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Denitrification Potential in Stormwater Control Structures and Natural Riparian Zones in an Urban Landscape

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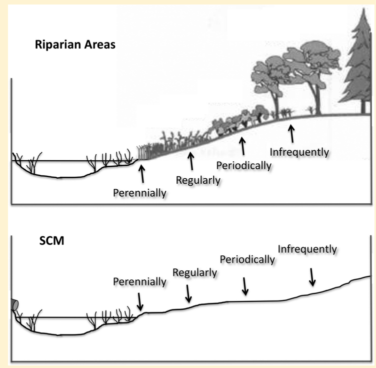
Ⓢ *Supporting Information*

ABSTRACT: Humans have significantly altered urban landscapes, creating impervious surfaces, and changing drainage patterns that increase volume and velocity as well as frequency and timing of runoff following precipitation events. These changes in runoff have impaired streams and riparian areas that previously reduced watershed nitrogen (N) flux through uptake and denitrification. Stormwater control measures (SCM) are used most frequently to mitigate these hydrologic impacts. While SCM control runoff, their ability to remove N compared to natural riparian areas is not well-known. In this study we compared potential denitrification [as denitrification enzyme activity (DEA)] in five types of SCM (wet ponds, dry detention ponds, dry extended detention, infiltration basin, and filtering practices) and forested and herbaceous riparian areas in Baltimore, MD. DEA was higher in SCM (1.2 mg N kg^{-1} hr^{-1}) than in riparian areas (0.4 mg N kg^{-1} hr^{-1}). While DEA was highly correlated with soil moisture, organic matter, microbial biomass, and soil respiration areas across sites, it was always higher in SCM at equivalent levels of these variables. SCM appear to function as denitrification hotspots and, despite having similar microbial biomass, have higher potential denitrification than natural riparian areas.



■ INTRODUCTION

The amount of urbanization in the United States over the second half of the 20th century was dramatic. Between 1950 and 2000 the amount of land classified as urban (>1 housing unit per acre) and exurban (between 1 unit per acre and 1 unit per 40 acres) increased 5 fold.[1] Urbanization increases both the type and amount of pollution that runs off into nearby aquatic ecosystems. This runoff includes pollutants such as sediments, road salts, heavy metals, hydrocarbons, and nutrients that are washed off buildings and roads.[2] The amounts of these pollutants are higher (A) because there are more sources in urban areas and, (B) because there is less opportunity for these pollutants to be removed by plants and soil before they reach aquatic ecosystems. With urbanization projected to continue to increase in the future[3] there is widespread concern about its effects on water quality.

Urbanization has been shown to have a particularly significant impact on the nitrogen (N) cycle.[4] Nitrogen emissions from fossil fuel combustion are higher in urban areas than in nonurban areas.[5] These emissions are in turn deposited on parking lots,[6] roads,[7] and along gradients away from roadways[8] causing urban areas to have 2−4 times more deposition than in nearby rural areas.[9,10] In addition to high deposition, fertilizer additions can be significant in urban areas.[11,12] Septic systems can be a significant source of N in suburban areas[13] and leaky sanitary sewer infrastructure can be important in more densely settled areas.[14]

In addition to cities being hotspots of input, their ability to process and retain N is also diminished compared to non-urban areas. Humans have significantly altered the landscape in urban areas by creating impervious surfaces, and modifying the drainage network (e.g., degrading and removing wetlands, burying and channelizing streams).[15] These landscape alterations result in lower watershed N retention because they change the amount and timing of runoff following precipitation events, resulting in "flashier" hydrology with higher peak flows than nonurban systems.[16] Increases in the volume and velocity of runoff associated with urbanization have also had dramatic effects on stream geomorphology by increasing scour and removing key retention structures such as large woody debris dams. These impacts are so common and characteristic across urban environments that Walsh et al. (2005) coined the term "urban stream syndrome" to describe this process.[17] One of the impacts of urban stream syndrome is that stream channels become incised,[18,19] lowering the water table in adjacent riparian zones and reducing connections between the riparian zone, the stream, and the uplands. The riparian zone normally functions as a "sink" for NO_3^- in watersheds by removing waterborne N through denitrification (the anaerobic microbial conversion of nitrate (NO_3^-) to nitrogen (N) gases) before N reaches the stream.[20−22] Denitrification, unlike plant uptake, results in permanent removal of N from aquatic systems, and is thus considered an important ecosystem function. However, stream incision and associated lower riparian water tables and

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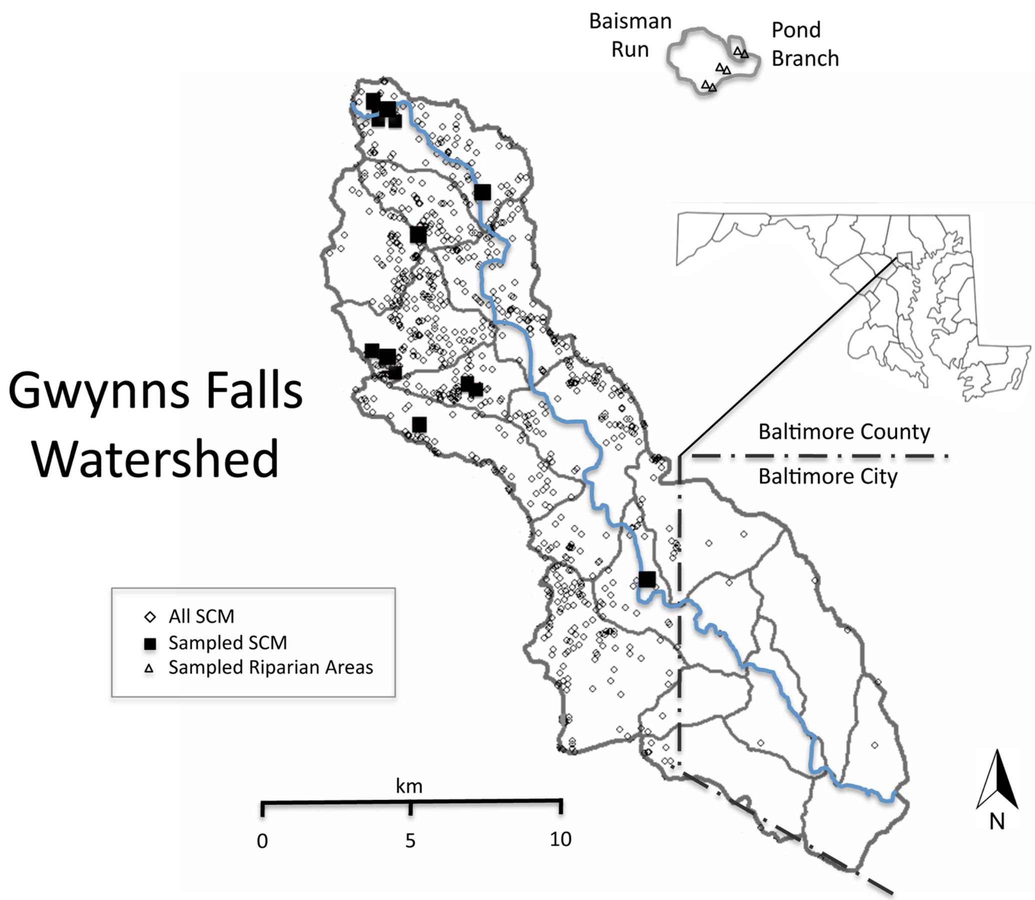

Figure 1. Map of the Gwynns Falls watershed spanning the urban−rural gradient from Baltimore City to Baltimore County showing all SCM (open circles) and sampled locations (closed squares).

soil moisture reduce this function causing the amount of N removed by denitrification to decrease.[23]

In urbanized watersheds with impaired streams and riparian zones, managers have turned to engineering solutions to replace the ecosystem functions previously performed by forests and riparian zones, such as stormwater infiltration and N removal. The primary method to control stormwater discharges is the installation of stormwater control measures (SCM),[24] which includes many different types of engineered structures designed to reduce peak discharge and/or remove pollutants associated with sediments. The different SCM designs allow each state to manage for their individual stormwater control goals (erosion and sedimentation control, recharge/base flow, water quality, channel protection, and flooding events) in the most cost-effective manner.[25] SCM can be grouped into five classes: (A) wet ponds, such as shallow marsh and wet ponds, which have a permanent pool of water, (B) dry detention ponds, which have pools that dry out between storms, (C) dry extended detention basins, which are designed to store runoff and then drain over an extended period of time (usually 24 h), (D) infiltration practices, such as swales, infiltration basins and trenches, which are designed to infiltrate stormwater into the soil, and (E) filtering practices such as sand filters and bioretention areas, which are designed only for sediment removal, and do not reduce peak flows.[2]

While SCM are primarily designed to control the hydrological impact of urbanization by reducing peak discharge and removing pollutants through settling of suspended sediments, they also have the potential to have a biogeochemical impact by increasing denitrification in several different ways. Denitrification, which is the oxidation of organic matter under low O_2 conditions when NO_3^- instead of O_2 is used by microbes as the terminal electron acceptor, is controlled by O_2 concentration, carbon availability, and NO_3^- concentration. Low $O_{2\,(aq)}$ conditions occur in saturated soils, because as O_2 is consumed by respiration water reduces diffusion of additional $O_{2\,(gas)}$ into soils. In SCM, the intermittent wetting and drying of soils due to fluctuating water levels results in a range of O_2 conditions both over time in between storm events and over space within an individual SCM. This range in O_2 concentration within the sediments of the SCM allows both anaerobic processes, such as denitrification, and aerobic processes, such as decomposition and nitrification, to occur simultaneously or in close proximity. Both decomposition, which is the breakdown of organic matter and nitrification, which is a microbial process that converts NH_4^+ to NO_3^- are likely to increase denitrification by increasing the amount of carbon and nitrate available to denitrifiers. Finally, by collecting and holding water, SCM facilitate interaction between denitrifiers in sediments and nitrate in the water, increasing the potential for denitrification.

Although SCM clearly have the potential to increase denitrification in urban landscapes,[26] there is great uncertainty about how their N removal capacity compares to the natural riparian areas and wetlands that are lost or degraded by urbanization. Furthermore, the variability in SCM design likely creates variation in N removal efficiencies both within and among different types of SCM.

In this paper, we compare potential denitrification in the most common types of SCM within the Gwynns Falls watershed in Baltimore County, MD, USA. SCM types included shallow marsh, wet pond, dry detention ponds, extended detention structure dry, extended detention, infiltration basin, and filtration basin. These SCM were compared with two types of natural riparian areas (forested and herbaceous). We measured potential denitrification using denitrification enzyme assays (DEA) as well as a series of microbial and biogeochemical parameters that influence DEA including soil moisture, soil organic matter content, soil inorganic N levels, microbial biomass carbon, microbial biomass N, microbial respiration, potential net nitrogen mineralization, and potential net nitrification. We also measured nitrate concentrations of the water in the inlet basins of the stormwater structures or streams adjacent to riparian areas. Our objectives were to (1) determine if SCM have high potential denitrification relative to natural riparian zones, and (2) assess if variations in SCM design influence this potential. These objectives represent the first step in understanding the influence of SCM on N removal and are crucial to constructing comprehensive watershed N budgets in urban areas, which will also include accumulation of N in plant biomass and soil organic matter.

■ MATERIALS AND METHODS

We sampled thirteen SCM and six riparian areas just outside of Baltimore, MD, USA on September 13 and 14, 2011 (Figure 1). The SCM structures were within the Gwynns Falls Watershed (76°30′, 39°15′), which spans a land use gradient from urban Baltimore to rural suburban fringe in Baltimore County.[27]

The thirteen SCM consisted of three from type A (2 shallow marsh, 1 wet pond), two from type B (dry detention ponds), five from type C (3 extended detention structure dry, which dry out completely between events, 2 extended detention, which might contain a wetland area in the bottom stage of an extended detention basin to increase sedimentation), one from type D (infiltration basin), and two from Type E (filtration basin). The SCM, which received all their inputs from surface runoff, had drainage areas ranging from 0.9 to 14 ha.

The six riparian sites (three forested and three herbaceous) were along three streams draining subwatersheds within a pair of watersheds in Baltimore County (~ 10 km away from the SCM). The rural watershed (Pond branch) is a forested watershed used as a reference watershed by the LTER; the adjacent watershed (Baisman Run) is classified as suburban, with large-lot housing development. The three streams drained areas that differed in extent of development, in this case large-lot single-family housing units containing some structures and vegetation, usually lawns. The streams were chosen to span a range of urbanization from undeveloped space (Pond Branch, 40 ha, 0% developed); mildly developed (Baisman 1, ~4 ha, 32% developed), and highly developed (Baisman 2, ~10 ha, ~42% developed).[28] Along each stream a pair of forested and herbaceous riparian areas was sampled, with the herbaceous areas originally created by forest cutting for a 50-m wide power line right of way that traverses the forested area.

We took water samples either from the inlet basin of the SCM or from the stream traversing the riparian area at all but one site (one of the type C extended detention SCM), which had no standing water. This water had been affected by its residence time in the inlet basin or passage through the riparian zone and its chemistry is thus a product of watershed conditions and riparian or SCM processing. We filtered (0.45-μm pore size) and stored samples at 4 °C until analysis (< 30 days) with a Lachat QuikChem flow injection analyzer for NO_3^-.

To capture the variability in soil wetness conditions and thus allow for a more robust comparison, we sampled along moisture gradients in the SCM and natural riparian zones (see diagram in Supporting Information). In all riparian areas and in all but one SCM, in which the perennially and regularly wet sites were inaccessible, we sampled at four locations (perennially wet, regularly wet, periodically wet, and infrequently wet) based on physical location and vegetation type. In the SCM, the perennially wet sites were located at the inlet and often had wetland vegetation, e.g., *Typha*, present. Regularly wet sites were on the bench above the inlet (<0.3 m difference in elevation) and often had tussock sedge (*Carex*) present. Periodically wet sites were in the basin bottom (0.3–1.2 m in elevation above inlet), and often had switchgrass (*Panicum*) or rushes (*Juncus*) present. Infrequently wet sites were in the middle of the slope along the bank of the SCM (> 1.2 m in elevation above the inlet) and usually had native grasses (*Agrostis*) present. In the riparian areas, the 4 sites were located along a transect perpendicular to the stream with the perennially wet sites within 10 cm of the stream edge, the regularly wet sites within 0.5 m (< 0.1 m difference in elevation), the periodically wet sites were within 2 m (< 0.5 m in elevation above inlet), and infrequently wet sites were upslope (> 0.5 m above the stream).

At each of the four moisture gradient locations we took three 3.0-cm diameter cores with a JMC Backsaver soil sampler. The top 5 cm of each of the three cores were combined to form a single composite sample to minimize analytical costs while providing adequate resolution to characterize a spatially heterogeneous area.[29] The samples were stored at 4 °C until processing (< 1 week), hand-sorted (i.e., large roots and rocks were removed similarly to Metcalfe[30]), mixed, and subsamples were taken and analyzed for soil moisture, soil organic matter, microbial biomass C and N, inorganic N (NH_4^+ and NO_3^-), potential net nitrification, and potential net mineralization, and denitrification potential according to methods described and referenced in Groffman et al.[31]

We determined soil moisture content by drying subsamples at 60 °C for 48 h and soil organic matter content by loss on ignition (LOI) at 450 °C for 4 h.[32] We measured microbial biomass C using the chloroform fumigation incubation method.[33] This involved fumigating samples with chloroform to kill and lyse microbial cells, inoculating them with fresh soil, and incubating them for 10 days, during which time microorganisms killed by chloroform were mineralized to CO_2 and NH_4^+. The amount of CO_2 and 2 M KCL extractable inorganic N produced during the incubation is proportional to the amount of C and N in the microbial biomass. A proportionality constant of 0.45 was used to calculate biomass C from CO_2, which we measured using a gas chromatograph.

We also measured the amount of CO_2 and 2 M KCL extractable NH_4^+ and NO_3^- in unfumigated "control" samples over a 10-day incubation. The amount of CO_2 was used to estimate microbial respiration. The amounts of NH_4^+ and NO_3^- and NO_3^- alone were used to calculate potential net N mineralization (conversion of organic N to inorganic N) and nitrification (transformation of NH_4^+ to NO_3^-).

Potential denitrification was measured using the DEA assay,[34] in which all the limiting factors of denitrification (O_2,

NO_3^-, and carbon) are removed, bacterial growth is inhibited by the addition of chloramphenicol, and the production of nitrogen gas is measured as the accumulation of N_2O in the presence of acetylene, which blocks the conversion of N_2O to N_2. Soil samples were incubated under anaerobic conditions, gas samples were taken at 30 and 90 min, stored in evacuated glass vials, and analyzed for N_2O by electron capture gas chromatography.

The statistical program JMP was used for all data analysis.[35] We used a one-way analysis of variance (ANOVA) to test for differences between stormwater structures and riparian areas in DEA, DEA:microbial biomass, and nitrate. We used a used a two-way ANOVA with interactions (inundation frequency) to test for differences in soil moisture between the SCM and riparian areas along sampling transects. To determine if differences among SMC and riparian areas were significant after correcting for the effects of the soil moisture, we used a two-way analysis of covariance (ANCOVA) with soil moisture as a covariate followed by a Tukey HSD post hoc analysis to test for differences among stormwater structures and riparian areas in DEA, microbial biomass C and N, microbial respiration, DEA:microbial biomass, potential net N mineralization, and nitrification. We evaluated the relationships between variables ((DEA:soil moisture), (DEA:soil organic matter), (DEA:microbial biomass), and (DEA:respiration)) with correlation and regression analysis.

■ RESULTS

There was significant variation in hydrologic conditions within the stormwater control structures, such that soil moisture declined along the sampling transect running along the designed gradient from perennially to infrequently inundated zones (Figure 2). In contrast, there was no statistically significant difference in soil moisture along the sampling transects in natural riparian zones.

There were significant differences in DEA and associated microbial variables between SCM and natural riparian areas and among the different SCM types and different types of natural riparian areas. Potential denitrification (DEA) in the top 5 cm of soil ranged from 0.005 to 1.75 mg N kg^{-1} hr^{-1} in the riparian areas and from 0.01 to 10.25 mg N kg^{-1} hr^{-1} in the stormwater structures. Overall when the SCM are compared to the riparian areas, potential denitrification was significantly ($p < 0.0197$) higher in the stormwater structures (1.2 mg N kg^{-1} hr^{-1}) than in the riparian areas (0.4 mg N kg^{-1} hr^{-1}) (Figure 3A). The ratio of DEA to microbial biomass C (DEA:MBC), which serves as an index of the importance of denitrifiers in the total microbial biomass, was significantly ($p < 0.0002$) higher in the stormwater structures (1.4) than in the riparian areas (0.3) (Figure 3B). The average nitrate concentration of the inlet basins in the stormwater structures was significantly ($p <$

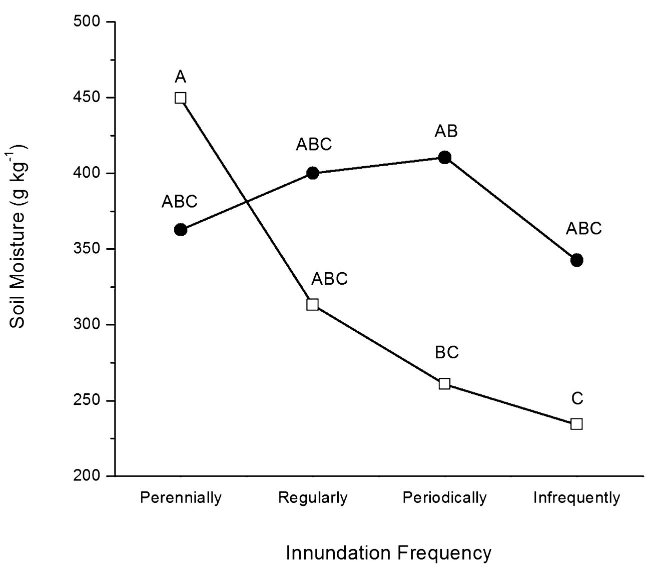

Figure 2. Soil moisture along sampling transects in SCM (open squares) and riparian areas (closed circles). Means with different letters are significantly different ($p < 0.0428$).

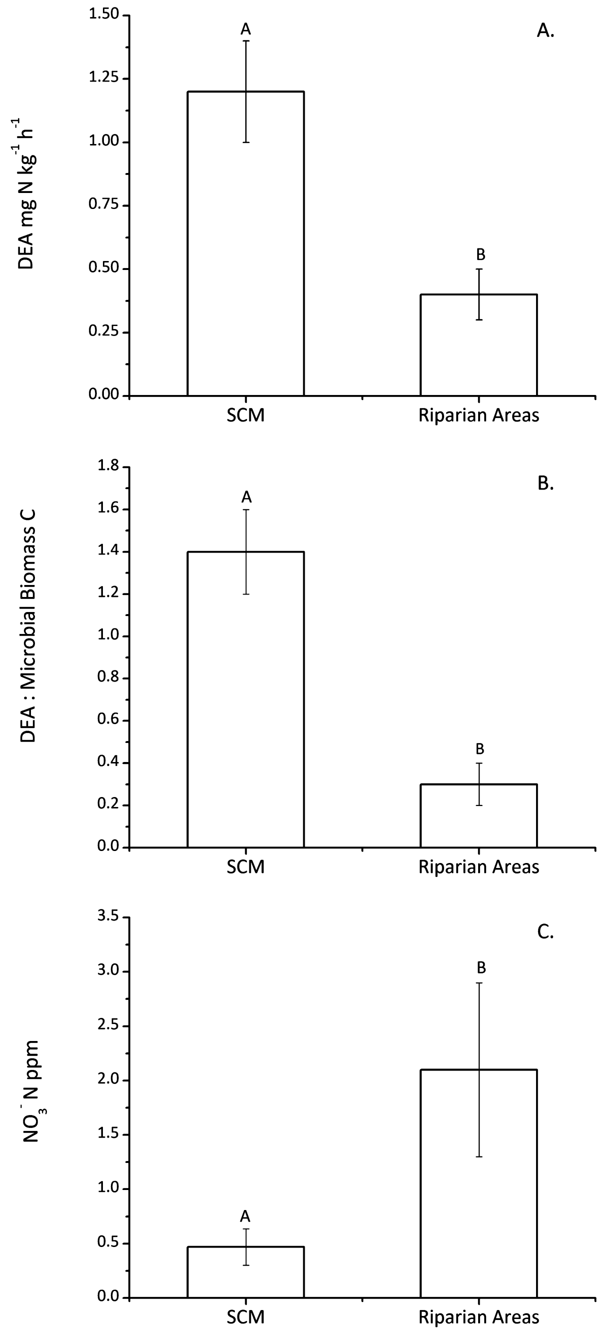

Figure 3. Potential denitrification (A), ratio of DEA:microbial biomass C (B), and nitrate concentration (C) in SCM and natural riparian areas.

Table 1. Soil Variables (± SE) in Stormwater Management Control Structures and Riparian Areas[a]

		soil moisture (g kg^{-1})	soil organic matter (g kg^{-1})	DEA (mg N kg^{-1} hr^{-1})	microbial biomass C (mg C kg^{-1})	microbial biomass N (mg N kg^{-1})	soil respiration (μg C g^{-1} d^{-1})	potential net N mineralization (μg N g^{-1} d^{-1})	potential net N nitrification (μg N g^{-1} d^{-2})	DEA:microbial biomass C
SMC type	A (Wet) (n = 12)	318 (24)	72 (6)^{B}	1.07 (0.25)^{B}	792 (75)	39 (8)	19.85 (1.80)^{B}	0.13 (0.19)	0.03 (0.19)	1.45 (0.36)^{AB}
	B (Dry) (n = 8)	352 (46)	86 (14)^{B}	1.49 (0.45)^{AB}	1113 (237)	61 (8)	27.83 (7.58)^{AB}	0.41 (0.53)	0.34 (0.53)	1.54 (0.26)^{AB}
	C (Dry Ext Det) (n = 20)	302 (24)	81 (12)^{AB}	1.43 (0.53)^{A}	933 (155)	37 (5)	22.52 (4.28)^{AB}	0.13 (0.07)	0.003 (0.07)	1.26 (0.25)^{AB}
	D (Infiltration) (n = 4)	240 (33)	48 (4)^{B}	0.18 (0.15)^{AB}	397 (77)	10 (5)	12.18 (3.35)^{AB}	0.05 (0.06)	0.06 (0.05)	0.31 (0.23)^{AB}
	E (Filtration) (n = 6)	325 (57)	74 (19)^{B}	1.00 (0.56)^{AB}	604 (104)	40 (8)	24.47 (8.00)^{AB}	0.21(0.12)	0.14 (0.19)	2.32 (1.27)^{A}
Riparian Type	Herbaceous (0%)[b] (n = 4)	520 (78)	125 (21)^{AB}	0.49 (0.18)^{AB}	1182 (81)	66 (14)	37.55 (9.58)^{AB}	−0.03 (0.02)	−0.46 (0.29)	0.43 (0.15)^{AB}
	Herbaceous (32%)[b] (n = 4)	271 (22)	40 (13)^{AB}	0.21 (0.11)^{AB}	653 (248)	653 (248)	15.05 (3.49)^{AB}	0.41 (0.15)	0.28 (0.11)	0.28 (0.09)^{AB}
	Herbaceous (42%)[b] (n = 4)	280 (51)	44 (23)^{B}	0.53 (0.41)^{AB}	730 (393)	730 (393)	20.11 (9.64)^{AB}	0.12 (0.05)	0.14 (0.07)	0.52 (0.16)^{AB}
	Forested (0%)[b] (n = 4)	552 (53)	206 (16)^{A}	0.70 (0.34)^{AB}	2453 (631)	2453 (631)	67.45 (10.26)^{A}	0.25 (0.25)	−0.28 (0.52)	0.41 (0.23)^{AB}
	Forested (32%)[b] (n = 4)	334 (41)	98 (35)^{AB}	0.07 (0.03)^{B}	1205 (365)	1205 (365)	25.89 (7.30)^{AB}	−0.01 (0.004)	0.09 (0.05)	0.13 (0.10)^{B}
	Forested (42%)[b] (n = 4)	315 (60)	76 (30)^{B}	0.15 (0.10)^{B}	824 (429)	824 (429)	9.53 (2.61)^{B}	0.57 (0.40)	0.56 (0.04)	0.13 (0.05)^{B}

[a]Means with different superscripts are significantly different (p < 0.05). [b]Percent developed area in watershed.

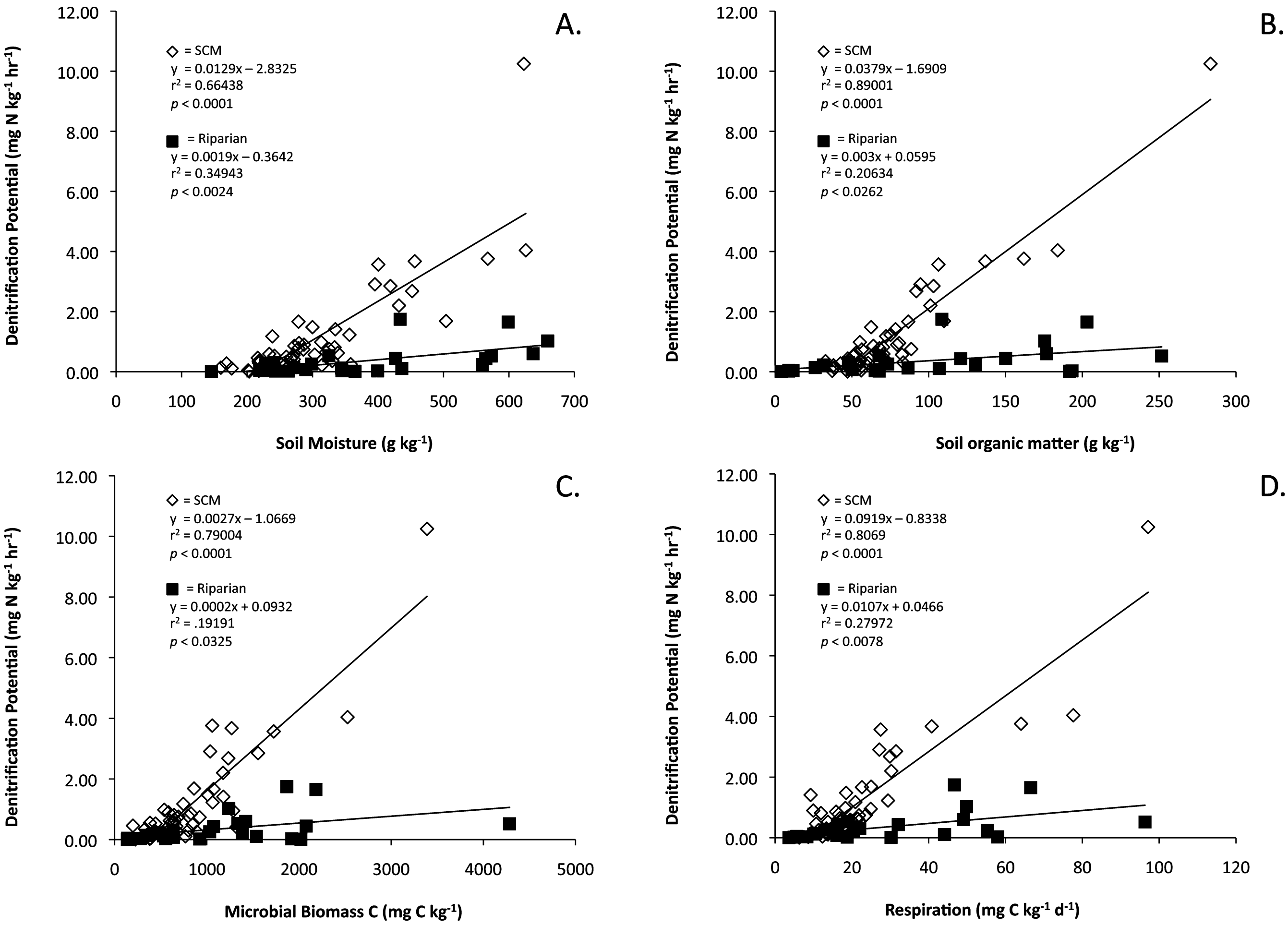

Figure 4. Regression of potential denitrification against soil moisture (A), soil organic matter (B), microbial biomass (C), and microbial respiration (D) in stormwater control structures and riparian areas (n = 50 and n = 24 for SCM and riparian areas, respectively).

0.0122) lower (0.47 ± 0.2 ppm NO_3^- - N) than in the streams traversing the riparian areas (2.13 ± 0.8 ppm NO_3^- - N) (Figure 3C).

When the different types of SCM and riparian areas were compared, there were significant ($p < 0.05$) differences in some (DEA, soil organic matter, soil respiration, and DEA:MBC) but not all (microbial biomass C and N, potential net N mineralization and nitrification) measured variables (Table 1). DEA was higher in SMC type C (dry extended detention) than in type A (wet pond) and forested riparian sites in both mildly and highly developed areas. Soil organic matter was higher in forested riparian sites of undeveloped areas compared to the herbaceous and forested riparian sites of highly developed areas, and SCM types A, B, D, and E (Table 1). Soil respiration was higher in undeveloped forested riparian areas compared to highly developed forest riparian areas and SMC type A. DEA:MBC was higher in type E (filtration) than in mildly and highly developed forest riparian areas.

DEA was highly correlated with multiple soil variables (Figure 4) in both SCM and riparian areas. There were strong relationships between DEA and soil moisture (A), soil organic matter (B), microbial biomass (C), and microbial respiration (D) in both SCM and natural riparian areas. The strength of these relationships varied markedly between SCM and riparian areas, with much steeper slopes in the SCM (Figure 4).

DISCUSSION

Our objectives were to compare the denitrification potential of SCM used to control the hydrological impacts of urbanization to natural riparian zones and to assess how different SCM designs influence denitrification. We also wanted to capture the spatial heterogeneity in the physical and biological drivers of denitrification caused by fluctuating water levels within the SCM. We used the DEA assay, which is a widely used integrative measure of potential denitrification.[36] Although DEA rates are likely to vary throughout the year due to changes in temperature and soil moisture, the assay provides an index that integrates long-term variation in the factors that control denitrification, because all the limiting factors, such as nitrate and carbon, are removed at the time of sampling. It has thus proven useful for comparison of different ecosystem types when frequent sampling is not possible

Our data showing higher DEA in the SCM compared to the riparian areas indicate that SCM have the potential remove more N per gram soil or per m^{-2} than natural riparian areas. Moreover, the higher DEA:MBC, which normalizes DEA to the amount of microbial biomass in the SCM, suggests that denitrifying organisms are a larger component of the microbial biomass in the SCM than in natural riparian areas.[37,38]

These results indicate that the SCM may function as hotspots of denitrification[39] in urban watersheds; a somewhat surprising result, given that the key controllers of variation in riparian denitrification (soil moisture and organic matter)[31] were not significantly different between the SCM and the natural riparian areas. The most likely explanation for the higher denitrification potential in the SCM compared to the riparian areas is the design of the SCM, which although originally engineered to control the hydrological impact of urbanization by reducing peak discharge are also facilitating the interaction of nitrate-laden stormwater with denitrifying sediments. In natural riparian areas, especially in urban watersheds, upland-derived nitrate often moves in channelized flow through the riparian zone, minimizing opportunities for interaction with denitrifying sediments. These results indicate that SCM are performing the same function that had previously been performed by riparian areas prior to their being degraded. It is interesting to note that we did not include any "bioretention" SCM in our study (due to accessibility limitations). This type of SCM is designed to maximize interaction of stormwater with sediments and may have even higher denitrification potential than the SCM sampled in this study.

The enhanced denitrification potential of the SCM is also shown by comparing relationships between DEA and controlling factors in SCM and riparian areas. DEA was much more responsive to soil moisture, soil organic matter, microbial biomass, and soil respiration (Figure 4A, B, C, D, respectively) in the SCM than in the natural riparian areas. This high responsiveness to moisture and organic matter in the SCM explains the apparent contradiction between our results showing high DEA and low NO_3^- concentrations in the SCM and other studies,[40,41,36] which found higher DEA in streams with higher NO_3^- concentrations. Because water in the inlet basin has been resident for some period, the nitrate concentration of this water is a function of the nitrate concentration of the water that flowed into the SCM as well as any processes that occur in the inlet basin prior to their being sampled. The relatively low nitrate concentrations found in the inlet basins are likely due to facilitation of high denitrification rates by the design of the SCM, which are intended to increase residence time and thus the interaction between upland-derived nitrate and denitrifying sediments. This is different from natural riparian zones, where the flow from the upland toward the stream is often channelized, reducing residence time and interaction of upland-derived water and nitrate with denitrifying sediments. While these rates do not appear to be high enough to completely deplete nitrate in the SCM and create nitrate limitation of denitrification, they do suggest that SCM have significantly better nitrate removal performance than natural riparian zones.

In addition to comparing potential denitrification between SCM and riparian areas we were also interested in assessing how SCM design or riparian type influences potential denitrification. Overall while there were large differences in both potential denitrification and soil variables among the different types of riparian areas and structures, very few of the differences were statistically significant. Among the different riparian areas, the only significant differences were between the undeveloped forested site and the highly developed forest and herbaceous sites in soil organic matter and soil respiration. Compared to the highly developed forest riparian area, the undeveloped forest riparian area had higher soil respiration and higher soil organic matter, and compared to the highly developed herbaceous area it had higher soil organic matter. Consistent with previous studies, we found no significant difference between forested and herbaceous riparian zones in denitrification potential.[31,42]

Although we expected to find differences among the different SCM, there were few differences in DEA among the different types of structures and no differences among the other variables (microbial biomass C and N, microbial respiration, DEA:microbial biomass, potential net N mineralization and nitrification, nitrate). Conceptually, we expected to measure high DEA in structures that drain more slowly (i.e., wet ponds (type A) and dry extended detention basins (type C)) because of extended interaction between the sediments and overlying water. The surprisingly low DEA in the wet ponds may be due to more permanently anaerobic conditions in these basins. While such conditions are optimal for denitrification of incoming nitrate, they are less effective at fostering coupled mineralization–nitrification–denitrification of other forms of N input.[43] We would expect high DEA in structures that alternated between wet and dry conditions (i.e., types B and C) when ammonia or organic forms of nitrogen are dominant and coupled nitrification/denitrification is needed for nitrogen removal. Structures that drain more quickly like infiltration (type D) or filtration (type E) should have lowest DEA because of decreased interaction between microbes in the sediments and nitrate in the pore water. While the DEA in type D was much lower than that of any of the other structures, likely due to the lower soil moisture and soil carbon, the only significant difference in potential denitrification was between the dry extended detention basins (type C) and wet ponds (type A) with the DEA being higher in dry extended detention (Table 1). It is likely that the sampling in this study was too limited to illustrate the effects of these complex dynamics on DEA. However, more intensive studies are underway to explore these dynamics in more detail.

The DEA rates reported here are similar to those reported in previous studies in the Baltimore region.[23,31] DEA values for our natural riparian areas were similar to other measurements made in riparian areas in forested reference areas (0.456 mg N kg^{-1} hr^{-1}) while the DEA estimates in the stormwater structures were similar to measurements made in suburban riparian areas (1.66 mg N kg^{-1} hr^{-1}) but not as high as in urban riparian areas (2.20 mg N kg^{-1} hr^{-1}).[23] The DEA values reported here (with the exception of type D) were within the range (0.390–1.15 mg N kg^{-1} hr^{-1}) reported by Zhu et al. for retention basins in Phoenix AZ.[26]

To estimate the potential impact that the SCM might have on nitrogen flows in the Gwynns Falls watershed, we can calculate an area-weighted estimate of their potential N removal using general removal efficiencies for each type of SCM along with their drainage areas. In the Gwynns Falls watershed there are 827 SCM, which collectively drain an area equivalent to 21% of the watershed (Figure 1). The general removal efficiencies used by the Chesapeake Bay program, which are calculated as a percent removal of N using influent and effluent concentrations for the different structures are as follows: wet ponds and wetlands (20%), dry detention, hydrodynamic structure (5%), dry extended detention (20%), infiltration practices (swale, porous pavement, infiltration trench, and infiltration basin, 70%, 80%, 80%, and 85% respectively) and filtering practices (sand filter, bioretention, dry well, 40%, 80%, and 85%, respectively).[47] If we apply the corresponding value of removal for each of these structure types to their areal extent in the Gwynns Falls watershed, we get an area-weighted N removal estimate of 3.3%, which is not insignificant considering that parts of the watershed have very few SCM (there are fewer SCM in areas with infrastructure built prior to SCM being required).[24] Watershed nitrogen retention in the Gwynns Falls, which includes soil storage, plant uptake, and denitrification losses, ranges from 35% in wet years to 85% in dry years,[47] so SCM could be responsible for anywhere from 4 to 9% of the N retained in the watershed. Evidence for N retention by SCM in the Gwynns Falls can also be taken from the difference in nitrogen concentrations between the SCM and the streams traversing natural riparian zones. These results suggest that SCM reduce the concentration of nitrate flowing across the landscape by approximately 50%. And if SCM treat 21% of the surface area of the Gwynns falls watershed, these results suggest a 10% reduction in nitrogen flow in runoff at the watershed scale.

While it is apparent that the SCM have high denitrification potential, exactly how much of an impact these SCM are having on watershed N removal is uncertain. Numerous other studies using either data that they collected themselves[44] or influent and effluent concentrations they obtained from the international BMP database (www.bmpdatabase.org)[45,46] have shown that pollutant removal of SCM can vary by type[45,46] and season.[44] Barrett found that only wet ponds and sand filters removed significant amounts of TN, while the Center for Watershed Protection[46] showed that while some SCM (type A) removed 45−67% of the NO_3^- others either removed none (type D) or increased N concentration by 14% (type E). Rosenzweig et al. monitored influent and effluent N concentrations in an extended detention pond in New Jersey for three week periods during the spring, summer, winter, and fall seasons and found that NO_3^- was only retained during the summer sampling period.[44]

While the net effect of SCM on watershed N removal is unknown it appears that there is the potential to increase the amount of N removed by changing SCM type. Our data and a recent review by Collins et al. (2010) that considers some of the challenges and opportunities for managing N in urban stormwater found that several alternative SCM, such as bioretention, filters, and wetlands, show greater promise in their ability to remove N from stormwater than more conventional practices such as dry ponds and wet ponds.

These results indicate that SCM are denitrification hotspots and that installing more and/or more effective SCM could reduce urban watershed nitrogen exports. This hotspot behavior appears to be driven by the engineered interaction between upland-derived nitrate in stormwater and sediments with high denitrification potential. This reduction in watershed N flux has important implications for controlling coastal eutrophication. Nitrogen availability limits primary production in most coastal ecosystems in the temperate zone[49] and excess nitrogen now degrades more than half of all U.S. estuaries.[50] By altering the nature and extent of SCM, managers can decrease the amount of nitrogen pollution in coastal ecosystems affected to urban and suburban watersheds.

Although it is difficult to compare the impact of SCM vs riparian areas on watershed N budgets because of differences in their detention times and uncertainties in the amount of N removal in riparian areas due to subterranean flows, this preliminary work suggests that SCM have the potential to significantly influence nitrogen flows across the landscape. Further work that accounts for the actual residence time of water and nitrogen in detention basins and riparian zones, and that considers possible removal of N that leaves certain types of SCM, such as infiltration basins, is necessary for a complete evaluation of the importance of SCM to nitrogen mass balances in urban watersheds.

■ ASSOCIATED CONTENT

Supporting Information

Table of locations of sample sites. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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