TECHNICAL ARTICLES

MACROPOROSITY AFFECTS WATER MOVEMENT AND PORE WATER SAMPLING IN PEAT SOILS

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The measurement of chemical concentration profiles in pore water is a starting point for the analysis of biogeochemical processes in water-logged peat soils. Concentration patterns may be obscured when macro-porosity causes preferential flow in column experiments and when pore water is retrieved from the peat by suction. To investigate the magnitude of such effects, we used LiBr as a tracer in peat columns at outflow rates of 0, 2–3, and 8 mm d^{-1}. The results were compared with modeled advective-diffusive migration rates. Twenty to fifty percent of the tracer was recovered from depths at which the tracer would have been absent if preferential flow had not occurred. At the high flow rate, the prefer-ential flow was stronger, and the retrieved pore-water was probably in disequilibrium with the matrix. When pore water was retrieved by suc-tion, linear concentration gradients decreased by about 30% through the recovery of water from different depths, and the quality of fitted linear gradients decreased from $R^2 = 0.99$ to $R^2 = 0.82$. When flow rates are low (<3 mm d^{-1}) and pore water concentration values from samplers are aggregated or regressed, the obtained concentration profiles seem to rep-resent the vertical distribution of chemical species reasonably well. The use and interpretation of pore water profiles in peat soils is problematic if flow rates are higher and if vertical gradients are based on individual or few data points that have been obtained by suction samplers. (Soil Sci-ence 2002;167:98–109)

Key words: Peatland, macroporosity, pore water, bromide, dissolved inorganic carbon.

WETLANDS are important sources, sinks, and reservoirs within global biogeochemical cycles, especially with respect to methane (CH_4) and carbon dioxide (CO_2) (Gorham, 1991). The focus of biogeochemical research in peatlands is shifting toward process-based modeling (e.g., Arah and Stevens, 1998; Walter and Heimann, 2000), but empirical data to parameterize and validate these models is sparse as empirical studies of car-bon (C) cycling have concentrated on the ecosys-

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tem scale (e.g., Frolking et al., 1998) or on the identification of basic processes and controls (e.g., Dunfield et al., 1993). Modeling of pore water profiles from both controlled column experi-ments and from field sites may help overcome these problems inasmuch as pore water profiles re-flect the *in situ* turnover patterns of chemical species. Pore water modeling has often been used successfully to quantify biogeochemical processes in sediments and aquifer materials (e.g., Furrer and Wehrli, 1996; Furrer et al., 1996). However, wetland soils are heterogeneous, and the turnover patterns are highly variable in time. This might se-verely constrain the use of pore water modeling in this environment. Whether pore water modeling offers the potential for the *in situ* determination of biogeochemical turnover rates depends on the ac-

curacy of pore water sampling techniques and experimental functioning and on the spatial and temporal variability of the processes.

Macroporosity is a ubiquitous feature in peat deposits and is important for the transport characteristics of solutes (Reeve et al., 2001). It also indirectly influences trace gas exchange with the atmosphere (Siegel et al., 1995). Macroporosity is particularly problematic in column studies because it may cause preferential flow (Ours et al., 1997) leading to biogeochemical patterns that are not primarily vertical. This makes pore water modeling difficult. Moreover, if pore water is retrieved from a heterogeneous medium by suction, it represents a mixture of pore water from different depths and pore sizes. In field investigations, suction can be avoided by the diffusion equilibration technique (e.g., Brandl and Hanselmann, 1991), but it cannot be applied repeatedly to one particular spot. This is a problem in column experiments and in field measurements, where processes are highly variable in space.

The effects of macro porosity on small-scale flow dynamics in peat have been studied primarily from a hydraulic perspective (e.g., Ingram et al., 1974; Chanson and Siegel, 1986; Ours et al., 1997), but the results of these studies cannot easily be translated into a biogeochemical context for two reasons. First, in studies with a hydraulic focus, wall effects are often avoided by using sealant, such as polyurethane, to prevent seepage at the interface (Ours et al., 1997), but this cannot be used in biogeochemical studies because of chemical contamination of the peat. Second, in hydraulic studies, high flow velocities, often 5 to >100 cm d^{-1}, are used (Chason and Siegel, 1986; Ours et al., 1997). These rates are faster than desirable for the investigation of many biogeochemical processes.

We investigated basic limitations of sampling techniques and vertical flow on pore-water concentration measurements in peat soils as a step toward the biogeochemical modeling of pore-water profiles in this environment. We assumed that water movement and concentrations of a conservative tracer sampled in column experiments would be affected (i) by preferential flow along column walls, (ii) by preferential flow within the peat, and (iii) by mixing effects caused by suction during sampling. We were interested specifically in the magnitude of these effects at flow rates of a few mm d^{-1} and in vertical sampling resolution of centimeters because such a setting might typically be encountered, or used, in biogeochemical studies of peatlands. The magnitude of these effects under these conditions

needs to be known when pore water profiles are obtained and interpreted or used for turnover estimates and pore water modeling.

METHODS AND MATERIALS

Sites

Peat cores were obtained from two sites. One site, Mer Bleue (MB) near Ottawa, eastern Ontario, Canada, is an open, slightly domed, oligotrophic peatland that is dominated by mosses (e.g., *Sphagnum rubellum, S. angustifolium, S. magellanicum* and *Polytrichum strictum*) and shrubs (e.g., *Ledum groenlandicum, Chamaedaphne calyculata,* and *Kalmia angustifolia*). The peat depth was about 4 m. The hydrology of the site has been described previously (Fraser, 1999; Fraser et al., 2001a and b). The second site near Kenora, northwestern Ontario, Canada, is a small oligotrophic peatland located in the northwestern watershed of Lake 239 (ELA, Experimental Lake Area) on the Precambrian Shield (Bayley et al., 1986). The peatland, several meters deep, is dominated by black spruce (*Picea mariana*) and mosses (*S. magellanicum, S. angustifolium* and *S. fuscum*).

Experimental Design

Seventeen peat cores, 20 cm in diameter $\times$ 75 cm in length, were extracted in sharpened PVC tubes from hollows in two peatlands from late summer to fall. To this end, the tubes were placed vertically on top of the peat surface, and the upper layer of the prospective peat core was dissected from the surrounding peat by sawing with a wood saw around the PVC tube. The tube was then driven manually into the peat and dug out with a spade until it could be recovered. Vertical compaction was generally small, less than 15% of the core length, as inferred by comparing the moss surfaces inside and outside the tube. Immediately after retrieval, a drainage mesh was placed over the base of the peat cores, which were capped with epoxy glue and sealed from the outside with silicone. For the first set of experiments, 35 to 37 22-cm-long samplers (Bev-Line IV, Cole Parmer, 7-mm outer diameter, 3-mm inner diameter, ca. 30 perforations per sampler) were inserted every 2 cm in three rows (0, 45, and 90°) at 6-cm intervals in each row (Fig. 1). The perforated part of the samplers covered the inner 15 cm of the cores. A flexible tube with a perforated end was inserted ca. 5 cm above the outflow to serve as a water table and suction indicator (Fig. 1). To assess wall effects, we inserted samplers that allowed retrieval of pore water from the area adjacent to the inner PVC-wall (3 cm), the inner 10
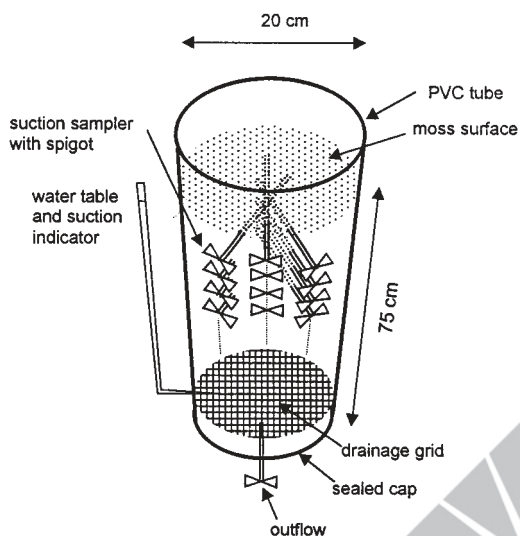
Fig. 1. Schematic of the column setup used.

cm, and a full horizontal cross–section within the core. Vertical water flow was induced by adding solution at the top with a sprinkler once a day and retrieving water with a syringe from the bottom. During water retrieval, the induced suction generally lowered the water table in the water table indicator tube (Fig. 1) by 20 to 70 cm. The cores were filled with distilled water up to 2–6 cm below the plant cover.

As an alternative method for obtaining pore water, we employed the equilibrium diffusion technique (peepers), consisting of small chambers filled with deionized water, covered by a semiper-meable membrane, and incubated in waterlogged substrate until equilibrium between inner and outer solution composition is reached (Hesslein, 1976; Brandl and Hanselmann, 1991). We used two models of 50-cm length, 1-cm resolution, cellulose-mixed ester membrane of 0.45-μm pore diameter, and 5–10-ml cell volume.

We conducted the following experiments:

(1) LiBr was added to one peat column at an inflow rate of 11 mm d^{-1} and an outflow rate of 8 mm d^{-1}. Pore-water profiles were sampled every other day for 8 days.

(2) To assess preferential flow at concentration and advection rates more representative of natural conditions in a peatland, a one–time pulse of 30 mm LiBr (1 mM) was applied to 16 cores. Pore-water profiles were sampled at six depths (12, 24, 36, 48, 60, and 74 cm) every 3 to 5 days for a period of 35 days, and further samples were taken after 50, 190, 210, and 250

days. The outflow rate in this experiment, initially 3 mm d^{-1}, was decreased to 2 mm d^{-1} after 50 days. The sampled volume per sampling date and depth segment was 2.5 mL, overall, resulting in a loss of ca. 4% of the inflowing water. The flow rates were selected as a compromise between the average runoff rate at the site (ca. 1 mm d^{-1}, based on a 8-month unfrozen period, Fraser et al., 2001a) and the necessity for faster vertical migration rates in biogeochemical column experiments.

(3) To compare pore water Br$^-$ concentration profiles sampled by the suction and equilibration technique, we sprinkled 21 mm of 1M LiBr solution on top of six cores. Three of these cores had been prepared with both samplers and a small type of pore water peeper (5 mL cell volume). The cores without peepers were sampled immediately. Two different volumes were extracted to examine whether concentrations were dependent on the extracted volume. The others cores were sampled with both suction and equilibration technique after 10 days.

Br$^-$ was determined either by injecting 2.5 mL of pore-water into a 10 mL syringe containing a mini-stirrer and an ion selective electrode (Cole Parmer) or by using ion chromatography (IC, Dionex, Metrosep Anion Dual 1, at 0.5 mL min$^-$1 flow rate and chemical suppression). The quantification limit was ca. 10–15 μmol L^{-1} for both methods. Below these levels, concentrations were systematically overestimated. As a species of biogeochemical interest, we determined dissolved CO_2 (dissolved inorganic carbon, DIC) using a headspace technique. A total of 0.5 mL of sample was retrieved from the pore water samplers and pore water peepers and filled in gastight GC vials (HP) and equilibrated and stored before analysis. The vials were previously spiked with 20 μL of HCl (4M) to inhibit microbial activity and to convert HCO_3^- and CO_3^{2-} to H_2CO_3. The samples were analyzed on a Shimadzu Mini 2 gas chromatograph with methanizer. The original dissolved concentration was determined from the gaseous concentration using Henry's law (K$_H$ = 10−1.5 (mol L^{-1} atm^{-1})) for CO_2. The time necessary for sampling the peeper was less than 10 min so that diffusive losses through the membrane can be ignored (Brandl and Hanselmann, 1991).

Model Calculations

To compare Br$^-$ migration in peat cores and theoretical migration without macroporosity ef-

fects, we simulated the Br^- migration using a simple box model that consisted of 16 fully mixed reservoirs. The change in reservoir size was calculated from the diffusion and an advective exchange of water with the adjacent reservoirs.

$$\Delta S_{Br,z}/\Delta T = D_{Br,z} (S_{Br,z-1} - S_{Br,z-1})/(z - z_{-1}) + v S_{Br,z-1} - D_{Br,z+1} (S_{Br,z} - S_{Br,z+1})/(z_{+1} - z) - v S_{Br,z} \quad (1)$$

$\Delta S_{Br/\Delta} T$: change of Br^- in a reservoir at depth z in time interval T (μmol cm^{-3} d^{-1}), D_{Br}: diffusion coefficient of Br at depth z^- (cm^2 d^{-1}), v: advective exchange rate between reservoirs (d^{-1}).

A source function was implemented at the uppermost layer, simulating the inflow of the tracer. The advective flow was time–invariant throughout the simulation. Mechanical mixing of the solute was not explicitly included into the model but was implicitly represented by using the mixed reservoir approach (van Ommen, 1985). Although we were aware of the effects of lateral and longitudinal dispersive mixing (e.g., Reeve et al., 2001), we chose this simple model because centimeter-scale pore water modeling is typically based on numerical box models, with the assumption of transport by simple diffusion and advection (e.g., Furrer et al., 1996). The diffusion coefficient D_{Br} was set to 1.036 cm^2 d^{-1}, which

is the approximate mixed diffusion coefficient of LiBr at 10° in water (Lerman, 1979). Diffusion coefficients were adjusted to porosity by reducing D_{Br} by a factor (porosity)^2 (Lerman, 1979). Porosity was calculated from measured bulk density (Fig. 2) and by assuming a specific density of the peat solids of 1.5 g cm^{-3} (Weiss et al., 1998). For comparison with the empirical experiments, the reservoirs were transformed into concentrations based on the geometry of the peat columns. Effects of ionic strength and charge balances on the diffusion coefficient were neglected. The calculations were done in Stella (High Performance Systems Inc., release 5.1.1).

Physical Characteristics of the Peat

At both sites, the peat decomposition on the von Post scale (von Post, 1922) increased from 2 to 3 in the upper 10 cm to about 6 to 9.5 at a depth of 70 cm (Fig. 2). The ELA peat was, on average, less decomposed at depth than the Mer Bleue peat. Fibric layers and poorly decomposed woody remains were frequently encountered at depth in the ELA cores and occasionally in MB cores. Graminoid roots occurred throughout the cores.

Bulk densities of the sampled peat columns were determined on depth increments of the columns after the end of the experiments. The
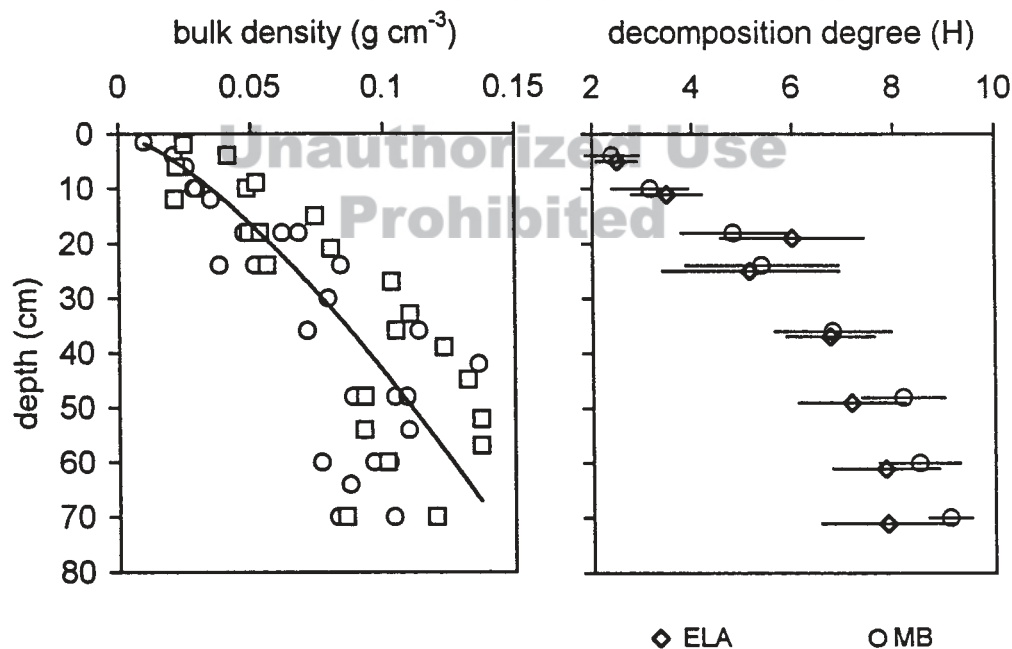

Fig. 2. Bulk density (Bd) and decomposition degree of the used peat cores. Bars indicate standard deviations. For modeling purposes the bulk density was expressed as a function of depth as Bd = 0.0107×$^{0.567}$ with R^2 = 0.79 (α < 0.05)

bulk density increased with depth from 0.01–0.05 in the uppermost 10 centimeters to 0.08–0.14 at lower depths (Fig. 2). The bulk density data were fitted to a quadratic function ($R^2 = 0.79$), which was used to calculate bulk density for the model calculations.

Horizontal hydraulic conductivity (K_H) in the peat previously been determined by Fraser (1999) at the MB sampling site, using piezometer bail tests after Hvorslev (1951). K_H was $2.7 \ 10^{-4}$ m s^{-1} ± $4.7 \ 10^{-4}$ m s^{-1} (± standard deviation, $n = 4$) at a depth of 0.5 m, and $7.4 \ 10^{-8}$ ± $4.6 \ 10^{-8}$ (± standard deviation, $n = 4$) at a depth of

0.75 m below the soil surface. K_H was not determined at the ELA site but was presumably larger due to the more fibrous nature of the peat at depths > 40 cm (Fig. 2).

RESULTS AND DISCUSSION

Preferential Flow in Column Experiments

The experimental results showed that with a column diameter of 20 cm and an output rate of 8 mm d^{-1}, wall effects occurred but were not very substantial (Fig. 3). In the poorly decomposed upper section of the peat column, Br$^-$ concen-
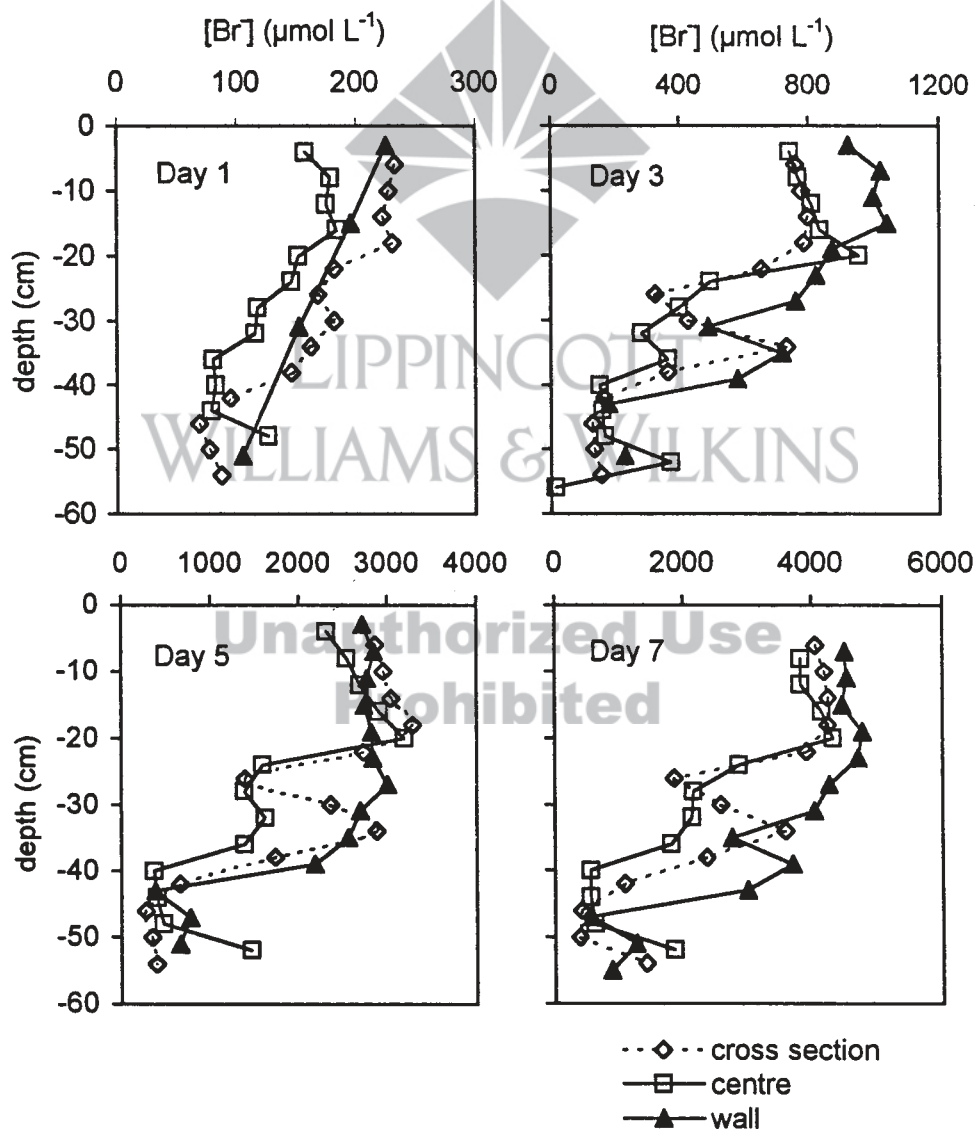

Fig. 3. Tracer migration in a peat column (Mer Bleue) at outflow rate of 8 mm d^{-1}. *Center* represents the inner 10 cm of the column, *wall* the outer 3 cm, and *cross section* the entire breadth of the column.

trations were similar throughout the core after about 6 days. Concentration differences occurred mainly in the moderately decomposed section between 25 and 45 cm depth. At greater depths, the very plastic consistency of the peat probably prevented preferential flow near the wall. The strong preferential flow occurring throughout the peat core, comparing the modeled and measured Br^- concentration profiles (Fig. 4), has to be attributed to internal flow paths in the peat column. Despite an advection rate of only about 10 mm d^{-1}, the tracer had migrated through the entire peat column after 8 days. Below a depth of

22 cm, 43–53% of the added Br^- was found, whereas modeling predicted that only about 1.6% of Br^- should have been present.

There may be disequilibrium between pore water chemistry and the peat matrix and macropores (Ours et al., 1997) when solutes migrate preferentially in larger pores and diffuse from there into the peat matrix. Our results are in agreement with this for the used flow rate of about 8 mm d^{-1}. After 8 days, 116% of the added Br^- was recovered, based on the central part of the core, 138% based on the cross-section, and 176% based on the wall area. Within the accuracy
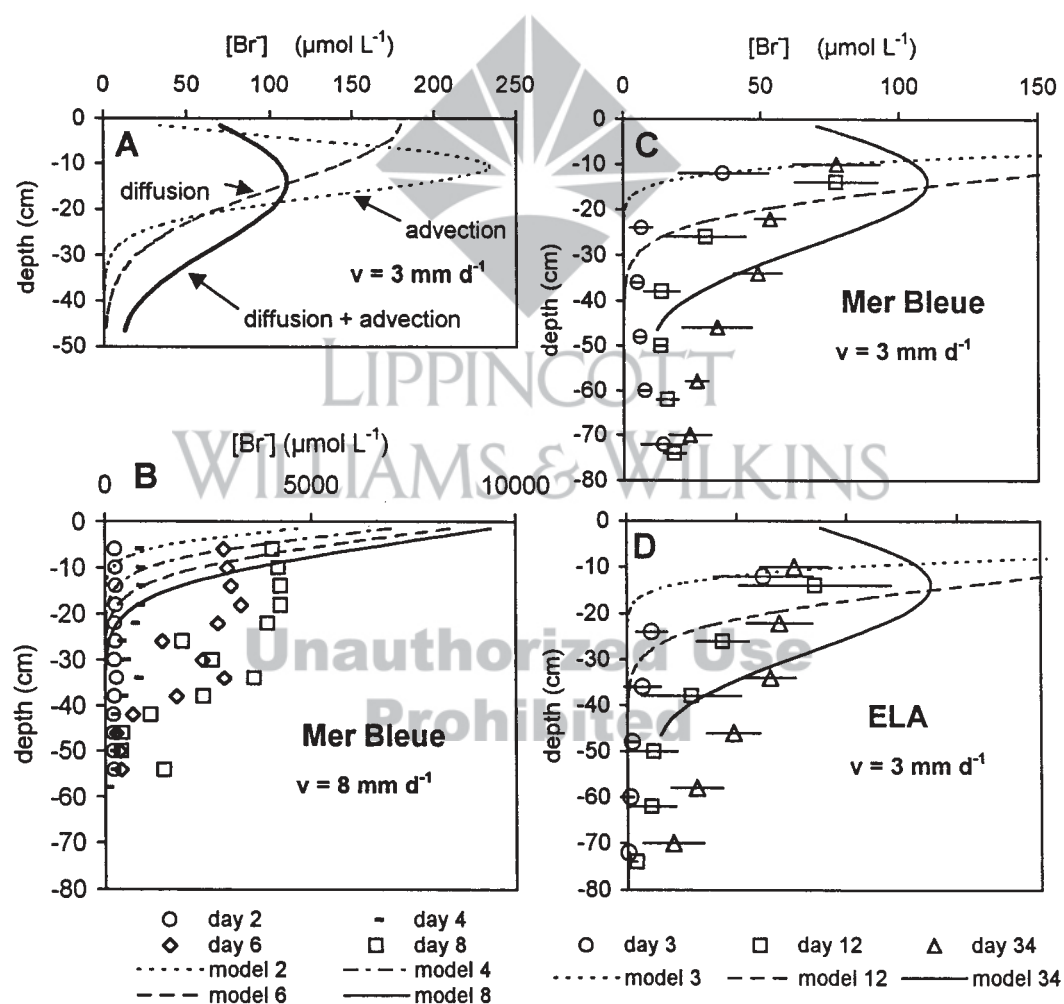

Fig. 4. Tracer migration in model calculations and at outflow rates of 8 and 3 mm d^{-1}. Model calculations show the tracer distribution after 34 days. Error bars represent the standard deviation of six to eight replicates. **Panel A** shows modeled advective and diffusive migration rates at an advection rate of 3 mm d^{-1}. Both processes contribute similarly to the overall migration. **Panel B** shows modeled and measured concentration profiles in one core from the Mer Bleue site at an advection rate of 8 mm d^{-1}. The more rapid migration in the measured profiles indicates preferential flow in the core. **Panel C and D** show measured and modeled migration in cores from Mer Bleue and ELA at flow rates of 3 mm d^{-1}. Preferential flow is indicated by the more rapid migration of the tracer compared with the modeled values.

of the analytical technique used, recoveries greater than 100% indicate that sampled water is in disequilibrium with the matrix. For flow rates < 8 mm d^{-1}, this might not apply. In the main tracer experiment, at flow output rates of 3 mm d^{-1}, the average Br$^-$ recovery after 5 weeks and in 16 cores was between 85 and 90% of the 1 mM LiBr application. This number is, however, relatively uncertain because of the limited vertical resolution of the measurements in this experiment.

To mimic realistic conditions, we carried out the main tracer tests at a column outflow rate of about 3 mm d^{-1}, which is equivalent to a net infiltration rate of 720 mm yr^{-1}, assuming 4 months with frozen ground. At such rates, the migration of a conservative species is controlled by both advective and diffusive migration, as is seen from the modeled migration patterns in Fig. 4 A. We also kept the initial input pulse of LiBr small to avoid disturbing biogeochemical processes in the columns, which were investigated simultaneously (Blodau, 2001), and any significant effects of the ionic strength on the porosity characteristics of the peat (Ours et al., 1997).

At these low advective flow rates, preferential flow still occurred. Assuming that the loss from the columns was negligible after 34 days, about 20% of the Br$^-$ tracer in the Mer Bleue cores and 30% in the ELA cores had migrated deeper than 42 cm. Modeling predicted, in contrast, that Br$^-$ should be nearly absent at these depths. The variability in concentration profiles among columns was substantial, but the basic patterns were consistent (Fig. 4 C, D and 5). The differences in tracer migration were initially fairly small between the two sites (Fig. 4 C, D). After 50 days, the variability in concentrations in the ELA columns was larger than in the Mer Bleue columns, possibly a result of the more heterogeneous nature of the ELA peat at intermediate and larger depths (Fig. 5 A, B). After several months, the Br$^-$ passing through the columns had peaked and concentrations decreased (Fig. 5). The larger measured than modeled concentrations indicate that either the movement of the tracer in the leaching phase was retarded or an additional source of Br$^-$ was present (Fig. 5).

The motivation for the experiments lay in exploring open-system column studies for the determination of biogeochemical turnover rates in peat. Pore water modeling, which involves the determination of mass balances for depth segments of the column, is often applied to groundwater systems (e.g., Furrer et al., 1996). In such approaches, preferential flow is problematic be-

cause it can cause sampled pore water to be chemically different from the moving pore water. This would cause errors in the calculated mass balances. Our results suggest that the preferential flow was considerably smaller at a flow rate of 3 mm d^{-1} compared with that at 8 mm d^{-1} (compare Fig. 5 B and 5 C and D). This result was obtained although the duration of the 3 mm d^{-1} experiment was longer, and a larger percentage of the tracer reached depths (25 to 35 cm) at which dual porosity begins to occur. The preferential flow might have been reduced further if a smaller and constant suction had been applied rather than the manual method applied here. Furthermore, at the low flow rate, there was no indication of disequilibrium between peat matrix and flow paths in the peat, as mentioned previously. Modeled tracer migration rates, which did not include preferential flow, were also in reasonable agreement with the measured rates (Fig. 5), suggesting that the movement of water could be explained without preferential flow in the column.

Although preferential flow still occurs at flow rates of 2 to 3 mm d^{-1}, the data suggest that it should not be a major source of error in the determination of turnover rates using pore water modeling in peat columns. However, low flow rates have disadvantages as neither advection nor diffusion can be neglected (Fig. 4 A), which makes model calculations more complicated. The time taken to adjust the column to the desired experimental conditions, e.g., input of solutes, also becomes very long. At a flow rate of 3 mm d^{-1}, the residence time of a solute would be about 7 months in a peat column of 60 cm long and a porosity of 0.8. The experimental design of column studies to study the effects of chemical inputs on the biogeochemical processes in peat is, therefore, constrained by preferential flow at high flow rates and biogeochemical response times at low flow rates.

Effects of Macroporosity on the Sampling of Pore Water

When pore water is retrieved from a dual porosity medium by suction, it might represent a mixture of pore water from different depths and pore sizes, depending on the volume that is extracted. Using 6 of 16 cores from the low-flow tracer experiments, we investigated the magnitude of these effects on concentration gradients of Br$^-$ and DIC. In three cores, pore water peepers were installed to compare concentration gradients derived from samplers and peepers. To attain different DIC levels, the columns were ex-
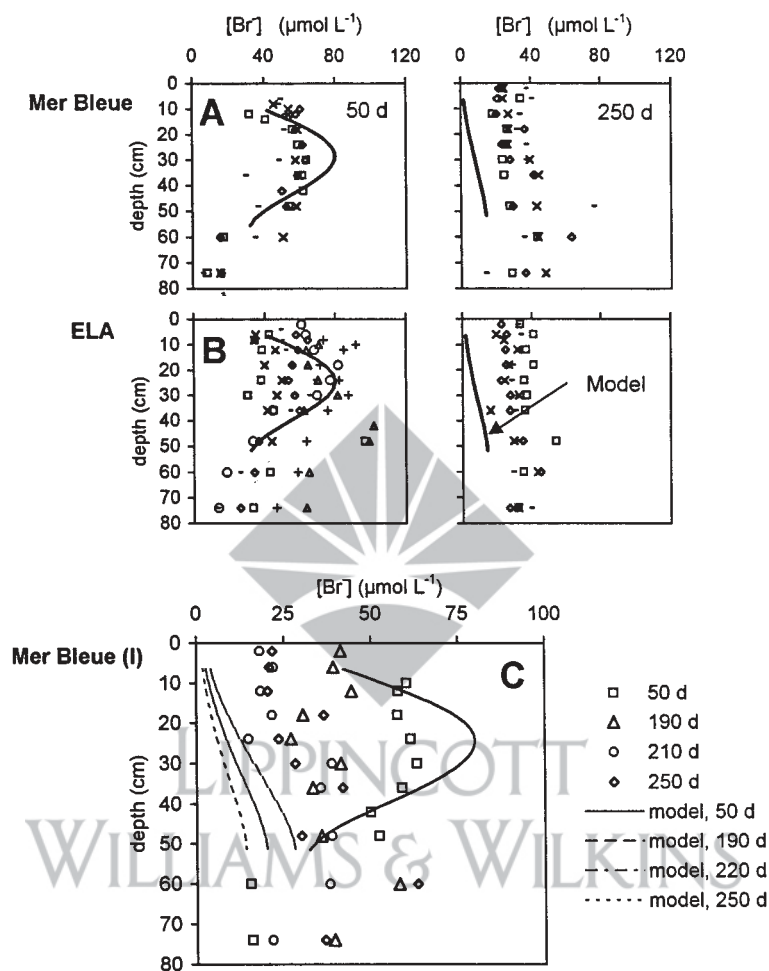
Fig. 5. Calculated and measured tracer migration at outflow rates of 2–3 mm d^{-1} over a period of 250 days. **Panel A** (Mer Bleue) shows the distribution of measured and modeled Br$^-$ concentrations in Mer Bleue peat cores after 50 and 250 days. Higher measured than modeled concentrations at lower depths at day 50 indicate preferential flow in the columns. Higher measured than modeled concentrations at day 250 might indicate retention of Br$^-$ in the profile. Symbols represent replicate cores and show the fairly large variability between cores. **Panel B** (ELA) provides the same information for peat cores from the ELA site. **Panel C** (Mer Bleue I) presents a time series of measured and modeled Br$^-$ profiles for one Mer Bleue peat core, showing basically the same tracer migration pattern as in Panel A but also the relatively large variability in this pattern through time within a single core.

posed to different equilibration times under saturated conditions. We created a strong Br$^-$ concentration gradient by sprinkling 21 mm of 1 M LiBr on top of the cores.

The higher specific density (1.085 g cm^{-3}) of the applied 1 M LiBr solution probably caused an initial, advective, density-driven flow into the columns, as indicated by the rapid initial movement of the tracer after application (Fig. 6). After sufficient dilution of the applied solution, the migration of the tracer was probably diffusion driven. This was also suggested by modeling,

which was able to reproduce both the flat part of the profiles and the concave profile section at lower depths (data not shown).

Assuming 10 days is an adequate equilibration time for the pore water peepers (Brandl and Hanselmann, 1991), the concentration in peeper samples should represent the average matrix composition of pore water. By comparing peeper and sampler profiles, the effect of suction on the true chemical depth gradients in the peat core can be estimated. Following this reasoning, suction primarily caused a decrease in the gradient
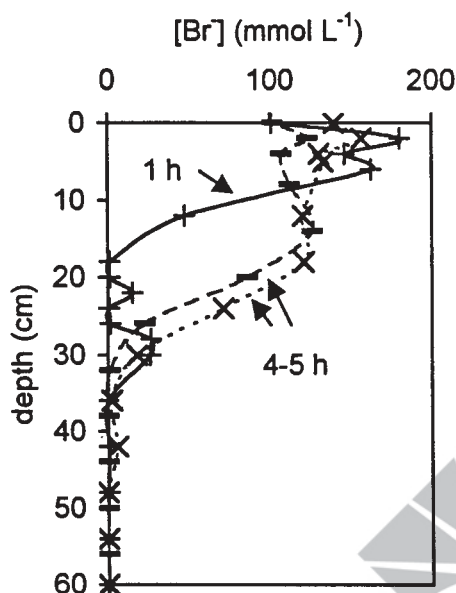
Fig. 6. Profiles of Br⁻ in pore water obtained from suction samplers following the application of 21 mm of 1 M LiBr solution to the top of three peat cores. Advective flow by drainage from the bottom was absent. The profiles show the rapid occurrence of Br⁻ at depths of up to 30 cm, 1 to 5 h after application of the tracer. This phenomenon might have been caused by a specific density-driven flow in macropores and/or preferential suction of water from macropores.

and scattering of the overall tracer gradients in the lower section of the columns (Fig. 7). Based on linear regression, the gradients decreased, on average, by 30%, and coefficients of determination (R^2) decreased, on average, from 0.99 (peepers) to 0.82 (samplers). The decrease indicates that the retrieved pore water was a mixture of water from both larger and lower depths than the sampled one. Immediately after application of the tracer to the peat core surfaces, the sampled concentrations of Br⁻ in surface peat also increased with the extracted volume. This also suggests that the extracted pore water was such a mixture of water (data not shown).

Furthermore, the scatter in the sampler data, compared with the peeper data (Fig. 7), indicates that each sampler obtained an *individual* mixture of water from different depths. Moreover, in the upper part of the profile, the concentration in the pore water from samplers was, on average, lower than that in the peepers. In two cases the deviation was fairly small (5–10%), but in another it was quite substantial (30–40%) (Fig. 7). Peat matrix and macropores in this section were apparently not fully in equilibrium with respect to the tracer concentration.

The DIC concentrations in the sampler pore water were, on average, higher than in the peepers at all three concentration levels (Fig. 8). The
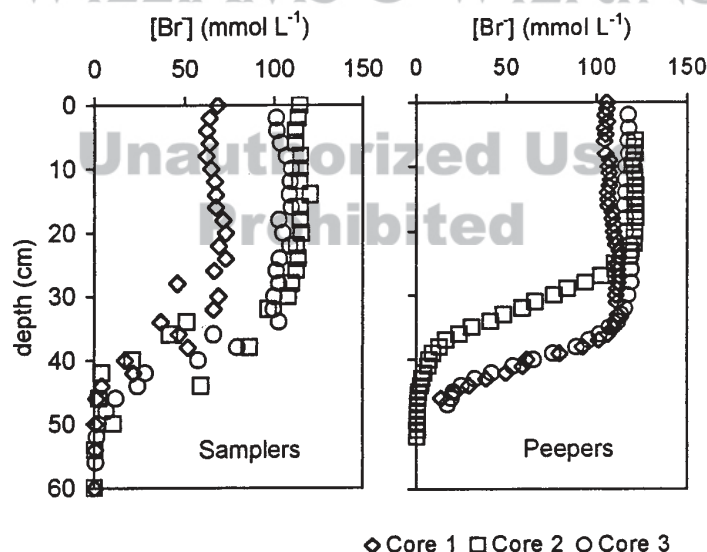

◇ Core 1 □ Core 2 ○ Core 3

Fig. 7. Profiles of Br⁻ in pore water obtained from suction samplers and diffusive equilibration peepers 10 days after the application of 21 mm of 1 M LiBr solution to the top of three peat cores. Advective flow by drainage from the bottom was absent. Each symbol represents values from one individual core. Filled symbols represent concentration values that were obtained from peepers, and open symbols concentration values from suction samplers. Samplers produce a larger variability in individual concentration values and less steep concentration gradients compared with peepers.
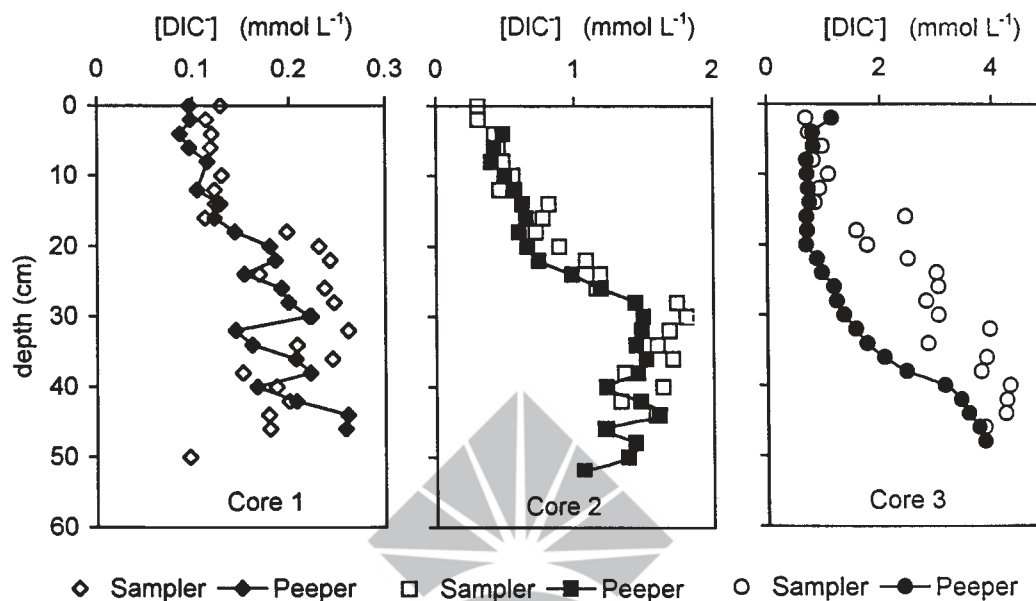
Fig. 8. Profiles of DIC in pore water obtained from suction samplers and diffusive equilibration peepers 10 days after the insertion of the pore water peepers into three peat cores.

deviation was smallest at intermediate concentrations, and the profiles were nearly replicated, but at high concentrations, peeper values were only 30 to 45% of the sampler concentrations. Such large differences cannot be explained by a lack of diffusive equilibration after a 10-day period, as was shown on experimental and theoretical grounds (e.g., Carignan, 1984; Brandl and Hanselmann, 1991). In peat, C dynamics can vary substantially on the centimeter scale (Blodau et al., manuscript in preparation), and heterogeneity, a lack in equilibrium between macropores and matrix, as well as between peeper and matrix solution, may contribute to this phenomenon.

As a consequence of the use of suction samplers, the described artifacts have an affect on the calculation of mass balances from pore water profiles because the biogeochemical zonation in the peat is obscured. As a result of the individual nature of water mixtures in each sampler, the concentrations in the profile do not represent the average concentration at that depth. Apparent concentration gradients on the basis of individual concentration values might be artifacts (Fig. 7). If mass balances are calculated from such profiles, this scatter requires strong agglomeration of data, or curve fitting, and diminishes the resolution of the measurements. Hence, there are limits to the scale on which processes can be identified

through pore water concentration measurements with samplers. For our peat columns, this limit would be on the order of several centimeters.

The observed artifacts were probably caused, at least in part, by preferential flow in macropores when water was extracted. This seems likely based on the flow experiments that were discussed earlier. However, it must also be considered that part of the observed scatter in bromide concentrations profiles was likely caused by the experimental setup. Disassembling the columns showed that several samplers had been bent downwards by the insertion of the peepers. The high tracer concentrations that were used might also have caused an artificial flow that was picked up in samplers but less so in the peepers. In reality, the effects of suction samplers on concentration profiles might be smaller than determined here, especially in coarse surface peat, which is often of primary biogeochemical interest and often does not exhibit a dual porosity.

Overall, *in situ* sampling of detailed pore water profiles in peatland soils is a trade-off between different sources of error: that caused by the soil structure when suction sampling is used and that caused by the biogeochemical variability on scales of meters when pore water peepers are used repeatedly. Pore water peepers obtain more representative pore water solutions, but the temporal

trends are confounded with spatial variability be-
cause the common models of peepers cannot be
applied repeatedly to the same location. This
problem is avoided by using permanently installed
suction samplers. To obtain time series of repre-
sentative pore water, a sampling method has not
yet been developed that combines the diffusion
equilibration technique with a nondestructive in-
sertion of the sampling cells into the peat.

CONCLUSIONS

The results presented suggest that the move-
ment of solutes caused by preferential flow in
peat is significant at high flow rates (>3 mm
d^{-1}), but it becomes insignificant at rates less than
this. Preferential flow along natural flow paths
seems to be more important than along the in-
terface between peat and column walls. At low
flow rates, water in the peat matrix and flow paths
seems to be close to chemical equilibrium, which
is necessary for the accurate determination of
vertical mass balances from pore water profiles,
and for the application of 1-dimensional pore
water modeling. Macroporosity effects probably
limit the use of pore water samplers in peat. At
depths below about 30 cm, each sampler obtains
an individual mixture of water from different
depths. Apparent concentration gradients on the
basis of individual samples are, therefore, not reli-
able. This diminishes the vertical resolution of
pore water profiles obtained with the suction
technique. To alleviate this problem, a sampling
technique is needed that is (i) based on diffusion
equilibration with the peat matrix and (ii) can
obtain pore water from identical locations in the
soil or sediment repeatedly.

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