Spatial and Temporal Patterns of Nutrient Loading, Nutrient Sourcing, and Stream Metabolism in Restored and Unrestored Urban Stream Reaches of Charlottesville, Virginia

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Abstract

Since the mid-1900s, humans have significantly accelerated the nitrogen (N) cycle by more than doubling N input into natural systems. Common sources of enhanced N include fertilizers, animal waste, septic systems, sanitary sewers, fossil fuel combustion, untreated stormwater, and atmospheric deposition. There is particular concern about increased nitrogen loads in streams and their link to riverine and estuarine eutrophication. Stream restoration and stormwater control measures (SCMs) are common practices to reduce nitrate loads in streams. This research explores the downstream trends in inorganic N concentrations, loads, and retention in seven restored and unrestored stream sections of the Meadow Creek watershed in Charlottesville, Virginia, in addition to adjacent riparian pond and wetland. We further track the dissolved inorganic nitrogen (DIN) sources to these sites through isotopic analysis, and analyze stream metabolism patterns through seasons and sites of different restoration status.

Water samples for nitrate + nitrite, and dual isotope analysis of $\delta^{15}NO_3$ and $\delta^{18}O$ were collected. Photosynthetically active radiation, dissolved oxygen, conductivity, water temperature, water level, and atmospheric pressure sensors were deployed. These variables were used as inputs in the Bayesian Single-Station estimation (BASE) model to generate gross primary productivity and ecosystem respiration.

Restoration was found to be effective at sequestering nitrogen with an enhanced effect in the summer. Pond and wetland studies also showed a water treatment effect through inlet and outlet nitrate + nitrite concentration and load comparisons. However, enhanced denitrification was not supported by the isotopic analysis of these samples. Sanitary effluent was the dominant nitrate source to our sites at baseflow conditions, yet this signal seems to be diluted at hurricane scale flows. Some stream metabolic activities had seasonal variability with peaks in the summer, which is the reverse pattern to nutrient concentration seasonality. These results have implications on the potential of stream restoration and SCMs to decrease excess nutrient loads into downstream systems, as well as to maintain or recover the various ecosystem services provided by streams.

Introduction

Since the mid-1900s, humans have significantly accelerated the nitrogen cycle by more than doubling N input into natural systems (Galloway et al., 2004; Burns et al., 2009). Urban watersheds are significant nutrient sources to streams through a complex mix of fertilizers, animal waste, septic systems, sanitary sewage leaks, fossil fuel combustion, untreated stormwater, and atmospheric deposition (Mayer et al., 2002; Elliott et al., 2007; Kaushal et al., 2006). Surveys of lawn fertilization in residential areas have shown that this can be a significant component of nitrogen input to urban and suburban watersheds (e.g., Fraser et al., 2013). In many cases, these applications exceed the nitrogen maximum permitted by law (Fraser et al., 2013). In addition, there are less opportunities for nutrient removal by plants and soil in urban areas (Bettez and Groffman, 2012). Besides untreated runoff, sediments also play a large role in water pollution. According to The Environmental Protection Agency (EPA), sediment is the most common pollutant of rivers, streams, and lakes by being a source of nutrients as well as other pollutants. 70% of the total sediment in the United States comes from human induced erosion. Nutrients transported to water bodies by runoff and sediments can lead to algal blooms, oxygen depletion, and mortality of aquatic organisms. Impaired waterways do not meet the water quality standards for at least one pollutant; currently, more than one-third of U.S. rivers are classified as impaired or polluted (Bernhardt et al, 2005). This research will examine the downstream evolution of nitrogen under different flows and seasons in an urban watershed in Charlottesville, Virginia, and the effectiveness of stream restoration as well as stormwater control measures (SCMs) at reducing nitrate concentrations in urban streams. We hope to shed light on their potential to decrease excess nutrient loads into downstream systems, as well as to maintain or recover the various ecosystem services provided by streams.

Urban Watershed Hydrology

During heavy rainfall events, paved surfaces prevent stormwater from infiltrating the soil. Instead, the water draining upstream lands is channeled through stormwater systems and discharged at great volumes and speed into receiving water bodies. This results in a condition described as the “urban stream syndrome” in waterways that run through modern cities (Walsh et al., 2005). This condition includes bank erosion, channel incision, altered channel morphology, altered hydrological regime, and reduced biotic richness and function. Channel incision is associated with lower riparian water tables, and the erosive enlargement of channels can also threaten adjacent infrastructure and properties. The biological effect of this is the creation of riparian aerated zones that favor nitrification over denitrification, therefore reducing retention and amplifying nutrient concentrations that are discharged into streams (Bettez and Groffman, 2012). Over time, urban streams become unsuitable for sensitive macroinvertebrates, and impose threats to clean water supply. In addition, the decrease in ground permeability linked to urbanization may lead to a reduction in groundwater recharge (Bhaskar et al. 2018). The impacts of the urban stream syndrome combined with the loss of ecological and social services provided by streams such as flood control, maintenance of water quality, habitat for plants and animals, and recreational opportunities for humans, have led to the practice of stream restoration and the construction of SCMs.

Stream Restoration

Stream restoration has gained popularity since the mid-1990s (Bernhardt et al., 2005). Restoration of streams is a major economic investment, with billions of dollars spent each year in the United States (Reisinger et al., 2019). The practice aims to return an impaired stream toward its pre-development hydrological and ecological potential. Although the true “natural potential” of a stream may be impossible to determine, attempts to its estimation include the study of comparable hydro-ecosystems, information about regional environmental conditions, as well as analysis of ecological, cultural, and historical reference information (Shields et al., 2003). This goal is achieved through methods such as bank stabilization, floodplain reconnection, creation of meanders to promote the dissipation of the water energy, riparian zone restoration, aquatic organism habitat creation, and the placement of carbon substrate in the stream to enhance microbial processes such as denitrification and biotic assimilation. This approach recognizes that stream ecosystems benefit from dynamic channels and complex morphology. Some efforts to enhance stream dynamics include localized bed and bank treatments, installing constructed riffles, and allowing streams to self-adjust (Vietz et al.,2015). Unfortunately, most restoration projects, especially small-scale ones, are not adequately monitored. This makes it difficult to understand which strategies are accomplishing their goals (Bernhardt et al., 2005). In addition, many stream restoration projects fail as stream channels begin to redevelop urban stream syndrome if the contributing watershed runoff and nutrient loading regimes are not managed (Shields et al., 2008).

Stormwater Control Measures

Rain gardens, urban tree canopy, bioswales, retention ponds, and constructed wetlands are examples of watershed management practices designed to control stormwater volumes and peak rates from upland areas and retain nutrients before discharging into water bodies. These practices promote infiltration, resulting in a slower and more continuous discharge of stormwater into streams, returning flow duration curves closer to natural conditions, which in turn decrease erosion and the amount of nutrients and sediment getting into the channel. In addition, some of these SCM act as temporary stormwater storage, which increase water residence time and contact time with the microbial community promoting processes such as denitrification. SCMs are a way to treat the upland drainage area as opposed to stream restoration, which is a local mitigation. The two practices may yield better results if applied conjointly.

Ecosystem Productivity

There are two ways nitrogen can be removed from the aquatic ecosystem; biological uptake by algae and other aquatic plants, and denitrification by microbes. The first is a temporary solution, while the latter permanently removes N from the system. Ecosystem nutrient cycling and uptake in streams is affected by riparian vegetation, point-source nutrient input, autotrophic and heterotrophic demand, organic carbon quantity and quality, as well as spatial and seasonal factors such as temperature and light availability (Hoellein et al., 2007). Each of these processes promote either sequestration or release of nutrients. Nutrient availability, especially nitrogen and phosphorus, is a major constraint to photosynthesis. Therefore, the stream metabolism has important interactions with nutrient cycling. Gross primary productivity (GPP) is the amount of chemical energy that autotrophs produce through the process of photosynthesis. This can be represented as a quantity of carbon or oxygen as these elements are sequestered or produced, respectively, by photosynthesis. Respiration refers to the conversion of organic carbon to carbon dioxide by organisms in a system. Ecosystem respiration (ER) is the summation of autotrophic respiration, the respiration of C by plants as well as other autotrophs, and heterotrophic respiration (Hall and Beaulieu, 2013). Respiration consumes oxygen (O_2), such that the GPP, ER, and net ecosystem production (the difference between GPP and ER), can be estimated in units of O_2. Net ecosystem production (NEP) can be used as an estimate of the organic carbon and nutrient cycling in a stream reach, as well as C available for storage, transport and nonbiological processes in the stream ecosystem (Lovett et al., 2006). When NEP is positive, the system is autotrophic. In this scenario, the stream produces more energy than it consumes. Autotrophic conditions are enhanced with the presence of algae and aquatic vegetation. When NEP is negative, as is the case for most streams and lakes, the system is heterotrophic. In this scenario, the stream consumes more energy than it creates. NEP fluxes, and related cycling of nutrients, vary throughout seasons (Hall and Beaulieu, 2013).

Isotopic Nutrient Sourcing

It is important to distinguish the various nitrate sources from different land use types to identify the appropriate course of action to reduce nitrogen loading in streams. Dual isotope analysis of NO_3^- allows for better interpretation regarding sources, sinks, and transport processes of nitrogen. $\delta^{15}NO_3$ is useful for identifying nitrate sourced from ammonium-bearing fertilizer, soil organic matter, sewage effluent, and animal manure. On the other hand, $\delta^{18}O$ is used for distinguishing nitrate sourced from nitrate-bearing fertilizer and atmospheric deposition (Burns et al., 2009). Aerobic conditions in sewers allow for mineralization of organic matter and nitrification of organic N. This is consistent with the gain of isotopically light nitrogen in the nitrate. This signal is reflected in receiving streams, but it may be weakened with increasing distance downstream as a result of in-stream denitrification (Divers et al., 2014) and dilution. Anaerobic conditions in wetlands promote denitrification by anaerobic microbes, which results in fractionation and a $\delta^{15}NO_3$ signal that is enriched with N-15. Isotopic signals are dependent on streamflow conditions. The Damkohler number is the ratio used to relate the chemical reaction time scale to the transport time scale (Yu and Hunt, 2017). In our case, the ratio between the flow time scale to the chemical reaction time scale is larger at baseflow conditions and smaller at stormflow conditions. This means that at baseflow conditions, denitrification and nitrification processes have a better chance to achieve a full conversion and should be evidenced by isotopic fractionation signals. Baseflow isotopic signal is generally dominated by the most constant nutrient source (groundwater) to the stream. However, stormflow can show up to 50% atmospheric deposition influence, but is quickly changed back to the baseflow signal after peak flow (Anisfeld et al., 2007; Kaushal et al., 2011).

Research Questions

Our research questions are as follows:

1. How do dissolved inorganic nitrogen (DIN) concentrations and loads evolve downstream through mixed land use catchments, stormwater control measures (SCMs), restored versus unrestored stream sections, between flow conditions, and among seasons?

2. What are the nitrate sources from different subcatchments at different flow conditions?

3. How do gross primary productivity (GPP) and ecosystem respiration (ER) patterns vary downstream among unrestored and restored sites of different restoration ages, and how do these influence nitrate concentrations and loads?

Regarding our first research question, we expect to see a positive correlation between nutrient concentration and cumulative drainage area percent impervious cover obtained from GIS data. We also hypothesize that inorganic nutrient concentrations will be reduced at sites influenced by restoration due to increased water residence time, greater light availability due to riparian canopy removal, enhanced microbial processes, and decreased bank erosion. For the same reasons, we expect to see a high denitrification signal in samples collected in the pond and wetland, especially in the summer when flows are reduced, and microbes are active. Under stormflow conditions, we expect to see a high degree of nutrient dilution in the samples compared to baseflow samples.

Regarding our second research question, we hypothesize that subcatchments with high tree cover percentage will be dominated by the soil organic matter isotopic signal. Samples taken in the wetland and in the pond, as well as receiving subcatchments, are expected to present a strong denitrification signal. Assuming that impervious cover is a surrogate for sanitary sewer density and leakage, we hypothesize that subcatchments with the highest percentages will be dominated by human waste isotopic signal. In addition, we expect stormflow samples, especially samples collected during the category 4 Hurricane Laura (08/31/2020), to have a strong atmospheric deposition signature.

Our third research question connects to the first question as algae is a major sink of nitrate. Metabolism data should provide important information regarding the uptake of nutrients from algae growth. We hypothesize that sites influenced by restoration will present higher GPP rates compared to the unrestored sites due to increased water residence times and increased photosynthetically active radiation (PAR). When comparing the results at the restored sites of different ages, we expect the newly restored site to show the highest GPP rates as an effect of the canopy clearing, widening of the channel, lower depths, and velocities as a result of the restoration. However, it may take time for effective biofilms and uptake capacity to develop in the streams following restoration. We hypothesize that water temperature and PAR will be the main drivers of GPP. Therefore, we expect GPP/ER would increase in the summer and decrease in the fall and winter when temperatures are lower, and vegetation is dormant. Therefore, we expect nitrate concentrations to be lower in the warmer months when plants and algae are actively taking up nutrients from the water. Conversely, if we assume that nutrient sources to the stream remain constant throughout the year, we expect concentrations to be higher in the winter, as ecosystem uptake of nutrients and denitrification are reduced.

Literature Review

Stream Nutrient Concentration Studies

Thompson et al. (2011), used a meta-analysis of a large number of long term studies of stream chemistry in disturbed catchments to suggest that catchments with high loading of nutrients tend to develop chemostatic behavior. Chemostasis is a transport limited phenomenon, which refers to invariant changes in concentration over different discharge rates. In the case of nitrate in urban watersheds, this implies that the long-term release of this anthropogenically-sourced solute ended up developing subsurface stores, which act as constant sources to streams through groundwater if groundwater remains the primary water source to streams. Duncan et al. (2017), in a study of urban catchments in Baltimore found a distinct pattern of nitrate concentration with different flow conditions. While baseflow nitrate concentrations were in the 1-2 mg L^{-1} range, these concentrations were quickly diluted to approximately 0.2-0.5 mg L^{-1} at the onset of large storm events. However, in the case of smaller storm events, nitrate increased with increasing discharge, then decreased with decreasing stream discharge over the entire event duration. In addition, the urban stream nitrate concentrations were higher in the winter and lower in the summer in contrast to forested catchments. This agrees with other studies which commonly find that when nutrient sources to streams are (relatively) constant throughout the year, N export in streams is highest in the winter, due to reduced plant and microbial uptake. In contrast, nitrate excess, and therefore loss from the system, is minimum in the summer as plants and microbes are active.

In Baltimore, considerable variability in seasonal patterns of stream nitrate in a forested catchment with a riparian wetland has been observed (Duncan et al., 2015). In addition to the effects of the anthropogenic sources of N to streams, forest composition, age, and the presence of wetlands are strong controls on the magnitude and seasonality of stream nutrients. Many forest watersheds in temperate climates have peak nitrate in the summer at low baseflow levels, which is an unusual behavior. In the summer, shallow well water concentrations were similar to dormant season stream concentrations. In addition, riparian hollow subsurface water became aerobic, leading groundwater NO_3^- concentrations to increase enough to coincide with summer stream concentrations. In contrast, upland concentrations were higher in the winter, spring, and late fall, suggesting that nitrate inputs from riparian zones outweigh nutrient uptake during the summer.

Yet another study in Baltimore showed that restored urban stream reaches had significantly higher NO_3^- uptake compared to unrestored urban reaches at baseflow (Reisinger et al., 2019). However, this comparison was done with newly restored reaches with open canopy cover and unrestored reaches with closed canopy cover. Therefore, the resulting nitrate uptake differences may be an effect of canopy cover rather than restoration itself. A study in Charlotte, NC, regarding the effect of age of restoration on denitrification in near-stream soils, found that denitrification potential responded as a function of soil organic matter (McMillan and Noe, 2017). During the construction phase of restoration, soils are re-graded, homogenized, and compacted leading to low soil carbon (~ 1.1%), TN (0.08%), as well as low denitrification potential in newly restored sites. In contrast, the highest denitrification potential, soil organic and nutrient content was found at a site that had its restoration completed six years prior. There is a clear recovery time after restoration that should continue to be monitored in upcoming research.

Although the implementation of SCMs in fact reduced mass export of dissolved (e.g., soluble reactive phosphorus and nitrate) and particulate pollutants, the driver of this reduction was largely hydrological rather than biogeochemical as SCMs are linked to the reduction in runoff (Jefferson et al., 2017). In contrast, a study in a forested watershed in Baltimore, was able to show that riparian wetland hollows, which are zones of lower topographic position dominated by anoxic conditions, are sinks of NO_3^-, and can account for over 99% of the total denitrification (Duncan et al., 2013).

A BES study in Baltimore, MD, comparing how SCMs within a watershed of land use varying from urban to rural perform in terms of denitrification relative to natural riparian areas found that potential denitrification was significantly higher in SCMs (1.2 mg N kg^{-1} hr^{-1}) compared to riparian zones (0.4 mg N Kg^{-1} hr^{-1}) (Bettez and Groffman, 2012). This is likely due to the way they are engineered, which facilitates the interaction of nitrate laden stormwater with denitrifying sediments. In the absence of SCMs, upland-derived nitrate is many times channelized through riparian areas, bypassing these areas, and reducing residence time, limiting the interaction with denitrifiers. Regarding the different types of SCMs, structures that were permanently wet presented low potential denitrification rates because they are less effective at fostering coupled mineralization-nitrification-denitrification of N input. Potential denitrification is high in structures that oscillate between wet and dry cycles, and therefore promote the coupled nitrification/denitrification needed for nitrogen removal.

Stream Metabolism Studies

GPP in streams draining urban watersheds in North Carolina ranged from 0 to 9.1 g O_2 m^{-2} d^{-1}, with February through April being the most productive months (as temperatures are warming, but prior to leaf-out), while August through November were the least productive months (Blaszczak et al., 2019). This could also be due to the supply of organic matter from leaves which provides the stream with nutrients, but such supply is exhausted by the end of the summer. The least flashy streams had the most pronounced GPP peaks, and the headwater streams had the lowest GPP median. ER ranged from 0.01g O_2 m^{-2} d^{-1} to 25.3 g O_2 m^{-2} d^{-1}. The second least flashy stream had the highest rates of respiration, while two of the flashiest streams had the lowest ER medians. An interesting finding of this study was that antecedent light conditions explained more of the variation in GPP than light conditions measured on the same day. Antecedent GPP as a proxy for autotrophic biomass accrual explained the most variation in GPP, and its explanatory power declined with increasing hydrologic flashiness. Overall, streamwater temperature was a stronger predictor than GPP of within-stream variation in ER. However, these only explained around 25% of ER variation, which suggested that ER was not driven by in-stream productivity but by external inputs of organic matter.

Diel variability in nitrate concentrations relates to stream metabolism in a Baltimore urban watershed (Duncan et al., 2017). Nitrate was lower in daylight hours when being consumed, and higher at night when stream ecosystem uptake was at a minimum. This variability was washed out during storms due to the scour of in-stream primary producers, but quickly recovered as stormflow receded. In addition, instantaneous GPP variability was highly correlated to subdaily changes in PAR. Both mean daily GPP and ER reached maximum values in the spring, and minimum values in the summer. Similarly, a study in a forested headwater system inTennessee found that ER rates were the highest in the spring and autumn, and lowest in the summer (Roberts et al., 2007). GPP rates were highest under spring open canopy conditions, dropping to its minimum upon canopy closure in the summer. During the spring, GPP and ER rates were similar, but the reach was heterotrophic most of the year. Very few autotrophic days happened during the months of February, March, and April. This is consistent with most freshwater studies which show that daily ER rates usually exceed GPP (Marcarelli et al., 2011). A positive correlation between GPP and PAR was found, where PAR explained over 70% of the variance in GPP. Urban stream restoration influenced the nutrient and energy dynamics of the stream through a combined analysis of continuous GPP, ER, and nutrient spiraling (Roberts et al., 2007). In newly restored sites, the clearing of riparian canopy cover alters the light regime of the stream, which enhances autotrophic productivity and N assimilation. Autotrophic production adds a new carbon source to streams. This can play a significant role for streams with limited carbon sources. However, as restoration ages and canopy cover regrow, this effect may diminish. In terms of ER, on the other hand, the results were not affected by restoration, canopy cover, their interaction, or season.

Baseflow estimations of metabolism were compared to estimated results before and after Hurricane Sandy in 2012 at another BES study (Reisinger et al., 2017). Prior to the hurricane, suburban and urban streams were heterotrophic, where mean GPP was 0.70 and 1.80 g O_2 m^{-2} d^{-1}, and mean ER was 4.12 and 2.62 g O_2 m^{-2} d^{-1}, respectively. After the hurricane, the streams experienced significant decrease in metabolism, with GPP reductions of 84% in the suburban site, and 92% in the urban site. ER reductions were lower (72% in the suburban site and 86% in the urban site). It took around two weeks for metabolism rates to go back to pre-flood levels.

The study in Tennessee also looked at the metabolism responses to two different storms in a forested headwater stream (Roberts et al., 2007). A large spring storm suppressed both GPP and ER, with GPP taking a longer period to return to pre-flood levels. Photosynthetic efficiency (GPP/PAR) exhibited a similar behavior as GPP. ER rates decreased dramatically on the day of the storm likely as a result of the reduction in autotrophic activity. After the storm passed, ER rates recovered and even exceed pre-flood levels. This caused a decoupling of GPP and ER. The response patterns were reversed during an autumn storm. GPP rates increased after the storm because of increased light availably from the clearing of floating leaf material. GPP/PAR showed a similar pattern. ER was suppressed as a response to the autumn storm, although not as drastically as during the spring storm. This study is perhaps unique in the sense that it showed the effect of storms of different seasons on stream metabolism.

Isotopic Sourcing of Stream Nutrients

A BES study done to identify sources and transformations of N in Baltimore watersheds found export of total N as well as sample nitrate concentrations were highest in agricultural followed by exurban and urbanized watersheds, and lowest in the forested catchment (Kaushal et al., 2011). In the forested watershed, N derived from soil and rain, and in low density residential and agricultural watersheds, N derived from soil/fertilizer and wastewater. In contrast, significant contributions from wastewater and mixing with atmospheric sources were seen in urbanized watersheds. When looking at samples collected during three storm events at six locations, low to moderate flows presented isotope values within the wastewater range. Stormflow presented isotope values within the atmospheric deposition range. High stormflow presented isotope values within the soil and wastewater range, as well as some mixing with atmospheric sources of nitrate.

A study of nitrate sources in precipitation, stormwater, soil water, and groundwater found that precipitation samples collected in a subtropical stormwater infiltration basin located in a residential area indicated a strong atmospheric source of NO_3^- (O'Reilly et al., 2012). On the other hand, groundwater samples and one soil water sample were indicative of nitrification of one or more of the following: atmospheric or fertilizer derived NH_4^+, soil nitrogen or organic waste. Through a comparison of $\delta^{18}O[NO_3^-]$ and $\delta^{18}O[H_2O]$, these researchers were able to provide additional evidence that the nitrate oxygen in the water samples was derived from nitrification. This was possible from the knowledge that nitrifiers source oxygen in the following manner: In $NH4^+$ oxidation to NO_2^-, *Nitrosomonas* uses one oxygen from water and one from O_2, and in NO_2^- oxidation to NO_3^-, *Nitrobacter* uses one oxygen from water (Kendall, 1998).

A study in Connecticut of mixed land-use (including agricultural, urban, and suburban) river baseflow versus stormflow identified three nitrate sources: atmospheric deposition, microbial nitrification, and sewage (Anisfeld et al., 2007). Stormflow samples generally had lower $\delta^{15}N$ and higher $\delta^{18}O$ values than baseflow, indicating a weaker influence of sanitary effluent and stronger influence of atmospheric deposition. In addition, there was a weak relationship between land use and isotopic values.

Methods

Study Site

The study site is a 14 km^2 subsection of the Meadow Creek watershed in Charlottesville, VA. Charlottesville is in the upper Piedmont Plateau at the foothills of the Blue Ridge Mountains. The city is at the headwaters of the Rivanna River and is dominated by metamorphic rocks. The watershed is urban with 38% impervious area, including a mix of commercial, university, residential, and parkland land uses. Meadow Creek was classified as an impaired waterway by the Virginia Department of Environmental Quality, mainly due to excessive sedimentation from stream bank erosion caused by stormwater runoff. The catchment underwent a 3.95-million-dollar restoration, which aimed to stabilize the stream, improve water quality, and enhance aquatic and forested habitat (Nature Conservancy, 2013). Two sets of stream channel restoration were carried out in 2012 (referred to as old restoration), and then in 2020 (referred to as new restoration). Restoration practices included the creation of meanders and riffles/pool sequences, placement of large woody debris and boulders in the stream, revegetation of the banks, and floodplain reconnection.

The sites are characterized in table 1, and figures 1 through 3. There are seven stream sites, in addition to pond and wetland inlets and outlets. MC2 was originally one of the stream sites, but it was discontinued due to unreliable data collection conditions. MC1 is the headwater reach. It is within a lower density development area, composed of larger forest and lower impervious area. MC3 is within a popular disc golf course. The riparian area is highly vegetated, the stream is incised with steep, eroding banks. Although the stream channel at MC4 is straight, which is an urban stream characteristic, the banks are level with the floodplain. This makes stormflow dissipation into the floodplain much easier than at MC3. Further downstream, the channel restored through a series of constructed meanders and riffle/pool reaches through sites MC5, MC6, and MC7, with an interruption between sites MC5 and MC6. There is still active construction within MC5, which suppresses tree cover recovery. This most recent restoration section is represented by the site “MC5d” in our metabolism analysis, which is 200 meters downstream from MC5. Sites MC6 and MC7 are within a park where tree cover is present as this section has regrown from the 2012 restoration.

Table 1: Meadow Creek site characterizations. The numbers out of the parentheses are the individual subcatchment percentages. The numbers inside parentheses are percentages of the cumulative areas.

	Streams						
Land cover %	**MC1**	**MC2**	**MC3**	**MC4**	**MC5**	**MC6**	**MC7**
Impervious	13.7 (13.7)	24.8 (21.4)	38.2 (33.6)	32.3 (33.4)	46.1 (33.8)	43.5 (37.7)	14.3 (37.5)
Tree	74.5 (74.5)	51.2 (58.3)	41.8 (46.3)	48.6 (46.8)	37.8 (46.4)	39.7 (43.7)	64.3 (43.9)
Herbaceous	11.8 (11.8)	21.0 (18.2)	20.0 (19.5)	18.7 (19.4)	13.5 (19.1)	16.2 (17.9)	13.3 (17.9)
Pasture	0.0 (0.0)	0.4 (0.3)	0.0 (0.1)	0.0 (0.1)	0.0 (0.1)	0.0 (0.03)	0.0 (0.03)
Wetlands	0.0 (0.0)	2.6 (1.8)	0.0 (0.5)	0.4 (0.5)	1.0 (0.5)	0.4 (0.5)	6.1 (0.5)
Water	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	1.6 (0.1)	0.3 (0.2)	2.1 (0.2)
Soil type	fine sandy loam	loamy	silt loam	silt loam	silt loam	silt loam	silt loam
Flow path slope	0.002	0.001	0.003	-0.002	0.000	-0.013	0.000
Restoration Status	Unrestored	Unrestored	Unrestored	Unrestored	New Restored	Affected by Restoration	Old Restored
Additional Sites	**Pond:**	MC5Pin Inlet	MC5Pout Outlet	**Wetland:**	MC7Win Inlet	MC7Wout Oulet	MC6/7 Untreated Outlet

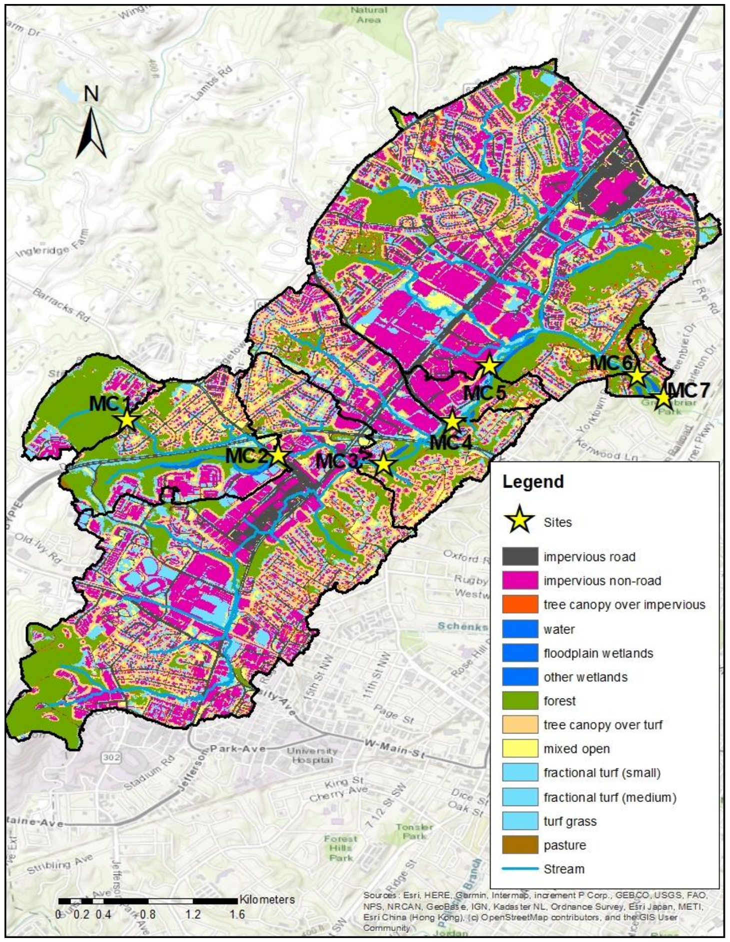

Figure 1: Meadow Creek subcatchments and sampling sites.

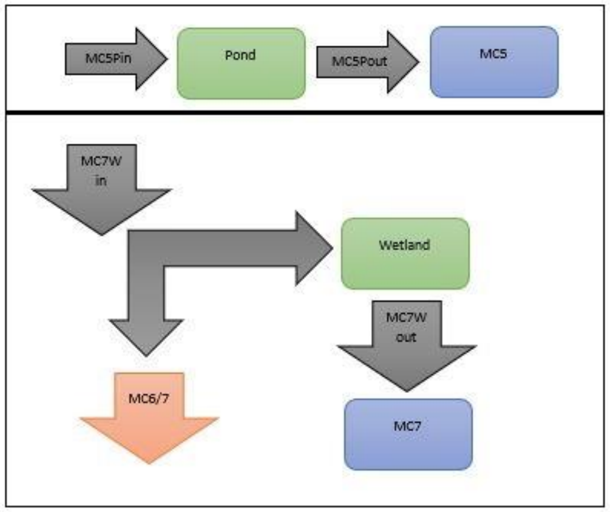

Figure 2: Schematic of the drainage positions of the pond sites (at the top), and wetland sites (at the bottom). Arrows represent inlets and outlets. The untreated outlet is illustrated by the red arrow. SCMs are illustrated by green rectangles, and the stream sites are illustrated by blue rectangles.

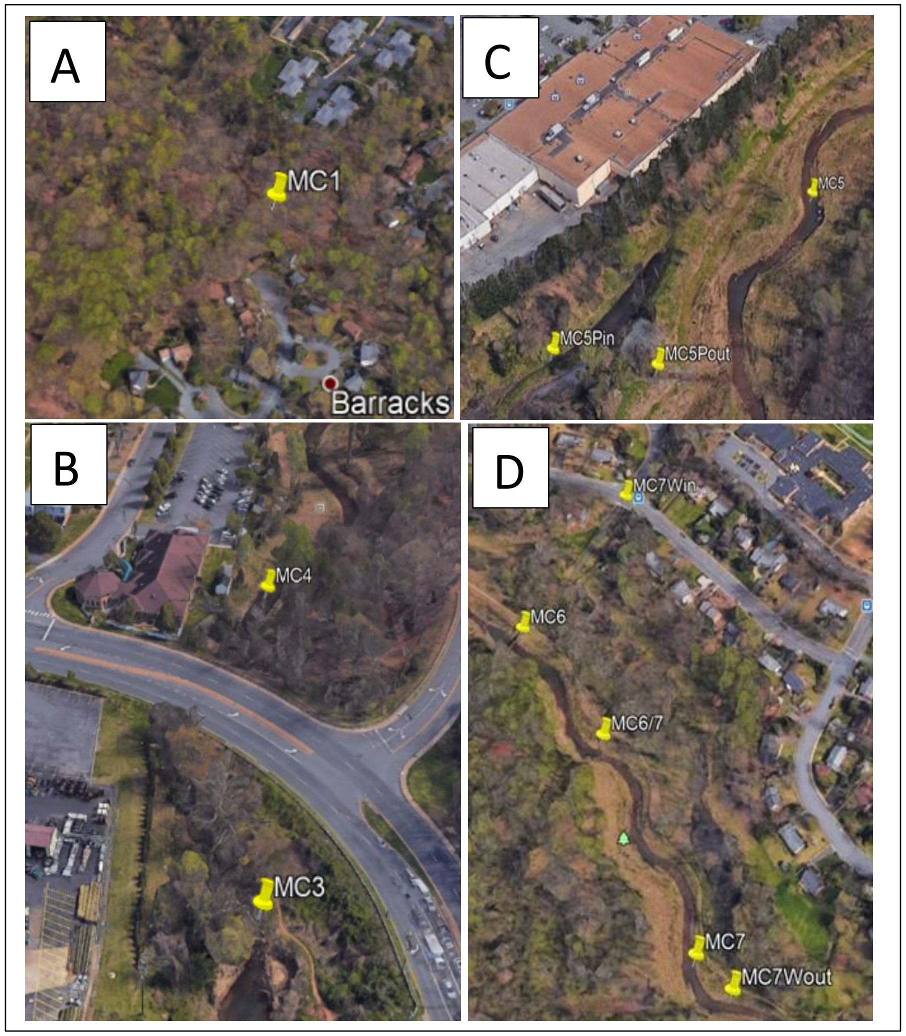

Figure 3: A) location of MC1. B) locations of MC3 and MC4. C) pond inlet and outlet locations relative to the stream station MC5. D) wetland inlet, outlet, as well as untreated outlet MC6/7, and nearby stream stations MC6 and MC7 (source: Google Earth).

Field Sampling

Field work started in November of 2019 and ended in January of 2021. We collected grab samples and measured streamflow at seven sites biweekly through the spring. We increased the sampling frequency to a weekly basis starting in the summer of 2020. Sample bags were rinsed with stream water three times, and then filled. Samples were filtered through a 0.45 µm GF or nylon filter. Centrifuge tubes were rinsed three times with filtered water, and then filled up to the 45 mL mark. Water samples were stored frozen and later run locally on a Lachat nutrient analyzer (NH_4^+ detection range: 0.36 to 42.86 µM N/L. PO_4^{3-} detection range: 0.16 to 12.91 µM P/L. NO_2^- + NO_3^- detection range:0.36 to 28.6 µM N/L). Duplicates were collected every other week starting in April of 2020. These were collected, filtered, and stored according to the same protocol described above, and some were selected for isotopic analysis in a manner to best represent the range of discharges in the dataset.

These were sent to The Regional Stable Isotope Lab for Earth and Environmental Science Research in Pittsburgh, Pennsylvania, for analysis of $\delta^{15}N$ and $\delta^{18}O$.

Streamflow was measured with a Sontek Flow Tracker 2 (SonTek FlowTracker 2 (FT2) handheld Acoustic Doppler Velocimeter (ADV®) | Xylem Singapore) using the velocity-area method. The channel cross section was divided into 3-10 subsections of equal width depending on each channel size. Midpoint water depth was recorded, and midpoint velocity was measured at 0.4 depth of each subsection. The Flow Tracker calculates individual discharge as $area_{subsection}$ x $velocity_{subsection}$. Total stream discharge was calculated as the summation of all subsection discharges. Throughout the research period, rating curves were developed for each site by plotting measured discharges versus water levels. These rating curves were fit with 2nd order polynomial regressions and were used to estimate discharge when there was sufficient data to develop a strong r^2 (>0.8).

Sites were selected to represent the unrestored (MC4), new restored (MC5d), and old restored (MC7) stream sections. Water level and temperature, dissolved oxygen, conductivity, and photosynthetically active radiation HOBO data loggers (www.onsetcomp.com) were deployed to record at a 15 minute interval at each site. One pressure transducer remained suspended in air and measure atmospheric pressure to represent such parameter for all sites. Sensor data was downloaded every two weeks. Dissolved oxygen and conductivity sensors were calibrated each time after download. Instrumentation was cleaned and maintained at each site visit.

Data Processing and Analysis

We note that all restored sites are downstream, and all unrestored sites are upstream, and therefore results reflect both local conditions and downstream evolution of stream chemistry and ecosystem conditions. Throughout the data collection period, we had a few problematic sites that caused difficulty in obtaining reliable discharge measurements. The analysis of nutrient load was only done for periods with reliable discharge data.

Nutrient loads (mg s^{-1}) were calculated as nutrient concentrations (mg L^{-1}) x 1000 (L m^{-3}) x discharge (m^3 s^{-1}) and normalized by upstream area to overcome the impact of downstream increase in discharge. Segment loads/concentrations/discharge changes in between each stream section as well as pond and wetland sites were calculated by subtracting the load/concentration/discharge of the downstream site from the load/concentration/discharge of the site directly upstream. These results were plotted to show periods of nutrient increases and decreases from site to site. As a quality control measure, for the stream sites, only data for periods of positive segment discharge were analyzed. In addition, baseflow nitrate + nitrite mean concentrations as well as loads were plotted for the stream sites against cumulative percent impervious, and cumulative percent tree cover to analyze land use effects. However, there is little variation in segment land cover from MC3 to MC7, so the sampling design does not support the analysis of the land use effect well.

To answer research question 1 (How do dissolved inorganic nitrogen (DIN) concentrations and loads evolve downstream through mixed land use catchments, stormwater control measures (SCMs), restored versus unrestored stream sections, between flow conditions, and among seasons?), mixed ANOVAs were run on the baseflow untransformed nitrate + nitrite concentrations as well as logarithmic transformed loads of the stream sites (MC1, MC3, MC4, MC5, MC6, and MC7) to test for differences in nutrient distributions by the site, season, and the interaction between site and season. An orthogonal comparison between restored versus unrestored sites was also run. For the SCMs analysis, we tested for differences in nutrient distribution by site and season at the pond sites with a mixed ANOVA on the square root transformed baseflow nitrate + nitrite concentrations. The ANOVA had contrast statements to analyze the following: 1) Pond outlet (MC5Pout) versus pond inlet (MC5Pin). 2) Pond outlet versus the stream reach immediately downstream (MC5). These comparisons were not orthogonal, and the p-value was adjusted to 0.025. Nonparametric statistics do not estimate means or variances, instead, they rank data in some way to evaluate differences in location. A Kruskal-Wallis test was performed on the baseflow nutrient loads, which is a direct analog to a parametric ANOVA. Another Kruskal-Wallis analysis of variance was run on the baseflow nitrate + nitrite concentrations to test for differences in distribution at the wetland inlet (MC7Win), outlet that does not pass through the wetland and is therefore considered to lack biologic treatment (MC6/7), wetland treated outlet (MC7Wout), and stream reach immediately downstream from the outlets and adjacent to wetland (MC7).The discharge data at the wetland sites were often so low as to be unmeasurable. When that was the case, the wetland output was effectively zero, indicating complete loss as surface flow. This prevented us from conducting a nutrient load analysis.

To answer research question 2 (What are the nitrate sources from different subcatchments at different flow conditions?) nitrate derived nitrogen and oxygen isotope values for five baseflow collection dates, and two stormflow dates, including Hurricane Laura, at all stream sites and pond sites were compared to known isotope ranges taken from Zhang et al. (2019), and against denitrification lines. Our $\delta^{18}O$ values were all lower than 14‰, which put us in the nitrogen fertilizer, soil organic nitrogen, and sewage isotope ranges. There is some overlap as well as local variation in these different categories.

To answer research question 3 (How do gross primary productivity (GPP) and ecosystem respiration (ER) patterns vary downstream among unrestored and restored sites of different restoration ages, and how do these influence nitrate concentrations and loads?), sensor derived

DO, salinity (converted from conductivity), water temperature, discharge, and PAR data were used as input in the Bayesian Single-Station estimation (BASE) model package in RStudio to generate gross primary productivity and ecosystem respiration at the three instrumented sites (MC4, MC5d, and MC7) for baseflow conditions. BASE estimates single-station whole-ecosystem rates of metabolism in a Bayesian framework. BASE assumes steady discharge. In addition, no other physical processes are assumed to contribute to change in DO, such as inputs from tributaries or groundwater with different DO concentrations (Grace et al., 2015).

Mean daily GPP and ER values that were over three standard deviations were removed, as well as extreme low values that were induced by storms as the assumption of steady flow precludes analyzing stormflow. The model outputs GPP and ER values in units of $mgO_2\ L^{-1}d^{-1}$. These were multiplied by the mean daily water level in meters to obtain GPP and ER in areal rates ($gO_2\ m^{-2}d^{-1}$), which allows for a comparison between sites. To test for differences in GPP distribution by site and season, a mixed ANOVA was run on the square root transformed GPP. Contrast statements were run to analyze the following: 1) Unrestored site (MC4) versus restored sites (MC5d and MC7). 2) New restored (MC5d) versus old restored site (MC7). These comparisons were orthogonal. A Kruskal-Wallis analysis of variance was run to test for all pairwise comparisons of ER scores. GPP/ER ratios were calculated for each site. This ratio allows us to understand whether a stream reach is autotrophic or heterotrophic. In addition, we produced a monthly average analysis of the three months of the fall season on GPP and ER to investigate the effect of leaf on/leaf off cycle on stream metabolism.

Results

Data Distribution at the Stream Sites

An overall nutrient concentration dilution pattern is seen as discharge increases at all sites (figure 4). Note that most storms occurred in the summer and fall; therefore, the baseflow to stormflow concentration transitions are clearer for these seasons. MC1 concentrations resembles semi-log reduction pattern with peak concentration of 0.89 mg L^{-1} in the summer. MC3, MC4, and MC5 plots have an envelope pattern, with peak concentrations in the winter of 1.05 mg L^{-1} at 0.99 mm day^{-1} at MC3, 1.04 mg L^{-1} at 0.78 mm day^{-1} at MC4, and 0.99 mg L^{-1} at 0.59 mm day^{-1} at MC5, excluding outliers. The MC3 and MC4 outliers happened on the same day of 07/22/2020 (summer) and may have been diluted by the time it reached MC5. The plots for MC6 and MC7 are more scattered. Peak concentrations of 0.88 mg L^{-1} at 0.46 mm day^{-1} at MC6, and 0.87 mg L^{-1} at 0.82 mm day^{-1} at MC7 are seen in the winter, excluding a fall outlier on 12/17/2020 of 0.90 mg L^{-1}. This decreasing trend with a maximum concentration of around 1 mg L^{-1} is similar to patterns seen in sites from the Baltimore Ecosystem Study (BES) such as Duncan et al., (2017).

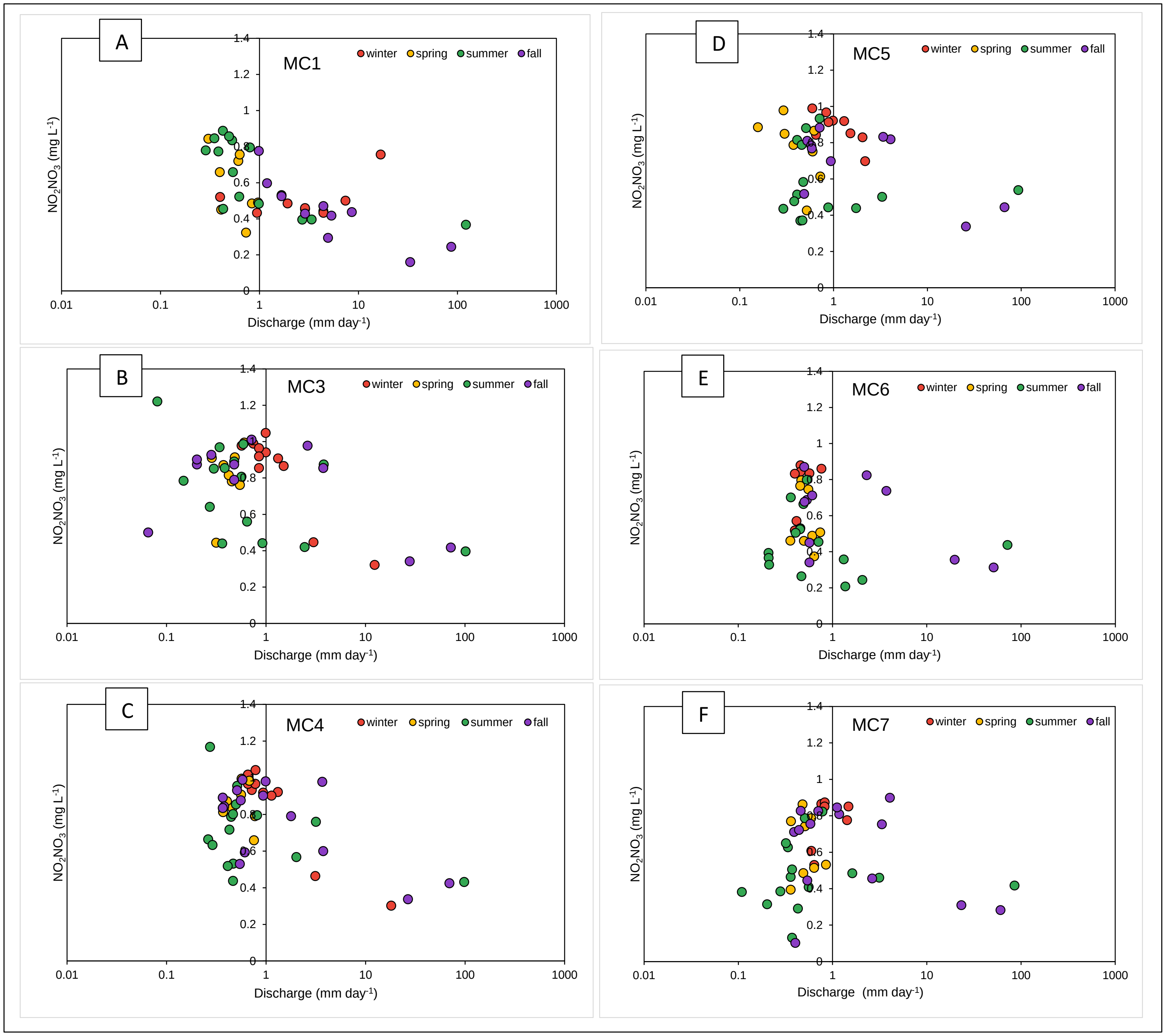

Figure 4: Nitrate + nitrite concentrations versus discharge on a logarithmic scale at A) MC1 B) MC3 C) MC4 D) MC5 E) MC6 F) MC7 from 11/22/2019 to 01/25/2021 in the winter (red), spring (yellow), summer (green), and fall (purple).

In plots of segment changes in load/concentrations (figure 5) , negative numbers indicate a load/concentration reduction in the downstream direction, while positive numbers indicate a load/concentration increase. All data in the unrestored section between sites MC1 and MC3 (e.g., load at MC3 minus load at MC1, which is represented as MC3-MC1) present a load increase, which agrees with the segment concentration trend in which 90.3% of the data present an increase. 89.7% of the data in the unrestored section between sites MC3 and MC4 (MC4-MC3) present a load increase despite 58.6% of the segment concentration data presenting a reduction.

76.5% of the data in the new restored section between sites MC4 and MC5 (MC5-MC4) present a load increase despite 64.7% of the segment concentration data presenting a reduction. 90% of the data in the section affected by restoration between MC5 and MC6 (MC6-MC5) present a load increase with 70% of the segment concentration data presenting a reduction. Finally, 90.9% of the data in the old restored section between MC6 and MC7 (MC7-MC6) present a load increase, which agrees with the segment concentration trend, in which 63.6% of the data present an increase. More detail can be found in table 2.

Table 2: Segment concentration and load change.

Segment	Concentration 10th Percentile (mg L^{-1})	Concentration 90th Percentile (mg L^{-1})	Load 10th Percentile (mg s^{-1} km^{-2})	Load 90th Percentile (mg s^{-1} km^{-2})
MC3-MC1	0.006	0.51	1.5	10.5
MC4-MC3	-0.107	0.078	0.34	23.6
MC5-MC4	-0.24	0.12	-6.6	37.8
MC6-MC5	-0.45	0.086	-0.18	7.57
MC7-MC6	-0.07	0.33	31.6	730

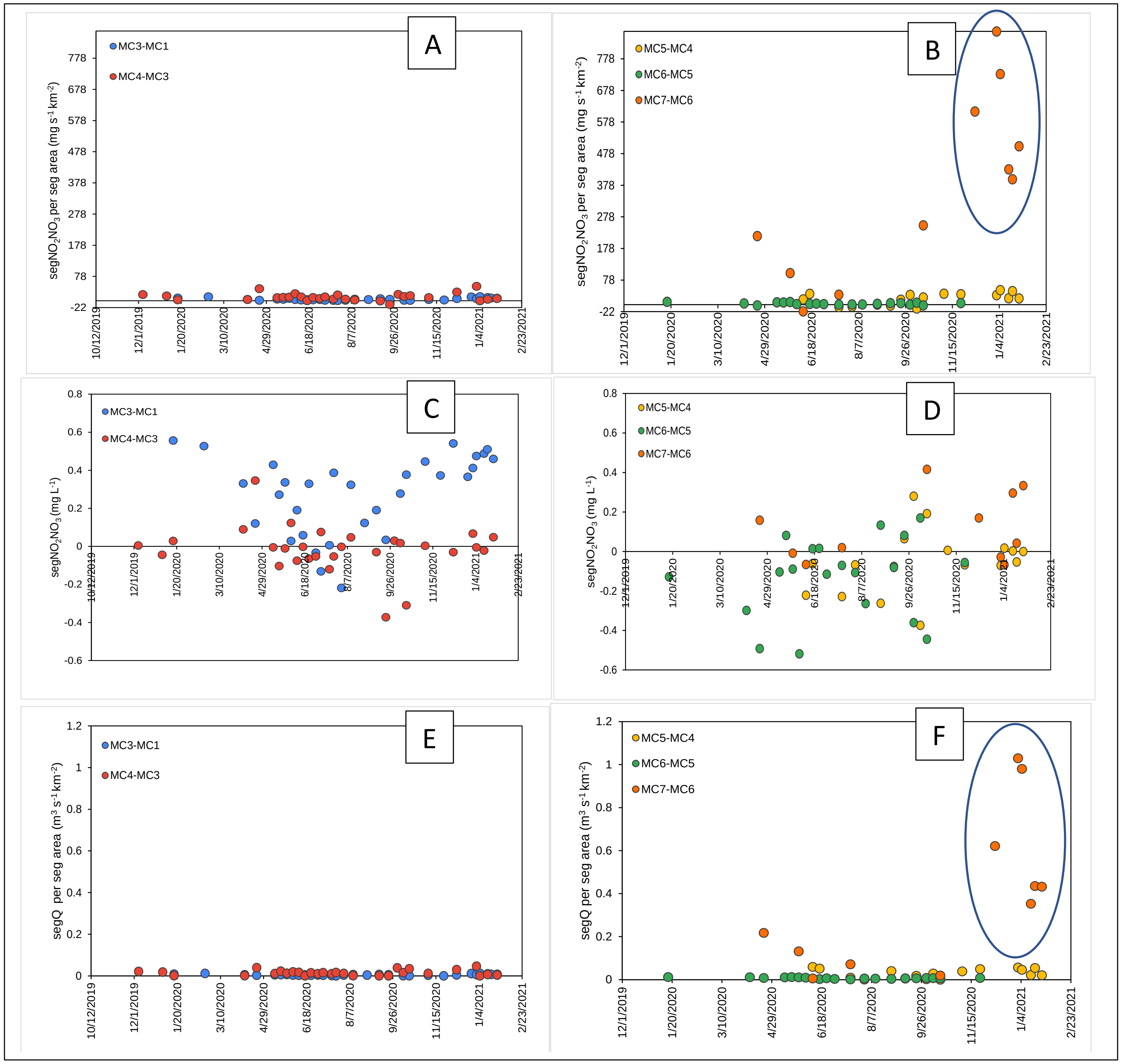

Figure 5: Baseflow segment A & B) loads C & D) concentrations E & F) discharges at the unrestored (MC3-MC1 and MC4-MC3) and restored (MC5-MC4, MC6-MC5, and MC7-MC6) stream sections. High values that stand out in the segment MC7-MC6 are circled.

Nutrient Concentrations and Loads at the Stream Sites

Site MC3 has the largest decrease in nitrate concentration at stormflow discharges, while MC7 has the lowest decrease (figure 6). There is a general pattern between the interaction of season and restoration status at the stream sites (figure 7). Restored sites show decreased mean nitrate + nitrite concentrations throughout all seasons except in the winter compared to unrestored means. The largest difference is seen in the summer, when the restored mean is 0.26 mg L^{-1} (33.8%) lower than the unrestored mean. The smallest difference is seen in the winter, when the restored mean is 0.03 mg L^{-1} (3.8%) greater than the unrestored mean. At the restored sites, the lowest mean concentration is seen in the summer (0.51 mg L^{-1}), while the highest mean is seen in the winter (0.82 mg L^{-1}). At the unrestored sites, the lowest mean concentration is seen in the spring (0.75 mg L^{-1}), and the highest mean is seen in the winter (0.79 mg L^{-1}). The statistical analysis is presented in table 3. The seasonal trend is maintained throughout sites when the dependent variable is changed to load. However, normalized restored load means are higher than unrestored loads at all seasons except in the summer. The normalized loads that have the highest weight in these results are likely the ones from MC5 and MC7 (figure 6). The statistical analysis is presented in table 4.

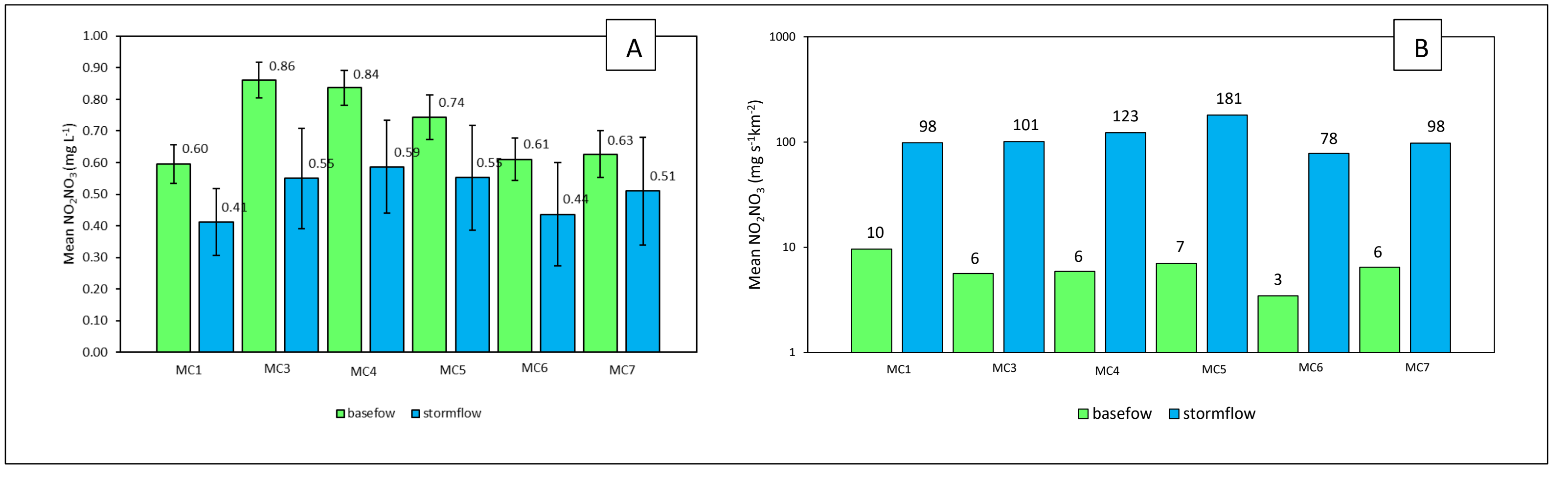

Figure 6: Mean baseflow and stormflow nitrate + nitrite A) concentrations B) loads per unit area on a logarithmic scale at the stream sites. The labeled numbers are the means, and the error bars represent the 95% confidence intervals.

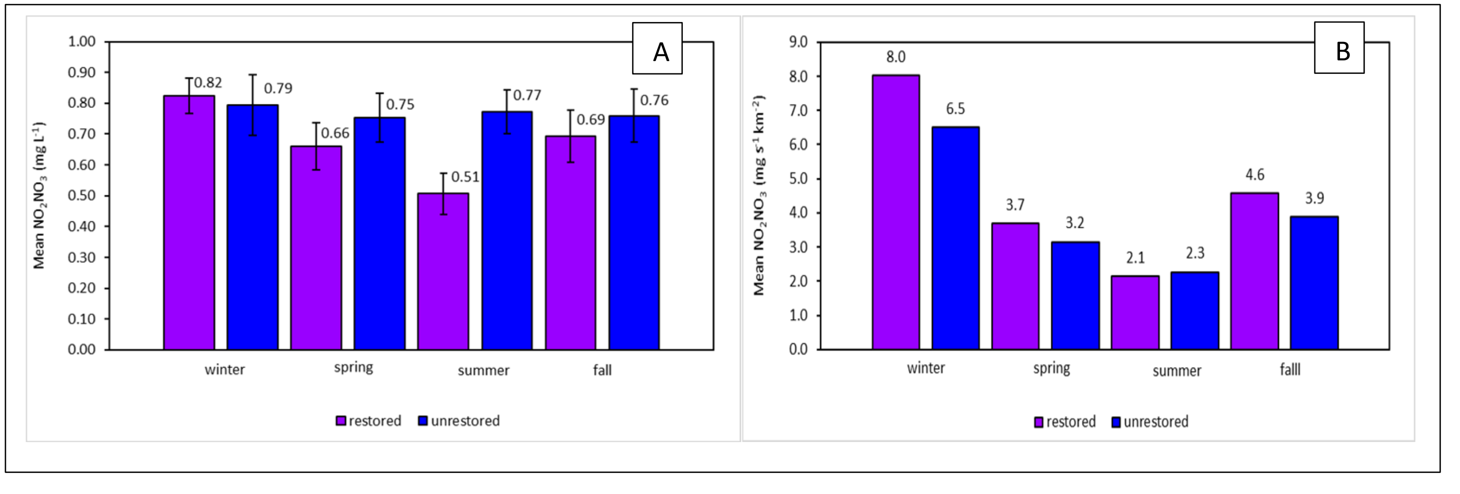

Figure 7: Combined effect of season and restoration on mean baseflow nitrate + nitrite A) concentrations B) loads per unit area at the stream sites. The labeled numbers are the means, and the error bars represent the 95% confidence intervals.

Table 3: Statistical analysis of baseflow nitrate + nitrite concentrations at the stream sites. The star represents the interaction between the two effects.

Effect	P-value	Contrast Statement	P-value	Mean (mg L^{-1})
Site	<0.0001	Unrestored v. Restored	0.0001	0.77 v. 0.66
Season	0.0006	New Restored v. Old Restored	0.003	0.74 v. 0.63
Site*Season	0.0001			

Table 4: Statistical analysis of baseflow nitrate + nitrite loads at the stream sites. The star represents the interaction between the two effects.

Effect	P-value	Contrast Statement	P-value	Mean (mg s^{-1})
Site	<0.0001	Unrestored v. Restored	0.0215	29.7 v. 63.7
Season	0.0018	New Restored v. Old Restored	0.0112	58 v. 90
Site*Season	0.0107			

In terms of land use, MC1 has significantly lower cumulative impervious cover (13.7%) and higher cumulative tree cover (74.5%) compared to the other sites (figure 8). Sites MC3, MC4, and MC5 are within a close range for both cumulative impervious cover (33.4% to 33.8%), and cumulative tree cover (46.3% to 46.8%). MC6 and MC7 have the highest cumulative impervious percentages (37.7% and 37.5%), and the lowest cumulative tree cover percentages (43.7% and 43.9%). Mean nitrate concentrations are lowest at MC1 (0.60 mg L^{-1}), increase at MC3 through MC5 (0.74 mg L^{-1} to 0.86 mg L^{-1}) and drop at MC6 and MC7 to concentration levels similar to MC1. This happens despite MC6 and MC7 having cumulative impervious percentages of over twice the percentage at MC1, and tree cover approximately 1.7 times lower.

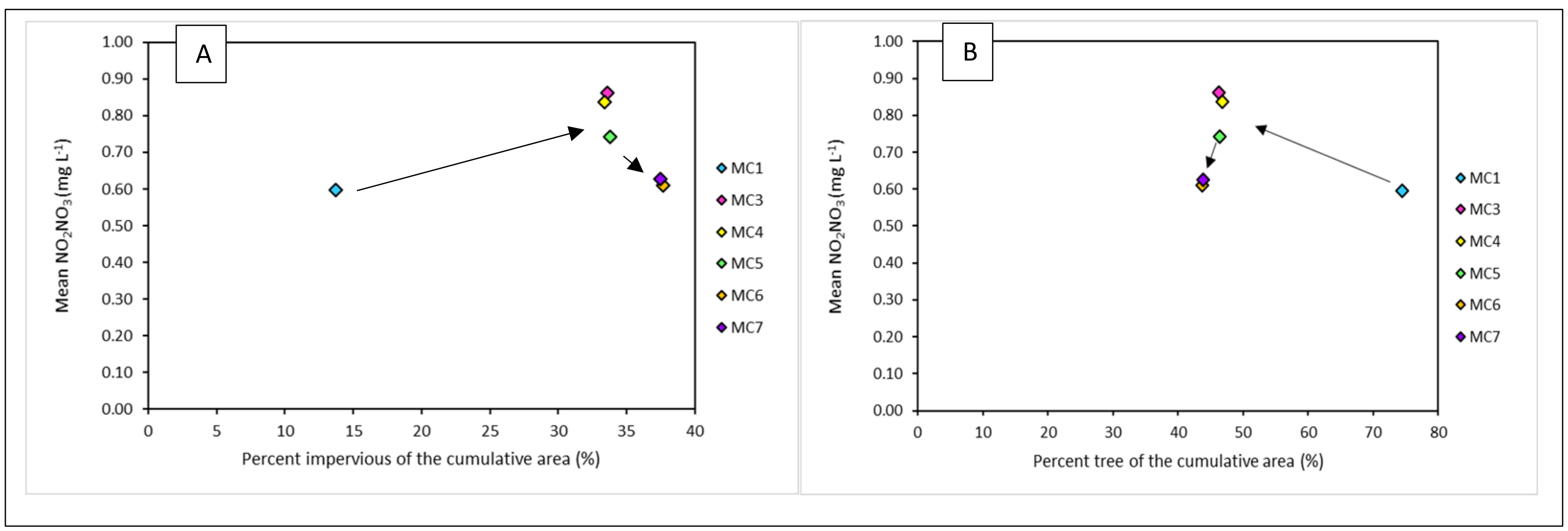

Figure 8: Mean baseflow nitrate + nitrite concentrations versus A) percent impervious B) percent tree cover of the cumulative areas draining to the stream sites.

Nutrient Concentrations and Loads at the Pond Sites

The pond outlet has the largest decrease in nitrate concentration at stormflow discharges, with a 49.7% decrease from mean baseflow concentration to mean stormflow concentration (figure 9). There is a 43.4% decrease from mean baseflow to mean stormflow at the inlet, and a decrease of 21% at MC5. The MC5 stormflow mean differs slightly from figure 6 because that figure has three additional sampling dates (11/22/19, 08/29/20, and 08/31/20) in which no samples were collected for MC5Pin and MC5Pout. Therefore, these were not included in this part of the analysis.

A general seasonal pattern of nitrate + nitrite concentrations and loads can be observed in these sites (figure 10) . Mean concentrations peak in the winter at MC5 (0.93 mg L^{-1}) and MC5Pin (0.62 mg L^{-1}). Peak concentration at MC5Pout is seen in the spring (0.48 mg L^{-1}), and the second highest value occurred in the winter (0.45 mg L^{-1}). The lowest concentrations are seen in the summer at all sites (0.57 mg L^{-1} at MC5, 0.54 mg L^{-1} at MC5Pin, and 0.36 mg L^{-1} at MC5Pout). At MC5 and MC5Pin mean concentrations progressively decrease from the winter through the summer, then start to recover in the fall. The statistical analysis is presented in table 5. Loads at MC5 also show a similar decreasing seasonal trend. In contrast, MC5Pin shows a mean load higher in the spring compared to the winter. This is a reflection of a slightly higher spring discharge (~0.005 m^3 s^{-1}) compared to winter discharge (~0.004 m^3 s^{-1}). The seasonal trend changes completely at MC5Pout. The mean loads decrease throughout the seasons. This is a reflection of the overall decreasing seasonal discharge (winter: ~0.011 m^3 s^{-1}, spring: ~0.003 m^3 s^{-1}, summer: ~0.003 m^3 s^{-1}, and fall: 0.001 m^3 s^{-1}). The statistical analysis is presented in table 6.

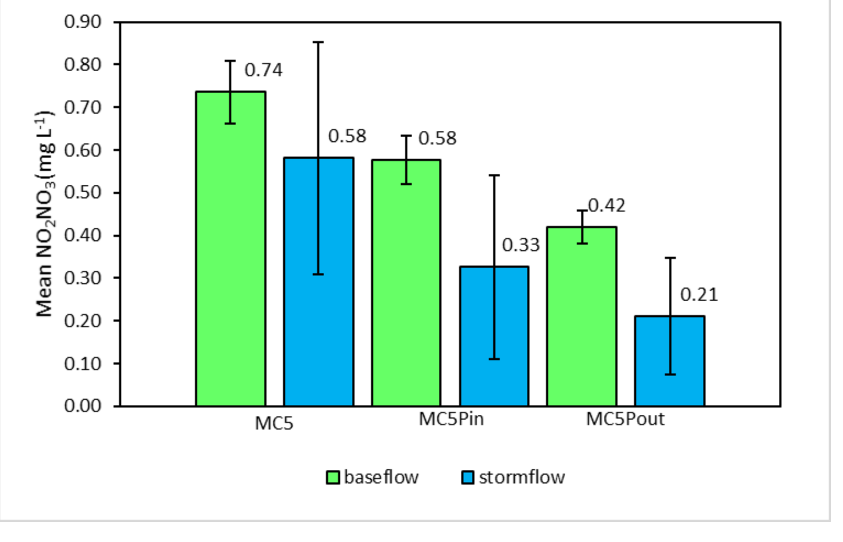

Figure 9: Mean baseflow and stormflow nitrate + nitrite concentrations at the pond sites. The labeled numbers are the means, and the error bars represent the 95% confidence intervals.

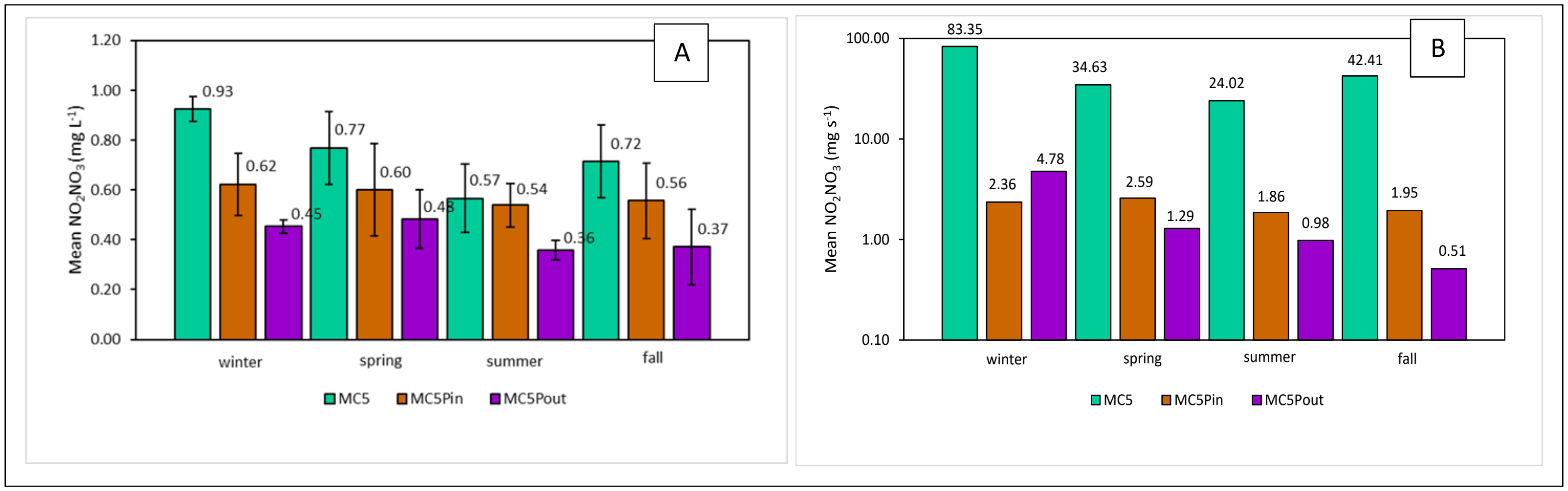

Figure 10: Effect of season on mean baseflow nitrate + nitrite A) concentrations B) loads on a logarithmic scale at the pond sites. The labeled numbers are the means, and the error bars represent the 95% confidence intervals.

Table 5: Statistical analysis of baseflow nitrate + nitrite concentrations at the pond sites. The star represents the interaction between the two effects.

Effect	P-value	Contrast Statement	P-value	Mean (mg L^{-1})
Site	<0.0001	MC5Pout v. MC5Pin	<0.0001	0.42 v. 0.58
Season	0.0008	MC5Pout v. MC5	<0.0001	0.42 v. 0.74
Site*Season	0.2618			

Table 6: Statistical analysis of baseflow nitrate + nitrite loads at the pond sites.

Contrast Statement	P-value	Wilcoxon Scores
MC5 v. MC5Pin	<0.0001	72.8 v. 38.5
MC5 v. MC5Pout	<0.0001	72.8 v. 21.3
MC5Pin v. MC5Pout	0.0003	38.5 v. 21.3

The segment graphs (figure 11) show incremental load and concentration increases/reductions from pond inlet to outlet. Note that negative segment discharges may indicate pond infiltration losses. It is important to point out that the discharge at MC5Pout at baseflow conditions is about 0.67% the baseflow discharge at MC5. At stormflow conditions, the discharge at MC5Pout is about 2.6% the stormflow discharge at MC5. Therefore, the effect of any biological treatment from just one pond on MC5 is limited.

96.3% of the segment load data present a reduction from MC5Pin to MC5Pout. The 90th percentile is -0.37 mg s^{-1}, while the 10th percentile is -2.1 mg s^{-1}. This is due to both the segment discharge and segment concentration data being mostly negative (81.5%). As far as segment concentration change, the 90th percentile is 0.05 mg L^{-1}, while the 10th percentile is -0.31 mg L^{-1}.

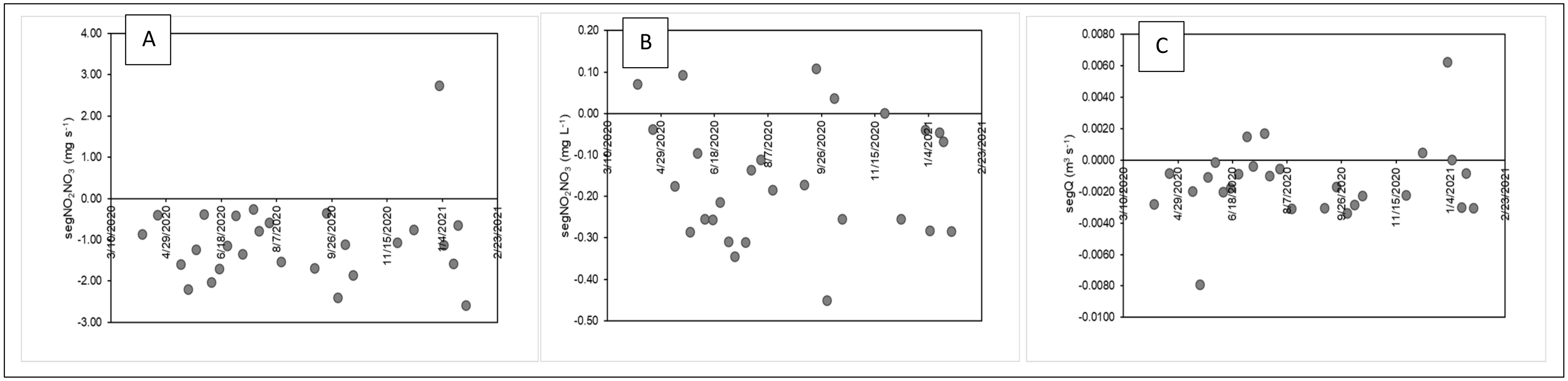

Figure 11: Baseflow segment A) loads B) concentrations C) discharges at the pond sites (MC5Pout-MC5Pin). Negative discharge numbers indicate that the pond is infiltrating water.

Nutrient Concentrations at the Wetland Sites

MC7Win and MC7Wout have unusual concentration patterns with discharge, showing 49.9% and 710.6% increases in mean stormflow concentrations compared to mean baseflow concentrations (figure 12). Large decrease in nitrate + nitrite concentration at stormflow discharges is seen at MC6/7 (58.6%). MC7 shows a decrease of 10.3%. Note that the stormflow sample size is 7 for each site compared to sample sizes of up to 31 at baseflow conditions. This caused wide stormflow 95% confidence intervals. The MC7 means shown in this figure differ from figure 6 due to three additional sampling dates (12/06/19, 08/31/20, and 09/18/20) in which no samples were collected for MC7Win, MC6/7 and MC7Wout. Therefore, these were not included in this part of the analysis.

In terms of the seasonal analysis, the sample sizes for MC7Win in the fall (n=5) and MC7Wout in the spring (n=2) impose constraints to the interpretation of the results (figure 13). MC7Win was moved upstream mid-fall for logistical reasons, which may contribute to the large confidence interval. The wetland was dry for a large portion of the spring, which prevented further sampling. The same decreasing concentration trend from winter to summer with a recovery in the fall that was discussed in previous sections is seen at MC7Win, and again at MC7. MC7Wout does not present a seasonal pattern. This site seems to stay at constant low levels throughout the year, with a slight increase in the spring mean.

MC6/7 presents a decreasing trend from spring to fall. The statistical analysis is presented in table 7.

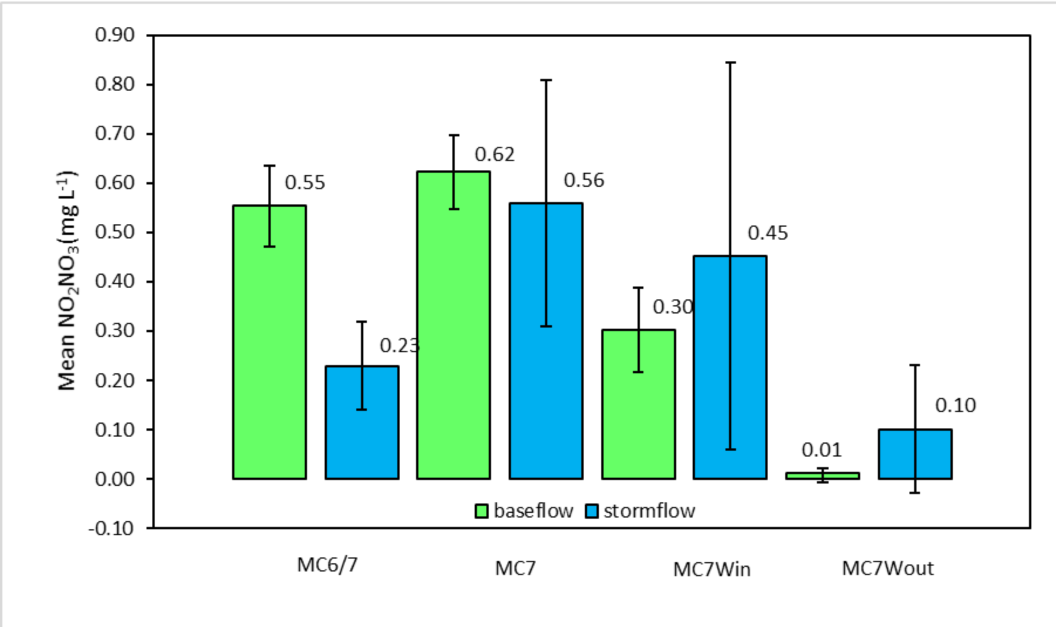

Figure 12: Mean baseflow and stormflow nitrate + nitrite concentrations at the wetland sites. The labeled numbers are the means, and the error bars represent the 95% confidence intervals.

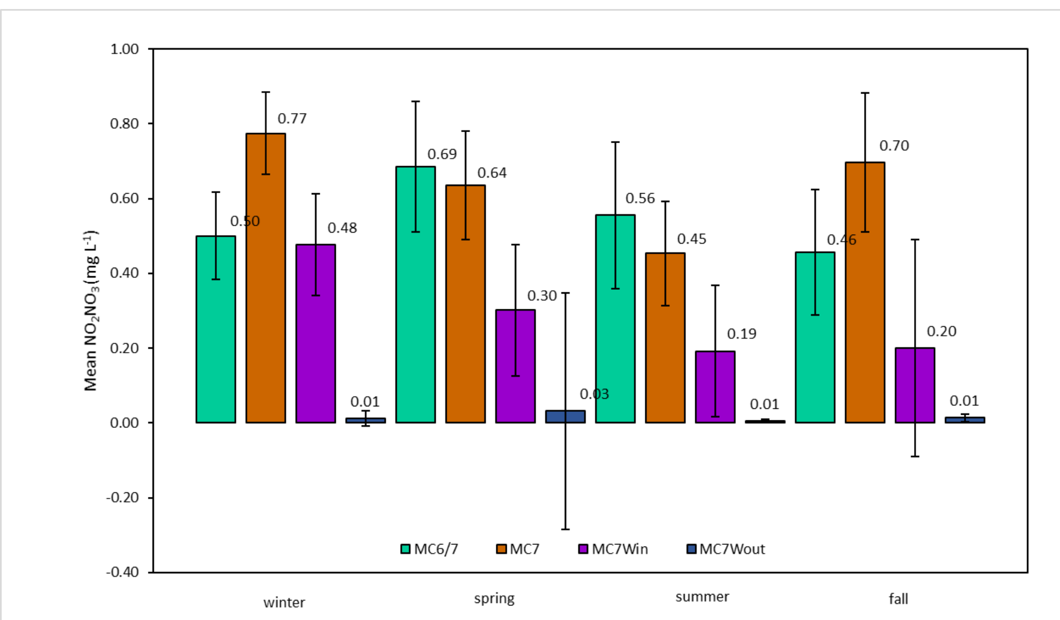

Figure 13: Effect of season on mean baseflow nitrate + nitrite concentrations at the wetland sites. The labeled numbers are the means, and the error bars represent the 95% confidence intervals.

Table 7: Statistical analysis of baseflow nitrate + nitrite concentrations at the wetland sites.

Contrast Statement	P-value	Wilcoxon Scores
MC6/7 v. MC7	0.5768	71.1 v. 78.7
MC6/7 v. MC7Win	0.0016	71.1 v. 47.1
MC6/7 v. MC7Wout	<0.0001	71.1 v. 12.3
MC7 v. MC7Win	<0.0001	78.7 v. 47.1
MC7 v. MC7Wout	<0.0001	78.7 v. 12.3
MC7Win v. MC7Wout	<0.0001	47.1 v. 12.3

Again, the goal of the segment graph is to identify incremental concentration reduction and increase from inlet (MC7Win) to untreated outlet (MC6/7) and treated outlet (MC7Wout) (figure 14). It is important to point out that the discharge at MC6/7 varies from 0.02% to 0.07% the discharge at MC7. The discharge at MC7Wout varies from 0.004% to 0.03% the discharge at MC7. Therefore, the effect of any nitrification from MC6/7 or biological treatment from the wetland on MC7 is limited but may be expanded by development of similar sites.

80% of the concentrations at the outlet MC6/7 are enriched in nitrate + nitrite compared to the concentrations at the inlet MC7Win. The 90th percentile is 0.67 mg L^{-1}, while the 10th percentile is -0.05 mg L^{-1}. By comparison, 95% of the concentrations at the outlet MC7Wout are lower than concentrations at the inlet MC7Win. The 90th percentile is -0.019 mg L^{-1}, while the 10th percentile is -0.54 mg L^{-1}.

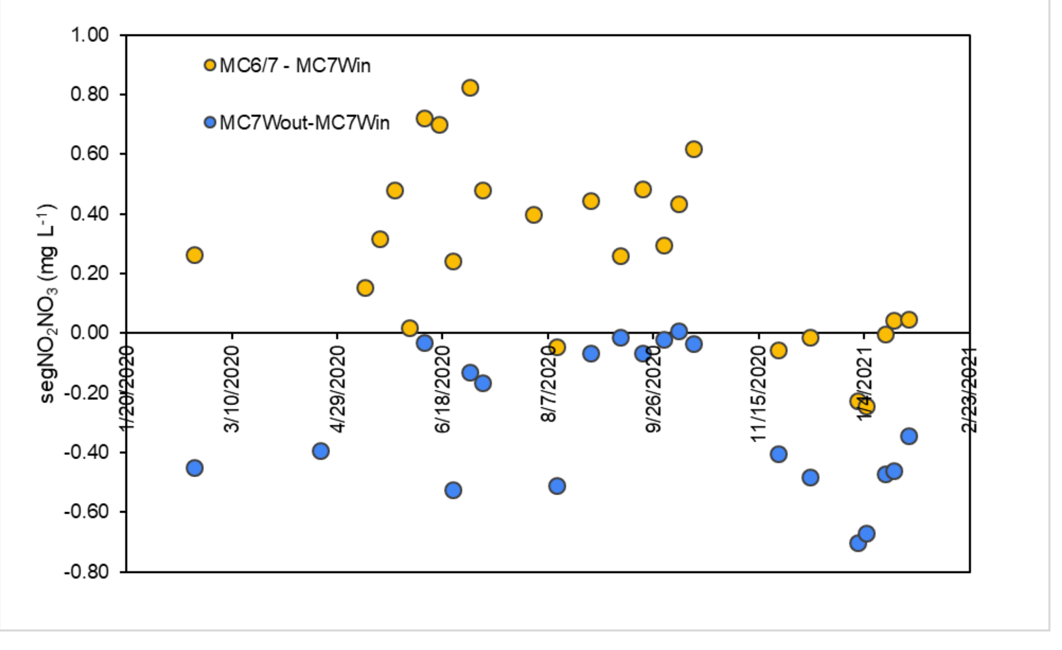

Figure 14: Baseflow segment concentrations at the wetland sites.

Isotope Nutrient Sourcing Analysis

The result from the isotopic analysis for five baseflow events, and two stormflow events with one being Hurricane Laura (8/31/2020) is shown in figures 15 and 16, and table 8. Sewage is the most abundant nitrate source at baseflow conditions. At the moderate storm event (8/29/2020), MC1 maintains the sewage signal, MC3 still presents sewage, but it becomes mixed with fertilizer and soil. MC4, MC5, MC6, and MC7 no longer present sewage signal, but only fertilizer and soil. Hurricane flows are up to three orders of magnitude higher than the moderate flows (figure 16). All of these samples consist of fertilizer and soil only, with negligible sewage presence.

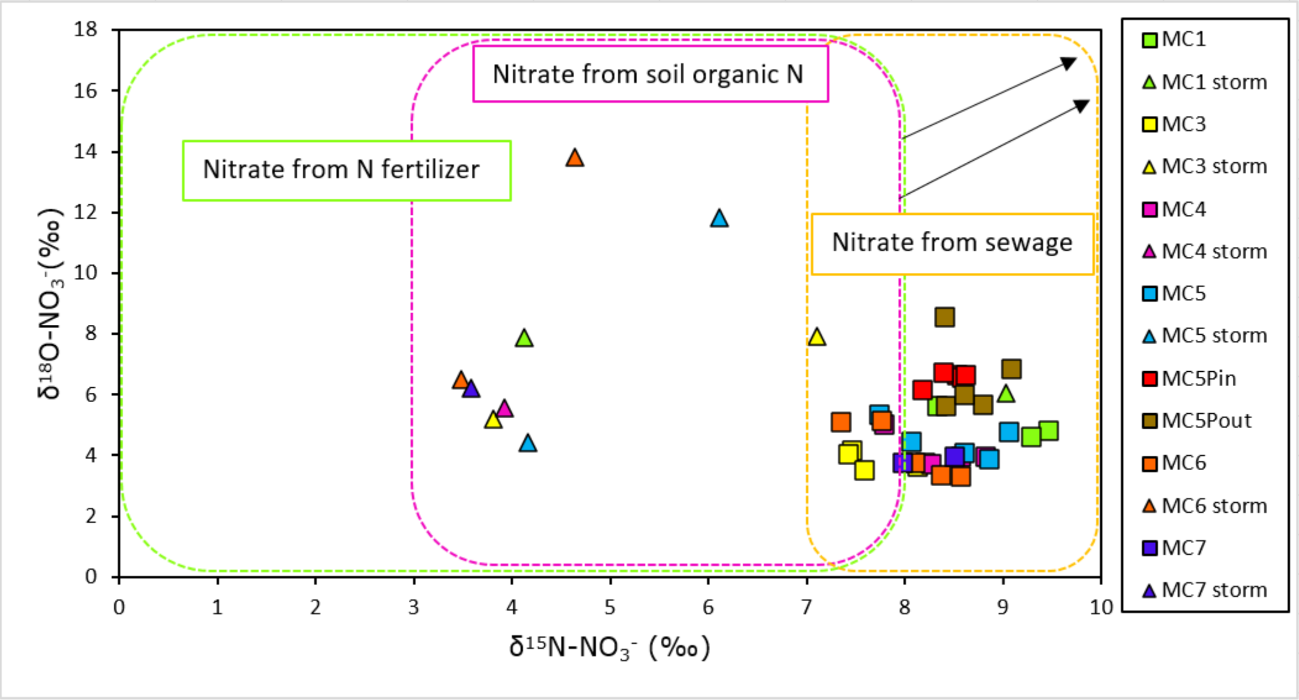

Figure 15: Distribution of $\delta^{15}N$ and $\delta^{18}O$ from different nitrate sources. The isotope ranges and denitrification lines were taken from Zhang et al., 2019.

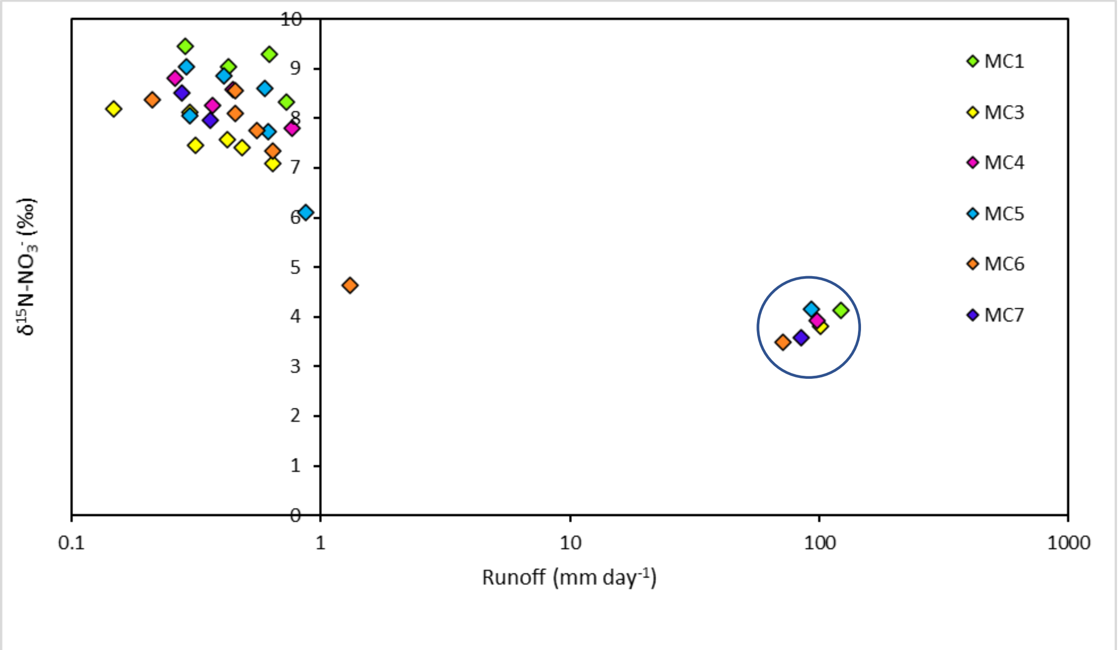

Figure 16: Distribution of $\delta^{15}N$ across different discharge rates on a logarithmic scale. Hurricane samples are circled.

Table 8: Number of samples for each nitrate source. The star represents the intersection between signals.

Site	Flow Type	Isotopic Signal	Number of Samples
MC1	Baseflow	Sewage	All
MC3	Baseflow	Sewage	2
MC4	Baseflow	Sewage	3
MC5	Baseflow	Sewage	4
MC5Pin	Baseflow	Sewage	All
MC5Pout	Baseflow	Sewage	All
MC6	Baseflow	Sewage	3
MC7	Baseflow	Sewage	1
MC3	Baseflow	Fertilizer*Soil*Sewage	3
MC4	Baseflow	Fertilizer*Soil*Sewage	1
MC5	Baseflow	Fertilizer*Soil*Sewage	1
MC6	Baseflow	Fertilizer*Soil*Sewage	2
MC7	Baseflow	Fertilizer*Soil*Sewage	1
MC1	Stormflow	Fertilizer*Soil	1
MC3	Stormflow	Fertilizer*Soil	1
MC4	Stormflow	Fertilizer*Soil	All
MC5	Stormflow	Fertilizer*Soil	All
MC6	Stormflow	Fertilizer*Soil	All
MC7	Stormflow	Fertilizer*Soil	All
MC1	Stormflow	Sewage	1
MC3	Stormflow	Fertilizer*Soil*Sewage	1

Stream Metabolism Analysis

Mean GPP is the highest in the summer at all sites, with an increasing trend downstream (figure 17). MC4 has a different seasonal trend compared to the other sites, where the mean is the highest in the summer, drops in the fall, and starts to recover in the winter. MC5d and MC7 present a progressively decreasing trend from summer to winter. The highest GPP mean in the dataset is seen at MC7 in the summer (1.47 gO_2 $m^{-2}d^{-1}$). The lowest GPP mean is seen at MC4 in the fall (0.52 gO_2 $m^{-2}d^{-1}$). The statistical analysis is presented in table 9. MC4 and MC5d do not present a significant seasonal variation in ER. MC7, on the other hand, presents a decreasing trend in ER from summer to winter. MC4 has means in the 2.84 to 2.88 gO_2 $m^{-2}d^{-1}$ range, MC5d in the 1.52 to 1.63 gO_2 $m^{-2}d^{-1}$ range, and MC7 in the 2.10 (winter) to 3.00 gO_2 m^{-2} d^{-1} (summer) range. The statistical analysis is presented in table 10. The GPP/ER plot presents the same seasonal trends as the GPP plot, except that this time the peak is seen at MC5d in the summer (0.92), although this site is the one with the widest 95% confidence interval due to a small sample size of 16.

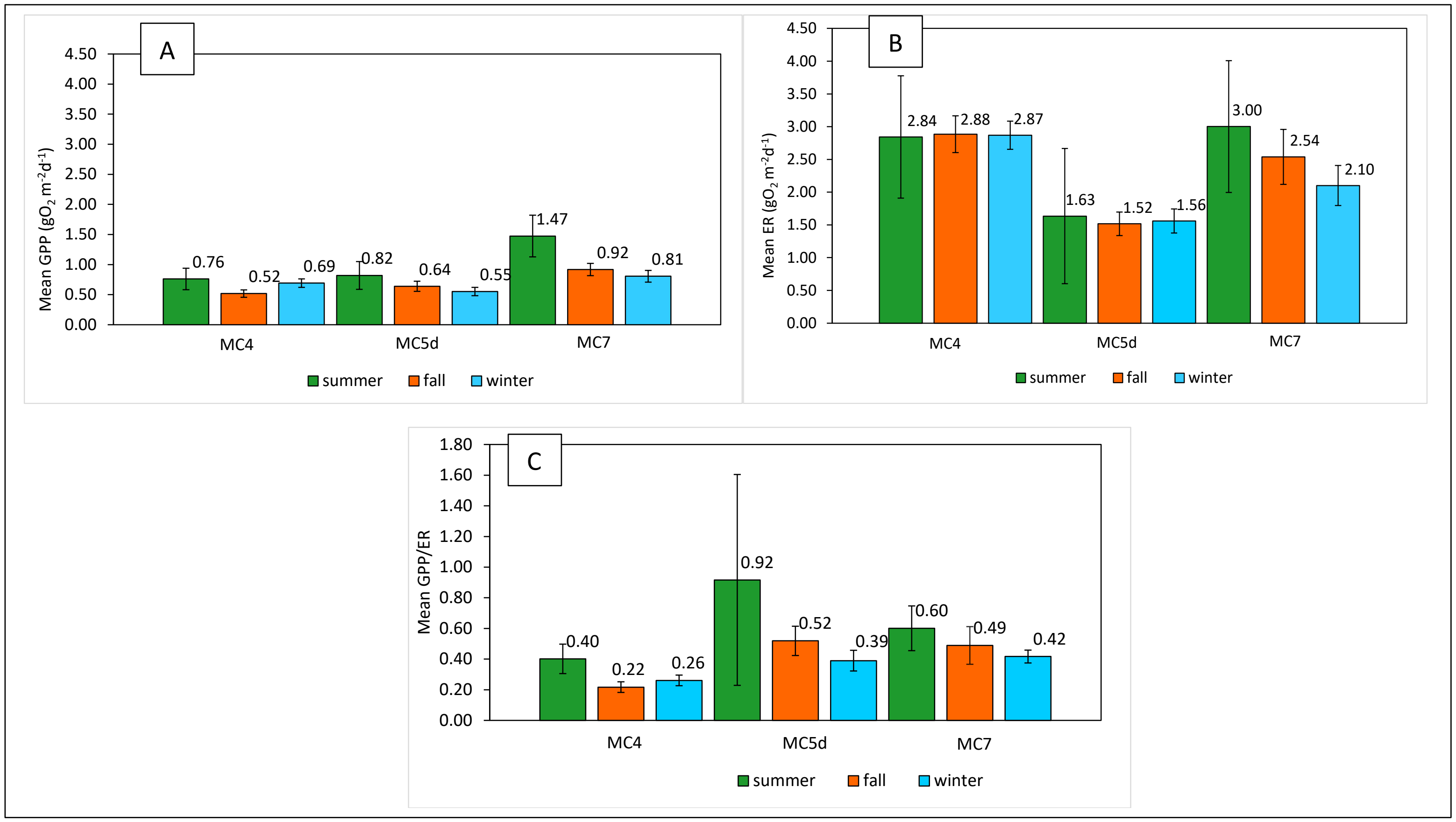

Figure 17: Combined effect of season and restoration on mean A) GPP B) ER C) GPP/ER at the metabolism sites. The labeled numbers are the means, and the error bars represent the 95% confidence intervals.

Table 9: Statistical analysis of GPP. The star represents the interaction between the two effects.

Effect	P-value	Contrast Statement	P-value	Restoration Class	Mean ($gO_2\ m^{-2}d^{-1}$)
Site	<0.0001	Unrestored v. Restored	<0.0001	Unrestored	0.62
Season	<0.0001	New Restored v. Old Restored	<0.0001	New Restored	0.63
Site*Season	0.0011			Old Restored	0.96

Table 10: Statistical analysis of ER.

Contrast Statement	P-value	Wilcoxon Scores	Restoration Class	Mean ($gO_2\ m^{-2}d^{-1}$)
MC4 v. MC5d	<0.0001	263 v. 122.6	Unrestored	2.87
MC4 v.MC7	0.0004	263 v. 214.1	New Restored	1.54
MC5d v. MC7	<0.0001	122.6 v. 214.1	Old Restored	2.48

The fall is interesting because contrary to the other seasons, the beginning and the end of the season can cause opposing stream metabolic effects. Senescing leaves become an additional carbon source to streams, which combined with the still warm temperatures of early fall, can result in a biological activity boost. As the fall progresses, and temperatures drop, biological activity slows. Figure 18 shows monthly average GPP and ER for the fall season (09/22/2020 to 12/21/2020).The monthly averages were divided as follows: First month- 09/22/2020 to 10/20/2020, second month- 10/21/2020 to 11/18/2020, and third month- 11/19/2020 to 12/20/2020. At MC4, the fall GPP mean is the highest in the first month (0.63 $gO_2\ m^{-2}d^{-1}$), followed by a statistically insignificant drop in the second month (0.39 $gO_2\ m^{-2}d^{-1}$) , and a statistically significant increase in the third month (0.54 $gO_2\ m^{-2}d^{-1}$). The monthly means progressively decrease at MC5d, with the change from the second month (0.72 $gO_2\ m^{-2}d^{-1}$) to the third month (0.39 $gO_2\ m^{-2}d^{-1}$) being statistically significant. At MC5d, the first month mean GPP (0.84 $gO_2\ m^{-2}d^{-1}$) slightly exceeds its summer mean (0.82 $gO_2\ m^{-2}d^{-1}$). The monthly means also progressively decrease at MC7, however, none of these changes are significant.

Fall ER behaves very differently from site to site. At MC4, ER increases from the first (2.21 $gO_2\ m^{-2}d^{-1}$) to the second month (3.20 $gO_2\ m^{-2}d^{-1}$), but it remains the same in the third month. None of these changes are statistically significant. At MC5d, there is a slight monthly average decrease over time, which is statistically insignificant. At MC7, the lowest ER mean occurs during the first month (1.90 $gO_2\ m^{-2}d^{-1}$), which is followed by a statistically significant peak in the second month (3.53 $gO_2\ m^{-2}d^{-1}$), and a statistically insignificant drop in the third month (2.24 $gO_2\ m^{-2}d^{-1}$)

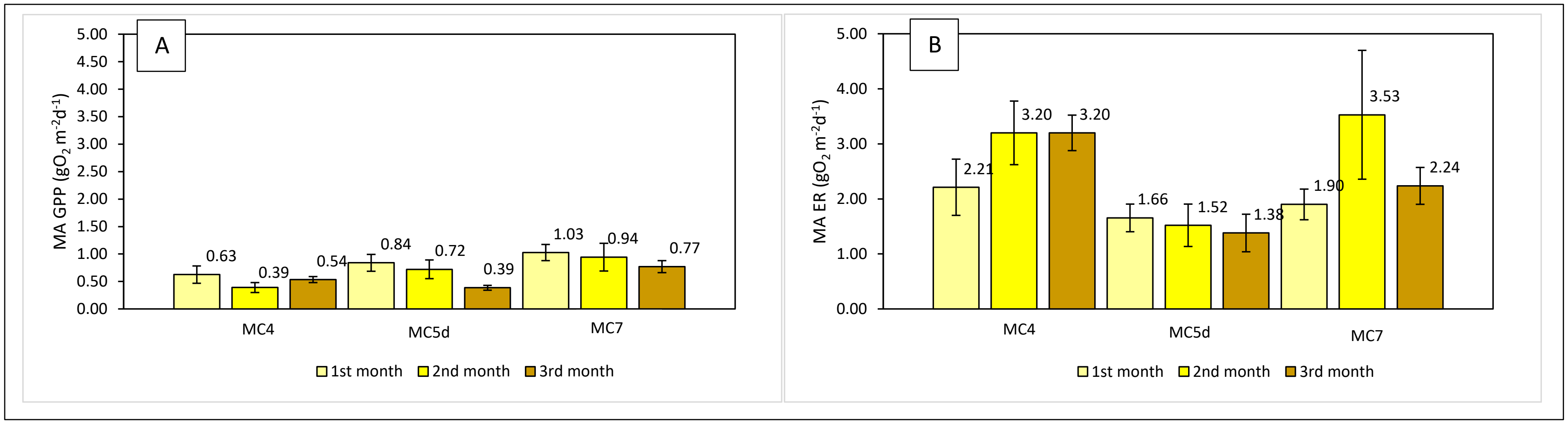

Figure 18: Fall monthly averages A) GPP B) ER where the first month goes from 09/22/2020 to 10/20/2020, second month goes from 10/21/2020 to 11/18/2020, and third month goes from 11/19/2020 to 12/20/2020. The labeled numbers are the means, and the error bars represent the 95% confidence intervals.

Discussion

Research question #1: How do dissolved inorganic nitrogen (DIN) concentrations and loads evolve downstream through mixed land use catchments, stormwater control measures (SCMs), restored versus unrestored stream sections, between flow conditions, and among seasons?

When analyzing each stream segment load and concentration between stations at baseflow conditions (figure 5), we observed the following: 1) All of the load data in the unrestored section between sites MC1 and MC3 presented an increase, which follows the concentration pattern. 2) 89.7% of the load data in the unrestored section between sites MC3 and MC4 presented an increase. Conclusions 1 and 2 are mostly a result of increasing discharge, as 58.6% of the concentration data presented a reduction trend. 3) 76.5% of the load data in the new restored section between sites MC4 and MC5 presented an increase. Conclusion 3 is also a result of increasing discharge, as 64.7% of the concentration data presented a reduction trend. 4) 90% of the load data in the restored section between sites MC5 and MC6 presented an increase. Conclusion 4 is also a result of increasing discharge, as 70% of the concentration data presented a reduction trend. 5) 90.9% of the load data in the old restored section between sites MC6 and MC7 presented an increase. which follows the concentration pattern, where 63.6% of the dataset presented an increase. Conclusions 3 and 4 lead us to believe that stream restoration in these sections has a positive effect on water quality. Since the old restored section did not follow the same trend, conclusion 5 suggests that there is an additional nutrient local source, such as a leaky sewer, between MC6 and MC7 which is not offset by restoration. This is supported by field observations of manholes near the sampling area.

A statistically significant difference was found between baseflow nutrient concentrations at restored sections (mean ~ 0.66 mg L^{-1}) versus unrestored sections (mean ~ 0.77 mg L^{-1}). The effect of season was also significant (p= 0.0006). Restoration seems to be the most effective at lowering concentrations in the summer (33.8% decrease compared to unrestored sites) when plants and microbes are active, and the soil is dry enough to infiltrate nutrient rich runoff more efficiently, while it has no effect in the winter (figure 7). At restored sites, nutrient concentrations were high in the winter and progressively decreased through the summer, with a recovery seen starting in the fall. This trend is kept in the load analysis. However, the area normalized restored loads were greater than the unrestored loads, which may reflect the apparent leaky sewer at MC7, which is also shown in the segment plots (inside the circles), and/or the increase in impervious area. In the summer, the loads reversed, suggesting biological sink that agrees with the concentration patterns. Regarding the land use analysis (figure 8), it is possible that we are seeing a combination of the effects of: 1) Restoration helping to achieve concentration levels similar to the headwater site (MC1) even at high cumulative impervious and low cumulative tree covers at the downstream most sites, and 2) Dilution from the large increase in discharge at these downstream areas. Finally, all sites presented decreased nutrient concentrations at stormflow compared to baseflow conditions (figure 6). This is sufficient evidence to support that our sites do not exhibit chemostasis, as they present load and concentration variability across different discharges and seasons.

For the SCMs analysis, we evaluated the effect of a pond and wetland. At the pond sites, mean baseflow concentrations were statistically lower at the outlet (0.42 mg L^{-1}) compared to inlet (0.58 mg L^{-1}) (figure 9). This could be a result of uptake processes such as algae growth. This is supported by the segment data, which showed that 96.3% of the load data in the section between MC5Pin and MC5Pout present a reduction, as well as 81.5% of the concentration data (figure 11). As far as the effect of discharge on nutrient distribution, the outlet and inlet presented 49.7% and 43.4% decreases, respectively, from mean baseflow concentration to mean stormflow concentration. As the dilution would be similar at the inlet and outlet, this may be explained by reduced pond retention at higher flows, following the Damkohler Number. The effect of season was also statistically significant (p= 0.0008) (figure 10). Similar to the seasonal trend at the stream sites, the summer mean concentrations at the pond sites were lower than all other seasons. The mean seasonal concentration of the inlet peaked in the winter, but at the outlet, the peak occurred in the spring, with the second highest mean occurring in the winter as well. This may be because the higher flows in the winter combined with lower temperatures reduce nitrate retention rates. In addition, there may also be flushing of stored or mineralized N in the pond.

The load seasonality trends are different. For MC5Pin, the mean was the highest in the spring. At MC5Pout, the mean loads decreased throughout the seasons from winter to fall. These reflect seasonal discharge trends.

At the wetland sites, mean baseflow concentrations were statistically lower at the treated outlet (0.01 mg L^{-1}) compared to the inlet (0.30 mg L^{-1}), as well as between the treated outlet compared to the untreated outlet (0.55 mg L^{-1}) (figure 12). Similar to the pond study, this is likely telling us that the wetland is a significant nitrate sink. This is supported by the 80% concentration data increase in the section between MC7Win and MC6/7, and the 95% concentration data reduction in the section between MC7Win and MC7Wout (figure 14). An interesting finding was that the mean concentration at the untreated outlet was almost double the mean concentration at the inlet. This is, again, likely being caused by sewer leakage. Contrary to any other site in this study, the mean stormflow concentration at MC7Win and MC7Wout showed 49.9% and 710.6% increases compared to the baseflow means. This is indicative of greater amounts of nutrients being delivered to the stream through the pipe system during storms, which is captured by MC7Win. We can also conclude that there is a flushing effect taking place at the wetland during storms, which is captured by MC7Wout. MC7Win had a decreasing trend starting in the winter, with a recovery in the fall (figure 13). MC7Wout stayed at constant low concentration levels throughout the year, with a slight increase in the spring. MC6/7 peaked in the spring and dropped in the fall. MC6/7 showed higher mean concentrations compared to its inlet throughout the year, even exceeding the stream site (MC7) means during the spring and summer.

Research question #2: What are the nitrate sources from different subcatchments at different flow conditions?

Sanitary effluent was the dominant nitrate source at baseflow conditions, even at MC1, which is our low density, higher forest cover site (figure 15). This could potentially be evidence of sewer leaks in that residential area. At the downstream sites starting at MC3, we started to see fertilizer and soil nitrate contribution to the isotopic signal in addition to sanitary effluent. Sanitary effluent was the sole nitrate source to the pond samples, and surprisingly, these did not fall within the denitrification lines. Similarly to Jefferson et al. (2017), this indicates that, in addition to uptake by algae, the reduction of nitrate mass export found in the pond was directly connected to the reduction in runoff provided by this SCM.

Samples collected during the two storm events, including Hurricane Laura, did not present an atmospheric deposition signal. There was an interesting relationship between nitrate sourcing and flow (figure 16). Under moderate flows, the headwater site MC1 consisted of only sewage, which was likely derived from mobilization of sanitary system nitrate. The next site MC3, consisted of residual sewage mixed with fertilizer and soil nitrate. All downstream site samples consisted only of mixed fertilizer and soil nitrate, indicating a dilution of sewage. At hurricane flows, the sewage signal completely disappears from all sites. Although it is common to see evidence of sewer overflow during large storms, as seen in Kaushal et al. (2011), figure 3B and D, it is possible that the runoff produced by Hurricane Laura expanded the variable source area to a much larger size. Since sewage effluent is a finite quantity, it was likely diluted to negligible amounts compared to other land derived nitrate sources such as fertilizer and soil. The same likely happened to the atmospheric deposition signal. Our sample size is limited, and further sampling would be beneficial for the isotopic analysis.

Research question #3: How do gross primary productivity (GPP) and ecosystem respiration (ER) patterns vary downstream among unrestored and restored sites of different restoration ages, and how do these influence nitrate concentrations and loads?

From the metabolism data (figure 17), we observed a statistically significant seasonal variability in GPP at the sites MC4, MC5d, and MC7, where GPP was the highest in the summer. The summer has a reverse trend in nutrients; it is the season with the lowest nutrient concentrations, discharges, and therefore, nutrient loads. As the optimal conditions for GPP occur in the summer (e.g., high temperatures, and plant and microbial activity), autotrophs consume the nutrients available in the water to fuel photosynthesis, acting as significant sinks. The low flows in the summer also favor this process by allowing biofilms and aquatic vegetation to grow, which increases their contact time with the nutrients, and allow them to grow. Conversely, GPP was the lowest in the winter at the two restored sites. This matches the reverse pattern for nutrient concentrations and loads. However, at the unrestored site, the minimum GPP occurred in the fall. There was a statistically significant difference in GPP between all the site classes, where GPP at the old restored site exceeded all of the others, particularly in the summer season. This does not support our hypothesis that the newly restored site would present the highest rates, and may be indicative of a cumulative effect of the total area on the old restored site, or the lag in the development of biofilms at the newly restored site. GPP was the lowest at the unrestored site as we predicted.

ER was fairly constant at all seasons at MC4 and MC5d, but it presented a decreasing trend at MC7 from summer to winter. This decreasing trend in ER from summer to winter, perhaps relates to the seasonal nutrient distributions the same way as GPP. There was an interesting ER trend across sites where the upstream most site MC4 had the highest mean, following by a decrease of 45% at MC5d, then an increase of 62% at MC7.This may be indicative of greater amounts of labile organic carbon available for decomposition at the end of the unrestored section at MC4, leaving mostly recalcitrant material, and therefore more resistant to decomposition, to make it to MC5d. At some point between MC5d and MC7, there is a recovery in ER, which may indicate additional carbon supply from the riparian vegetation regrowth. There was a statistically significant difference between all pairwise comparisons. We expected GPP/ER ratios to be higher in the summer compared to the fall. That held true for all sites. All sites were heterotrophic regardless of season, and MC5d was the site that got the closest to being autotrophic in the summer. This is likely due to the abundant amount of algae that were present in the site during the summer and the limited local input of organic matter.

Regarding the fall monthly average analysis (figure 18), many different effects are likely taking place. During the first month, leaves were still on the trees. Leaves started falling either early or late October. Therefore, our second month should have a greater impact on metabolism by boosting both GPP and ER. By the third month, these biological activities should decline due to decreased surface water temperatures. From figures 1 and 3a-d, we observe that MC4 has a great deal of riparian cover. Therefore, this site should reflect the "leaf off effect" well. For the monthly average GPP, there was a drop from the first to the second month, which could be a reflection of high leaf material floating on the stream, which further blocked sunlight, and kept autotrophs from performing photosynthesis. There was an increase from the second month to the third which could be a temporary effect of the leaves being washed out, allowing sunlight to reach the stream. The monthly average ER somewhat supports this hypothesis as there was an increase from the first month to the second, which could potentially indicate higher rates of decomposition of leaf material in the stream. MC7 is within a regional park with good tree cover. Therefore, it should behave similarly to MC4. From the monthly average GPP, there was a gradual decrease throughout the months. From first to second month, this could be due to leaves blocking sunlight, or the effect of canopy closure, and from the second to the third month, it could be due to temperatures being too low to support biological activity. The monthly average ER was the lowest in the first month, which could still be a reflection of summer canopy closure. Then again, the mean increased from the first to the second month, potentially indicating a boost in decomposition from leaf loading, and it dropped from the second to the third month, indicating a biological slowdown from possibly a combination of lower water temperatures and the scouring of leaf debris through higher flows. Finally, MC5d is located on a clear floodplain with some herbaceous cover. Senescence should not be a significant factor. Both moving average GPP and ER have a decreasing trend throughout the months, which is the natural effect of the transition from summer to fall on stream biological activity.

Conclusions

Nutrient concentrations decreased downstream, even when the land use went from high forest and low impervious to low forest and high impervious. This could either be a result of restoration, or a dilution, or a combination of both. The area between stations MC6 and MC7 presented increased concentrations and exceptionally high loads. This is likely due to leaky sewers in the area, which is supported by field observations and sewer isotopic signal in samples. There is a seasonality trend in both loads and concentrations, where values were generally the lowest in the summer, and the highest in the winter suggesting that restoration is the most effective in the summer. Sample concentrations decreased significantly at stormflow compared to baseflow. At both the pond and wetland study cases, outlet concentrations were statistically lower than inlet concentrations. At the pond, this was caused by algae uptake and runoff reduction. In the case of the wetland, the treated outlet mean concentration was statistically lower than the untreated outlet mean, while both are fed by the same inlet. This is indicative of denitrification coupled with a set of other processes; however, we were not able to conduct an isotopic analysis of these sites. In addition, the untreated outlet presented concentrations higher than inlet's. This is, again, likely due to leaky sewers.

Sanitary effluent was the dominant nitrate source to all stream sites, regardless of land use, and pond sites at baseflow conditions. The signal was attenuated in two storm events, one of moderate size, and a near complete dilution at hurricane scale flow. The same likely happened to the atmospheric nitrate signal during the two storms with the nitrate sources shifting to fertilizer and soil, which are land derived. These observations suggest the response of the watershed is not chemostatic across different flows, with shifts in both the concentrations and sources of nitrate.

Gross primary productivity followed a reverse pattern to nutrient seasonality. It was the highest in the summer when concentrations, discharges, and loads were the lowest. The opposite was true in the winter. Restored sites had greater GPP, at least partially due to differences in illumination. The GPP sequestered nitrate, and converted it to organic form, which is a temporary, not a permanent, removal. Ecosystem respiration had a similar trend as GPP at the old restored site, but it remained mostly constant at the other two. MC5d almost reached an autotrophic state in the summer, likely due to dense algae layers and lack of local organic matter input to fuel respiration. Otherwise, all sites remained heterotrophic throughout the year. Monthly fall metabolism analysis reflected the role of leaf senescence as either metabolic boosters by serving as nutrient supply to the stream, or as metabolic inhibitors by blocking sunlight.

Stream channel restoration has become a widespread practice to protect adjacent infrastructure, reduce sediment sourced from eroding banks, and reduce nutrient loads to receiving water bodies. This study focused on a set of restored and unrestored stream reaches in the Meadow Creek watershed in Charlottesville, VA. While this restoration was originally designed primarily to reduce sediment from eroding banks, it also has the potential to provide nutrient load reduction. Sampling and analysis of stream discharge, dissolved inorganic nitrogen (DIN) concentrations, and isotopic composition showed that stream restoration works moderately well at reducing DIN. The treatment provided was most effective in the summer, but much lower in the winter, higher in restored sites with open canopies compared to closed canopy sites, and higher during low flow conditions. This highlights the important role of vegetation and algal nitrogen uptake in DIN reduction. As the stormwater production by the surrounding urban watershed is not impacted by channel restoration, high flow bypass of biological uptake remains a major limitation on restoration effectiveness. The pond and wetland proved effective, providing DIN reduction year-round by direct surface runoff reduction and biological uptake. Although enhanced denitrification is likely, especially in the wetland, we were not able to show evidence of this process in isotopic analysis.

Stream restoration is clearly contributing to the goal of DIN sequestration, but results would be enhanced if this practice is coupled with the implementation of SCM within the drainage area. Stream channel restoration effectiveness is limited as it largely addresses the problem on a local scale, as the dominance of vegetation and algal uptake does not constitute permanent removal as organic forms of N can remineralize further downstream. SCM such as ponds, wetlands, tree canopy and other green infrastructure (GI) promote the attenuation of peak flows and potentially runoff volume throughout the upland drainage area, causing nearby water bodies to receive more manageable discharge volumes and reduced nutrient loads. The coupling of the two practices has the potential to maximize the positive results to water quality and ecosystem restoration in urban watersheds. Lastly, we found that leaky sewers are a major source of nutrients to this urban stream, even in subcatchments with greater tree canopy cover, consistent with studies in other watersheds. There is a continuing need for sanitary sewer inspection and maintenance in urban catchments to control the dominant DIN source. Our results show that there is no one solution to recover an impaired stream, instead, this is a challenge that requires a coordinated treatment of both watershed runoff and nutrient loading regimes, sanitary infrastructure, and channel, riparian, and floodplain restoration to reduce downstream impacts.

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