3-2008

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Clay P. Arango

J. L. Tank

J. N. Am. Benthol. Soc., 2008, 27(1):90–107

DOI: 10.1899/07-024.1
Published online: 21 December 2007

Land use influences the spatiotemporal controls on nitrification and denitrification in headwater streams

C. P. Arango[1] AND J. L. Tank[2]

Department of Biological Sciences, University of Notre Dame, Notre Dame, Indiana 46556 USA

Abstract. N and C cycles in headwater streams are coupled, and land use can modify these cycles by increasing N availability and removing riparian vegetation. To increase our understanding of how land use modifies the controls on N cycling, we quantified rates of 2 microbial N transformations in a total of 18 agricultural and urban streams (with and without riparian buffers) for 3 y to examine how riparian vegetation and land use influence sediment nitrification and denitrification. Nitrification rates were highest in agricultural streams in late spring. Nitrification was not related to streamwater NH_4^+ concentrations but was positively related to sediment C content (linear regression, $r^2 = 0.72$, $p < 0.001$). This result suggests that benthic decomposition provided NH_4^+ (via mineralization) to increase sediment nitrification. Denitrification rates did not differ among landuse types but were positively related to sediment C content and streamwater NO_3^- concentration (multiple linear regression, $R^2 = 0.78$, $p < 0.001$). Sediment C content, the primary predictor of denitrification rates, did not differ among land uses, but streamwater NO_3^- concentration, the secondary predictor of denitrification rates, was highest in winter and in agricultural streams, indicating that land use and season were more important determinants of denitrification than coupled nitrification. Substrate availability (N and C) for N transformations generally did not differ between buffered and unbuffered streams within a similar landuse type, probably because of the confounding influence of tile drainage systems, which effectively decouple stream channels from their riparian zones. Land use influenced the delivery of the necessary substrates for N transformations but decreased the role of riparian zones in stream N cycling by simplifying the drainage network of headwater streams.

Key words: nitrogen, denitrification, nitrification, riparian zones, agricultural streams, urban streams.

N frequently limits productivity in terrestrial and aquatic ecosystems, and humans have effectively doubled N availability by fixing N industrially on a large scale (Vitousek et al. 1997). Over ½ of anthropogenically derived N is applied as nitrogenous fertilizers in agricultural or urban settings, where application frequently exceeds demand (Vitousek et al. 1997) and excess N is exported from the landscape (Carpenter et al. 1998). As a consequence, streams that drain agricultural and urban catchments often have elevated dissolved inorganic N (DIN) concentrations that modify internal N cycling and transformation rates relative to streams draining less modified landscapes (Bernot and Dodds 2005). Most streams in the continental US are heavily modified through anthropogenic changes in land use (Meyer and Turner 1994), but much of our understanding of stream N cycling comes from studies in relatively pristine systems where biotic processing can control N flux to downstream ecosystems (Peterson et al. 2001).

Anthropogenic activities can increase both NH_4^+ and NO_3^- concentrations in stream water, but most of the increased N load occurs as NO_3^- (Peierls et al. 1991). Therefore, we quantified nitrification and denitrification rates, which can directly influence NO_3^- concentrations, albeit in opposing directions. During nitrification, CO_2 fixation is coupled to the oxidation of NH_4^+ to NO_3^-, potentially increasing NO_3^- concentrations and releasing N_2O as a by-product. In contrast, during denitrification, NO_3^- reduction is coupled to organic C oxidation, potentially decreasing stream NO_3^- concentrations by producing nitrogenous gases (N_2O and N_2). Nitrification requires NH_4^+ (supplied from the water column or mineralized in the sediments through decomposition of organic matter) as an energy source, and denitrification requires organic C as an energy source. These 2

[1] Present address: Department of Geography and Land Studies, Central Washington University, Ellensburg, Washington 98926 USA. E-mail: arangoc@cwu.edu
[2] E-mail address: jtank@nd.edu

N transformations are linked through the stream C cycle (Bernhardt and Likens 2002). Therefore, agricultural or urban landuse practices can influence the N cycle directly by increasing NH_4^+ or NO_3^- availability or indirectly by altering the C cycle.

Leaf inputs provide an important source of organic C in forested stream ecosystems. Vegetation typically is removed from stream banks when land is converted to agricultural and urban uses. Removal of riparian vegetation reduces inputs of allochthonous C (Golladay et al. 1989) and increases the importance of autochthonous C in the stream food web (Quinn et al. 1997). Removal of riparian vegetation also reduces periodic inputs of large wood to streams and changes C cycling indirectly by decreasing organic matter retention (Bilby 1981). Intact riparian vegetation can moderate daily temperature fluctuations (Abell and Allan 2002), improve water quality by retaining N as it moves from uplands to the stream (Peterjohn and Correll 1984), and alter organic matter dynamics. Therefore, riparian buffer zones often are used to mitigate stream degradation associated with urban and agricultural land uses (Naiman and Decamps 1997).

Seasonal changes in riparian vegetation influence N and C cycles of forested streams in temperate regions. Forested streams typically are detritus-based ecosystems. However, autotrophy can be important before leafout in spring (Mulholland et al. 2006) when assimilatory demand for N by rapidly growing algae can drive N uptake and reduce N availability for heterotrophic microbes (Mulholland 1992). After leaffall in autumn, assimilatory demand for N by fungal and bacterial biofilms on leaves can dominate N uptake (Tank and Webster 1998). Discharge in temperate streams typically varies in response to seasonally shifting precipitation patterns, and seasonal variation in discharge has important consequences for N cycling. For example, nutrient concentrations typically are controlled by hydrology in agricultural catchments, especially those with subsurface tile drains that shorten terrestrial water residence time (Petry et al. 2002, Royer et al. 2004).

To improve our understanding of how land use alters N cycling in headwater streams, we quantified rates and controls on nitrification and denitrification in basins that have been heavily modified by agricultural and urban land uses. Studies done only during summer overlook temporal dynamics that can have important implications for N cycling, and few studies have addressed how riparian buffers influence sediment nitrification and denitrification in streams. Therefore, we used a year-round sampling regime to investigate how nitrification and denitrification rates (N transformation rates) vary among forested and urban and agricultural streams with and without riparian buffers. We hypothesized that: 1) higher DIN concentrations in agricultural and urban streams would lead to higher N transformation rates compared to forested streams; 2) riparian buffers on agricultural and urban streams would decrease DIN concentrations relative to concentrations in unbuffered streams, and this decrease would lead to N transformation rates more similar to rates in forested streams; and 3) high assimilatory N demand by algae in the spring and decomposers in the fall would reduce overall DIN availability and decrease dissimilatory N transformation rates compared to summer and winter.

Methods

Landuse classification

All 18 study streams were within the Kalamazoo River catchment in southwestern Michigan (Fig. 1), where historical land cover was mixed-deciduous forest, oak woodlands, and wetlands; land use today is a mix of row-crop agriculture and remnant forest patches. The surficial geology in this region consists mostly of glacial outwash deposits, and most soils are alfisols of the Southern Michigan and Northern Indiana Drift Plains ecoregion. We defined landuse types as agricultural, urban, forested, buffered-agricultural, buffered-urban, or distal-agricultural (Fig. 2A–F) by considering land use in the whole catchment and within the 100-m buffer adjacent to the stream channel and extending upstream to the stream source along the mainstem and any tributaries (100-m buffer). We categorized streams that drained catchments in which the predominant (generally >70% of the catchment) land use was agriculture or forest as agricultural or forested, respectively (Fig. 2A, C). In contrast, we categorized streams that drained catchments in which urban land use was relatively low (15–49% of the catchment) as urban (Fig. 2B) because even small amounts of urban land use can have a disproportionate influence on streams (Paul and Meyer 2001). We further classified agricultural streams as buffered-agricultural (Fig. 2D) if they drained agricultural catchments, but their 100-m buffers were predominantly forested. We further classified urban streams as buffered-urban (Fig. 2E) if they drained urban catchments but their 100-m buffers were forested or a city park. We used the designation distal-agricultural (Fig. 2F) when streams drained catchments that were largely forested but had small percentages of agricultural land use not adjacent to the stream.

We used ArcGIS 8.2 (Environmental Systems Re-

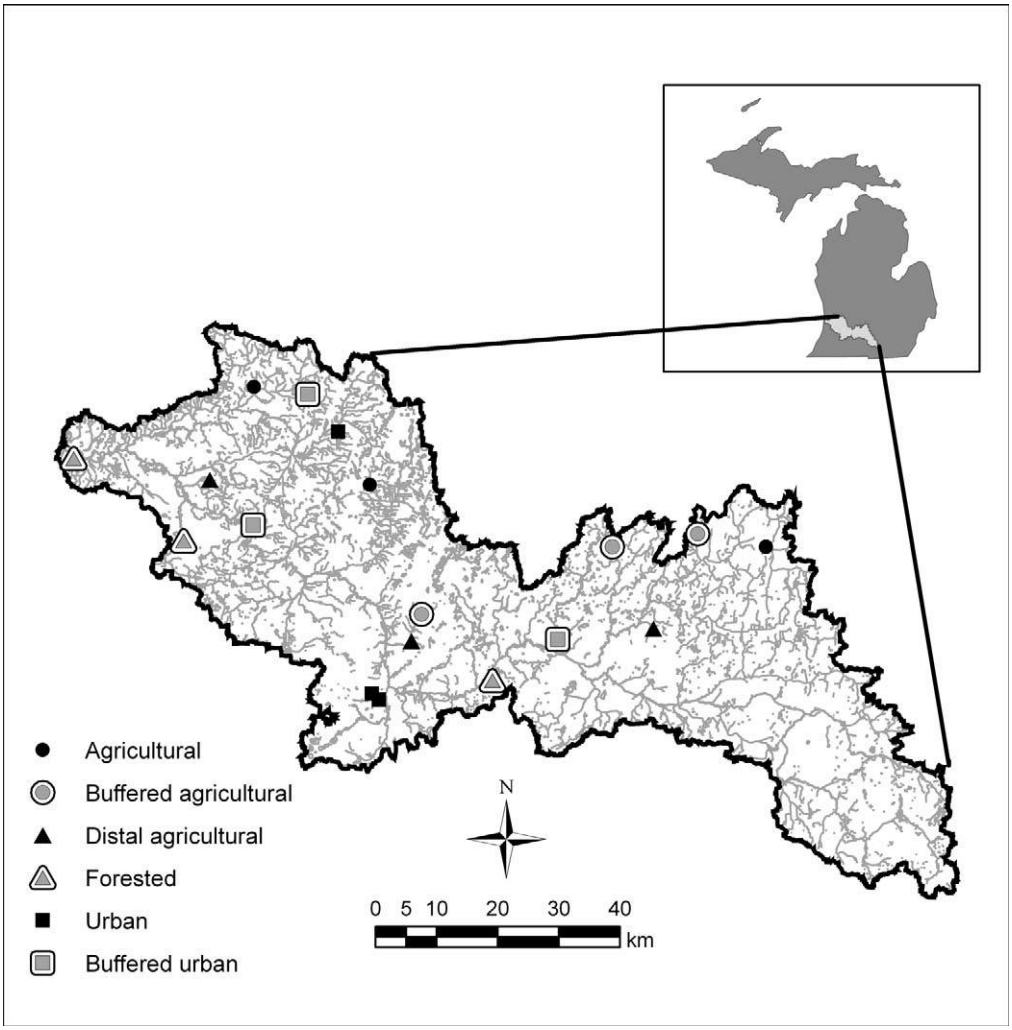

FIG. 1. Study sites in the Kalamazoo River catchment, southwestern Michigan.

search Institute, Redlands, California) to select candidate streams using data downloaded from the National Land Cover Database (reclassed Landsat Thematic Mapper imagery from 1992; Vogelmann et al. 2001). Our decision to use satellite data was problematic for 3 reasons: 1) the 10-m pixel size of the raw data can distort landuse percentages within a catchment; 2) the source imagery was acquired by satellites in 1992, but our study began in 2003, so 11 y of potential landuse change is not reflected in the catchment landuse statistics; and 3) the automated procedure used to distill satellite data into land-cover classes can misclassify land uses. To minimize these problems, we visited each stream to confirm the landuse configuration of the candidate streams and selected 3 streams that best represented each of the 6 landuse types. We attribute apparent discrepancies between our classifications and the landuse data (Table 1) to problems associated with using satellite imagery. For example, Bullet Brook was located entirely within a military training area with no agricultural activity, but the land-cover data classify its catchment as 28% agricultural.

We attempted to select streams that drained subcatchments between 100 and 1000 ha in area, and 15 of our study sites met this criterion (range: 127–896 ha; Table 1). However, lack of access to private property constrained our ability to sample in ideal sites, so 3 subcatchments were >1000 ha (Table 1). The larger subcatchments had relatively high discharge compared to the other sites, but average annual discharge was still fairly low, and the larger streams were not outliers with respect to the DIN and sediment characteristics most likely to control N transformations (Table 2).

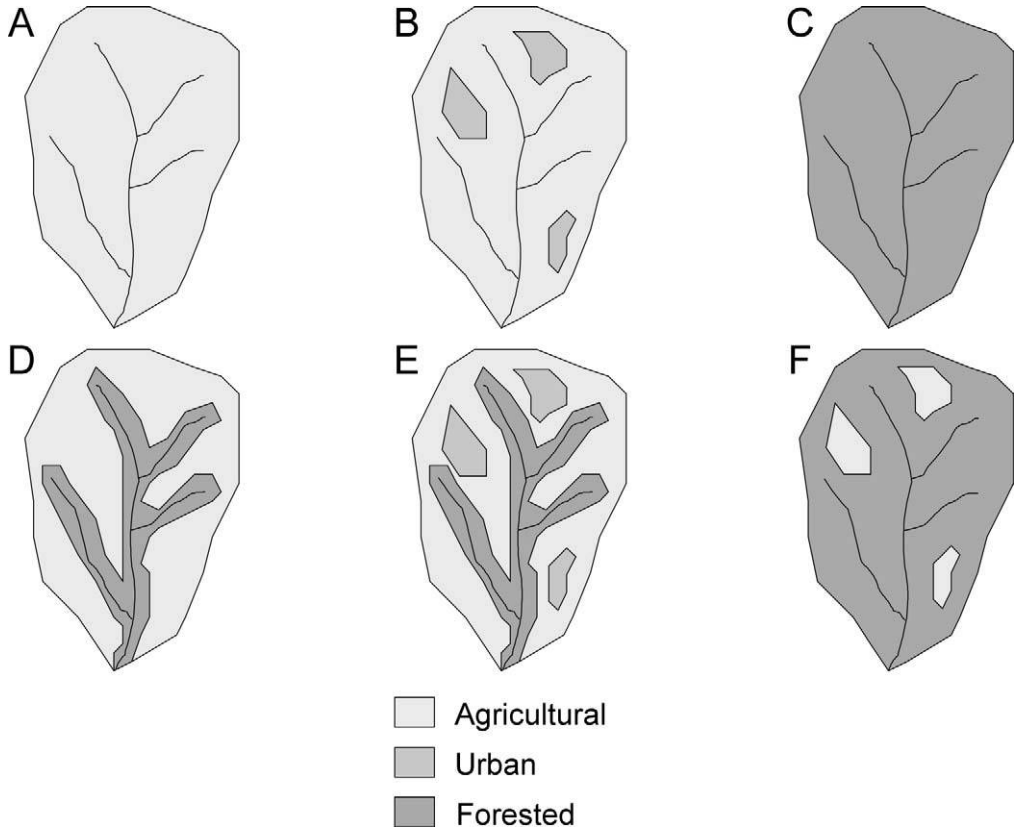

FIG. 2. Idealized landuse classification system showing agricultural (A), urban (B), forested (C), buffered-agricultural (D), buffered-urban (E), and distal-agricultural (F) streams.

Sediment nitrification assays

Sand was the predominant substratum in the low-gradient streams we studied, and we rarely observed gravel or cobble in the inorganic bedload; however, each stream had varying proportions of fine benthic organic matter and silt. We collected monthly sediment samples for laboratory N transformation assays. We ensured that the samples reflected the different proportions of inorganic and organic streambed materials by taking 25 cores (30 $cm^2 \times 2$ cm deep) from a 100-m stream reach. We pooled the cores into 5 separate samples (~300 mL each). We stored samples on ice, returned them to the laboratory, and began the assays immediately. We used the nitrapyrin-inhibition method (Hall 1984, Kemp and Dodds 2001, Strauss et al. 2004) to measure sediment nitrification rates in the study streams. We used 25 mL of sediment from each pooled sample and added 50 mL of unfiltered stream water to make a 75-mL slurry in each of 2 flasks. We designated one flask as the production flask and added 10 μL of a 10% solution of nitrapyrin dissolved in dimethyl sulfoxide (DMSO), an organic solvent that delivered nitrapyrin across the cell membrane where it blocked the conversion of NH_4^+ to NO_3^-. We designated the other flask as the control and added 10 μL of DMSO without nitrapyrin so that nitrification was not blocked. During method development, we found that assays run for periods ranging from 24 to 120 h yielded the same estimate of nitrification rate, so we incubated the flasks for 24 to 48 h on a rotary shaker at 150 rpm. At the end of the assay, we added 25 mL of 2M KCl and shook the flasks for 10 min to flush NH_4^+ from cation exchange sites. We centrifuged the entire slurry and filtered the supernatant into bottles that we froze for future NH_4^+ analysis (described in *Physiochemical variables* below). We calculated nitrification rate as the difference between NH_4^+ in the production and control flasks and scaled this value by the dry mass (DM) of sediment in the assays and the assay duration (units: μg N g^{-1} DM h^{-1}). We calculated the nitrification rate for a given month in a given stream as the average of the 5 sets of paired flasks. We acknowledge that nitrification rates measured with this method are probably higher than ambient rates because they were measured in oxygenated slurries (Strauss et al. 2004), but we emphasize that they do not represent maximum potential rates because we did not amend them with NH_4^+. In addition, we incubated

TABLE 1. Landuse characteristics of the study streams.

Stream	Catchment area (ha)	Year of study	Catchment			100-m riparian buffer		
			Forest + wetland (%)	Agricultural (%)	Urban (%)	Forest + wetland (%)	Agricultural (%)	Urban (%)
Agricultural								
Burnips	298	1	2	98	0	5	95	0
Shelbyville	154	2	3	97	0	9	91	1
Sherman	260	3	5	95	0	1	99	0
Buffered agricultural								
Spicerville	680	1	30	70	0	65	35	0
Richland	1312	2	26	73	0	44	56	0
Ellis	366	3	22	78	0	68	32	0
Urban								
Wayland	201	1	31	20	49	49	21	31
Arcadia	3639	2	44	40	15	17	14	67
Axtell	435	3	39	10	48	19	35	46
Buffered urban								
Dorr	233	1	13	73	14	24	73	3
Allegan	127	2	20	72	7	48	47	5
Urbandale	1824	3	48	45	4	73	22	3
Forested								
Swan	896	1	71	27	0	86	9	0
Bullet	359	2	64	28	5	85	15	0
Tannery	240	3	72	17	2	77	12	2
Distal agricultural								
Bellevue	528	1	44	55	0	75	25	0
Springbrook	358	2	49	49	0	92	8	0
Weber	128	3	48	52	0	71	29	0

sediment slurries at room temperature to minimize variability not associated with substrate and sediment characteristics, and we might have overestimated in situ rates when ambient stream temperatures were cool.

Sediment denitrification assays

We used the chloramphenicol-amended acetylene-block technique (Smith and Tiedje 1979, Royer et al. 2004, Inwood et al. 2005, Arango et al. 2007) to estimate sediment denitrification rates in the laboratory. Acetylene (C_2H_2) blocks the conversion of N_2O to N_2 by denitrifying bacteria, allowing N_2O to accumulate in the assay bottles. Adding chloramphenicol inhibits de novo synthesis of denitrifying enzymes and reduces bottle effects associated with laboratory assays (Brock 1961, Smith and Tiedje 1979, Royer et al. 2004). We took 25-mL sediment subsamples from the same pooled samples used in the nitrification assays (5 per stream) and added 50 mL of unfiltered site water with chloramphenicol at a final concentration of 0.3 mM in the 75-mL slurry. We sealed the bottles with septum caps for headspace sampling and purged them with ultrahigh-purity He for 5 min, shaking periodically to induce anoxia. After purging the bottles, we returned them to ambient atmospheric pressure and added 15 mL of C_2H_2, generated by reacting calcium carbide with deionized water, for a 10% atmosphere of C_2H_2 in the assay bottle. We shook the bottles for several seconds to equilibrate dissolved gases with the headspace before collecting gas samples. We then removed a 5-mL headspace subsample and injected 4 mL of the sample into a 3-mL evacuated vial for later N_2O analysis. We maintained constant pressure in the assay bottles by replacing each headspace subsample with 5 mL of 10% C_2H_2 in He balance. We collected multiple gas samples during the 4.25-h incubation. We took the 1st sample after 15 min had elapsed and took additional samples every hour thereafter.

We analyzed N_2O concentrations in headspace samples by manually injecting 100 μL of sample into a Varian Star 3600 gas chromatograph (Varian, Inc., Palo Alto, California) with a Porapak Q column and electron capture detector (Varian, Inc.) (injector temperature = 120°C, column temperature = 40°C, detector temperature = 320°C, with a 5% CH_4/95% Ar carrier gas at 30 mL/min), with a valve to vent C_2H_2 away from the detector. We used Bunsen coefficients to calculate total N_2O produced in the bottle, plotted N_2O production against time, and calculated the N_2O production rate as the slope of the line of best fit ($r^2 > 0.92$). We determined denitrification rates by dividing the N_2O production rate by the mass of

sediment in the assay bottle and assay duration (units: μg N g^{-1} DM h^{-1}). We calculated rates for a given month in a given stream as the average denitrification rates calculated from the 5 assay bottles. Again, we recognize that the denitrification rates might be higher than ambient rates because we measured them in anoxic slurries (Groffman et al. 2006); however, the sandy sediments in our study streams are naturally unconsolidated, and we incubated them with chloramphenicol to limit the response of the microbial community to the ideal anoxic conditions (Brock 1961, Smith and Tiedje 1979, Bernot et al. 2003). As with nitrification assays, we incubated sediment slurries at room temperature to minimize variability not associated with substrate and sediment characteristics, and we might have overestimated in situ rates when ambient stream temperatures were cool. We point out that the reported denitrification rates do not represent maximum potential rates because we did not amend incubations with additional NO_3^- or organic C.

Sediment characterization

We dried replicate 5-mL subsamples from each pooled sediment sample to constant mass in a 60°C oven, and then weighed the subsamples to obtain DM for scaling the N-transformation assays. We also fumigated oven-dried samples in a dessicator with concentrated HCl to purge inorganic C from the sediments (Hedges and Stern 1984). We combusted fumigated samples in a Costech elemental analyzer (Costech, Valencia, California) to measure sediment organic C (% C) and N (% N) content, from which we calculated molar sediment C:N. For a subset of samples in the 3-y data set (91 of 216 samples), we collected an additional sediment core for analysis of exchangeable NH_4^+. We added 25 mL of 2M KCl to a sediment core, collected as described above, in the laboratory, and shook the slurry on a rotary shaker at 150 rpm for 10 min. We centrifuged the entire slurry, filtered the supernatant (Pall A/E glass-fiber filter, 1 μm nominal pore size; Pall Corporation, East Hills, New York) and froze it for future NH_4^+ analysis (described in *Physiochemical variables* below). We expressed exchangeable NH_4^+ as the mass of NH_4^+-N per volume of sediment (μg N/mL sediment).

Physiochemical variables

At each site, we measured streamwater velocity (Marsh–McBirney 200; Marsh–McBirney, Frederick, Maryland), width, and depth to calculate discharge, and we used a Hydrolab Minisonde (Hach Environmental, Loveland, Colorado) to measure temperature, specific conductance, pH, and dissolved O_2. We filtered stream water through Pall A/E glass-fiber filters (1 μm nominal pore size) into high-density polyethylene bottles that were prerinsed with filtered stream water. We stored the samples on ice and returned them to the laboratory, where we froze them for future analyses.

We analyzed multiple sample types (streamwater, exchangeable, and nitrification assay samples) with the same chemical methods. We used the phenate method (Solorzano 1969, APHA 1995) to measure NH_4^+ concentrations on a Shimadzu UV-1601 spectrophotometer (Shimadzu, Columbia, Maryland) at 630 nm, and we used the molybdate method (Murphy and Riley 1962, APHA 1995) to measure soluble reactive P at 885 nm. We measured NO_3^- (USEPA 1993) with a Dionex 600 ion chromatograph (Dionex, Sunnyvale, California), and we quantified water-column dissolved organic C (DOC) by acidifying samples to pH <2 and analyzing them on a Shimadzu TOC-500 C analyzer using the combustion infrared method (APHA 1995).

We calculated average volume-weighted (AVW) nutrient concentrations so that we could compare water-chemistry variables among study streams that varied in catchment size. We used discharge measurements to calculate daily water volume discharged from each study catchment. We multiplied nutrient concentrations by the volume discharged to obtain the daily mass of nutrients exported. For each site, we summed the daily masses of nutrients exported and divided daily masses by the sum of the daily water volume discharged to obtain AVW nutrient concentrations (Table 2). Most of our sampling dates occurred when stream discharge was near baseflow. Therefore, our reported AVW concentrations characterize baseflow nutrient export rather than nutrient loss over an annual cycle, which would have been much greater had we included samples taken during storm flows.

Statistical analyses

We used either $\log_{10}(x)$ transformation or $\log_{10}(x)$ followed by power transformation of nonnormal data to meet the assumptions of parametric statistics. Because we sampled the same streams over a 1-y period, we analyzed how nitrification and denitrification rates and physiochemical independent variables differed among landuse types and through time using repeated-measures analysis of variance (rmANOVA) (SAS, version 9.1; SAS Institute, Cary, North Carolina) blocked by year to partition interannual hydrologic variation. We used linear regressions (SYSTAT, version 11; SYSTAT, San Jose, California) to identify evidence of coupled nitrification/denitrification within and

TABLE 2. Mean (SE) values of water-chemistry and sediment variables at each study site. Values for the individual streams are means of monthly values ($n = 12$ per stream), and mean values for each landuse type are means of the monthly means from the individual streams ($n = 3$ per landuse type). Q = discharge, DO = dissolved O_2, SRP = soluble reactive P, DOC = dissolved organic C, DM = dry mass. − indicates the variable was not measured.

Stream	Q (L/s)	DO (mg/L)	DO (% saturation)	pH	NH_4^+-N (μg/L)[a]	NO_3^--N (mg/L)[a]	SRP (μg P/L)[a]	DOC (mg C/L)[a]
Agricultural								
Burnips	12 (6.0)	6.8 (0.2)	72.7 (3.3)	8.0 (0.3)	554	10.8	413	11.0
Shelbyville	9 (1.8)	9.1 (0.7)	82.6 (4.1)	8.1 (0.1)	13	19.5	5	5.4
Sherman	3.0 (1.0)	9.1 (1.2)	92.7 (11.3)	7.6 (0.1)	24	6.23	36	4.5
Mean	**8.2 (2.7)**	**8.4 (0.8)**	**83.6 (5.8)**	**7.9 (0.2)**	**197 (178)**	**12.2 (3.9)**	**151 (131)**	**7.0 (2.0)**
Buffered agricultural								
Spicerville	23 (9.8)	7.6 (0.5)	90.8 (8.0)	8.0 (0.2)	44	3.28	47	10.1
Richland	48 (2.5)	8.6 (0.4)	75.7 (4.2)	7.9 (0.1)	15	1.63	5	1.2
Ellis	20 (2.1)	8.5 (0.7)	80.9 (3.4)	8.0 (<0.1)	30	0.57	11	2.1
Mean	**31 (8.9)**	**8.2 (0.3)**	**82.5 (4.4)**	**8.0 (<0.1)**	**30 (8)**	**1.83 (0.8)**	**21 (13)**	**4.5 (2.8)**
Urban								
Wayland	19 (5.3)	9.6 (0.7)	113 (6.6)	8.2 (0.3)	240	0.79	28	6.1
Arcadia	57 (4.8)	9.4 (0.6)	84.6 (4.1)	7.9 (0.1)	43	1.03	8	1.1
Axtell	33 (2.3)	7.3 (0.4)	69.3 (2.8)	7.7 (<0.1)	81	0.18	29	0.9
Mean	**36 (11)**	**8.7 (0.7)**	**89.0 (12.8)**	**7.9 (0.2)**	**121 (61)**	**0.67 (0.25)**	**22 (7)**	**2.7 (1.7)**
Buffered urban								
Dorr	26 (5.1)	8.3 (0.3)	87.3 (5.0)	8.3 (0.2)	91	1.84	11	2.1
Allegan	20 (3.8)	9.9 (0.9)	87.0 (5.5)	8.2 (0.1)	26	2.06	17	2.9
Urbandale	38 (5.3)	8.6 (0.7)	80.3 (3.3)	8.0 (<0.1)	53	0.39	8	3.5
Mean	**28 (5.2)**	**8.9 (0.5)**	**84.9 (2.3)**	**8.2 (0.1)**	**57 (19)**	**1.43 (0.52)**	**13 (3)**	**3.2 (0.2)**
Forested								
Swan	19 (3.3)	7.4 (0.3)	77.1 (3.2)	7.7 (0.2)	39	0.53	15	4.1
Bullet	4.6 (1.0)	10 (0.8)	84.2 (6.0)	8.2 (0.1)	9	0.41	4	0.8
Tannery	7.8 (3.3)	7.3 (1.5)	62.3 (11.4)	7.4 (<0.1)	36	0.18	3	4.9
Mean	**10 (4.2)**	**8.2 (0.9)**	**74.5 (6.4)**	**7.8 (0.3)**	**28 (9)**	**0.37 (0.10)**	**8 (4)**	**3.3 (1.2)**
Distal agricultural								
Bellevue	33 (13)	7.8 (0.3)	84.4 (4.7)	8.2 (0.3)	12	0.13	9	5.9
Springbrook	17 (0.7)	9.5 (0.4)	84.2 (4.2)	8.1 (0.1)	11	0.68	4	0.8
Weber	6.8 (2.2)	6.2 (0.7)	58.1 (4.5)	7.3 (0.1)	22	0.05	6	4.3
Mean	**19 (7.6)**	**7.8 (1.0)**	**75.6 (8.7)**	**7.8 (0.3)**	**15 (3)**	**0.29 (0.20)**	**6 (1)**	**3.7 (1.5)**

[a] Annual volume-weighted concentration

among streams, multiple linear regressions (MLRs) to identify which physiochemical variables were significantly related to nitrification and denitrification rates, and nonlinear regression (SigmaPlot, version 10; SYSTAT, San Jose, California) to describe the relationship between nitrification rates and sediment C:N. We used MLRs to analyze the relationship between N transformation rates and physiochemical variables, using annual mean values of each physiochemical variable from each stream to avoid pseudoreplication.

We condensed the landuse attributes from each catchment (i.e., catchment area, % of catchment in agriculture, urban, forest, and wetland land-cover classes, and % of 100-m buffer in agriculture, urban, forest, and wetland land-cover classes) into continuous, uncorrelated ordination axes using principal components analysis (PCA) (PCord; MjM Software Design, Gleneden Beach, Oregon), and we used the PCA axes as independent variables in linear regressions to identify relationships between catchment land use and nitrification and denitrification rates and key independent variables (SYSTAT 11).

Results

Landuse and seasonal patterns in N transformations

Sediment nitrification rates varied over 2 orders of magnitude (Table 2) and were significantly greater in agricultural than in distal-agricultural streams (rmA-

TABLE 2. Extended.

Sediment				
Exchangeable NH_4^+-N (μg/mL sediment)	Organic C content (%)	Molar C:N	Nitrification (μg N g^{-1} DM h^{-1})	Denitrification (μg N g^{-1} DM h^{-1})
—	3.6 (0.3)	17.7 (0.8)	0.54 (0.13)	1.88 (0.21)
0.14 (0.03)	2.1 (0.3)	23.9 (1.4)	0.23 (0.07)	0.34 (0.08)
2.42 (0.58)	4.8 (0.3)	15.0 (0.8)	1.03 (0.19)	1.31 (0.66)
1.28 (1.14)	**3.5 (0.8)**	**18.9 (2.6)**	**0.60 (0.23)**	**1.12 (0.45)**
—	7.1 (0.2)	16.6 (0.5)	0.24 (0.10)	1.05 (0.29)
0.33 (0.10)	1.2 (0.2)	16.5 (0.7)	0.15 (0.05)	0.18 (0.02)
0.98 (0.14)	5.3 (1.3)	17.3 (1.1)	0.40 (0.09)	0.18 (0.09)
0.65 (0.33)	**4.5 (1.7)**	**16.8 (0.3)**	**0.26 (0.07)**	**0.47 (0.29)**
—	1.2 (0.3)	41.5 (3.7)	0.11 (0.04)	0.09 (0.02)
0.40 (0.16)	1.6 (0.2)	127.7 (18.5)	0.07 (0.02)	0.06 (0.01)
0.48 (0.07)	1.1 (0.1)	74.6 (10.2)	0.07 (0.01)	0.05 (0.01)
0.44 (0.04)	**1.3 (0.1)**	**81.3 (25.1)**	**0.08 (0.01)**	**0.07 (0.01)**
—	0.6 (0.1)	21.3 (0.8)	0.09 (0.04)	0.11 (0.02)
0.04 (0.01)	0.3 (0.1)	30.9 (2.2)	0.01 (<0.01)	0.02 (0.01)
0.34 (0.04)	0.8 (0.1)	26.7 (2.0)	0.08 (0.02)	0.06 (0.01)
0.19 (0.15)	**0.6 (0.2)**	**26.3 (2.8)**	**0.06 (0.02)**	**0.07 (0.03)**
—	2.7 (0.3)	17.2 (0.7)	0.07 (0.02)	0.11 (0.06)
0.25 (0.05)	1.5 (0.2)	24.9 (1.2)	0.17 (0.03)	0.09 (0.01)
0.15 (0.04)	0.3 (<0.1)	20.2 (0.8)	0.03 (0.01)	0.03 (<0.01)
0.20 (0.05)	**1.5 (0.7)**	**20.8 (2.2)**	**0.09 (0.04)**	**0.08 (0.02)**
—	1.4 (0.3)	21.6 (2.4)	0.08 (0.05)	0.02 (<0.01)
0.08 (0.02)	0.6 (0.2)	20.1 (1.0)	0.04 (0.01)	0.03 (<0.01)
0.34 (0.06)	0.3 (0.1)	18.0 (0.8)	0.06 (0.02)	0.02 (<0.01)
0.21 (0.13)	**0.8 (0.3)**	**19.9 (1.0)**	**0.06 (0.01)**	**0.02 (0.01)**

NOVA, $p = 0.019$; Fig. 3A). Sediment nitrification rates were significantly higher in May, June, and December than in March (rmANOVA, $p = 0.008$; Fig. 3A). Stream temperatures associated with winter (November–February; mean = 3.6°C), summer (May–August; 17.5°C), and transitional seasons (March, April, September, October; 10.5°C) were statistically distinct (rmANOVA, $p < 0.0001$; data not shown). We used these seasons as a proxy variable for ambient temperature and found that nitrification rates were significantly higher in summer than in other seasons (rmANOVA, $p = 0.004$). Temporal differences in nitrification rates were driven by patterns in agricultural and buffered-agricultural streams, which always had the highest nitrification rates. Pairwise comparisons indicated that buffered and unbuffered streams in the same broad landuse category (agricultural or urban) had similar nitrification rates.

Denitrification rates also varied over 2 orders of magnitude (Table 2). Denitrification rates did not differ among landuse types (rmANOVA, $p = 0.17$; Fig. 3B), but they were significantly greater in December, January, and February than in June (rmANOVA, $p = 0.004$; Fig. 3B). We used seasons as a proxy variable for ambient temperature and found that denitrification rates were significantly higher in winter than in summer (rmANOVA, $p < 0.0001$). Temporal differences in denitrification rates were driven by patterns in agricultural and buffered-agricultural streams, but

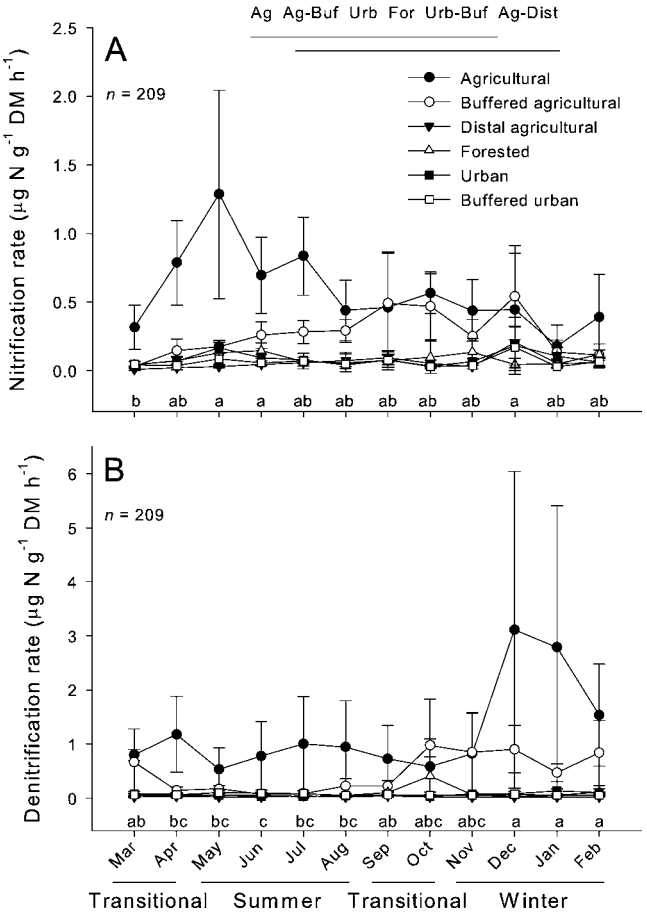

FIG. 3. Seasonal and landuse patterns in monthly mean (±1 SE) nitrification (A) and denitrification (B) rates during 3 seasons (summer, winter, transitional) defined on the basis of periods of statistically distinct stream temperatures. *Transitional* corresponds to March, April, September, and October. Months with the same letters are not significantly different. Lines beneath landuse types in (A) group statistically similar land uses. Ag = agricultural, Ag-Buf = buffered-agricultural, Ag-Dist = distal-agricultural, Urb = urban, Urb-Buf = buffered-urban, For = forested. See text and Fig. 2 for explanation of landuse types. $n = 3$ for each datum.

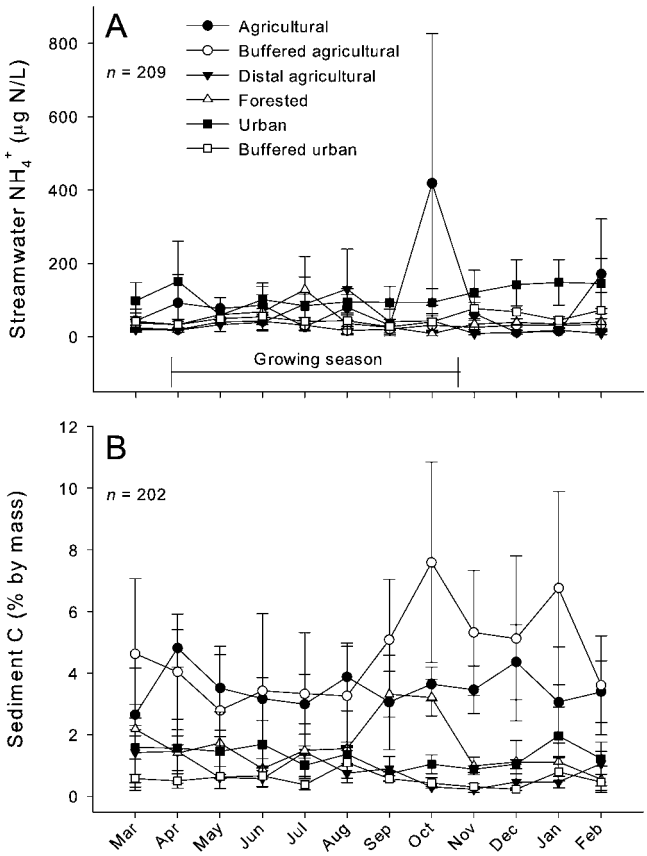

FIG. 4. Seasonal and landuse patterns in monthly mean (±1 SE) NH_4^+ concentrations (A) and sediment C content (B). Months with the same letters are not significantly different. Abbreviations are as in Fig. 3. See text and Fig. 2 for explanation of landuse types. $n = 3$ for each datum.

differences among landuse types were obscured by high winter variability in agricultural streams.

Agricultural and buffered-agricultural streams always had the highest N transformation rates, but nitrification and denitrification were temporally decoupled. Nitrification rates were highest in summer, whereas denitrification rates were highest in winter. N transformation rates were positively related (across all sampling events, excluding 3 statistically identified outliers; $n = 213$ cases), but the relationship explained little of the overall variability in the data (linear regression, $r^2 = 0.07$, $p < 0.001$; data not shown). N transformation rates were never positively related within streams. Coupled nitrification/denitrification occurs more frequently when streamwater NO_3^- concentrations are <150 µg N/L (Seitzinger et al. 2006), so we selected the 34 (of 216) cases that met this criterion among streams and reran the analysis. N transformation rates were not correlated in this subset of cases.

Land use and seasonal patterns of DIN and organic C

Streamwater NH_4^+ concentration tended to be higher in urban streams than in streams in other landuse types (Table 2), but NH_4^+ concentrations did not differ significantly among landuse types (rmANOVA, $p = 0.06$; Fig. 4A) or through time (rmANOVA, $p = 0.11$; Fig. 4A). Analysis of only those data collected during the growing season (April–October) showed that NH_4^+ concentrations were similar in buffered and unbuffered streams within the same broad landuse category (Fig. 4A). Analysis of the same data subset

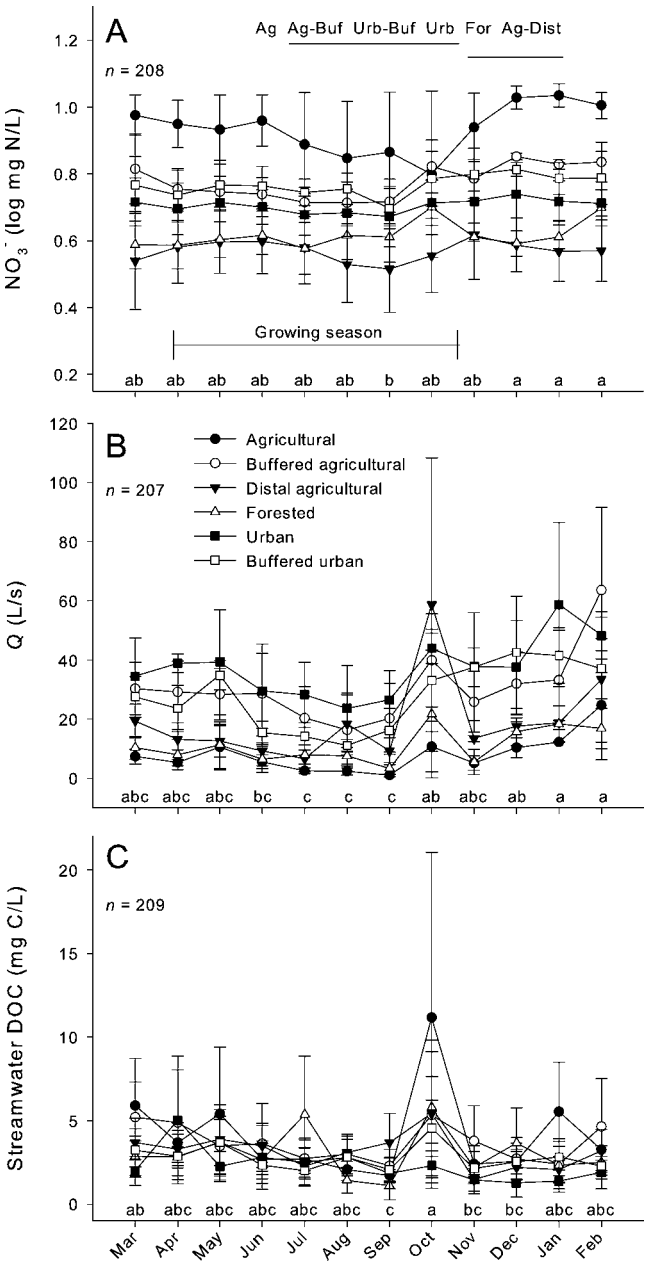

FIG. 5. Seasonal and landuse patterns in monthly mean (±1 SE) NO_3^- concentration (A), discharge (Q) (B), and dissolved organic C (DOC) (C) concentration. Months with the same letters are not significantly different. Lines beneath landuse types in (A) group statistically similar land uses. Abbreviations are as in Fig. 3. See text and Fig. 2 for explanation of landuse types. $n = 3$ for each datum.

showed that NH_4^+ concentrations were significantly lower in streams studied in year 2 than in streams studied in years 1 and 3 (rmANOVA, $p = 0.001$), but that nitrification rates did not differ among years. Analysis of the full data set showed that sediment % C tended to be higher in agricultural and buffered-agricultural streams than in streams in other landuse types (rmANOVA, $p = 0.08$; Table 2, Fig. 4B) but did not vary through time (rmANOVA, $p = 0.75$; Fig. 4B).

Streamwater NO_3^- concentrations were an order of magnitude higher in agricultural streams than in streams in other landuse types (rmANOVA, $p < 0.0001$; Table 2, Fig. 5A). In pairwise comparisons, NO_3^- concentrations were significantly lower in buffered-agricultural streams than in agricultural streams, but NO_3^- concentrations did not differ between buffered-urban and urban streams. Analysis of only those data collected during the growing season (April–October) showed that NO_3^- concentrations were similar in buffered and unbuffered streams within the same broad landuse category. Streamwater NO_3^- concentrations were significantly higher in winter than in other seasons (rmANOVA, $p = 0.001$; Fig. 5A) in streams in nearly all landuse types and were associated with higher stream discharge in the winter (rmANOVA, $p < 0.0001$; Fig. 5B). DOC did not differ among landuse types (Table 2, Fig. 5C), but DOC concentrations were significantly higher in October, corresponding to autumn leaf abscission, than in other months (rmANOVA, $p < 0.001$; Fig. 5C).

Factors controlling N transformation rates

Annual mean nitrification rates were positively related to sediment % C (MLR, $r^2 = 0.72$, $p < 0.0001$, $n = 18$; Fig. 6A) but not streamwater NH_4^+ concentration, sediment C:N, or ambient stream temperature. In year 1, we found no relationship between nitrification rates and streamwater NH_4^+ concentration ($n = 6$), so we began sampling exchangeable NH_4^+ in the sediment. In years 2 and 3, we found a significant positive relationship between nitrification rates and exchangeable NH_4^+ ($r^2 = 0.67$, $p = 0.001$, $n = 12$; Fig. 6B), but we found no relationship between nitrification rates and streamwater NH_4^+ concentration ($n = 12$). Taken together, the results from the 3-y data set and the 2-y data set suggested that decomposition of organic C in the sediment provided a benthic NH_4^+ source for nitrification. We examined this hypothesis using the 2-y data set and found a positive relationship between exchangeable NH_4^+ and sediment % C ($r^2 = 0.56$, $p = 0.005$; Fig. 6C), supporting a link between NH_4^+ production and decomposition of organic C.

Sediment C:N was not significantly related to nitrification rate in an MLR, but we found a significant negative exponential relationship between these variables ($r^2 = 0.42$, $p = 0.016$; Fig. 7). Our data set based on annual means was too small to detect a significant threshold using a 2-dimensional Kolmogorov–Smirnoff threshold test, but the data suggest a break at C:N

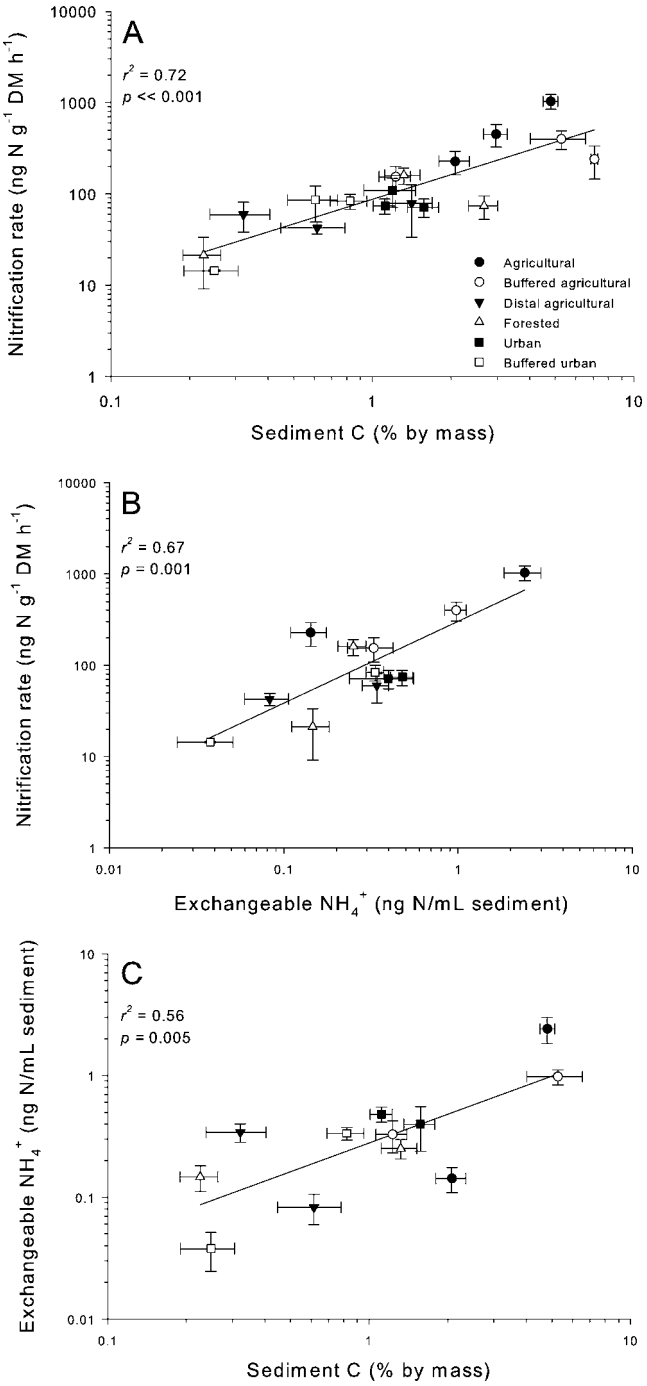

FIG. 6. Relationships between mean annual (±1 SE) nitrification rates and sediment C content (A), nitrification rate and exchangeable NH_4^+ (B), and exchangeable NH_4^+ and sediment C content (C). We sampled exchangeable NH_4^+ in only 12 streams.

≈ 20. Below this value, nitrification rates decrease with increasing C:N, and above this value nitrification rates are generally low and have no relationship with sediment C:N (Fig. 7).

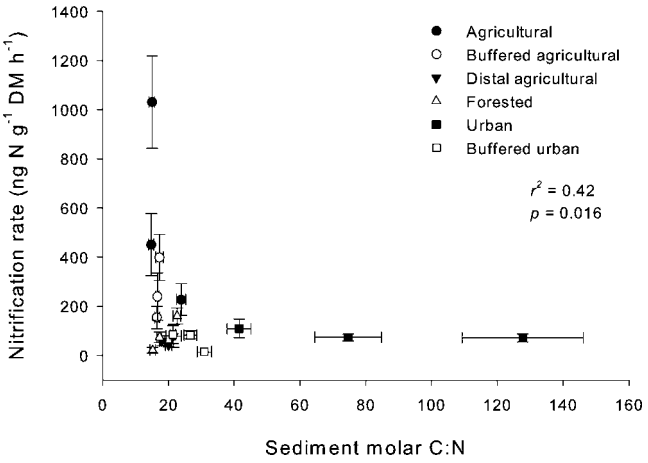

FIG. 7. Relationship between mean annual (±1 SE) nitrification rates and sediment C:N. The relationship is described by a significant negative exponential decay function, but the line of best fit is not included for clarity. $n = 12$ for each datum.

Annual mean denitrification rates were positively related to sediment % C and streamwater NO_3^- concentration (MLR, $R^2 = 0.78$, $p < 0.0001$, $n = 18$; Table 3) but not to streamwater DOC concentration or ambient stream temperature. Sediment % C had the most explanatory power based on coefficient of determination ($r^2 = 0.62$; Fig. 8).

Relationship between landuse metrics and N transformations

PCA identified 3 gradients that explained 83.7% of the variability in the landuse data. Axis 1 was an agriculture–forest gradient (45.8% of the variability), Axis 2 was a wetland gradient (23.1%), and Axis 3 was an urban gradient (14.8%). The agriculture–forest gradient (represented by Axis 1 scores) was significantly related to mean annual nitrification ($r^2 = 0.32$, $p = 0.015$; Fig. 9A) and denitrification ($r^2 = 0.41$, $p = 0.004$; Fig. 9D) rates, with higher transformation rates associated with more agricultural land use. We also regressed nitrification and denitrification rates against

TABLE 3. Partial coefficients of determination for independent variables that significantly affect denitrification rates (μg N g^{-1} DM h^{-1}). The overall regression model for denitrification had $R^2 = 0.78$ and $p < 0.001$. All variables are $\log_{10}(x)$ normalized. DOC = dissolved organic C, × = no relationship, n.s. = not significant ($p > 0.05$).

Independent variable	Correlation	Partial R^2	p value
Sediment % C	+	0.62	<0.001
Streamwater NO_3^-	+	0.16	0.004
Streamwater DOC	×	×	n.s.
Streamwater temperature	×	×	n.s.

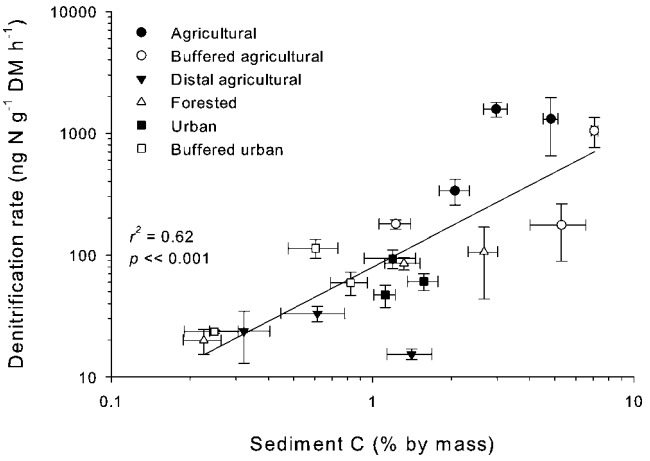

FIG. 8. Relationship between mean annual (±1 SE) denitrification rates and sediment C content. $n = 12$ for each datum.

the fractional measures of agricultural land use in the whole catchment (Fig. 9B, E) and within the 100-m buffer (Fig. 9C, F), but these alternate independent variables did not increase explanatory power relative to the ordination axis.

Sediment % C was not explained by the agriculture–forest gradient (Axis 1) or fractional measures of agricultural land use in the catchment or 100-m buffer (Fig. 10A–C). However, streamwater NO_3^- concentration was significantly related to the agriculture–forest gradient ($r^2 = 0.55$, $p < 0.001$; Fig. 10D) and both fractional measures of agricultural land use (catchment: $r^2 = 0.47$, $p = 0.001$; 100-m buffer: $r^2 = 0.38$, $p = 0.006$; Fig. 10 E, F).

Discussion

Seasonal patterns in sediment nitrification rates

Mean annual nitrification rates spanned 2 orders of magnitude (Table 2), and nitrification rates were

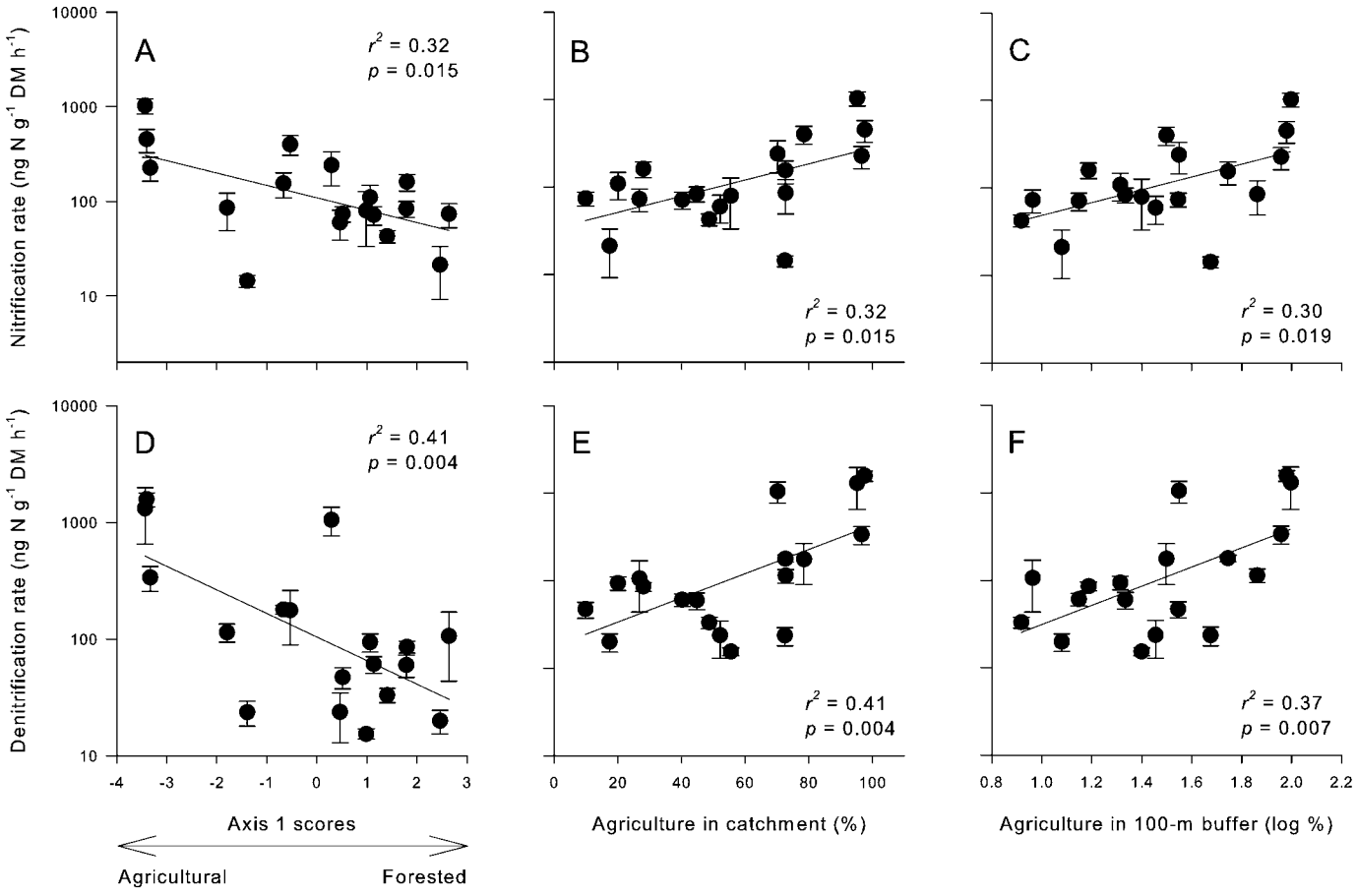

FIG. 9. Relationships between mean annual (±1 SE) nitrification and denitrification rates and a gradient of agricultural–forested land use based on principal components analysis (PCA) Axis 1 scores (A, D), % agricultural land use in the catchment (B, E), and % agricultural land use in the 100-m riparian buffer (C, F). See text for definition of 100-m riparian buffer and ordination details. $n = 12$ for each datum.

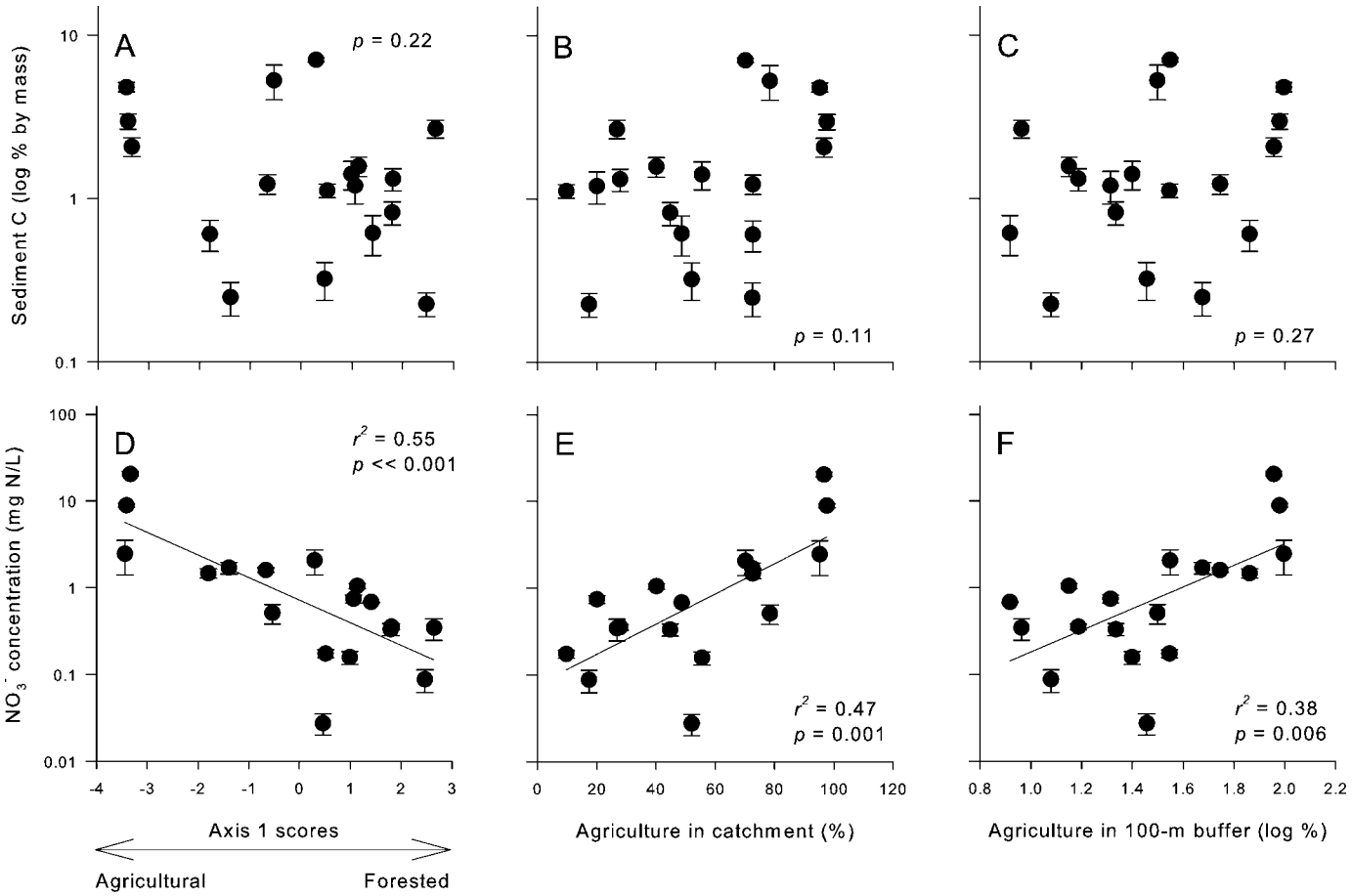

FIG. 10. Relationship of mean annual (±1 SE) sediment C content and NO_3^- concentrations with a gradient of agricultural–forested land use based on principal components analysis (PCA) Axis 1 scores (A, D), % agricultural land use in the catchment (B, E), and % agricultural land use in the 100-m riparian buffer (C, F). See text for definition of 100-m riparian buffer and ordination details. $n = 12$ for each datum.

highest in spring (Fig. 3A). We multiplied our biomass-scaled rates (μg N g^{-1} DM h^{-1}) by standing stocks (g DM/m^2) to convert them to areal units (0.4–9.0 mg N m^{-2} h^{-1}). Our values spanned roughly the same range as values measured over a year in Appalachian mountain streams (0.4–2.0 mg N m^{-2} h^{-1}; Starry et al. 2005), Kansas prairie streams (2.2–4.6 mg N m^{-2} h^{-1}; Kemp and Dodds 2002), and the Upper Mississippi River (4–15 mg N m^{-2} h^{-1}; Strauss et al. 2004). These studies all reported highest nitrification in the late spring or early summer. The reasons for the high rates varied among sites but included temperature and NH_4^+ availability (Starry et al. 2005), increased O_2 and NH_4^+ availability (Kemp and Dodds 2002), or temperature alone (Strauss et al. 2004).

Nitrification is a metabolic process controlled by substrate availability, specifically O_2 (Kemp and Dodds 2001) and NH_4^+ (Strauss et al. 2002). Primary producers can stimulate nitrification by affecting the depth to which O_2 is found in the sediment (Rysgaard et al. 1994). If O_2 regulates nitrification, then peak nitrification rates should be associated with high primary producer biomass. Autotrophs were abundant at our study sites in early spring when riparian canopies were open and light levels were increasing, but nitrification rates were highest in the late spring (Fig. 3A) when the canopy was closed and primary producer biomass was declining. We measured nitrification in oxic assays, and thus, might have overestimated in situ rates, but the presence of abundant nitrifying bacteria in sediments at a time when benthic O_2 production was relatively low (late spring) suggests that other factors than O_2 (e.g., NH_4^+ availability or warm temperatures) probably influenced nitrification rates. Seasonal patterns in nitrification rates were not related to streamwater NH_4^+ concentrations, but they were related to sediment exchangeable NH_4^+ and sediment % C.

Influence of land use on nitrification controls

Nitrification rates were highest in agricultural streams. The positive association between nitrification and agricultural land use is probably the result of numerous factors that increase decomposition rates in agricultural streams. For example, nitrification rates were strongly related to sediment % C, which tended to be higher in agriculturally influenced streams than in urban or forested streams (Fig. 4B), probably because agricultural fields in the Midwest frequently are sited on drained wetlands that have highly organic soils (Mitsch et al. 2001), and cultivation increases soil erosion (Jones et al. 2001). Decomposition of sediment C produces exchangeable NH_4^+, which increases nitrification rates in other midwestern streams (Strauss et al. 2002) and in large rivers (Strauss et al. 2004). In addition, water temperatures frequently are high in agricultural streams because the absence of riparian vegetation allows greater light penetration to the stream channel (Osborne and Kovacic 1993). Temperature controls rates of microbial metabolism and can influence nitrification rates directly (Sheibley et al. 2003) or indirectly by increasing decomposition rates (Webster and Benfield 1986), which subsequently increases NH_4^+ production.

Sediment C:N can control nitrification indirectly because heterotrophic microbes outcompete nitrifying bacteria for NH_4^+ when C:N is high (>20), but not when it is low (<20) (Strauss and Lamberti 2002). We found a significant negative exponential relationship between nitrification rates and sediment C:N (Fig. 7). We were unable to quantify a significant threshold in this relationship, but a break in the data close to C:N = 20 corresponds closely to thresholds observed in studies of small streams (C:N = 15, Kemp and Dodds 2002; C:N = 20, Strauss and Lamberti 2002) and forest soils (C:N = 22, Ollinger et al. 2002). High sediment C:N might have conferred a competitive advantage to heterotrophic microbes, especially in urban streams, where C:N was sometimes very high (Fig. 7).

Seasonal patterns of denitrification rates

Denitrification rates spanned nearly 2 orders of magnitude and showed a significant seasonal pattern characterized by highest rates in winter and lowest rates in summer (Fig. 3B). A meta-analysis of denitrification in aquatic habitats (i.e., oceans, coastal environments, estuaries, lakes, and rivers) with a relatively broad range of NO_3^- concentrations (0.01–13.58 mg N/L) showed that denitrification rates were highest in summer when water temperatures were high (Piña-Ochoa and Álvarez-Cobelas 2006). In our study, denitrification rates were highest in winter (Fig. 5A) when NO_3^- concentrations were high, a result suggesting that seasonal changes in NO_3^- delivery might regulate denitrification. Our N transformation assays were done at room temperature, so we cannot determine the extent to which cool stream temperatures would dampen denitrification responses to higher NO_3^- concentrations. However, cold temperatures limit denitrification despite high NO_3^- availability in other systems (Pattinson et al. 1998).

A distinct NO_3^- pulse coincided with the first significant runoff in late autumn and early winter (Fig. 5A, B). Southwestern Michigan has a humid climate with relatively regular rainfall, but the summers of our study were characterized by below-average precipitation. NO_3^- produced by terrestrial nitrification accumulates in soil water during dry periods. When rain flushes this concentrated soil solution into streams, streamwater NO_3^- concentration can increase dramatically (Morecroft et al. 2000). Hydrologic flushing of NO_3^- by spring runoff increased NO_3^- concentration up to 3 orders of magnitude over baseflow concentrations in agricultural streams in Illinois (Royer et al. 2006). Our observation that peaks in denitrification followed pulses of NO_3^- caused by flushing of soil NO_3^- after a dry summer and autumn suggests that sediment denitrification is subject to seasonal NO_3^- limitation in regions characterized by seasonal drought. This observation emphasizes the importance of streamwater NO_3^- concentration as a significant predictor of denitrification in our study streams (Table 3), and it highlights the importance of hydrology in controlling the delivery of NO_3^- for denitrification.

Landuse influence on the controls of denitrification

Denitrification rates did not differ among landuse types, but mean annual denitrification rate was positively related to agricultural land use when agriculture was treated as a continuous variable (Fig. 9A–C). Moreover, the 2 highest monthly denitrification rates in our agricultural streams (1.31 and 1.88 μg N g^{-1} DM h^{-1}; Table 2) approached the highest rates seen in Illinois agricultural streams (2.3 μg N g^{-1} DM h^{-1}; Schaller et al. 2004). Our rates are among the highest ever reported in studies based on the method we used.

Agricultural streams frequently have high NO_3^- concentrations (e.g., Johnson et al. 1997, Inwood et al. 2005, Dodds and Oakes 2006) because of excess fertilizer application to adjacent crops (David et al. 1997) and tile drainage systems that rapidly deliver terrestrial N to streams (Royer et al. 2004). NO_3^- concentration explained 70% of the variability in denitrification rates in the meta-analysis done by

Piña-Ochoa and Álvarez-Cobelas (2006), but it explained only 16% of the variability in denitrification rates among our streams (Table 3). NO_3^- concentration might have been a weak predictor of denitrification rates in our data set because we sampled in all seasons (cf. summer only in the meta-analysis) and included "hot and cold moments" (sensu McClain et al. 2003) of denitrification. NO_3^- concentrations in most systems included in the meta-analysis were relatively low (<1.5 mg N/L; Piña-Ochoa and Álvarez-Cobelas 2006), so denitrification might have been limited by NO_3^- in those systems, whereas denitrification might have been limited by C in our streams where NO_3^- concentrations were high. This explanation is consistent with the strong relationship between denitrification rate and sediment % C in our study (Fig. 8).

Streamwater DOC concentration peaked sharply during leaf abscission in October (Fig. 5C). DOC in leachate from freshly abscised leaves ranges from low to high lability (Strauss and Lamberti 2002), so the autumn pulse of DOC could have contributed a relatively labile C source capable of stimulating denitrification. However, we did not observe a peak in denitrification associated with the autumn peak in DOC concentration. Mean annual DOC concentrations were positively related to % wetlands in the catchment ($r^2 = 0.33$, $p = 0.01$; data not shown), but DOC derived from wetlands often contains a high proportion of refractory humic substances (Qualls and Richardson 2003), which might not be ideal C sources for denitrification. Overall, our data suggest that denitrifiers derive the bulk of their C from sediment pools (Fig. 8).

Coupled nitrification and denitrification

Our data suggest limited coupling of nitrification and denitrification in our study streams. Although nitrification and denitrification rates were positively related among streams, this relationship probably reflected the influence of sediment % C on both N transformations (Figs 6A, 8) rather than coupled nitrification/denitrification processes. For example, agricultural and buffered-agricultural streams had the highest nitrification and denitrification rates (Fig. 3A, B), but they also tended to have the highest sediment % C (Fig. 4B). Furthermore, NO_3^- concentrations were >150 μg N/L in 176 of 216 samples, and NO_3^- concentrations >150 μg N/L discourage coupled nitrification/denitrification (Seitzinger et al. 2006). However, we cannot exclude the possibility that coupled nitrification/denitrification occurred in study streams with low NO_3^- concentrations (e.g., Bellevue or Weber; Table 2) because redox-optimized laboratory slurries (the method we used) are not ideally suited to detect coupled N transformations.

Effect of riparian buffers on nitrification and denitrification

NO_3^- concentrations differed significantly between agricultural and buffered-agricultural streams, but not between urban and buffered-urban streams. Riparian buffers had no effect on NO_3^- concentration during the growing season, and % agricultural land use in the 100-m riparian buffer was only weakly related to streamwater NO_3^- concentration. Collectively, these results suggest that riparian buffers have limited influence on water and sediment chemistry or their effects on N transformations in our study streams. Riparian buffers can moderate stream temperatures (Abell and Allan 2002), reduce sedimentation (Hubbard et al. 1990), and decrease nutrient flux from terrestrial to stream ecosystems (Peterjohn and Correll 1984), but the effectiveness of riparian buffers is dictated by their interaction with the hydrosystem (e.g., Houser et al. 2005). All of our study catchments had tile drains or simplified drainage networks that quickly routed runoff and shallow groundwater to the streams and decreased interaction of runoff and shallow groundwater with riparian buffers. Hydrologic flushing of soil-water NO_3^- in autumn and rapid routing of upland sediment to streams probably were augmented by these simplified hydrosystems (e.g., David et al. 1997, Royer et al. 2004). Thus, anthropogenic modification of the hydrosystems uncoupled riparian buffers from the stream channels, with the consequence that riparian buffers had little influence on the variables we studied, and hydrology became the most important factor controlling delivery of substrates for N transformations to the streams.

The absence of spatiotemporal patterns in sediment C content provides further evidence of the overriding importance of hydrology in these streams. Natural leaf packs were present in all streams during our autumn field sampling, and we expected sediment % C to increase in autumn and early winter as the leaves were incorporated in the sandy sediments during fragmentation and breakdown. Sediment % C did not differ among months (Fig. 4B) or between streams with and without riparian buffers, despite obvious differences in riparian vegetation. Managing agricultural and urban streams as drains requires channel straightening, subsurface tile drains, and periodic dredging to remove large wood. All but 1 of the distal-agricultural and forested streams in our study were also managed as drains though they did not include subsurface tiles. Drain management practices increase the frequency and magnitude of peak flows, decrease channel

complexity, and reduce the capacity for organic matter retention (e.g., Bilby 1981, Allan et al. 1997). Thus, landuse practices that simplify catchment hydrology and in-channel complexity might constrain N transformations by reducing organic matter retention in these streams.

Riparian zones reduce nutrient and sediment transport from uplands to streams (Peterjohn and Correll 1984, Osborne and Kovacic 1993, Lee et al. 2003, Sabater et al. 2003), but the benefits of riparian buffers were small in these streams with anthropogenically modified hydrosystems. Landuse practices can disconnect riparian zones from the hydrosystem, with the consequences that the streams are loaded with sediment and NO_3^-, and DIN concentrations remain high despite high N transformation rates. These results do not mean that riparian buffers should be disregarded as tools to mitigate water-quality degradation. Instead, hydrologic connectivity between uplands and riparian zones in landscapes heavily modified by human activity should be reestablished and maintained as a way to restore the functions of riparian zones.

Studies in relatively pristine streams show that substrate availability governs N transformations (Jones et al. 1995, Kemp and Dodds 2002, Piña-Ochoa and Álvarez-Cobelas 2006). Landuse-modified streams do not differ fundamentally from pristine streams. Substrate availability still controls N transformation rates, but land use governs substrate availability. Routing solutes and organic matter through the drainage network can overwhelm the influence of riparian zones and leave hydrology in control of substrate delivery to the stream. N application to uplands increases NO_3^- concentrations and uncouples denitrification and nitrification, with the consequence that C limits denitrification. Our results confirm that streams are integrated with the landscape (Hynes 1975, Vannote et al. 1980), and they highlight the importance of understanding how land use mediates N transformations.

Acknowledgements

We thank the many landowners who graciously granted us access to their property. The Drain Commissions of Allegan, Kalamazoo, Eaton, Calhoun, and Barry counties, the City of Kalamazoo, and Fort Custer Training Center helped us coordinate site access. Melody Bernot provided advice during the planning stages of this study, and Jake Beaulieu, Carrie DePalma, and John Hallock helped in the field and laboratory. Dennis Birdsell, Jon Loftus, and Rian Galloway assisted with sample analysis at Notre Dame's Center for Environmental Science and Technology. Comments by J. Beaulieu, F. Triska, P. Silver, and 2 anonymous referees improved earlier versions of this manuscript. CPA was funded by the Arthur J. Schmidt Presidential Fellowship and Bayer Predoctoral Fellowship. Additional funding was provided by National Science Foundation grant DEB 0111410.

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Received: 12 March 2007
Accepted: 6 November 2007