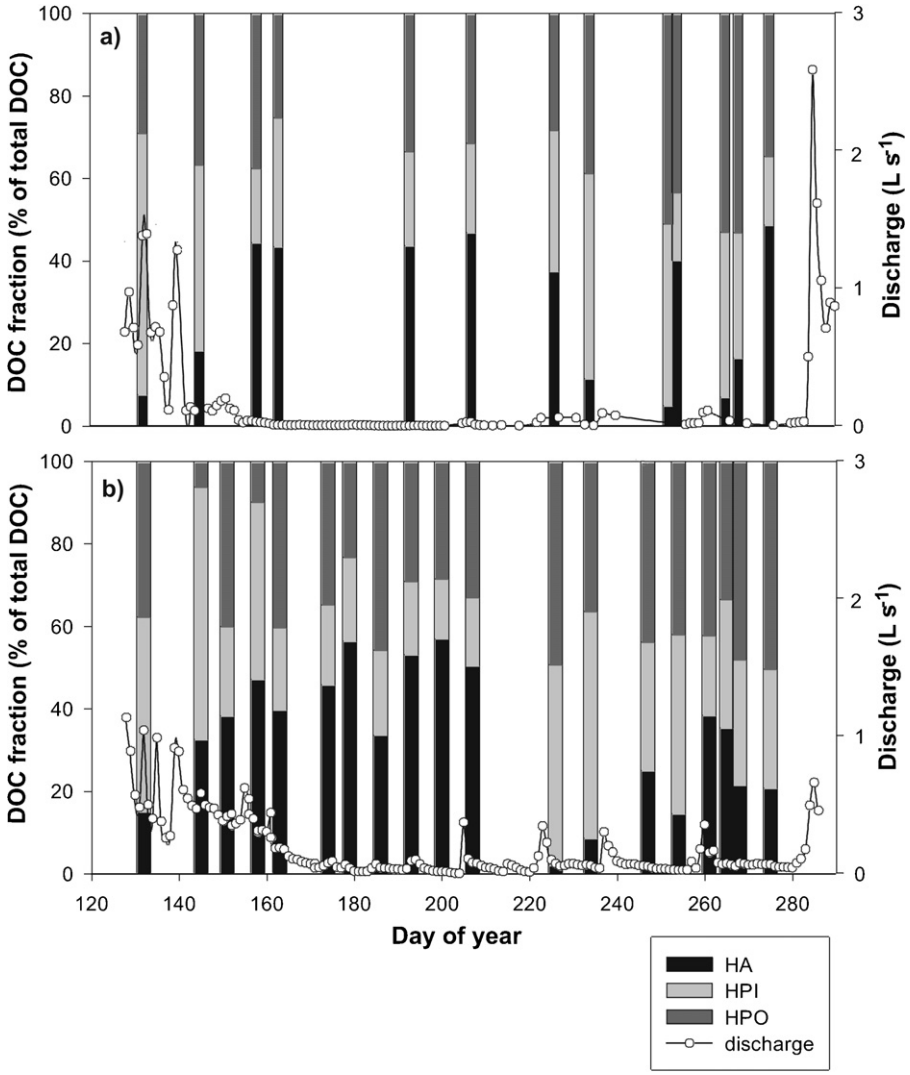

Fig. 4. Discharge and DOC fractions at the (a) cutover and (b) restored sites in 2000. Black, light grey, and dark grey bars refer to the HA, HPI, and HPO fractions, respectively.

of DOC while the largest component was the HPI fraction ranging between 56 and 60%, with HPO making up only 11–15%.

There was only a small change in DOC character released from shrub vegetation at 7 °C at day 8 and day 21 of the incubation (data not shown). The HA fraction decreased slightly (32–28%) while the HPO fraction increased from 11% to 14% and the HPI fraction remained essentially unchanged (56–57%). In contrast temporal DOC character changes were more pronounced at 22 °C as the HA fraction decreased from 36% to 24%, while both the HPI and HPO fractions increased from 56% to 60% and 8% to 16%, respectively.

Peat leachates were quite variable in their relative proportions of the three fractions and showed temperature dependence (Fig. 3). At 22 °C the HA fraction was a more important component of DOC (3–23%) but it was absent in some peat samples at 7 °C (10% for deep peat) (Fig. 3). The HPO fraction was a large component of DOC ranging from 36 to 96% of the DOC released and also showed temperature effects with more HPO at 7 °C compared to 22 °C. The HPI fraction was also substantial, ranging from 14 to 60% of DOC, with samples incubated at 7 °C having a lower percentage than samples incubated at 22 °C (Fig. 3).

A higher percentage of HPO and lower percentage of HPI were released from anoxic deep peats compared with oxic peats (Fig. 3). The HPO fraction increased by 9–15% at 7 °C, and by 21% at 22 °C; however, comparison could not be made at 22 °C at the restored site (data not available). The HPI fraction dropped from 33 to 28% at 7 °C and from 43 to 39% at 22 °C. HA was more readily produced by samples incubated under oxic than anoxic conditions. At 22 °C HA made up 21% of the DOC under oxic conditions while it was only 3% under anoxic conditions.

3.3. Seasonal DOC runoff quality

DOC concentration in discharge and total DOC export from this site were reported in Waddington et al. (2008). In summary, for the 2001 study season average DOC concentration in discharge was 76.9–121.0 and 58.5–149.3 mg L^{-1} with DOC export of 6.2 and 3.5 g C m^{-2} at the cutover and restored sites, respectively. The humic acid (HA) fraction of DOC in discharge ranged from 4.7 to 48.5% with a mean of 26.3 ± 18.3% at the cutover site (Fig. 4b). At the restored site, the HA fraction ranged from 1.9 to 56.7% with a mean of 33.2 ± 16.4% (Fig. 4b). DOC quality was not significantly different (Student's *t*-test; $p < 0.05$) between the two sites. Seasonal trends in HA were similar at the two sites with low proportions in the spring and fall when discharge was greatest and higher proportions in the summer months. At the restored site, on two occasions, HA was

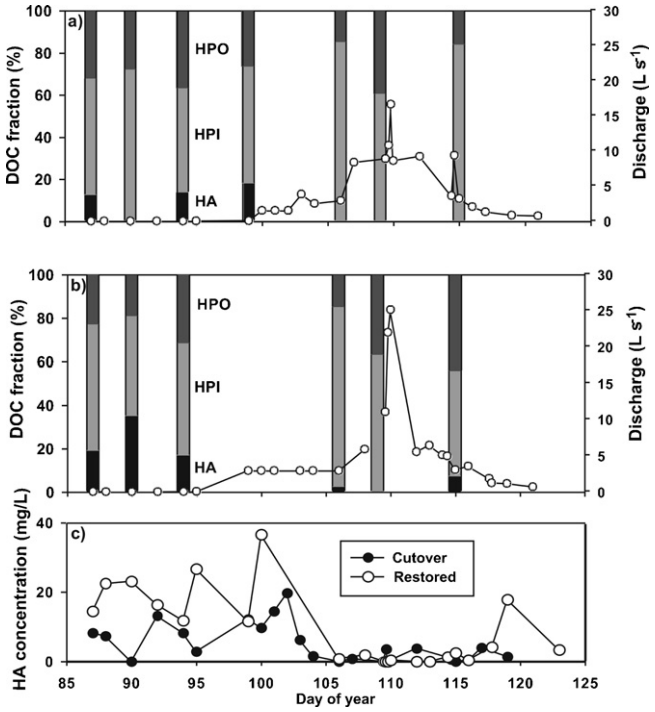

Fig. 5. Discharge and DOC fractions during the 2001 snowmelt period at the: (a) cutover and (b) restored sites. Discharge values are inserted as a reference. The main melt event took place between DOY 105 and 115. Black, light grey, and dark grey bars refer to the HA, HPI, and HPO fractions, respectively. Higher frequency HA concentrations are presented in panel (c).

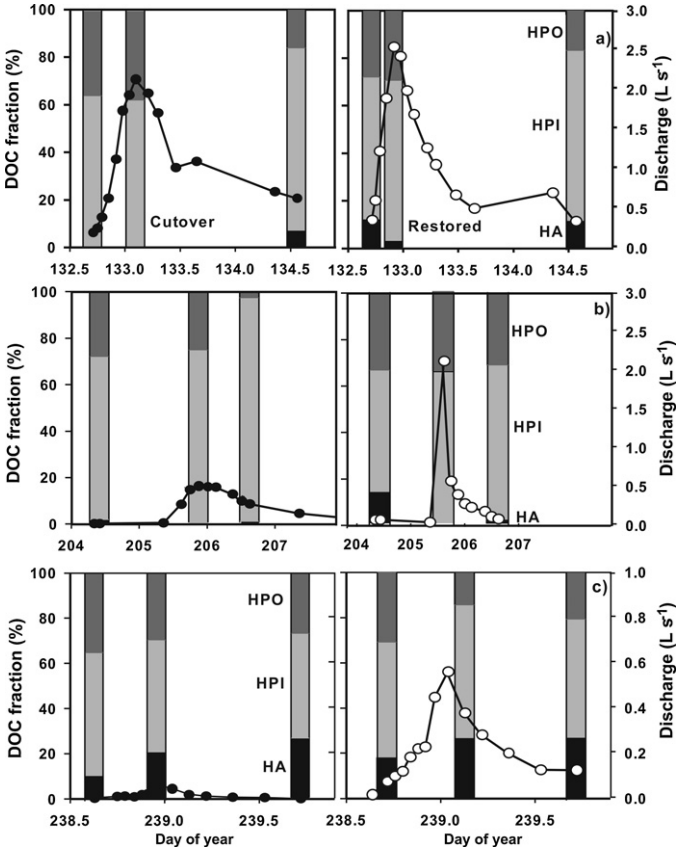

Fig. 6. Discharge and DOC fractions during three summer of 2001 storm events: (a) medium-intensity storm with wet antecedent conditions in May (DOY = 132–133), (b) high-intensity storm with dry antecedent conditions in July (DOY = 205), and (c) medium-intensity storm with dry antecedent conditions in August (DOY = 238–39). Note the difference in the scale for discharge on (c). Black, light grey, and dark grey bars refer to the HA, HPI, and HPO fractions, respectively.

lower during the summer and more characteristic of spring and fall values. This occurred following larger storm events in mid-August and early September.

The HPO fraction represented 38.0 ± 9.2% and 35.7 ± 12.1% of DOC at the cutover and restored sites, respectively (Fig. 4). There were two days when HPO fractions at the restored site were noticeably low (May 22nd and June 7th, DOY = 142 and 158), which coincided with storm events. Maximum proportions of this component were observed in the fall (53.4% and 50.6% at the cutover and restored sites, respectively). Lowest proportions (12.5% and 6.5% at the cutover and restored sites, respectively) occurred in the spring to early summer months.

The HPI fraction represented 35.7 ± 16.4% and 31.7 ± 14.4% of DOC at the cutover and restored sites respectively over the study season. Proportions were high in the spring when the maximum value was reached at the restored site (61.2%, Fig. 4b) and high in the fall when the maximum was reached at the cutover site (66.0%, Fig. 4a). This fraction decreased in the early summer period when the minimum values were observed at the cutover site (16.3%) and at the restored site (14.5%), followed by an increase in mid-August and early September (Fig. 4).

3.4. DOC runoff quality during snowmelt

Before snowmelt, discharge from the restored and cutover sites was low (~0.05 L s^{-1}) and discharge increased during the main snowmelt period in mid April (days 101–115) at both sites to a peak of 16.6 and 25.1 L s^{-1} (0.83 and 5.0 mm h^{-1}) at the cutover and restored sites, respectively (Fig. 5). The restored site returned to baseflow conditions faster than at the cutover site. Prior to snowmelt all three DOC fractions were present in the runoff at both sites (Fig. 5). At the restored site DOC was distributed more evenly among the three components while at the cutover site the HA fraction accounted for a smaller proportion. The HA fraction was larger prior to snowmelt with maximum concentrations of 36.6 and 19.7 mg L^{-1} making up 60 and 18% of the DOC at the restored and cutover sites, respectively (Fig. 5c). This fraction decreased to near zero values during the main melt event between DOY 101 and 115 and increased once again after the melt subsided. Of the other two fractions HPI was the more dominant component, representing maximum proportions of 88.8 and 71.4% of DOC during the melt event at the cutover and restored sites, respectively (Fig. 5). It remained high during the lag part of the melt at the cutover site and decreased to pre melt values at the restored site. The HPO component accounted for approximately 33% of the DOC prior to snowmelt at both sites. Once discharge increased, HPO reached maximum values at 39.4 and 31% of DOC at the cutover and restored sites, respectively (Fig. 5). Following snowmelt HPO decreased to 14% which coincided with another peak in discharge at the cutover site. In contrast, at the restored site HPO reached maximum proportions (44%) following the melt (Fig. 5b).

3.5. DOC runoff quality during stormflow

DOC quality was variable during storm events with all three fractions present prior to the event although HPI and HPO were generally more dominant than HA (Fig. 6). During peak discharge HPI comprised the highest proportion of DOC.

Discharge at the cutover site during the May storm increased from 0.18 to 2.12 L s^{-1} (0.86–10.2 mm d^{-1}) in 9.4 h while at the restored site discharge started off higher, increasing from 0.35 to 2.5 L s^{-1} (0.42–3.0 mm d^{-1}) in 4.8 h. The HPI fraction was the most dominant fraction during this event representing 60–70% of DOC. The HPI fraction increased slightly at the restored site but not at the cutover site during peak flow (Fig. 6a). Following the event HPI increased by 15 and 5% at the restored and cutover sites, respectively. The HPO fraction, which represented about 20–30% of the DOC, did not change during peak flow and decreased slightly during the lag part of the event (Fig. 6a) at both sites.

The July storm (DOY = 205) was a high-intensity thunderstorm (peak rainfall intensity of 18.1 mm in 30 min). This storm followed a ten-day period when the total precipitation was 8.9 mm. Discharge at the cutover site prior to the storm was low (0.006 L s^{-1}; 0.03 mm d^{-1}) and at the restored site it was ten times higher (0.05 L s^{-1}; 0.06 mm d^{-1}). Discharge increased quickly at the restored site reaching the peak of 2.5 L s^{-1} (3.0 mm d^{-1}) in 1.2 h while at the cutover site, peak discharge (0.57 L s^{-1}; 2.7 mm d^{-1}) was reached in 4.3 h. Prior to the storm the HA fraction at the cutover site was very low (Fig. 6b). HA was higher at the restored site and represented approximately 13–17% of DOC. During peak discharge this fraction decreased to zero at the restored site. It increased slightly following the storm at the cutover site and more significantly at the restored site. HPI was the dominant component at both sites representing 70–90% of DOC at the cutover site and 50–70% at the restored site. The largest increase in HPI fraction occurred at the cutover site during the lag part of the hydrograph when it reached 96.3% (Fig. 6b). The HPO fraction, representing approximately 30% of DOC, did not change significantly at the restored site during the July-storm but in contrast decreased to only 2.7% at the cutover site during the lag part of the storm (Fig. 6b).

The August storm event lasted 12 h during which time 22.6 mm of rain fell. Discharge at the cutover site increased from 0.002 to 0.06 L s^{-1} (0.01–0.30 mm d^{-1}) in 7.9 h (Fig. 6c). The restored site had higher discharge (0.01 L s^{-1}; 0.01 mm d^{-1}) before the storm, which increased to a peak of 0.56 L s^{-1} (0.67 mm d^{-1}) in 9.8 h (Fig. 6c). DOC quality patterns during this low-intensity storm were slightly different from the previous two storms. The HA fraction at the cutover site fluctuated between 10 and 30% of DOC during the event and did not decrease during peak discharge. At the restored site the range was similar except that it disappeared during peak discharge (data not shown) and then increased at the lag part of the hydrograph to greater values than before the storm event (Fig. 6c). Both HPI and HPO fractions remained in the same range at the cutover site during the entire storm while at the restored site the HPI fraction increased during the event.

4. Discussion

The quality of DOC released from soil will depend on not only the substrate type but also the conditions of temperature and physical and chemical characteristics of the soil in which it is produced and consumed (Kalbitz et al., 2000). Differences in quality of DOC exported following peatland restoration will result from both shifts in net DOC production, as controlled by changing substrate availability and chemistry, and shifts in hydrology, linked to ditch blocking and higher water table position. The nature of hydrologic events, such as snowmelt and storms, will also impact the quality of DOC exported given differences in mobility of the DOC fractions. The relative importance of these factors for interpreting the results is discussed below.

4.1. DOC production and quality

The release of DOC in incubation experiments represents the balance of production, desorption, adsorption and microbial utilization (Moore and Dalva, 2001). While microbial production and consumption of DOC will be temperature dependent, sorption will be independent of temperature (Kalbitz et al., 2000) and thus the effect of temperature on DOC production has varied between studies. For example, Gödde et al. (1996) and Moore and Dalva (2001) reported Q_{10} values of 1.5–2.0 and Christ and David (1996a) found a constant Q_{10} close to 2 was appropriate over a wide range of temperatures. In contrast, MacDonald et al. (1999) reported little change with incubation temperature. In the present study temperature was a significant explanatory variable for both initial and final net DOC production rates although the rate for individual substrates was not significantly different between the temperature treatments. Calculated Q_{10} values were similar to those previously reported.

Temperature had little effect on quality of DOC released from vegetation samples. In contrast warmer temperatures resulted in a larger proportion of HA and less HPO from peat samples. The observed shift in DOC fractions at different temperatures in peat is consistent with findings by Christ and David (1996a). In their study of spodosol leachates at different temperature and moisture conditions, HPO was found to be more abundant in samples incubated at lower temperature while HPI had higher concentrations at higher temperature. Microbial activity can certainly be the cause of this shift as at higher temperatures microbes are more active and can degrade large molecules like HPO to smaller ones such as HPI (Bourbonniere, 1989; Guggenberger et al., 1994). The presence of the more hydrophobic, higher molecular weight HA (Bourbonniere, 1989) indicates that either the dissolution of this component is enhanced by increased temperature or that it is formed from metabolites released in the degradation of the organic samples through oxidative polycondensation. The lack of HA produced at 7 °C under anaerobic conditions, and its appearance for cutover peat under aerobic conditions suggest that at least some is produced through oxidative polycondensation (Fig. 3). The effect of increased dissolution of HA was also evident in this study as a small amount was produced even under anaerobic conditions from samples incubated at 22 °C.

Christ and David (1996a) concluded that cool and wet conditions favouring anoxia would produce the highest amount of DOC. In contrast, as with Moore and Dalva (2001), no significant difference was found between initial release rate of DOC from samples incubated under oxic and anoxic conditions in the present study. It is likely that both DOC production and consumption increase under oxic conditions eliminating any effect on net DOC production. In contrast, we observed significantly higher rates of release under oxic conditions over the full 25 days of the incubation.

There were clear differences in the DOC net production rate and quality from different vegetation types. Shrub vegetation and to a lesser extent herbaceous vegetation showed an initial high net production of DOC followed by a decrease, suggesting a large pool of readily soluble DOC. Christ and David (1996b) determined that most DOC released initially is part of an adsorbed DOC reservoir that can be easily mobilized upon water addition. The decrease in DOC released by shrubs through time, once the initial pool of DOC was released suggests it was not produced quickly enough to offset DOC degradation. This suggests that DOC initially released from shrub material is highly labile and easily mobilised. DOC produced by both shrubs and herbaceous plants contained all three DOC fractions. It is likely that the HA produced by these substrates are "precursor" molecules as research by Gonet and Debska (1998) suggests that HA extracted from fresh material differs from the

traditionally accepted character of HA. The shift in shrub leachate towards lower HA and higher HPI and HPO fractions over time indicates degradation of this precursor HA component. Christ and David (1996a,b) observed a similar trend towards lower HPO and HA with increasing incubation time in spodosol leachates.

Moss samples produced the least DOC of all substrates investigated in this study and the initial release rates (101–133 $\mu g\,DOC\,g^{-1}\,d^{-1}$) were similar to those reported by Moore and Dalva (2001) (100 $\mu g\,DOC\,g^{-1}\,d^{-1}$). Mosses released all three fractions of DOC but the amount of HA was minimal and attributed to microbial action and the formation of HA from polycondensation. The high proportion of HPI in DOC released from moss is consistent with the findings of Wickland et al. (2007) who reported that HPI accounted for 73 and 48% of DOC produced by *Sphagnum* and feathermosses, respectively.

All peat samples collected in this experiment (shallow and deep) were formerly pre-cutover anoxic (catotelm) peat samples that have been exposed to aeration and an increase in bulk density; however, DOC net production rates calculated in this experiment (34–94 $\mu g\,DOC\,g^{-1}\,d^{-1}$) correspond well with those reported by Moore and Dalva (2001) for hemic peat (25–41 $\mu g\,DOC\,g^{-1}\,d^{-1}$). Moreover, the effect of temperature on the release of DOC from peat is consistent with the observations of Moore and Dalva (2001). No direct conclusion can be made on whether the controlling factor in this release is physical leaching or microbial degradation. However, more DOC was produced over the 25-day period by peat at the restored site compared to the cutover site (Fig. 2) and there are clearly biochemical and physical differences between these two sites. For example, Andersen et al. (2006) found higher microbial biomass carbon and nitrogen in surface peats at the restored site. Alternatively, the restoration measures, including the mechanical tilling of the peat layer to level the surface at the restored site, may have exposed "fresher" peat layers compared to the cutover site, thus providing a better source for DOC production. Productivity of new vegetation at the restored site probably also provides a source of DOC to the near surface peat (e.g. Trinder et al., 2008) that was rapidly leached upon wetting. Shallow restored peat produced more HA than shallow cutover peat (Fig. 3) and given the importance of HA in DOC produced by shrub and herbaceous substrate, this could indicate the input of new substrate at the restored site.

Straw was utilized to improve the physical conditions for *Sphagnum* re-growth at the restored site. Based on our study and the fact that there is about 300 $g\,m^{-2}$ of mulch spread over the peatland (Petrone et al., 2001) and using our net production results from the incubation study, the potential for DOC production under ideal conditions over one growing season (May–October) would be approximately 3.3 $g\,DOC\,m^{-2}$. This indicates a large potential DOC source at the Bois-des-Bel peatland, approximately equivalent to the total DOC export calculated for the restored site (Waddington et al., 2008), and will dominate the initial export of DOC from restored peatlands. DOC produced from incubated straw had a high HPI content, indicating that it is readily decomposable. Moreover, high proportions of HPI in exported DOC could indicate an influence of straw on DOC export following restoration.

4.2. DOC runoff quality – impact of restoration

There are limited studies of DOC quality in peatland export, particularly under different disturbance and restoration regimes. However, the quality of DOC exported from sites is important because the molecules that comprise DOC have different chemical characters and can affect natural water system processes to varying extents. Based on results of DOC quality produced by substrate incubation, increasing moss cover and straw application at the restored site could result in shifts in DOC exported towards higher HPI content. Although both sites have herbaceous plants and shrubs present, the coverage of these also increased following restoration (Waddington et al., 2010) and this could increase the importance of HA in exported DOC.

We found no significant difference in DOC quality between the restored and the cutover sites. Similarly, Glatzel et al. (2003) did not find a difference in DOC quality exported from cutover and restored peatlands. Given the differences in DOC quality produced by the variety of substrates available at the restored site, it may be that the averaging of these components leads to no substantial change in the quality of DOC exported. Also, as vegetation cover and productivity are still developing at these initial stages of restoration (e.g. Waddington et al., 2010), the influence of these new substrates may remain minimal compared to the large volume of residual peat. We hypothesize that the character of DOC exported from the restored site will change over time as a new vegetation layer develops. The cutover site, on the other hand, will probably not change but will remain an active source of DOC since the vegetation growing on it promotes water table draw-down helping to maintain aeration of the peat (Van Seters and Price, 2001).

Another possible explanation for the lack of difference between the restored and cutover sites is that hydrologic controls on the export of the various fractions are more important than the relative availability of each fraction.

4.3. Hydrological controls on DOC export quality

Strong seasonality was observed in HPI and HA fractions, while the HPO fraction did not change significantly (Fig. 4). A strong hydrological control was evident with periods of high flow characterised by lower HA and higher HPI, and low flow by higher HA and lower HPI. The nature of these fractions can explain this relationship. HA is the most hydrophobic portion of DOC and contains large molecules that are highly oxidized with a strong aromatic character (Bourbonniere, 1979). Due to these properties, this fraction is difficult to dissolve into the aqueous phase, particularly at the pH normally found in peatlands. Using sand-peat columns Stutter et al. (2007) investigated DOC release mechanisms and suggest that its release is diffusion limited with longer water–soil contact time required for larger molecules to be released. Therefore, in systems where water passes through the matrix quickly, very little HA will be able to enter the solution, while during stagnant periods increased amounts can be mobilized. In contrast, HPI has a low molecular weight, readily dissolves in water and thus can be easily mobilized, even when water moves quickly through the peat matrix. Christ and David (1996a) found that this fraction was increasingly mobilized during frequent rewetting. Consequently, the seasonal trend in these fractions during the transition from spring to fall can be explained by the increased flushing of the HPI fraction during high flow periods. HA is subsequently released during the summer when the HPI pool is depleted; however, the input of HPI continues in the summer, due to increased microbial activity, and HPI is flushed again during high-intensity storm events and high flow periods in the autumn. This is consistent with the observation of Evans et al. (2007) that baseflow releases old, soil derived DOC while high flow periods release younger DOC likely derived from recent plant matter. Moreover, deep water table position in summer suggests that water flow will be through deeper, older peat that is likely to supply more HA than shallower layers.

Hydrological control of DOC quality was apparent during most events, but the low-intensity August storm revealed a different pattern as DOC quality changed little during the event (Fig. 6c). While earlier storms rapidly flushed water from the site, the August storm was low-intensity and lasted longer increasing the infiltration of water into the peat matrix making the connection of different DOC

pools possible and enhancing movement of the less mobile HA and HPO fractions.

4.4. Biogeochemical controls on DOC quality

While hydrological controls appear to be the most important control on DOC quality during events, seasonal shifts in baseflow DOC chemistry suggest that biogeochemical controls may also be important. The HPI fraction is a dominant component in all samples and becomes even more prevalent during the high flow period of the snowmelt. This result is consistent with other studies (Kaiser et al., 2001, 2002; Urban et al., 1989), which found this component to be a large proportion in winter and spring soil samples. Kaiser et al. (2002) suggested that this fraction contained labile carbohydrates that were not degraded by microbes during the winter. Furthermore, Kaiser et al. (2001) suggested that winter production of this fraction is also the result of the disruption of microbial and plant cells due to freezing and thawing.

Although HPI was found to account for a larger proportion of DOC during summer months in some peatlands (Bourbonniere, 1989; Scott et al., 1998) others have observed an increase in HPO and humic substances during the summer in peatlands and forests (Kaiser et al., 2001; Sachse et al., 2001) likely due to higher microbial activity resulting in polymerization (Urban et al., 1989). Fenner et al. (2001) reported an enrichment of low to mid molecular weight DOC in the spring and fall and a sharp decrease in summer, while Höll et al. (2009) observed an increase in the humification index of peatland DOC during summer. DOC fractions at the restored and cutover sites are more consistent with these latter studies with increases in the proportion of HA and HPO in summer months.

The increase in HA and HPO during the summer supports the two general theories on the formation of the HA fraction: (1) release from plants through successive microbial degradation and (2) building up from smaller components through polycondensation. The changes that are mirrored between HA and HPI suggest a transformation of HPI fraction to HA. This is further supported by the warm, dry conditions that exist during the summer period producing an environment where oxidative polycondensation, a process that can produce HA, is favoured. Additionally, during incubations of peat under a range of temperatures Fenner et al. (2005) found a positive correlation between phenol oxidase activity and concentrations of phenolic compounds. They suggested that at higher temperatures the phenolic substances were being cleaved from the peat faster than they could be consumed by the microbial community and a similar mechanism could be at play for the HA fraction in the current study. Finally, higher summertime HA concentrations may also be linked to leaching from vegetation. Since the incubation study found HA to be an important component of leachate from both shrubs and herbaceous vegetation and these are only present during the summer months, shifts in discharge DOC quality are likely linked to the growth of these vegetation types on the site.

5. Summary and conclusions

The net DOC production experiment indicated that there is a large potential for all vegetative components to release DOC at both the cutover and restored sites. On a short time scale herbaceous and shrub vegetation exhibited greatest net DOC production with highest net production on a longer time scale by peat which is found in much larger quantities compared to the other substrate and thus could persistently produce DOC.

Fractionation of DOC produced by the different vegetation samples indicates that all components have the potential to release the three fractions of DOC studied in this experiment. At cooler temperatures HA is more likely to be produced by shrub and herbaceous plant material than by peat, moss and straw. In contrast, at this cooler temperature peat samples are more likely to produce HPO while straw and mosses produce about the same proportion of both HPO and HPI. At warmer temperatures the HPI fraction increases in importance while the HPO fraction decreases possibly due to an increased importance of microbial activity. Finally, oxic conditions were found to result in a larger HA fraction compared with anoxic conditions.

The Bois-des-Bel peatland was restored with the aim of improving the hydrological and biogeochemical conditions that would favour the reestablishment of *Sphagnum* species. While there was an improvement in the hydrological conditions at the site and moss and vascular plant cover have increased in abundance, DOC quality in runoff was not significantly affected. This limited effect could result from an averaging of the chemistry of the DOC produced by the variety of substrates available at the restored site and could change as the emerging vegetation develops and increases in productivity. Quality of the DOC in discharge varied both during hydrological events (snowmelt and storms) and seasonally indicating the importance of both hydrological and biogeochemical controls on the quality of exported DOC. Rapid flushing of water through the peatland favoured the export of HPI over HA. An increase in the fraction of DOC as HA in midsummer suggests the importance of polycondensation and vascular plant productivity on DOC quality.

As the vegetation community on the restored site continues to develop with an associated increase in productivity and the accumulation of litter as new peat, hydrologic pathways and DOC production and export may also be altered. Continued study is required to understand the trajectory of DOC dynamics with time following peatland ecosystem restoration. As an important part of the ecosystem carbon balance and because of its important effects on downstream ecosystems, DOC production rates, export and DOC quality should be considered when developing peatland management plans and monitoring restoration success.

Acknowledgements

This research was supported by a NSERC-CRD grant to JMW and the Peatland Ecology Research Group. We would like to thank Sarah Day and Jamee DeSimone for field and lab assistance and Yoseph Zuback for producing the site map. Comments on an earlier draft by Alona Armstrong, Evan Kane, Merritt Turetsky, Tim Moore and an anonymous reviewer are greatly appreciated.

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