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Hydrology and dissolved organic carbon biogeochemistry in an ombrotrophic bog

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Abstract:

At the Mer Bleue bog, Ontario, Canada, DOC export measured at the basin outflow was $-8\cdot3 \pm 3\cdot7$ g C m^{-2} yr^{-1}, and DOC loading via precipitation was estimated to be $1\cdot5 \pm 0\cdot7$ g C m^{-2} yr^{-1}. Discharge and DOC export calculated using a Dupuit–Forchheimer approximation compared well (within 1 g C m^{-2} yr^{-1}) to outflow estimates of DOC export, and confirmed that outflow measurements were a suitable proxy for DOC seepage at the peatland margins. DOC export was 12% of the magnitude of the residual carbon sink measured at the peatland. The [DOC] across groundwater transects decreased with depth, and [DOC] sampled below 0·75 m depths remained fairly constant over the study period. However, [DOC] exported through the acrotelm (0 to 0·45 m peat depth) was variable, ranging from 40 mg l^{-1} after snowmelt to 70 mg l^{-1} during the growing season. Fluorescence analysis revealed that exported DOC was 'allochthonous-like', whereas DOC in the catotelm (deeper layers of peat) became more 'autochthonous-like' with depth. A conceptual model is developed to summarize the hydrological processes and controls which affect DOC biogeochemistry at the Mer Bleue.

KEY WORDS DOC; peatlands; carbon budgets; groundwater; flowpath

INTRODUCTION

Best estimates of global carbon (C) fluxes suggest that contemporary changes in land-use and fossil fuel emissions are sources of atmospheric C, whereas the biosphere and oceans are net sinks (Schimel, 1995). However, the balance of the global C budget is dependent upon a northern hemisphere terrestrial sink 1–3 Gt C yr^{-1} (Tans *et al.*, 1990; Siegenthaler and Sarmiento, 1993; Ciais *et al.*, 1995). Preliminary studies have shown that C-cycling in northern ecosystems is transient and poorly understood, and have suggested that increased C sequestration in northern ecosystems could be a function of nitrogen (N) deposition (Schimel *et al.*, 1996; Schindler and Bayley, 1993); carbon dioxide (CO_2) fertilization (McGuire *et al.*, 1997); and climate variability (Dai and Fung, 1993; Schimel *et al.*, 1996; Randerson *et al.*, 1997). Ecosystem scale measurements of C fluxes are needed to determine the rates and controls on contemporary C sequestration. In this paper we examine the role of hydrology as a control on dissolved organic carbon (DOC) biogeochemistry in a northern peatland.

The saturated and anoxic conditions found in peatlands give slow decomposition rates and lead to substantial C storage. Gorham (1991) estimated this C reservoir to be 455 Gt, or one-third of the global soil C store (Schimel, 1995). Paleoreconstructions show long-term C accumulation rates in peatlands are $\sim$20–30 g C m^{-2} yr^{-1} or globally $\sim$0·076–0·096 Gt C yr^{-1} (Clymo, 1984; Gorham, 1991), corresponding to $\sim$10% of the missing terrestrial C sink (Gorham, 1995). Annual C sequestration is the difference between C uptake (gross production) and C losses through root respiration, soil respiration, CH_4 emission and DOC export.

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Table I. Summary of DOC export and runoff measurements from wetland and forested-wetland catchments in the literature

Study	Type of catchments location	Run off (mm)	Export (g C m^{-2} yr^{-1})
Mulholland (1981)	Creeping Swamp, North Caroline, USA	485[a]	21
Naiman (1982)	boreal forest, Septlles, Quebec, CAN	570–1640[b]	2·5–48·4
McKnight *et al.* (1985)	Thoreau's Bog, Massachusetts, USA	240	8·4
Moore (1987)	subarctic peatland, Schefferville, Quebec, CAN	302–389	1·1–1·9
Collier *et al*(1989)	Three wetlands, Westland, NZ	1120–1104	28·7–37·8
Moore (1989)	Forested Westland, NZ	137–1755	8–21
Moore and Jackson (1989)	Forested Larry River, NZ	1023–1253	30·6–43·8
Urban *et al.*(1989)	Peatlands, Minnesota, USA and Kenors, Orsario, CAN	224–1410	3–4
Koprivnjak and Moore (1992)	Subarctic fen, Schefferville, Quebec, CAN	111[c]	1·2
Gorham (1995)	'Typical' northern peatland	N/A	20
Carroll Crill (1997)	Salliès fen, Barrington, New Hampshire, USA	1071[d]	3·4
Scott *et al.* (1998)	Upland peat complex, North Penninex, UK	798–1799[d]	7–15
Elder *et al.* (2000)	Allequash Creek basin, north-central Wisconsin, USA	170–390	<26

[a] Runoff was estimated to be −37%of annual precipitation (1310 mm) in this study.

[b] Runoff estimates were calculated from reported mean annual estimates of discharge and basin area estimates.

[c] Runoff and export estimates are for a three-month study period.

[d] Estimates of runoff were not reported in these studies, therefore annual precipitation was cited.

The chemistry of humic substances is complex, therefore DOC has been the focus of studies for several reasons. For example, DOC influences the cycling of heavy metals (Thurman, 1985; Malcolm, 1993); minimizes UV-B penetration in lakes (Schindler and Curtis, 1997; Williamson *et al.*, 1996); and affects water quality and acidity transport (Urban *et al.*, 1989; Huber *et al.*, 1994). DOC also affects the C budgets of peatlands (Table I). Estimates of DOC export range from 1 to 48 g C m^{-2} yr^{-1}, and Gorham (1995) estimated that DOC export from a 'typical' northern peatland is approximately equal to the long-term sink term (20 to 30 g C m^{-2} yr^{-1}).

Some of the export values (Table I) are large (e.g. Naiman, 1982; Urban *et al.*, 1989), but the export varies with catchment properties and hydrogeologic setting. Large export terms ($>$20 g C m^{-2} yr^{-1}) are a function of high water yields that result from precipitation$\gg$evapotranspiration (e.g. Moore, 1989; Collier *et al.*, 1989); or upland$\gg$wetland area (Naiman, 1982; Urban *et al.*, 1989) such that annual runoff is $>$500 mm yr^{-1}. In contrast, DOC export terms are smaller when the catchment is dominated by peatland, relief is negligible, and/or $P \cong ET$ (i.e. runoff $<$ 250 mm yr^{-1}). In such hydrogeologic settings, export terms similar to McKnight *et al.* (1985), Moore (1987) and Koprivnjak and Moore (1992) are plausible ($<$10 g C m^{-2} yr^{-1}).

Here, we report on the hydrology and DOC biogeochemistry of the Mer Bleue bog, a large (25 km^2) northern peatland, near Ottawa, Ontario, Canada. Our objectives were to: (1) quantify the net exchange of DOC from a subcatchment of the Mer Bleue and compare the magnitude of the DOC source/sink to the measured trace gas source/sink; (2) compare the magnitude of DOC exported at the catchment outflow to seepage flux of DOC at the peatland margins; and (3) describe the hydrobiogeochemical linkages which control *in situ* DOC concentrations and DOC export at the Mer Bleue. We hypothesized, based on the hydrologic processes observed at the Mer Bleue, that the DOC export should be of a similar magnitude as that of other large arctic and subarctic peat complexes—e.g. $\sim$10 g C m^{-2} yr^{-1}. Since Mer Bleue dominated the catchment and it has an easily measured outflow, unusual for most peatland, we compared the DOC export measured at the outflow and DOC losses estimated by seepage calculations and DOC concentration in the peatland itself. It is often implicitly hypothesized out of necessity that measures of internal flow and DOC concentrations are 'representative' of DOC loss at the outflow, or that the net loss of DOC measured at a basin outflow that has a peatland present is 'representative' of peatland DOC loss (e.g. Moore, 1987; Urban *et al.*, 1989; Waddington and Roulet, 1997). We also hypothesized that DOC quality measured in the peatland and at the outflow is a function of the residence time of water in the peatland. A test of this is to compare DOC quality *in situ*, with runoff volume and position of the water table generating the runoff. Finally, we hypothesized that the annual DOC export is large enough to be considered in the quantification of the net annual sink or source of carbon in a peatland.

STUDY SITE

The north-draining basin (4·8 km^2) of the Mer Bleue bog complex (45° 30′ N and 75° 25′ W) was instrumented for this study (Figure 1). The basin is characterized by several raised peat domes, and the major hydraulic gradients controlling groundwater seepage from the peatland are oriented north–south along the length of the drainage basin. Ground and surface water leaving the peatland enters a continuous network of beaver ponds along the perimeter of the peatland, and exits the bog complex through a single outflow at the western extent of the drainage basin (east–west gradient $\sim$0·0008). Upland and hillslope contributing areas contain Dystric and Eutric Brunisols, and have negligible area because they are well drained away from the peatland by networks of ditches. The peatland is underlain by continuous, marine clay deposits that range in thickness from 12 to 45 m (Hobson, 1969; Belanger and Harrison, 1977). K_h estimates of the underlying marine clay were $\ll 10^{-10}$ m s^{-1} ($n = 4$), and head measurements were higher in the peatland than in the clay. Since the marine deposits are continuous and thick, hydraulic gradients are from the peat to clay, and the K_h of the marine clay is very small, the flux of water into the peatland from the underlying aquiclude was assumed to be zero. For further details on deeper groundwater flow patterns and the geochemistry of the Mer Bleue area see Fraser *et al.* (2001).

The climate of Mer Bleue is classified as cold humid continental, and mean annual temperature, mean annual precipitation and growing season length recorded at a nearby weather station are 5·8 °, 910 mm and 193 days, respectively (Environment Canada, 1998). Dominant species on the bog are mosses (*Sphagnum magellanicum* and *Sphagnum rubellum*), and shrub and graminoid species such as labrador tea (*Ledum groenlandicum*), leatherleaf (*Chamaedaphne calyculata*), blueberry (*Vaccinium myrtilloides*), cotton grass (*Eriophorum spp.*)

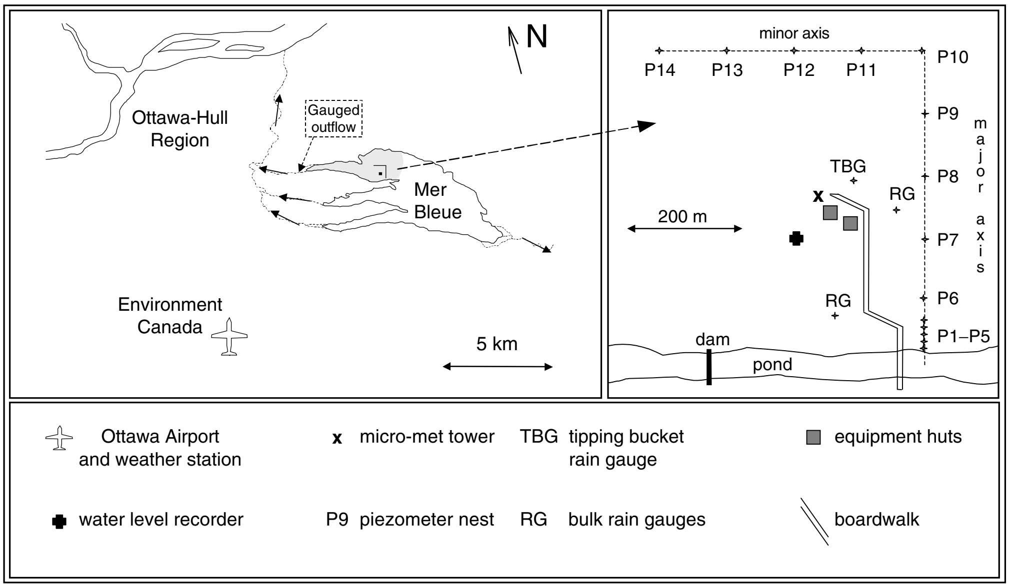

Figure 1. Map (left) of the Mer Bleue showing proximity to Ottawa, Ontario, Canada, the direction of surface water flow from the peatland and the location of the gauged outflow used in this study. A schematic showing field instrumentation is at the right of the figure

and sedge (*Carex oligosperma*) dominate the lower canopy. The canopy species are black spruce (*Picea mariana*), tamarack (*Larix laricina*) and grey birch (*Betula populifolia*).

METHODS

Hydrology

Runoff (R), evapotranspiration (ET) and precipitation (P) were measured over the hydrological year ending May 22, 1999. Stream velocities were gauged at the basin outflow and runoff estimates were determined from rating curves and basin contributing area. ET was estimated from continuous eddy covariance measurements of the latent heat flux (Q_E) (P. Lafleur, personal communication). Rainfall measurements from two bulk gauges a tipping bucket rain gauge and detailed rainfall data from a nearby Environment Canada weather station (Figure 1) were used to estimate total rainfall at the Mer Bleue bog. Snowfall was measured using a snow gauge equipped with a Nipher shield, and snow water equivalent (SWE), snow depth and snow density estimates were completed over a snow course.

Piezometers and wells were inserted across the major and minor axes of the peat dome (see Figure 1). Piezometers were constructed from 1·25 cm ID SCH 80 PVC pipe, coupled to 20 cm long slotted heads, and sheathed with 40 μm Nitex mesh. Manual observation wells were constructed from 5 cm ID PVC pipe (nests P6–P14, Figure 1). A well situated near the micrometeorological tower, and wells at nests P1–P5 were constructed from 15 cm ID PVC pipe and instrumented with water level recorders. Four drive-point piezometers were inserted to the underlying marine clay to sample interstitial pore waters and assess groundwater exchange across the base of the peatland. The drive-point apparatus consisted of 30 cm Waterloo drive-point heads with 180 μm shields, clean sampling tube and 2 cm ID galvanized pipe.

Piezometer elevation and peatland topography were measured. A steeper gradient ~0·03 was found at the bog margin near the beaver pond, whereas a lesser gradient ~0·001 extended from nest P3 to the topographic maxima ~450 m away. Horizontal and mean hydraulic conductivities (K_h and K_m) at nests were calculated from bail tests after Hvorslev (1951). Mean hydraulic conductivities (K_m) were calculated at two nests from piezometers constructed without slotted heads. Vertical hydraulic conductivities were calculated from:

$$K_m = \sqrt{(K_h \times K_v)} \tag{1}$$

after Freeze and Cherry (1979).

Sampling and chemical analyses

Surface water from beaver ponds and the basin outflow were sampled weekly over the study period. Head and chemistry measurements were made bimonthly across the groundwater network for the ice-free season. A peristaltic pump was used to bail and obtain peat pore water samples. Some of the recharged water was pumped to clean Nalgene bottles for DOC analysis. A precipitation collector (Nitex covered) was used to sample DOC in snow and rainfall. All DOC samples were filtered with 0·45 μm membrane filters and analysed shortly thereafter.

DOC measurements were made using a Shimadzu 5050 Total Organic Carbon analyser. DOC samples were acidified with 2 N HCl to pH 2 and sparged by an N_2 carrier gas to remove dissolved inorganic carbon prior to measurement. Samples were then combusted at 680 °C to produce CO_2 gas which was measured by an infrared gas analyser. Averages of six injections per sample were made, or extra injections were performed by default until the coefficients of variance were less than 1%.

Fluorescence scans of 70 water samples were measured with a Shimadzu RF-1501 scanning spectrofluorometer, and used to determine differences in DOC quality of source waters (precipitation, deep groundwater, surface water) across the basin. Excitation radiation was fixed at 370 nm and scans were performed from 370 to 650 nm. Variations in spectral intensity were corrected for with scans of standard 1 μg l^{-1} quinine sulphate solution in 0·1 N H_2SO_4 (Donahue *et al.*, 1998). Scans of sample blanks (distilled deionized water) were used to find and remove scattering by subtracting the blank fluorescence values from the emission scans, and the ratio of 450 : 500 nm wavelength emission intensity was calculated. Low magnitude quotients ($\sim$1·4) typify terrestrially-derived allochthonous organic carbon, whereas high quotients ($\sim$1·9) typify microbially-derived autochthonous organic matter (McKnight *et al.*, in press). Allochthonous-like DOC has also been reported to have an enhanced ability to absorb visible and ultraviolet radiation, compared to autochthonous-like DOC (Donahue *et al.*, 1998).

Error analysis

Discharge error was determined from the standard errors of rating curves, such that minimum and maximum daily discharges were calculated using stages that ranged ±0·0041 m, ±0·021 m and ±0·020 m about the best-fit curve for ice-free, winter and spring melt rating curves, respectively. A GPS survey of the Mer Bleue area allowed for accurate delineation of the subcatchment. Therefore, a ±5% error in drainage basin area was used in runoff calculations. Total precipitation from the Mer Bleue and an Environment Canada weather station (Ottawa International Airport) were within 16%. Instrument errors (<5%) were determined after Winter (1981), and errors associated with networked weather stations (5–10%) were determined after Winter (1981) and Dingman (1994). Since errors from obstructions, occult precipitation and low intensity rain were believed to be minimal at the Mer Bleue, we believed it was appropriate to ascribe a ±15% uncertainty to our annual measurements of P. The error associated with the micrometeorological and eddy covariance measurement of ET ranges from 10 to 20%.

Coefficients of variance of DOC measurements were low (<1·0%), therefore we had confidence in our analytical measurements. However, we were limited by the number of outflow DOC measurements ($n = 40$), and curve fitting was required to obtain daily estimates of DOC concentration. Uncertainty in daily [DOC] values was determined using minimum and maximum estimates of [DOC] for 14-day periods over the hydrological year. Minimum and maximum [DOC] were then multiplied by minimum and maximum daily water yields to obtain an error estimate of DOC load. Error attributed to DOC loading via precipitation was calculated using minimum and maximum estimates of precipitation and [DOC] ranging from 1 to 3 mg l^{-1} (Thurman, 1985; Dalva and Moore, 1991; Neal and Hill, 1994).

RESULTS

Macroscale hydrology and biogeochemistry

The water balance and runoff record for the Mer Bleue are shown in Figure 2. Annual P, ET and R were 757, 598 and 222 mm respectively, yielding a residual (ΔS) of −63 mm (Figure 2a). Agreement between peatland water table position and ΔS from start to completion of the study gave confidence in P, ET and R measurements. ΔS also agreed with SWE measurements made during winter months.

The runoff record was dominated by snowmelt runoff (84 mm; March 16 to April 20, 1999), and by a mid-winter melt (34 mm; January 7 to February 19, 1999). The two melt events accounted for 53% of runoff measured over the hydrological year (Figure 2b). A summer runoff peak (June 14 to July 19, 1998) coincided with unusually high P compared to 52-year normals from the Ottawa International Airport (Environment Canada, 1998). We estimate that measured P was 179 mm, whereas ‘normal’ P is 90–100 mm for this time period. Drought from July 19 to August 23, 1998 depleted basin storage and runoff was negligible at that time ($P = 46$ mm; $ET = 92$ mm).

DOC concentrations were lowest during spring melt when groundwater from the peatland and beaver ponds mixed with melting snow ([DOC] $\sim$ 1–4 mg l^{-1}) to yield [DOC] $\sim$ 20–23 mg l^{-1} (Figure 2b). Highest [DOC] were observed mid-June and December 1998, and ranged from 55 to 60 mg l^{-1}. There was a relationship ($p < 0.001$) between [DOC] and basin runoff over the hydrological year (Figure 3), but the

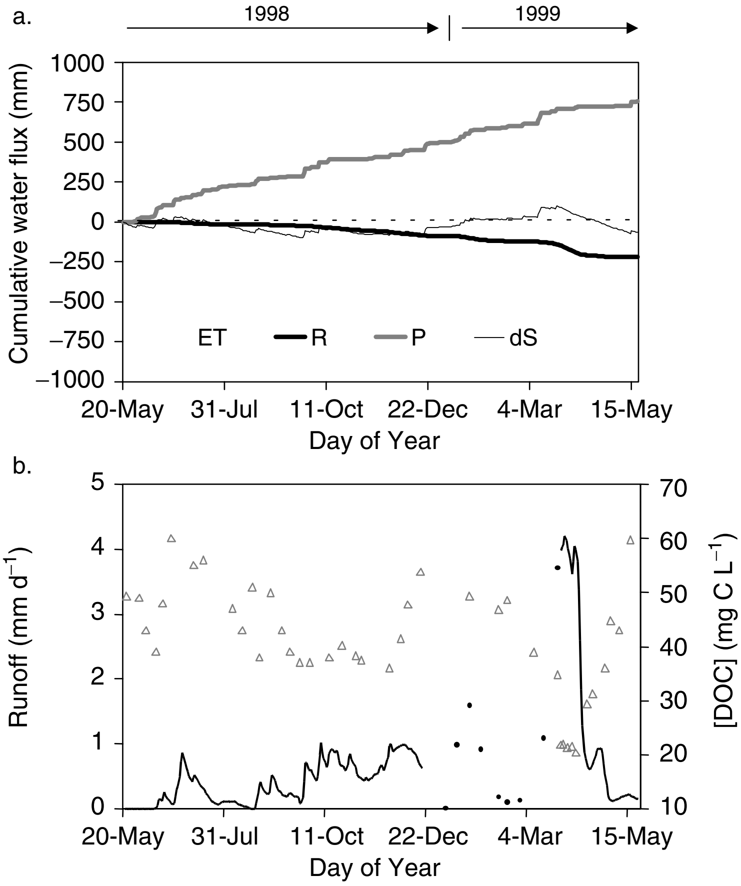

Figure 2. (a) Components of the water balance measured at the Mer Bleue bog. ΔS is the residual of the measured components where $\Delta S = P - ET - R$. Water fluxes (P, ET and R) are cumulative fluxes in mm. (b) Runoff and DOC concentrations measured at the basin outflow. DOC concentrations are denoted by triangles (mg l^{-1}), whereas the black line and black filled circles denote continuous and point measurements of runoff respectively (mm day^{-1})

relationship was solely controlled by snowmelt 1999 outliers. There was no [DOC] : runoff relationship after removing these outliers. Mean annual flow-weighted [DOC] was 37 ± 5 mg l^{-1}. Snow and rain samples were collected and analysed for [DOC] on five occasions (mean [DOC] = 2·8 mg l^{-1}; SD = 1·33 mg l^{-1}), and agreed with [DOC] ranges (1 to 3 mg L^{-1}) reported by Thurman (1985), Dalva and Moore (1991) and Neal and Hill (1994).

Seasonal and annual hydrochemical fluxes and errors are reported in Table II, where loadings and exports of water and DOC are reported as positive and negative fluxes respectively. Final estimates of DOC export and loading were $-8{\cdot}3 \pm 3{\cdot}7$ g C m^{-2} yr^{-1} and $1{\cdot}5 \pm 1{\cdot}1$ g C m^{-2} yr^{-1} (Table IIb), thus the net DOC loss was $-6{\cdot}8 \pm 4{\cdot}8$ g C m^{-2} yr^{-1}. DOC loading via precipitation ($\sim$0·4 g C m^{-2}) was constant over the year, owing to an even distribution of annual precipitation between seasons. Although runoff was greatest in the spring (90 mm), DOC export was greatest during the summer (2·6 g C m^{-2}).

Hydrology and DOC at the peatland margin

The beaver ponds at the margins of the subcatchment store $\sim$5–10 mm of water (pond storage prorated to peatland area). Since $>$50% of annual runoff (118 mm of 222 mm yr^{-1}) was measured during melt events, the ponds were flushed $\sim$10 times during this time. With frequent pond flushing, we were confident that

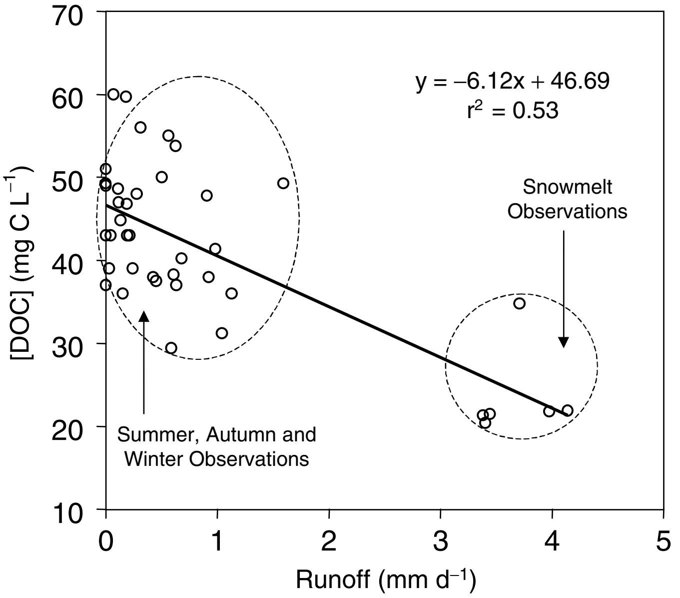

Figure 3. Regression of [DOC] and runoff for 40 observations over the hydrological year ($r^2 = 0.53$; $F = 42.81$; $p < 0.001$). The relationship is significant, but controlled by snowmelt 1999 outliers. After removal of snowmelt observations, the relationship between [DOC] and runoff was not significant ($r^2 = 0.03$; $F = 0.78$; $p = 0.385$)

Table II. (a) Water balance error analysis for the Mer Bleue bog. Inputs are reported as positive fluxes, and outputs are reported as negative fluxes. (b) DOC balance error analysis where inputs are reported as positive fluxes and exports are reported as negative fluxes

(a)	Season	P (mm)	R (mm)	ET (mm)	Storage change (mm)
	Spring	170 ± 26	−89·5 ± 27	−217 ± 33	−136·5 ± 81·5
	Summer	184 ± 28	−22·5 ± 6·6	−271 ± 41	−109·5 ± 74·5
	Autumn	189 ± 28	−62 ± 9·6	−81 ± 12	46 ± 46·5
	Winter	214 ± 32	−48 ± 29·4	−29 ± 4	−137 ± 63
	Annual	757 ± 114	−222 ± 72·6	−598 ± 90	−63 ± 276·6

(b)	Season	DOC loading (g C m^{-2})	DOC export (g C m^{-2})	Net DOC sink sources (g C m^{-2})
	Spring	0·3 ± 0·2	−1·1 ± 1·8	−0·8 ± 2·0
	Summer	0·4 ± 0·3	−2·6 ± 0·3	−2·2 ± 0·6
	Autumn	0·4 ± 0·3	−2·2 ± 0·3	−1·8 ± 0·6
	Winter	0·4 ± 0·3	−2·4 ± 1·3	−2·0 ± 1·6
	Annual	1·5 ± 1·1	−8·3 ± 3·7	−6·8 ± 4·8

water yields and chemical loads measured at the outflow were representative of the hydrochemical processes occurring across the basin. In contrast, we hypothesized that longer pond residence times owing to growing season drought would increase the potential for DOC transformations (flushing time ~6 weeks) across the basin. Therefore, we believed it was important to determine if the DOC flux measured at the basin outflow was a suitable proxy for seepage flux and *vice versa* during the growing season; and to isolate the controls on DOC export and DOC biogeochemistry.

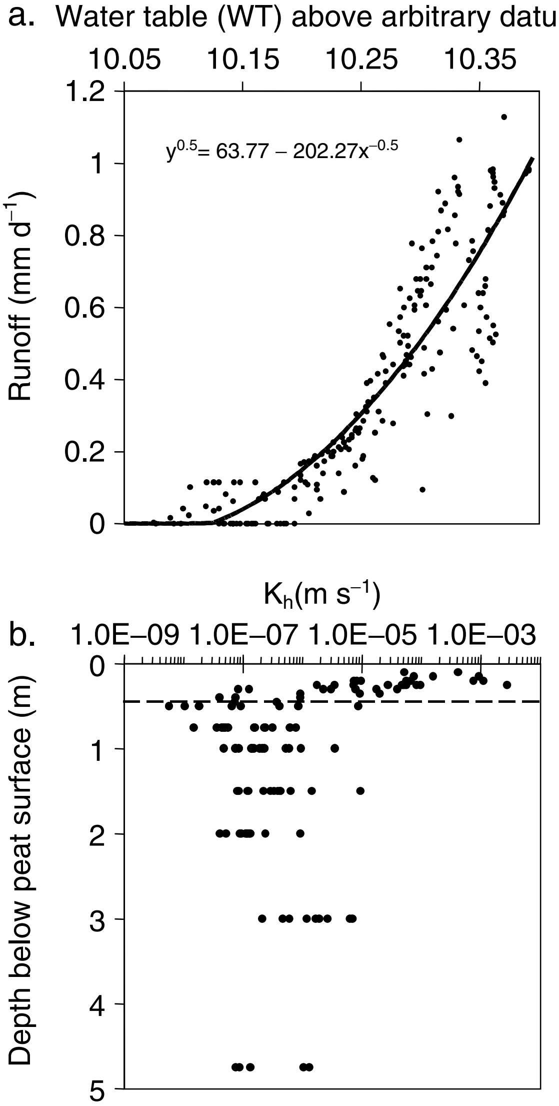

Figure 4. (a) Regression analysis of basin runoff and peatland water table position for the ice-free season ($r^2 = 0{\cdot}79$; $F = 785{\cdot}6$; $p < 0{\cdot}001$). (b) Patterns of horizontal hydraulic conductivity (K_h) with depth across the groundwater network. The acrotelm and catotelm are separated by a dashed line (∼0·45 m below the peat surface)

Field measurements showed that highest peatland water table position (May 21 to December 9, 1998) coincided with greatest basin runoff (Figure 4a). K_h at the peatland margin increased several orders of magnitude toward the peat surface (Figure 4b). Acrotelm (peat surface to ∼0·45 m peat depth) K_h at the Mer Bleue bog ranged from 10^{-7} to 10^{-3} m s^{-1} ($n = 36$), and increased toward the peat surface, whereas K_h of catotelm peat ranged from 10^{-8} to 10^{-6} m s^{-1} ($n = 86$) and showed no pattern with depth across the groundwater network. Owing to the empirical relationship between runoff and water table position, and the K_h pattern in the acrotelm, a Dupuit–Forchheimer (D–F) approximation and groundwater chemistry were used to compare groundwater seepage and DOC loads at the peatland margins to discharge and loads measured at the basin outflow ∼4 km downstream (Figure 1).

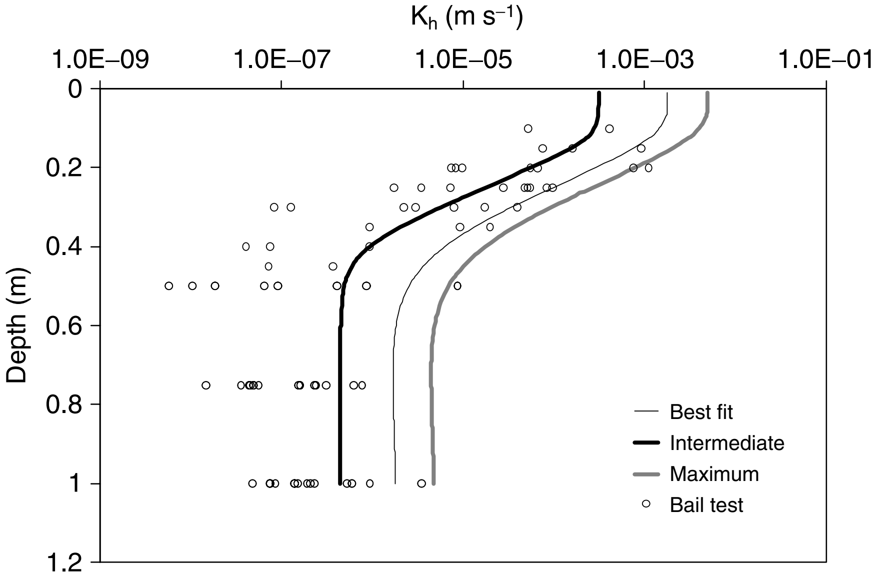

Figure 5. K_h estimates at the peatland margin and K_h profiles fit to the measurements. The 'Intermediate', 'Best fit' and 'Maximum' profiles were obtained by curve fitting through the K_h distribution such that the K_h differences between the acrotelm and catotelm were preserved

Piezometric data from nests P1–P5 confirmed the existence of a seepage face at the peatland margin, showing horizontal groundwater flow at the peatland margin during the growing season (Fraser, 2000). The persistence of horizontal flow yielded constant water table gradients between P1–P3, where average water table and surface gradients were estimated to be ~0·022 and ~0·03 respectively. Field measurements of water table position, hydraulic gradient, and a depth profile of K_h (Figure 5) were incorporated into D–F approximations to estimate discharge at the peatland margin (Kirkham, 1967; Gafni and Brooks, 1990). Discharge from May 21 to December 9, 1998 was computed for 0·01 m thick layers between the water table and a peat depth of 1·0 m. Estimates of discharge were scaled to basin size using the peatland perimeter (11 000 m), and scaled to units of runoff using the subcatchment area (4·8 km^2).

Estimated runoff agreed with runoff measured at the basin outflow (80 mm versus 77 mm) using the 'best fit' profile of K_h (Figure 6a). Regression analysis (not shown) of measured versus approximated runoff had an $r^2 = 0{\cdot}74$, $F = 562{\cdot}6$, $p < 0{\cdot}001$. D–F approximations indicated that ~95% of the discharge at the peatland margin was transmitted between 0·05–0·30 m depths below the peat surface. Further, approximations constrained by 'intermediate', 'best fit' and 'maximum' K_h profiles (Figure 5) illustrate the sensitivity of the D–F approximation to the K_h–depth profile (Figure 6b).

D–F approximated groundwater discharge and records of [DOC] from piezometer nest P1 and the beaver pond (~30 m downstream of P1; Figure 1) were used to estimate DOC loads attributed to seepage from the peatland, but the measurements from P1 were used cautiously because of the limited number of observations ($n = 13$). D–F approximated DOC export was determined using daily discharges from the 'best fit' D–F approximation (scaled by basin perimeter), and curve fitting was used to obtain daily [DOC]. Minimum and maximum export ranges were calculated from 14-day minimum and maximum [DOC] observations.

D–F approximated DOC export for the 203-day growing season was 4·2 ± 0·7 g C m^{-2} using [DOC] from the pond, whereas DOC export measured at the outflow was 3·3 ± 0·8 g C m^{-2} for the same period. D–F approximated export was 4·4 ± 0·7 g C m^{-2} when [DOC] from piezometers at P1 were used in budget calculations. The ~21% discrepancy between the measured and D–F approximated DOC export was a function of the differences in [DOC] measured near groundwater transects compared to the outflow in autumn 1998 (Figure 6a).

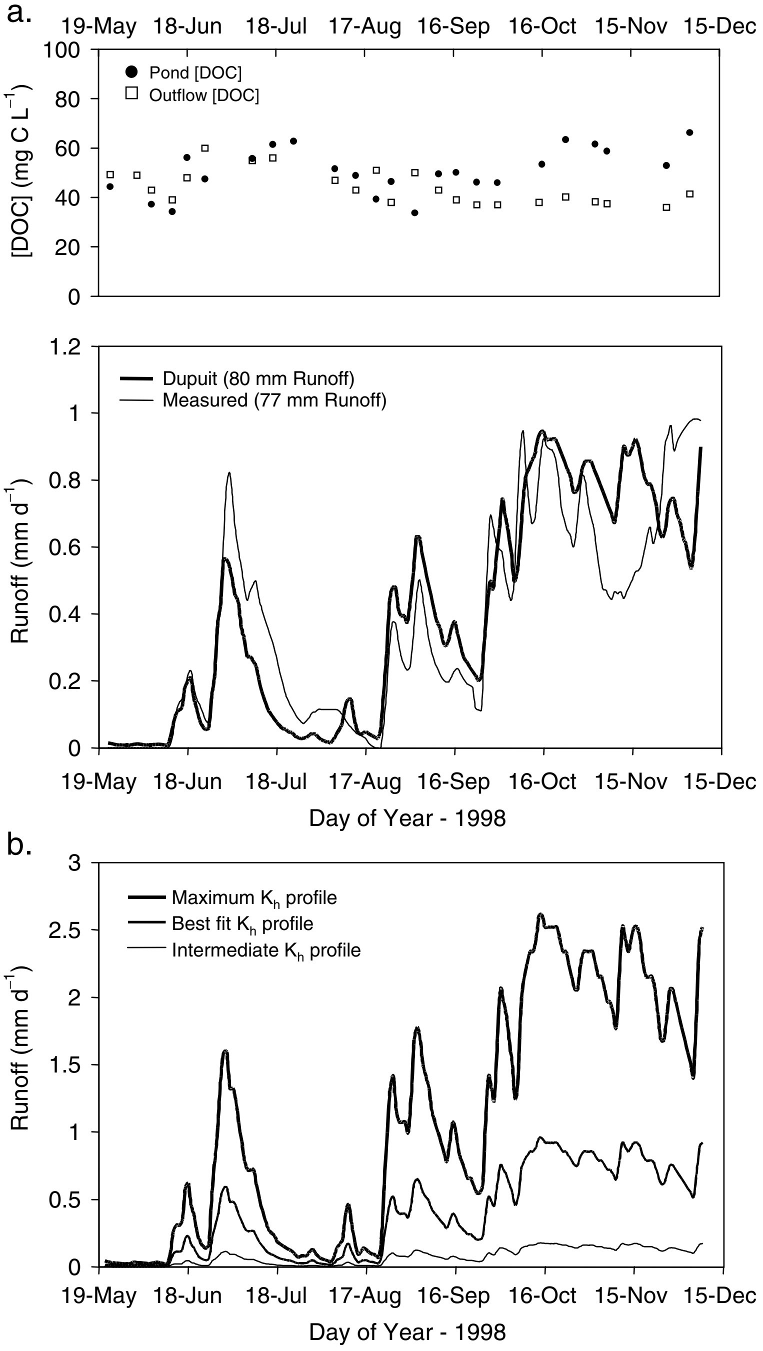

Figure 6. (a) A comparison of [DOC] and runoff at the beaver pond near P1 and the basin outflow. D–F and measured runoff were 80 and 77 mm respectively ($r = 0{\cdot}86$; $F = 562{\cdot}6$; $p < 0{\cdot}001$). (b) Sensitivity of D–F approximations constrained by the K_h functions in Figure 5. Runoff predictions based on 'Intermediate', 'Best fit' and 'Maximum' K_h profiles were 15, 80 and 218 mm respectively

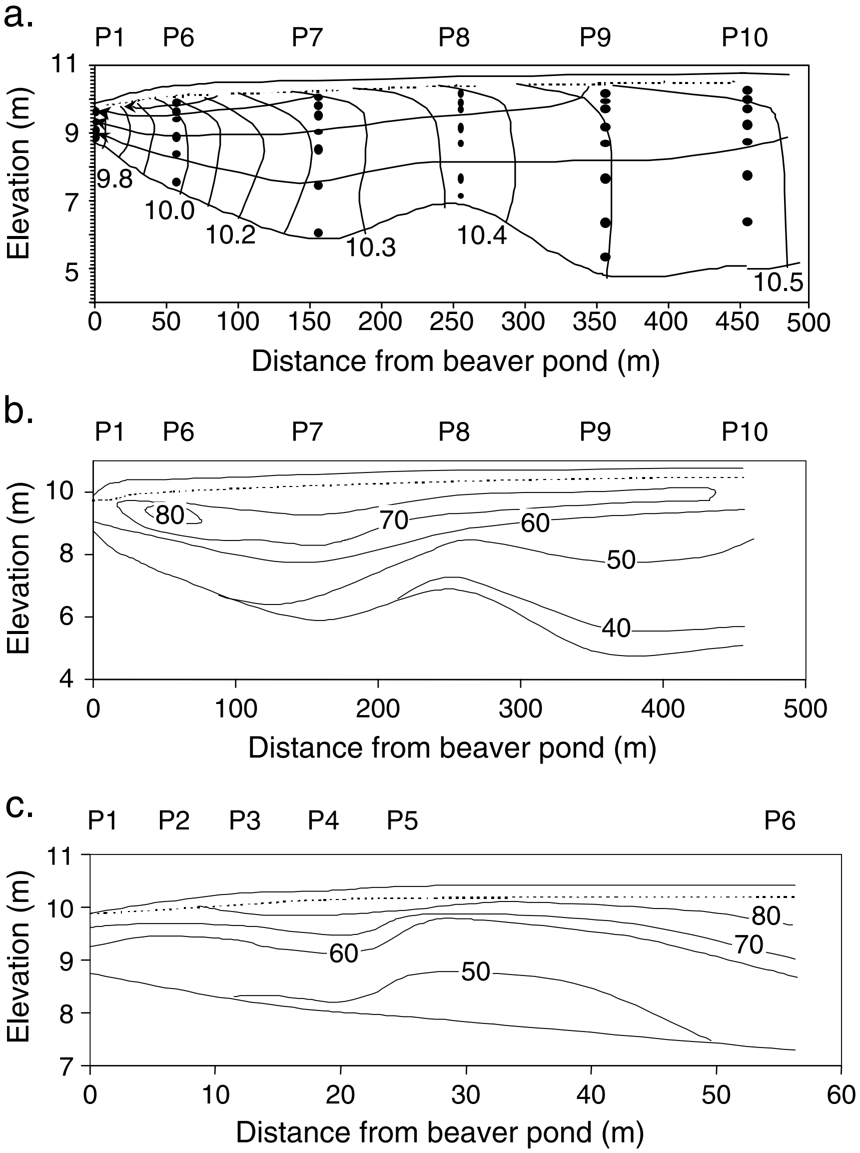

Figure 7. (a) A flownet showing groundwater recharge across the major axis (August 26, 1998). Flownets were drawn after Freeze and Cherry (1979) with vertical exaggeration equal to 20 (see Fraser *et al.*, 2001 for more details). (b) DOC isopleth across the major axis on July 22, 1998. The isopleth was constructed using [DOC] from nests P1 and P6–P10. (c) DOC isopleth across the peatland margin on July 22, 1998. The isopleth was constructed using [DOC] from nests P1–P6

Hydrology and DOC within the peatland

Groundwater flow patterns across the major axis of the peatland were distinctly different from patterns observed at the peatland margin. Equipotentials were always vertical near the peatland margin, whereas equipotentials across the major axis varied between recharge and discharge, depending on the timing and magnitude of precipitation (*P*) and evapotranspiration (*ET*) (Fraser *et al.*, 2001). When $ET >> P$ in the summer, flow patterns reversed from recharge to discharge and were sustained for approximately 40 days. However, geochemical reconstructions of groundwater flow patterns using *in situ* Na^+ tracing showed that

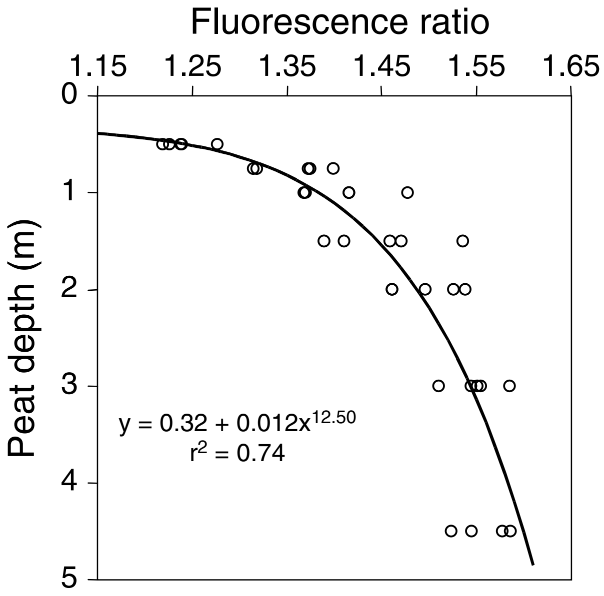

Figure 8. Change in fluorescence quotient with peat depth across the major axis of the Mer Bleue bog ($r^2 = 0{\cdot}74$; F-stat = 50·37; $p < 0{\cdot}001$). The quality of DOC became more 'autochthonous' with increased depth into the peatland compared to the 'allochthonous' fluorescence signal found near the water table

the Mer Bleue bog is on average a long-term recharge system (Fraser *et al.*, 2001). A flownet illustrating groundwater recharge at the Mer Bleue bog is shown in Figure 7a.

Spatial changes in [DOC] are shown for the major axis and peatland margin in Figure 7b. Chemopleths across the major axis ($n = 10$ sample dates; July 22, 1998 shown) showed that [DOC] increases slightly between the peat surface and 1·5 m depth, then decreases with depth (Figure 7b). Concentrations decreased with depth at the peatland margin (Figure 7c), but there was no evidence of a concentration inversion similar to that on the major axis. Exportable [DOC] (DOC in the upper ~0·45 m of the peat profile) was variable over the hydrological year, where [DOC] ranged from ~40 mg l^{-1} following spring melt to ~70 mg l^{-1} during the growing season. During the growing season, [DOC] in the upper 0·75 m of the peat profile usually increased in response to rainfall events. However, [DOC] in the upper profile did not correlate with water table position, suggesting that concentration changes were dependent on confounding factors such as substrate availability, temperature, and DOC partitioning through respiration and methanogenesis. Patterns and [DOC] below 0·75 m peat depth did not vary significantly.

DOC 'quality' changed with increased peat depth across the major axis (Figure 8). Fluorescence quotients increased with depth from ~1·2 (allochthonous DOC) at the peatland surface to ~1·6 (more autochthonous DOC) in deeper peats (3 to 5 m depths). The fluorescence quotient of surface water samples and discharge water at the basin outflow ranged from 1·2 to 1·3 ($n = 10$), whereas the fluorescence quotient of water sampled from the drive-point piezometers inserted beneath the peatland ranged from 1·5 to 1·7 ($n = 10$). The quotients of rain samples were ~1·5 to 1·6, in agreement with measurements made in other boreal ecosystems (W. F. Donahue, unpublished data).

DISCUSSION

DOC export at the Mer Bleue bog

Measured and D–F estimated DOC export were within 21% or 1 g C m^{-2} at the Mer Bleue bog. Therefore, we believe the outflow record of DOC export ($-8{\cdot}3 \pm 3{\cdot}7$ g C m^{-2} yr^{-1}) is a suitable proxy for DOC export from this subcatchment. The discrepancy between measured and D–F approximated export is small, but could be explained by hydrobiogeochemical processes that occur across the basin. For example, photodegradation, methanogenesis and flocculation/sedimentation along the pond network could account for some of the decrease in [DOC]. Additionally, hillslope contributions from uplands may have diluted pond water through contributions of low [DOC] ($\sim$10–20 mg l^{-1}) across the basin length. However, the upland mineral soils have low K values, small area and are well ditched away from the peatland, so we believe the magnitude of dilution is small.

Measured P over the hydrological year was $\sim$17% or 153 mm below the long-term average for the region (Environment Canada, 1998). Therefore, we assume that DOC export would be larger than our estimates suggest during a 'normal' year. We calculate a runoff ratio of 0·3 for the Mer Bleue, while for this part of eastern Canada it has been estimated to be 0·4 (Hare and Thomas, 1979). Thus, a more 'normal' summer discharge of 46–62 mm yr^{-1} ([DOC] = 55 mg l^{-1}) would yield an additional 2·5–3·4 g C m^{-2} yr^{-1} of DOC export, a 'normal' winter storage of snow of 153 mm ([DOC] = 20 mg l^{-1} based on pond estimates at snowmelt) would give an additional 3·1 g C m^{-2} yr^{-1} of DOC export. Therefore, under 'normal' hydrological conditions at the Mer Bleue, we would expect DOC export, precipitation loading and DOC loss to be of the order of $\sim$12, $\sim$2 and $\sim$10 g C m^{-2} yr^{-1}, respectively.

Groundwater flow paths and DOC biogeochemistry

The temporal patterns of DOC export and transport within the peatland can be explained by considering dominant flow paths. During winter and spring melt, runoff occurs as fast flow over the peat surface, owing to the development of ice at the peat–snow interface [Figure 9(1)]. Exportable [DOC] during spring melt was controlled by the SWE of the snow pack, availability of fresh substrate and pond mixing. Mixing calculations using snow ($\sim$200 mm, 1–4 mg l^{-1}) and pond ($\sim$5–10 mm, 50 mg l^{-1}) storage capacities and [DOC], suggest there is available substrate for DOC production during melt, despite the low temperatures. If DOC production were negligible, spring melt [DOC] would have been lower than 20 mg l^{-1}, which was not the case (Figure 2b). [DOC] increased once substrate contact in the upper 0·45 m of the peat profile occurred following ground thaw.

Water table position controls the amount of peatland area contributing to DOC export, because of the exponential decrease in K_h with depth. For example, if the water table position is near the peat surface, DOC can be exported through an acrotelm 'wedge' the length of the major axis [Figure 9(2)]. However, if water table position is low, piezometric data show that the area contributing to DOC export can be reduced to a distance <15 m from the margin of the peatland [Figure 9(3)]. DOC 'quality' of export water through the acrotelm was allochthonous-like (i.e. fluorescence quotient = 1·2 to 1·3), thus the Mer Bleue transforms the quality of DOC from $\sim$1·6 (precipitation) to $\sim$1·2–1·3 (DOC export from the peatland).

Water and substrates that are not partitioned to acrotelm runoff are recharged through the peatland [Figure 7a, Figure 9(4) and (5)]. In general, [DOC] in the recharge system decreased with peat depth, and did not change between successive sampling dates. Fluorescence quotients of DOC increased in magnitude with peat depth (Figure 8) in a predictable fashion. Larger magnitude fluorescence quotients (1·6 to 1·7) correspond to more autochthonous-like DOC, and have lower aromaticity and fulvic fraction than allochthonous DOC (Dianne McKnight, personal communication). Therefore, fluorescence and groundwater data suggest that decreases in [DOC] with depth may be attributed to *in situ* microbial consumption of available DOC while recharged through the peatland. Water and substrates entering the recharge system are eventually discharged at the peatland margin [Figure 9(5)], by horizontal flow. Exportable [DOC] was fairly constant in the catotelm, and fluorescence quotients increased with peat depth. Therefore, DOC exported through the catotelm has lower 'quality' or UV absorbing properties than DOC exported through the acrotelm. We conjecture that prolonged drought would reduce DOC export through the acrotelm, in effect reducing the amount of allochthonous-like DOC exported to downstream aquatic ecosystems. However, prolonged drought would also reduce the importance of DOC export to the carbon budget of the Mer Bleue bog, because seepage would also be reduced.

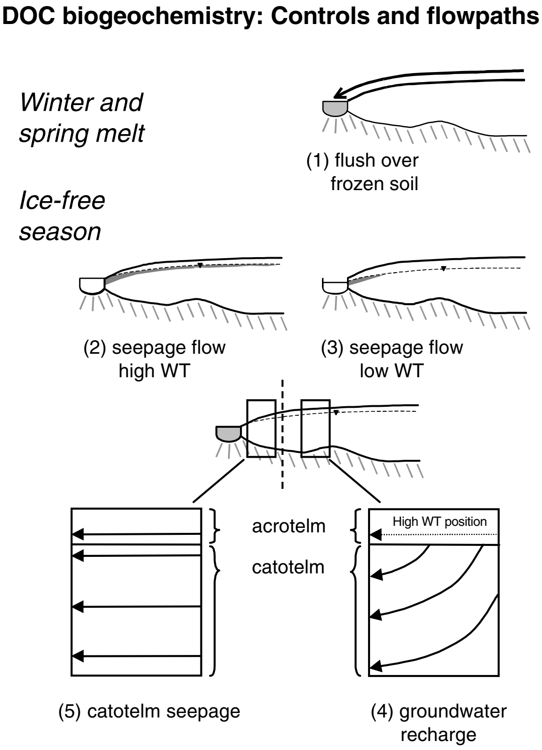

Figure 9. Conceptual diagram illustrating hydrological pathways and controls on DOC biogeochemistry at the Mer Bleue bog. Contributing areas of seepage flow are shown in flow paths (2) and (3) with grey shading

DOC export and carbon budgets of peatlands

DOC export from the Mer Bleue bog ($-8{\cdot}3$ g C m^{-2} yr^{-1}) was slightly larger than estimates from subarctic peatlands (Moore, 1987; Koprivnjak and Moore, 1992) and a mid-latitude fen (Carroll and Crill, 1997), but similar to estimates from other peatland-dominated catchments (McKnight *et al.*, 1985; Moore, 1989; Scott *et al.*, 1998). However, our export term was less than estimates from mid-latitude wetlands (Naiman, 1982; Urban *et al.*, 1989) and a 'typical' northern peatland (Gorham, 1995). Waterborne losses by DOC reported in the literature (1 to 50 g C m^{-2} yr^{-1}; Table I) represent a range of between ~13 to 250% of the long-term C sequestration in peatlands (20–30 g C m^{-2} yr^{-1}; Gorham, 1991). In contrast, our estimate of DOC export was 12% of the measured annual net ecosystem exchange at the Mer Bleue bog (71 g C m^{-2} yr^{-1}; Lafleur *et al.*, 2001), or 28 to 42% of long-term C sequestration.

The importance of DOC export to carbon budgets is dependent, in part, on hydrogeologic setting. In a peatland that is surrounded by a large area of upland, DOC biogeochemistry should be important to the carbon budget (e.g. Naiman, 1982; Urban *et al.*, 1989) because large DOC export terms (up to 50 g C m^{-2} yr^{-1}) will systematically affect the carbon budget, particularly if NEE is small. However, we argue that DOC export terms (>15 g C m^{-2} yr^{-1}) are unrealistic for a large percentage area of northern peatlands, specifically peat-dominated catchments with low relief. Mean annual flow-weighted [DOC] at the Mer Bleue bog was 37 ± 5 mg l^{-1}, which is similar to estimates reported for other peat-dominated catchments (i.e. 30 to 40 mg l^{-1}; Mulholland, 1981; McKnight *et al.*, 1985; Dalva and Moore, 1991). Assuming the [DOC] of export water is 30–40 mg l^{-1}, ~375–500 mm yr^{-1} of runoff is required to yield 15 g C m^{-2} yr^{-1}. We acknowledge that runoff of this magnitude is plausible in certain regions of North America, but unrealistic in most places with peatlands. For example, P and R in the Hudson Bay Lowlands and the Western Boreal

Forest range from 400–800 mm yr^{-1} and 120–380 mm yr^{-1} (Hare and Thomas, 1979; National Wetlands Working Group; 1988). Expected range of DOC export in these regions is $\sim$3·6–11·4 g C m^{-2} yr^{-1} based on concentration data and mean runoff.

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