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Influence of Geomorphological Variability in Channel Characteristics on Sediment Denitrification in Agricultural Streams

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ABSTRACT

Within fluvial systems, the spatial variability of geomorphological characteristics of stream channels and associated streambed properties can affect many biogeochemical processes. In agricultural streams of the midwestern USA, it is not known how geomorphological variability affects sediment denitrification rates, a potentially important loss mechanism for N. Sediment denitrification was measured at channelized and meandering headwater reaches in east-central Illinois, a region dominated by intensive agriculture and high NO_3–N stream export, between June 2003 and February 2005 using the chloramphenicol-amended acetylene inhibition procedure. Sediment denitrification rates were greatest in separation zones, ranging from 0.6 to 76.4 mg N m^{-2} h^{-1}, compared with riffles, point bars, pools, and a run ranging from 0 to 36.5 mg N m^{-2} h^{-1}. Differences in benthic organic matter (r = 0.70) and the percentage of fine-grained sediments (r = 0.93) in the streambeds controlled much of the spatial variations in sediment denitrification among the geomorphological features. Although two meandering study reaches removed 390 and 99% more NO_3–N by sediment denitrification than adjacent channelized reaches, NO_3–N loss rates from all reaches were between 0.1 and 15.7% d^{-1}, except in late summer. Regardless of geomorphological characteristics, streams in east-central Illinois were not able to process the high NO_3–N loads, making sediment denitrification in this region a limited sink for N.

STREAM GEOMORPHOLOGY is an important component of fluvial ecosystems (Cirmo and McDonnell, 1997; Fisher et al., 1998; Rhoads et al., 2003) that contributes to the spatial diversity in physical attributes of the riverine landscape (Ward et al., 2002). This diversity in part includes in-stream geomorphic features (e.g., riffles and pools), floodplains, and hyporheic zones. The variability in hydraulic conditions, sediment properties, and organic-matter retention among various geomorphic features may cause spatial differences in nutrient processes, such as denitrification.

In the upper Midwest, agriculture is the primary source of N delivered to the Mississippi River basin (Rabalais et al., 2002). Between 1980 and 1996, Illinois and Iowa were the source of 35% of the N discharged to the Gulf of Mexico at the mouth of the Mississippi River (Goolsby et al., 2001). Intensive agriculture in Illinois has contributed to total N exports as great as 40 kg N ha^{-1} yr^{-1} during wet years (David and Gentry, 2000), with N export during more typical years averaging >15 kg N ha^{-1} yr^{-1} (Goolsby et al., 1999). Intensive fertilization, subsurface drainage, and stream channelization have led to increasingly larger riverine exports of N from Illinois since the 1880s (David et al., 2001). Subsurface drainage and channelization decrease water residence time compared with natural drainage conditions, thereby reducing N retention within watersheds.

Several studies have examined hydrogeomorphic controls of nutrients and trace metals (Meyer, 1979; Klotz, 1985; Chambers et al., 1992; Rhoads and Cahill, 1999) but none have examined the linkage between in-stream geomorphology and sediment denitrification. Sediment denitrification is a unique process in nutrient chemistry, in that it permanently removes N from the aquatic system. Previous studies (Royer et al., 2004; Schaller et al., 2004) using the acetylene inhibition technique amended with chloramphenicol examined sediment denitrification in agricultural streams of Illinois and measured sediment denitrification rates >5 mg N m^{-2} h^{-1}, substantially higher than denitrification rates in most aquatic systems (Seitzinger, 1990). Other studies have reported a broad range of in-stream denitrification rates (<1–29.7 mg N m^{-2} h^{-1}; Seitzinger, 1990; Inwood et al., 2005). Environmental controls of denitrification identified in previous studies include hydrology (Richardson et al., 2004), sediment properties (Garcia-Ruiz et al., 1998; Wall et al., 2005), water temperature (Pfenning and McMahon, 1996), and organic C and N availability (Pfenning and McMahon, 1996; Inwood et al., 2005).

In a study linking stream geomorphology to trace elements, Rhoads and Cahill (1999) identified sediment relationships with trace elements and suggested that the geomorphology of a stream could influence how trace elements are distributed downstream from their sources. For example, Rhoads and Cahill (1999) determined that streams having greater diversity in geomorphic features and sediment properties could be greater sinks for nutrients and trace elements than channelized streams that exhibit uniform bed properties. Geomorphic features that promote the accumulation of fine sediments and benthic organic matter may enhance the retention of nutrients and trace elements through adsorption or biological uptake (Rhoads and Cahill, 1999). These conclusions were supported by Garcia-Ruiz et al. (1998), who identified a positive correlation between sediment denitrification rate and the percentage of fine (<100-μm) particles in the sediment. Garcia-Ruiz et al. (1998) further concluded that the greatest denitrification rates were associated with sediments high in organic matter. These studies suggest that riffles and points bars, which

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Abbreviations: EBE_C, East Branch Embarras channelized site; EBE_M, East Branch Embarras meandering site; EMB_C, Embarras channelized site; EMB_M, Embarras meandering site.

are comprised of relatively coarse sediments, may have lower sediment denitrification rates than pools and separation zones, which typically contain fine sediments, with greater organic matter concentrations in the separation zones. In meandering streams, separation zones, also called *recirculation eddies* or *slack waters*, typically occur just upstream of the bend apex along the outer bank or just downstream of the apex along the inner bank (Hodskinson and Ferguson, 1998). These zones are areas of recirculating flow "separated" from the fast-moving flow in the main channel by a bounding shear layer.

For headwater agricultural streams, our objectives were to: (i) determine how spatial variability in stream-channel geomorphological characteristics affects sediment denitrification rates; and (ii) quantify differences in the effectiveness of denitrification in removing NO_3–N from channelized and natural meandering reaches. By examining the influence of geomorphic characteristics on sediment denitrification, this study provides new evidence on how a stream's geomorphic structure affects sediment denitrification and the ultimate impact on N loads in headwater agricultural streams.

MATERIALS AND METHODS

Study Sites

This study was conducted at two channelized and two meandering stream sites in the headwaters of the Embarras River basin in Champaign County, east-central Illinois (Fig. 1). The surrounding agricultural landscape supports >90% row crop agriculture consisting mainly of corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.] (David et al., 1997). Headwater streams in this region exhibit characteristics of low-energy fluvial systems, with gradients between 0.0001 and 0.001 m m^{-1} (Rhoads and Herricks, 1996). Sand and gravel particles dominate the streambed and riparian vegetation is limited to grass buffer strips and sparsely scattered trees.

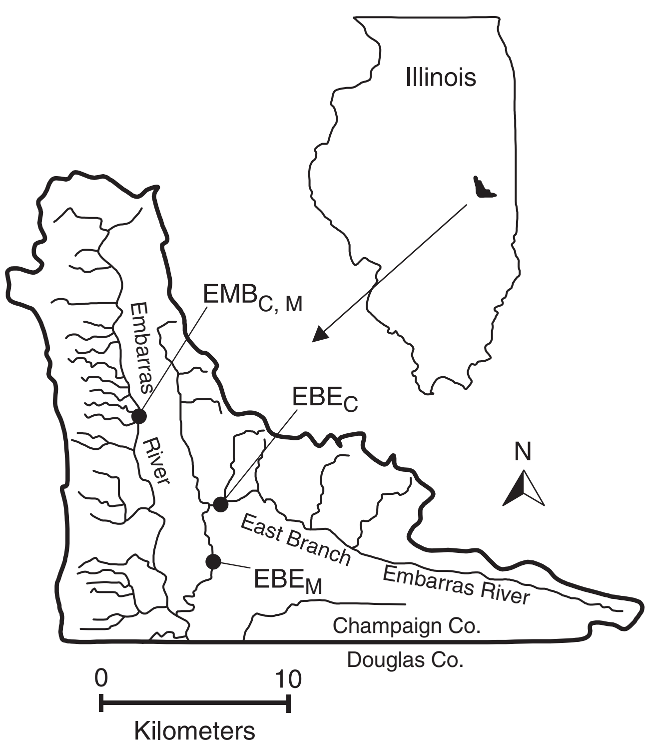

Fig. 1. Location of study reaches in Champaign County, east-central Illinois. Subscripts C and M indicate channelized and meandering reaches, respectively.

Two paired channelized and meandering stream reaches in the Embarras River basin were selected based on their geomorphic properties and availability in a largely agricultural region that has few meandering reaches (Fig. 2). Channelized reaches in east-central Illinois are identified by straight, trapezoidal-shaped channels with flat, uniform beds lacking riffle–pool sequences (Rhoads and Herricks, 1996). Meandering reaches are sinuous channels that exhibit considerable diversity in geomorphic features, including well-developed pool–riffle sequences, point bars, and zones of flow separation. The paired channelized (EMB_C, 39°58′56″ N, 88°12′23″ W) and meandering (EMB_M) reaches on the Embarras River were 0.5 km apart. They averaged 4 m wide with depths typically between 27 and 74 cm during sampling events. Study lengths of the channelized and meandering reaches were 100 and 420 m, respectively. The meandering reach had a sinuosity of 1.9, determined from surveying efforts. Fifty-three percent of the meandering reach consisted of riffles, which occurred between meander bends; 20% point bars, which occurred on the inside of meander bends; 18% cut-bank pools, which occurred on the outside of meander bends, and 9% separation zones, which occurred mainly in the lee of point bars.

The paired channelized (EBE_C, 39°56′48″ N, 88°08′29″ W) and meandering (EBE_M) reaches on the East Branch Embarras River were separated by a distance of 3 km. They averaged 8 m wide with depths typically between 51 and 80 cm during sampling events. Study lengths of the channelized and meandering reaches were 100 and 150 m, respectively. The meandering reach had a sinuosity of 1.1. Twenty-three percent of the meandering site consisted of riffle, 64% run, and 13% separation zones. The reach did not contain well-developed pools. The reaches on the East Branch Embarras River were situated within an area of extensive fine-grained glacial lacustrine deposits, which provided an opportunity to investigate sediment denitrification in fine sediments compared with the coarse sediments in the Embarras River. For greater detail on the geomorphic characteristics of our study sites, refer to Rhoads and Herricks (1996) and Rhoads et al. (2003).

Field Measurements

All study reaches were extensively mapped in the summer of 2004, and wetted streambed surface area measurements were conducted at the channelized reaches when sampling for sediment denitrification between June 2003 and February 2005. The channelized reaches were relatively uniform and did not contain any prominent in-stream geomorphological features. Measurements in these reaches focused on characterization of the wetted streambed area for estimation of total removal of NO_3–N from the water column by sediment denitrification. In contrast, the meandering reaches contained prominent in-stream geomorphological features. The boundaries and spatial extent of riffles, point bars, cut-bank pools, runs, and separation zones were determined based on spatial variations in water depth, velocity, and sediment composition. The surface area of the streambeds in the straight and meandering reaches, and the surface area for each geomorphic feature in the meandering reaches, were simultaneously determined in the summer of 2004. For all other times when sediment samples for denitrification were collected, the surface areas of the meandering sites were estimated by calcu-

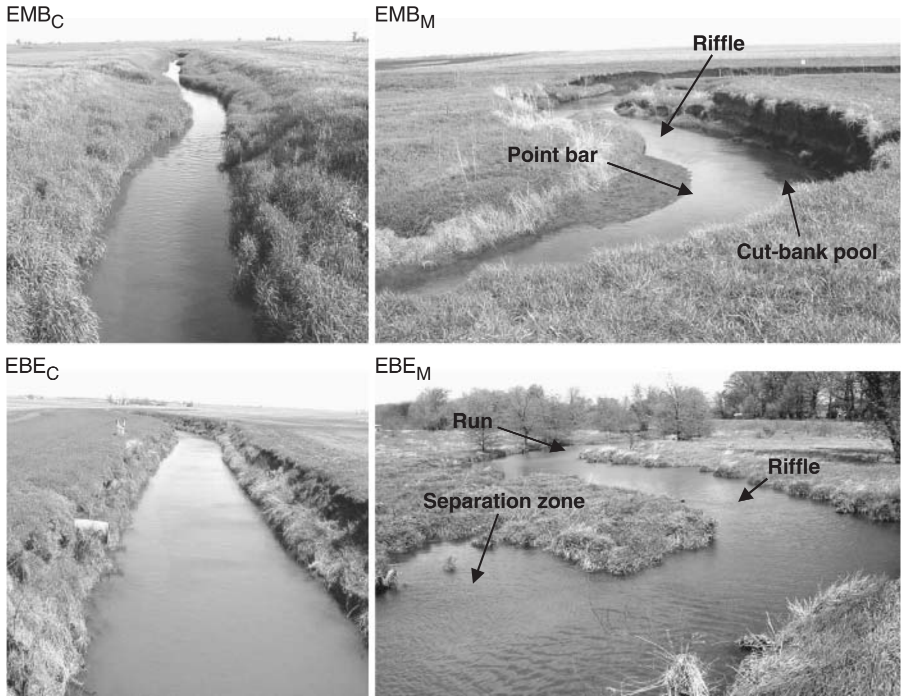

Fig. 2. Photographs of the channelized (subscript C) and meandering (subscript M) stream sites on the Embarras (EMB) and East Branch Embarras (EBE) rivers. Geomorphic features at the meandering sites are labeled on the photographs.

lating the ratio of the meandering reach to the surface area of its paired channelized reach as determined in the summer of 2004, and multiplying that ratio by the surface area of the channelized reach measured during each sampling event for denitrification. The surface area measurements were used to estimate the removal of NO_3–N from the water column by sediment denitrification. Selected geomorphic features were mapped during sampling events for sediment denitrification to confirm the accuracy of estimated surface areas for the meandering reaches.

A Marsh-McBirney (Frederick, MD) Model 2000 Flo-Mate was used to measure stream velocity at half the water depth in 10 equal increments across the width of the channels. Discharge for each sampling event was calculated from these measurements. In addition, velocities were measured at various locations throughout the meandering reaches to determine the boundaries and spatial extent of in-stream geomorphic features. Daily average discharge was also measured for the Embarras River basin near Camargo, IL (390°47′30″ N, 880°11′10″ W, basin area = 481 km^2), located 25 km downstream from the EMB$_C$ study site to provide a more complete picture of hydrologic conditions between sampling dates. Discharge between 1 June 2003 and 28 Feb. 2005 was acquired from the U.S. Geological Survey and stream NO_3–N concentrations were measured from periodic grab samples collected from the center of the stream.

The sediment composition of streambed material was determined in November 2004. Sediment samples were scooped from the upper 5 cm of the streambed using plastic sampling bottles within 0.5 m of where cores were extracted for sediment denitrification measurements, with three replicates per stream site or geomorphic feature. Samples were homogenized, dried at 60°C, and then combusted at 550°C in a muffle furnace. After eliminating organic matter, sediment aggregates were broken apart using a rolling pin. Sediment samples were then sieved into six particle classes: coarse and medium gravel (>4 mm), fine gravel (4–2 mm), coarse sand (2–0.5 mm), medium sand (500–200 μm), fine sand (200–53 μm), and silt and clay (<53 μm).

Additional field measurements at all geomorphic features throughout the study included water temperature and concentrations of NO_3–N and dissolved organic C (DOC). For NO_3–N and DOC, surface water grab samples were collected from the center of the stream and stored at freezing temperatures for NO_3–N and acidified for DOC. Analyses for NO_3–N and DOC were conducted on a Dionex (Sunnyvale, CA) DX-120 ion chromatograph and a Dohrmann (Mason, OH) DC-80 carbon analyzer, respectively.

Sediment Denitrification Measurements

Seasonal sediment denitrification rates were measured between June 2003 and February 2005, with three sediment samples per channelized reach or geomorphic feature within the meandering reaches collected approximately once a month. Bed material was collected from the study reaches midmorning and returned to the laboratory within 3 h for measuring sediment denitrification rates.

At the channelized reaches, three transects, 50 m apart, were established at least 100 m from any bridges. At each transect, three sediment cores were collected at equal intervals across the width of the stream and homogenized into one sample. Sediment samples were extracted from the upper 5 cm of the streambed using polyvinyl chloride tubing, which had a surface area of 7 cm^2. At the meandering reaches, three or more geomorphic features of each type (riffle, point bar, cut-bank pool, run, or separation zone) were sampled within a day of the adjacent channelized reaches. For each type of feature, three or more random sediment cores were collected and homogenized into one sample.

Denitrification rates were measured using the acetylene inhibition technique (Tiedje et al., 1989; Knowles, 1990) as modified by Royer et al. (2004). Although this method is inappropriate in sediments with low NO_3–N or coupled nitrification–denitrification (Rudolph et al., 1991; Seitzinger et al., 1993), NO_3–N >10 μ*M* and the addition of chloramphenicol improve the estimates of measuring in situ denitrification rates (Smith and Tiedje, 1979; Royer et al., 2004). Chloramphenicol is an antibiotic that inhibits the activity of existing denitrification enzymes when acetylene inhibition techniques are used. This benefits denitrification assays where sediment cores are converted to slurries for determining denitrification rates because it prevents an increased response in denitrification rates to a disruption in redox conditions, anaerobic conditions caused by purging samples with He before analysis, and optimal exposure of denitrifiers to NO_3^- and organic C. We have used these techniques successfully as documented in greater detail by Royer et al. (2004), and our denitrification rates are similar to other published studies that report in situ denitrification rates using chloramphenicol (Royer et al., 2004; Schaller et al., 2004; Inwood et al., 2005).

Twenty-five cubic centimeters of sediment, excluding particle sizes ≥4 mm, from each homogenized sediment sample was transferred to individual 150-mL flasks equipped with a butyl septum lid for gas sampling. The sediments were then diluted to 75 mL with stream water taken from the same locations as the sediment samples ($n = 3$ per site or habitat and date). Sediment particle sizes ≥4 mm were considered too large to support a significant enough population of denitrifying bacteria to affect sediment denitrification rates. Chloramphenicol was then added to each flask at a concentration of 5 m*M* to suppress de novo enzyme synthesis, which reduces bottle effects and improves estimates of in situ denitrification rates (Brock, 1961). Bottles were purged with He, and acetylene gas (C_2H_2, 10% v/v) was added to block the transformation of N_2O to N_2. Flasks were incubated at stream temperature and headspace gas samples were collected four times during a 2-h period with a gas-tight syringe. Before gas sampling, flasks were shaken to release N_2O from sediments; otherwise flasks were left undisturbed throughout the incubation period. Time series experiments conducted by Smith and Tiedje (1979) identified that a 2-h incubation period, when used with chloramphenicol, was effective at inhibiting N_2 formation and producing a linear accumulation of N_2O with time. All denitrification rates reported in the results exhibited a linear production of N_2O for 2 h.

Gas samples were analyzed for N_2O on a Varian (Palo Alto, CA) Model 3600 gas chromatograph equipped with an 80/100-mesh Porapak Q column and a ^{63}Ni electron-capture detector. Column and detector temperatures were 70 and 300°C, respectively. Sediment denitrification rates were calculated as the linear rate of N_2O accumulation with time multiplied by the Bunsen solubility coefficient (Tiedje, 1982) and expressed per gram of ash-free dry mass (AFDM) of subsample substrate. After completion of sediment denitrification assays, subsamples and their parent homogenized sediment samples were dried at 60°C to determine dry mass and combusted at 550°C in a muffle furnace to determine AFDM. Total benthic organic matter for each homogenized sediment sample, before separating out subsamples for sediment denitrification assays, was determined by adding the AFDM measured from the subsample to the AFDM measured from its parent, homogenized sediment sample. To express sediment denitrification on an areal basis, rates were multiplied by the sum of the AFDM of the parent homogenized sediment sample and its extracted subsample.

Calculating Nitrate-Nitrogen Removal by Sediment Denitrification

Nitrate-N removal by sediment denitrification was calculated at the channelized reaches as the product of the mean sediment denitrification rate and the streambed surface area scaled to 200 m per sampling date and then averaged per season. A 200-m distance was chosen because it was the average distance among the straight-valley lengths of the channelized reaches and the meandering reaches. For the meandering reaches, mean sediment denitrification rates per sampling date were calculated by multiplying the mean sediment denitrification rates of each geomorphic feature by the percentage of the total bed surface area that a geomorphic feature covered and summing the results for all geomorphic features within the reach. The area of each geomorphic feature relative to the total bed surface area was determined when the meander reaches were mapped in the summer of 2004. The percentages for the meandering reach on the Embarras River reflect the total surface area of the meander reach after removing small areas of exposed, compacted lacustrine hard clay that were experimentally found to have low denitrification rates near detection limits. The amount of NO_3–N removed by sediment denitrification was calculated by multiplying the mean sediment denitrification rate and the streambed surface area scaled to 200 m per sampling date and then averaged per season. Only data collected from February 2004 to February 2005 were included in NO_3–N removal estimates at EMB_M due to the absence of sampling of point bars before February 2004.

Statistical Analyses

Statistical analyses were performed using SAS (SAS Institute, 1990). Sediment denitrification rates were initially tested for normality and homogeneity of variance using Levene's test. Although square-root transformation of sediment denitrification rates from EMB and log transformation of sediment denitrification rates from EBE met the normality criterion, they failed Levene's test for homogeneity of variance. Therefore, for determining significant differences in sediment denitrification rates between five seasons (spring, early summer, late summer, fall, and winter), nonparametric statistics (Kruskal–Wallis) were used. Nonparametric statistics were also used for determining significant differences in sediment denitrification rates between different geomorphic features.

Sediment denitrification rates from EMB were square-root transformed and EBE were log transformed to conduct a simple linear regression to test for a relationships between sediment denitrification rates and benthic organic matter concentrations. Stream NO_3–N concentrations <1 mg L^{-1} and measurements obtained in February when water temperatures were <5°C were excluded from the linear regression analyses. At low stream NO_3–N concentrations and water temperatures, sediment denitrification rates were near detection limits and would have obscured relationships between denitrification rates and benthic organic matter concentrations. Linear regression was also used to examine relationships between benthic organic matter and silt and clay percentages. Benthic organic matter concentrations and silt and clay percentages met normality criteria.

RESULTS

Field Measurements

The mean streambed surface area calculated for a straight-valley length of 200 m at EMB_C was 940 m^2 compared with 1200 m^2 at EMB_M, and 1500 m^2 at EBE_C compared with 2500 m^2 at EBE_M. Sediment composition was coarser and there was less benthic organic matter at the reaches on the Embarras River compared to

Table 1. Streambed characteristics of channelized (subscript C) and meandering (subscript M) reaches of the Embarras (EMB) and East Branch Embarras (EBE) rivers, including the streambed area of geomorphic features at the meandering reaches. Sediment composition was measured in November 2004 (n = 3 per site/habitat) and mean benthic organic matter between June 2003 and February 2005.

Site (% of streambed area)	Coarse and medium gravel (>4 mm)	Fine gravel (4–2 mm)	Coarse sand (2–0.5 mm)	Medium sand (500–200 μm)	Fine sand (200–53 μm)	Silt + clay (<53 μm)	n	Benthic organic matter
	%							%
EMB_C	30 (6)†	15 (1)	43 (6)	8 (1)	3 (<1)	1 (<1)	38	1.6 (0.1)
EMB_M								
Riffle (53)	60 (16)	8 (5)	22 (6)	6 (3)	3 (1)	1 (<1)	32	2.0 (0.1)
Point bar (20)	18 (3)	10 (2)	56 (2)	9 (<1)	5 (4)	2 (<1)	24	1.5 (0.1)
Cut-bank pool (18)	44 (6)	11 (1)	20 (<1)	8 (2)	7 (1)	9 (4)	40	2.5 (0.1)
Separation zone (9)	5 (3)	7 (3)	39 (16)	34 (16)	11 (4)	5 (2)	571	2.2 (0.1)
EBE_C	7 (4)	7 (2)	60 (5)	18 (1)	5 (3)	3 (1)	30	2.5 (0.1)
EBE_M								
Riffle (23)	12 (4)	14 (3)	42 (4)	18 (3)	11 (1)	3 (<1)	26	2.4 (0.1)
Run (64)	2 (1)	3 (1)	31 (4)	22 (3)	23 (3)	19 (5)	24	4.1 (0.2)
Separation zone (13)	1 (6)	2 (1)	29 (6)	23 (4)	28 (6)	18 (5)	84	5.0 (0.2)

† Values in parentheses are one standard error.

those on the East Branch Embarras River (Table 1). At both meandering reaches, riffles or point bars had the coarsest sediments and the lowest concentration of benthic organic matter, whereas separation zones had the finest sediments and the highest concentrations of benthic organic matter.

Water temperature and water chemistry were similar between the paired channelized and meandering reaches (Table 2). Throughout the study, stream NO_3–N concentrations were typically >5 mg L^{-1}, except during late summer when they were <2 mg L^{-1} (Fig. 3). There were no consistent patterns of greater or lesser stream NO_3–N concentrations in any geomorphic feature within the meandering reaches for any given sampling date. Stream NO_3–N concentrations varied little between the upstream sampling locations and downstream sampling locations at EMB_M but there was a decrease in concentrations of 0 to 0.2 mg L^{-1} within a reach length of 67 m at EBE_M. Stream NO_3–N concentrations also decreased by 0.2 to 1.2 mg L^{-1} between the channelized reach and the meandering reach on the East Branch Embarras River.

Table 2. Physiochemical characteristics of channelized (subscript C) and meandering (subscript M) reaches of the Embarras (EMB) and East Branch Embarras (EBE) rivers averaged by season from June 2003 to February 2005.

Site	n	Water temperature	Discharge	NO_3–N	Dissolved organic C
		°C	$m^3\ s^{-1}$	mg L^{-1}	
			April–May		
EMB_C	2	12.8 (3.1)†	1.08 (0.34)	6.7 (1.1)	2.8 (1.1)
EBE_C	2	12.6 (2.7)	1.14 (0.07)	13.5 (0.3)	1.7 (0.1)
EBE_M	2	13.6 (2.2)	1.66 (0.04)	12.8 (0.7)	1.8 (0.2)
			June–July		
EMB_C	4	20.0 (0.5)	0.73 (0.10)	7.7 (1.1)	2.2 (0.2)
EBE_C	3	19.2 (0.6)	0.83 (0.08)	12.0 (1.1)	1.9 (<0.1)
EBE_M	3	18.9 (0.6)	1.18 (0.11)	11.2 (1.1)	2.8 (0.4)
			August–September		
EMB_C	2	25.7 (2.3)	0.03 (0.01)	0.7 (0.6)	3.5 (0.2)
EBE_C	2	24.0 (0.6)	0.02 (< 0.01)	1.9 (1.6)	3.4 (0.3)
EBE_M	2	24.1 (1.2)	0.02 (0.01)	1.8 (1.4)	3.6 (0.3)
			October–November		
EMB_C	4	9.8 (2.3)	0.29 (0.10)	4.2 (0.6)	3.1 (0.7)
EBE_C	3	11.6 (0.6)	0.30 (0.15)	7.9 (1.2)	2.0 (0.4)
EBE_M	3	11.8 (0.7)	0.53 (0.21)	7.0 (1.2)	2.0 (0.2)
			February		
EMB_C	2	1.5 (1.4)	0.35 (0.08)	6.0 (0.4)	2.0 (0.2)
EBE_C	1	4.1	0.39	10.9	1.3
EBE_M	1	3.7	0.59	10.1	1.4

† Values in parentheses are one standard error.

Sediment Denitrification

Sediment denitrification rates ranged from 0.1 to 1.9 mg N m^{-2} h^{-1} at EMB_C. At EMB_M, sediment denitrification rates ranged from 0 to 2.6 mg N m^{-2} h^{-1} in the riffles and point bars, 0 to 3.6 mg N m^{-2} h^{-1} in the cut-bank pools, and 1.9 to 39.8 mg N m^{-2} h^{-1} in the separation zones (Fig. 4). Denitrification rates were greatest in the separation zones and least in the riffles and point bars throughout all seasons, with a significant difference between separation zones and riffles and point bars in the spring, early summer, and fall (Kruskal–Wallis, $P < 0.007$). By season, mean sediment denitrification rates (±SE) were greatest between June and September, averaging 1.0 ± 0.5 mg N m^{-2} h^{-1} at EMB_C and 0.9 ± 0.3 mg N m^{-2} h^{-1} in the riffles and point bars, 1.7 ± 0.4 mg N m^{-2} h^{-1} in the cut-bank pools, and 11.0 ± 2.6 mg N m^{-2} h^{-1} in the separation zones at EMB_M. Sediment denitrification rates measured in February were <0.2 mg N m^{-2} h^{-1} at EMB_C

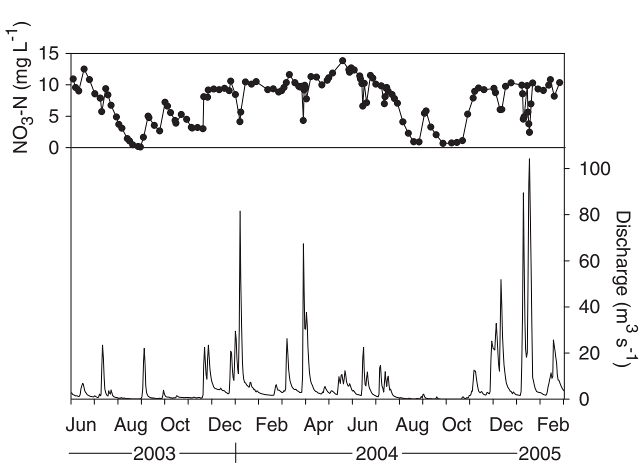

Fig. 3. Daily average discharge and stream NO_3–N concentrations for the Embarras River basin near Camargo, IL, from 1 June 2003 to 28 Feb. 2005.

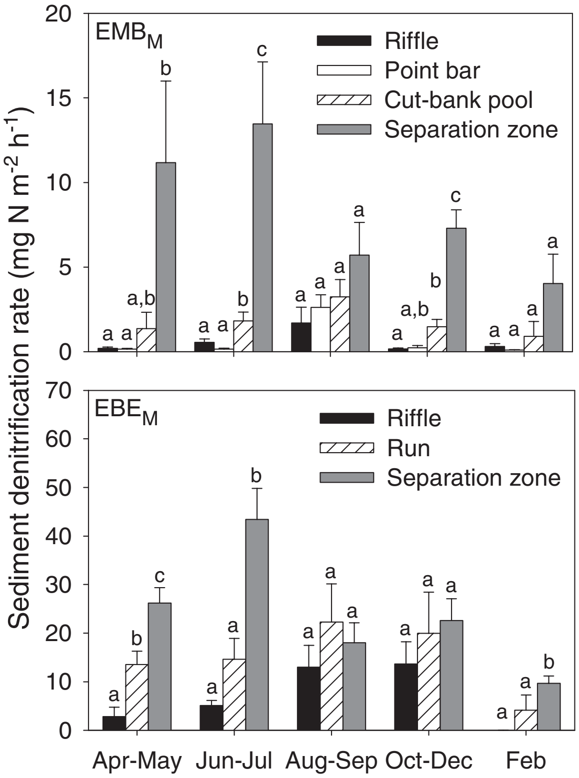

Fig. 4. Mean sediment denitrification rates (one standard error) for geomorphic features at the meandering reaches of the Embarras (EMB) and East Branch Embarras (EBE) rivers averaged by season from June 2003 to February 2005. Different letters indicate significant differences between means for a specific season (Kruskal–Wallis, $P < 0.05$).

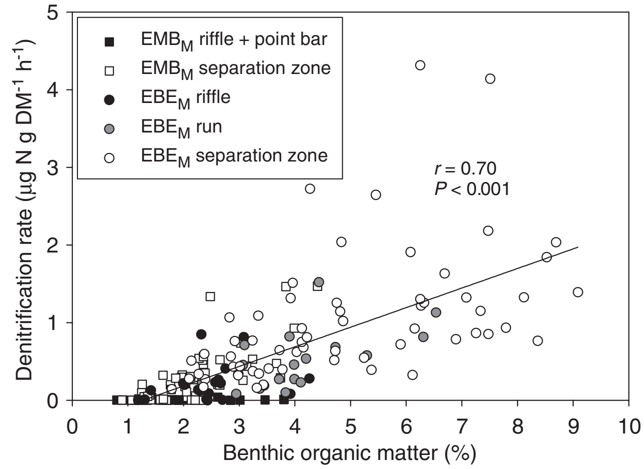

Fig. 5. Relationship between sediment denitrification rates for geomorphic features at the meandering reaches of the Embarras (EMB) and East Branch Embarras (EBE) rivers and benthic organic matter. Figure excludes sediment denitrification rates measured in February and when stream NO_3–N concentrations were <1 mg L^{-1}.

and in the riffles and point bars at EMB$_M$, and averaged 0.8 ± 0.7 mg N m^{-2} h^{-1} in the cut-bank pools and 4.0 ± 1.6 mg N m^{-2} h^{-1} in the separation zones at EMB$_M$.

At EMB$_M$, benthic organic matter concentrations were positively correlated with sediment denitrification rates in the riffles and point bars (linear regression, P = 0.04, r = 0.33) and separation zones (P < 0.0001, r = 0.75). Figure 5 shows the relationship between benthic organic matter concentrations and sediment denitrification rates for those geomorphic features at the Embarras and East Branch Embarras meandering reaches that exhibited significant relationships. A linear regression analysis resulted in a P < 0.001 and r = 0.70 when data were combined in Fig. 5.

Sediment denitrification rates and NO_3–N removal calculated for the entire meandering reach at EMB$_M$ were greater than denitrification rates and NO_3–N removal at the channelized reach (EMB$_C$) during all sampling dates (Table 3). Separation zones accounted for 58% of the total NO_3–N removed at EMB$_M$, even though the collective surface area of the separation zones was only 9% of the total streambed area. Riffles and point bars accounted for 26% and cut-bank pools accounted for 16% of the total amount of NO_3–N removed, which were values equal to the percentage of the surface area these features occupy. The percentages were consistent throughout the seasons, except in late summer when 58% of the total NO_3–N removed from the meandering reach was from riffles and point bars and 22% from separation zones, and in winter, when cut-bank pools accounted for 2% and separation zones accounted for 73% of the total NO_3–N removed. In addition to an increase in NO_3–N removal due to geomorphic features between EMB$_C$ and EMB$_M$, the large bed surface area associated with a sinuosity of 1.9 at EMB$_M$ increased total NO_3–N removal by 91% on average compared with total NO_3–N removal if the meandering reach had a sinuosity of 1.0.

At EBE$_C$, sediment denitrification rates ranged from 0 to 71.5 mg N m^{-2} h^{-1}. Denitrification rates ranged from 0 to 26.4 mg N m^{-2} h^{-1} in the riffle, 2.0 to 36.5 mg N m^{-2} h^{-1} in the run, and 0.6 to 76.4 mg N m^{-2} h^{-1} in the separation zones at EBE$_M$ (Fig. 4). Separation zones had significantly greater sediment denitrification rates than any other type of geomorphic feature in the spring, early summer, and winter (Kruskal–Wallis, P < 0.03). The lowest denitrification rates occurred in the riffle throughout all seasons. Sediment denitrification rates were greatest between June and September, averaging 26.5 ± 12.3 mg N m^{-2} h^{-1} at EBE$_C$, 8.4 ± 2.2 mg N m^{-2} h^{-1} in the riffle at EBE$_M$, 18.0 ± 4.2 mg N m^{-2} h^{-1} in the run at EBE$_M$, and 32.5 ± 4.5 mg N m^{-2} h^{-1} in the separation zones at EBE$_M$. Denitrification rates measured in February were <0.1 mg N m^{-2} h^{-1} at EBE$_C$, <0.1 mg N m^{-2} h^{-1} in the riffle at EBE$_M$, 4.1 mg N m^{-2} h^{-1} in the run at EBE$_M$, and 9.7 mg N m^{-2} h^{-1} in the separation zones at EBE$_M$.

A significant positive correlation existed between benthic organic matter and sediment denitrification rates for EBE$_M$ when data from all geomorphic features were combined (linear regression, P < 0.001, r = 0.70), but not for EBE$_C$, when samples from February and when stream NO_3–N concentrations were <1 mg L^{-1} were excluded (Fig. 5). Significant correlations did not exist when each geomorphic feature was analyzed separately.

Sediment denitrification rates for the entire reach at EBE$_M$ were greater than those for EBE$_C$ in fall and winter (Table 3), and NO_3–N removal by sediment deni-

Table 3. Removal of stream NO_3–N by sediment denitrification at the channelized (channel) and meandering (meander) reaches of the Embarras and East Branch Embarras rivers scaled to a straight-valley length of 200 m. Seasonal means include measurements from February 2004 to February 2005 on the Embarras River and from June 2003 to February 2005 on the East Branch Embarras River.

Season	n	Sediment denitrification		NO_3–N load		NO_3–N removed		NO_3–N load removed	
		Channel	Meander	Channel	Meander	Channel	Meander	Channel	Meander
		mg N m^{-2} d^{-1}		kg d^{-1}		g d^{-1}		%	
Embarras River									
Apr.–May	2	3	33	590		3	44	<0.001	0.007
June–July	2	3	32	610		3	41	<0.001	0.007
Sept.	1	19	78	3		15	78	0.57	2.9
Nov.	1	4	25	81		4	32	0.006	0.04
Feb.	1	3	16	180		3	21	0.002	0.006
East Branch Embarras River									
Apr.–May	2	440	300	1300	1800	710	800	0.06	0.04
June–July	3	800	380	870	1100	1200	970	0.13	0.09
Aug.–Sept.	2	390	350	3	5	580	850	14	21
Oct.–Nov.	3	210	400	230	240	310	960	0.25	0.49
Feb.	2	1	94	360	520	1	230	<0.01	0.04

trification was greater at EBE_M than at EBE_C during every season except early summer. The run accounted for 64% of the total NO_3–N removed, covering 64% of the total streambed at EBE_M. Respectively, the separation zones and the riffle accounted for 25 and 11% of the total NO_3–N removed, covering 13 and 23% of the total streambed at EBE_M. The percentages were consistent throughout the seasons, except in late summer when 23% of the total NO_3–N removed from the meandering reach was from the riffle and 9% from separation zones, and in winter when the riffle accounted for <1% of the total NO_3–N removed. A sinuosity of 1.1 at EBE_M increased total NO_3–N removal by 13% on average compared with a sinuosity of 1.0.

A significant positive correlation existed between mean benthic organic matter and silt and clay percentage at both channelized reaches and for all geomorphic features at the two meandering reaches. Linear regression analysis identified a P value of <0.001 and $r^2 = 0.87$.

DISCUSSION

The results of this study indicated that sediment denitrification at the meandering reaches removed on average 390% (Embarras) and 99% (East Branch Embarras) more stream NO_3–N than the channelized reaches when comparing straight-valley reach lengths of 200 m. Two characteristics associated with variability in stream-channel geomorphology—separation zones, which were "hot spots" of sediment denitrification activity, and sinuosity, which increased the surface area of the streambed—were the primary factors leading to greater in-stream NO_3–N removal from meandering reaches than channelized reaches. At EMB_M, separation zones were only 9% of the total surface area of the meandering reach, but accounted for 59% of the mean NO_3–N removed by sediment denitrification. Riffles and point bars at EMB_M only accounted for 26% of the mean NO_3–N removed by sediment denitrification, despite the fact that these features covered 73% of the bed. Although the magnitude of difference between the surface area of separation zones and riffle and the amount of NO_3–N removed from them was less at EBE_M than at EMB_M, separation zones still contributed significantly to the amount of NO_3–N removed from EMB_M. Besides separation zones, sinuosity was also an important factor in denitrification; EMB_M, which had a sinuosity of 1.9, accounted for 91% more mean NO_3–N removal than if it had a sinuosity of 1.0.

In a study by Richardson et al. (2004) on the Upper Mississippi River, sediment denitrification activity was found to be greatest in the backwater lakes and lowest in the main channel. They concluded that denitrification activity was largely a function of high-C sediments related to NO_3–N delivery and hydraulic retention time (Richardson et al., 2004). Further evidence of benthic organic matter acting as a control on sediment denitrification has been reported by Wall et al. (2005) and Kemp and Dodds (2002). The relatively large amounts of fine sediments and benthic organic matter in separation zones, compared with other geomorphic features, explains why these locations are "hot spots" for denitrification. The recirculating flow within the separation zones causes these geomorphic features to be sinks for both benthic organic matter and fine-grained sediments. During base flow conditions in late summer, however, separation zones had decreased sediment denitrification rates compared with spring, early summer, and fall, whereas riffles had increased in sediment denitrification rates. This may suggest that hydraulic connectivity between the main channel and these two geomorphic features differ during base flow, which could account for lower sediment denitrification rates in the separation zones caused by a greater depletion of NO_3–N due to higher water temperatures than was being replaced by upstream delivery. Conversely, riffles were receiving greater NO_3–N loads, contributing to greater sediment denitrification rates.

The relationship between sediment size and sediment denitrification was confirmed by the high rates of denitrification at the East Branch Embarras reaches, which had relatively fine bed material associated with lacustrine deposits, compared with the Embarras reaches, which contained relatively coarse sediment associated with reworked fluvioglacial deposits. The relatively high concentrations of benthic organic matter and finer grained sediments at the channelized and meandering reaches on the East Branch Embarras River resulted in more than six times more NO_3–N removed from these paired reaches than the paired channelized and meandering sites on the Embarras River. This disparity illustrates the importance of the textural composition of bed material on denitrification. Separation zones at EBE_M did not have as great of an influence on differences in NO_3–N removal between EBE_M and EBE_C as these zones did between EMB_M and EMB_C. The greater overall abundance of fine-grained sediments and benthic organic matter throughout the channelized and meandering sites on the East Branch Embarras River may have reduced the influence of separation zones on whole-reach denitrification rates. Thus, the presence of separation zones within meandering reaches of predominantly coarse-grained sediments seems to have a greater influence on the removal of NO_3–N than it does within straight and meandering reaches of predominantly fine-grained bed material.

A significant positive correlation existed between the abundance of silt and clay and the mean concentration of benthic organic matter for all geomorphic features in the meandering reaches and for the uniform streambed at the channelized reaches (Fig. 6). Compared with coarse sediments, fine sediments have a larger surface area per unit weight or volume, provide more abundant microbial habitats (Ranjard et al., 2000), reduce O_2 diffusion from the surface waters into the underlying sediment due to the presence of a viscous boundary layer (House, 2003), and enhance the development of anoxic microenvironments. Several studies have linked high denitrification rates with fine-grained soils in floodplains and streams (Garcia-Ruiz et al., 1998; Pinay et al., 2000; West, 2001). This study has shown that the same relationship holds for sediment denitrification and that spatial variability in sediment denitrification is a function of parent streambed material and the presence of in-stream geomorphological structures. Homogenous channelized reaches have spatially uniform sediment denitrification rates, whereas the spatial variability of in-stream geomorphological structures in meandering reaches, which produces spatial variability in hydraulic conditions, sediment sorting, and organic matter accumulation, leads to spatial variability of sediment denitrification rates within these reaches.

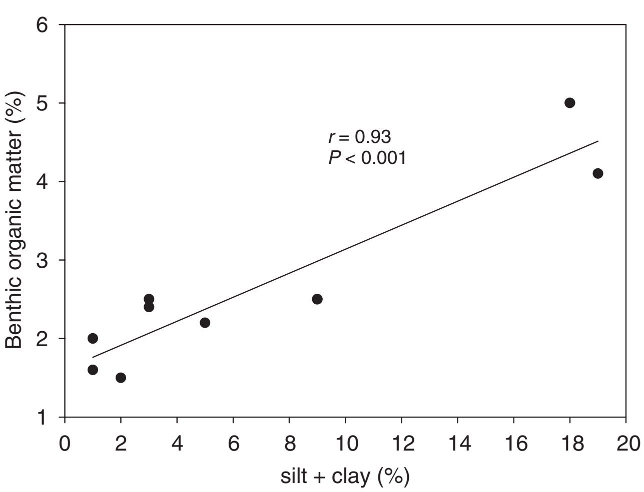

Fig. 6. Relationship between mean benthic organic matter of sediment samples collected between June 2003 and February 2005 and silt and clay in sediments measured in November 2004. Each value represents a channelized reach or geomorphic feature within a meandering reach on the Embarras and East Branch Embarras rivers.

Because of widespread stream channelization for land drainage (Rhoads and Herricks, 1996), headwater meandering reaches in east-central Illinois rarely exceed a straight-valley length of a few hundred meters. For 100% of the measured NO_3–N in the reaches of the Embarras River to be removed by sediment denitrification, straight-valley lengths of 40 000 km of straight channel or 2900 km of meandering channel would be required during the spring. In late summer, these distances reduce to 35 km of straight channel and 6.9 km of meandering channel. For the East Branch Embarras River, straight-valley lengths of approximately 400 and 1.1 km are required for both reaches during the spring and late summer, respectively. Drain-tile outlets, which convey N-rich subsurface water, occur at many locations along headwater streams in east-central Illinois, however, adding N to these streams from numerous sources. These contributions overwhelm the capacity of sediment denitrification to remove a significant percentage of the total NO_3–N. Royer et al. (2004) determined that loss rates for NO_3–N in streams throughout the region were $<5\%\ d^{-1}$, except in late summer. They concluded that most NO_3–N in the headwater streams was exported to downstream water bodies rather than being denitrified (Royer et al., 2004). From this study, loss rates for NO_3–N at the two channelized reaches, computed by dividing mean sediment denitrification rates by stream NO_3–N concentrations and stream depth, ranged from 0.1 to 1.4% d^{-1} at EMB_C and 1.3 to 15.7% d^{-1} at EBE_C, except in late summer. These percentages were similar to those for adjacent meandering sites, suggesting that sediment denitrification in headwater streams of east-central Illinois has little impact on NO_3–N loads.

CONCLUSIONS

This study has shown that meandering reaches of headwater streams in the agricultural environment of east-central Illinois remove more in-stream NO_3–N than adjacent channelized reaches. The difference in N removal is related to the greater diversity of in-stream geomorphological structure of the meandering reaches, which are sinuous and contain pools, riffles, point bars, and separation zones, compared with the channelized reaches, which are straight and have uniform, flat beds. In particular, geomorphic characteristics, channel sinuosity, and the presence of separation zones contribute substantially to the relatively high rates of N removal in the meandering reaches. Separation zones, which occurred mainly in the lee of point bars, were areas of flow recirculation where benthic organic matter and fine-grained sediments preferentially accumulated. Thus, separation zones were "hot spots" for sediment denitrification in meandering reaches. Channel sinuosity, which increases the total surface area of the streambed per unit valley length, is also an important contributor to total N removal. The influence of geomorphic structure on in-stream denitrification operates through its effects on hydraulic conditions, sediment sorting, and organic matter accumulation, as confirmed by the positive correlations between sediment denitrification and concentrations of benthic organic matter and fine sediments.

Sediment denitrification rates were similar between the paired channelized and meandering reaches with abundant fine sediments and benthic organic matter, but denitrification rates were much greater than those paired channelized and meandering reaches with relatively coarse sediments. Thus, sediment properties, including those associated with parent materials, were a strong control of sediment denitrification rates. Geomorphic variability, by producing local in-stream accumulations of fine sediments and benthic organic matter, such as separation zones, had the greatest influence on denitrification rates in reaches with relatively coarse sediments. Within the context of a particular type of parent material, stream geomorphology serves as a template that controls spatial differences in sediment denitrification, both locally within reaches and between different types of reaches.

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