DIFFERENTIAL CONTROLS OF DENITRIFICATION IN RIPARIAN ZONES AND STREAMS ALONG AN URBAN TO EXURBAN GRADIENT

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Abstract. The large increase in impervious surface cover due to urbanization leads to "flashier" storm flows and increased runoff. This altered hydrology causes channel incision in urban stream channels and lower water tables in the riparian (next to the stream) zone. In turn, these physical changes alter many stream processes, including denitrification. Denitrification is the anaerobic microbial process that transforms nitrate (NO_3^-) to N_2 gas. It is particularly important, as it is one of the primary sinks of nitrogen, and excess nitrogen loading can lead to eutrophication and hypoxia in coastal areas. We might expect there to be more sources of nitrogen from exurban areas than urban areas, as exurban land use is often agricultural, with substantial fertilizer runoff, and houses in these areas are on septic tanks, which are another large nitrogen source. Depending on the extent of these nitrogen sources, and on the availability of carbon, denitrification will either be carbon or nitrogen limited. This study, therefore, sought to determine if denitrification in riparian zones and streams was limited by carbon or nitrogen and whether these limitations varied over an urban to exurban gradient. Denitrification potential and a suite of related variables (microbial biomass carbon and nitrogen content, potential net nitrogen mineralization and nitrification, microbial respiration, inorganic nitrogen pools) were measured in forested and herbaceous riparian soils and stream sediments from debris dams and pools in four different watersheds (urban, suburban, exurban, and forested reference) in and around Baltimore, MD. Denitrification potential was highest in herbaceous riparian soils and lowest in pool sediments. In general, we observed highest denitrification rates in the exurban habitats, while the other watersheds did not differ. Finally, denitrification potential was carbon-limited in all exurban habitats, where rates were significantly higher when carbon was added but not when nitrogen was added. These data suggest that despite the large nitrogen loading from the exurban watershed, some of the load is effectively being denitrified. Further, these results show that stream restoration efforts should focus on bringing more carbon into these systems, which should result in even higher denitrification rates.

INTRODUCTION

The consequences of excess nitrogen (N) loading to ecosystems can be detrimental and can lead to eutrophication in adjacent coastal waters and estuaries (Carpenter et al., 1998), acidification of freshwater systems (Driscoll et al., 1987), contamination of drinking water (US EPA, 1990), N saturation in forests (Aber et al., 1989), and shifts in plant community composition (Tilman, 1984). In efforts to minimize such effects, it is necessary to consider both N sources and sinks. The primary anthropogenic sources of N are fertilizer, sewage, and atmospheric deposition (Carpenter et al., 1998). N sinks include assimilation, storage in sediments, and denitrification (Lowrance et al., 1997; Seitzinger et al., 2006).

Denitrification, the anaerobic microbial process that consumes nitrate (NO_3^-) and releases N_2 gas back to the atmosphere, is a preferred sink because it removes NO_3^- from the system completely, as opposed to immobilizing it temporarily. This process only occurs under specific conditions, i.e. where there is sufficient NO_3^- or nitrite (NO_2^-), low oxygen concentrations, and labile carbon (C) (Seitzinger et al., 2006). Like many biogeochemical processes, denitrification often occurs within hotspots, small areas

where rates are elevated (McClain et al., 2003). Riparian zones and stream sediments are commonly considered hotspots of denitrification (Vidon et al., 2010; McClain et al., 2003); therefore, developing a greater understanding of denitrification in these systems is essential to understanding N processing in ecosystems and landscapes.

Urbanization has greatly impacted riparian zone and stream ecosystems and their ability to process and retain N. In particular, reduced upland infiltration and flashy storm flows due to higher impervious surface cover results in the geomorphic and hydrologic alteration of urban ecosystems (Walsh et al., 2005). As a result, ecological structure and function is often changed in urban streams and riparian zones. Walsh et al. (2005) coined the phrase "urban stream syndrome" to describe characteristics of urban streams, such as channel incision, high peak flows, fewer geomorphic features, and high stream N concentrations. In addition to high N concentrations, the modified structure of stream channels and riparian zones may result in reduced N retention in these systems. Consequently, there is great interest in understanding N cycling in urban streams and riparian zones, particularly those which feed into coastal waters that are susceptible to eutrophication (NRC, 2000).

In riparian zones, the potential for denitrification is typically highest in subsurface soils, where organic C is available (Gold et al., 2001; Hedin et al., 1998). However, incised stream channels and reduced upland infiltration in urban watersheds (Wolman, 1967; Henshaw and Booth, 2000) can lead to hydrologic drought in urban riparian area, reducing groundwater table levels near urban streams. When the water table is low, groundwater will not interact with the surface horizons with the highest denitrification potential (Groffman et al., 2002). Despite low water tables, riparian zones and streams can maintain high denitrification rates in urban area due to higher NO_3^- concentrations that comparatively pristine land uses (Mulholland et al., 2008).

In streams, geomorphic features with high organic matter (OM), such as organic debris dams, can be hotspots for denitrification (Groffman et al., 2005). However, debris dams are frequently displaced in urban streams due to high storm flow. Where debris dams are maintained, however, the high NO_3^- concentrations in urban streams can stimulate denitrification, resulting in higher rates than in dams in non-urban streams (Hale and Groffman, 2006; Groffman et al., 2005). In addition to debris dams, sediments in stream pools may also function as denitrification hotspots. While denitrification rates in pool sediments are typically lower than those in debris dams, pool sediments cover much more stream area, particularly in urban streams (Groffman et al., 2005, Harrison et al., 2012). Further, water residence time is much longer in pools (days to weeks) compared to debris dams (minutes to hours; Hall et al., 2002). Extended residence time leads to higher OM accumulation, which should support anaerobic conditions and microbial activity (Kemp and Dodds, 2001). Therefore, low but significant denitrification rates in urban pool sediments over long intervals may result in considerable amounts of NO_3^- removal (Triska et al., 1993; Hall et al., 2002).

In this study, we examined both riparian zones and stream sediments in urban, suburban, and exurban ecosystems to assess their ability to function as denitrification hotspots. While much recent research has focused on urban and suburban areas, exurban streams and riparian zones have receives less attention (Paul and Meyer, 2001). Exurban land (less than one housing unit per hectare) occupies five times the area of urban land uses (Theobald, 2001), and is quite dynamic, as it intersects urban and rural land uses, and contains both protected and human-dominated areas (Hansen et al., 2002; Theobald, 2004). Even so, exurban areas have more recently been recognized as perhaps the most understudied landscape along the urban-rural gradient (Theobald, 2004). As suburban and exurban areas are rapidly expanding, often faster than urban zones, a complete understanding of the effects of urban land use change requires consideration of exurban areas (Pickett et al., 2011).

Both C and N can limit rates of denitrification, and such limitation may vary over an urban to exurban gradient. C is a key regulator of denitrification, as it provides the energy source for heterotrophic denitrifiers. C also drives other microbial activity that both immobilizes inorganic N, and consumes O_2, providing the anaerobic conditions necessary for denitrification. Groffman et al. (2002) showed that OM was lower in urban and suburban riparian soils compared to a forested reference site. This was likely due to a lower water table, which leads to the consumption of OM in the larger aerobic zone. Additionally, exurban land use is predominantly agricultural, which is often associated with depleted levels of C (Parton et al., 1987). Therefore, exurban soils may have low OM as well.

While levels of C may be relatively low in exurban areas, N loading may be particularly high in these areas due to fertilizer inputs from agricultural fields and leaching from septic systems. Kaushal et al. (2011) showed that in urban watersheds, N sources are dominated by atmospheric deposition and wastewater discharge. In suburban watersheds, fertilizer runoff from residential lawns may be an important source. However, N from fertilizers can be retained in lawns, and may contribute insignificant loading (Raciti et al., 2008).

Differential control of denitrification by C and N may underlie variation in stream and riparian zone denitrification performance in urban, suburban and exurban ecosystems. However, as the controls of denitrification vary seasonally, particularly C, N, and groundwater level, it is necessary to consider that denitrification rates and controls may vary over the year. For instance, water tables and NO_3^- concentrations are typically lower in summer due to elevated evapotranspiration and plant uptake (Kellogg et al., 2008). Likewise, the addition of leaf fall in autumn contributes a significant carbon flux into the system, while lower temperatures during this time may reduce microbial activity (Bernhardt et al., 2005).

Understanding these limitations can help enhance denitrification through stream and riparian restoration efforts, and help mitigate N transport to coastal waters. We aimed to determine if N or C controls of denitrification in streams and riparian zones vary along an urban to exurban gradient, and whether these limitations changed seasonally. We sampled two ecotypes (riparian zones and streams), and two habitats within each ecotype. Within the riparian ecotype, we examined (1) forested and (2) herbaceous habitats. Within the stream ecotype we examined (1) debris dams and (2) pools. We samples all habitats in urban, suburban, exurban, and forested reference sites in the Baltimore metropolitan area in both June and November, 2012. These sites are part of the Baltimore Ecosystem Study Long-term Ecological Research (LTER) project (http://www.beslter.org). Our objectives were to: (1) determine if denitrification, and its control by C or N, varied between ecotypes and habitats, (2) assess if and how denitrification and its limitations vary over an urban to exurban gradient, and (3) assess how seasonality affects denitrification and its limitations, and whether these patterns vary over an urban to exurban gradient.

METHODS

We sampled riparian zone soils and stream sediments from urban, suburban, exurban, and forested reference watersheds in the Baltimore metropolitan area in June and November, 2012. Additionally, we completed a riparian and stream assessment in July 2012 which included identification of riparian vegetation, stream substrates, flow types, and habitats, as well as measurements of stream bank width and depth.

Sampling Sites

Glyndon (suburban) is the headwater reach of the Gwynns Falls watershed, which extends from the urban center of Baltimore City through older suburban and rural areas into the Patapsco River, and ultimately to the Chesapeake Bay (Fig. 1). Dead Run (urban) is a tributary to the Gwynns Falls. Cranberry Branch,

which is surrounded by exurban land use, is a recent addition to the BES stream sites, and drains into the Patapsco River basin as well. Pond Branch, a forested reference site for BES, is in the Gunpowder watersheds, adjacent to the Gwynns Falls.

Dead Run is a 3rd-order stream, and its watershed is the most impervious of our sites (Table 1), with highly dense residential and commercial land use, including the Baltimore Beltway. As a result, this stream channel is degraded and exhibits channel incision. Additionally, sections of the channel have been straightened or modified, including reaches that have been lined with concrete or culverted (Harrison et al., 2012). In addition to atmospheric deposition and runoff from impervious surfaces, nutrients enter Dead Run's stream and riparian zones from leaks in sanitary sewer infrastructure (Kaushal et al., 2011). Additionally, as large sections of the stream do not have woody riparian vegetation, there is little organic matter from the watershed that can contribute to debris dam formation.

The Glyndon watershed, although the second most impervious, does not display the expected channel incision of other suburban streams, demonstrated by its comparatively high bank width: depth ratio (Table 2). This watershed is primarily residential and sewered, with 3.9 houses per ha, and 15% lawn area (Law et al., 2004). Despite watershed differences, Glyndon and Dead Run had very similar stream NO_3^- concentrations, approximately 0.5 mg N L^{-1} in the summer and 2 mg N L^{-1} in the fall (Table 1).

Land use in Cranberry Branch is 51% agricultural and only 2.9% urban (USGS Survey, 2006). The primary agricultural activities are row crop and livestock, including three animal feeding operations within the watershed (McCoy, 2001). The stream had high NO_3^- concentrations (>4 mg N L^{-1}) likely due to inputs from fertilizer and manure. Stream channels in this watershed are relatively intact.

The Pond Branch watershed is almost entirely forested, and the stream is a narrows 1st order stream that flows through Oregon Ridge Park in Baltimore County. The only herbaceous area within the watershed is a narrow strip of cleared forest, which is maintained for a power line. In both June and November, stream NO_3^- was below detection (<0.05 mg N L^{-1}).

Sampling

We selected three replicate riparian sites along each stream where there was both herbaceous and forested cover. In both June and November, soils were collected at each site from herbaceous and forested riparian zones. Additionally, we sampled sediments from an organic debris dam and pool in the stream at each of these sites. At each riparian site, we collected three soil cores 5 m from the stream bank with a "bulb corer," sampling 10 cm depths, and combined the replicates in a plastic bag. Only one herbaceous riparian site was sampled at Pond Branch, as the remainder of the riparian zone is forested.

Organic debris dam and pool sediments were collected using a trowel. Debris dams were defined as accumulated fresh and decomposed organic matter in the stream channel, and pools were considered quiescent areas in the main channel, as described by Groffman et al. (2005). In addition to soil and sediment, we collected stream water samples that were filtered (0.45 μm pore size) in the field and stored at 4 °C until analysis (<2 weeks) with a Lachat QuickChem flow injection analyzer for NO_3^-.

We completed a stream and riparian assessment of Cranberry Branch, Glyndon, and Dead Run (Table 2). This protocol was modified from the EPA's stream habitat assessment protocol (Barbour et al., 1999). We recorded substrates, flow types, habitats, wetted width, bankful width, bankful depth, and riparian vegetation. Substrates were determined based on size, and included silt, sand (<2mm), gravel (2mm-1cm), pebble (1-6.4 cm), cobble (6.4-25.6 cm), boulder (>25.6 cm), bedrock, and concrete/riprap. Flow types were described as either pool, riffle, run, or fall. Habitat features included logs, loose woody debris, aquatic vegetation, live root balls, debris dams, muck, leaf packs, and algal mats. We assessed channel

geometry by measuring wetted width, bankful width, and bankful depth. Riparian vegetation was assessed by identifying all woody plants within a 30 x 10 m transect of the stream bank.

Laboratory Analysis

We transported samples on ice to the Cary Institute of Ecosystem Studies in Millbrook, New York where they were stored at 4 °C until analysis (<2 weeks). Soil and sediments were hand sorted and homogenized, and rocks, roots, and other debris was removed.

Soil moisture was measured by drying at 60 °C for 48 h (McInnes et al., 1994), and % organic matter content (%OM) was measured by loss on ignition at 450 °C for 4 h (Nelson and Sommers, 1996). Soil and sediment NO_3^- and NH_4^+ were extracted from soils using $2M$ KCL and analyzed using a flow injection analyzer.

We measured denitrification potential with the short-term anaerobic denitrification enzyme activity (DEA)) assay developed by Smith and Tiedje (1979), as described by Groffman et al. (1999). In this assay, sieved soils are amended with NO_3^-, dextrose, chloramphenicol, and acetylene, and incubated under anaerobic conditions for 90 minutes. We took gas samples at 30 and 90 minutes, and stored them in evacuated glass tubes, prior to analysis for N_2O by electron capture gas chromatography. To assess the factors limiting denitrification, we repeated this assay in the absence of either NO_3^- or dextrose and with both NO_3^- and dextrose omitted.

Microbial biomass C and N content were measured by the chloroform fumigation-incubation method (Jenkinson and Powlson, 1976). Soil and sediment samples were fumigated to kill and lyse microbial cells and subsequently inoculated with fresh soil. Over a 10-day incubation, there is substantial microbial growth in the inoculated soil, due to the readily available substrate produced by fumigation. Following the incubation, flushes of carbon dioxide (CO_2) and $2M$ KCl extractable NO_3^- and NH_4^+ released by the growing cells are assumed to be directly proportional to the amount of microbial C and N in the original sample. CO_2 was measured by thermal conductivity gas chromatography. CO_2 was converted to microbial biomass C using a proportionality constant (0.45).

Rates of potential net N mineralization were calculated as the accumulation of total inorganic N and potential net nitrification as the accumulation of NO_3^- a 10-day incubation of unfumigated soil. Soil respiration was estimated as the accumulation of CO_2 during this incubation.

Statistical Analysis

Watershed, habitat, ecotype, date, and DEA treatment were compared with multiple factor analysis of variance, with interactions. Duncan's multiple range test was used to determine specific differences between watersheds and treatments. We additionally performed parametric (Pearson) and nonparametric (Spearman) correlation analyses. The Statistical Analysis System (SAS Institute; 1988) was used for all analyses.

RESULTS

Seasonal Differences (June vs. November)

In all four DEA treatments, denitrification potential was significantly higher in June compared to November (Table 3). Similarly, in riparian soils only, June denitrification potential rates exceeded those

in November for all four DEA treatments (Fig. 2A). In stream sediments, denitrification potential was higher in June in the $+C$ treatment, but there were no seasonal difference in other treatments (Fig. 2B).

Denitrification in riparian soils appeared to be C-limited (i.e. rates were increased by C but not by N additions) in June and November, but possibly more so in June when rates from the $+C$ treatment equaled those in the $+C+N$ treatment (Fig. 2A). The addition of C to stream sediments did not enhance denitrification potential more than the N addition in June or November. However, sediment denitrification potential from the $+C$ treatment was equivalent to the $+C+N$ treatment in June, suggesting some C-limitation in the summer, and jointly limited by C and N (i.e. rates only increased by C and N additions) in the fall (Fig 2B).

In riparian soils, June microbial biomass C and N exceeded those in November ($p<0.0003$ and $p<0.039$), as did soil NO_3^- concentration ($p<0.0003$). In stream sediments, sediment NO_3^- concentration was significantly higher in June than November ($p<0.042$).

Ecotype Comparison (Riparian vs. Stream)

Denitrification potential was significantly higher in riparian soils than in stream sediments in all but the $+N$ DEA treatment (Fig. 3). Riparian soils were C-limited, while sediments were not. %OM, microbial biomass C and soil/sediment NO_3^- concentration were also significantly higher in riparian soils.

In riparian soils only, denitrification potential was positively correlated with soil NO_3^- concentration ($r^2=0.38$, $p<0.0103$). In contrast, the correlation between denitrification potential and microbial biomass was significant for both soils and sediments ($r^2= 0.38$, $p< 0.0126$ and $r^2=0.77$, $p< 0.0001$). Similarly, riparian soil and stream sediment denitrification potentials from the control and $+C$ DEA treatments were correlated to soil/sediment NO_3^- concentration (soils: $r^2=0.477$, $p<0.0011$ and $r^2=0.52334$, $p<0.0003$; sediments: $r^2=0.74$; $p<0.0001$ and $r^2=0.877$, $p<0.0001$). Additionally, stream sediment denitrification potential from the $+N$ DEA treatment was correlated to C variables (microbial biomass C: $r^2= 0.864$, $p<0.0001$ and sediment respiration: $r^2= 0.85$, $p< 0.0001$) while the $+C$ and reference treatments were not.

Riparian Soils Across Watersheds

Rates of denitrification potential in riparian soils were similar across the four watersheds (Table 4). However, there were watershed differences in the limitation tests, particularly in the $+C$ and reference DEA treatments (Table 4). Riparian soil NO_3^- concentrations differed across watersheds, as did SOM, where the forested reference soils were higher than the urbanized watersheds (Table 5). The exurban, suburban, and urban riparian soil denitrification potentials were C-limited, while the forested reference riparian soils were not nutrient limited (Table 4).

Riparian Habitat Comparison (Forested vs. Herbaceous)

Overall, rates of denitrification potential in forested and herbaceous riparian soils were similar. However, concentrations of soil NO_3^- and NH_4^+ in the herbaceous riparian soils exceeded those of the forested soils ($p< 0.0008$ and $p< 0.0026$). Denitrification potential in the forested riparian soils was positively correlated to soil NO_3^- concentration ($r^2=0.627$, $p<0.001$), while denitrification potential in the herbaceous riparian soils was correlated with microbial biomass C ($r^2=0.572$, $p<0.0105$).

In the $+C$ DEA treatment, denitrification potential in the herbaceous riparian soils was higher than in forested riparian soils ($p< 0.0133$; Fig. 4), although both the forested and herbaceous riparian soils appeared to be C-limited. In the forested riparian soils, denitrification potentials from the $+C$, $+N$, and reference DEA treatments were correlated with soil NO_3^- concentrations ($r^2=0.74$, $p<0.0001$; $r^2=0.441$,

$p<0.0307$ and $r^2=0.787$, $p<0.0001$). These correlations were not significant in the herbaceous riparian soils bu denitrification potential from the $+C$ treatment was correlated with microbial biomass C ($r^2 = 0.461$, $p < 0.469$) in these soils.

In the forested riparian soils, denitrification potential from all DEA treatments except $=N$ was highest in the exurban watershed (Table 6). The exurban, suburban, and forested reference forested riparian soils all showed differences across DEA treatments, although only the exurban forested riparian soils were C-limited. In contrast, denitrification potentials in the suburban and forested reference forested riparian soils were limited by both C and N.

Exurban, urban, and suburban herbaceous riparian soil denitrification potential differed across DEA treatments, and these soils all showed C-limitation. In both the forested and herbaceous riparian soils, microbial biomass C was highest in the forested reference watershed (Table 7). However, only the suburban soils had significantly lower microbial biomass C that the forested reference in the forested soils, while all three urbanized herbaceous riparian soils had lower microbial biomass C than the forested reference herbaceous riparian soils.

Denitrification rates in the urban forested and herbaceous riparian soils were correlated to soil NO_3^- concentration ($r^2=0.82$, $p<0.0438$ and $r^2= 0.95$, $p<0.0043$). In the herbaceous riparian soils, denitrification potential was correlated to microbial biomass C in both the exurban and urban watersheds ($r^2=0.89$, $p<0.175$ and $r^2=0.89$, $p<0.0433$), and to soil respiration in the suburban watershed ($r^2=-0.82$, $p<0.0447$).

Stream Sediments Across Watersheds

There was no significant difference in stream sediment denitrification potential ($+C+N$ DEA treatment) across the four watersheds (Table 8). However, there were differences in the $+C$ and reference (no addition) treatments, where higher rates were found in the urban sediments compared to the suburban and forested reference sediments (Table 8). DEA treatment differences were found in the exurban, suburban, and forested reference watersheds, and showed a C-limitation in exurban sediment denitrification and an N-limitation (i.e. rates are increased by N but not by C additions) in the suburban and forested reference sediments.

Sediment microbial variables differed across watersheds, particularly microbial biomass C, sediment NH_4^+ concentration, potential net N mineralization, and potential net nitrification (Table 9). The forested reference and suburban sediments had higher microbial biomass C and sediment NH_4^+ concentration, while the urban and exurban sediments had higher rates of potential net N mineralization and potential net nitrification. Similarly, sediment %OM was higher in the forested reference watershed than the urban or exurban, but did not differ from suburban sediments (Table 9).

The $+C+N$ and $+N$ treatment sediment denitrification potentials were highly correlated to C variables (microbial biomass C: $r^2=0.77$, $p<0.0001$ and $r^2=0.86$, $p<0.0001$; and sediment respiration: $r^2=0.86$, $p<0.0001$ and $r^2=0.85$ and $p<0.0001$). In comparison, stream sediment denitrification potentials from the reference and $+C$ treatments were highly correlated to sediment NO_3^- concentration ($r^2= 0.74$, $p<0.0001$ and $r^2=0.88$, $p<0.0001$).

Stream Habitat Differences (Debris Dams vs. Pools)

Denitrification potential was significantly higher in debris dam material than in pool sediments (Fig. 5) but the difference was only significant in the $+C+N$ and no addition treatments. Rates in both debris dam and pool sediments were correlated with C variables (microbial biomass C: $r^2=0.82$, $p<0.0001$ and

$r^2=0.78, p<0.0001$; sediment respiration: $r^2=0.86, p<0.0001$ and $r^2=0.85, p<0.0001$). In both debris dam and pool sediments, denitrification potential was higher in the $+C+N$ treatment and the other treatments did not differ ($p<0.0004$ and $p<0.0263$), demonstrating joint C and N limitation.

Denitrification potential from the $+N$ DEA was highly correlated with C variables in both debris dam and pool sediments (microbial biomass: $r^2=0.82, p<0.0001$ and $r^2=0.90, p<0.0001$; sediment respiration: $r^2=0.80, p<0.0001$ and $r^2=0.97, p<0.0001$). Debris dam sediment denitrification potentials from the $+C$ and reference DEA types were positively correlated with sediment NO_3^- concentration ($r^2=0.94, p<0.0001$ and $r^2=0.83, p<0.0001$), but this relationship was not observed in pool sediments.

Debris dam sediment denitrification potentials from the $+C$ and control DEA treatments varied across watersheds (Table 10). In both treatments, rates were higher in urban sediments. In addition, rates in exurban sediments exceed that in suburban and forested sediments in the $+C$ treatment. In pool sediments, only the $+C$ treatment showed watershed differences, with denitrification potential highest in exurban sediments (Table 10).

In the exurban and urban debris dam sediments, denitrification was C-limited ($p<0.0175$ and $p<0.0001$), where potentials from the $+C$ DEA treatment exceeded those from the $+N$ and reference treatments. Contrary to the C-limitations observed in other habitats, in suburban debris dam sediments, the $+C+N$ treatment produced higher denitrification potentials than the $+C$ and reference potentials ($p<0.05$), but was similar to that from the $+N$ DEA treatment. The forested reference sediments were jointly limited by C and N, as the $+C+N$ treatment denitrification potentials exceeded the other treatments, which were all similar ($p<0.0242$).

DEA treatment differences were identified in the exurban and urban pool sediments ($p<0.0242$ and $p<0.0001$). The exurban pool sediments were C-limited, and the $+C$ DEA treatment produced higher ($p<0.05$) rates of denitrification than $+N$ and reference treatments. Neither C nor N limited urban pool sediment denitrification, as the $+C+N$ DEA treatment had the highest denitrification potential, and the limiting DEA treatments did not differ.

Debris dam microbial biomass C and sediment NO_3^- concentration varied across watersheds as well ($p<0.0379$ and $p<0.0001$) (Table 10). The forested reference microbial biomass C surpassed the urbanized watersheds' debris dam sediments, and the exurban debris dams had the lowest microbial biomass C. The highest debris dam sediment NO_3^- concentration was in the urban watershed, the forested reference concentrations were second highest, and the suburban and urban debris dam sediment NO_3^- concentrations were similarly low. Pool sediments did not show any differences in these parameters.

DISCUSSION

Our data show that urban, suburban, and exurban riparian zones and streams can function as denitrification hotspots. We revealed variation in denitrification and its nutrient limitations within ecotypes and habitats, across an urban to exurban land use gradient, and between summer and fall. We found that riparian soil denitrification potential was higher than stream sediments, and that exurban denitrification was often higher than urban and suburban habitats. Denitrification was frequently C-limited in most habitats and in both the summer and fall.

Denitrification between ecotypes and habitats

Our first objective was to examine possible differences in denitrification potential of ecotype, habitat, and C or N limitation. We found riparian soil rates exceeded those in stream sediments. This is likely due to higher soil NO_3^- concentration (on average about 4 μg N g^{-1}) compared to sediment NO_3^- (less than 1 μg N

g^{-1}), as well as higher %OM in riparian soils. We also found riparian soils were C-limited, in contrast to sediments which did not demonstrate a nutrient limitation.

Harrision et al. (2011) suggested that microbial biomass N might be a strong predictor of denitrification potential, as it represents both C and N pools. Consistent with this hypothesis, mean riparian soil microbial biomass N (about 50 μg N g^{-1}) was four times that of stream sediments, while microbial biomass C of riparian soils was not even twofold higher. These data suggest that not only is microbial biomass N a strong predictor of denitrification, but a low ratio of microbial biomass C:N may be associated with the observed C-limitation in riparian soils. This C-limitation was consistent with Groffman and Crawford (2003), who showed that C variables were more important controllers of denitrification in urban riparian soils than N variables.

Similar to previous studies (Bettez and Groffman, 2012; Mayer et al., 2007; Groffman and Crawford, 2003; Addy et al., 1999; Clement et al., 2002; Lowrance et al., 1995; Haycock and Pinay, 1993; Schnabel et al., 1996), denitrification potential was similar in herbaceous and forested riparian soils. The herbaceous soils were more C-limited than forested riparian soils, likely due to the elevated soil NO_3^- concentration in the herbaceous soils.

Higher soil N pools in the herbaceous riparian zones may be due to N additions from fertilizer, as the urban, suburban, and exurban herbaceous riparian zones are lawns. However, even if fertilizer input is minimal, in comparison to forested vegetation, herbaceous biomass has little or no woody material, and is therefore higher in N, with a lower C:N ratio. High N content in herbaceous litter should reflect N content in organic matter and soil N pools, which are higher than forested riparian soils. While denitrification potential from the +C DEA treatment was related to microbial biomass C in herbaceous soils, it was related to soil NO_3^- concentration in the forested soils. These data suggest that despite similar denitrification potentials, there are differential controls of denitrification between the riparian vegetation types.

As expected, we observed higher denitrification potential in debris dams compared to pools, likely due to more labile carbon. This result is consistent with Harrison et al. (2011) and Groffman et al. (2005), and our measurements of debris dam and pool sediment microbial biomass C, sediment NO_3^- concentration, and denitrification potentials are similar to values in Harrison et al. (2011). In contrast to fairly homogenous riparian soil, factors controlling denitrification may be highly variable in stream sediments, and we observed no distinct nutrient limitation in debris dam or pool sediments.

Denitrification across the urban to exurban gradient

Exurban areas have very low-density housing and large swaths of open lawn and agricultural fields. While elevated N loads in urban areas are typically associated with high population density, exurban land use produces even larger N loads (Table 1). However, as exurban watersheds have very low impervious surface cover, exurban streams and riparian zones remain hydrologically connected to the uplands, and streams are minimally degraded. While we expected higher denitrification potentials in the exurban riparian zones due to the high NO_3^- concentrations and maintained hydrologic structure, denitrification potentials did not differ across the urban to exurban gradient. While it has been suggested that NO_3^- concentration is a strong predictor of denitrification (Pina-Ochoa and Alvarez-Cobelas, 2006; Mulholland et al., 2009), the exurban riparian soils may have reached a NO_3^- concentration where denitrification is not N-limited (Roley et al., 2012; Inwood et al., 2005; Wall et al., 2005).

This hypothesis is supported by the C-limitation of exurban riparian denitrification, although the suburban and urban riparian soils were C-limited as well. The forested reference riparian soil denitrification was not C-limited, suggesting that depleted levels of OM and elevated soil NO3- concentrations in the urbanized watersheds may explain the C-limitations.

When riparian soils were divided between forested and herbaceous habitats, differing patterns of C-limitation across the urban to exurban gradient were revealed. In the forested riparian soils, the exurban soils were C-limited and produced higher denitrification potentials than the other watersheds, synchronous with elevated soil NO_3^- concentrations in the exurban forested riparian zones.

In comparison to the observed C-limitation of forested riparian soil denitrification and its relationship to watershed N loads, the urban, suburban, and exurban herbaceous riparian soils were all C-limited. Herbaceous riparian soil NO_3^- concentrations were equal across watersheds, and %OM and microbial biomass C were more likely drivers of the C-limitation in herbaceous soils, as these were highest in the forested reference watersheds, and equivalent in the urbanized watersheds.

Although forested and herbaceous riparian soil denitrification potentials were equivalent, the urban land uses that were C-limited differed, as well as the observed drivers of this limitation. This finding suggests that vegetation cover is a significant control of denitrification nutrient limitation in urbanized watersheds, where the C-limitation of denitrification is controlled by N variables in forested riparian zones and by C variables in herbaceous riparian zones.

In the urban, suburban, and exurban riparian sites, the herbaceous riparian zone land use was residential lawns. Lawn vegetation and management practices may explain some of the C-limitation in these watersheds. The lack of variation in soil NO_3^- concentration across the watersheds may be due to similar NO_3^- inputs from fertilizer applications to the urban, suburban, and exurban lawns. This direct N source to lawn riparian soils may negate the influence of differential N loads from surrounding watersheds.

In addition, lawn management typically includes the removal of woody and leafy litter (Harivandi et al., 2001), which constitutes a significant C export from the system (Kaye et al., 2005) and prevents the accumulation of soil organic matter and soil C pools. These management practices, which may elevate soil N and reduce soil C stocks, as well as the ecological resemblance of lawns across urban land uses, may explain the C-limitation across the three urbanized herbaceous riparian zones. Further, the lack of variation in N and C pools, as well as microbial variables in the lawn riparian zones suggests that the lawn cover vegetation may be a more important control of denitrification compared to the degree of urbanization and associated nutrient loads of the surrounding watershed. In contrast, variation in forested riparian zone denitrification rates and nutrient limitations was more related to the degree of watershed urbanization, revealing that forested riparian soil denitrification potentials may be more influenced by differences along an urban to exurban gradient, compared to lawn riparian zones.

Denitrification potential in stream sediments did not differ across the urban to exurban gradient, and when separated by habitat, both debris dam and pool sediments produced similar denitrification potentials across the four watersheds. Our denitrification potentials of exurban stream sediments from the $+C+N$ and $+C$ DEA treatments are similar to those reported by Roley et al. (2012) from an agricultural stream, however our $+C$ treatment produced lower potentials than that in Roley et al. (2012), suggesting that the exurban stream was more C-limited than the agricultural stream. While it has been documented that pool sediment denitrification potentials are similar across an urban to rural gradient (Groffman et al., 2005), previous studies have found higher rates of denitrification in urban dams compared to forested reference debris dams (Hale and Groffman, 2006; Groffman et al., 2005), which is contrary to our results.

Although denitrification potentials were similar across watersheds in debris dam sediments, there was variation in the nutrient limitations across the watershed transect, where the exurban and urban dams were C-limited. These limitations are possibly explained by elevated NO_3^- concentrations in urban debris dams, and reduced exurban debris dam sediment microbial biomass C, which was the lowest of the

watersheds. Additionally, %OM was lowest in the exurban and urban sediments, which provides further evidence of the observed C-limitation.

While we expected suburban denitrification to function similarly to exurban and urban sediments, we found the suburban debris dam sediment denitrification potential to be N-limited. This suggests that N loads to the suburban stream are minimal and are likely being retained in lawns and riparian zones. In examining the same suburban stream, Hale and Groffman (2006) hypothesized that the culvert size of the stream, plus the storm water controls in the watershed may provide conditions for maintaining geomorphic features and minimal urban stream syndrome, despite urbanization. These site differences may provide an explanation for the N-limitation, as well as other measurements of microbial activity in the suburban stream that were similar to the forested reference stream. Moreover, these results demonstrate that site-specific features, including water table dynamics, geomorphology, geology, and land use history, must be considered in examining riparian and stream denitrification and microbial activity, and ascribing generalizations about riparian and stream functioning to a specific land use type would be imprudent.

Seasonal impact on denitrification and its limitations

Our third objective was to assess how seasonality affects denitrification, its limitations, and whether the temporal variation differs over an urban to exurban gradient. As we only sampled in the summer and fall, and only once in each season, our interpretation of seasonal effects is limited. However, we observed interesting variation in denitrification potential and its controls between seasons, which may have been linked to temporal shifts in C and N flow and other direct and indirect controls of denitrification.

In riparian soils, denitrification potential was higher in June than November. This is likely due to higher microbial biomass C, microbial biomass N, and soil NO_3^- concentration in June. As we hypothesized, riparian denitrification was more C-limited in June compared to November. This was demonstrated by equal rates from the +C DEA and +C+N treatment in June, while the +C DEA treatment potentials in November were lower in comparison. While riparian denitrification potential was still C-limited in November, it is likely that the C input from leaf fall reduced this limitation.

In stream sediments, our data suggested that denitrification was C-limited in the summer, but had no nutrient limitation in the fall. This is consistent with our data demonstrating elevated sediment NO_3^- concentration in June compared to November. There was little seasonal variation of stream sediment microbial variables across watersheds, although the C-limitation of exurban stream sediment denitrification potential was somewhat stronger in June. We did not observe differences in the denitrification potential of stream sediments between June and July, which is surprising as sediment denitrification has been thought to fluctuate across seasons depending on stream temperature (Wall et al., 2005; Jorgenson, 1989).

Conclusions

This study has direct implications for urban stream management and restoration. Our results showed that the controls and regulating factors of denitrification are dynamic, and in order to enhance denitrification hotspots in these systems, restoration efforts should focus on the differential controls of denitrification across habitats, urban land use types, and seasons. For example, while debris dam sediments had higher rates of denitrification potential than pool sediments, they were difficult to find in urban streams. The restoration of urban hydrology, paired with planting woody vegetation in the uplands should promote and maintain debris dams in urban streams. Pool sediments, which cover much more stream area compared to debris dams, also demonstrated good denitrification performance. Therefore, managing for pool formation and maintenance in streams will create denitrification hotspots and may be a more practical strategy for enhancing N retention compared to targeting debris dams.

We observed a C-limitation in urban, suburban, and exurban riparian soil denitrification potentials. This finding suggests that in order to increase denitrification, management practices should aim to elevate soil C levels, resulting in improved water quality and reduced N loading to coastal areas. Higher soil C levels should increase denitrification regardless of habitat, by promoting decomposition and anaerobic conditions. Still, the urban, suburban, and exurban herbaceous riparian soils and the exurban forested riparian soils should be targeted, as our findings showed that denitrification potentials in these habitats were C-limited.

As soil C pools can be difficult to manage in urban riparian zones (Pouyat et al., 2002), restoration projects should include the implementation of engineered artificial structures, such as OM-filled trenches (Schipper et al., 2005) and permeable reactive barriers (Blowes et al., 2000). While conventional stream restoration projects focus on aesthetic and structural repair, the creation of artificial denitrification hotspots should be included in these efforts. Enhancing and artificially creating N sinks may be a more effective approach to nutrient management than attempting to limit nonpoint N sources (Mitsch et al., 2001). This is particularly true across the urban to exurban gradient, where N sources vary substantially within a relatively small land area.

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APPENDIX

TABLE 1. Characteristics of Baltimore metropolitan area watersheds and stream NO_3^- concentration of sampling sites.

Stream (lat,long)	dominant land use	catchment area (ha)	population density (per ha)	% land use			% impervious surface	Stream NO_3^- (mg/L)	
				forested	residential	agricultural		June	November
Pond Branch 39°28'49"N, 76°41'16"W	forested	32.3[a]	0[a]	100[c]	0[c]	0[c]	0[a]	<0.05	<0.05
Dead Run 39°17'45"N, 76°44'38"W	urban	2034[a]	12.6[a]	9[c]	42[c]	3[c]	41[a]	0.45	2.14
Glyndon 39°28'18"N, 76°49'02"W	suburban	81[a]	9.4[a]	10[c]	37[c]	0[c]	32[a]	0.64	2.06
Cranberry Branch 39°35'36"N, 76°58'03"W	exurban	1070[b]	NA	NA	NA	NA	0.6[d]	4.4	4.78

Data from Law et al. (2004)[a], USGS Survey (2006)[b], Kaushal et al. (2011)[c], Homer et al. (2004)[d]

Stream NO3- data was measured in this study.

NA = data not available

TABLE 2. Results of stream and riparian zone assessment of Cranberry Branch, Glyndon, and Dead Run sites.

Stream	Predominant Land Use	Riparian Vegetation	Substrates	Flow Types	Habitats	Wetted width (m)	Bankful Width (m)	Bankful width: depth	other observations	Dominant woody species
Cranberry Branch	exurban	Forested	cobble, gravel, clay, sand	run, pool	leaf pack, large woody debris	2.8	6.2	6.6	restored, exposed matting	Fraxinus pennsylvanica Juglans nigra Lindera sp.
		Herbaceous	cobble, gravel, pebble, boulder	run	log, debris dam, leaf pack, large woody debris	2.1	6.9	6.6	restored, exposed matting, riprap	Acer rubrum Liriodendron tuilipifera Cornus sp.
Glyndon	suburban	Forested	fine silt, cobble, gravel, sand,	run, pool	live root ball, muck, large woody debris, leaf pack	0.9	3.9	8.2	trash and bricks in stream	Acer rubrum Fraxinus pennsylvanica Ulmus americana
		Herbaceous	pebble, cobble, gravel, sand	pool, riffle, run	large woody debris, debris dam	0.9	7.2	10.4	trash in stream	Acer saccharinum Betula nigra Rosa multiflora
Dead Run	urban	Forested	bedrock, pebble, cobble,	pool, riffle	large woody debris, leaf pack, debris dam,	2.8	8.5	4.9	concrete and trash in stream	Rosa multiflora Lindera sp. Ulmus americana
		Herbaceous	cobble, pebble, gravel, sand	run, riffle	leaf pack, large woody debris, debris dam	1.8	4.7	4.9	trash in stream	Acer rubrum Pinus strobus Quercus rubra

TABLE 3. Mean (SE) denitrification potential of riparian soils and stream sediments across DEA treatments in June (n=44) and November (n=46), from four watersheds in the Baltimore metropolitan area (1-way ANOVA).

DEA Treatment	Denitrification potential (ng N g^{-1} hr^{-1})		P
	June	November	
+C+N	901 (127)	534 (93)	0.015
+C	801 (193)	238 (56)	0.003
+N	193 (34)	117 (23)	0.064
reference	143 (29)	56 (11)	0.002

TABLE 4. Mean (SE) denitrification potential of riparian soils across DEA treatments from four watersheds in the Baltimore metropolitan area. Values followed by different letters within a column (lower-case letters) or row (upper-case letters) are significantly different at $p<0.05$ (1-way ANOVA and Duncan's Multiple-Range test). Exurban, suburban, urban n =12. forested reference n=8.

DEA Treatment	Denitrification potential (ng N g^{-1} hr^{-1})			
	Exurban	Suburban	Urban	Forested Reference
+C+N	1200 (271) a A	927 (95) a A	796 (226) a A	628 (124) a A
+C	1675 (408) a A	1088 (130) a B	418 (401) b AB	6 (3) b B
+N	152 (27) b A	180 (26) b A	130 (33) c A	170 (35) b A
reference	273 (78) b A	140 (271) b AB	165 (37) c AB	11 (11) b B

TABLE 5. Mean (SE) percent organic matter and soil NO_3^- concentration of riparian soils from four watersheds in the Baltimore metropolitan area. Values followed by different letters within a column are significantly different at *p<0.05* (1-way ANOVA and Duncan's Multiple-Range test). *n* ranges from 8 to 10.

Watershed	Soil organic matter (%)	Soil NO_3^- (μg N g^{-1})
Exurban	8.1 (0.3) b	8.0 (1.8) a
Suburban	7.1 (0.3) b	2.8 (0.8) bc
Urban	8.0 (0.5) b	4.3 (1.0) b
Forested Reference	13.7 (1.7) a	0.7 (0.1) c

TABLE 6. Mean (SE) denitrification potential (ng N g^{-1} hr^{-1}) of forested and herbaceous riparian soils across DEA treatments from four watersheds in the Baltimore metropolitan area. Values followed by different letters within a column (lower-case letters) or row (upper-case letters) are significantly different at *p<0.05* (1-way ANOVA and Duncan's Multiple-Range test). Forested *n=6*. Exurban, suburban, urban herbaceous *n=6*, forested reference herbaceous *n=2*.

Habitat	Watershed	Denitrification potential (ng N g hr)			
		+C+N	+C	+N	*reference*
Forested	Exurban	1194 (319) a A	1625 (389) a A	161 (52) a B	356 (136) a B
	Suburban	602 (148) b A	241 (101) b B	104 (38) a B	170 (50) ab B
	Urban	583 (169) b A	352 (257) b AB	145 (46) a B	132 (54) b B
	Forested Reference	590 (118) b A	6.3 (2.7) b B	142 (38) a B	15 (13) b B
Herbaceous	Exurban	1206 (471) a AB	1725 (762) a A	144 (22) a B	190 (66) a B
	Suburban	989 (56) a A	595 (228) a B	156 (36) a C	160 (26) ab C
	Urban	1272 (385) a A	1825 (651) a A	214 (47) a B	148 (55) ab B
	Forested Reference	741 (381) a	6.7 (10) a	253 (8.8) a	-0.58 (0.58) b

TABLE 7. Mean (SE) microbial biomass C of forested and herbaceous riparian soils across four watershed in the Baltimore metropolitan area. Values followed by different letters within a column are significantly different at $p<0.05$ (1-way ANOVA and Duncan's Multiple-Range test). Forested $n=3$, herbaceous exurban, suburban, and urban $n=3$, forested reference $n=1$.

Watershed	Microbial Biomass C (ug C g^{-1})	
	Forested	Herbaceous
Exurban	1033 (119) ab	1236 (329) b
Suburban	574 (187) b	743 (134) b
Urban	1208 (291) ab	1093 (190) b
Forested Reference	1515 (297) a	2198 (849) a

TABLE 8. Mean (SE) denitrification potential of stream sediments across DEA treatments from four watersheds in the Baltimore metropolitan area. Values followed by different letters within a column (lower-case letters) or a row (upper-case letters) are significantly different at $p<0.05$ (1-way ANOVA and Duncan's Multiple-Range test). Exurban, suburban, forested reference $n=12$, urban $n=10$.

DEA Treatment	Denitrification potential (ng N g^{-1} hr^{-1})			
	Exurban	Suburban	Urban	Forested Reference
+C+N	332 (99) a A	603 (257) a A	306 (136) a A	820 (283) a A
+C	289 (66) a AB	14 (3.0) b B	377 (325) a A	47 (20) b B
+N	61 (21) b A	176 (75) b A	73 (40) a A	284 (110) b A
reference	44 (16) b AB	16 (3.5) b B	68 (3.5) a A	36 (16) b AB

TABLE 9: Mean (SE) sediment NO_3^-, sediment NH_4^+, sediment percent organic matter, and microbial process variables in sediments from four watersheds in the Baltimore metropolitan area, June and November 2012. Values followed by different letters within a column are significantly different at $p<0.05$ (1-way ANOVA and Duncan's Multiple-Range test). Exurban, suburban, forested reference $n=12$, urban $n=10$.

Watershed	Microbial biomass C (μg C g^{-1})	Sediment NO_3^- (μg N g^{-1})	Sediment NH_4^+ (μg N g^{-1})	Potential net N mineralization (μg N g^{-1} d^{-1})	Potential net nitrification (ug N g^{-1} d^{-1})	Sediment organic matter (%)
Exurban	410 (104) b	0.60 (0.18) a	1.2 (0.33) b	0.02 (0.06) a	0.11 (0.06) ab	2.4 (0.2) b
Suburban	664 (169) ab	0.59 (0.17) a	2.6 (0.81) ab	-0.18 (0.09) ab	0.02 (0.04) b	5.0 (1.3) ab
Urban	419 (161) b	1.2 (0.09) a	0.40 (0.09) b	0.17 (0.05) a	0.17 (0.05) a	2.7 (0.7) b
Forested Reference	1090 (308) a	0.47 (0.06) a	5.0 (2.1) a	-0.27 (0.19) b	.002 (0.003) b	8.2 (2.1) a

TABLE 10. Mean (SE) denitrification potential across DEA treatments, microbial biomass C, and sediment NO_3^- in debris dam and pool sediments in four watersheds in the Baltimore metropolitan area, June and November 2012. Values followed by different letters within a column (lower-case letters) or row (upper-case letters) are significantly different at $p<0.05$ (1-way ANOVA and Duncan's Multiple-Range test). $n=6$, except urban debris dam sediments $n=4$.

| Habitat	Watershed	Denitrification potential (ng N g^{-1} hr^{-1}) DEA Treatment +C+N	+C	+N	reference	Microbial biomass C (μg C g^{-1})	Soil NO_3^- (μg N g^{-1})
Debris Dam	Exurban	464 (163) a A	340 (130) b A	86 (37) a B	71 (29) b B	249 (76) b	0.29 (0.01) c
	Suburban	679 (359) a A	15 (4.0) c B	188 (84) a A	17 (6.4) b B	784 (281) ab	0.40 (0.07) c
	Urban	575 (312) a B	886 (805) a A	144 (95) a C	140 (101) a C	607 (407) ab	2.4 (2.1) a
	Forested Reference	1250 (429) a A	54 (36) c B	346 (92) a B	53 (27) b B	1211 (271) a	0.55 (0.06) b
Pool	Exurban	201 (97) a AB	238 (36) a A	37 (18) a BC	1838 (4.1) a C	571 (178) a	0.91 (0.33) a
	Suburban	526 (400) a A	14 (4.8) b B	165 (133) a B	14 (3.4) a B	544 (201) a	0.79 (0.33) a
	Urban	136 (17) a A	37 (16) b A	26 (5.6) a A	19 (3.5) a A	293 (63) a	0.49 (0.15) a
	Forested Reference	389 (308) a A	40 (22) b A	222 (209) a A	20 (16) a A	969 (582) a	0.39 (0.09) a
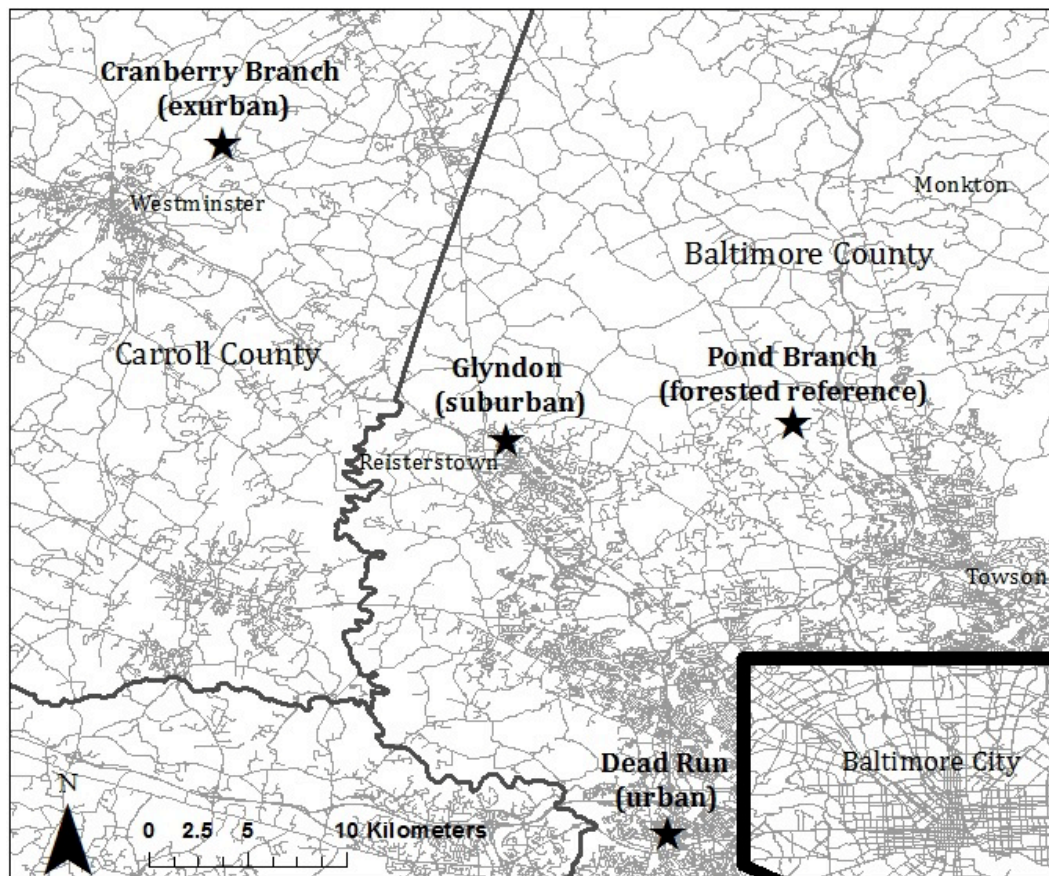
FIGURE 1. Map of Baltimore Metropolitan area, showing the four streams sampled along the urban to exurban gradient.
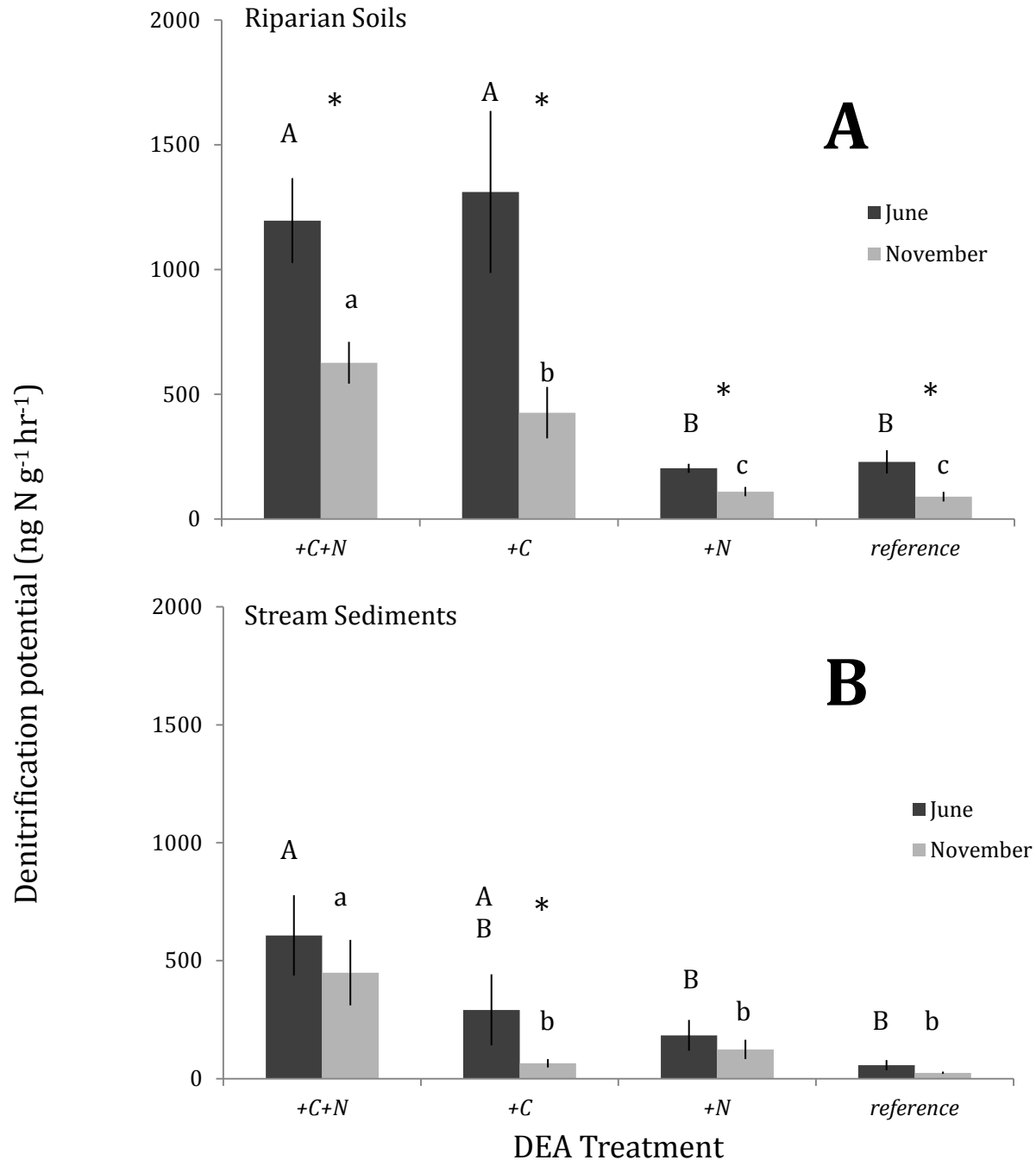
FIGURE 2. Mean (±SE) denitrification potential across DEA treatments in (A) riparian soils and (B) stream sediments in June and November 2012, in the Baltimore metropolitan area. Asterisks indicate significant differences between June and November. Different letters above bars indicate significant differences between DEA treatments at *p < 0.05* (1-way ANOVA and Duncan's Multiple-Range test). Upper-case letters indicate differences in June and lower-case letters indicate differences in November. *n* ranged from 22 to 24.
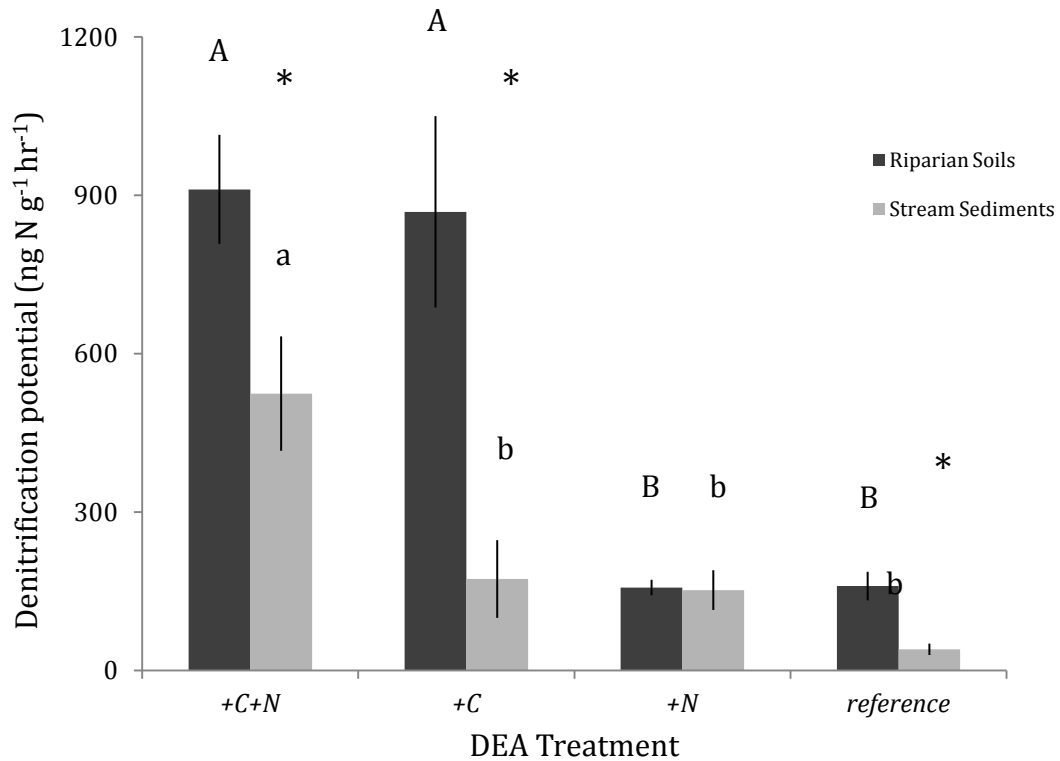
FIGURE 3. Mean (±SE) denitrification potential across DEA treatments in riparian soils (*n*=44) and stream sediments (*n*=46), from four watersheds in the Baltimore metropolitan area, June and November 2012. Riparian habitats are pooled and stream habitats are pooled. Asterisks indicate significant differences between riparian soils and stream sediments. Different letters above bars indicate significant differences between DEA treatments at *p < 0.05* (1-way ANOVA and Duncan's Multiple-Range test). Upper-case letters are differences in riparian soils and lower-case letters are differences in stream sediments.
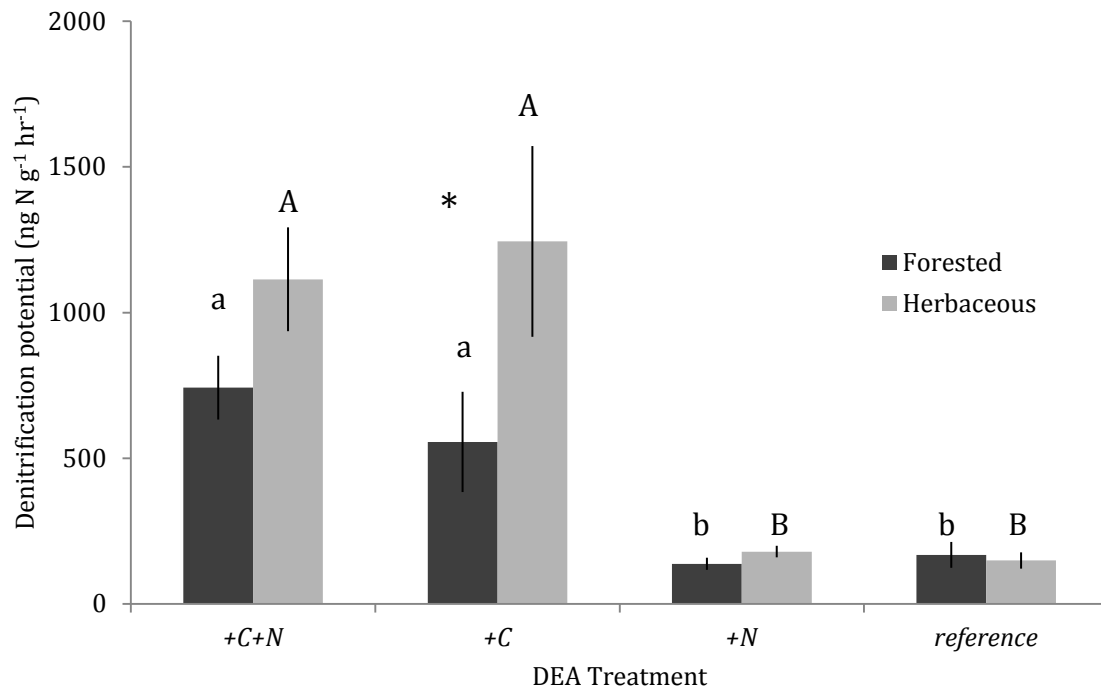
FIGURE 4. Mean (±SE) denitrification potential across DEA treatments of forested (*n*=24) and herbaceous (*n*=20) riparian soils from four watersheds in the Baltimore metropolitan area, June and November 2012. Asterisks indicate significant differences between forested and herbaceous riparian soils. Different letters above bars indicate significant differences between DEA treatments at *p < 0.05* (1-way ANOVA and Duncan's Multiple-Range test). Upper-case letters are differences in herbaceous riparian soils and lower-case letters are differences in forested riparian soils.
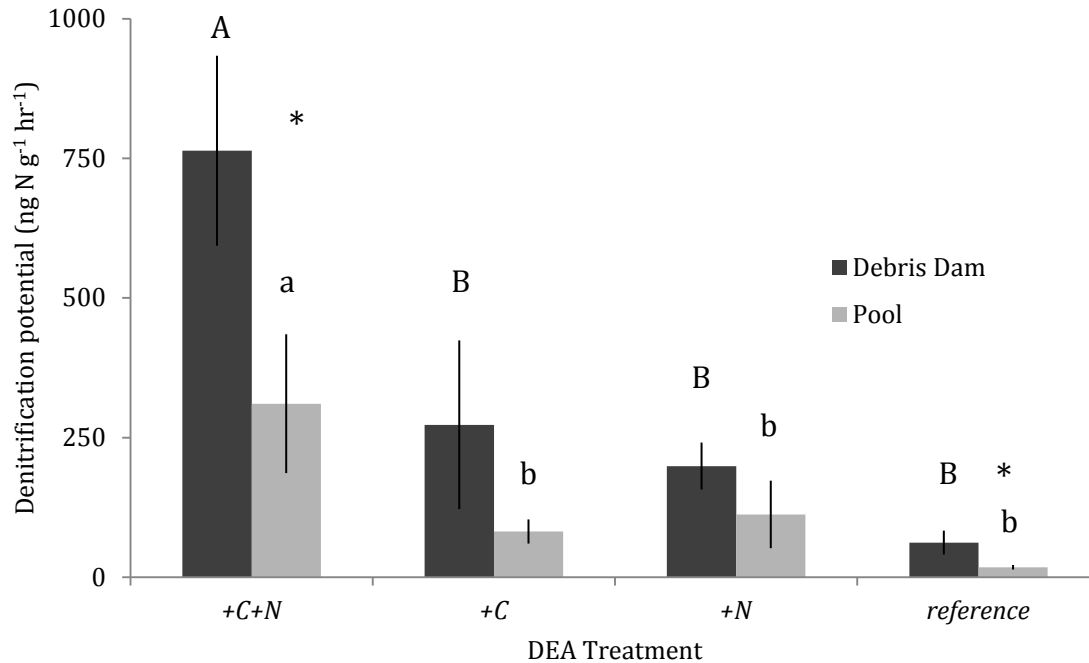
FIGURE 5. Mean (±SE) denitrification potential across DEA treatments of debris dam (*n*=22) and pool (*n*=24) stream sediments from four watersheds in the Baltimore metropolitan area, June and November 2012. Asterisks indicate significant differences between debris dam and pool sediments. Different letters above bars indicate significant differences between DEA treatments at *p < 0.05* (1-way ANOVA and Duncan's Multiple-Range test). Upper-case letters are differences in debris dam sediments and lower-case letters are differences in pool sediments.