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Dissolved organic carbon dynamics in the peat–streamwater interface

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Abstract. A series of experiments were conducted to address the fate of dissolved organic carbon (DOC) in the peat–stream interface zone linking a minerotrophic poor fen and an ombrotrophic mire with surrounding stream water in the drainage area of Lake Örträsket in northern Sweden. Transport and mineralisation of DOC were quantified in peat–stream interface cores in response to variations in pore water velocity, DOC concentration and the molecular size and source of DOC. Mineralisation and CH_4 production were positively correlated with pore water velocity at rates between 0.08 and 0.20 cm h^{-1} and negatively correlated at rates between 0.20 and 0.40 cm h^{-1}. The DOC concentration of the effluent from the peat cores was independent of the pore water velocity but proportional to the DOC concentration of the source water. Higher concentrations of DOC were exported from than imported to the peat cores, and the cores exported DOC molecules of smaller average molecular size than received. Carbon mineralisation in the peat, assessed in a static system, was independent of the concentration of DOC. DOC with a nominal cutoff at 100 Da was mineralised faster by streamwater bacteria than DOC dialysed with a cutoff at 3500 Da, and their mineralisation rate was positively correlated with the DOC concentration. Streamwater bacteria mineralised streamwater DOC at a lower rate than the peat–stream interface zone pore water DOC. The pattern of velocity dependence of mineralisation was the same for both sources of peat DOC but the mineralisation rates, average molecular size, and bioavailability of DOC were different, emphasising the importance of the compositional heterogeneity of the peat–stream interface zone for the DOC budget of streamwater.

Introduction

Allochthonous terrestrial organic matter and macrophytic aquatic plants of wetlands and littoral communities are considered to be the main sources of dissolved organic carbon (DOC) to streams in upland and wetland areas, exceeding the contribution of phytoplankton by several folds to several orders of magnitude (Wetzel 1992; Hope et al. 1997; Schiff et al. 1997; Aitkenhead et al. 1999). Two pools of DOC have been identified in upland streams (Schiff et al. 1997). One, which is often greater than 50%, is derived from recently fixed, younger and more labile DOC, which has been leached from the A horizon or litter layer of soil and peatlands via shallow flow paths. Discharging groundwater, with low ^{14}C content (old DOC) and a low proportion of labile functional groups, is the source of the second pool.

Hydrological links between groundwater and surface water are through upwelling and downwelling areas (Vaux 1968) in the hyporheic zone, which is

characterised by high metabolic activity (Grimm and Fischer 1984; Pusch 1996) and by its function as a source or sink for DOC depending on discharge of groundwater, DOC concentration, and biological activity (Findlay et al. 1993; Hornberger et al. 1994; Brunke and Gonser 1997). The zone adjacent to streams in peatlands (here defined as the peat–stream interface zone) shares some characteristics with the hyporheic zone. It is a permanently dark habitat in hydrological contact with both shallow groundwater and surface water (Brunke and Gonser 1997). DOC transported to/from peatlands may be immobilised to a large extent in this zone, as is the case in hyporheic habitats, where 45–80% of DOC can be immobilised by biotic and abiotic processes (Wallis et al. 1981; Ford and Naiman 1989; Fiebig 1995).

Water and organic carbon are transferred in both directions between peatlands and groundwaters in boreal systems (Siegel and Glaser 1987; Charman et al. 1994). Mobile peat DOC can result from fermentation of sedimentary organic matter in conjunction with methane generation and release of organic acids as intermediate products (Aravena and Wassenaar 1993), or from oxidation of soil organic matter in the upper aerobic part of the peat profile (Palmer et al. 2001). Palmer et al. (2001) used ^{14}C analyses to show that pore water DOC in peat was significantly younger than the peat OC itself. The recent origin of pore water DOC was suggested to be near-surface peat sources, and the presence of young DOC in adjacent streamwater was traced to pore water DOC moving down the peat profile.

The transport of DOC from peatland to surface water is a quantitatively important process on a watershed scale (Dillon and Molot 1997), which has been a point of departure for a recent discussion on the explanation of long-term trends of DOC export in a global warming context (Freeman et al. 2001; Evans et al. 2002; Tranvik and Jansson 2002). Potential large-scale contributions of peatlands as a DOC source for heterotrophic food webs in streams inspired this research. The goals were to elucidate relationships between mineralisation of DOC in the peat–stream interface zone and three environmental factors known to vary spatially and temporally in a peat environment. The first factor was pore water velocity, which may vary within shallow and deep subsurface zones in peatlands (Quinton et al. 2000) and proposed to have a major influence on microbial and biogeochemical processes in the hyporheic zone (Findlay 1995). In general, lower pore water velocity is positively (Stepanauskas et al. 1996; Willems et al. 1997) and higher pore water velocity negatively (Kelsey and Alexander 1995) correlated with DOC degradation per unit time. The sign of the correlation depends on the size of some other variables, such as residence time of DOC, suspended microbial biomass (Palazzi et al. 1999), the thickness of the mass transfer boundary layer (De Beer et al. 1996), and concentration of DOC (Pignatello and Xing 1996). We hypothesised that the correlation between pore water velocity and mineralisation of DOC was dependent on the density of suspended biomass and the concentration of DOC. Because redox conditions in peat vary (Clymo 1992), saturated and limited oxygen conditions were used to test the hypothesis.

The second factor was the concentration and bioavailability of DOC. Several observations (Bridgham and Richardsson 1992; Schmidt et al. 2000) suggest that

peat microflora activity is limited by the availability of labile DOC. Therefore, we tested peat DOC mineralisation by peat and stream microflora in response to different DOC concentrations. We also tested the mineralisation of peat DOC with a molecular weight above 3500 D (MW > 3500) versus DOC with a molecular weight above 100 D (MW > 100) by the peat microflora. We hypothesised that the peat-stream interface zone would be a source of low molecular weight DOC for streamwater as a result of preferential mineralisation of high molecular weight DOC (Fiebig and Lock 1991; Amon and Benner 1996).

Finally, the third factor we compared was the bioavailability of the peat DOC with that of streamwater for streamwater bacteria. The main assumption was that peat DOC would sustain faster mineralisation rates due to its younger oxidation age compared with streamwater DOC derived from a mixture of sources, including older DOC from deeper groundwater (Schiff et al. 1997). In addition, we tested whether mineralisation by streamwater bacteria of MW > 3500 and MW > 100 DOC from the same sources would conform to the size reactivity continuum model (Amon and Benner 1996), in which organic matter continuously becomes less bioavailable and smaller in size during decomposition.

The work was an attempt to quantitatively integrate hydrological, biogeochemical, and microbial processes by addressing interactions between pore water velocity and transport and mineralisation of DOC. A special effort was made to use ranges of velocity and DOC concentration that were sufficiently large to represent field scale variability such that correlations found at the laboratory scale would be useful in models predicting transport and fate of DOC at the field scale. To account for heterogeneity in other characteristics of the peat hyporheic zone as a source of DOC for streamwater, we tested the relationships in three adjoining peat cores from two contrasting peatlands, the minerotrophic fen Skarda and the ombrotrophic mire Östra Björntjärn, in the same river system.

Materials and methods

Study area

Lake Örträsket is a large (7 km^2) humic lake (DOM 813 $mg\,l^{-1}$) with two major inlets, River Vargån (DOM 8–40 $mg\,l^{-1}$) and River Örån (DOM 5–30 $mg\,l^{-1}$), and one major outlet, River Öre. The drainage area (2174 km^2) is mainly covered by coniferous forests and mires (Jansson et al. 1996) with granite and gneiss as dominant bedrock and negligible anthropogenic influence on water quality. One sampling site (Skarda, 64°13′N, 18°49′E) is a small (15 ha) *Sphagnum* sp. and *Carex* sp. dominated minerotrophic poor fen located along a small river, Skardaån, which is a tributary to River Örån. Shallow groundwater supplies the fen with enough nutrients (Table 1) so that primary production is in equilibrium with decomposition, and no net accumulation of carbon takes place in the system. The other sampling site (Ö. Björntjärn, 64°08′ N, 18°49′E) is located in a larger (30–50 ha) complex of poor fens draining into three small lakes (Björntjärnarna) that

Table 1. Physiochemical properties of filtered (0.22 µm Millipore GS filter) peat pore water from Skarda and Östra Björntjärn. The elemental analysis was made by Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Perkin Elmer, Optima 3000 DV). The standards were atomic spectroscopy standards from Perkin Elmer, SPEX, Accustandard, and Merck. The instrument was calibrated with a mixed multi-component standard at three concentrations within a factor of 50, and the calibrations were controlled with independent standards. The measurements of nitrate, ammonium, and phosphate were made with a Technicon Autoanalyzer II flow injection analyser (FIA). Average and standard error (SE) of three replicates are shown.

	Skarda		Ö. Björntjärn	
	Average	SE	Average	SE
Porosity (%)	72	11	82	14
pH	6.1	0.1	4.4	0.8
Conductivity $\mu S\,cm^{-1}$)	59.6	1.8	39.1	5.5
DOC ($mg\,l^{-1}$)	20.7	2.3	44.7	13.6
K ($mg\,l^{-1}$)	3.0	1.4	0.53	0.2
Ca ($mg\,l^{-1}$)	3.2	0.4	1.4	0.03
Na ($mg\,l^{-1}$)	5.7	2.4	1.8	0.3
Total – P ($mg\,l^{-1}$)	0.2	0.1	0.8	0.4
S ($mg\,l^{-1}$)	1.8	0.6	0.8	0.1
Al ($mg\,l^{-1}$)	0.2	0.03	0.1	0.01
Fe ($mg\,l^{-1}$)	0.6	0.3	0.5	0.2
Mn ($mg\,l^{-1}$)	0.05	0.01	0.0	0.0
Si ($mg\,l^{-1}$)	1.1	0.3	1.2	0.5
Mg ($mg\,l^{-1}$)	0.5	0.1	0.3	0.05
Cr, Cu, Ni, Pb, Zn, Hg ($mg\,l^{-1}$)	0.5	0.2	0.1	0.1
PO_4-P ($\mu g\,l^{-1}$)	82	21	10	3.2
NO_3-N ($\mu g\,l^{-1}$)	110	33	28	5.1
NH_4-N ($\mu g\,l^{-1}$)	84	17	43	29

ultimately drain into Lake Örträsket. The fen consists of ombrotrophic hummock strings dominated by *Sphagnum acotifolium* sp. and *Calluna sp.* The rate of decomposition is slow mainly because of poor nutrient conditions (Table 1), but also because of antimicrobial properties of the Sphagnum mosses. The rate of plant production exceeds the rate of structural carbon decomposition and the system has a net accumulation of carbon (Clymo 1992).

Sampling

The sampling was carried out on 19–23 October 1998, following the first heavy snowfall of the season. Three peat cores were collected less than 2 m apart in the zone adjacent to Skardaån and a brook draining the mire at Ö. Björntjärn (defined as the peat–stream interface zone). Litter and peat was removed to a depth of 40–60 cm less than 1 m from the water's edge until the water saturated peat in the catotelm was uncovered. The peat cores were collected using a stainless steel

cylindrical corer (10 cm diameter) with a serrated cutting edge that was gently cutting out the peat core as it was moved into the cylinder. A sufficient quantity of the surrounding peat was then cut out to release the vacuum and lift the cylinder and the core to the surface.

The peat core (>20 cm in length) was transferred to a 10 cm diameter PVC tube and tightly sealed with two black plastic bags. The cores were kept outdoors (<5 °C) for two days until transported to the laboratory and stored at −15 °C until the experiment commenced (3 months later). The storage conditions represented natural conditions since peatlands in northern Sweden are frozen for months each year. Several studies have shown that microbial populations in frozen peat are active at temperatures well below −10 °C (Panikov 1999). Seventy litres of water from each site were collected from the excavated pits. Stream water was also collected at each site. The water was filtered (Whatman GF/F) and stored at 4 °C until used in the experiments.

Continuous flow experiment

The relationship between pore water velocity and carbon mineralisation in the peat cores was examined in a continuous flow column experiment. A 5 cm thick segment was removed with a band saw from each of six frozen peat cores (three from Skarda and three from Ö. Björntjärn) at 15 cm depth. The frozen core segments were placed in PVC columns with an inner height of 5 cm and an inner diameter of 10 cm. The columns were sealed at the ends with sintered plastic plates (100 µm pore size) milled into PVC end plates with a short pipe in the middle for tubing connections. The end plate was attached to the column with brass bolts and secured with brass wing nuts. The columns were connected to a continuous flow system as shown in Figure 1.

Filtered (Whatman GF/F) peat water from Skarda and Ö. Björntjärn was used as feed solution and kept in 10 l flasks placed on magnetic stirrers. The flasks were connected by 1 mm i.d. Teflon tubings to a peristaltic pump (Ismatec MV) with 0.75 mm i.d. Teflon tubing. The pumps were placed 30 cm below the feed solution to maintain a sufficient pressure head for bubble free feed delivery. The pump tubings were connected with Teflon tubings to the bottom end plate of the columns. The top end plate of the column was connected with Teflon tubings to a 3 mm i.d., 50 mm long glass tube inserted and sealed in a rubber stopper in a 500 ml glass bottle. A septum (HP 4 mm solsept) for gas sampling was placed in a pre-bored hole in the rubber stopper and sealed with silicone. All other connections in the set-up were sealed with silicone, and the whole system remained gas tight for the duration of the experiment. The columns were maintained by pumping feed water from bottom to top at 0.08–0.40 cm h^{-I}, which is within the range of hydraulic conductivities commonly found in peat groundwater (Chason and Siegel 1986; Quinton et al. 2000). After the porosity of the cores had been determined, the conditions for the experiments were first oxygen limited and then oxygen saturated. All six columns were run in parallel at 15 °C in a temperature-controlled room,

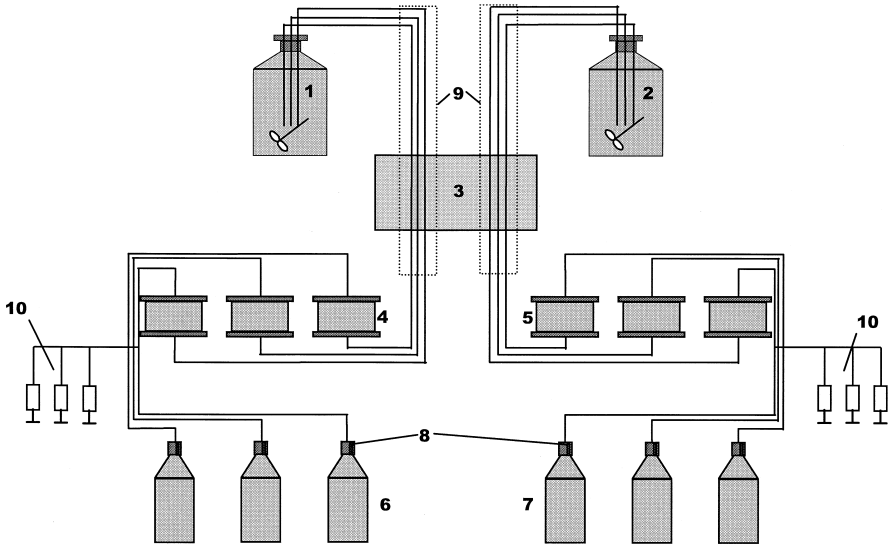

Figure 1. Schematic drawing of the design of the continuous flow experiment. (1) Feed water from Skarda (2) Feed water from Östra Björntjärn (3) Peristaltic pump (4) PVC columns with hyporheic peat cores from Skarda (5) PVC columns with hyporheic peat cores from Ö. Björntjärn (6) and (7) Collection bottles for effluent water from the cores (8) Septa for gas sampling (9) PVC tubings filled with N_2 and enclosing Teflon tubings in the oxygen limited experiment (10) 50 ml collection syringes.

which was also used for subsequent batch experiments. This temperature is representative for those peatlands during summer.

The peat porosity was calculated from a breakthrough curve of $^3H_20$ (25 mCi ml^{-1}) added to the feed water (final activity of 5000 dpm ml^{-1}) that was pumped through the columns at 10 ml h^{-1}. The ^3H activity was quantified by manually collecting 1 ml of effluent water, mixing it with 4 ml of Beckman ReadySafe liquid scintillation cocktail, and counting on a Beckman LS 6500 liquid scintillator. Pore water velocity was calculated from the weight of the collected water and the time between water collections.

To remove residues of oxygen from the peat columns during the oxygen limited experiment, the feed solution was flushed with N_2 for 2 h each day. This left the feed solution with 0.1–0.5% O_2 saturation. The teflon tubings upstream of the columns were enclosed in 10 mm i.d. PVC tubings filled with N_2 and sealed at both ends with silicone. The peat columns were left for 4 days with feed solution saturated with N_2 and both tubing connections closed. During the oxygen saturated experiment, the N_2 filled PVC tubings were removed and the feed solution was flushed with O_2 for 2 h each day to give an oxygen saturation of 98.5–99.5%. To create aerobic conditions in the peat, oxygen saturated water was pumped through the columns at 0.2 cm h^{-1} for 4 days before the measurements commenced.

At each flow rate, approximately 700 ml (two pore volumes) of feed solution were pumped through the core and discarded to ensure that the entire pore volume

was replaced. The density of bacteria in the effluent during the replacement period was measured by acridine orange staining and enumeration with an epifluorescence microscope (Zeiss Axiolab HBO50). The cell density stabilised in the effluent before the replacement period ended, indicating that the system was in a steady state. Portions of 100–250 ml of effluent were collected in 500 ml bottles from each column at each pore water velocity. To eliminate microbial activity, sodium azide was added to the empty bottles before each sampling to give a final concentration of 0.5% in the collected effluent. The bottles were prepared by flushing with N_2 to remove all CO_2 from the headspace.

Ten millilitres of headspace were withdrawn from the collection bottles through the septum in the rubber stopper and injected through a 1 ml sample loop of a Shimadzu 17A gas chromatograph for analysis of CO_2 and CH_4. The GC was equipped with a flame ionisation detector and a Porapak Q column. Injection/detection and oven temperatures were 140 °C and 70 °C, respectively, and helium was used as a carrier gas at 40 ml min^{-1}. The injected gas sample passed through a Shimadzu methaniser, which reduced CO_2 to CH_4. Dissolved CO_2 and CH_4 in the effluent solution was quantified by adding 5 ml to septum sealed 20 ml serum bottles, which had been flushed with N_2 after sealing to remove CO_2 in the headspace. The pH of the solution was lowered to <2 with 2 M HCl and the bottles were thoroughly shaken by hand for 1 min to transfer CO_2 and CH_4 to the gas phase. Five millilitres of the gas phase were withdrawn with a syringe and analysed for CO_2 and CH_4 as described before. The CO_2 and CH_4 concentrations were measured in the feed solution in the same way.

The rate of CO_2 production was calculated at each pore water velocity as:

$$(CO_2)_{prod} = \frac{\{([CO_2]_{hspbottle} \times V_{hspbottle}) + ([CO_2]_{hspsera} \times V_{hspsera} \times \\ \times (V_{effluent}/0.005))\} - \{[CO_2]_{feed} \times V_{hspsera} \times (V_{effluent}/0.005)\}}{t \times w_{peat}} \quad (1)$$

where $(CO_2)_{prod}$ is the rate of CO_2 production (mg CO_2 h^{-1} g $peat^{-1}$), V is volume (l), t is the time (h) elapsed during collection of effluent solution and w_{peat} is the dry weight (g) of the peat cores. The subscripts $_{hspbottle}$, $_{hspsera}$ and $_{effluent}$ denote the headspace of the collection bottle and the serum bottle, and the effluent solution, respectively. The rate of CH_4 production was calculated in the same way.

At each velocity, the DOC concentration, average DOC molecular size, pH, electrolytic conductivity, oxygen saturation (using a WTW Oxi 323 microprocessor oxi-meter connected to a WTW Cellox 325 oxygen sensor), and cell density of the effluent were measured in aliquots from a separate collection syringe that was filled by the pressure of the water flow, thus ensuring that there was no headspace. The collection syringe was placed upstream of the collection bottle. Water from the same syringe was used in the bioavailability assay described below. Subsamples for DOC measurements were filtered (Millipore 0.22 µm) and quantified by a Shimadzu TOC-500 total carbon analyser. At least three replicate injections were made of each sample, giving a standard deviation of $< 2\%$. The molecular weight

and degree of aromaticity of DOC was calculated from Chin et al. (1994):

$$M_{\mathrm{w}} = \frac{3.99 \times (\mathrm{UVA}_{280}/\mathrm{DOC} \times l) + 490}{1000} \tag{2}$$

$$\text{Aromaticity}(\%) = 0.05 \times \frac{\mathrm{UVA}_{280}}{\mathrm{DOC} \times l} + 6.74 \tag{3}$$

where M_{w} is the average molecular weight (kilo Daltons, kDa), UVA_{280} is the ultraviolet absorption at 280 nm (measured on a Pharmacia Biotech Ultrospec 3000 spectrophotometer using a 1 cm analysis cell), DOC is the dissolved organic carbon concentration ($\mathrm{mol\,l^{-1}}$) and l is the measurement cell path length (cm).

Bacterial cell density was measured by flow cytometry (del Giorgio et al. 1996). Fifty microlitres SYTO 13 stain (50 µM, Molecular Probes) and 50 µl fluoresbrite carboxy YG microspheres (1.58 µm diameter, ca. $3\times10^5\,\mathrm{ml^{-1}}$ – quantified by epifluorescence microscopy) were added to 1 ml of filtered (Millipore 0.8 µm) effluent water. The resulting suspension was counted in a Beckton Dickinson FacSort flow cytometer at a sample water velocity of $12\,\mu\mathrm{l\,min^{-1}}$. The CellQuest 1.2 software was used to control the flow cytometer and calculate the cell density. Bacterial cells and microspheres were separated in a log–log scattergram of green fluorescence intensity (FL1) and side light scattering (SSC) with voltages for these parameters set to 560 and 400, respectively. The samples were run until 10,000 events had occurred or until 1 min had elapsed. The cell density in each sample was calculated by using the microspheres as an internal standard.

Batch experiment 1 – DOC mineralisation in peat

This experiment was designed to assess the influence of concentration and molecular size of DOC on carbon mineralisation in peat. Filter sterilised (0.22 µm Millipore GS filter) water from the excavated pit (peat water) was vacuum centrifuged in a Savant SpeedVac SS32 system with the concentrator enabled and the drying rate set to high. Vacuum centrifugation was always terminated when less than 0.5 ml remained in the centrifuge tubes but before reaching dryness. The resulting concentrate had $850\,\mathrm{mg\,l^{-1}}$ (Skarda) and $1180\,\mathrm{mg\,l^{-1}}$ (Ö. Björntjärn) of DOC. The concentrate was added to 10 mm wide dialysis bags (Spectra/Por cellulose ester membrane) with a cutoff at 3500 or 100 Da and dialysed in 10 l flasks filled with ultra pure Milli-Q water under continuous stirring with a magnetic bar. As long as the electrolytic conductivity of the dialysate continued to decrease in response to the daily replacement of the Milli-Q water, the concentrate was transferred to new dialysis bags to avoid clogging of the membrane pores. This procedure was repeated until no further changes in conductivity were observed.

The ion depleted DOC concentrates (MW > 100 and MW > 3500) were added to filter sterilised (0.22 µm Millipore GS filter) artificial peat water previously prepared based on the elemental (ICP-ES) and ion (FIA) composition of the peat water (Table 1). As a result of the preparations, 10 solutions from each field site were

obtained with the same elemental and inorganic ion composition but with DOC concentrations varying between 10, 20, 30, 40 and 50 mg l^{-1} and molecular sizes of >100 Da and >3500 Da. Any differences in response to treatments of these two DOC fraction would results from the presence of 100–3500 MW DOC in the >100 MW fraction. Each of the solutions was added to a 200 ml flask placed 15 cm above a PVC tube (height 15 cm, inner diameter 1.2 cm) and connected to it with 1 mm i.d. Teflon tubing. The PVC tube contained a peat core that was thawed and then stored at 15 °C 1 week prior to pore water replacement to ensure that the initial burst of CO_2 release often observed in thawed peat would not affect the bioassay. Three pore volumes of interstitial peat water, corresponding to 192 ml, were then replaced with a DOC solution at 15 ml h^{-1}. A breakthrough curve of $^3H_20$ (25 mCi ml^{-1}, final activity of 4000 dpm ml^{-1} in feed water) was established to ensure that three pore volumes were sufficient to replace all of the interstitial water. The peat cores with replaced pore water were stored at 2 °C until the bioassay started.

Portions of 5–7 g wet weight of peat with replaced pore water were added to 300 ml glass jars with tight fitting lids. More DOC solution was added to obtain a gravimetric moisture content of 1250% of dry weight. Four replicates of each DOC concentration and molecular size range were prepared. The jars were placed in a constant temperature room at 15 °C in large covered plastic basins. Tap water was added to the bottom of the basins to maintain a high humidity and reduce water evaporation from the samples. CO_2 production in the peat was measured after 2, 4, and 8 days of incubation. Each time a measurement was made, a 12 mm diameter butyl septum was inserted in a hole in the lid, and 5 ml of headspace was withdrawn with a syringe after 20 min, 6, and 14 h. CO_2 was analysed by gas chromatography as described above. Before the septum was installed, the headspace was flushed with synthetic air containing 350 ppm CO_2. The slope of the regression of the change in CO_2 concentration with time was mostly linear, and the linear slope was used to calculate CO_2 production rate (mg CO_2 g^{-1} h^{-1}). All measurements with $r^2 < 0.9$ were considered erroneous and excluded.

Batch experiment 2 – bioavailability of peat and stream DOC

The purpose of this experiment was to assess differences in bioavailability between peat DOC (Skarda and Ö. Björntjärn) and stream DOC (river Skardaån). Peat water collected at Skarda and Ö. Björntjärn and stream water collected in river Skardaån was filter sterilised (0.22 µm Millipore GS filter) and concentrated and dialysed in DOC fractions with nominal cutoff at 100 and 3500 Da. The concentrates were mixed with the artificial stream water prepared as described before, with the exception of the concentrations of NO_3^-, NH_4^+ and PO_4^{3-}, that were three times as high as the natural concentrations to avoid nutrient limitation in the bioassays. Aliquots of the >100 and >3500 Da DOC concentrates were added to 80 ml of artificial river Skardaån water in 100 ml serum bottles to give final concentrations of 0, 15, 30, 45, 60 and 75 mg l^{-1} of DOC. The >3500 Da treatment of river

Skardaån was lost by accident. Water from Skardaån (initial bacterial density 0.8×10^6 cells ml^{-1}) was filtered (0.6 µm Millipore cellulose ester filters) to remove bacterivores and then centrifuged at $8000 \times g$ at 1–4 °C for 15 min in a Sorvall RC 5B Plus centrifuge (DuPont, Newtown). The cells were resuspended in filtered (0.22 µm Millipore GS) river water, centrifuged once more and resuspended in a small volume of filter sterilised river water. An aliquot of the suspension was inoculated to the serum bottles at a density of 2×10^6 cells ml^{-1}. This level was approximately twice as high as the *in situ* density and sufficiently high to respire detectable CO_2 amounts during the short term incubations. The headspace was flushed with synthetic air containing 350 ppm CO_2 before the incubation started after which the bottles were sealed with rubber septa and aluminium caps. The bottles were gently shaken (3 rpm) on a Sorvall shaker during incubation in darkness at 15 °C. After 12, 48, and 84 h, three bottles (replicates) of each DOC concentration, DOC size and origin were sampled. Each time a sample was taken, HCl was injected through the septum in the bottle to acidify the solution ($pH < 2$) and transfer the CO_2 to the headspace. Headspace samples were then withdrawn and injected on the GC. As with the peat batch incubation, the slope of the linear regression of the change in CO_2 concentration with time was mostly linear and used to calculate the CO_2 production rate (mg CO_2 g^{-1} h^{-1}).

Batch experiment 3 – carbon utilisation in effluent water

Finally, we compared respiration and total carbon utilisation in effluent water from peat cores at varying pore water velocities. Aliquots of effluent water from the peat cores in the continuous flow experiment were sampled upstream of the collection flasks except for the effluent at 0.4 cm h^{-1} in Skarda which was lost due to mishandling. After filter sterilising (0.22 µm Millipore GS filter) the effluent sample, 30 ml from each flow velocity were added in triplicate to 50 ml serum bottles. Inoculates from the river Skardaån were prepared as described before and added to the bottles to obtain an approximate density of 0.1×10^6 cells ml^{-1}. The bottles were incubated and sampled after 12, 48, and 84 h as in the second batch experiment, except that a 3.5 ml aliquot of the water was taken before acidification to determine bacterial cell density and biovolume.

The cell density was measured at the beginning and end of an assay by flow cytometry. Two milliltres of water was stained with acridine orange to determine the average bacterial cell size. The stained water was filtered through a 0.2 µm polycarbonate filter (Poretics), and the filters were viewed with an epifluoroescence microscope (Zeiss Axiolab) connected to video scanning equipment. The scanned images were transferred to a computer, and the cell size was determined using an image analysis program (IPLab Spectrum(tm), Signal Analytics Corporation). One filter was analysed for each flow velocity, and the average cell volume was found to be similar (0.28 μm^3, CV = 10%). Bacterial biomass was calculated by assuming that the carbon content of the cells was 0.308 pg μm^{-3} (Fry 1988) which is within the range (0.106 – 0.720 pg μm^{-3}) of a number of volume to carbon conversion

factors found for acridine orange stained bacteria (Posch et al. 2001). Bacterial secondary production in each bottle (BP, $\mu g\,C\,l\,h^{-1}$) was calculated as:

$$BP = \frac{BB - BB_0}{t} \tag{4}$$

where BB is the final bacterial biomass ($\mu g\,C\,l^{-1}$), BB_0 is the initial bacterial biomass and t is time (h). Bacterial respiration (BR) was measured and calculated as in the second batch experiment. Total bacterial carbon utilisation (A) was calculated at each flow velocity as:

$$A = BP + BR \tag{5}$$

and the bacterial growth efficiency (BGE) was calculated as:

$$BGE = \frac{BP}{BP + BR} \tag{6}$$

Statistical analysis

Differences between sites and oxygen treatments in the column experiments were tested with repeated measures ANOVA, using pore water velocity as a fixed treatment effect and columns as a random replicated factor. Repeated measures polynomial contrasts were used to test for linear or non-linear relationships between pore water velocity and carbon gas production, pore water cell density, effluent DOC concentration and DOC molecular weight. Repeated measures ANOVA was also used to test for changes in peat batch respiration over time. One-way ANOVA was used to test for differences between treatments and sites in the batch experiments. Linear contrasts were used to test for effects of specific DOC concentrations in the peat batch experiment, while linear regression was used to test for relationships between treatments and mineralisation rates in the water batch experiments.

Results

Continuous flow experiment

Mineralisation rate in the peat cores varied in a non-linear way with pore water velocity, regardless of the source of the peat and the O_2 concentration (Figure 2). Maximum mineralisation was obtained for intermediate velocities, at 0.16–0.24 $cm\,h^{-1}$, for both oxygen saturated and oxygen limited conditions (Figure 2a and b). Methane production in peat cores from Skarda was related in a similar way to the pore water velocity, with a maximum at 0.16–0.24 $cm\,h^{-1}$ (Figure 2c and d). The mineralisation rates varied with the source of peat but were invariant with the O_2 concentration. The mineralisation rates in the Skarda peat were 2–15 times faster and the CH_4 production rates 10–100 times faster than in the Ö. Björntjärn

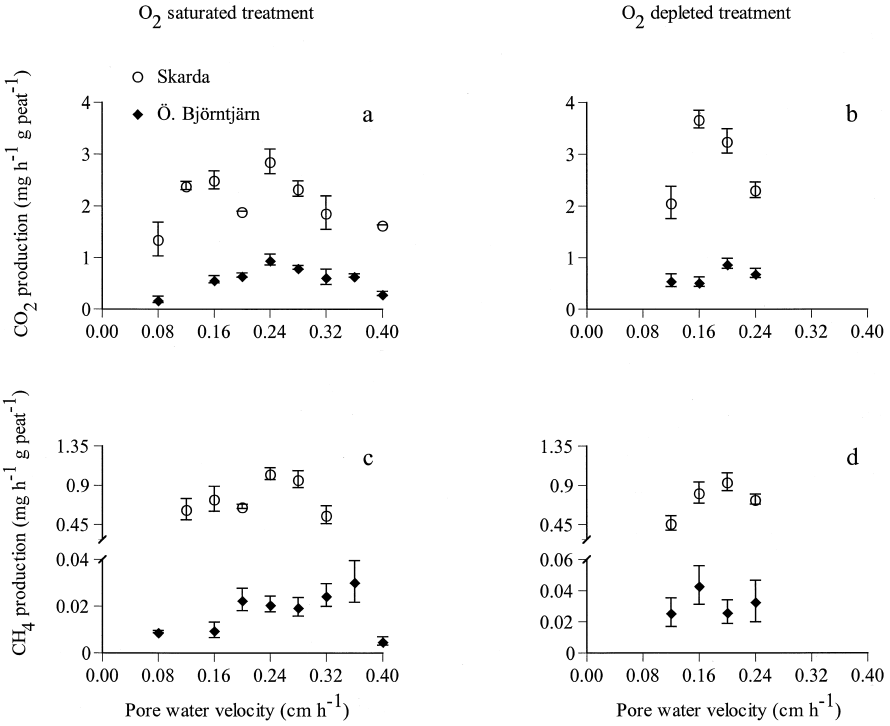

Figure 2. Respiration (a and b) and methane production (c and d) in hyporheic peat cores in response to velocity in O_2 saturated or depleted feed solution. Pore water velocity had a significant ($p < 0.05$) effect on respiration and methane production under oxygen saturated conditions (a, d) but only respiration was significantly affected by velocity under oxygen limited conditions ($p < 0.05$) (b and e). Respiration and methane production were greater in peat cores from Skarda compared to Östra Björntjärn ($p < 0.001$) but no differences were found between oxygen saturated and oxygen limited conditions ($p > 0.05$). Average and standard errors are shown.

peat. The same quantities of C were emitted as CO_2 and CH_4 from the Skarda peat, whereas one order of magnitude more C came from CO_2 compared with CH_4 in the Ö. Björntjärn peat.

The density of bacteria was significantly higher in the effluent water from the Skarda peat cores than from those taken at Ö. Björntjärn (Figure 3a). However, the differences in mineralisation and methane production rates between the peat sources were smaller respectively, larger when they were expressed on a per cell basis (Figure 3b and c). This indicates that aerobic metabolism of cells in the pore water of the Skarda peat was less active and the anaerobic metabolism was more active than in cells in the Ö. Björntjärn peat. Cell density in the effluent water was unaffected by the pore water velocity increase from 0.08 to 0.4 cm h^{-1}.

DOC concentrations of the effluent from peat cores were independent of the pore water velocities but proportional to the DOC concentration of the source water

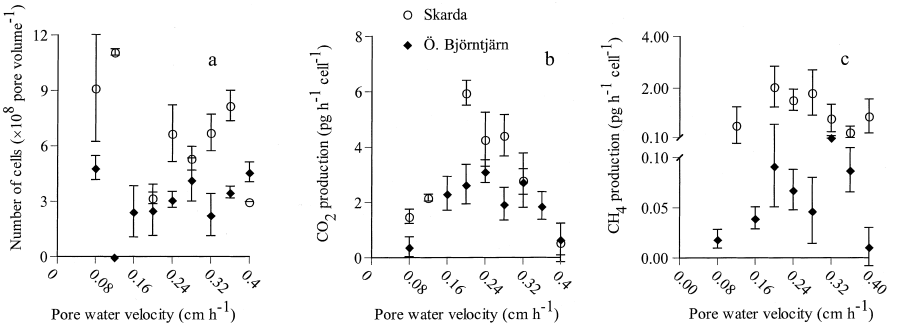

Figure 3. Bacterial density in effluent water from peat cores and cell averaged respiration and methane production in the cores in response to pore water velocity under oxygen saturated conditions. The cell density was not dependent on velocity but higher in the effluent from the peat cores of Skarda than in that of Östra Björntjärn ($p < 0.05$). The respiration per cell was affected in a linear manner by velocity in Skarda ($p < 0.05$) and in a non-linear manner ($p < 0.05$) by velocity in Ö. Björntjärn. The methane production varied in a non-linear manner with velocity in Skarda ($p < 0.05$) but not in Ö. Björntjärn. There was no significant difference in respiration between the sites (b) but a large difference in methane production $p < 0.01$ (c) Average and standard errors are shown.

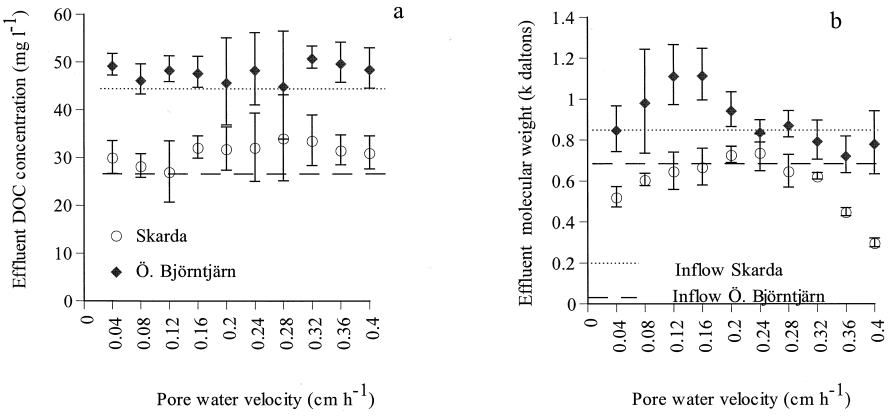

Figure 4. DOC concentrations (a) and average molecular size (b) in source (dotted and hatched line) and effluent water of the peat cores at different velocities. DOC concentrations were independent of velocity and significantly higher in Östra Björntjärn than in Skarda ($p < 0.001$). The average DOC molecular weight was significantly higher in Ö. Björntjärn than in Skarda ($p < 0.001$). Average and standard errors are shown.

(Figure 4a). The DOC concentrations in the effluent from both the Skarda and the Ö. Björntjärn cores were 0–10% higher than concentrations in the influent. Consequently, the net DOC export increased with the flow rate and was of similar size from both sources (Figure 5). The average molecular weight of DOC in the effluent water varied with pore water velocity and was lowest for the lowest and highest

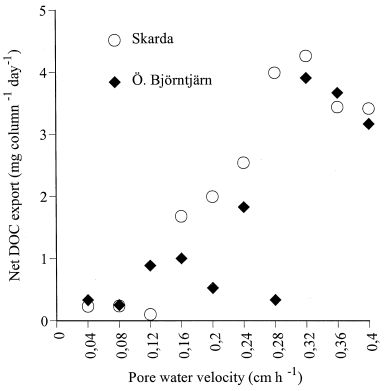

Figure 5. Net DOC export from the peat cores at different pore water velocities. Net DOC export was calculated as $(V \times C_{\text{outlet}}) - (V \times C_{\text{inlet}})$, where V is the volume of water transported through the column per day ($1\,\text{day}^{-1}$) and C is the concentration of DOC in the inlet and outlet water, respectively ($\text{mg}\,\text{l}^{-1}$). Average of three replicates is shown.

velocities (Figure 4b) where the cores exported smaller molecules than they received. The molecular size of DOC of the source and effluent water of Skarda was smaller than that of Ö. Björntjärn, so that molecular size and concentration were positively related to each other.

Batch experiment 1 – DOC mineralisation in peat

Carbon mineralisation in the peat samples was independent of the source of the peat and of the DOC concentration of the added water, except for the highest DOC concentration in Ö. Björntjärn (Figure 6). The mineralisation rate was higher for MW > 100 than MW > 3500 DOC in the Skarda peat (except for the last day). The MW > 100 DOC was mineralised at a higher rate at the beginning of the incubation than at the end.

Batch experiment 2 – bioavailability of peat and stream DOC

The mineralisation of the MW > 100 DOC from the peat core effluents and from the stream by the stream water bacteria was positively correlated with the DOC concentration, regardless of the source (Figure 7). The most bioavailable DOC was from the Ö. Björntjärn core effluent while stream DOC was the least bioavailable. MW > 100 DOC was more bioavailable than MW > 3500 DOC. However, the conversion of MW > 100 stream DOC to CO_2 was equal to or even less than that of the MW > 3500 peat DOC by the streamwater bacteria. The mineralisation rate normalised for DOC concentration ($\text{mg}\,CO_2\,\text{h}^{-1}$ $\text{mg}\,\text{DOC}^{-1}$) was negatively

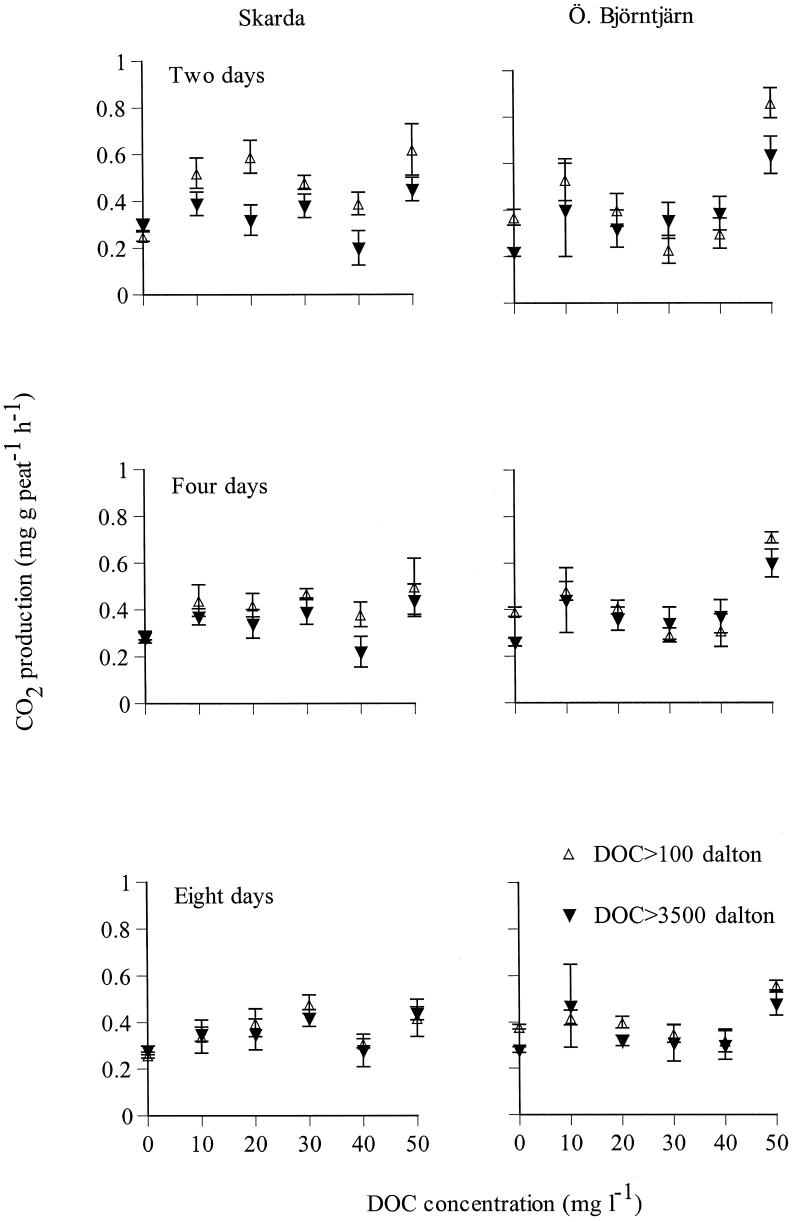

Figure 6. Rate of mineralisation in microcosms made from peat and hyporheic water with different concentrations and ranges of apparent molecular sizes of DOC and after incubation for 2, 4 and 8 days. The DOC concentration had no significant effect on the mineralisation rate in Skarda (one way ANOVA, $p > 0.05$) and a significant effect only at the highest DOC concentration in Ö. Björntjärn (Tukey test, $p < 0.05$). The mineralisation rate was greater with the MW > 100 compared with the MW > 3500 DOC after 2 and 4 days in Skarda ($p < 0.05$) and rate of mineralisation was lower after 8 days compared with 2 days for MW > 100 DOC in Skarda ($p < 0.05$). Average and standard errors are shown.

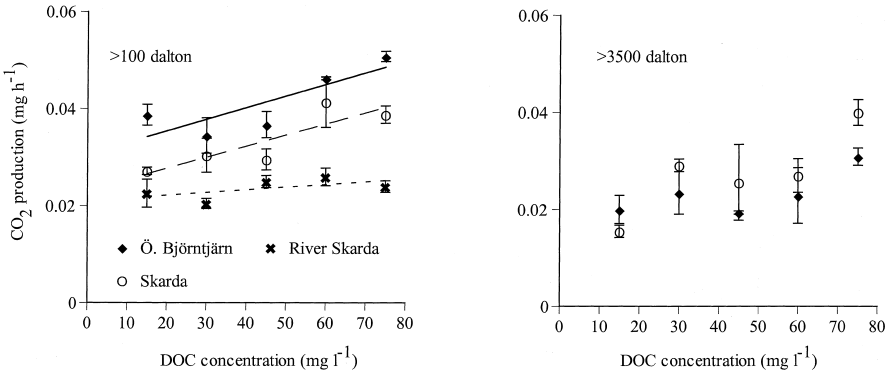

Figure 7. Rate of mineralisation by streamwater bacteria in response to concentrations of DOC isolated from the peat hyporheic zones and the river and added to artificial river water at two ranges of apparent molecular sizes. For the MW > 100 DOC, the mineralisation was significantly faster with Ö. Björntjärn DOC than with Skarda DOC ($p < 0.05$) and with Skarda DOC compared with river DOC ($p < 0.001$). The mineralisation rate was significantly (Skarda and River DOC: $p < 0.01$, Ö. Björntjärn DOC: $p < 0.05$) dependent on the DOC concentration (Ö. Björntjärn DOC, $r^2 = 0.68$; Skarda DOC, $r^2 = 0.75$; river DOC, $r^2 = 0.34$). There was no significant effect of the DOC concentration on the mineralisation for molecular sizes > 3500 Da. Finally, the mineralisation rate was faster with MW > 100 DOC compared to MW > 3500 DOC (Ö. Björntjärn $p < 0.01$, Skarda $p < 0.05$) Average and standard errors are shown.

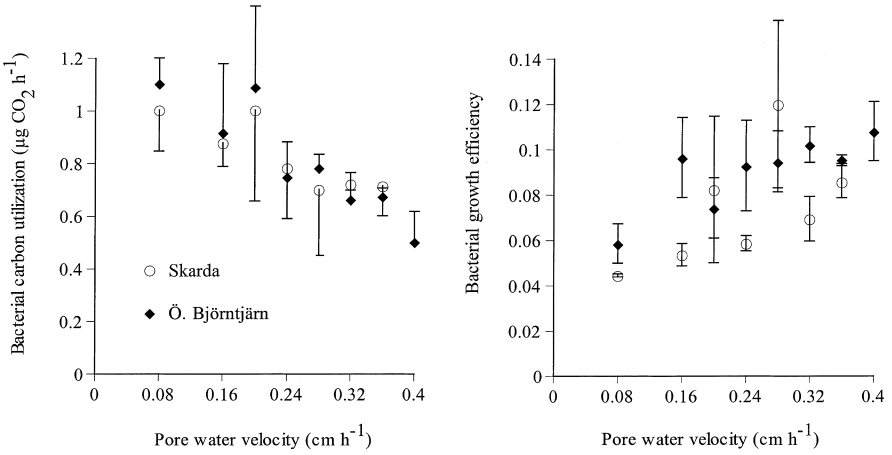

Figure 8. Bacterial carbon utilisation (*A*) and growth efficiency (BGE) with effluent DOC at various pore water velocities. The velocity had a significant effect on the utilisation of DOC from Skarda ($p < 0.05$, $r^2 = 0.32$). Average and standard errors are shown.

correlated with DOC concentration (Skarda, $R^2 = 0.85$; Östra Björntjärn $R^2 = 0.74$), suggesting that stream water bacteria were less efficient in using higher concentrations of DOC.

Table 2. Average values of oxygen, pH and conductivity at all pore water velocities in the source and effluent water of the oxygen saturated and oxygen limited columns. Values in parentheses are the standard errors.

	Skarda				Östra Björntjärn			
	Oxygen saturated		Oxygen limited		Oxygen saturated		Oxygen limited	
	In	Out	In	Out	In	Out	In	Out
O_2 (% saturation)	98 (3.2)	85 (12)	1.7 (2.0)	2.3 (3.1)	98 (3.5)	87 (16)	1.1 (1.2)	2.1 (0.8)
pH	6.4 (0.2)	6.1 (1.1)	6.3 (0.3)	5.8 (0.9)	4.4 (0.2)	4.1 (0.7)	4.4 (0.3)	3.9 (0.8)
Conductivity ($\mu S\,cm^{-1}$)	59 (2.1)	74 (12)	59 (1.8)	69 (10)	39 (2.4)	64 (8.5)	39 (2.0)	62 (9.9)

Batch experiment 3 – carbon utilisation in effluent water

Bacterial carbon utilisation (A) by the stream water bacteria in peat core effluent water was negatively correlated with pore water velocity, while growth efficiency was positively influenced (Figure 8). However, the large variation of the growth efficiency data made this relationship insignificant.

Discussion

The response of peat respiration to the pore water velocity in the continuous flow experiment supported our hypothesis and agreed to some extent with findings in other column studies, in which microbial activity was positively (Stepanauskas et al. 1996; Willems et al. 1997) or negatively (Kelsey and Alexander 1995; Langner et al. 1998; Brusseau et al. 1999) correlated with velocity. The work by Willems et al. (1997) is especially illuminating since they show that the sign of the correlation seems to depend on the magnitude of velocity, temperature, and porosity. High flow velocities often found in hyporheic gravel bed material tend to be positively correlated with biological activity. For instance, Fiebig (1995) used a laboratory experiment with sandy hyporheic cores to show that DOC immobilisation was proportional to groundwater discharge rate in upwelling areas of a small stream. Likewise, Baker et al. (2000) found that hyporheic sediment collected at peak discharge in a stream had about 30% higher respiration than sediment collected at base flow (1/100 of peak), and Battin (2002) showed that microbial activity in incubated streambed sediment was positively correlated with Darcian velocity of the site at which the sediment was collected.

Observations showing a negative correlation between DOC immobilisation and velocity were made at higher velocities than in our work, but Willems et al. (1997) and Stepanauskas et al. (1996) found a positive correlation between net DOC immobilisation and velocity between 0.15 and 3.4 $cm\,h^{-1}$. The change in sign of the correlation may occur when velocity exceeds a value at which the residence time of

organic molecules and suspended cells becomes shorter than required for membrane transport and enzymatic reactions in a cell. Beyond that limit, degradation and velocity will be negatively correlated because the residence time decreases with velocity, as suggested by Langer et al. (1998) and by the bioreactor theory (e.g., Harder et al. 1977).

The work by Willems et al. (1997) demonstrates the influence of porosity and temperature on the correlation between activity and velocity. Whereas the correlation is mainly negative at lower temperature (8 °C) and steeper and mainly positive at higher temperature (20 °C), it can be both positive and negative at 15 °C. Likewise, soils with higher porosity (80%) have a steeper and more extended range of positive correlation than soils with lower porosity (40–50%). The high porosity of our peat cores and those of Stepanauskas et al. (1996) (70–80%) compared with the soils used by Langner et al. (1998) and Brusseau et al. (1999) (30–40%) adds to the explanation of the differences in sign of the correlation between velocity and degradation.

Invariance of mineralisation and CH_4 production with oxygen conditions (Figure 2) was not expected from the generally acknowledged dependence of bacterial growth and activity of methanogens and heterotrophs on oxygen concentration (Harvey et al. 1995) or from the observations by Öquist and Sundh (1998) that CO_2 production was highest in oxic and CH_4 production highest in anoxic peat slurries. However, Bastviken et al. (2001) challenged this relationship. They found alike growth and activity in oxic and anoxic conditions in limnic systems and suggested that organic matter may be more bioavailable in an anoxic environment. The same similarities between oxic and anoxic mineralisation were found by Dauwe et al. (2001) and Kristensen et al. (1995) for marine sediments. Our results for the peat material may depend on the complexity of its pore system, in which pores that are disconnected from advective flow may store large amounts of CH_4 (Brown and Overend 1993), CO_2 and O_2 (Hoag and Price 1997) that can diffuse to the advective pores. This gas buffering system may provide small amounts of oxygen for aerobic metabolism even when the source water is kept oxygen free.

One of the suggested mechanisms for the relationship between respiration rate and pore water velocity, microbial density variations, could be sorted out because the number of cells in pore water was independent of velocity (Figure 3). A careful equilibration of the core system at each pore water velocity was performed to obtain steady state conditions, such that variations in total cell numbers would correspond with variations in suspended cell numbers. The suspended biomass carbon, calculated from data in Figure 3(a), an average cell volume of $0.28\ \mu m^{-3}$, and a cell carbon concentration of $0.31\ pg\ \mu m^{-3}$ (Fry 1988), accounted for only $1/20$ to $1/50$ of the CO_2 production (Figure 2). The remaining was due to cells associated with solid material or dead end pores. The highest velocity used in our experiment, $0.4\ cm\ h^{-1}$, was probably too low to cause shear effects in the peat material and below the velocity at which Palazzi et al. (2000) started to observe a decrease in effluent cell density with velocity. It was probably also too low to compress the hydrodynamic boundary layer sufficiently to enhance adsorption of cells, resulting in the kind of positive correlation between velocity and number of adsorbed cells possibly responsible for observations made by Kelsey and Alexander (1995).

A second suggested mechanism accounting for the association between respiration rate and pore water velocity, a positive correlation between pore water velocity and concentration of DOC, could also be ruled out because effluent DOC concentrations were independent of velocity (Figure 4a). However, net DOC export from the peat cores was positively correlated with pore water velocities, suggesting that catchment hydrology may have a great influence on DOC transport in streamwater. The third potential mechanism was the residence time, which was not tested explicitly and cannot be rejected as an explanation. The dual porosity nature of peat with inter-connected pores that actively transmit advective flow and pores that may become closed at low pore water velocity and act as a sink for the solute (Hoag and Price 1997), makes it especially sensitive to variations in pore water velocity. As velocities increased above $0.24\,\mathrm{cm\,h^{-1}}$ (Figure 2), the closed pores may have become less accessible, the effective residence time decreased and the total respiration rate became negatively correlated with the velocity.

Diffusion most likely limited degradation in the batch experiments with zero pore water velocity, and peat respiration in the batch experiments were $1/10$ of that in the continuous flow experiment (Figures 2 and 6) and $1/100$ times of that in Christensen et al. (1999). Diffusion limitation may be one of several reasons for the invariance of peat respiration with DOC concentration. The microbial preference often found for monomers, such as glucose, compared with more complex carbon sources, such as humic acid and leaf leachate (e.g., Magill and Aber 2000), was also evident in the peat batch bioassay, in which respiration in the Skarda peat was higher with $\mathrm{MW} > 100$ than $\mathrm{MW} > 3500$ DOC (Figure 6).

A potential limitation of the assay was an underdose of the isolated DOC. Between 0.9 and 4.4 mg of DOC were added to each jar. After 2 days, 19–24 mg CO_2 had been respired per gram of peat (Figure 6), corresponding to 26–33 mg C per jar. Even if the entire of added DOC were respired, the peat itself would have had to provide respiratory organic C during the bioassay to make the magnitude of respiration possible. This C contribution from the peat during the bioassay, for example, from the polysaccharide matrix of sorbed microorganisms (Freeman and Lock 1995) and from particulate organic matter (Brugger et al. 2001; Fischer et al. 2002), should account for respiration in the treatment without DOC added, which was often comparable to the bioassays with $\mathrm{MW} > 3500$ DOC added (Figure 6).

A comparison of the metabolism of DOC in the peat batch and water batch bioassays (Figures 6 and 7) revealed some of the described characteristics of the peat–stream interface zone. First, there was larger respiration of $\mathrm{MW} > 100$ DOC in comparison with $\mathrm{MW} > 3500$ DOC, regardless of the source of peat DOC. The characterisation of the peat DOC by the UVA_{280} measurements showed its aliphatic origin and relatively low average molecular size (0.4–1.2 kDa), similar to that found by Schindler and Krabbenhoft (1998) in hyporheic pore water. The dependence of respiration on molecular size of DOC may be related to this aliphatic characteristic.

Second was the correlation between DOC concentration and respiration for the streamwater bacteria (Figure 7). The carbon utilisation was uncoupled from the DOC concentration when the streamwater bacteria were assayed with effluent from the peat cores without nutrient amendment (Figure 8). Carbon utilisation

represented the increase in biomass C and respiration, but only the former, which was up to twice as large as respiration (data not shown), was responsible for the negative correlation between pore water velocity and carbon utilisation. Because the respiration rates on the peat core effluent DOC were about 1/5 of the respiration rate on the same concentration of DOC prepared by dialysis of peat pore water (Figure 7), it seems as if mineralisation of exported DOC by streamwater bacteria was limited by other components than DOC. Some possibilities are velocity dependent nutrient limitation or inhibitory phenolic components (Freeman et al. 2001), but we do not have the data to test this hypothesis.

A third achievement was the demonstration of discrimination in streamwater bacteria between $MW > 100$ DOC from three different sources, especially as it pertains to the metabolism of streamwater DOC compared with peat derived DOC. This agrees with, but does not support, other observations that ^{14}C enriched components of DOC (young DOC) are utilised by streamwater bacteria (Raymond and Bauer 2001), and that DOC moving from peat areas into streams is of recent origin (Schiff et al. 1997; Palmer et al. 2001).

Heterogeneity in carbon quality among peaty soils was emphasised by Updegraff et al. (1995) who found that most of the variation in carbon mineralisation between the soils was due to differences in a relatively small labile pool. Since the bacteria from the peat stream interface zone of Ö. Björntjärn were not discriminating between $MW > 100$ and $MW > 3500$ (Figure 4) and had a lower cell specific utilisation rate than the bacteria from Skarda (Figure 2), it is possible that the DOC pool of Ö. Björntjärn had a lower fraction remaining of labile $MW > 100$ DOC than the DOC pool of Skarda. This difference between DOC pools corresponds with observations of lower microbial activity and decomposition rates in ombrotrophic systems, such as Ö. Björntjärn, compared with minerotrophic mires, such as Skarda (Szumugalski and Bayley 1995).

Our results show that $MW > 100$ DOC may be released from the peat–stream interface zone and become more readily utilised by streamwater bacteria than the $MW > 3500$ DOC, in accordance with the decomposition model presented by Saunders (1976). While this source of reactive $MW > 100$ DOC is readily consumed when entering the surface water, the portion of the remaining $MW > 100$ DOC (River Skarda DOC in Figure 6) that converts to CO_2 becomes equal to or even less than that of the peat derived $MW > 3500$ DOC in the streamwater (Figure 7). This gradual degradation of the bioreactivity of the $MW > 100$ DOC fraction during its processing in the streamwater is in accordance with the size-reactivity continuum model introduced by Amon and Benner (1996). By this export, the peat–stream interface zone provides allochthonous carbon for utilisation by freshwater bacteria (Bano et al. 1997) and represents an important source of the heterotrophic base of humic lakes and rivers (Hessen 1992; Jansson et al. 1999).

Seasonal variation of heterotrophic activity of planktonic microbial populations in an oligotrophic stream ecosystem is primarily controlled by the availability of labile DOC (McKnight et al. 1993). Our study demonstrates the influence of some characteristics of heterogeneity on the mineralisation and export of DOC to surface water in the peat–stream interface zone of a stream ecosystem surrounded by mires.

It follows that the peat–stream interface zone may be an important allochthonous carbon source supporting concentration dependent microbial growth and metabolism in oligotrophic rivers and lakes.

Acknowledgements

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