Mitigation of Shallow Groundwater Nitrate in a Poorly Drained Riparian Area and Adjacent Cropland

Jennifer H. Davis, Stephen M. Griffith,* William R. Horwath, Jeffrey J. Steiner, and David D. Myrold

ABSTRACT

Riparian ecosystems, through their unique position in the agricultural landscape and ability to influence nutrient cycles, can potentially reduce NO_3 loading to surface and ground waters. The purpose of this study was to determine the fate of NO_3 in shallow groundwater moving along a lateral flowpath from a grass seed cropping system through an undisturbed mixed-species herbaceous riparian area. Soil A (30–45 cm) and C horizon (135–150 cm) NO_3, dissolved oxygen, and nitrous oxide concentrations were significantly higher in the cropping system than the adjacent riparian area. Nitrate concentrations in both horizons of the riparian soil were consistently at or below 0.05 mg N L^{-1} while cropping system concentrations ranged from 1 to 12 mg N L^{-1}. Chloride data suggested that NO_3 dilution occurred from recharge by precipitation. However, a sharp decrease in NO_3/Cl ratios as water moved into the riparian area indicated that additional dilution of NO_3 concentrations was unlikely. Riparian area A horizon soil water had higher dissolved organic carbon than the cropping system and when the riparian soil became saturated, available electron acceptors (O_2, NO_3) were rapidly reduced. Dissolved inorganic carbon was significantly higher in the riparian area than the cropping system for both horizons indicating high biological activity. Carbon limitation in the cropping system may have led to microbial respiration using primarily O_2 and to a lesser degree NO_3. Within 6 m of the riparian/cropping system transition, NO_3 was virtually undetectable.

T$_{\text{HE}}$ presence of high NO_3 in ground and surface water can, under certain conditions, be associated with agricultural sources including the use of fertilizer N (Goldstein et al., 1998). Overuse of fertilizer, poor timing of applications, and the temporary nature of the crop sink for N all contribute to potential excess NO_3 in agricultural landscapes (Davis, 2003). On-farm reduction and optimization of fertilizer N applications are potential remedies for elevated NO_3 concentrations in water supplies; however, the relatively low cost of fertilizer N makes these approaches difficult to justify (Martin et al., 1999). Riparian zones, which can potentially mitigate NO_3, are receiving increased interest as alternatives for protecting and improving water quality (Hill, 1996).

The effectiveness of riparian zones at decreasing NO_3 concentrations during transport from upland agricultural fields to streams can depend on the extent, management, and type of vegetation as well as the topography and hydrology of the site (Young et al., 1980; Peterjohn and Correll, 1984; Lowrance et al., 1984b; Dillaha et al., 1989;

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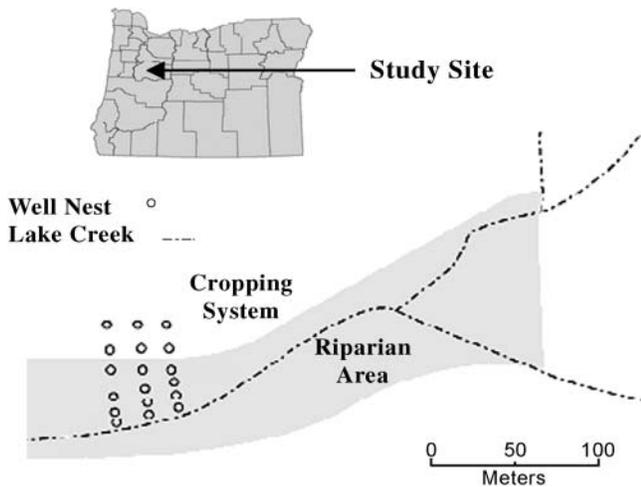
Haycock and Pinay, 1993; Groffman et al., 1996; Schnabel et al., 1996; Martin et al., 1999; Wigington et al., 2003). Both biological and physical processes can be responsible for the observed reductions in riparian soil water NO_3 concentrations. Biological processes of NO_3 removal include immobilization by plants (Peterjohn and Correll, 1984; Haycock and Pinay, 1993) and microbes, denitrification (Jacobs and Gilliam, 1985; Lowrance, 1992), and dissimilatory NO_3 reduction to NH_4 (DNRA) (Hill, 1996). Denitrification results in the net loss of N from the ecosystem whereas plant or microbial uptake and DNRA would result in retention. Physical processes include the mixing of water at converging flow paths, divergence of high NO_3 groundwater around a dense soil layer, or upwelling of older, low NO_3 groundwater (Böhlke et al., 2002; Puckett et al., 2002; Israel et al., 2005). These processes can be misinterpreted as biological consumption of NO_3 and loss from the system (Mengis et al., 1998). Dominant processes will affect how and if riparian areas can be managed for NO_3 removal. For example, if physical processes dominate, vegetation management (type of vegetation, width of area, etc.) would be a less effective tool in reducing NO_3 concentrations.

Most riparian studies have been conducted in the eastern coastal plain of the United States (Hill, 1996). In the Willamette Valley, Oregon, soil and climatic conditions are very different. Nitrate can accumulate in soils during the dry warm summers and then be exported in shallow groundwater during the cool wet winters, sometimes at levels exceeding the EPA limit of 10 ppm NO_3–N (Davis, 2003).

The primary purpose of this study was to determine the transport and fate of NO_3 in the A and C soil horizons as water moves from an intensively managed cropping system through an undisturbed mixed-species, herbaceous riparian area. Specifically, we wanted to determine the efficacy of the seasonally saturated riparian area at mitigating shallow groundwater NO_3 concentrations and determine underlying biotic and/or physical mechanisms. We also evaluated the contribution of NO_3 to the riparian area from the transition of a fourth year perennial ryegrass (*Lolium perenne* L.) crop to no-till clover (*Trifolium repens* L.) cropping system.

MATERIALS AND METHODS

Site Description

Experiments were conducted from fall 1997 through the early summer 1999 on a tributary of Lake Creek in Linn County, Oregon, USA (44°32′ N, 123°03′ W) (Fig. 1). The

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Abbreviations: DIC, dissolved inorganic carbon; DNRA, dissimilatory nitrate reduction to ammonium; DOC, dissolved organic carbon; DO, dissolved oxygen; ECD, electron capture detector.

Fig. 1. Location of the study site in Linn County, OR and placement of three transects of wells, running perpendicular to the stream from the cropping system through the riparian area to Lake Creek.

study site consisted of an ephemeral stream bordered on both sides by an uncultivated, herbaceous, mixed species riparian area that buffered the stream from an adjacent intensively managed perennial ryegrass seed production field. Water quality was reported for the site in the previous 2 yr (fall of 1995 to summer 1997) by Wigington et al. (2003). Topography at the Lake Creek site is quite flat, with slopes <3% and the dominant soils at the site are poorly drained (Dayton-Holcomb series). Dayton soil series (fine, smectitic, mesic Vertic Albaqualfs) extended into the riparian area approximately 25 m. The Holcomb soil series (fine, smectitic, mesic Typic Argialbolls) occupies the upland position extending from the Dayton soil into the cropping system. The presence of a restrictive, clay IIB_t horizon below the A and E horizons in Dayton and Holcomb soils results in perched water tables that persist during the wet season (Boersma et al., 1972). These restrictive horizons are underlain by silty clay loam or silt loam IIIC horizons.

The riparian area was 30 to 48 m wide and vegetated predominantly with grasses and fewer forbs, sedges, and rushes (McAllister et al., 2000). The riparian area had not been cultivated since 1975, although the vegetation was occasionally mowed and removed before 1995. In the fall of 1998, the cropping system started its fourth year in perennial ryegrass seed production and received 173 kg N ha^{-1} as a urea-ammonium sulfate solution in split spring applications (3 Mar. 1998 and 11 Apr. 1998). In September 1998, the ryegrass seed crop was sprayed with glyphosate and direct seeded with clover. Vigorous plant growth of the clover did not begin until April 1999, leaving the soil essentially barren during the fall, winter, and early spring. The clover crop received 90 kg N ha^{-1} as urea in spring 1999.

Total annual precipitation was 1524 mm in 1998 and 1265 mm in 1999, 93% of which occurred between November and June (Hyslop Field Station, Benton County, OR; 44°38′ N, 123°11′ W) (Oregon Climate Service, 2005). More importantly, total precipitation for water year 1997–1998 (Sept. 1997 to Sept. 1998) was 1250 mm and water year 1998–1999 (Sept. 1997 to Sept. 1998) was 1518 mm. As usual for this region's marine climate, little precipitation occurred from June to October both years; thus the soil became dry and cracked and the water table dropped below 1.5 m during these periods. Consistent seasonal precipitation began in October and stream flow started in November (Wigington et al., 2003).

During the wet winter (November to February), the water tables remained close to the soil surface and soils of both the riparian area and cropping system were saturated. As spring precipitation decreased, water tables fluctuated, and wet/dry cycles occurred in the surface soils. Data from Wigington et al. (2003) indicated that when soils were saturated, water moved through the soil along a downslope hydraulic gradient through these poorly drained soils from the upland cropping system through the riparian area to the stream. Only a small proportion of stream flow came from this flow path. Most stream water originated from overland flow through ephemeral swales in the grass seed cropping system.

Sample Collection

In 1997, three transects of closed-headspace sampling wells, approximately 17.5 m apart, were installed perpendicular to the stream (Fig. 1). Each transect consisted of six sampling points. At each sampling point (well nest), a pair of wells were installed to collect water from the A horizon (30–45 cm) and the C horizon (135–150 cm). Rows of well nests ran parallel to the stream. Two rows were in the Dayton soil of the riparian area (0.5 and 8–9 m from the stream), the riparian area with Holcomb soil (15–17 and 24–32 m from the stream), and the cropping system with Holcomb soil (36–44 and 51–58 m from the stream). Closed-headspace sampling wells were installed 1 m from existing open headspace wells (Wigington et al., 2003). The closed headspace wells (Fig. 2) containing Argon allowed sampling of soil water, under low redox conditions, that had not been exposed to the atmosphere. These wells have been shown to contain lower, probably more realistic concentrations of NO$_3$ (Baham et al., 1999) and also permitted the sampling of dissolved gases. The sampling wells consisted of
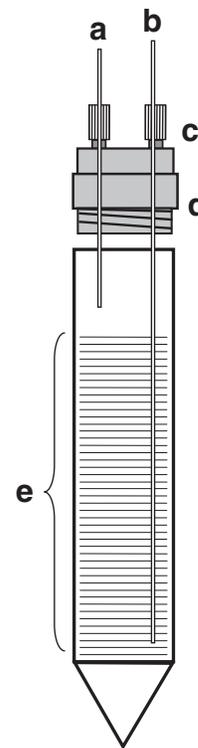
Fig. 2. Closed-headspace well showing (a) inlet for the introduction of Argon gas, (b) water sample collection tube, (c) plastic compression fitting, (d) screw top to well, (e) 15 cm screening (Baham et al., 1999).

5.1 cm i.d. PVC pipes with a slot width of 0.25 mm and a slot-screening interval of 15 cm. The tops of the sampling wells were sealed except for two lengths of 3.2 mm o.d. Teflon tubing extending from the well bottom to the soil surface. In the fall of 1998, three pairs (A and C horizon) of open-headspace piezometers were installed on the center transect equidistant between the last row of riparian wells and first row of cropping system wells, the central pair being located on the riparian/cropping system border.

When water was present, samples were collected weekly from November 1997 to June 1998 (water year 1997/1998) and November 1998 to May 1999 (water year 1998/1999), alternating weekly between the A and C horizon. Before sampling, three well volumes were removed with a stainless steel hand pump. During sampling, the vent tube (Fig. 2) was connected to an inner tube containing high-grade argon gas. Samples to be analyzed for NO_3, dissolved organic carbon (DOC), and Cl were collected directly into an open 250 mL amber glass bottle. After this sample was collected, a septum was placed on the sample tube and a 50-mL volume of water was drawn into a syringe and discarded. Another 40 mL of water was immediately collected and injected into a 12-mL vial whose headspace had been evacuated and flushed with high-grade helium several times. Two volumes of water were flushed through the vial before a sample was kept. This procedure was repeated with a 20-mL vial. Water from the 12-mL vials was analyzed for dissolved oxygen (DO) using Chemet kits K-7501 (detection limit: 0.025 mg O_2 L^{-1}) and K-7512 (detection limit: 1 mg O_2 L^{-1}) (CHEMetrics, Inc., Calverton, VA) and dissolved inorganic C (DIC) using the Dohrman DC-190 total organic carbon analyzer (detection limit: 0.1 mg C L^{-1}) (Tekmar-Dohrman, Cincinnati, OH). Water from the 20-mL vials was analyzed for dissolved N_2O. In the laboratory, 8 mL of water were removed and simultaneously replaced with high-grade helium. The remaining 12 mL were incubated at 25°C for 1 h to allow for headspace equilibration before gas samples were removed for analysis of N_2O on an HP6890 GC equipped with a ^{63}Ni ECD (detection limit: 0.9 μg N L^{-1}) (Agilent Technologies, Inc., Palo Alto, CA).

Samples collected for NO_3 and DOC analyses were filtered through 0.45-μm polycarbonate filters. Filters were washed before use by soaking in a sequence of two double-deionized water baths for a minimum of 24 h. Analyzing sample blanks validated the filter washing procedure. DOC was quantified by high temperature catalytic combustion on the Dohrman DC-190 total carbon analyzer (detection limit: 0.1 mg C L^{-1}) (Tekmar-Dohrman, Cincinnati, OH). Soil NO_3 was determined colorimetrically using QuikChem method 10-107-04-1-A (NO_3–N) (detection limit: 0.05 mg N L^{-1}) on a flow injection autoanalyzer (Lachat Instruments, Milwaukee, WI).

Water samples collected in 1998–1999 were filtered and analyzed as described above in addition to being analyzed colorimetrically for Cl using QuikChem method 10-117-07-1-C (detection limit: 0.02 mg Cl L^{-1}) (Lachat Instruments, Milwaukee, WI). Ratios of NO_3/Cl were calculated to determine if NO_3 disappearance was due to either biological or physical phenomena (Gast et al., 1974; Lowrance et al., 1984a; Martin et al., 1999). Chloride served as a conservative tracer for NO_3 because they are transported similarly, but Cl is biologically inactive. Along a hydrologic flowpath, if NO_3 concentrations decline and Cl concentrations stay constant, then NO_3 was likely removed biologically. If Cl concentrations change in tandem with NO_3 concentrations, then the decline in NO_3 concentrations is most likely due to either a dilution from low NO_3 groundwater (Mengis et al., 1998) or stream water (Pinay and DeCamps, 1988), or to a divergence of the flow path (Cey et al., 1999).

Data Analysis

Differences in means between the sites (cropping system vs. riparian area) and depths (A vs. C horizon) were determined by analysis of variance using a modified split-plot design, with site as the main plot and depth as subplots using SPSS statistical software (SPSS Inc., 2002). The model for this design was:

$$y_{ijkl} = \mu + S_i + B_j + SB_{ij} + \delta_{(ij)} + T_k + ST_{ik} + SBT_{iJk} + \varepsilon_{(ijk)}$$

where S is site, B is block, and T is depth. The restrictions on randomization were represented by: $\delta_{(ij)}$ the restriction error. The mean square (MS) for SB was used to test S main effect, and the MS for SBT used to test the T main effects and ST interaction. Means separations were done using Fisher's Protected Least Significant Difference test (Sokal and Rohlf, 1981). Data were not transformed. All differences were significant at $p \leq 0.001$, unless otherwise stated.

RESULTS

Nitrate

Soil pore water NO_3 concentrations from closed-headspace wells were significantly ($p \leq 0.001$) higher in the cropping system than the riparian area for A (30–45 cm) and C horizons (135–150 cm) both years (Fig. 3). Significance of main effects and interactions are shown in Table 1. Mean A and C horizon soil water NO_3 concentrations in the riparian area were consistently low (≤ 0.05 mg NO_3–N L^{-1}). The mean and standard error of NO_3 concentrations in the A horizon of the cropping system (years pooled) were 4.19 ± 0.18 mg NO_3–N L^{-1} and in the C horizon were 5.62 ± 0.13 mg NO_3–N L^{-1}. Data collected in 1998–1999 from
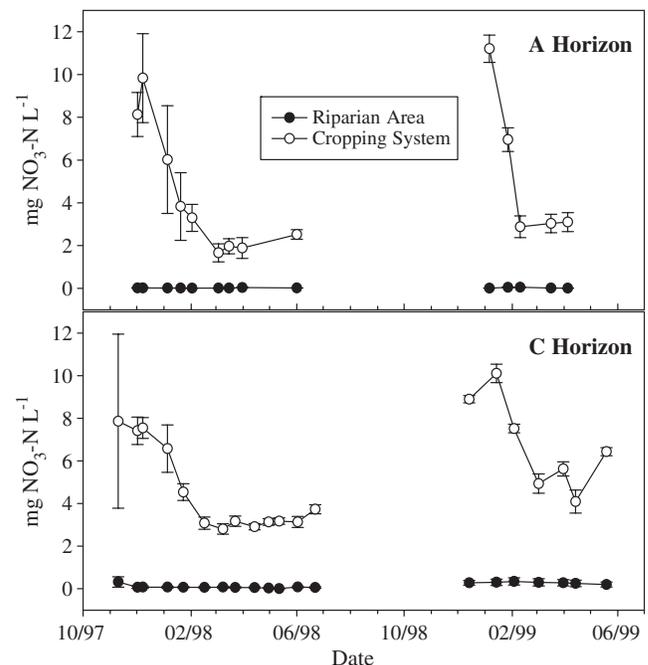

Fig. 3. Mean and standard error of nitrate concentrations in the soil pore water of the A and C horizons of the riparian area and cropping system.

Table 1. Statistical summary of main effects and interactions of site and depth.†

| Parameter	NO$_3$	DOC	N$_2$O	DO	DIC	Cl
Site	***	***	***	***	***	ns§
Depth	***	***	***	***	***	***
Site × depth	***	***	***	***	ns	***

*** $p = 0.001$.

† DOC, dissolved organic carbon; DO, dissolved oxygen; DIC, dissolved inorganic carbon.

§ ns, $p > 0.05$.

three evenly spaced, open-headspace piezometers placed between the fourth (riparian) and fifth (cropping system) rows showed that in the A horizon, NO$_3$ concentrations dropped immediately within the transition zone (Fig. 4). In the C horizon, there was a more gradual decrease in NO$_3$ concentrations as water moved from the cropping system into the riparian area. In the cropping system, A and C horizon NO$_3$ concentrations were highest after fall wet-up and decreased over the water year (Fig. 3). Elevated NO$_3$ concentrations after fall wet-up were most likely due to the movement of mineralized and nitrified N that accumulated in the soil over the warm, dry summer (Nelson et al., 2006). Higher C horizon soil water NO$_3$ reflected movement of NO$_3$ below the root zone and the reduced biological activity of subsoils (Böhlke and Denver, 1995).

Cropping system NO$_3$ concentrations were significantly higher in 1998–1999 (6.66 ± 0.17 mg NO$_3$–N L^{-1})
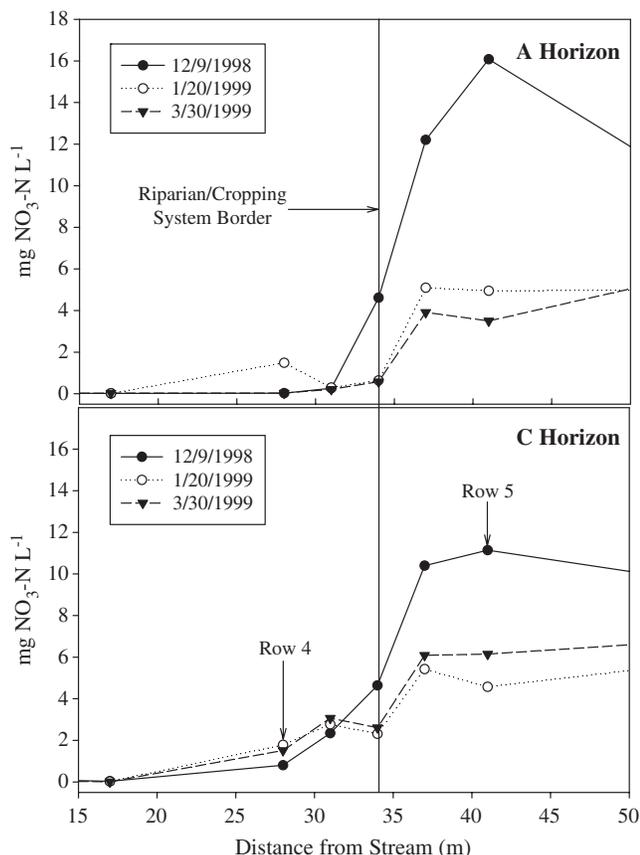
(first-year clover crop) than 1997–1998 (3.15 ± 0.15 mg NO$_3$–N L^{-1}) (fourth year perennial ryegrass seed crop). Differences most likely resulted from the transition to a new crop in the fall of 1998. The clover planting was sparsely established with no more than a few leaves per plant present until April the following spring.

Chloride

Unlike NO$_3$, Cl concentrations were not significantly different between the riparian area and cropping system (Table 1). A horizon soil water showed a consistent decrease in Cl concentrations over the 1998–1999 water year (Fig. 5). The decrease in Cl coincided with the decrease seen in cropping system NO$_3$, where concentrations decreased until April and then remained relatively constant until June (Fig. 3). The percentage drop from January to April in NO$_3$ (73 ± 2.9%) was higher than Cl (51 ± 6.4%). These data suggested that dilution of A horizon soil water Cl and NO$_3$ occurred through inputs of precipitation but that biological consumption of NO$_3$ also occurred, further decreasing concentrations. C horizon Cl concentrations also decreased over the water year by 29% (± 6.0%), suggesting that dilution by recharge was also occurring in the C horizon. However, a greater decrease in cropping system NO$_3$ concentrations (60 ± 4.5%) again suggested that biological processes were also responsible for reducing NO$_3$ concentrations.

Spatial patterns of NO$_3$/Cl ratios can indicate the relative importance of biological consumption and dilution of NO$_3$ along the hydrologic flow path (Gast et al., 1974; Lowrance et al., 1984a). Martin et al. (1999) and Lowrance (1992) studied NO$_3$ dynamics in grass and wooded riparian areas and, based on decreases in the NO$_3$/Cl ratio within the riparian area, concluded that biological consumption was primarily responsible for decreased riparian NO$_3$ concentrations. Nitrate/Cl ratios (Table 2) in the A and C horizons at Lake Creek showed a dramatic and consistent decrease in NO$_3$ relative to Cl, as water moved into the riparian area. Nitrate was consistently low throughout the riparian area, whereas Cl remained relatively high. This trend was consistent
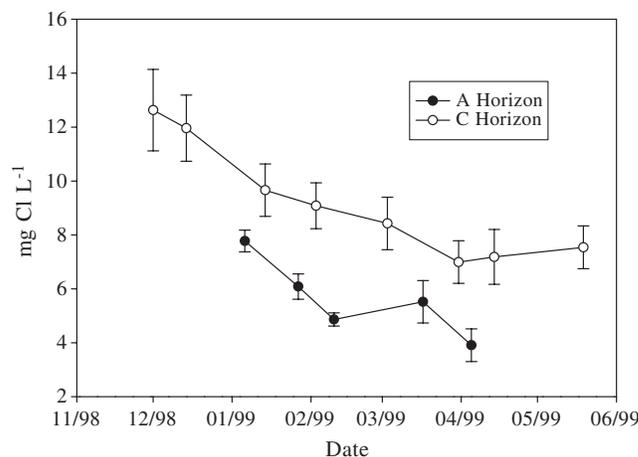

Fig. 4. Nitrate concentrations in open-headspace wells installed in the fall of 1998 between rows 4 (riparian) and 5 (cropping system) on the center transect.

Fig. 5. Mean and standard error of chloride concentrations in the soil pore water of the A and C horizons during water year 1998–1999.

Table 2. Mean and standard error of nitrate/chloride ratios (mg N L^{-1}/mg Cl L^{-1}) in the riparian area (RA) and the cropping system (CS) for water year 1998–1999 in the A and C horizons.

Distance from stream	Area	A Horizon (30–45 cm)	C Horizon (135–150 cm)
m			
0.5	RA	0.01 (0.00)	0.02 (0.01)
9	RA	0.01 (0.00)	0.01 (0.00)
17	RA	0.01 (0.00)	0.01 (0.00)
28	RA	0.01 (0.00)	0.17 (0.02)
41	CS	0.79 (0.11)	1.1 (0.07)
55	CS	0.82 (0.11)	1.1 (0.07)

with biological consumption of NO_3 along the flow path as opposed to dilution from a converging or diverging flow path.

Dissolved Organic Carbon

Soluble organic C is one potential source of energy for microbes and has been used as an indicator of the potential for biological activity in the soil profile, particularly for denitrification (Meek et al., 1970). Opposite of temporal NO_3 trends, DOC concentrations (depths pooled) were higher in 1997–1998 than 1998–1999 for the cropping system and especially the riparian area (Fig. 6). Greater rainfall in the summer of 1997 (189 mm in June, July, and August) than the summer of 1998 (50 mm) (Oregon Climate Service, 2005), may have increased wet-dry cycles, enhancing organic matter decomposition, leading to higher dissolved C concentrations (Reddy and Patrick, 1975; Aulakh et al., 1992). Mean A horizon concentrations in 1997–1998 were 13.3 mg C L^{-1} in the riparian area and 6.61 mg C L^{-1} in the cropping

Fig. 6. Mean and standard error of dissolved organic carbon (DOC) concentrations in the soil pore water of the A and C horizons of the riparian area and cropping system.

system compared with 5.14 mg C L^{-1} in the riparian area and 3.25 mg C L^{-1} in the cropping system in 1998–1999.

Spatial trends in A horizon DOC were also opposite of NO_3, with significantly higher DOC in the riparian than the cropping system for both years. Higher riparian DOC most likely reflected permanent vegetation (larger root biomass) (Tufekcioglu et al., 1999) and lack of soil disturbance (Balesdent et al., 1990). In the C horizon, there was no difference in DOC concentrations between the riparian area and cropping system and annual mean DOC concentrations were all below 5 mg C L^{-1}. Although mean annual C horizon DOC concentrations were in the range to limit denitrification, point concentrations in the riparian area reached 14 mg C L^{-1} before decreasing in late spring. The DOC concentrations in the riparian area were higher in the A than the C horizon. We hypothesized that the riparian surface soils had higher levels of DOC from the decomposition of plant residues, building and degrading of soil organic matter, and the release of root exudates. DOC concentrations in the cropping system were similar between the A and C horizons.

In 1997–1998, A horizon DOC concentrations gradually increased until March and then decreased between March and June (Fig. 6). As DOC concentrations increased, NO_3 and Cl concentrations decreased from dilution by precipitation and presumably biological consumption of NO_3. The infiltration of precipitation may have transported DOC from the surface down into the soil profile, increasing concentrations at 30- to 45-cm depth over the fall and winter. The C horizon had a similar but delayed increase in DOC but also had a dramatic decrease around the same time as in the A horizon. A horizon DOC concentrations in the second year (1998–1999) started out low, similar to those of the previous spring, increased slightly in early spring and then decreased. In 1998–1999, C horizon DOC concentrations decreased from December to January and remained consistently low for the rest of the water year. The smaller pulse of DOC in 1998–1999 may reflect potentially less organic C mineralization in the dry summer of 1998 compared with 1997.

Dissolved Oxygen

Dissolved oxygen, the electron acceptor that yields the most energy for microbial respiration, can be an indicator of potential NO_3 reduction through denitrification or DNRA. A and C horizon soil water DO concentrations, measured in 1998–1999, had temporal and spatial patterns similar to NO_3 (Fig. 7). A horizon DO generally decreased over the sampling season and was higher in the cropping system than the riparian area ($p \leq 0.001$). The DO concentrations inside the riparian area were generally <1.0 mg O_2 L^{-1} except in wells next to the stream where concentrations were 2.5 to 6 mg O_2 L^{-1}. Water in the A horizon sampling wells next to the stream mixes with well-aerated stream water (Wigington et al., 2003). A horizon riparian area DO was low by January and temporal changes were minor. A horizon DO in the cropping system started out higher
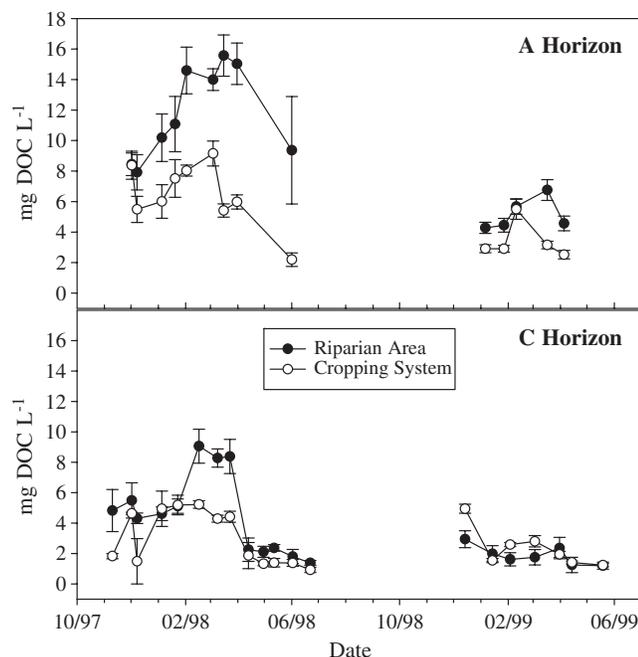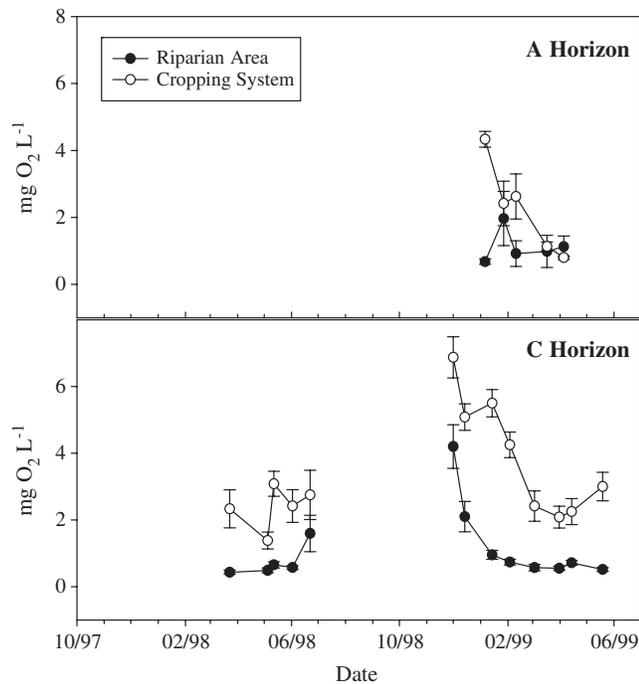
Fig. 7. Mean and standard error of dissolved oxygen concentrations in the soil pore water of the A and C horizons of the riparian area and cropping system.
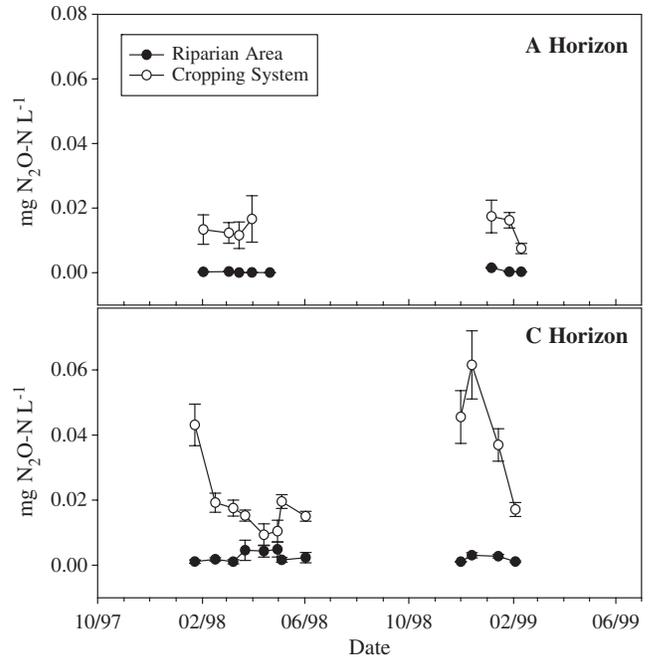

Fig. 8. Mean and standard error of dissolved nitrous oxide concentrations in the soil pore water of the A and C horizons of the riparian area and cropping system.

but dropped by 3.7 mg L^{-1} from January to April. This decrease was not the result of dilution by precipitation because water entering the soil profile would have had approximately 11 mg O$_2$ L^{-1} (equilibrium with the atmosphere at 10°C) (Weiss, 1970).

Spatial and temporal patterns for C horizon soil water DO were similar to those of the A horizon, with two exceptions. In January 1999, DO concentrations were lower in A horizon than C horizon wells presumably from higher biological activity and O$_2$ consumption. A second difference between A and C horizon DO was low concentrations (0.9 mg O$_2$ L^{-1}) in the C horizon wells closest to the stream where there was less mixing with stream water. Otherwise, C horizon DO concentrations were spatially similar to NO$_3$ wherein DO dropped significantly as water moved from the cropping system into the riparian area ($p \leq 0.02$). C Horizon DO was relatively high in December 1998 but by January, concentrations dropped significantly in the riparian area to below 1 mg O$_2$ L^{-1} and remained low through late spring. Cropping system DO in the C horizon decreased gradually until April and then increased in May and June. The same pattern was seen in limited data collected in 1997–1998. Increased late spring DO was most likely from the start of wet/dry cycles in the surface soils. The riparian area maintained low DO conditions but the cropping system did not.

Dissolved Nitrous Oxide

Nitrous oxide, an intermediate product of denitrification, followed spatial patterns similar to NO$_3$ (Fig. 8). There was more NO$_3$ and N$_2$O in the cropping system

than in the riparian area for both A and C horizon soil water in both years of the study. Nitrous oxide in soil water containing relatively high NO$_3$ provided indirect evidence that denitrification was a potential mechanism of NO$_3$ reduction.

Inorganic Carbon

Dissolved inorganic carbon (DIC), a byproduct of organic matter oxidation, can be indicative of biological activity in soils. Dissolved inorganic carbon was significantly higher in the riparian area than the cropping system for both horizons (Fig. 9). A horizon DIC concentrations increased over the spring presumably from increased activity with soil warming with the increase being much greater in the riparian area. Dissolved inorganic carbon in the C horizon also increased in the riparian soil in the spring while the cropping system did not. Although DIC could come from the dissolution of carbonates in the riparian area, the seasonal and spatial trends in DIC in combination with trends in NO$_3$, DO, and DOC indicate that the oxidation of organic C to support microbial respiration is occurring, especially in the riparian soil.

DISCUSSION

Higher NO$_3$ concentrations in cultivated compared with riparian shallow groundwater, have been well documented (Lowrance et al., 1984b; Verchot et al., 1997; Mengis et al., 1998). Differences have been attributed to biological processes (Peterjohn and Correll, 1984; Lowrance et al., 1984b; Jacobs and Gilliam, 1985; Haycock and Pinay, 1993), hydrological processes (Böhlke
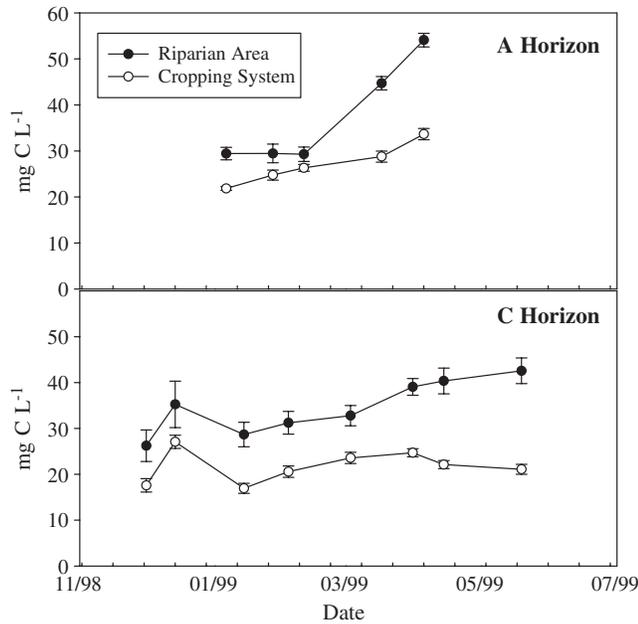
Fig. 9. Mean and standard error of dissolved inorganic carbon concentrations in the soil pore water of the A and C horizons of the riparian area and cropping system.

et al., 2002; Puckett et al., 2002), or both (Israel et al., 2005). At the Lake Creek site, the hydraulic gradient implied flow paths from the cropping system, through the riparian area, to the stream (Wigington et al., 2003). Greater piezometric head in deeper wells than in surface water can indicate discharge of and dilution by deeper groundwater (Böhlke et al., 2002; Puckett and Hughes, 2005). Head measurements made in open piezometers in the C horizon at the Lake Creek site did not indicate upwelling of deeper groundwater (Wigington et al., 2003). In addition, the dramatic and consistent decrease in NO_3 relative to Cl concentrations as water moved into the riparian area provided additional evidence that dilution from a converging or diverging flow path was not a major factor contributing to low riparian NO_3, suggesting NO_3 removal during transport. Decreases in both Cl and NO_3 concentrations in the cropping system over the water year suggested dilution from recharge; however, greater decreases in NO_3 concentrations in relation to Cl in the cropping system pointed to additional reduction in NO_3 concentrations from biological consumption as well. Plant uptake has been shown to be a significant sink for NO_3 in the A horizon of both the riparian area and cropping system (perennial ryegrass) especially in late spring with the significant growth and N uptake of grass species (Davis et al., 2006). In the winter, during fallow periods, and below the root zone, microbial processes are responsible for the bulk of reductions in NO_3 concentrations.

The riparian area and cropping system are two distinct systems connected by lateral water flow. Consistently low riparian NO_3 concentrations are a reflection not only of the lack of direct fertilizer applications but to the ability of the riparian soils to process NO_3. In 1997–1998, although riparian DOC concentrations were

higher than in the cropping system, both areas were above the 2 to 5 mg C L^{-1} range found to limit denitrification in groundwater microcosms (Groffman et al., 1996) and more in line with groundwater DOC concentrations of Israel et al. (2005) (12 to 14 mg C L^{-1}) where denitrification was thought to have led to low riparian NO_3 groundwater concentrations in one transect of wells. When the soil at the Lake Creek site became saturated in the fall, available O_2 in the riparian area was most likely consumed through microbial and root respiration (A horizon), as evinced by concomitant increases in DIC, creating a strong redox gradient between the riparian area and cropping system. Dissolved oxygen concentrations were sufficiently low (<2 mg O_2 L^{-1}) to then promote respiration using NO_3 as an electron acceptor (Gillham, 1991; Cey et al., 1999). In addition, Baham et al. (1999) showed evidence of Fe and Mn reduction in the riparian soil with maximum reduction occurring at a soil depth of 10 to 20 cm. Baham et al. (1999) also found that shallow groundwater of the riparian area contained higher concentrations of Fe(II) and Mn(II) than the cropping system with peak concentrations in the spring reaching 1500 μM Fe(II) and 150 μM Mn(II). Denitrification is not dependant solely on the availability of organic C as an electron donor; reduced inorganic Fe, Mn, and S can also supply electrons for NO_3 reduction (Korom, 1992; Tesoriero et al., 2000). Upon entering the Fe- and Mn-reducing riparian area, NO_3 in incoming groundwater would likely be reduced through autotrophic and/or heterotrophic denitrification (Korom, 1992). It is also likely that labile organic C in the solid phase provided electrons for microbial respiration (Tesoriero et al., 2000; Puckett et al., 2002). The availability of reduced Fe and Mn (Baham et al., 1999) and other forms of organic C could account for the sustained reduction in NO_3 concentrations within the riparian area when DOC concentrations were low, such as in water year 1998–1999 and in the subsoil. A similar upstream site on Lake Creek, which did not have a naturally vegetated riparian area (cropped to stream edge), was found to be more frequently flooded than our riparian site, but was also found to have higher redox values and higher NO_3 concentrations (Wigington et al., 2003). The effect the riparian area had on water quality (low NO_3 concentrations) was not due only to the proximity of the riparian area to the stream but to whole ecosystem dynamics.

The cropping system had lower DOC and higher NO_3 and DO than the riparian area most likely from periodic disturbance and direct applications of fertilizer N (Bauder et al., 1993). The cropping system soil (10–30 cm) has been shown to contain larger available N pools with slower turnover than the riparian area (Davis et al., 2006). Potentially lower microbial activity (lower DIC) in the cultivated soils (Horwath et al., 1998) may have led to microbial respiration using primarily O_2, and to a lesser degree, NO_3. Since Fe(II) and Mn(II) concentrations were much lower in the cropping system compared with the riparian area, autotrophic denitrification might not have played a large role. In the cropping system, DOC concentrations in 1997–1998 were

relatively high (>5 mg C L^{-1}) in winter when NO_3 reduction was occurring. The rapid spring drop in DOC did not occur with a significant drop in NO_3 concentrations. As soils warmed, aerobic respiration likely led to the spring decrease in cropping system DOC. However, even when cropping system concentrations of DO were relatively high (>2 mg O_2 L^{-1}), soil heterogeneity most likely would have allowed for some portion of NO_3 to be consumed by denitrification in localized zones or hotspots (Groffman et al., 1996; Cey et al., 1999). Gambrell et al. (1975) reported NO_3 reduction in an aerobic soil (redox 500–600 mV) and concluded that denitrification occurred in anaerobic microsites.

Even though subsoils have been shown to have lower microbial activity compared with surface soils (Parkin and Meisinger, 1989; Lowrance, 1992), C horizon NO_3 and DO were consumed in the C horizon over the water year in both the riparian area and cropping system. However, significantly lower NO_3 and DO concentrations in the riparian area shows that the redox gradient between the riparian area and cropping system existed even to this depth. Wells placed between the last row of riparian and first row of cropping system wells show that the decrease in NO_3 was more gradual in the C horizon, indicating slower processing with depth. Lower Fe(II) and Mn(II) concentrations in the C compared with the A horizon showed that the subsoil was not as highly reduced as the surface soil.

The near-fallow conditions present during the transition from perennial ryegrass seed to no-till clover in the cropping system in combination with lower DOC were most likely responsible for higher NO_3 on site in 1998–1999. Even though no-till soils generally produce lower NO_3 levels than conventionally tilled soils (Fenster and Peterson, 1979), soil disturbance with direct drilling of clover seed in early fall of 1998, compared with 4 yr of no disturbance, may have contributed some NO_3 from the mineralization of microbial biomass and soil organic matter N. Nitrate concentrations have been shown to be higher in fallow periods than where a crop was established (Khanna, 1981). Since clover establishment was poor until late spring 1999, plant N uptake would have been negligible during fall and winter, resulting in greater N loss to soil water. Therefore, higher NO_3 concentrations in water year 1998–1999 were likely due to a greater supply of NO_3 than demand for it (Nelson et al., 2006). A greater load of NO_3 from the cropping system to the riparian area in 1998–1999 did not increase NO_3 concentrations within the riparian soil indicating that the riparian area was capable of processing increased NO_3 loads.

One scenario to consider was that water flowed slow enough through the soil that NO_3–laden groundwater did not travel very far into the riparian area during the water year and that with these slow flow rates, DO and NO_3 were consumed even in soil with low DOC (Puckett et al., 2002) and microbial activity (subsoil). Groundwater velocity was calculated using saturated hydraulic conductivity estimates from the same region and soil type and at similar depths as our current study (Warren, 2002), a hydraulic gradient of 0.02 and a porosity of 0.44.

Velocity estimates in the A horizon ranged from 0.4 to 1.1 m d^{-1}, indicating that water could move from 48 to 133 m over the course of the saturated period (121 d). Since the riparian area is only 30 to 48 m wide, even low velocity estimates would allow shallow groundwater containing NO_3 in the cropping system to move completely through the riparian area. Because of the highly reduced conditions in the riparian soil, it is likely that when NO_3 entered the riparian area in groundwater from the cropping system, it was quickly consumed. In the C horizon, velocity ranged from 0.01 to 1.68 m d^{-1} indicating that water could move as little as 1.2 m and up to 203 m over the saturated period. This wide range of values makes it difficult to determine if low C horizon DO and NO_3 in the riparian area was due to sufficient biological activity or to slow water movement. It was likely that the actual velocity was somewhere in the middle of the range. Either way, the C horizon soil was capable of removing nitrate in incoming groundwater. Wigington et al. (2003) found that most stream water at this site originates from overland flow through the cropping system. Although only a small portion of incoming water interacts with the riparian soils, this poorly drained riparian system was very efficient at removing NO_3 from shallow groundwater.

Additional research is required to better evaluate surface and subsurface NO_3 consuming process rates and their controlling factors, especially the dominant electron donors. Determining the significance of denitrification vs. dissimilatory nitrate reduction to ammonium would also add to the understanding of the ability of these systems to process or retain N.

CONCLUSIONS

Data from this study suggest that both dilution from precipitation in the early water year and biological consumption, most likely plant uptake (A horizon only) and denitrification, were responsible for decreases in soil water NO_3 seen as water moved from the cropping system into the riparian area. The riparian area had biologically active A and C horizons. Oxygen and NO_3 were consumed early in the water year, creating a reductive zone where incoming NO_3 was rapidly consumed. Although the transition of the cropping system from a fourth year perennial ryegrass crop to no-till clover produced higher groundwater NO_3 concentrations, the A and C horizon riparian soil remained efficient, able to process all incoming NO_3, limiting the contribution of groundwater at this site to NO_3 in stream flow. However, stream flow at this site is dominated by overland runoff, greatly limiting the impact the riparian area can have on surface water quality.

ment or approval by the United States Department of Agriculture or the Agricultural Research Service of any product or service to the exclusion of others that may be suitable.

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