

Landscape and Watershed Processes

Dissolved Organic Carbon Dynamics in a Riparian Aquifer: Effects of Hydrology and Nitrate Enrichment

P.-A. Jacinthe,* P. M. Groffman, and A. J. Gold

ABSTRACT

The capacity of riparian soils to remove nitrate (NO_3^-) from ground water is well established, but the effects of ground water NO_3^- -enrichment on C dynamics are not well studied. We incubated horizontal cores of aquifer material extracted from beneath moderately well-drained (MWD) and poorly drained (PD) soils in a riparian forest in Rhode Island, USA for 132 d, and dosed (flow rate, 170 mL d^{-1} ; dissolved O_2 , 2 in PD and 5 mg L^{-1} in MWD cores) with ground water amended with either Br^- , $\text{Br}^- + \text{NO}_3^-$ (10 mg N L^{-1}), or $\text{Br}^- + \text{NO}_3^- + \text{DOC}$ (20 mg C L^{-1}). The DOC was extracted from forest floor material and added during the first 56 d of the experiment. Addition of NO_3^- had limited effect on CO_2 production while DOC amendment had a significant effect in the PD but not in the MWD mesocosms. Total CO_2 production ($\text{mg CO}_2\text{-C kg}^{-1}$ soil) was 6.3, 7.0, and 10.1 in the PD and 3.6, 4.0, and 4.5 in the MWD cores amended with Br^- , $\text{Br}^- + \text{NO}_3^-$, and $\text{Br}^- + \text{NO}_3^- + \text{DOC}$, respectively. Carbon balance ($C_{\text{bal}} = \text{DOC}_{\text{in}} - (\text{DOC}_{\text{out}} + \text{CO}_2\text{-C})$) showed a net C retention of 8.0 mg C kg^{-1} soil in the DOC-amended MWD cores (equivalent to 50% of the DOC added), and a net C loss of 8.3 mg C kg^{-1} soil in similarly treated PD cores. The lack of C retention in the PD cores was ascribed to reductive dissolution of minerals implicated in DOC sorption. These findings underscore that there is marked variation in C dynamics in riparian aquifers that has the potential to influence the fate of NO_3^- and DOC in the landscape.

LOCATED AT THE UPLAND–AQUATIC SYSTEM interface, riparian ecosystems play important roles in the maintenance of water quality through biogeochemical processing of pollutants, in particular the removal of nitrate (NO_3^-)—a widespread ground water contaminant (Nolan and Stoner, 2000). This function has been ascribed to biological denitrification (Groffman et al., 1992; Hill, 1996), and NO_3^- uptake by the riparian vegetation (O'Neill and Gordon, 1994). Studies of the capacity of riparian zones to act as *sinks* for ground water NO_3^- have been an active area of research (Hill, 1996; O'Neill and Gordon, 1994; Haycock and Pinay, 1993).

Ground water denitrification is frequently limited by the availability of organic carbon (C) to support ground water microbial activity (Bradley et al., 1992; Groffman et al., 1996; Hedin et al., 1998). Dissolved organic C (DOC) is a mobile and an important C source in the subsurface, but there remains uncertainty about the pro-

duction, bioavailability, and transport of DOC through soils into aquatic systems (Qualls and Haines, 1992; Boyer and Groffman, 1996; Kalbitz et al., 2000). In addition to DOC biochemical attributes, sorption processes are major controllers of DOC mobility and availability to subsurface microbes (Qualls and Haines, 1992; Hagedorn et al., 2000; McCracken et al., 2002). Iron- and Al-oxides provide most of the DOC sorption sites in soils and sediments (Kaiser and Zech, 1996; Kaiser and Zech, 1998). Work by McCracken et al. (2002) has demonstrated the role of organo-mineral coatings (formed through DOC and Fe co-precipitation) in C retention in soils. McClain et al. (1997) reported DOC concentrations one order of magnitude higher in ground water underneath oxide- and clay-poor Spodosols than Oxisols in central Amazonian forests. Metal oxides are variable-charge minerals, which at pH below their zero point of charge (Sposito, 1989), develop positive charges allowing sorption of DOC and anions (e.g., SO_4^{2-}). Competition between sulfate (SO_4^{2-}) and DOC for sorption sites is a well documented phenomenon (Guggenberger and Zech, 1992); however due to the greater affinity of DOC for the binding sites (Kaiser and Zech, 1998), a net displacement of SO_4^{2-} is most often observed (Kaiser and Zech, 1996, 1998). Studies (Carlyle and Hill, 2001; Knapp et al., 2002) of elements distribution in ground water systems have reported higher dissolved Fe^{2+} concentrations and lower anion retention in anaerobic than in aerobic regions of ground water. Likewise, Hagedorn et al. (2000) noted that DOC efflux from forest soil profiles was higher under reduced than aerobic conditions, and was positively correlated with dissolved Fe^{2+} concentrations. The lower anion and DOC retention in anaerobic environments was attributed to a loss of sorption surfaces due to reductive dissolution of Fe oxides (Hagedorn et al., 2000; Carlyle and Hill, 2001; Knapp et al., 2002). These research findings suggest that soil redox state plays an important role in determining the translocation of DOC and associated nutrients, and could indirectly influence the quality and biogeochemistry of connected water systems.

Riparian ecosystems are characterized by seasonally variable water tables which, through periodic contact with the more biologically active upper layers of soils, could influence C supply to subsurface microbes. Water

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Abbreviations: DO, dissolved oxygen; DOC, dissolved organic carbon; DOC_{in} , dissolved organic carbon in input solution; DOC_{out} , dissolved organic carbon in core effluent; MBC, microbial biomass carbon; MWD, moderately well drained; PD, poorly drained; PDOM, patches of decomposed organic materials; SOC, soil organic carbon.

table drawdown and leaching can also assist in the transport to depth of NO_3^- and organic substrates, thereby altering substrate availability and biological activities in the subsurface. In addition, these substrates and microbial products are transported in near-surface and subsurface flows to neighboring streams and rivers. This hydrological connectivity between shallow aquifers, overlying soils, and surface waters has implications for the biogeochemical cycling of carbon (C) and nitrogen (N) in riparian ecosystems.

For more than a decade, we have conducted field and laboratory studies in several New England riparian forests to examine biological NO_3^- removal in these ecosystems (Groffman et al., 1992; Nelson et al., 1995; Gold et al., 1998; Groffman et al., 1998; Jacinthe et al., 1998; Addy et al., 1999). Biological N transformation processes are relatively well studied; however, still remaining unexplored are questions related to C dynamics in the subsurface of riparian forests. These questions include (i) the importance of surface-derived DOC as a C source for subsurface microbes; (ii) the capacity of riparian forest subsoils to retain and degrade DOC, and thus control DOC transport to aquatic systems; and (iii) the alteration of C metabolism in riparian aquifers exposed to NO_3^- -enriched ground water. We hypothesized that (i) soil drainage characteristic is a primary controller of DOC mobility in riparian ecosystems, and (ii) input of NO_3^- to riparian aquifers enhances microbial activity and CO_2 production.

In this study we used mesocosms of aquifer material collected along a soil drainage class gradient to investigate C dynamics and the fate of DOC in NO_3^- -enriched ground water. Sulfate dynamics in the mesocosms were also analyzed, to gain insight into DOC sorption-desorption processes. Aquifer material sampling strategy, mesocosm design, and dosing were designed to simulate the exchange of DOC between the forest floor and the shallow aquifer underneath, to maintain in situ ground water conditions characterized in previous studies (Nelson et al., 1995; Groffman et al., 1992), and to capture the spatial variation in biogeochemical processes associated with hydrology. Our specific objectives were to (i) quantify CO_2 production in a riparian aquifer and evaluate the effect of NO_3^- and DOC additions on this production, and (ii) to determine, through C budgeting, the fates (decomposition, sorption) of DOC added to aquifer materials extracted from different soil drainage classes in a riparian forest.

MATERIALS AND METHODS

Collection of Cores and Instrumentation

Undisturbed cores (40 cm long, 15 cm diam.) of aquifer material were obtained from beneath poorly drained (PD) and moderately well drained (MWD) soils in a riparian forest near the campus of the University of Rhode Island (Kingston, RI). The drainage classes were delimited based on field observation of redoximorphic features of the soil profile. The distance between the two drainage class locations was about 30 m with the MWD soil at the transition between wetland and upland. The soils in the riparian zone are coarse-textured

Endoaquepts derived from glaciofluvial deposits of granitic and loamy sands. Natural vegetation was a second-growth forest with a mixture of red maple (*Acer rubrum* L.) and white oak (*Quercus alba* L.) dominating its upland edge (MWD soils) and red maple the dominant vegetation in the PD section. The aquifer mean annual temperature (upper 1 m) is 11°C. Dissolved oxygen concentrations (DO) average 2 and 5 mg L^{-1} in the PD and MWD sections, respectively (Nelson et al., 1995). Water table depth during the dormant season fluctuates between 20 and 40 and 90 and 110 cm below surface in the PD and MWD sections, respectively (Gold et al., 1998).

At each drainage class location, three pits were randomly located and excavated to depths below the mean elevation of the water table (PD, 0.61 m; MWD, 1.55 m). All pits were dug through the C horizon, which consists of medium to fine sand parent material. Three cores were extracted from each pit using an 8-ton hydraulic jack to horizontally push the PVC pipes along an exposed side of the pit. The subsoil was moist at the time of sampling, thereby easing pipe insertion and reducing compaction. Subsequent bromide (Br^-) breakthrough curve analysis (Gold et al., 1998) confirmed that the structural integrity of the aquifer material was adequately maintained. Once extracted, cores were fitted at both ends with a Plexiglas plate perforated with a 0.32-cm hole and a PVC endcap. The core endcaps were drilled to accommodate a 0.16 cm barbed fitting connected to dosing (inlet) and sampling (outlet) tubing (Fig. 1). Cores were stored for 60 d in the laboratory at 4°C before ground water dosing began.

Experimental Design

Mesocosm setup was designed to simulate biological processes in the riparian aquifer under conditions (temperature, DO, flow rate) similar to ambient. Triplicate mesocosms for each soil drainage class were dosed for 132 d with ground water collected every 4 to 6 wk from shallow wells within each drainage class. The first batch of ground water was collected in October 1995 while the last batch was obtained in February 1996. Background DOC concentrations averaged 1.3 ± 0.2 mg C L^{-1} in the shallow ground water beneath the MWD soil. In the PD section of the riparian forest, ground water DOC was 1.5 ± 0.6 mg C L^{-1} in early autumn and 3.8 ± 0.4 mg C L^{-1} in late fall to early winter. Background NO_3^- was 0.1 ± 0.1 in the PD and 0.3 ± 0.2 $\text{mg NO}_3\text{-N L}^{-1}$ in the MWD sections of the ground water. During that period, ground water SO_4^{2-} averaged 2.4 ± 0.3 and 3.3 ± 0.1 $\text{mg SO}_4\text{-S L}^{-1}$ in the PD and MWD areas, respectively.

Ground water was transferred into 10 L polypropylene carboys, purged with Ar and Ar- O_2 mixtures to yield DO concentrations of 2 (PD) and 5 mg L^{-1} (MWD), and amended with (i) Br^- (control), (ii) $\text{Br}^- + \text{NO}_3^-$, and (iii) $\text{Br}^- + \text{NO}_3^- + \text{DOC}$. Inflow concentrations were Br^- (10 mg Br L^{-1}), NO_3^- (10 mg N L^{-1}), and DOC (20 mg C L^{-1}).

Dissolved organic carbon (DOC) was obtained by water extraction of forest floor material (1:3 soil/water ratio), followed by overnight (4°C) decantation, and successive filtration through Whatman GF/A (1.6 μm) and GF/F (0.7 μm) filters. An aliquot of the filtrate was analyzed for DOC content, and an appropriate volume of DOC extract (taking background DOC into account) was added to the carboys to yield a target concentration of 20 mg C L^{-1} . Dissolved organic C was only added during the first 56 d of the experiment. The residual effect of the DOC addition was monitored for the remaining 72 d of the experiment.

A noncirculating continuous flow through system (Fig. 1), using an Ismatec multichannel peristaltic pump (Cole Parmer, IL), was designed to deliver (average flow 170 mL d^{-1}) the

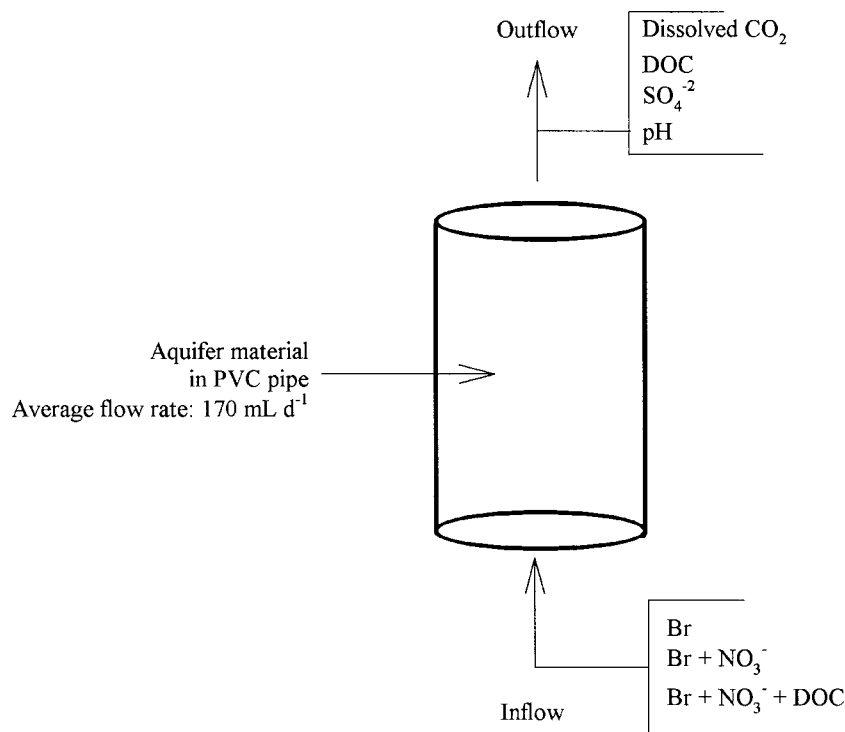


Fig. 1. Schematic representation of the mesocosm dosing setup.

amended ground water to the cores. Pore water velocity was 2.5 cm d^{-1} , within the range measured in a previous ground water study at the site (Nelson et al., 1995). During dosing, the cores were positioned vertically. Ground water entered the bottom of the cores while effluent was collected on top in acid-washed vessels. Effluent volume from each core was regularly (every other day on average) recorded and samples were taken for chemical (NO_3^- , NH_4^+ , pH, SO_4^{2-} , and DOC) analyses. The inorganic N transformation data are available elsewhere (Gold et al., 1998; Jacinthe et al., 1998).

Given the incubation temperature (11°C), O_2 partial pressure in the carboy headspaces was set at 12.9 and 4.7 kPa, respectively, to maintain the targeted DO levels. To avoid creation of vacuum in the carboys as solution was being pumped out into the cores, and also to maintain a constant DO in the carboy headspace, an Ar-O_2 mixture was continuously supplied to the carboy at a rate of approximately 0.5 mL min^{-1} (Fig. 1). Dissolved O_2 level in the carboys was regularly monitored and adjusted as needed. Measured DO concentrations in the carboys feeding the PD and the MWD cores averaged 2.2 and 5.4 mg L^{-1} , respectively during the course of the experiment.

Monitoring of Dissolved Gases Production

A silicone-based sampler was used to collect dissolved gases in the core effluents (Fig. 1). Briefly, core effluent was channeled into an enclosure with a silicone cell at its center. Gases in solution diffuse through the silicone membrane, accumulate in the silicone cell (20-mL volume, 10-cm length) until equilibrium between the liquid and gas phases are established as dictated by Henry's law. Gas phase concentration, obtained through sampling of the silicone cell headspace, was converted into dissolved gas concentration. Further information regarding the construction and operation of this sampler is available elsewhere (Jacinthe and Groffman, 2001).

Soil Organic and Microbial Biomass Carbon

At the end of the experiment, each core of aquifer material was sliced into 5 cm long sections to determine whether or not patches of decomposed organic material (PDOM) were present; PDOM identification was based on color, signs of illuviation and secondary mineral accretion, and decomposed organic materials (e.g., root fragments). When present, patches were isolated and characterized. Soil matrix samples were also taken. Fresh PDOM and soil matrix samples were assayed for microbial biomass C using the chloroform-fumigation-incubation procedure (Jenkinson and Powlson, 1976). Finely ground ($<250 \mu\text{m}$) air-dried samples were also used for organic C determination.

Biodegradability of Water-Extractable Forest Floor Carbon

The biodegradability of the DOC extracted from the forest floor was measured using the method described by Boyer and Groffman (1996). Briefly, duplicate 20 mL DOC extracts were amended with NH_4 ($0.5 \text{ mg NH}_4\text{-N L}^{-1}$), inoculated with 0.1 mL ($1.6 \mu\text{m}$ filtrate) of ground water and incubated aerobically in the dark for 10 to 14 d. Depending on the batch, initial DOC concentration of the extract ranged between 52 and 106 mg C L^{-1} (mean, $78 \pm 17 \text{ mg C L}^{-1}$). At regular time intervals, duplicate samples were taken to determine remaining DOC concentration in the incubation vessels.

Analytical Procedures

Dissolved organic C was determined with a Shimadzu 5050 carbon analyzer (Shimadzu Scientific Instruments, Columbia, MD) using high-temperature (680°C) catalytic oxidation of H_3PO_4 -treated samples. Organic C content of soil matrix and PDOM samples was determined by combustion with a Carlo Erba CN analyzer. Sulfate analysis was conducted on a Dionex 500 ion chromatograph (Dionex, Sunnyville, CA) equipped

Table 1. Carbon dioxide production in aquifer mesocosms taken from beneath poorly drained (PD) and moderately well-drained (MWD) soils in a riparian forest and amended with Br, Br + NO₃, and Br + NO₃ + DOC. Values are mean (SD) of 60 to 69 observations.

Treatment	Dosing period, 0–56 d		Dosing period, 70–132 d	
	PD	MWD	PD	MWD
	— μg CO ₂ -C kg ⁻¹ soil d ⁻¹ —			
Br	74 (10)b	38 (3)a	31 (5)b	22 (2)a
Br + NO ₃	84 (10)b	45 (2)a	30 (4)b	24 (3)a
Br + NO ₃ + DOC	119 (2)a	53 (15)a	51 (8)a	27 (6)a

† Values in the same column followed by different letters are significantly different at $P < 0.05$.

with an AS4A column with Na₂CO₃ (1.8 mM) and NaHCO₃ (1.7 mM) as the mobile phase (flow rate, 2 mL min⁻¹). Analysis of CO₂ was performed on a Tracor (Austin, TX) gas chromatograph equipped with a thermal conductivity detector. Column (300 cm long, 0.2 cm i.d. Porapak Q 80/100, Alltech, Deerfield, IL) and detector temperatures were 70 and 50°C, respectively. The carrier gas was Ar-CH₄ at a flow rate of 30 cm³ min⁻¹.

Data Analysis

Dissolved CO₂, DOC, and SO₄²⁻ concentrations were converted into mass kg⁻¹ soil using dissolved concentration, flow rate, and weight of cores (avg. 11.7 kg). Given the daily pattern of CO₂ production and nutrient concentration in the core effluents observed during the 132-d study, and consistent with previous reports from this experiment (Gold et al., 1998; Jancinthe et al., 1998), the data for each mesocosm were divided into a series of 10-d periods. There were 2 to 9 observations per mesocosm within each 10-d period. No measurement was made between Days 60 and 70.

Data were analyzed using a repeated measures analysis of variance (Littell, 1989) with soil drainage and treatment as main factors and sampling period as the repeated measures factor. Huynh-Feldt adjusted values were used to test the statistical significance of sampling period and interactions. Where indicated, separate analyses were performed for each soil drainage class and treatment. Statistical analyses were performed using SAS (SAS Inst., 1990). Unless noted otherwise, statistical significance was determined at the 95% level.

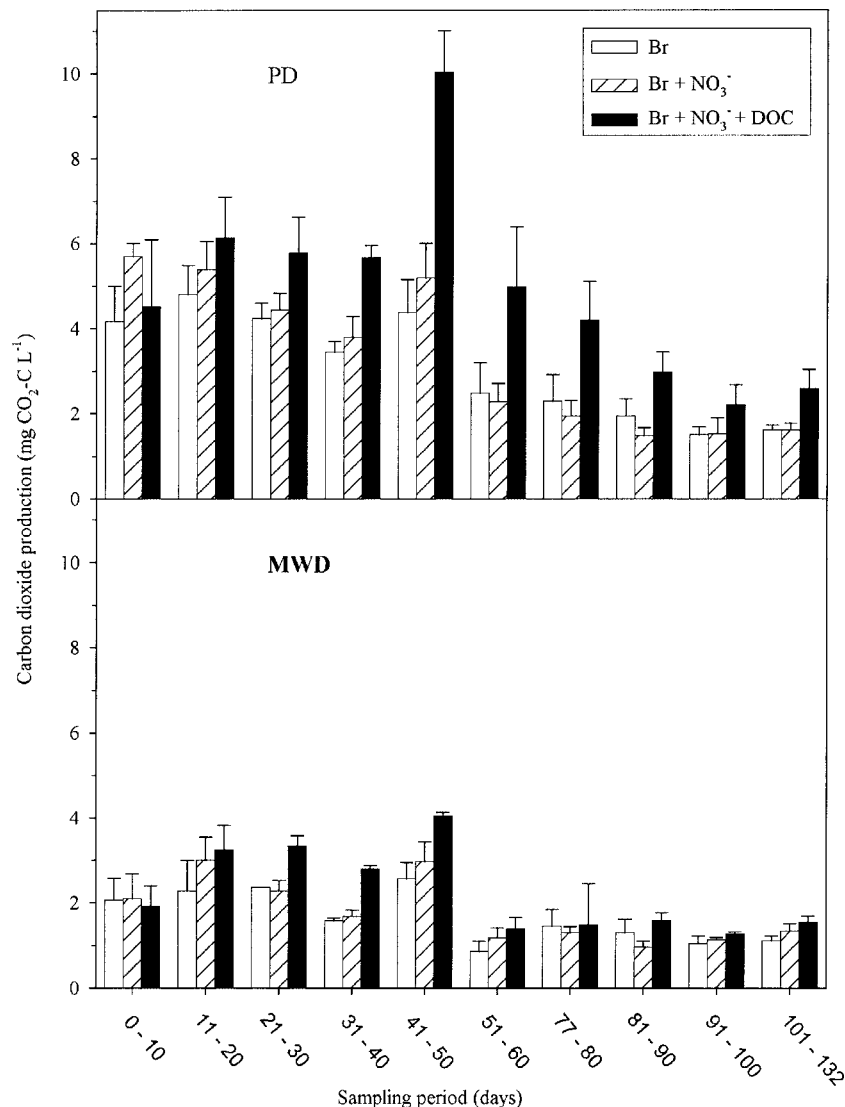


Fig. 2. Carbon dioxide (CO₂) production in poorly drained (PD) and moderately well-drained (MWD) mesocosms as affected by soil drainage class, nitrate (NO₃⁻), and dissolved organic C (DOC) addition. Vertical bars represent standard deviation of the mean ($n = 6$ to 27 observations).

Table 2. Carbon budget for mesocosms taken from beneath the poorly drained (PD) and moderately well-drained (MWD) soils in a riparian forest and amended with Br, Br + NO₃, and Br + NO₃ + DOC. Amendment with DOC occurred only during the 0- to 56-d dosing period. Values are the mean ± SD of triplicate cores.

Treatment	Dosing period, 0–56 d				Dosing period, 70–132 d			
	DOC _{in} †	DOC _{out}	CO ₂ -C	C balance	DOC _{in}	DOC _{out}	CO ₂ -C	C balance
	mg C kg ⁻¹ soil							
Br	2.4 ± 0.1	6.9 ± 0.6	4.3 ± 0.4	-8.8 ± 0.8	5.3 ± 0.2	5.5 ± 0.2	2.0 ± 0.3	-2.2 ± 0.1
Br + NO ₃	2.6 ± 0.1	6.7 ± 0.9	5.1 ± 0.4	-9.1 ± 1.3	4.8 ± 0.1	6.9 ± 0.8	1.9 ± 0.3	-4.0 ± 0.8
Br + NO ₃ + DOC	13.3 ± 0.5	7.7 ± 0.9	6.7 ± 0.2	-1.1 ± 0.3	6.0 ± 0.3	9.8 ± 0.6	3.4 ± 0.4	-7.2 ± 0.2
Br	1.7 ± 0.2	2.6 ± 0.4	2.3 ± 0.1	-3.2 ± 0.1	1.3 ± 0.1	2.9 ± 0.2	1.3 ± 0.2	-2.9 ± 0.4
Br + NO ₃	1.6 ± 0.0	2.5 ± 0.1	2.6 ± 0.1	-3.5 ± 0.2	1.4 ± 0.1	2.5 ± 0.1	1.4 ± 0.1	-2.5 ± 0.1
Br + NO ₃ + DOC	15.5 ± 2.9	2.8 ± 0.4	3.0 ± 0.7	+9.7 ± 1.8	2.5 ± 0.5	2.6 ± 0.5	1.5 ± 0.4	-1.7 ± 0.4

† DOC_{in} and DOC_{out} = dissolved organic carbon in input solution and effluent, respectively.

RESULTS

Carbon Dioxide Production

There were statistically significant effects of soil drainage class ($P < 0.001$), treatment ($P < 0.007$), and sampling period ($P < 0.03$) on CO₂ production. The pattern of CO₂ production was similar in all the mesocosms with production 1.5 to 4 times higher during the first 56 d of dosing than during the later part of the experiment (Table 1 and Fig. 2). Between Days 0 and 56, CO₂ production averaged 94 and 45 μg CO₂-C kg⁻¹ d⁻¹ in the PD and MWD mesocosms, respectively (Table 1). Carbon dioxide production dropped significantly between days 70 to 132 averaging 37 in the PD and 24 μg CO₂-C kg⁻¹ d⁻¹ in the MWD mesocosms.

With NO₃⁻ addition, CO₂ production rates increased (although not significantly) by 15% on average during the 0- to 56-d dosing period (Table 1). However, in the 70- to 132-d period, CO₂ production rates were similar in the control (Br⁻ only) and in the NO₃⁻ treatment, regardless of drainage class. When ground water was amended with DOC, CO₂ production significantly ($P < 0.05$) increased in the PD but not in the MWD mesocosms (Tables 1 and 2, Fig. 2).

During the course of the experiment, CO₂ production (mg CO₂-C kg⁻¹ soil) totaled 6.3, 7.0, and 10.1 in the PD and 3.6, 4.0, and 4.5 in the MWD cores amended with Br⁻, Br⁻ + NO₃⁻, and Br⁻ + NO₃⁻ + DOC, respectively. Carbon dioxide production (Y) was weakly ($R^2 <$

0.20) related to DOC in the input solution. However, positive relationships with effluent DOC (X) were found. The strength of the relationships varied with treatment being greatest for the Br⁻ + NO₃⁻ and lowest for the Br⁻ + NO₃⁻ + DOC treatments (Fig. 3).

Biodegradability of Forest Floor Dissolved Organic Carbon Extract

The amount of DOC extracted from the riparian forest floor varied with soil drainage class and time of forest floor collection. In the PD area, DOC decreased from 277 to 194 mg C kg⁻¹ soil between October and December, whereas in the MWD area, it increased from 270 to 320 mg C kg⁻¹ soil during the same period. Degradation of DOC generally followed a first order kinetic. Decomposition rate constants (k) exhibited seasonal variation (Fig. 4), but rates were generally 1.3 to 5 times greater in the PD than the MWD extracts.

Dissolved Organic Carbon and Sulfate

In the control and NO₃⁻ treatments, DOC concentrations in the effluent (DOC_{out}) often exceeded inflow (DOC_{in}) concentrations (Fig. 5), resulting in a net DOC loss from the aquifer material. For the whole experiment, losses of DOC in these two treatments averaged 5.4 and 2.6 mg C kg⁻¹ soil in the PD and MWD cores, respectively (Table 2). In the cores receiving external DOC input, net gains of DOC (PD, 5.6; MWD, 12.7 mg

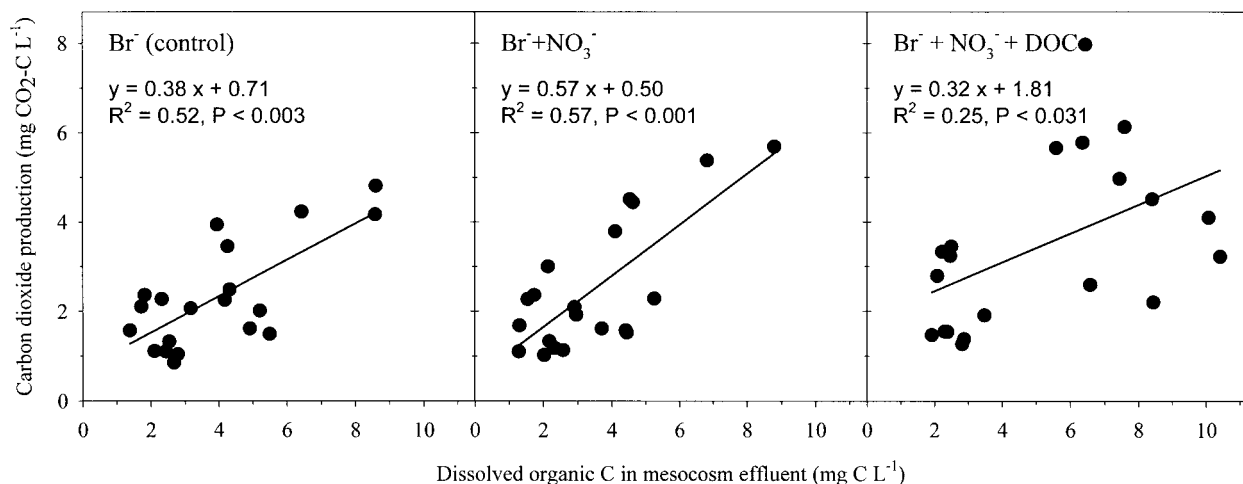


Fig. 3. Relationships between carbon dioxide (CO₂) production and dissolved organic carbon (DOC) in mesocosm effluent.

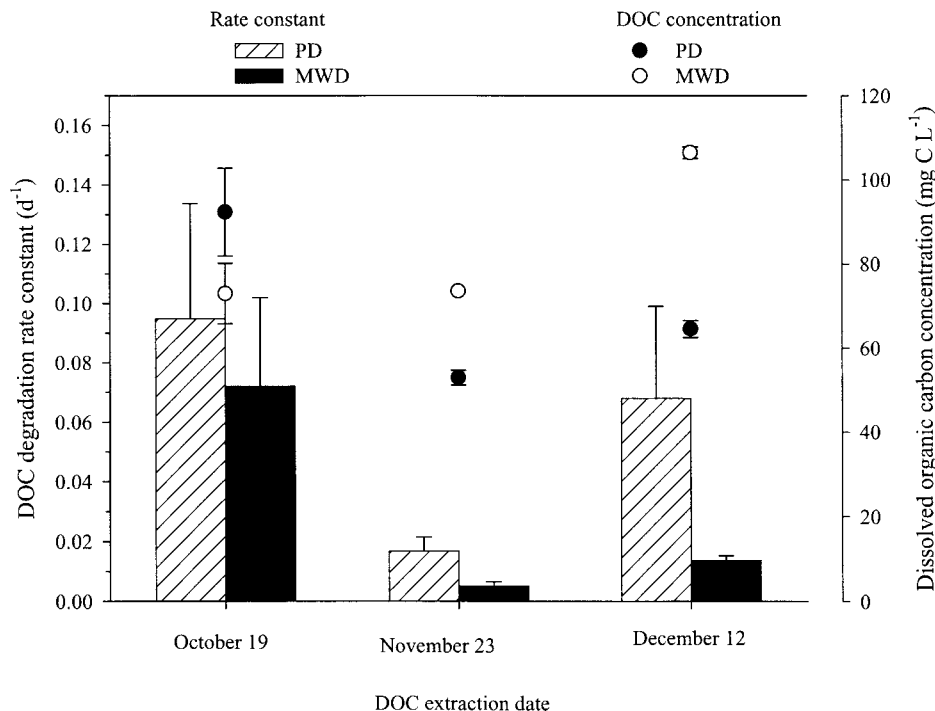


Fig. 4. Degradation rate constants (d^{-1}) of dissolved organic carbon (DOC) and concentration of DOC (right scale) in extracts obtained through suspension in ground water (soil/water ratio 1:3) of forest floor materials taken from poorly drained (PD) and moderately well-drained (MWD) sections of the riparian forest. The DOC extracts were amended with NH_4 ($0.5 \text{ mg } NH_4\text{-N } L^{-1}$) and incubated aerobically in the dark for 14 d.

$C \text{ kg}^{-1}$ soil) were recorded during the first 56 d of the experiments. However, with cessation of the DOC amendment after Day 60, DOC_{out} became greater than DOC_{in} in the PD cores, whereas in the MWD cores, DOC_{out} and DOC_{in} were in balance (Table 2). The net loss of DOC ($3.8 \text{ mg } C \text{ kg}^{-1}$ soil) recorded in the PD cores during that second period represented 70% of the DOC gained during the first part of the experiment.

Concentrations of SO_4^{2-} in core effluents tended also to be greater than inflow concentration (Fig. 6). Sulfate concentrations in the MWD core effluents were 1.5 to 2 times higher than in the PD cores. During the course of the experiment, a net SO_4^{2-} loss averaging 1.1 and $4.4 \text{ mg } SO_4\text{-S } \text{kg}^{-1}$ soil in the PD and MWD cores, respectively, was recorded. In the PD cores, the SO_4^{2-} loss was higher in the DOC-amended than in the other treatments (Table 3).

Carbon Balance

For each 10-d dosing period, mesocosm C balance (C_{bal}) was computed as:

$$C_{bal} = DOC_{in} - (DOC_{out} + CO_2\text{-C})$$

where DOC_{in} , and DOC_{out} represent the mass of C as DOC ($\text{mg } C \text{ kg}^{-1}$) in the mesocosm inflow and effluent, respectively, and $CO_2\text{-C}$ is the mass of CO_2 produced ($\text{mg } CO_2\text{-C } \text{kg}^{-1}$). In the control and NO_3^- treatment, $DOC_{out} + CO_2\text{-C}$ were 1.5 to 2 times DOC_{in} (Table 2 and Fig. 4), resulting—in almost all cases—in a negative C balance (Table 2). The C deficit was generally greater in the PD cores, and increased slightly with amendment of these cores with NO_3^- (Table 2 and Fig. 5). The overall

C balance was also negative (net loss of $8.4 \text{ mg } C \text{ kg}^{-1}$), even with amendment of the PD mesocosms with external DOC. However, the overall C balance was positive (net gain of $8.1 \text{ mg } C \text{ kg}^{-1}$) in the DOC-amended MWD cores.

Organic C (SOC) content and microbial biomass-C (MBC) in the PD and MWD matrix samples were similar (Table 4). Patches of decomposed organic matter (PDOM) were absent in all the MWD cores but were found in all the PD cores. Organic C content and MBC were 3 to 5 times higher in the PDOM compared with the matrix samples.

DISCUSSION

The ground water dosing experiment reported here aimed to evaluate the importance of natural soil drainage characteristics—landscape position and the effects of NO_3^- enrichment on C dynamics in a riparian aquifer. The results show that there is marked variation in C dynamics in riparian aquifers that has the potential to influence the fate of NO_3^- and DOC in the landscape.

We hypothesized that increased NO_3^- availability would stimulate microbial activity and alter C mineralization, affecting the C balance of the riparian aquifer. We found that CO_2 production increased, but not significantly, with NO_3^- addition. This finding does not entirely support but is in line with the hypothesis. It also suggests the presence of a reservoir of labile organic compounds in the riparian aquifer. In the NO_3^- -enriched mesocosms, CO_2 production was 57% of the DOC in the core effluents as opposed to 38% in the control (Fig. 3).

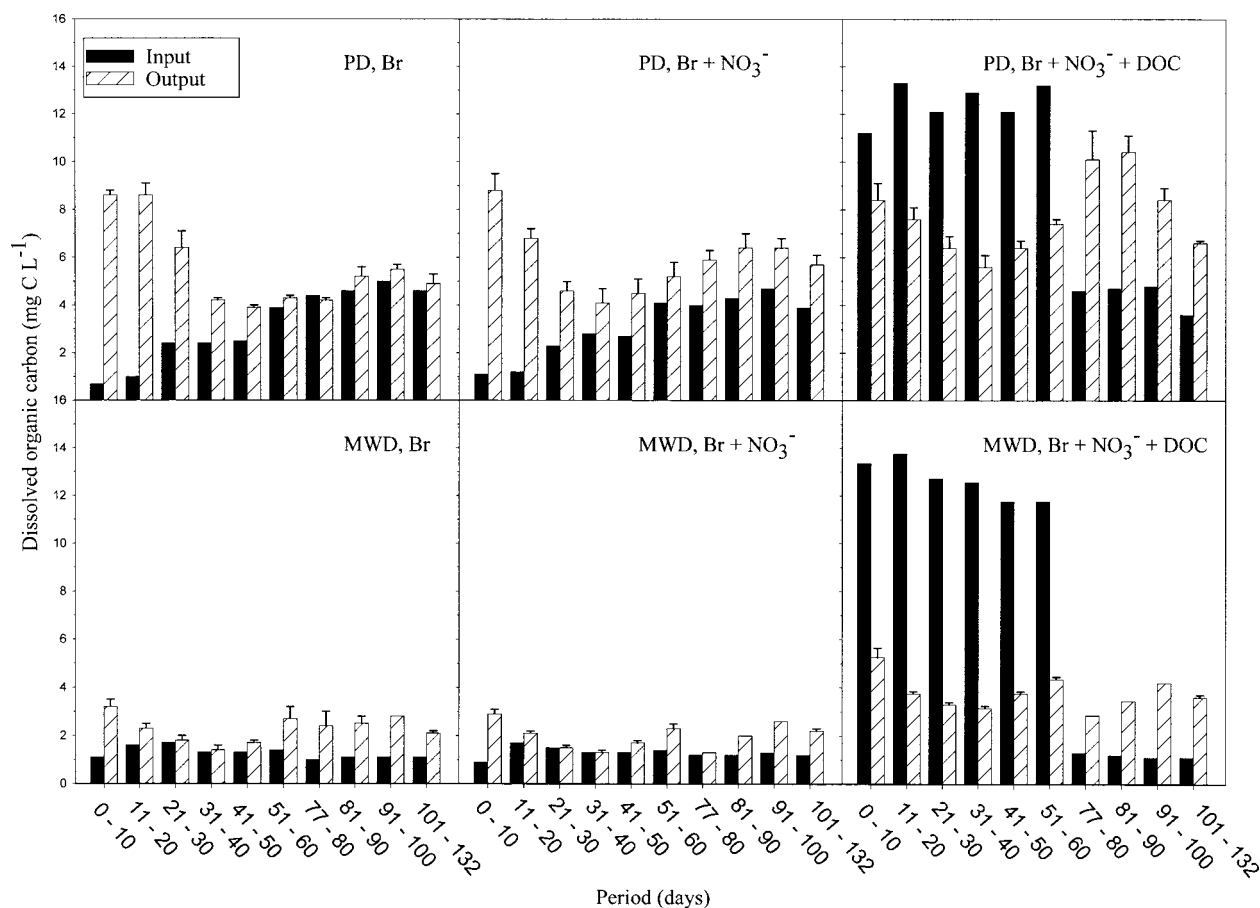


Fig. 5. Dissolved organic carbon (DOC) concentrations in the inflow and outflow of poorly drained (PD) and moderately well-drained (MWD) mesocosms. Vertical bars represent standard deviation of the mean ($n = 6$ to 27 observations).

These conversion rates of available DOC are within the range reported for methanol (50%, Grguric et al., 2000), and hyporheic DOC (>50%, Findlay and Sobczak, 1996), but lower than reported for acetate (approximately 100%, Baker et al., 1999).

Although CO_2 production significantly increased in the PD cores with DOC amendment, the conversion rate of DOC in the NO_3^- plus DOC treatments was much lower than in the control and the NO_3^- -amended treatment (Fig. 3). The additional CO_2 produced in response to DOC amendment accounted for only 15% (PD) and 3% (MWD) of the DOC added. These findings suggest that the daily addition of approximately 0.3 mg C kg^{-1} as DOC may have exceeded the C miner-

alization capacity of the riparian aquifer heterotrophic community.

During the dosing experiment, water flow rate (pore water velocity, 2.5 cm d^{-1}), temperature, and DO conditions were similar to those measured in the field (Nelson et al., 1995). Nonetheless, net C removal as DOC from the mesocosms was noted. These losses, in addition to respiratory loss as CO_2 , would lead over time to a gradual depletion of the mesocosm C stocks. Therefore, to maintain the system at steady state, a sustained process of subsurface C replenishment is needed. In our treatments with added DOC, the C budget in the PD cores was almost in balance (a deficit of only 1.1 mg C kg^{-1} soil), whereas an estimated 9.7 mg C kg^{-1} soil was re-

Table 3. Sulfate budget for mesocosms taken from beneath poorly drained (PD) and moderately well-drained (MWD) soils in a riparian forest and amended with Br, Br + NO_3 , and Br + NO_3 + DOC. Units are $\text{mg SO}_4\text{-S kg}^{-1}$ soil. Values are the mean \pm SD of triplicate cores.

Treatment	Dosing period, 0–56 d		Dosing period, 70–132 d		Whole experiment sulfate balance
	$\text{SO}_4\text{ in}$	$\text{SO}_4\text{ out}$	$\text{SO}_4\text{ in}$	$\text{SO}_4\text{ out}$	
Br	2.7 ± 0.1	3.0 ± 0.1	3.4 ± 0.1	3.2 ± 0.2	-0.2 ± 0.1
Br + NO_3	2.7 ± 0.1	3.2 ± 0.3	3.4 ± 0.1	3.6 ± 0.2	-0.7 ± 0.3
Br + NO_3 + DOC	2.7 ± 0.1	3.9 ± 0.1	3.4 ± 0.1	4.5 ± 0.2	-2.3 ± 0.1
Br	3.4 ± 0.2	6.5 ± 0.9	4.9 ± 0.2	6.8 ± 0.3	-5.0 ± 1.0
Br + NO_3	3.5 ± 0.1	6.3 ± 0.7	5.0 ± 0.1	6.6 ± 0.5	-4.4 ± 0.6
Br + NO_3 + DOC	3.2 ± 0.6	5.4 ± 1.5	4.6 ± 0.8	6.1 ± 1.1	-3.8 ± 0.6

† $\text{SO}_4\text{ in}$ and $\text{SO}_4\text{ out}$ = sulfate in input solution and effluent, respectively.

Table 4. Soil organic carbon (SOC) and microbial biomass C (MBC) in soil matrix and patches extracted from mesocosms of shallow aquifer material. Values are mean \pm SE with the number of determinations in parentheses.

Drainage class	Material	SOC	MBC
		g C kg ⁻¹	mg C kg ⁻¹
PD	Matrix	2.3 \pm 0.2 (9)	39.2 \pm 2.0 (36)
PD	Patch	12.1 \pm 2.7 (7)	103.1 \pm 2.8 (6)
MWD†	Matrix	2.0 \pm 0.1 (9)	41.5 \pm 0.9 (31)

† Patch was not found in any MWD core.

tained in the MWD cores (Table 2). This amount represents nearly half of the DOC (16.2 mg C kg⁻¹ soil) added to the MWD cores during the first 56 d of the experiment. In addition to the lower net DOC retention, it also appears that DOC is weakly retained in the PD cores. A comparison of the DOC balances between the first (0–56 d) and second part (70–132 d) of the experiment indicates that nearly 70% of the DOC retained in the PD cores during the first period may have been released with cessation of external DOC input during the second period.

Thus, there are clear differences between mesocosms from the two drainage classes with respect to the fates of added DOC with greater C decomposition in the PD and more C retention in the MWD soils. A summary of these differences may be as follows: (i) greater CO₂ production in the PD cores, (ii) generally greater biode-

gradability of DOC extracts from the PD forest floor, and (iii) limited DOC sorption and thus greater DOC availability in the PD cores. In addition, the PDOM-associated microbial biomass data (Table 4) also suggest the occurrence in the PD cores of a larger microbial population to metabolize the available DOC. Although PDOM account for <1 to 10% of the mesocosm mass (Addy et al., 1999), their presence in the PD cores and absence in all the MWD cores likely contribute to variation in CO₂ production and DOC fate in the mesocosms.

It is interesting to note that while addition of DOC increased CO₂ production, monitoring of N gas evolution has shown that addition of external DOC did not stimulate denitrification in these aquifer mesocosms (Jacinthe et al., 1998). Production of CO₂ is an index of overall microbial activity, while N gas production reflects the response of a special group of microbes, namely denitrifiers. This differential response (N gases vs. CO₂ production) to DOC addition suggests that denitrifiers can utilize a narrow range of substrates (not present in significant amounts in the DOC that was added) compared to the general heterotrophic population. It is also possible that denitrification is restricted to PDOM “hotspots” of activity, where C limitation is less of a factor.

Sources of DOC to a riparian forest shallow aquifer include forest floor leaching, stemflow, deep rhizode-

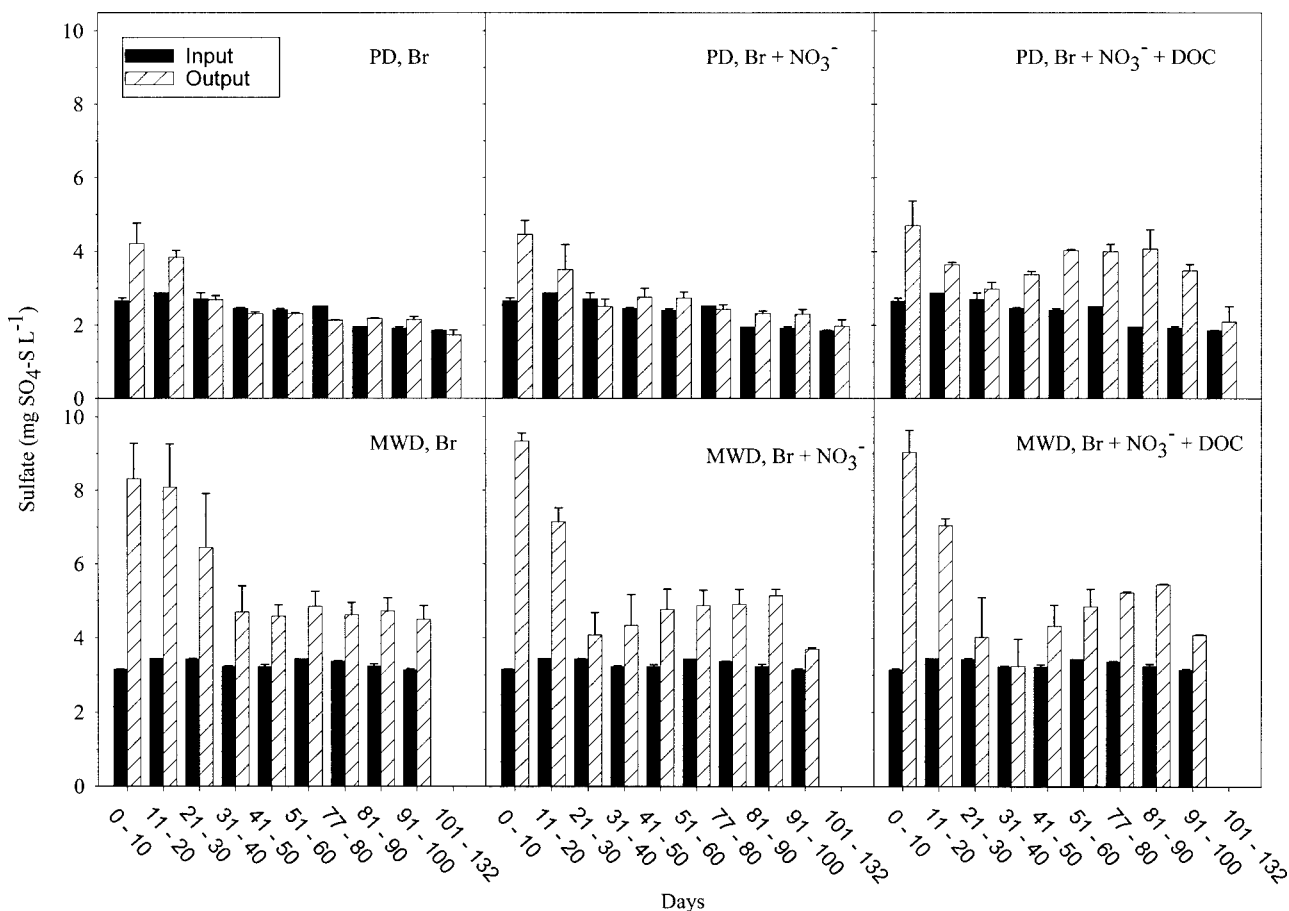


Fig. 6. Sulfate (SO₄²⁻) concentrations in the inflow and outflow of poorly drained (PD) and moderately well-drained (MWD) mesocosms. Vertical bars represent standard deviation of the mean ($n = 6$ to 27 observations).

position, and roots turnover (Haycock and Pinay, 1993). At our riparian forest site, annual forest floor flushing during snowmelt events may provide an important pathway for DOC delivery to the aquifer. While background aquifer DOC remained nearly constant ($1.3 \pm 0.2 \text{ mg C L}^{-1}$) in the area beneath the MWD soil, it increased from $1.4 \pm 0.6 \text{ mg C L}^{-1}$ in the early autumn to $3.8 \pm 0.8 \text{ mg C L}^{-1}$ in the late autumn–early winter in the area beneath the PD soil. This temporal variation of background DOC (Fig. 5) suggests that, during the dormant season, DOC leaching may have occurred to a greater extent in the PD than in the MWD area of the riparian forest. This variation is also consistent with our finding of greater DOC retention in the MWD than in the PD cores, and underscores the control of soil hydrology on DOC transport in riparian soils.

In addition to CO_2 production differences, the PD and MWD soils also differed with regard to their DOC-retention capacity, likely due to differences in the reactivity and availability of sorptive surfaces. Research has shown that Fe- and Al-bearing minerals are the most important solid phase surfaces controlling DOC sorption (Kaiser et al., 1996; Hagedorn et al., 2000), and that sorption intensity is often reduced due to coverage of sorption sites by organic compounds and DOC competition with inorganic ligands (NO_3^- , SO_4^{2-} , PO_4^{3-}) for sorption sites (Moore et al., 1992; Kaiser et al., 1996). Given SOC data (Table 4), and C balance similarities between the control and the NO_3^- treatment, these factors appear inadequate to explain the DOC retention difference between the PD and MWD cores. As previous studies have shown (Hagedorn et al., 2000; Carlyle and Hill, 2001; Knapp et al., 2002), reduced conditions ($\text{DO}, 2 \text{ mg L}^{-1}$) in the PD cores may have led to dissolution of mineral oxides resulting in a loss of mineral surfaces, which translated into limited capacity to retain DOC. The integrity of these mineral surfaces have probably been maintained in the MWD cores making DOC sorption possible. Furthermore, the greater release of SO_4^{2-} in the MWD cores would suggest that SO_4^{2-} may have been displaced during DOC sorption in the MWD cores (Vance and David, 1992; Kaiser and Zech, 1996, 1998). However, our data do not fully support that interpretation as SO_4^{2-} release was of similar magnitude in all the MWD cores regardless of treatments. It seems that internal SO_4^{2-} production rather than displacement is the contributing factor to the greater SO_4^{2-} release in the MWD cores.

The fate of CO_2 produced in riparian ecosystems is influenced by chemical, biological, and transport processes. Carbonate and secondary mineral formation (Chapelle, 2000) represent potential CO_2 sinks. In the present study, the pH of ground water inflow and outflow was in the 4.5 to 6.1 range (study wide avg. 4.9) with no difference due to soil drainage class, ground water amendment, and sampling period. In this pH range, dissolved inorganic C will occur predominantly as carbonic acid (H_2CO_3), with negligible amounts of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) (Sposito, 1989). Thus, formation of metal carbonates, as a potential CO_2 sink seems unlikely in this riparian system.

Although not quantified, utilization of CO_2 by autotrophic nitrifiers in the Calvin reductive pentose cycle (Schmidt, 1982) is a probable CO_2 sink as internal NO_3^- production in the range 6.3 to $25 \mu\text{g N kg}^{-1} \text{ d}^{-1}$ was measured during the first 40 d of the experiment (Jacinthe et al., 1998). However, this sink was likely important only for a limited period of time as net N nitrification was nil after 40 d of dosing.

The CO_2 produced in shallow riparian aquifers can be transported to neighboring streams and other surface water bodies when ground water emerges or, could be emitted at the soil surface. Which process is dominant depends primarily on hydrology, geomorphology, and climatic conditions. The sandy soil material overlying the riparian aquifer at this study site should offer limited restriction to CO_2 diffusion and emission. Likewise, CO_2 outgassing at ground water emergence sites could also be an important pathway of CO_2 return to the atmosphere as CO_2 supersaturation was observed throughout this study. Increased CO_2 production could also be expected when the water table reaches the near surface soil layers during the winter/spring season. However, low temperature during that period of the year may restrict biological activity in the shallow aquifer.

CONCLUSIONS

Although the PD and MWD cores were extracted from shallow aquifer sites only 30 m apart, their biological and physico-chemical properties with regard to C processing were quite distinct. The PD aquifer material was more biologically active, as determined by CO_2 production, and was more responsive to NO_3^- and DOC input than material from the MWD section of the riparian aquifer. Conversely, the MWD cores retained DOC more efficiently than the PD cores, suggesting that this drainage class may limit horizontal transfer of ground water DOC to other locations within the riparian zone. Previous research evaluating DOC dynamics and transport in terrestrial landscapes has primarily focused on the vertical movement, decomposition, and retention of DOC in different soil layers. The present study highlights the need for inclusion of a horizontal component in investigations of DOC transport and fate. Given the spatial distribution of soil drainage classes in riparian zones, knowledge of the biophysical diversity and the spatial relationships between these landscape units will further our understanding of the functioning and environmental benefits of riparian ecosystems.

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