



Dissolved organic matter properties and their relationship to carbon dioxide efflux from restored peat bogs

Stephan Glatzel^{a,*}, Karsten Kalbitz^b, Mike Dalva^c, Tim Moore^c

^a*Landscape Ecology Unit, Institute of Geography, University of Göttingen, Goldschmidtstrasse 5, 37077 Göttingen, Germany*

^b*Department of Soil Ecology, Bayreuth Institute for Terrestrial Ecosystem Research (BITÖK), University of Bayreuth, 95440 Bayreuth, Germany*

^c*Department of Geography and Centre for Climate and Global Change Research, McGill University, 805 Sherbrooke Street West, Montreal, QC, Canada H3A 2K6*

Received 30 December 2001; accepted 9 December 2002

Abstract

The effects of peat bog harvesting and restoration on dissolved organic matter (DOM) are poorly known although DOM represents the most mobile part of organic matter in peat. The aims of our study were: (i) to determine concentrations and properties of DOM in a series of natural, harvested, and restored peatlands in eastern Québec and (ii) to relate DOM to CO₂ efflux from these bogs. We sampled pore waters at eight peat bogs and determined dissolved organic carbon (DOC) concentrations, humification indices derived from synchronous fluorescence spectra (humification index (HIX), ratio of intensities at 470 and 400 nm), specific absorption at 280 nm, and the humic acid (HA) content. DOC concentrations ranged from 35 to 625 mg C l⁻¹. The highest values were observed at a block-cut (BC) site where the ditches had been closed to stimulate restoration. This resulted in limited external drainage, DOM accumulation in deeper horizons, and an enrichment of the poorly biodegradable humic acids to about 60% of the bulk DOM. DOC concentrations increased immediately during harvesting up to 188 mg C l⁻¹ as a result of this ecosystem disturbance. Afterwards, DOC concentrations decreased which might be due to a low content of potential DOM of the remaining little oxidised peat. The enhanced decomposition of the remaining peat during the restoration process seems to be important for a new build-up of potential DOM, which is indicated by reincreasing DOC concentration during the restoration process. We could not relate spectroscopic properties of DOM to peat harvesting and restoration. The portion of humic

* Corresponding author. Tel.: +1-49-551-398051; fax: +1-49-551-3912139.
E-mail address: sglatze@gwdg.de (S. Glatzel).

acids was inversely related to CO₂ efflux, indicating low substrate quality of humic acids in pore waters. The seasonal average humification indices of DOM where humic acids had been removed were positively correlated with the seasonal CO₂ efflux from the eight sites, indicating that high respiration results in an enrichment of more aromatic and complex DOM molecules. The relationships suggest that DOM composition affects CO₂ efflux from peat bogs and is also driven by respiration and CO₂ efflux.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Carbon dioxide efflux; Dissolved organic matter; Peatland; Restoration; Synchronous fluorescence spectroscopy; UV–VIS spectroscopy

1. Introduction

Peat harvesting is widespread in Europe, Asia, and North America. In 1998, the global annual peat production was at least 25×10^6 tons (Jasinski, 1999), of which 1.1×10^6 tons were extracted from 160 km² in Canada (Jasinski, 1999; Lappalainen, 1996). Until the late 1960s, peat was extracted on a small scale by a block-cutting technique, leaving a landscape consisting of ridges and trenches (Robert et al., 1999). Blocking of the drainage ditches results in natural revegetation. Since then, larger areas have been harvested by a vacuum technique. After drainage and removal of vegetation, they leave an even surface that is exposed to wind and water erosion and strong temperature fluctuations. Restoration of vacuum-harvested peatlands requires raising the water table, straw mulching, and the application of surface peat containing *Sphagnum* diaspores, vascular plant seeds, and remains (Ferland and Rochefort, 1997; Rochefort, 2001).

Peat harvesting and restoration measures should have a pronounced effect on C turnover. The CO₂ net ecosystem exchange (NEE) of restored bogs in Finland revealed a net sink of CO₂ (Komulainen et al., 1999; Tuitilla et al., 1999). High water table and colonization of harvested peat by *Eriophorum vaginatum* var. *spissum* (*E. spissum*) controlled the CO₂ NEE. In Canada, restoration of peat bogs was found to lower net CO₂ loss (Waddington and Price, 2000; Waddington and Warner, 2001). A soil moisture control on NEE was detected by Waddington and Warner (2001) and Waddington and Price (2000), stressing the significance of physical peat properties and root exudates on the C budget of restored bogs.

Dissolved organic matter (DOM) concentrations and properties may reflect land use changes in peatlands. Kalbitz et al. (1999) used DOM properties to differentiate degraded and intact peatlands caused by a different intensity of land use. They extracted DOM from peat and found degraded peatlands to have a higher specific UV absorption, a higher absorption at 1620 cm⁻¹ in Fourier-transformed infrared spectra, and a red shift in synchronous fluorescence spectra. The authors stated that these observations indicate increased aromaticity and humification of degraded peatlands.

DOM is also a source of respiration (Seto and Yanagiya, 1983; Zsolnay and Steindl, 1991; Qualls and Haines, 1992), therefore, the quantity and quality of DOM could partly explain CO₂ efflux from restored peatlands. However, the contribution of DOM to CO₂

efflux in restored bogs is unknown. In Finnish peat bogs, 35–45% of the respiration were derived from roots (Silvola et al., 1996) and between 50% and 70% of CO₂ efflux originated from recent photosynthates (Komulainen et al., 1999). Recent photosynthate such as root exudate is also a possible source of dissolved organic carbon (DOC) (Zsolnay, 1996). We believe that carbonate release in acidic bog ecosystems is a negligible source of CO₂, thus, a large fraction of evolved CO₂ could derive from DOM.

Fluorescence and UV spectroscopy have recently been used to establish differences in DOM composition. The specific absorption in UV light (e.g. 280 nm) corresponds to the aromaticity of DOM (Chin et al., 1994; McKnight et al., 1997). A “humification index” (HIX), which is the ratio of the intensity of emitted light at a long and a short excitation wavelength of synchronous fluorescence spectra, was proposed by Kalbitz et al. (1999, 2000a). Zsolnay et al. (1999) and McKnight et al. (2001) proposed two other HIX using fluorescence emission spectra. All these indices are based on the observation that a shift in maximum fluorescence intensity from shorter to longer wavelengths is associated with an increasing number of highly substituted aromatic nuclei and/or with conjugated unsaturated systems (Senesi et al., 1989; Miano and Senesi, 1992). Kalbitz et al. (1999) employed the HIX on peat pore-water samples (Kalbitz et al., 1999) and tested it on different fluorimeters (Kalbitz and Geyer, 2001). They found that a high HIX of DOM is related to strong humification of peat. For our examination, this suggests that the HIX of DOM should be related to the degree of decomposition of DOM. Therefore, DOM composition (e.g. HIX) could indicate the substrate value of DOM for respiration (Kalbitz et al., 2003) and could also be a consequence of respiration.

The goals of our study were twofold. First, we determined the variations in the concentration and composition of DOM in pore waters of a series of peatlands in eastern Québec that represent natural, drained, harvested, and restored bogs. Second, we related these variations in DOM concentration and chemistry to the seasonal efflux of CO₂ from these sites.

2. Materials and methods

2.1. Sites

The study area is located near Rivière du Loup, Québec, Canada, between the foothills of the Appalachians and the St. Lawrence River at 47°48' N and 69°28' W. The mean annual temperature is 4.2 °C with a January mean of –11 °C and a July mean of 19 °C. The mean annual precipitation is 930 mm, of which more than two-thirds fall as rain (Environnement Canada, 1993). The eight sites we used are classified as Atlantic boreal peatlands (National Wetlands Working Group, 1986).

The bog (BOG) which covers 0.03 km² is surrounded by peatlands that are being extracted and a drainage ditch that has probably lowered the water table (Table 1). The vegetation is dominated by shrubs (e.g. *Chamaedaphne calyculata* and *Kalmia angustifolia*) and *Sphagnum* spp. The actively harvested (H) site is part of a large vacuum-harvested complex covering 1.2 km², with 30-m-wide sections separated by ditches that have lowered the water table. Adjacent to H, there are three experimental sites where restoration started in 1999 (R99), 1997 (R97), and 1995 (R95), covering 0.02, 0.05, and

Table 1

Type of harvesting, sampling depth for the intersite comparisons, seasonal water table range, site-specific parameters for the CO₂ efflux model, and modelled seasonal CO₂ efflux at the experimental sites in 2000 in Rivière du Loup, Canada

Site/restoration	Type of harvesting	Sampling depth (cm below ground)	Seasonal water table range (cm below ground)	CO ₂ efflux model parameters (dimensionless)		Seasonal CO ₂ efflux (g C m ⁻²)
				<i>a</i>	<i>b</i>	
BOG: bog (reference)	no harvesting	50	0–75	50.35	0	587
H: actively harvested	vacuum-harvested	75	100–150	11.31	30.27	155
R99: start of restoration in 1999	vacuum-harvested	50	25–75	15.94	0	186
R97: start of restoration in 1997	vacuum-harvested	75	25–75	66.53	283.65	996
R95: start of restoration in 1995	vacuum-harvested	50	25–75	42.16	0	491
A: abandoned site	block-cut harvested	50	50–100	101.96	0	1189
BC: block-cut site; ditches closed	block-cut harvested	ridge: 75	ridge: 25–75	15.53	526.33	91
		trench: 50	trench: 0–35	40.42	113.11	559
I: inundated site	block-cut harvested	50	0	25.52	173.80	433

For intrasite comparisons, block-cut trench was sampled from 25- to 150-cm depth, and block-cut ridge was sampled from 75- to 150-cm depth. Differences in seasonal DOC efflux are significant between A and H and R99.

0.03 km², respectively. The vegetation at these three sites ranges from some patches of bryophytes at R99 under straw mulch, a site with large *E. spissum* tussocks (R97), and a site where the *E. spissum* tussocks are older and smaller (R95). Clayey deposits underlie R95, R97, and R99 at a depth of 0.5–1 m.

Three sites were harvested by manual block-cutting. The abandoned (A) site extends over 0.05 km² and has been left to succession 20 years before we started our measurements. It is covered by *E. spissum*, ericaceous shrubs, birch trees, and bare peat. At the block-cut (BC) site, which covers an area of 0.08 km², the ditches were partially closed 10 years before our measurements started. Hummocks and hollows have developed in the trench, occupied by a mixture of *E. spissum*, shrubs, and *Sphagnum* spp. (Robert et al., 1999). The ridge is vegetated by trees, shrubs, and lichens. At the inundated (I) site, which is 0.08 km² in size, the closure of the ditches raised the water table close to the ridge surface and the flooding of the trenches, resulting in *E. spissum*, shrubs, and *Sphagnum* spp.

At all sites, the high C/N ratio of the peat (80–22) and the tight N cycling of the prevailing vegetation (Stuart Chapin et al., 1993) suggest very low pore-water NO₃⁻ concentrations. In addition, we never noticed Fe³⁺ stains in the peat or ditches of our sites or in the sample vials. Thus, we assume that our spectroscopic measurements were not affected by the presence of nitrate or Fe²⁺ in the samples.

2.2. DOC sampling and analysis

For the comparison of DOC concentration and properties between sites, we installed piezometers at depths of 50 (BOG, R99, R95, A, BC trench sites) or 75 cm (H, R97, BC ridge, and trench sites). At the BC site, we installed additional piezometers at depths of 100 and 150 cm on the ridge and at 25, 100, and 150 cm in the trench (Table 1). The piezometers were installed in spring 1999, except at the R99 site, where installation was in autumn 1999. Before sampling the piezometers for the first time, we emptied them five times in order to rule out contamination due to disturbed peat. We sampled pore waters on May 24, July 16, August 21, September 12, and October 26, 2000.

We transported the samples on ice to the laboratory. There, we filtered them through 0.4- μ m glass fibre filters. Samples were stored at approximately 4 °C until analysis.

We examined the variation of DOC properties with samples from May and July, as we were not able to conduct the spectroscopic analyses on all samples. May was our first sampling date, and July, as the warmest month of summer, might represent a period of maximum microbial activity. At the BC site, we were able to conduct data analyses with samples from October as well.

We determined the DOC concentration on a Shimadzu TOC-5050 total organic carbon analyzer within 2 weeks of sampling. Following Kalbitz et al. (2003), who noticed the mineralization of just 5–9% of DOC from aqueous peat extracts within 90 days, we expect small C losses due to storage. The Shimadzu TOC-5050 determines nonpurgeable organic carbon, which was acceptable for our purpose since no volatile components were involved. The humic acid (HA) fraction was determined by subtracting the DOC concentration of the supernatant after acidification to pH 2 from the DOC concentration before acidification (Bourbonniere, 1989).

For spectroscopic measurements, the May samples were analyzed at McGill University whereas the July and October samples were frozen and transported to the University of Bayreuth (BITÖK). All samples (bulk DOM, DOM without HA) were diluted to 10 mg C l^{-1} . We determined the specific absorption at 280 nm (A 280) using a Perkin-Elmer Lambda 14 (McGill) and a BIO-TEK Instruments UVIKON 930 (BITÖK). Additionally, we recorded synchronous fluorescence spectra (300–550 nm, $\Delta\lambda$: 18 nm, 100 nm min^{-1}) using a SPEX Fluorolog-2 (McGill) and a BIO-TEK Instruments SFM 25 (BITÖK) and determined a humification index (HIX; Kalbitz et al., 2000a). Among the humification indices suggested by Kalbitz et al. (2000a), we chose the ratio of the intensity at the excitation wavelength at 470 nm over the one at 400 nm. Before transporting the July and October samples to Germany, we compared the specific absorption at 280 nm and the humification indices at both UV–VIS spectrometers and fluorometers with five water-soluble fulvic acids extracted from another peatland (Kalbitz and Geyer, 2001). The correspondence between the results at both instruments was satisfactory ($r^2=0.86^*$ for the UV–VIS spectrometers; $r^2=0.97^{**}$ for the fluorometers).

2.3. CO_2 efflux

Efflux of CO_2 was determined with a closed chamber technique (Hutchinson and Livingston, 1993) from late May to late September 2000 with several stationary collars at every site. We used opaque, cooled chambers placed on the collars to measure CO_2 efflux at approximately 2-week intervals from changes in CO_2 concentration at 0, 1, 2, 4, and 5 min using an EGM-3 infrared gas analyzer (IRGA) (PP systems, Haverhill, MA, USA). We calibrated the IRGA with external standards of 0 and $500 \mu\text{l l}^{-1} \text{CO}_2$ and detected an analytical precision of 2.6%.

We estimated the seasonal and weekly CO_2 efflux from a model based on the linear correlation between air temperature and individual efflux measurements from the collars that were closest to the piezometers at each site. The parameters of the equation:

$$y = ax + b \quad (1)$$

with $y = \text{CO}_2$ efflux ($\text{mg m}^{-2} \text{h}^{-1}$), $x = \text{air temperature (}^\circ\text{C)}$, a , $b = \text{parameters of the site-specific regressions (Table 1)}$, were applied to the hourly air temperature record from our weather station at BC for the entire season (day of year: 144–264). Finally, the seasonal CO_2 efflux, as well as the CO_2 efflux of the week previous to the May and July pore-water sampling, was put in relation to the DOC concentration, portion of HA, and to the HIX and the A 280 of the bulk DOM and the DOM without HA.

2.4. Statistical analyses

All statistical analyses were conducted using *Statistica '99 Editon*. For descriptive purposes, we calculated the mean DOC concentration and mean DOM quality parameters based on sampling site. Differences of DOM concentrations and properties between the sites were tested using the parameter-free Kruskal-Wallis rank test. In addition, the Mann–

Whitney *U*-test was performed to determine differences between two mean values. The employed significance level was 0.05.

The difference between the seasonal site-specific CO₂ efflux data was tested by adding and subtracting the standard error of the slope of the respiration model for every site from the seasonal CO₂ efflux. Carbon dioxide efflux between sites was considered significantly different if the larger efflux value minus the standard error was higher than the smaller efflux value plus the standard error. We tested the correspondence between DOC parameters and CO₂ efflux as well as sampling depth employing linear regressions.

3. Results and discussion

3.1. DOC concentrations

Seasonal average concentrations of DOC ranged from 35 to 110 mg C l⁻¹ (Fig. 1), which is somewhat higher to that found in other peatlands (Grieve, 1990; Moore, 1997; Fraser et al., 2001), where DOC concentrations are seldom >50 mg l⁻¹. Within site, DOC concentrations at the block-cut (BC) site showed much higher variability with DOC ranging from 40 to 625 mg C l⁻¹, some of the highest reported for natural environments (Fig. 2). Concentrations of DOC at the BC site increased with depth. This is in contrast to a natural peatland 700 km southwest of our research site, where DOC concentrations decreased with depth (Fraser et al., 2001).

The high DOC concentrations at the sites harvested by the block-cut technique (BC, A) could be due to residual DOC accumulation in the undrained system or preferential DOC release in an anaerobic environment compared to an aerobic one. In most cases, anaerobic conditions increase the release of DOC from soils because of less efficient

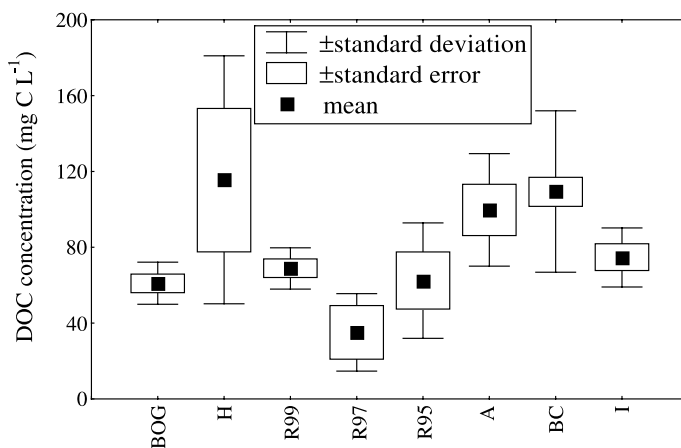


Fig. 1. DOC concentrations in 50- and 75-cm depths in the 2000 season at the sites in Rivière du Loup, Canada. Significant differences according to the Mann–Whitney *U*-test exist between BC and BOG, R99, R95, A, and I, as well as between A and BOG and R99.

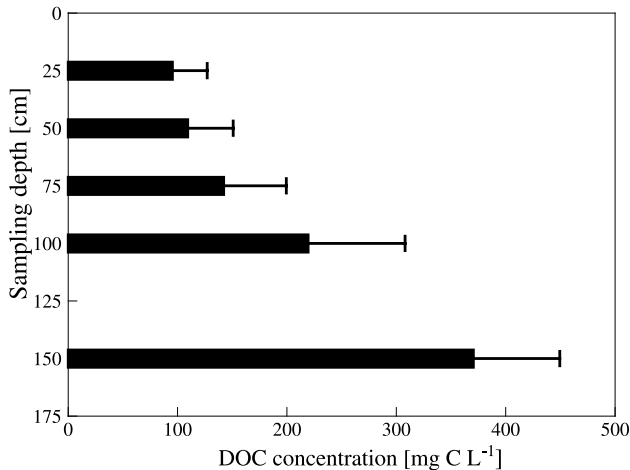


Fig. 2. Sampling depth and DOC concentrations of pore water at the block-cut site, Rivière du Loup, Canada. The bars and the error bars denote the mean and 1 S.D. of DOC concentrations for pore-water samples from all five sampling dates in the 2000 season.

decomposition than under aerobic conditions, resulting in higher proportions of water-soluble intermediate metabolites (Otsuki and Hanya, 1972; Mulholland et al., 1990; Sedell and Dahm, 1990; Homann and Grigal, 1992; Kalbitz et al., 1997). Furthermore, higher DOC concentrations under anaerobic conditions could be caused by decreased DOC adsorption (Kaiser and Zech, 1997; Chin et al., 1998; Hagedorn et al., 2000) and a slower conversion of released DOC to CO₂ (Moore and Dalva, 2001). However, a higher DOC release from plant tissues and soils under anoxic as compared to oxic conditions is not a general phenomenon (Moore and Dalva, 2001). Furthermore, at the inundated site, presumably the most anaerobic environment, DOC concentrations were lower than at the other two block-cut sites (BC, A). Therefore, the high DOC concentration and their increase with depth at the BC sites are rather a result of the undrained system (accumulation of DOM) than of anaerobic conditions. The relatively low DOC concentration at the inundated site is very close to the natural bog, indicating a successful restoration although it is probably due to a low density of vegetation and peat compared to the large volume of water.

To our knowledge, DOC concentrations in harvested and restored peat bogs have not been published before. Based on our results (Fig. 1), we propose the following conceptual model of changes in DOC upon harvesting and restoration. Harvesting of peat (site H) results in a large increase in DOC as a result of this “ecosystem disturbance”. In addition, after clear-cutting of forests, a large increase in DOC concentrations is reported (reviewed by Hope et al., 1994; Kalbitz et al., 2000b). Some time after harvesting (site R99), DOC concentrations decrease because of depletion of easily decomposable organic matter, the potential source of DOM (Tipping, 1998; Tipping et al., 1999; Qualls, 2000; Moore and Dalva, 2001). DOM release from the remaining little oxidised organic matter (R99, R97) is relatively low. However, our examinations indicate (increasing CO₂ efflux from R99 to

R95; see Section 3.3) that this organic matter might be oxidised resulting in replenishment of potential DOM, possibly promoted by root exudate-derived priming effects (Jones, 1998; Kuzyakov et al., 2000). This process would result in a reincrease of DOC concentrations with time (site R95).

Changes in hydrophysical peat properties during the restoration process affect contact time and area between the solid and the liquid phase (Heathwaite, 1995; Schouwenars and Vink, 1990) and, thus, could also be important controls of DOM release. These effects were not studied so far. Furthermore, we did not find any effects of the highly oscillating water tables at the H, R99, R97, and R95 sites which should result in drying–rewetting cycles and in increasing DOC concentrations (reviewed by Kalbitz et al., 2000b).

In summary, DOC concentrations increase immediately during harvesting as a result of this ecosystem disturbance. Afterwards, DOC concentrations decrease because of the probably low content of potential DOM of the remaining peat. The establishment of vegetation promotes a reincrease in DOC concentration. After block-cut harvesting and closing of the ditches, elevated DOC concentrations occur as a result of DOM accumulation in deeper horizons.

3.2. DOC properties

At all sites except block-cut (BC), the humic acid portions ranged between 0% and 83% (median 20%). At the BC site, the percentage of humic acids was much higher (median 46%). Seasonal average values for each site showed that the humification index (HIX) was 0.3–0.5 for all sites except R95 and A, where the HIX rose to 0.8 and 1.5, respectively. The HIX of the DOM samples after removing humic acids (average value: 0.47) was lower than the HIX of the bulk DOM (average value: 0.67), suggesting a more humified character of humic acids than of bulk DOM (Senesi et al., 1989). The specific absorption at 280 nm (A 280) of the pore-water samples ranged from 0.01 to 0.07 l mg C⁻¹ cm⁻¹. The seasonal average of A 280 for the sites was 0.03–0.04, except for R97, where it was 0.07. The A 280 of DOM samples after removing humic acids (average value: 0.028) was lower than the A 280 of bulk DOM (average value: 0.047), implying an increased aromaticity of humic acids (Chin et al., 1994).

The high humification of the peat at the A and R97 sites (highest von Post humification index of all sites; Glatzel, unpublished data) was reflected in highest A 280 and HIX values. However, we could not relate these spectroscopic properties to peat harvesting and restoration. Unlike Dai et al. (2001), who observed increased aromaticity and humification of DOM after clear-cutting of a forest stand, we found no such alteration of DOM after harvesting. Furthermore, the changing DOC concentrations after restoration (R99–R95) were not accompanied by changing DOM composition.

The per site average HIX of the DOM samples after removal of humic acids was not correlated to the per site average of the A 280 ($r^2=0.08$, $P=0.56$), but after exclusion of data from the A site, there was a significant correlation ($r^2=0.76$, $P=0.01$). The correspondence between a high humification index and a high specific absorbance at 280 nm at all other sites supports the idea that increasing humification is associated with increasing aromatic structures (Zech and Guggenberger, 1996; McKnight et al., 2001) and increasing complexity of the DOM molecules.

3.3. CO₂ efflux from the peat

The seasonal CO₂ efflux in 2000 ranged from <200 g C m⁻² at the H and R99 sites, through 490–1000 g C m⁻² at the BOG, BC, R95, I, and R97 sites, to a value of 1190 g C m⁻² at the A site (Table 1). The first 3 years of restoration of the peat result in an increase of CO₂ efflux from the H (160 g C m⁻²) through R99 (190 g C m⁻²), R97 (1000 g C m⁻²) and R95 (490 g C m⁻²) sites. The restoration process seems to enhance decomposition by establishing vegetation and the associated plant and rhizosphere respiration. Tuitilla et al. (1999) presented an evaluation of the role of vegetation on respiration. In Finnish block-cut and restored peatlands, they determined 300–630 g C m⁻² seasonal respiration on *E. spissum* tussocks compared to 80–250 g C m⁻² seasonal respiration on bare peat between the tussocks.

Our results are confirmed by Waddington et al. (2002), who report increased respiration of block-cut peat bogs in central Québec 7 or 8 years after cessation of harvesting compared to similar sites 2–3 years after cessation of harvesting. Waddington et al. (2002) explain the increased respiration at the older sites with stronger humification of the peat. Increased decomposition in peat with greater humification has also been reported by Stewart and Wheatley (1990) and Prevost et al. (1997).

3.4. CO₂ efflux in relation to DOC properties

There was no relationship between seasonal CO₂ efflux and DOC concentrations or May and July CO₂ efflux and DOC concentrations. The only DOM property with a significant relationship to the seasonal CO₂ efflux was the seasonal average humification index of DOM after removing the humic acids (Fig. 3). The relationship between this HIX

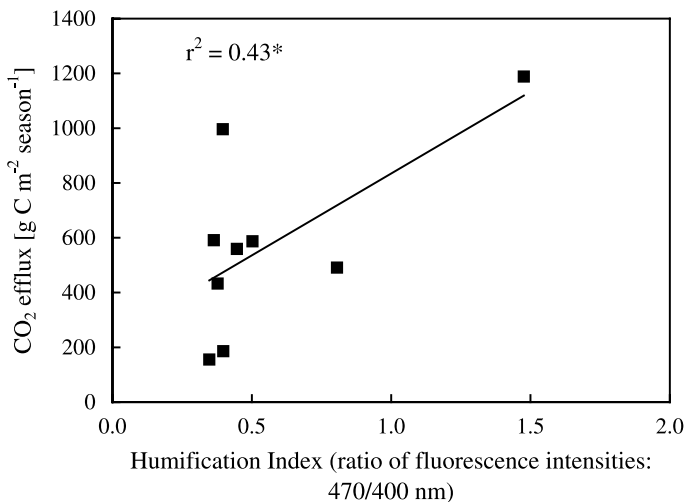


Fig. 3. Humification index of DOM from pore-water samples after removing humic acids in May and July in relation to seasonal carbon dioxide efflux in 2000 at the experimental sites in Rivière du Loup, Canada.

and CO₂ efflux suggests that the degradable fraction has already been oxidised, leaving a more stable DOC. Kalbitz et al. (2003) related a high content of aromatics, a high portion of hydrophobics, and a high humification index to a high microbial stability of DOC. UV absorbance and fluorescence data indicate an enrichment of aromatic moieties during biodegradation of dissolved organic matter (Zsolnay and Steindl, 1991; Hongve et al., 2000; Parlanti et al., 2000; Moran et al., 2000; Pinney et al., 2000). All of these studies support our idea that the positive relationship between the HIX of DOM (after removing the humic acids) and CO₂ efflux could be the result of high respiration followed by an accumulation of a more stable DOC.

In May and July, we found no significant correlation between CO₂ efflux and pore-water DOC concentration, A 280, and HIX (for bulk DOM and DOM after removing humic acids) using the single sampling dates. In May, a high proportion of HA was associated with low CO₂ efflux (Fig. 4). Unfortunately, there were too few samples in July to confirm this correlation. Nevertheless, the association of a high proportion of humic acids with low CO₂ efflux in spring indicates that humic acids are only a minor source for CO₂. This is in contrast to Boyer and Groffmann (1996), who found a higher microbial degradation of water-soluble HA compared to fulvic acids. However, the higher aromaticity and complexity of humic acids in comparison to the bulk DOM (Section 3.2) and the positive relationship between these properties and microbial stability of DOM (Kalbitz et al., submitted for publication) suggests that HA is a poor substrate for microorganisms. Furthermore, the huge accumulation of DOM at the poorly drained BC site and its increase with depth are accompanied by a strong increase in the portion of humic acids confirming the low substrate quality of humic acids.

At the BC site, the HIX of bulk DOC in May was higher than in July (Fig. 5). This could be the result of a physical release of strongly humified DOM from particulate organic matter during winter and early spring frost–thaw events (Kalbitz et al., 2000b). At both sampling dates, the HIX was elevated near the surface compared to the bottom. In

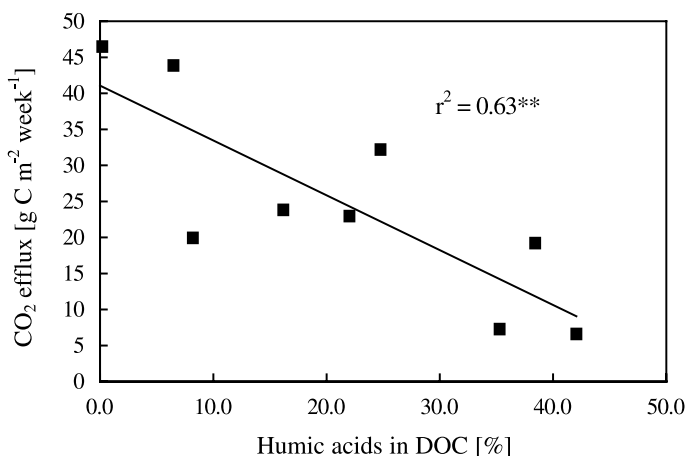


Fig. 4. Weekly carbon dioxide efflux in relation to the portion of humic acids in bulk DOM from pore-water samples at the experimental sites in Rivière du Loup, Canada, in May 2000.

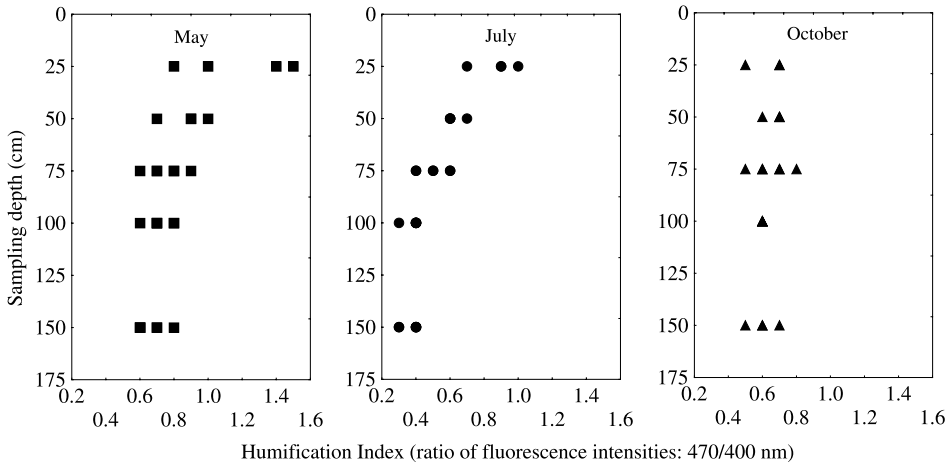


Fig. 5. Sampling depth and humification index of DOM from pore-water samples from May, July, and October 2000 at the block-cut site in Rivière du Loup, Canada.

October, the HIX at the BC site was similar at all depths. This means that the HIX of subsoil DOM was higher in October than in July. Thus, the zone with strong decomposition reached also the lower horizons between July and October as the higher HIX of DOM in the lower horizons suggests stronger decomposition. A now enhanced respiration activity in the deep horizons due to warmer temperatures led to a more even distribution of HIX throughout the profile. In addition, a slow mixing of water from shallow and deep horizons, which should be completed in fall, could be responsible for the consistent distribution of HIX throughout the profile in October.

In summary, our examinations of CO₂ efflux in relation to DOM properties show that DOM properties are both a consequence of and have an effect on respiration. High CO₂ efflux implies a residual accumulation of strongly humified DOM. The two indicators of a preferential stabilisation of humic acids are: (i) an inverse relationship to the CO₂ efflux and a high content at the BC site which increases with depth as a result of DOM mineralization and (ii) limited drainage followed by a high accumulation of stable DOM in the subsoil.

4. Conclusions

Peat bog harvesting and restoration is clearly reflected in DOC concentrations of peat pore waters but generally not in DOM composition. However, DOM composition affects CO₂ efflux from peat bogs under natural, harvested, and restored conditions and is also a consequence of respiration and CO₂ efflux. Compared to abandonment, inundation of block-cut harvested peat bogs seems to be a better way of restoration as indicated by DOC concentrations and CO₂ efflux that are closer to natural conditions. Prevention of external drainage in order to prevent C losses by surface water runoff results in high DOC concentration and an enrichment in relatively stable components like humic acids. The

future development of this C sink is unknown, but any drainage measure could lead to the instant release of this accumulated DOM.

Acknowledgements

We are grateful to M. Marinier and M. Langins for pore-water sampling. We acknowledge the help of A. Rodenhiser, P. Lim Soo, and D. Gray with the fluorospectroscopic measurements at PAPRICAN at McGill University. We thank D. LeQueré, B. Belanger, J. Gagnon, C. Samson, and R. Tanguay at Premier Tech Horticulture for access to the sites and technical support. We are grateful to two anonymous referees for their helpful comments. Funding was provided by the Natural Science and Engineering Research Council of Canada, the Canadian Sphagnum Peat Moss Association, the Centre for Climate and Global Change Research of McGill University, and the Deutsche Forschungsgemeinschaft.

References

- Bourbonniere, R.A., 1989. Distribution patterns of dissolved organic matter fractions in natural waters from eastern Canada. *Org. Geochem.* 14, 97–107.
- Boyer, J.N., Groffmann, P.M., 1996. Bioavailability of water extractable carbon fractions in forest and agricultural soil profiles. *Soil Biol. Biochem.* 28, 783–790.
- Chin, Y.-P., Aiken, G., Loughlin, E.O., 1994. Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. *Environ. Sci. Technol.* 28, 1853–1858.
- Chin, Y.-P., Traina, S.J., Swank, C.R., Backhus, D., 1998. Abundance and properties of dissolved organic matter in pore waters of a freshwater wetland. *Limnol. Oceanogr.* 43, 1287–1296.
- Dai, K.H., Johnson, C.E., Driscoll, C.T., 2001. Organic matter chemistry and dynamics in clear-cut and unmanaged hardwood forest ecosystems. *Biogeochemistry* 54, 51–83.
- Environnement Canada, 1993. Normales Climatiques au Canada, 1961–1990. Quebec. Service de l'environnement atmosphérique, Ottawa, ON.
- Ferland, C., Rochefort, L., 1997. Restoration techniques for *Sphagnum*-dominated peatlands. *Can. J. Bot.* 75, 1110–1118.
- Fraser, C.J.D., Roulet, N.T., Moore, T.R., 2001. Hydrology and dissolved organic carbon biogeochemistry in an ombrotrophic bog. *Hydrol. Process.* 15, 3151–3166.
- Grieve, I., 1990. Variations in chemical composition of the soil solution over a four-year period at an upland site in southwest Scotland. *Geoderma* 46, 351–362.
- Hagedorn, F., Kaiser, K., Feyen, H., Schleppe, P., 2000. Effects of redox conditions and flow processes on the mobility of dissolved organic carbon and nitrogen in a forest soil. *J. Environ. Qual.* 29, 288–297.
- Heathwaite, L., 1995. Problems in the hydrological management of cut-over raised mires, with special reference to Thorne Moors, Yorkshire. In: Wheeler, B.D., Shaw, S.C., Fojt, W.J., Robertson, R.A. (Eds.), *Restoration of Temperate Wetlands*. Wiley, Chichester, pp. 315–329.
- Homann, P.S., Grigal, D.F., 1992. Molecular weight distribution of soluble organics from laboratory-manipulated soils. *Soil Sci. Soc. Am. J.* 56, 1305–1310.
- Hongve, D., van Hees, P.A.W., Lundstrom, U.S., 2000. Dissolved components in precipitation water percolated through forest litter. *Eur. J. Soil Sci.* 51, 667–677.
- Hope, D., Billett, M.F., Cresser, M.S., 1994. A review of the export of carbon in river waters: fluxes and processes. *Environ. Pollut.* 84, 301–324.
- Hutchinson, G.L., Livingston, G.P., 1993. Use of chamber systems to measure trace gas fluxes. In: Rolston, D.E. (Ed.), *Agricultural Ecosystem Effects on Trace Gases and Global Change*. ASA Special Publ. 55. ASA, CSSA, and SSSA, Madison, pp. 63–78.

- Jasinski, S.M., 1999. Peat. Minerals Yearbook 1999. Metals and Minerals. Minerals and Information, vol. 1. U.S. Geological Survey, Reston, VA.
- Jones, D.L., 1998. Organic acids in the rhizosphere—a critical review. *Plant Soil* 205, 25–44.
- Kaiser, K., Zech, W., 1997. About the sorption of dissolved organic matter to forest soils. *J. Plant Nutr. Soil Sci.* 160, 295–301.
- Kalbitz, K., Geyer, W., 2001. Humification indices of water-soluble fulvic acids derived from synchronous fluorescence spectra—effects of spectrometer type and concentration. *J. Plant Nutr. Soil Sci.* 164, 259–265.
- Kalbitz, K., Popp, P., Geyer, W., Hanschmann, G., 1997. β -HCH mobilization in polluted wetland soils as influenced by dissolved organic matter. *Sci. Total Environ.* 204, 37–48.
- Kalbitz, K., Geyer, W., Geyer, S., 1999. Spectroscopic properties of dissolved humic substances—a reflection of land use history in a fen area. *Biogeochemistry* 47, 219–238.
- Kalbitz, K., Geyer, S., Geyer, W., 2000a. A comparative characterization of dissolved organic matter by means of aqueous samples and isolated humic substances. *Chemosphere* 40, 1305–1312.
- Kalbitz, K., Solinger, S., Park, J.-H., Michalzik, B., Matzner, E., 2000b. Controls on the dynamics of dissolved organic matter in soils: a review. *Soil Sci.* 165, 277–304.
- Kalbitz, K., Schmerwitz, J., Schwesig, D., Matzner, E., 2003. Biodegradation of soil-derived dissolved organic matter as related to its properties. *Geoderma* 113, 273–291 (this issue).
- Komulainen, V.-M., Tuitilla, E.-S., Vasander, H., Laine, J., 1999. Restored cut-away peatland as a sink for atmospheric CO₂. *J. Appl. Ecol.* 36, 634–648.
- Kuzyakov, Y., Friedel, J.K., Stahr, K., 2000. Review of mechanisms and quantification of priming effects. *Soil Biol. Biochem.* 32, 1485–1498.
- Lappalainen, E., 1996. General review on world peatland and peat resources. In: Lappalainen, E. (Ed.), *Global Peat Resources*. International Peat Society, Jyskä, Finland, pp. 53–56.
- McKnight, D.M., Harnisch, R., Wershaw, R.L., Baron, J.S., Schiff, S., 1997. Chemical characteristics of particulate, colloidal, and dissolved organic matter in Loch Vale Watershed, Rocky Mountain National Park. *Biogeochemistry* 36, 99–214.
- McKnight, D.M., Boyer, E.W., Westerhoff, P.K., Doran, P.T., Kulbe, T., Andersen, D.T., 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnol. Oceanogr.* 46, 38–48.
- Miano, T.M., Senesi, N., 1992. Synchronous excitation fluorescence spectroscopy applied to soil humic substances chemistry. *Sci. Total Environ.* 117, 41–51.
- Moore, T.R., 1997. Dissolved organic carbon: sources, sinks, and fluxes and role in the soil carbon cycle. In: Lal, R., Kimble, J.M., Follett, R.F., Stewart, B.A. (Eds.), *Soil Processes and the Carbon Cycle*. CRC Press, Boca Raton, FL, pp. 281–292.
- Moore, T.R., Dalva, M., 2001. Some controls on the release of dissolved organic carbon by plant tissue and soils. *Soil Sci.* 166, 38–47.
- Moran, M.A., Sheldon, W.M., Zepp, R.G., 2000. Carbon loss and optical property changes during long-term photochemical and biological degradation of estuarine dissolved organic matter. *Limnol. Oceanogr.* 45, 1254–1264.
- Mulholland, P.J., Dahm, C.N., David, M.B., Di-Toro, D.M., Fisher, T.R., Kögel-Knabner, I., Meybeck, M.H., Meyer, J.L., Sedell, J.R., 1990. What are the temporal and spatial variations of organic acids at the ecosystem level? In: Perdue, E.M., Gjessing, E.T. (Eds.), *Organic Acids in Aquatic Ecosystems*. Life Sciences Research Report, vol. 48. Wiley, Chichester, pp. 315–329.
- National Wetlands Working Group, 1986. *Canada Wetland Regions*. National Atlas of Canada, 5th ed. Department of Energy, Mines, and Resources, Ottawa, ON.
- Otsuki, A., Hanya, T., 1972. Production of dissolved organic matter from dead green algal cells: II. Anaerobic microbial decomposition. *Limnol. Oceanogr.* 17, 258–264.
- Parlanti, E., Worz, K., Geoffroy, L., Lamotte, M., 2000. Dissolved organic matter fluorescence spectroscopy as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs. *Org. Geochem.* 31, 1765–1781.
- Pinney, M.L., Westerhoff, P.K., Baker, L., 2000. Transformations in dissolved organic carbon through constructed wetland. *Water Res.* 34, 1897–1911.

- Prevost, M.P., Belleau, P., Plamondon, A.P., 1997. Substrate conditions in a treed peatland: response to drainage. *Écoscience* 4, 543–554.
- Qualls, R.G., 2000. Comparison of the behavior of soluble organic and inorganic nutrients in forest soils. *For. Ecol. Manag.* 138, 29–50.
- Qualls, R.G., Haines, B.L., 1992. Biodegradability of dissolved organic matter in forest throughfall, soil solution and stream waters. *Soil Sci. Soc. Am. J.* 56, 578–586.
- Robert, E.C., Rochefort, L., Garneau, M., 1999. Natural revegetation of two block-cut mined peatlands in eastern Canada. *Can. J. Bot.* 77, 447–459.
- Rochefort, L., 2001. Restoration écologique. In: Payette, S., Rochefort, L. (Eds.), *Écologie des Tourbières du Québec–Labrador*. Les Presses de l'Université Laval, Sainte-Foy, QC, pp. 449–504.
- Schouwenaars, J.M., Vink, J.P.M., 1990. Hydrophysical properties of peat relicts in a former bog and perspectives for *Sphagnum* regrowth. *Int. Peat J.* 4, 15–28.
- Sedell, J.R., Dahm, C.N., 1990. Spatial and temporal scales of dissolved organic carbon in streams and rivers. In: Perdue, E.M., Gjessing, E.T. (Eds.), *Organic Acids in Aquatic Ecosystems*. Life Sciences Research Report, vol. 48. Wiley, Chichester, pp. 261–279.
- Senesi, N., Miano, T.M., Provenzano, M.R., Brunetti, G., 1989. Spectroscopic and compositional comparative characterization of I.H.S.S. reference and standard fulvic and humic acids of various origin. *Sci. Total Environ.* 81/82, 143–156.
- Seto, M., Yanagiya, K., 1983. Rate of CO₂ evolution from soil in relation to temperature and amount of dissolved organic carbon. *Jpn. J. Ecol.* 33, 199–205.
- Silvola, J., Alm, J., Ahlholm, U., Nykänen, H., Martikainen, P., 1996. The contribution of plant roots to CO₂ fluxes from organic soils. *Biol. Fert. Soils* 23, 126–131.
- Stewart, J.M., Wheatley, R.E., 1990. Estimates of CO₂ production from eroding peat surfaces. *Soil Biol. Biochem.* 22, 65–68.
- Stuart Chapin III, F., Moilanen, L., Kielland, K., 1993. Preferential use of organic nitrogen for growth by a non-mycorrhizal arctic sedge. *Nature* 361, 150–153.
- Tipping, E., 1998. Modelling the properties and behavior of dissolved organic matter in soils. *Mitt. Dtsch. Bodenkdl. Ges.* 87, 237–252.
- Tipping, E., Woof, C., Rigg, E., Harrison, F., Inneson, P., Taylor, K., Benham, D., Poskitt, J., Rowland, A.P., Bol, R., Harkness, D.D., 1999. Climatic influences on the leaching of dissolved organic matter from upland UK moorland soils, investigated by a field manipulation experiment. *Environ. Int.* 25, 83–95.
- Tuitilla, E.-S., Komulainen, V.-M., Vasander, H., Laine, J., 1999. Restored cut-away peatland as a sink for atmospheric CO₂. *Oecologia* 120, 563–574.
- Waddington, J.M., Price, J., 2000. Effect of peatland drainage, harvesting, and restoration on atmospheric water and carbon exchange. *Phys. Geogr.* 21, 433–451.
- Waddington, J.M., Warner, K.D., 2001. Atmospheric CO₂ sequestration in restored mined peatlands. *Écoscience* 8, 359–368.
- Waddington, J.M., Warner, K.D., Kennedy, G.W., 2002. Cutover peatlands: a persistent source of atmospheric CO₂. *Glob. Biogeochem. Cycles* 16, 2-1–2-7.
- Zech, W., Guggenberger, G., 1996. Organic matter dynamics in forest soils of temperate and tropical ecosystems. In: Piccolo, A. (Ed.), *Humic Substances in Terrestrial Ecosystems*. Elsevier, Amsterdam, pp. 100–170.
- Zsolnay, A., 1996. Dissolved humus in soil waters. In: Piccolo, A. (Ed.), *Humic Substances in Terrestrial Ecosystems*. Elsevier, Amsterdam, pp. 171–223.
- Zsolnay, A., Steindl, H., 1991. Geovariability and biodegradability of the water-extractable organic material in an agricultural soil. *Soil Biol. Biochem.* 23, 45–50.
- Zsolnay, A., Baigar, E., Jimenez, M., Steinweg, B., Saccomandi, F., 1999. Differentiating with fluorescence spectroscopy the sources of dissolved organic matter in soils subjected to drying. *Chemosphere* 38, 45–50.