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N processing within geomorphic structures in urban streams

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Abstract. Stream water often diverges from the main channel into sediments below the stream surface, gravel bars next to the stream, or organic debris dams in the middle of the stream. These geomorphic structures have the potential to support processes that produce or consume inorganic N (NH_4^+, NO_3^-) and thus affect streamwater quality. We measured production (potential net mineralization and nitrification) and consumption (denitrification potential, net immobilization) of inorganic N, respiration, and organic-matter content in sediments from geomorphic structures in 4 streams in and around Baltimore, Maryland, USA. We sampled sediments from stream pools, riffles, gravel bars (vegetated and nonvegetated), and organic debris dams in forested reference and suburban catchments, and also sampled degraded (incised channel) and restored reaches of one stream. Denitrification potential was highest in organic debris dams and organic-rich gravel bars—structures with high organic matter content. Organic debris dams in suburban streams had higher denitrification than debris dams in the forested reference stream, likely because of higher NO_3^- concentrations in suburban streams. These results suggest that denitrification in debris dams increases in response to high NO_3^- levels and that denitrification may be an important sink for NO_3^- in urban or suburban streams. However, such denitrifying structures as organic debris dams may be difficult to maintain in urban streams because of high storm flows and downstream displacement. Geomorphic structures in N-rich streams also supported higher rates of nitrification than structures in a forested reference stream, suggesting that these structures can become sources of NO_3^-. The ultimate effect of different structures on NO_3^- concentrations in urban streams will depend on the balance of these production and consumption processes, which is a complex function of a stream's ability to retain organic matter and resist hydrologic changes associated with urbanization and elevated NO_3^- levels.

Key words: denitrification, nitrification, hyporheic, urban, nitrate, stream.

The ability of stream ecosystems to convert inorganic N into organic forms or N_2 is an important function (Burns 1998, Alexander et al. 2000, Peterson et al. 2001, Wollheim et al. 2001, Bernhardt et al. 2002). Inorganic N, especially NO_3^-, is of concern as a drinking water pollutant and as a cause of eutrophication in coastal waters (USEPA 1990, Howarth et al. 1996). Catchment-scale strategies to control N pollution focus on reducing sources (e.g., fertilizer, sewage) and/or increasing sinks of inorganic N (Mitsch et al. 2001, Driscoll et al. 2003, Galloway et al. 2003). Sinks are areas and/or processes that prevent movement of inorganic N to receiving waters (Mitsch et al. 2001), and include uptake by autotrophs, immobilization by heterotrophs, and denitrification, the anaerobic conversion of NO_3^- into N_2. Different components of stream ecosystems can function as either inorganic N sources or sinks, so there is great interest in understanding N processing within geomorphic structures of streams, and how such structures are affected by environmental variation, natural and human disturbance, and ecosystem management (Paul and Meyer 2001, Nilsson et al. 2003).

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The balance between N source and sink processes in streams is strongly influenced by C fluxes. Carbon is the energy source that drives microbial immobilization of inorganic N as well as most denitrification activity (Holmes et al. 1996, Bernhardt and Likens 2002, Strauss et al. 2002). High heterotrophic immobilization reduces nitrification, an aerobic process that produces NO_3^-. High activity by heterotrophs also consumes O_2, which fosters denitrification (Baker et al. 2000, Mulholland et al. 2000, Bernhardt et al. 2002). Any factors that influence accumulation and processing of C are therefore strong regulators of N dynamics in streams.

One approach to analysis of instream N sink and source dynamics is to consider different geomorphic structures, characterize microbial source and sink processes, and then quantify their importance in the overall flow of water (Munn and Meyer 1990, D'Angelo et al. 1991, Jones et al. 1995, Holmes et al. 1996, Martí and Sabater 1996, Fisher et al. 1998, Kemp and Dodds 2002a). Most stream water flows within the main channel, but water also flows into subsurface sediments, adjacent gravel bars or instream organic debris dams. Analysis of C and N dynamics in such structures may be useful for characterizing their potential to produce and consume inorganic N. An ecosystem-scale assessment requires coupling this analysis with hydrologic information on the amount of water passing through geomorphic structures (Duff and Triska 1990, Valett et al. 2002). Consideration of the natural and anthropogenic factors influencing the origin and maintenance of geomorphic structures, such as flow regime, riparian vegetation, and geologic substrate, is an additional requirement of these studies (Wollheim et al. 2001).

Urbanization is one of the major factors affecting stream ecosystems worldwide (Paul and Meyer 2001, Booth 2005, Grimm et al. 2005, Meyer et al. 2005, Walsh et al. 2005a). Increases in imperviousness associated with urbanization greatly alter stream flow and sediment regimes. Urbanization is also associated with increased chemical inputs and alteration of riparian vegetation and C input to streams (Paul and Meyer 2001, Nilsson et al. 2003). It is likely that hydrologic and biogeochemical changes associated with urbanization greatly alter occurrence and function of geomorphic structures, but there have been no studies designed to assess how C and N processes are affected within such structures in urban streams.

We present work from the Baltimore Ecosystem Study (BES, http://beslter.org), which, along with Phoenix, Arizona, is 1 of the 2 urban sites recently (1997) added to the US National Science Foundation's long-term ecological research (LTER) network (Pickett et al. 1997, 2001, Grimm et al. 2000). A major focus of BES research is analysis of N sources and sinks in urban and suburban catchments. Specific BES studies have quantified fertilizer inputs (Law et al. 2004), stream exports and input–output budgets (Band et al. 2001, Groffman et al. 2004), and riparian N processing (Groffman et al. 2002, 2003, Groffman and Crawford 2003). We describe a study designed to assess instream processing of N in urban catchments, based on a survey of denitrification, nitrification, mineralization, respiration, and organic content of sediments from 4 contrasting geomorphic structures (pools, riffles, organic debris dams, gravel bars) within suburban and forested reference streams. Our objectives were to 1) determine if geomorphic structures in urban streams could function as sources or sinks for NO_3^-, 2) examine controls on the potential for such sources or sinks, focusing on organic content and streamwater NO_3^- concentrations, and 3) assess the effects of stream geomorphic restoration on this potential.

Methods

We sampled sediments from 4 streams with contrasting land use in the Baltimore metropolitan area (Table 1). Glyndon, Pond Branch, and Baisman Run are long-term BES study sites (Groffman et al. 2004). Pond Branch and Glyndon are narrow (~1 m wide) 1st-order streams, and Baisman Run is a relatively larger (~3 m wide) 2nd-order stream; Pond Branch is a tributary to Baisman Run. Minebank Run is a 2nd-order, highly degraded (2–3 m of incision, 3–5 m wide) stream, which was the site of an intensive stream restoration study (Mayer et al. 2004). We studied both restored and unrestored sections of Minebank Run. The unrestored section was a typical incised, degraded urban stream (Walsh et al. 2005b). The upper reaches were restored in 2001 to improve geomorphic stability and reduce channel incision. Restoration involved reshaping stream banks to increase interaction between the stream channel and riparian zone, protecting stream banks against erosion, establishing pool and riffle zones, and aggressive revegetation of the riparian zone.

We examined sections of each stream for the presence of key geomorphic structures (hereafter ''structures'') shown in previous studies to have distinctive potential for processing of C

TABLE 1. Characteristics of study streams and their catchments. All sites are in Baltimore County, USA. Data are from Groffman et al. (2004). NA = data not available.

Stream (lat, long)	Predominant land use	Catchment area (ha)	% land use Forested	Residential	Agriculture	% catchment imperviousness
Gwynns Falls at Glyndon (39°28′18″N, 76°49′02″W)	Suburban	81	4	47	0	22
Pond Branch (39°28′49″N, 76°41′16″W)	Forested	32.3	100	0	0	0
Baisman Run (39°28′45″N, 76°40′42″W)	Suburban/forested	381	65	34	1	1
Minebank Run (39°23′34″N, 76°33′23″W)	Suburban	780	17	81	2	NA

and N along hydrologic flowpaths (Fisher et al. 1998, Kemp and Dodds 2002b). Structures included **gravel bars** (intermittently submerged coarse inorganic sediments), **vegetated gravel bars** (gravel bars containing herbaceous vegetation), **mucky gravel bars** (intermittently submerged fine and/or organic sediments), **organic debris dams** (accumulated fresh and decomposed organic matter in the stream channel), **pools** (quiescent areas in the main channel), and **riffles** (areas of rapid, turbulent flow interspersed among pools). Not all geomorphic structures occurred in every study stream (e.g., no organic debris dams occurred in Minebank Run).

We collected sediment samples from within each structure at 2 sites (≥5 m apart) per stream. We took sediments from 3 to 5 locations within each geomorphic structure with a hand trowel and composited all material into one sample bag in the field. When necessary, we excavated sediments to the minimum depth necessary (≤20 cm) to ensure all samples were saturated with stream water.

We collected all samples 1 July 2002 and transported them in zip-lock bags on ice to the laboratory, where they were refrigerated until analyzed (<2 wk). There, we sieved samples (6-mm mesh) to separate large rocks, sticks, and other debris from sediment. We measured % organic matter content (% OM) of sediment by loss on ignition (Felmer et al. 1998), burning samples at 550°C for 1 h. We measured denitrification potential using the denitrification enzyme activity (DEA) assay of Smith and Tiedje (1979), as described by Groffman et al. (1999). Briefly, we amended sieved sediments with NO_3^-, dextrose, chloramphenicol, and acetylene, and incubated them in sealed flasks under anaerobic conditions for 90 min. We took samples from the air space of flasks at 30 and 90 min, stored them in evacuated glass tubes, and then analyzed them for N_2O by electron capture gas chromatography.

We quantified potential net N mineralization and nitrification, and microbial respiration by measuring inorganic N and CO_2 production in 10-d incubations. We quantified microbial respiration by measuring the amount of CO_2 evolved, and potential net N mineralization and nitrification from accumulation of NH_4^+ + NO_3^-, and NO_3^- alone, over the incubation. We measured CO_2 by thermal conductivity gas chromatography (Holland et al. 1999), whereas we measured NH_4^+ and NO_3^- colorometrically with a flow-injection analyzer (APHA 1981).

We evaluated differences among streams and structures using 1-way ANOVA, or its nonparametric equivalent (Kruskal–Wallace test) when data were nonnormal and/or sample sizes were unequal (SAS 1988, release 6.03, SAS Institute, Cary, North Carolina). We examined relationships between denitrification, mineralization, nitrification, respiration, organic content, and streamwater NO_3^- with parametric (Pearson) and nonparametric (Spearman) correlation analyses (SAS 1988).

Results

Denitrification potential was highest ($p < 0.05$) in sediment within organic debris dams (Table 2, Fig. 1A). Sediments in mucky and vegetated gravel bars did not support as much denitrification as would be expected given their relatively high % OM (Fig. 1B) and microbial respiration (Table 2). In contrast, sediments from mineral gravel bars, pools, and riffles showed relatively low % OM and denitrification potential (Table 2).

There was significant among-stream variation in denitrification potential for sediment in organic debris dams (Table 2). Debris dams in the forested reference stream, Pond Branch, showed lower ($p < 0.05$) denitrification potential than debris dams in the suburban streams Baisman Run and Glyndon (Fig. 2A), even though % OM of debris dams did not differ among the 3 streams (Fig. 2B). There was a strong correlation between denitrification potential and streamwater NO_3^- concentration ($r = 0.98$, $p < 0.001$), suggesting that the high denitrification potential of debris dams in Baisman Run and Glyndon may be related to their exposure to relatively high NO_3^- concentrations (Fig. 2C). Internal production of NO_3^- from nitrification was not stimulated by high streamwater NO_3^- concentrations (Fig. 2C cf. 2D).

In contrast to debris dams, there were no differences in denitrification potential in pool and riffle sediments among streams (Fig. 3A, B), and there was no difference in denitrification potential (Fig. 3A) or potential net nitrification (Fig. 4A) between pools in restored vs unrestored reaches of Minebank Run. Pool ($p < 0.07$; Fig. 4A) and riffle ($p < 0.004$; Fig. 4B) sediments from the unrestored reach of Minebank Run had significantly higher rates of potential net nitrification than sediments from the other study streams.

Discussion

The ''urban stream syndrome'' predicts that streams in urban catchments will have a flashier hydrograph, elevated concentrations of streamwater nutrients, altered channel morphology and stability, and reduced biotic richness compared to streams in forested catchments (Paul and Meyer 2001, Meyer et al. 2005, Walsh et al. 2005b). Our results suggest that this syndrome also influences the capacity of stream geomorphic structures to function as sources and sinks for inorganic N in complex ways. Hydrologic changes associated with urbanization, especially high storm flows, may hinder development and maintenance of organic-rich, denitrifying debris dams, but chemical changes associated with urbanization, especially high streamwater NO_3^- concentrations, appear to induce a denitrification response in those organic-rich structures remaining in the system.

Organic content and denitrification

As expected, structures with high % OM, such as debris dams, showed higher denitrification potential compared with organic-poor structures such as gravel bars, pools, and riffles. Denitrification is an anaerobic, heterotrophic process, and debris dams provide C through decomposition. High microbial respiration rates in organic-rich debris dams contribute to the formation of an anaerobic environment through O_2 consumption (Bernhardt and Likens 2002). Debris dams thus have the potential to function as ''hot spots'' of denitrification (McClain et al. 2003) in urban streams. Factors regulating formation and retention of debris dams in urban streams (see below), therefore, may be of great interest in managing NO_3^--loading problems in urban catchments.

In addition to debris dams, vegetated and organic-rich, mucky gravel bars had high % OM relative to gravel bars, pools, and riffles. However, unlike debris dams, these structures did not support high denitrification potential. It is possible that OM in gravel bars was more decomposed and less labile and, therefore, less able to support denitrification and general O_2-consuming heterotrophs (Paul and Clark 1996).

Streamwater NO_3^- and denitrification

Denitrification potential in organic debris dams appeared to increase in response to high streamwater NO_3^- concentrations. Debris dams in the forest reference stream, which had low NO_3^- concentrations, supported significantly less denitrification than debris dams in the 2 suburban streams with higher NO_3^- concentra-

TABLE 2. Mean (SE) % organic matter and microbial process variables in sediments within geomorphic structures from 4 streams in the Baltimore (USA) metropolitan area. $n = 2$ replicate structures/stream.

Stream	Geomorphic structure	Organic matter (%)	Denitrification potential (μg N kg^{-1} h^{-1})	Potential net mineralization (mg N kg^{-1} d^{-1})	Potential net nitrification (mg N kg^{-1} d^{-1})	Microbial respiration (mg C kg^{-1} d^{-1})
Pond Branch	Debris dam	14 (4.0)	185 (31)	−2.30 (1.40)	0.05 (0.04)	55 (5.0)
	Pools	1.5 (0.5)	48 (33)	−0.01 (0.04)	0.03 (0.01)	5.8 (0.3)
	Riffles	0.9 (0.0)	15 (9)	0.03 (0.18)	0.13 (0.08)	4.7 (0.7)
	Gravel bar (mucky)	13 (6.0)	402 (107)	−2.50 (0.70)	0.04 (0.01)	29 (10.0)
	Gravel bar	1.0 (0.1)	8.1 (6)	−0.03 (0.03)	0.07 (0.03)	3.1 (0.6)
Baisman Run	Debris dam	26 (6.0)	1604 (76)	−2.70 (1.50)	0.05 (0.05)	68 (0.5)
	Pools	0.9 (0.3)	36 (30)	0.19 (0.08)	0.08 (0.04)	4.1 (0.7)
	Riffles	0.7 (0.1)	18 (7)	0.25 (0.18)	0.16 (0.05)	3.5 (0.2)
	Gravel bar	0.8 (0.2)	21 (15)	0.24 (0.06)	0.16 (0.04)	2.7 (0.9)
	Gravel bar (vegetated)	4.9 (4.0)	65 (60)	0.07 (0.31)	0.25 (0.23)	6.9 (4.3)
Glyndon	Debris dams	17 (4.0)	4955 (2460)	−3.00 (2.20)	1.10 (0.90)	46 (8.0)
	Pools	2.7 (0.5)	219 (216)	0.04 (0.04)	0.11 (0.06)	8.9 (4.5)
	Riffles	2.2 (0.6)	73 (69)	−0.2 (0.02)	−0.01 (0.03)	9.4 (0.7)
Minebank Run (unrestored)	Pools	1.1 (0.1)	21 (15)	1.10 (0.50)	1.40 (0.60)	8.8 (3.4)
	Riffles	2.1 (0.1)	7.6 (7)	0.50 (0.10)	0.70 (0.10)	6.8 (0.6)
	Gravel bar	1.3 (0.1)	16 (15)	0.20 (0.03)	0.20 (0.04)	3.8 (2.4)
	Gravel bar (vegetated)	1.2 (0.1)	45 (22)	−0.03 (0.04)	0.17 (0.10)	11 (0.9)
Minebank Run (restored)	Pools	1.4 (0.07)	7.9 (5)	0.40 (0.30)	0.40 (0.20)	3.5 (0.8)
	Gravel bar	1.9 (0.4)	2.6 (1)	0.14 (0.03)	0.22 (0.16)	2.7 (0.1)
	Gravel bar (vegetated)	3.0 (0.4)	7.6 (6)	−0.17 (0.11)	0.02 (0.02)	6.5 (0.4)

tions. Denitrification is frequently NO_3^--limited, and microbial activity is likely to be limited by fewer electron acceptors in anaerobic centers of debris dams (Holmes et al. 1996, Hedin et al. 1998, Thompson et al. 2000, Martin et al. 2001, Kemp and Dodds 2002b). Thus, a significant increase in denitrification potential in response to high NO_3^- concentrations was not surprising. Our results suggest that denitrification within organic debris dams may provide an important negative feedback function to high NO_3^- concentrations commonly observed in the urban stream syndrome.

It is important to note that high streamwater NO_3^- concentrations did not increase potential net nitrification rates in debris dams. This result was unexpected because NO_3^- in stream water can be immobilized and then later remineralized and nitrified (Bernhardt and Likens 2002). The fact that denitrification potential was stimulated by high streamwater NO_3^-, whereas nitrification was not, suggests that exposure of debris dams to high streamwater NO_3^- concentrations increases sink more than source processes. This result is important in a water-quality context because the increase in denitrification reduces streamwater NO_3^- levels. However, these patterns could vary with stream conditions, such as when debris dams dry out, which could cause nitrification (an aerobic process) of immobilized N to increase more than denitrification.

Importance of geomorphic features with low organic content

Denitrification potential in pool and riffle sediments was much lower than in debris dams, as would be expected from the low % OM within these structures relative to debris dams. However, although denitrification rates were low in pools and riffles, denitrification in these structures may be important as a sink for NO_3^- because of the high areal extent of pools and riffles compared with debris dams, especially in urban streams. Moreover, residence time of stream water in pools and riffles can be long (days to weeks vs minutes and hours in debris dams;

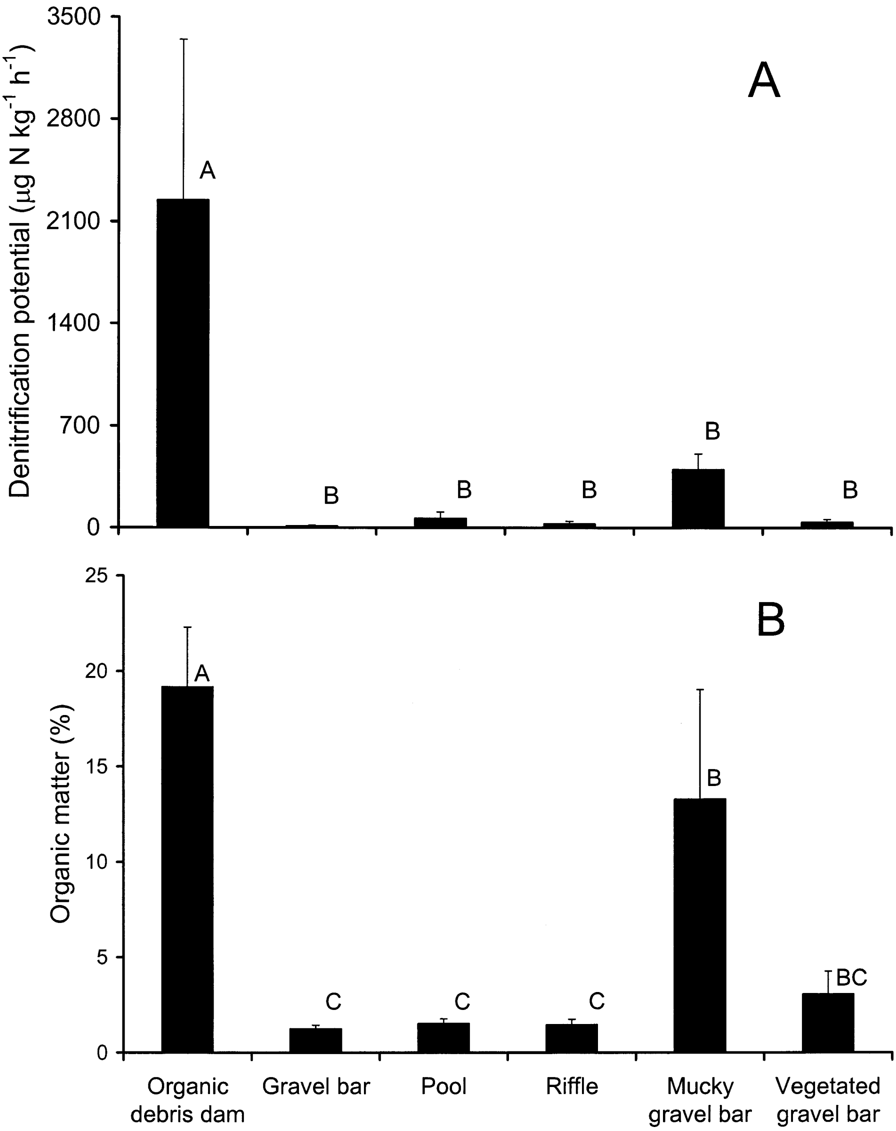

FIG. 1. Mean (+1 SE) denitrification potential (A) and % organic matter (B) of stream sediments sampled from geomorphic structures in 4 streams in the Baltimore metropolitan area, summer 2002. Different letters above bars indicate significant differences at $p < 0.05$ (1-way ANOVA and Duncan's Multiple-Range test). n ranged from 2 to 8.

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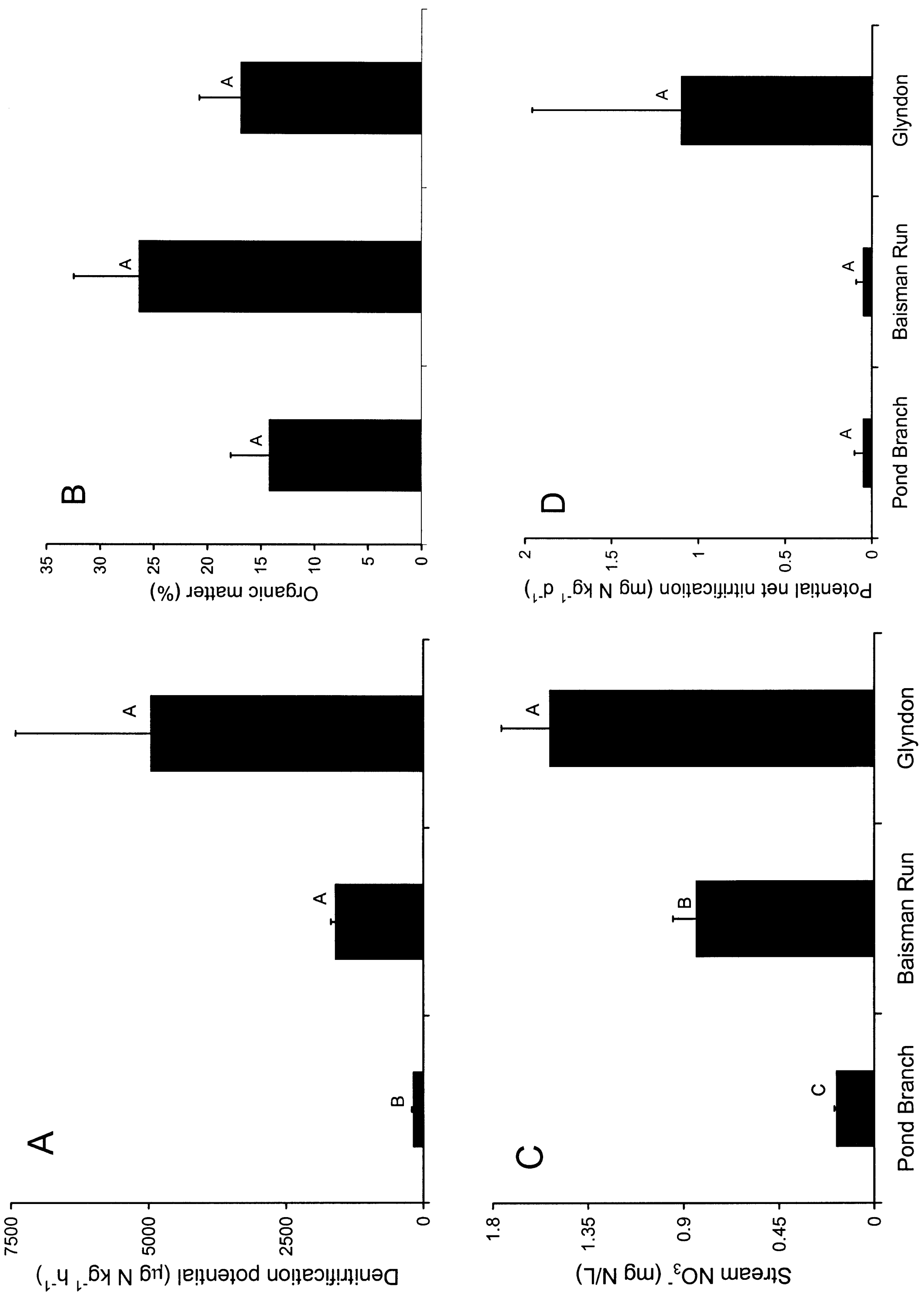
FIG. 2. Mean (+1 SE) denitrification potential (A), % organic matter (B), streamwater NO_3^- concentrations (C), and potential net nitrification (D) associated with sediment from debris dams in 3 streams in the Baltimore metropolitan area, summer 2002. Streamwater NO_3^- concentrations were from weekly samples in June and July 2002 (from Groffman et al. 2004). Debris samples were from 1 July 2002. Different letters above bars indicate significant differences at $p < 0.05$ (1-way ANOVA and Duncan's Multiple-Range test). $n = 3$ for A, B, and C, $n = 11$ for D.


A
B
C
D
Denitrification potential (μg N kg-1 h-1)
Organic matter (%)
Stream NO3- (mg N/L)
Potential net nitrification (mg N kg-1 d-1)
Pond Branch
Baisman Run
Glyndon
0
2500
5000
7500
0
5
10
15
20
25
30
35
0
0.45
0.9
1.35
1.8
0
0.5
1
1.5
2

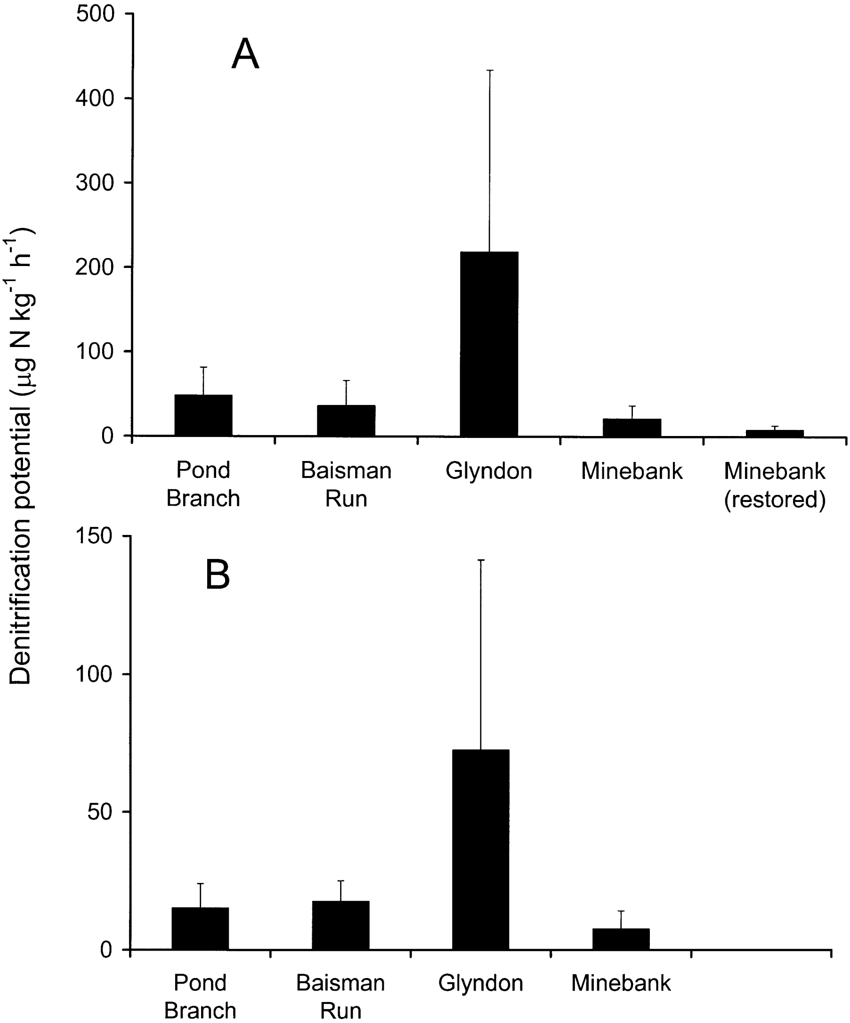


FIG. 3. Mean (+1 SE) denitrification potential in sediments from pools (A) and riffles (B) in 4 streams in the Baltimore metropolitan area, summer 2002. $n = 3$.

Hall et al. 2002). Thus, low denitrification rates over large areas and long intervals could remove significant amounts of NO_3^- (Triska et al. 1993, Grimaldi and Chaplot 2000, Hall et al. 2002). We are measuring in situ denitrification rates using more sensitive methods in other research at Minebank Run (Addy et al. 2002), including quantifying water residence time (Mayer et al. 2004), to provide a more comprehensive evaluation of the importance of pools and riffles to stream NO_3^- dynamics.

Surprisingly, potential net nitrification was not higher in pools and riffles within high-NO_3^- streams. However, the low % OM in these structures appears to make it unlikely for significant immobilization, remineralization, and nitrification to occur. These results were consistent with those observed from the debris dams, also suggesting that high streamwater NO_3^- concentrations increase sink processes more than source processes in geomorphic structures.

Effects of restoration on streamwater NO_3^-

We were able to compare pools in the restored and unrestored reaches of Minebank Run as a first step in evaluating effects of geomorphic restoration on streamwater NO_3^- dynam-

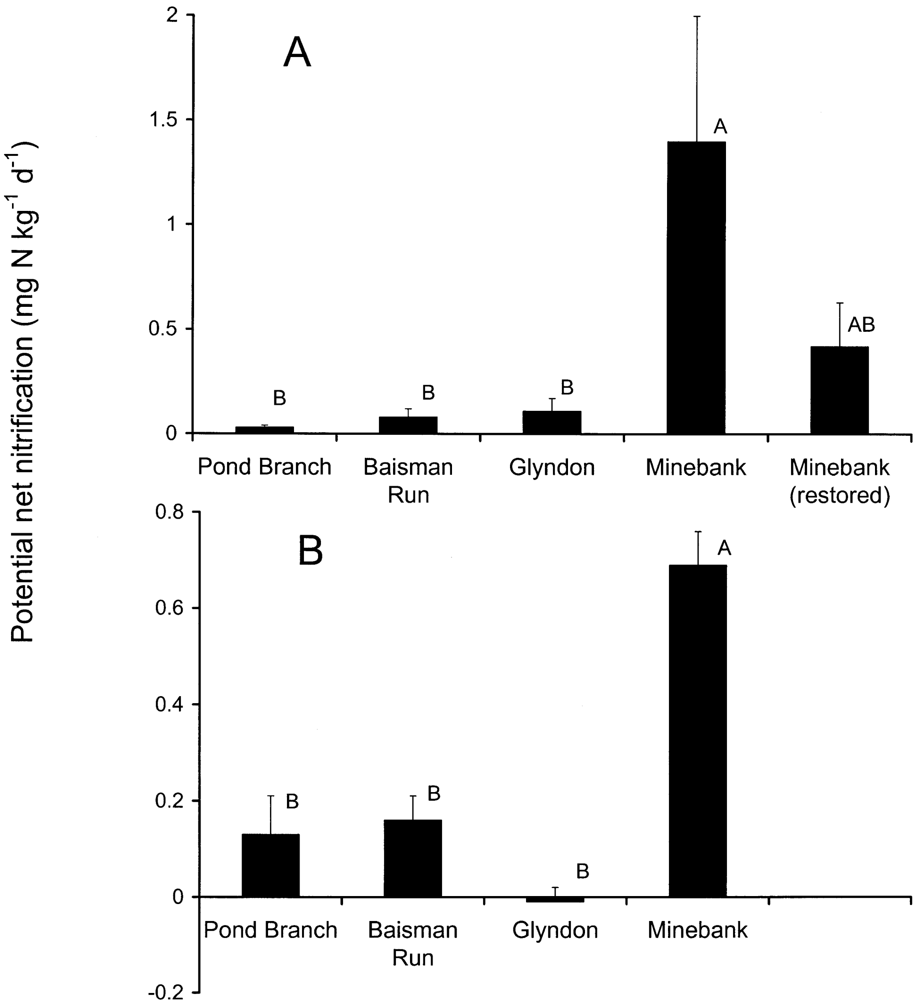


FIG. 4. Mean (+1 SE) potential net nitrification in pools (A) and riffles (B) in 4 streams in the Baltimore metropolitan area, summer 2002. Different letters above bars indicate significant differences at $p < 0.05$ (1-way ANOVA and Duncan's Multiple-Range test). $n = 3$.

ics. There was no difference in denitrification potential in sediments from pools between restored and unrestored reaches of Minebank Run, but potential net nitrification rates were lower in the restored than unrestored reach, and were similar to rates in more-forested and less-degraded streams (Pond Branch, Baisman Run). The greatest degree of difference in nitrification rates between restored and unrestored reaches occurred in pools: nitrification rates in the unrestored reach of Minebank Run were the highest measured, and were significantly higher than in pools in the restored reach. Although preliminary, these results suggest that geomorphic restoration may also provide a water-quality benefit by reducing instream nitrification. The mechanism for this effect would be increased production and retention of C in the stream/riparian ecosystem, which would promote increased immobilization of NH_4^+, thereby reducing the amount available to nitrifiers (Bernhardt et al. 2002, Strauss et al. 2002).

Our results suggest that restoration efforts to reduce NO_3^- concentrations should focus on establishment and retention of organic debris dams. This approach is challenging in urban streams because of high storm flows and flashiness (Booth 2005), and associated high potential to displace organic debris downstream (Paul and Meyer 2001, Meyer et al. 2005, Walsh et al. 2005a). Aggressive stormwater controls in urban catchments, which are often implemented to improve stream geomorphic stability and biological habitat, also could benefit water quality if they foster retention of debris dams. It is interesting to note that the Glyndon Stream had organic debris dams, despite being an urban catchment with >20% imperviousness (Table 1). Visual observation suggests that debris dams persisted in this stream because of several factors, including slope, soils and landuse history, and the presence of small culverts—several idiosyncratic factors that may have acted to mitigate high stormflows and reduce rates of channel incision in this stream. Understanding factors regulating the establishment, maintenance, and function of debris dams in urban streams should thus be a priority for research (Booth 2005).

Implications for future research

A more thorough understanding of N processing in geomorphic structures of urban streams will require several other types of studies beyond those we describe. Two key considerations are 1) a closer coupling of N processing data with hydrologic measurements, and 2) models that quantify amounts and residence times of water moving through different structures. There is also a need to evaluate several types of stream structures more closely, such as pools and riffles with low rates of N processing but with important hydrologic roles in the ecosystem. Analysis of these structures will require a focus on production, storage, and processing of benthic OM as a source of C to support microbial activity (Meyer et al. 2005, see also Harbott and Grace 2005). Future research also should consider dissolved organic N in addition to inorganic N because debris dams and other stream structures may have high potential to convert inorganic N to labile dissolved organic N that may be remineralized downstream (Kaushal and Lewis 2003). Our results suggest that such studies will be worthwhile and important. We have shown that urban streams support structures with significant amounts of N processing, including denitrification, and that this processing responds to streamwater NO_3^- concentrations and geomorphic restoration. Our results also suggest that instream processing should be an important component of efforts to evaluate and manage sources and sinks of N in urban catchments.

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