Biogeochemical Cycling And Nutrient Control Strategies For Groundwater At Stormwater Infiltration Basins

Andrew M. O'Reilly

University of Central Florida

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BIOGEOCHEMICAL CYCLING AND NUTRIENT CONTROL STRATEGIES FOR GROUNDWATER AT STORMWATER INFILTRATION BASINS

by

ANDREW M. O’REILLY
B.C.E. Auburn University, 1991
M.C.E. Auburn University, 1993

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ABSTRACT

Elevated concentrations of nutrients, particularly nitrate (NO$_3^-$), in groundwater and springs in Florida are a growing resource management concern. Stormwater infiltrations basins, which are a common stormwater management practice in the well-drained karst terrain areas of Florida, are a potentially important source of nutrients to the groundwater system because stormwater exits the basin by only evaporation or infiltration. To better understand the biogeochemical processes integrating stormwater infiltration impacts on groundwater resources in a field-scale setting, a combination of hydrologic, soil chemistry, water chemistry, dissolved and soil gas, isotope, and microbiological data was collected from 2007 through 2010 at two stormwater infiltration basins receiving runoff from predominantly residential watersheds in north-central Florida.

Substantially different biogeochemical processes affecting nitrogen fate and transport were observed beneath the two stormwater infiltration basins. Differences are related to soil textural properties that deeply link hydroclimatic conditions with soil moisture variations in a humid, subtropical climate. During 2008, shallow groundwater beneath the basin with predominantly clayey soils (median 41% silt+clay content) exhibited decreases in dissolved oxygen (O$_2$) from 3.8 to 0.1 mg L$^{-1}$ and decreases in nitrate nitrogen (NO$_3^-$-N) from 2.7 mg L$^{-1}$ to less than 0.016 mg L$^{-1}$, followed by manganese (Mn) and iron (Fe) reduction, sulfate (SO$_4^{2-}$) reduction, and methanogenesis. In contrast, beneath the basin with predominantly sandy soils (median 2% silt+clay content), aerobic conditions persisted from 2007 through 2009 (dissolved O$_2$ of 5.0–7.8 mg L$^{-1}$), resulting in NO$_3^-$-N of 1.3–3.3 mg L$^{-1}$ in shallow groundwater. Soil extractable NO$_3^-$-N was significantly lower and the copper-containing nitrite reductase gene
density was significantly higher beneath the clayey basin. Differences in moisture retention capacity between fine- and coarse-textured soils resulted in median volumetric gas-phase contents of 0.04 beneath the clayey basin and 0.19 beneath the sandy basin, inhibiting surface/subsurface O₂ exchange beneath the clayey basin.

Subsurface biogeochemical processes at the clayey stormwater infiltration basin were further analyzed to better understand the effects of the highly variable hydrologic conditions common in humid, subtropical climates. Cyclic variations in biogeochemical processes generally coincided with wet and dry hydroclimatic conditions. Oxidizing conditions in the subsurface persisted for about one month or less at the beginning of wet periods with dissolved O₂ and NO₃⁻ showing similar temporal patterns. Reducing conditions in the subsurface evolved during prolonged flooding of the basin. At about the same time O₂ and NO₃⁻ reduction concluded, Mn, Fe and SO₄²⁻ reduction began, with the onset of methanogenesis one month later. Reducing conditions persisted up to six months, continuing into subsequent dry periods until the next major oxidizing infiltration event. Evidence of denitrification in shallow groundwater at the site is supported by median NO₃⁻-N less than 0.016 mg L⁻¹, excess N₂ up to 3 mg L⁻¹ progressively enriched in δ¹⁵N during prolonged basin flooding, and isotopically heavy δ¹⁵N and δ¹⁸O of NO₃⁻ (up to 25‰ and 15‰, respectively). Isotopic enrichment of newly infiltrated stormwater suggests denitrification was partially completed within two days. Soil and water chemistry data suggest a biogeochemically active zone exists in the upper 1.4 m of soil, where organic carbon was the likely electron donor supplied by organic matter in soil solids or dissolved in infiltrating stormwater. The cyclic nature of reducing conditions effectively controlled the nitrogen cycle,
switching nitrogen fate beneath the basin from NO$_3^-$ leaching to reduction in the shallow saturated zone.

Soil beneath the sandy stormwater infiltration basin was amended using biosorption activated media (BAM) to study the effectiveness of this technology in reducing inputs of nitrogen and phosphorus to groundwater. The functionalized soil amendment BAM consists of a 1.0:1.9:4.1 mixture (by volume) of tire crumb (to increase sorption capacity), silt and clay (to increase soil moisture retention), and sand (to promote sufficient infiltration), which was applied to develop an innovative best management practice (BMP) utilizing nutrient reduction and flood control sub-basins. Construction and materials costs, excluding profit and permit fees, for the innovative BMP were about $US 65 m$^{-2}$ of basin bottom. Comparison of nitrate/chloride (NO$_3^-$/Cl$^-$) ratios for the shallow groundwater indicate that prior to using BAM, NO$_3^-$ concentrations were substantially influenced by nitrification or variations in NO$_3^-$ input. In contrast, for the new basin utilizing BAM, NO$_3^-$/Cl$^-$ ratios indicate minor nitrification and NO$_3^-$ losses with the exception of one summer sample that indicated a 45% loss. Biogeochemical indicators (denitrifier activity derived from real-time polymerase chain reaction and variations in major ions, nutrients, dissolved and soil gases, and stable isotopes) suggest NO$_3^-$ losses are primarily attributable to denitrification, whereas dissimilatory NO$_3^-$ reduction to ammonium and plant uptake are a minor processes. Denitrification was likely occurring intermittently in anoxic microsites in the unsaturated zone, which was enhanced by increased soil moisture within the BAM layer and resultant reductions in surface/subsurface O$_2$ exchange that produced conditions conducive to increased denitrifier activity. Concentrations of total dissolved phosphorus and orthophosphate (PO$_4^{3-}$) were reduced by more than 70% in unsaturated zone soil water, with the
largest decreases in the BAM layer where sorption was the most likely mechanism for removal. Post-BAM $\text{PO}_4^{3-}/\text{Cl}^-$ ratios for shallow groundwater indicate predominantly minor increases and decreases in $\text{PO}_4^{3-}$ with the exception of one summer sample that indicated a 50% loss. Differences in nutrient variations between the unsaturated zone and shallow groundwater may be the result of the intensity and duration of nutrient removal processes and mixing ratios with water that had undergone little biogeochemical transformation.

In order to quantify potential processes leading to observed nitrogen losses beneath the innovative BMP, an integrated infiltration basin–nitrogen reduction (IBNR) system dynamics model was developed. Based on two simulation periods, the IBNR model indicated denitrification accounted for a loss of about one-third of the total dissolved nitrogen mass inflow and was occurring predominantly in the BAM layer. The IBNR model results in combination with the field-based biogeochemical assessment demonstrated that the innovative BMP using the functionalized soil amendment BAM is a promising passive, economical, stormwater nutrient-treatment technology. Further field- and laboratory-scale research on the long-term sustainability of nutrient losses and further elucidation of causative physicochemical and biogeochemical mechanisms would contribute to improved BAM performance and green infrastructure development in the future.
In memory of Michael A. O’Reilly (1936–2007).

“…And sees before him, dale and plain,  
The pleasant land of counterpane.”  
  – Robert Louis Stevenson

May I find the journey, rather than the destination.
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Lastly, and most importantly, I must “Praise God from whom all blessings flow,” without whose creation I would be nothing and without whose Truth I would have nothing to seek.
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<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAO</td>
<td>acid-ammonium-oxalate</td>
</tr>
<tr>
<td>AEC</td>
<td>anion exchange capacity</td>
</tr>
<tr>
<td>BAM</td>
<td>biosorption activated media</td>
</tr>
<tr>
<td>BMP</td>
<td>best management practice</td>
</tr>
<tr>
<td>CDB</td>
<td>citrate-dithionite-bicarbonate</td>
</tr>
<tr>
<td>CEC</td>
<td>cation exchange capacity</td>
</tr>
<tr>
<td>DCIA</td>
<td>directly connected impervious area</td>
</tr>
<tr>
<td>DIC</td>
<td>dissolved inorganic carbon</td>
</tr>
<tr>
<td>DNRA</td>
<td>dissimilatory nitrate reduction to ammonium</td>
</tr>
<tr>
<td>DO</td>
<td>dissolved oxygen</td>
</tr>
<tr>
<td>DOC</td>
<td>dissolved organic carbon</td>
</tr>
<tr>
<td>EIA</td>
<td>effective impervious area</td>
</tr>
<tr>
<td>EMC</td>
<td>event mean concentration</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>HT</td>
<td>Hunter’s Trace</td>
</tr>
<tr>
<td>IBNR</td>
<td>integrated infiltration basin–nitrogen reduction</td>
</tr>
<tr>
<td>IC</td>
<td>inorganic carbon</td>
</tr>
<tr>
<td>IN</td>
<td>inorganic nitrogen</td>
</tr>
<tr>
<td>nirK</td>
<td>copper-containing nitrite reductase</td>
</tr>
<tr>
<td>NO(_3^–)</td>
<td>nitrate + nitrite nitrogen</td>
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<td>OC</td>
<td>organic carbon</td>
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xxx
<table>
<thead>
<tr>
<th>Acronym</th>
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<tbody>
<tr>
<td>ON</td>
<td>organic nitrogen</td>
</tr>
<tr>
<td>qPCR</td>
<td>quantitative real-time polymerase chain reaction</td>
</tr>
<tr>
<td>RMSE</td>
<td>root-mean-squared error</td>
</tr>
<tr>
<td>SMRC</td>
<td>soil moisture retention curve</td>
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<tr>
<td>SO</td>
<td>South Oak</td>
</tr>
<tr>
<td>TDN</td>
<td>total dissolved nitrogen</td>
</tr>
<tr>
<td>TDP</td>
<td>total dissolved phosphorus</td>
</tr>
<tr>
<td>TDR</td>
<td>time domain reflectometry</td>
</tr>
<tr>
<td>TEAP</td>
<td>terminal electron accepting process</td>
</tr>
<tr>
<td>TIC</td>
<td>total inorganic carbon</td>
</tr>
<tr>
<td>TN</td>
<td>total nitrogen</td>
</tr>
<tr>
<td>TOC</td>
<td>total organic carbon</td>
</tr>
<tr>
<td>TP</td>
<td>total phosphorus</td>
</tr>
<tr>
<td>USGS</td>
<td>U.S. Geological Survey</td>
</tr>
<tr>
<td>VWC</td>
<td>volumetric water content</td>
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CHAPTER 1: INTRODUCTION

Introduction

Material in this chapter is taken in large part from that presented by O’Reilly et al. (2012a,b,c) and has been reproduced here upon permission of the respective publishers (Appendix A).

Stormwater infiltration is a valuable water resource management practice for mitigating development impacts and increasing fresh water recharge worldwide (Clark and Pitt, 2007; Page et al., 2010). Yet, potential adverse environmental health effects on groundwater due to nutrient impacts must be recognized (Göbel et al., 2007; Taylor et al., 2005). Traditionally, stormwater has been managed from the perspective of surface-water impacts. More recently, the impacts of stormwater infiltration on groundwater quality have been more closely studied in regard to a variety of constituents, such as major ions, nutrients, trace metals, pesticides, and volatile organic compounds (Pitt et al., 1999; Fisher et al., 2003; Hatt et al., 2009; Zubair et al., 2010). However, little attention has been directed toward investigating nitrogen (N) and carbon (C) cycling beneath stormwater infiltration basins to improve best management practices (BMPs) for mitigation of environmental health impacts of stormwater on groundwater quality.

Biogeochemical processes occurring in the shallow subsurface can be an important determinant of groundwater quality beneath stormwater infiltration basins, and especially in the case when the coupled N and C cycles can serve to mitigate leaching of inorganic N species to groundwater in association with C mineralization (Kim et al., 2003; Cho et al., 2009). However, the highly dynamic nature of infiltrated water and groundwater beneath infiltration basins complicates
understanding of an already complex biogeochemical system (Cho et al., 2009; Datry et al., 2004). Little research at the field scale is available on the temporal variability of N cycling beneath stormwater infiltration basins.

A common constituent of concern is nitrate (NO$_3^-$), due to its worldwide prevalence in terrestrial and aquatic systems, influence on biogeochemical cycling from local to global scales, potential human health impacts, and the possibility for mitigation by denitrification (Vitousek et al., 1997; Seitzinger et al., 2006; Ward et al., 2005). Stormwater runoff is one of many sources of N (Schiffer, 1989; Kim et al., 2003; Taylor et al., 2005; Page et al., 2010) among others, such as septic tanks (Katz et al. 2010) and land-based application of reclaimed water (Sumner and Bradner, 1995) or fertilizer (Böhlke, 2002; Green et al., 2008a). Nitrogen, particularly NO$_3^-$, easily moves from terrestrial ecosystems into groundwater and surface waters (Baker, 1992; Kahl et al., 1993; Peterjohn et al., 1996). Contaminated stormwater runoff can contribute to elevated NO$_3^-$ concentrations in groundwater.

Because N often is the limiting nutrient for plants (Einsle and Kroneck, 2004), increased quantities of N in ecosystems alter competitive relationships among terrestrial and aquatic organisms (U.S. Environmental Protection Agency, 2005). Elevated NO$_3^-$-nitrogen (NO$_3^-$-N) concentrations exceeding 0.1 mg L$^{-1}$, a level representative of background conditions in the Upper Floridan aquifer in Florida (Katz, 1992; Maddox et al., 1992), are common in Florida groundwater (O’Reilly et al., 2007). Consequently, throughout much of Florida, NO$_3^-$-N concentrations have increased in many Upper Floridan aquifer springs since the 1950s, exceeding 1 mg L$^{-1}$ in recent years at some springs in central and north Florida (Katz et al., 1999, 2009; Katz, 2004; Phelps, 2004; Phelps et al., 2006; Knowles et al., 2010, St. Johns River
Water Management District, 2010). At present (2010), NO$_3^-$-N concentrations in Florida springs generally are well below 10 mg L$^{-1}$, the primary drinking water standard established by the U.S. Environmental Protection Agency (2010). Yet, elevated levels commonly above natural background concentrations can have deleterious effects on the environmental health of the fragile spring ecosystems and other downstream biota (Walsh et al., 2009). Walsh et al. (2009, p. 89) state that “increased nutrient input to Florida springs is the single greatest threat to the ecology of these systems.” In recognition of these factors, a NO$_3^-$-N (plus nitrite) concentration of 0.35 mg L$^{-1}$ was recently proposed as a protective criterion for aquatic life in Florida’s springs and clear streams (U.S. Environmental Protection Agency, 2011).

As competition increases for natural resources within society as well as between man and the environment, the importance of promoting green infrastructure in stormwater management is growing (Pataki et al., 2011). Assessment of the performance of stormwater BMPs, and urban infrastructure in general, from a biogeochemical cycling perspective is essential to gleaning a process-based understanding of nutrient dynamics in urban soils (Lorenz and Lal, 2009) and a more holistic determination of positive and negative feedbacks between the natural and built environment (Pataki et al., 2011). Borch et al. (2010) describe the importance of biogeochemical cycling on contaminant dynamics and the potential such understanding provides for development of engineered remediation strategies.

The existing design criteria for a typical stormwater infiltration basin involves excavation of a basin above the water table, leaving the natural soil profile unmodified except by possible incidental compaction during the construction process and the addition of vegetation on the sides and bottom such as sod. Stormwater runoff is directed to the infiltration basin for surface water
pollution reduction and flood control purposes, where stormwater exits the basin by only infiltration or evaporation. Therefore, impacts to groundwater can be substantial.

Alternative design criteria focus on functionalized soil amendments that can facilitate nutrient removal. In a functionalized soil amendment each component of the amendment mixture possesses particular functional characteristics to improve attenuation of a pollutant of concern in a specific environmental setting. Soil amendments commonly have been implemented in relatively small-scale applications (<1 ha drainage area), such as low-impact development bioretention cells and raingardens (Davis et al., 2009; Hunt et al., 2006). A full-scale application of this technology for regional stormwater infiltration basins serving watersheds >20 ha has received little or no attention. In order to serve the dual purpose increasingly required of stormwater BMPs to provide both water quality and water quantity control, application of innovative designs integrating sub-basins for nutrient reduction, which utilize functionalized soil amendments, and flood control are promising.

Design, development, and performance assessment of a stormwater BMP for mitigation of nutrient impacts on groundwater are complicated by the complex array of interacting processes that contribute to the net effects observed in field monitoring results. A need exists to quantify these processes in order to further the development of passive nutrient control strategies leading to improved stormwater infiltration BMPs. System dynamics, a methodology especially for better framing and understanding complex feedback systems, has been widely used to model such interactions in environmental/ecological studies. Xuan et al. (2009, 2010) recently applied system dynamics modeling for describing nutrient removal mechanisms in semi-enclosed subsurface treatment facilities and demonstrated that such quantitative analysis techniques are
well suited for studying N transformations in the subsurface. Such techniques can be applied to study N cycling beneath stormwater infiltration basins to aid in the development of innovative BMPs promoting nutrient reduction.

**Objectives**

To better understand the integration of the natural and built environments in the context of stormwater infiltration, a comprehensive study was conducted from 2007 through 2010. The intent of this study was to identify both the hydrologic conditions and the biogeochemical processes beneath two stormwater infiltration basins, with emphasis on nutrient fate, which impact groundwater resources in a humid, subtropical climate and to use these results to develop and test an improved BMP. The objectives of this research are as follows:

- demonstrate how differences in soil properties beneath two subtropical stormwater infiltration basins led to differences in N and C cycling and other relevant biogeochemical processes;
- elucidate the sequential biogeochemical processes occurring cyclically at seasonal or shorter time scales and demonstrate that such processes can effectively control N fate beneath a subtropical stormwater infiltration basin;
- develop an improved stormwater infiltration BMP utilizing an integrated design that incorporates both nutrient reduction and flood control and implement it in a full-scale field setting;
- develop biosorption activated media (BAM)—a functionalized soil amendment designed to mimic natural physicochemical and biogeochemical processes—and
demonstrate its potential for nutrient (N and P) removal by assessing its performance during a preliminary monitoring period; and

- quantitatively explore the changes observed after the addition of BAM and the N removal mechanisms of the innovative stormwater infiltration basin with the aid of a system dynamics model characterized by the collected field-scale dataset.

A combination of hydrologic, soil and water chemistry, dissolved and soil gas, isotopic, and microbiological data collected 2007–2010 during the study were used to provide a better understanding of controlling factors on groundwater quality. Results can inform development of improved BMPs to mitigate N and P impacts from stormwater infiltration basins.

Description of Study Area

Two stormwater infiltration basins located in the Silver Springs springshed approximately 2 and 9 km southwest of Silver Springs in north-central Florida, USA, were monitored during 2007–2010 to identify subsurface biogeochemical processes (Figure 1). The Silver Springs springshed is characterized by karst topography consisting of predominantly internal drainage into closed depressions or diffuse seepage into the highly permeable surficial sediments (Phelps, 2004); 1933–2007 annual mean discharge from the spring group was 21.7 m$^3$ s$^{-1}$ (Knowles et al., 2010). Climate of the area is humid subtropical, with hot, rainy summers and cool, relatively dry winters (Phelps, 2004). Long-term (1901–2010) annual averages indicate rainfall of about 1,360 mm yr$^{-1}$ and mean daily air temperature of about 22°C at the National Oceanic and Atmospheric Administration (NOAA) Ocala station (COOP ID 086414) approximately 7 and 13 km south of the two stormwater basins (National Climate Data Center,
2011). During the study (2007–2010), annual average rainfall ranged from 1,120 to 1,440 mm yr\(^{-1}\); minimum daily air temperature averaged about 15°C; and maximum daily air temperature averaged about 28°C. Potential evapotranspiration averaged about 1,250 mm yr\(^{-1}\) (1996–2010) based on daily values computed by using the Priestley-Taylor equation (Jacobs et al., 2008; Mecikalski et al., 2011) for a 2-km pixel covering the NOAA Ocala station (U.S. Geological Survey, 2011a, 2011b).
Figure 1: Locations of the South Oak and Hunter’s Trace stormwater infiltration basins. Upper map shows location of each watershed, and inset maps show the locations of residences and monitoring sites relative to each stormwater infiltration basin.

Note: Rain gages located at wells M-0511 and M-0505. Lysimeters, soil moisture probes, and soil temperature probes located at wells PW and M-0506.
North-central Florida is underlain by three principal hydrogeologic units in order from shallowest to deepest: (1) surficial aquifer system, consisting of varying amounts of sand, silt, and clay; (2) intermediate confining unit, which is predominantly clay; and (3) Floridan aquifer system, which is a thick sequence of carbonate formations. The surficial aquifer system and intermediate confining unit correspond to the post-Miocene and Miocene sediments, respectively, and are discontinuous and variable in thickness (Phelps, 2004). The Floridan aquifer system comprises the Upper and Lower Floridan aquifers. The Upper Floridan aquifer is generally 90 m thick in north-central Florida and serves as the primary source of fresh water for numerous springs as well as for drinking water and irrigation purposes (Phelps, 2004).

Both stormwater basins are located in watersheds that have transitioned from predominantly rural to residential land use during 1973–1990 and have remained residential to present day. In 1973, land use in the watershed draining to the South Oak (SO) basin was approximately 80% agricultural (nursery, specialty crops, and citrus) and 20% hardwood forest, and land use in the watershed draining to the Hunter’s Trace (HT) basin was approximately 70% pine forest and 30% low-density residential. In 2004, land use in the SO watershed was approximately 70% low-density residential and 30% medium-density residential, and land use in the HT watershed was approximately 70% medium-density residential and 30% undeveloped conservation area (pine forest). Soils in both watersheds are predominantly classified as hydrologic group A, indicating well drained behavior (Wanielista et al., 1997). Soils consist of Hague sand (loamy, siliceous, semiactive, hyperthermic Arenic Hapludalfs), Kanapaha fine sand (loamy, siliceous, semiactive, hyperthermic Grossarenic Paleaquults), and Kendrick loamy sand (loamy, siliceous, semiactive, hyperthermic Arenic Paleudults) in the SO watershed and Candler
sand (hyperthermic, uncoated Lamellic Quartzipsamments) in the HT watershed (Thomas et al., 1979). Soils in the immediate vicinity of the HT basin are consistent with those of its watershed, but soils at the SO basin are considerably finer-textured and poorly drained compared to those of its watershed. The SO basin is 1,600 m$^2$ in area with a watershed of 29 ha; the HT basin is 2,800 m$^2$ in area with a watershed of 23 ha (Figure 1). Both basins function to infiltrate stored water without surface outlets. The geometry of the SO basin was estimated from horizontal and vertical survey points, whereas original “as built” construction plans for the HT basin were available and were verified by surveying. The SO basin occupies a natural land-surface depression and was excavated to a depth of about 1 m. Although the SO basin overflows during prolonged or intense storm events, stormwater remains confined to the natural depression. The HT basin was excavated to a depth of about 3 m in a relatively flat terrain and stormwater remains confined to the basin boundaries even during extreme storm events. In the HT watershed, the stormwater conveyance system consists of curb-and-gutter roadway, whereas in the SO watershed roadside swales are the primary system used to convey runoff to the basin. Impervious area attributable to roadways is estimated to be 5% of the SO watershed and 10% of the developed portion of the HT watershed (6% of the entire watershed).
CHAPTER 2: MATERIALS AND METHODS

Introduction

Material in this chapter is taken in large part from that presented by O’Reilly et al. (2012a,b) and has been reproduced here upon permission of the respective publishers (Appendix A).

Hydrologic, soil, and water-quality conditions were monitored at both sites. Hydrologic conditions were monitored continuously 2008–2009 at the SO site and 2008–2010 at the HT site. A total of 24 sampling events were conducted during a variety of wet and dry hydroclimatic conditions from June 2007 through August 2010. The most frequent sampling (approximately monthly) was conducted November 2007 through December 2008 at the SO basin and November 2007 through September 2008 and November 2009 through August 2010 at the HT basin.

Hydrologic Monitoring

Hydrologic monitoring consisted of measurements of rainfall, basin stage (stored stormwater level), groundwater level, matric head, subsurface temperature, and volumetric moisture content. Rainfall was measured with a siphon-type tipping bucket gage (TR-525S, Texas Electronics, Inc., Dallas, TX), basin stage and groundwater level (wells M-0505, M-0506, M-0511, M-0512, and PW) were measured with submersible pressure transducers (MPSDIT.010, vented and temperature compensated, Rittmeyer Ltd., Zug, Switzerland), matric head (soil moisture pressure head) was measured using tensiometers equipped with pressure transducers,
temperature was measured using thermistors, and volumetric water content was measured using time domain reflectometry (TDR). TDR measurements were adjusted, as necessary, based on gravimetric measurement of volumetric moisture content on undisturbed soil cores at field and saturated moisture contents. Data were recorded at 5-minute intervals from December 2007 through December 2009 (SO site) and August 2010 (HT site). Additionally, periodic (approximately monthly) measurements of basin stage and groundwater level (all wells) were made from March 2007 through December 2009 (SO site) and August 2010 (HT site).

Monitoring wells were installed at each site by hollow-stem auger in March 2007 (Figure 1). The wells consisted of a 5.1-cm-diameter PVC casing with a 1.5-m-length screen. Wells were screened within 3 m below the water table with the exception of one well at each site which was screened approximately 5 m deeper than the shallow wells. The deep well at the SO site (M-0511) was not sampled due to low water yield. Suction lysimeters with a 20 cm long porous cup (model 1923, Soilmoisture Equipment Corporation, Santa Barbara, CA) were installed vertically at each site by hand excavation at depths of 0.5, 0.9, and 1.4 m (1.3 m at the HT site) adjacent to the well inside the basin in June 2008 (Figure 1). To minimize preferential flow paths, the porous cups of the lysimeters were embedded in a silica flour and deionized water slurry, overlain by a 15-cm thick layer of bentonite chips subsequently hydrated with deionized water, and backfilled to land surface in layers with careful tamping using native soil. TDR and thermistor probes (CS616-L and 107-L, respectively, Campbell Scientific, Inc., Logan, UT) were also installed in June 2008 adjacent to the deepest lysimeter and inserted horizontally into the undisturbed soil of the excavation wall at depths of 0.3, 0.6, and 0.9 m. Tensiometers (field tensiometer SW-03, Soil Measurement Systems, Tucson, AZ) with a 2.2-cm long porous cup were installed in July 2008.
adjacent to the lysimeters in a single borehole at depths of 0.3, 0.6, and 0.9 m; porous cups were embedded in silica flour slurry and bentonite chips were used to isolate monitoring zones.

Soil Physical, Mineralogical, and Chemical Properties

A combination of soil physical, mineralogical, and chemical properties was measured on samples collected at both sites. Soil samples were collected by hand auger, double-cylinder hammer-driven core sampler (Grossman and Reinsch, 2002), or split-barrel sampler (ASTM D 1586-84, American Society for Testing Materials, 1994) at depths ranging from 0.1 to 9.7 m.

Soil physical property measurements consisted of particle size gradation, particle density, soil moisture retention curve (SMRC), and saturated hydraulic conductivity. Textural analysis was based on dry mechanical sieving or a combination of wet sieving and centrifugation. Particle-size distributions were determined using techniques outlined in ASTM D 422-63 (American Society for Testing Materials, 1994). Samples for wet analysis were saturated with Na\(^+\) by rinsing with 1 M sodium chloride (NaCl) and then washing out the NaCl solution, centrifuging to decant supernatants in the process. The purpose of Na\(^+\) saturation was to promote dispersion in order to fractionate samples into sand (nominally, 2–0.05 mm), silt (nominally, 0.05–0.002 mm), and clay (nominally, < 0.002 mm). Sand and coarse fragments (nominally, >2 mm) were separated by wet sieving, and silt and clay, by centrifugation using a procedure outlined by Soukup et al. (2008). Particle density was determined using the pycnometer method (Flint and Flint, 2002; Naujock, 2008). SMRCs were measured for the main drying curve on undisturbed soil cores using the pressure cell method (Dane and Hopmans, 2002; Naujock,
Hydraulic conductivity was measured by Naujock (2008) on undisturbed soil cores using a falling head method similar to that described by Reynolds et al. (2002).

Soil mineralogical and chemical analyses were performed by the University of Florida Soil Core Laboratory in Gainesville, FL (W.G. Harris, personal communication, 2009, 2010, 2011). Twenty-four samples were analyzed for silt and clay mineralogy by X-ray diffraction analysis (Harris and White, 2008), iron (Fe) and aluminum (Al) oxyhydroxides using acid-ammonium-oxalate extraction (AAO) and citrate-dithionite-bicarbonate extraction (CDB), and phosphorus by CDB extraction. Twenty-two samples were analyzed for pH, electrical conductivity, cation-exchange capacity (CEC), and anion exchange capacity (AEC). Samples were collected by split-barrel sampler in March 2007 at depths corresponding to the screened interval of each well and stored at room temperature until analysis. At each site, samples at 1–3 m intervals were collected at one well through the full thickness of the unconsolidated sediments overlying the Upper Floridan aquifer.

Mineralogical analyses were performed on silt and clay fractions derived by the wet sieving and centrifugation technique described above. Clay mineralogy was determined by X-ray diffraction analysis of the clay fraction using diagnostic cation saturations (Mg$^{2+}$ and K$^+$), glycerol solvation, and heat treatments (thermogravimetry) for definitive phyllosilicate identification using techniques of Karathanasis and Harris (1994) and Harris and White (2008). Thermogravimetry was conducted on each clay-fraction sample and was used in some cases to quantitatively estimate mass percentages of kaolinite and gibbsite; high smectite presence confounds identification of kaolinite by thermogravimetry. Silt mineralogy was determined by X-ray diffraction.
Extractions of Al, Fe, and P by AAO were conducted in the dark (to minimize photolytic effects) using a procedure described by McKeague and Day (1966). The AAO extraction is selective for noncrystalline oxide forms (including oxyhydroxides and hydroxides) of these metals. Extractions of Al, Fe, and P by CDB were performed according to a procedure introduced by Mehra and Jackson (1960). The CDB extraction generally removes total Fe oxides (including crystalline forms), but is less definitive for Al oxides. The CDB extraction of P possibly came close to extracting total P because of the strong complexing tendency of the oxalate anion for both the Ca$^{2+}$ and Al$^{3+}$ with which P was associated. Both of the extraction procedures were modified slightly to accommodate sandy soils with relatively low quantities of extractable metals. Metal concentrations in AAO and CDB extracts were determined by inductively-coupled plasma spectrometry (EPA Method 200.7).

The pH and electrical conductivity of samples were determined in 1:1 soil:solution (deionized water) mass proportions using standard laboratory pH and electrical conductivity meters and electrodes. Effective CEC (the CEC most representative of the material in situ) was determined by using NH$_4^+$ to replace exchangeable cations on the soil exchange complex via mass action (Sumner and Miller, 1996). These cations (Al$^{3+}$, Ca$^{2+}$, Mg$^{2+}$, Na$^+$, and K$^+$) were measured in the exchange solutions via inductively-coupled plasma spectrometry. AEC of samples was determined using a method specified by Zelazny et al. (1996) by saturating the anion exchange with Cl$^-$ and displacement with NO$_3^-$.

Fifty-nine soil samples for analysis of C and N content were collected during four sampling events at the SO basin (March–December 2008) and seven sampling events at the HT basin (March 2008–August 2010) representing a variety of hydroclimatic conditions. Samples
were collected by hand auger or double-cylinder hammer-driven core sampler, placed in 500 mL polyethylene wide-mouth bottles, packed in ice in the field, and subsequently stored frozen until analysis. For each sampling event, soil samples were collected from a single borehole within 3 m of the well in the basin at depths from 0.1–2.3 m (wells PW and M-0506, Figure 1); the borehole was backfilled to land surface in layers with careful tamping using native soil. Soil solids were air-dried and ball-milled (to assure representative subsamples) in preparation for determination of organic carbon (OC), total carbon (TC), and total nitrogen (TN). Analysis of OC was performed by dichromate digestion (Walkley and Black, 1934). Analysis of TC and TN was performed by spectroscopic quantification of evolved combustion products using a carbon-nitrogen analyzer (Shimadzu TOC-V/SSM-5000A, Shimadzu Scientific Instruments, Columbia, MD). Inorganic carbon (IC) was computed as the difference between TC and OC. Two extractions were performed for each sample using 2M potassium chloride (KCl) and distilled water. Both KCl and water solutions were analyzed for NH$_4^+$ on a continuous-flow analyzer by the sodium phenate reaction method (EPA Method 350.1). These same solutions were analyzed for NO$_3^-$ plus NO$_2^-$ (denoted NO$_x$) on a continuous-flow analyzer by the cadmium reduction method (EPA Method 353.2), and for NO$_3^-$ by UV spectrophotometry (Norman and Stucki, 1981). External standards were used as a quality-control check, with error < ±10%. Water solutions were additionally analyzed for OC, TC, and TN by combustion-oxidation (Shimadzu TOC-V/CPH/CPN, Shimadzu Scientific Instruments, Columbia, MD). Inorganic N (IN) was computed as the sum of NH$_4^+$ and NO$_x$; organic N (ON) was computed as the difference of TN and IN. The KCl-soil solutions were shaken for 1 h on a reciprocating shaker before extraction; these analyses were performed to provide an estimate of concentrations based on analyte mass.
both adsorbed to soil particles and dissolved in soil pore water. The water solution extractions were performed to provide an estimate of analyte mass in soil pore water and perhaps more loosely sorbed, and thus were incubated without agitation for 48 h at 4°C (to minimize microbial activity) before extraction. The C and N concentrations in the sample-solution mixtures were presumed equilibrated after incubation. Moisture content by drying at 105°C was determined for each sample and used in the computation of final analyte concentration on a per mass basis for both extraction procedures. For comparison with other water samples, water extraction concentrations for NH$_4^+$, NO$_x$, and NO$_3^-$ were also expressed per volume of soil moisture originally entrained in each sample.

**Water Chemistry**

Water samples were collected for chemical analysis of precipitation, stormwater, soil water, and groundwater (June 2007–August 2010). Water samples were collected and processed following standard U.S. Geological Survey (USGS) protocol (U.S. Geological Survey, 1998). Monitoring wells were purged until at least three casing volumes of water were removed, and field properties (temperature, specific conductance, pH, dissolved oxygen (DO), and redox potential) had stabilized. Field properties were measured for all water samples using a YSI 556MPS multiparameter sonde with a polarographic DO sensor (prior to May 2008) and YSI 6920 V2 multiparameter sonde with an optical DO sensor (May 2008 and later) (YSI Incorporated, Yellow Springs, OH); a flow-through chamber was used for groundwater samples. Sondes were calibrated daily against known standards according to standard USGS protocols (Wilde and Radtke, 1998). When water was stored in the infiltration basins, stormwater samples
were collected at five locations within the basin (by wading) by filling a 1 L amber glass bottle (precombusted at 450°C) through the full depth of standing water and compositing by churn. Stormwater field properties (temperature, specific conductance, pH, DO, and redox potential) were measured at the same five locations and median values reported. Soil-water samples were collected by first purging the lysimeter and then applying a pressure of −60 kPa. Next, the lysimeter was allowed to fill for 6–48 h, depending on ambient soil moisture content. Atmospheric air was then used to apply a pressure to force the water from the lysimeter into a 1 L amber glass bottle (precombusted at 450°C) from which water was withdrawn by peristaltic pump for filtration and bottle filling. Field properties (temperature, specific conductance, and pH only) for soil-water samples were measured using a subsample from the 1 L bottle collected immediately after filling. Precipitation (bulk deposition) samples were obtained by collection in an 8 L plastic bucket from which field properties (temperature, specific conductance, and pH only) were measured and water was withdrawn by peristaltic pump for filtration and bottle filling. Alkalinity was determined for all samples by incremental titration with 0.16 N or 1.6 N sulfuric acid.

Water samples were collected for laboratory analysis of major ions, trace elements, nutrients, and carbon. Major ions included Ca\(^{2+}\), K\(^+\), Mg\(^{2+}\), Na\(^+\), Br\(^-\), Cl\(^-\), F\(^-\), SO\(_4\)^{2-}, Si, and alkalinity. Trace elements and nutrients included Al, B, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, V, W, and Zn. Nutrients included NH\(_4\)^+ as N, NO\(_3^-\) plus NO\(_2^-\) as N, NO\(_2^-\) as N, TN, orthophosphate as P, and total P. Carbon samples included total inorganic carbon (TIC), total organic carbon (TOC) and dissolved organic carbon (DOC).
Samples collected for analyses of major ions, trace elements, and nutrients were filtered through a 0.45-μm pore-size disposable encapsulated filter, rinsed with deionized and sample water. DOC samples were filtered through 0.45-μm pore-size disposable encapsulated filter, rinsed with water certified to be free of organic carbon and with sample water. Filtered samples for all analytes were collected for precipitation, soil water, and groundwater and unfiltered samples for TN and total P were collected for groundwater samples; both filtered and unfiltered samples for all analytes were collected for stormwater. All major ion, trace element, nutrient, and organic carbon samples were analyzed by the USGS National Water-Quality Laboratory in Denver, Colorado, using previously documented methods (Brenton and Arnett, 1993; Clesceri et al., 1998; Fishman, 1993; Fishman and Friedman, 1989; Garbarino et al., 2006; Garbarino and Struzeski, 1998; Hoffman et al., 1996; Patton and Kryskalla, 2003; Struzeski et al., 1996). USGS site identification numbers for sites where water samples were collected and information on obtaining laboratory results are provided in Appendix B. Analytical methods, method detection limits, and laboratory reporting levels for each analyte are listed in Appendix C. Water samples for TIC analysis were collected only at the HT site (May 2009–August 2010) and were analyzed at the USGS laboratory in Boulder, CO (R.L. Smith, personal communication, 2010), using the method described for dissolved inorganic carbon (DIC) by Antweiler et al. (2005).

Dissolved and Soil Gases

Water and soil gas samples were collected for analysis of gas concentrations dissolved in groundwater and present in the gas phase of the unsaturated zone. Measurement of DO in groundwater and basin stormwater was performed in the field using a polarographic sensor (YSI
556MPS) from June 2007 to April 2008 and an optical sensor (YSI 6920 V2) from May 2008 to August 2010 (YSI Incorporated, Yellow Springs, OH). A subset of groundwater samples collected between March 2008 and August 2010 were also analyzed for major dissolved gases (Ar, N₂, O₂, CO₂, CH₄) by gas chromatography (GC) by the USGS Chlorofluorocarbon Laboratory in Reston, Virginia (Busenberg et al., 2001). Duplicate dissolved gas samples were collected in 160 mL serum bottles that were filled gently to overflowing from the bottom while submerged in a larger container. When full, a thick butyl rubber stopper was inserted into the bottle with a syringe needle in place to permit excess water to escape. Samples were preserved by packing bottles in ice in the field and storing at 0–4°C until analysis (Böhlke et al., 2004). Lack of potassium hydroxide (KOH) preservation can allow microbial activity in the sample bottle to affect biogenic gas concentrations (P.K. Widman, personal communication, 2009). The primary analytes of interest are Ar and N₂ (from which excess N₂ attributable to denitrification can be estimated). Groundwater generally had low O₂ and NO₃⁻ concentrations, therefore nitrification/denitrification reactions in the sample bottles likely were minimal. CO₂ and CH₄ concentrations possibly could have been affected and were therefore interpreted qualitatively. Analysis of duplicate bottles indicated 2-sigma (σ) coefficients of variations for Ar, N₂, CO₂ and CH₄ of 0.4%, 0.5%, 1.4% and 1.7%, respectively. Large variations in GC-derived O₂ concentrations were noted, therefore only field measured O₂ concentrations were used. Additionally, groundwater samples were analyzed for nitrous oxide (N₂O) at the USGS laboratory in Boulder, Colorado (R.L. Smith, personal communication, 2010), based on the methods outlined by Antweiler et al. (2005) and Smith et al. (2004).
Soil gas samples were collected using a diffusion monitor device (Rolston, 2002) only at the HT site (November 2009–August 2010). Soil gas monitors were installed by hand excavation adjacent to the lysimeters during construction of the nutrient reduction basin at depths of 0.3, 0.5, 0.9, 1.3, and 1.8 m. Each soil gas monitor consisted of a buried, perforated 125 mL polyethylene bottle, connected to 1.6-mm (inside diameter) brass tubing extending to about 1.2 m above land surface. The bottle was used to facilitate collection of a passive sample by allowing soil gas to freely diffuse into the buried bottle between sampling events, thus when withdrawn the sample would be more representative of the ambient in situ soil gas. In contrast, sampling from open tubing may preferentially withdraw gas from larger soil pores (Rolston, 2002). The monitor tubing had a 3-way stopcock attached that was left closed between sampling events and was used to facilitate purging without disconnecting the syringe assembly. The syringe assembly consisted of a 30 mL plastic syringe with a 1-way stopcock and was used to purge the monitor tubing of at least two volumes of gas and then to slowly withdraw 30 mL of gas. Care was taken to collect gas in the syringe at approximately atmospheric pressure. After first closing the 1-way stopcock followed by closing the 3-way stopcock, the syringe assembly was removed and a needle attached. After expelling 3–5 mL of gas to clear the syringe needle, the needle was immediately inserted into a 30-mL stoppered serum bottle with a helium headspace and the entire contents of the syringe expelled. Duplicate samples were collected for each monitor. Soil gas samples were analyzed for Ar, N₂, O₂, N₂O, and CH₄ at the USGS laboratory in Boulder, Colorado (R.L. Smith, personal communication, 2010), based on the methods outlined by Antweiler et al. (2005), Smith et al. (2004), and Smith et al. (2005).
Stable Isotopes

Isotopic values are reported using standard delta (δ) notation (Clark and Fritz, 1997) as follows:

\[
\delta R_{\text{sample}} = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000
\]  

(1)

For \( \delta^{15}\text{N} \), \( R = ^{15}\text{N}/^{14}\text{N} \); for \( \delta^{18}\text{O} \), \( R = ^{18}\text{O}/^{16}\text{O} \); and for \( \delta^{13}\text{C} \), \( R = ^{13}\text{C}/^{12}\text{C} \). Results are reported in parts per thousand (per mil, ‰). N isotopes are reported relative to N\(_2\) in air (Mariotti, 1983); O isotopes are reported relative to Vienna Standard Mean Ocean Water (Coplen, 1988; Coplen, 1994); and C isotopes are reported relative to Vienna Peedee belemnite and normalized (Coplen et al., 2006). \( \delta^{15}\text{N} \) values of NO\(_3^-\) and dissolved N\(_2\), \( \delta^{18}\text{O} \) values for NO\(_3^-\) and H\(_2\)O, and \( \delta^{13}\text{C} \) values of DIC and DOC were determined.

Samples for isotopic analysis of NO\(_3^-\) were collected in opaque polyethylene bottles after filtration, packed in ice in the field, and subsequently frozen until analysis. Due to a change in protocol, samples collected prior to 2009 were filtered with a 0.45-μm pore-size disposable encapsulated filter and samples collected in 2009 and later were filtered with a 0.2-μm pore-size disposable encapsulated filter. NO\(_3^-\) samples were analyzed by bacterial conversion of NO\(_3^-\) to N\(_2\)O and subsequent measurement on a continuous flow isotope ratio mass spectrometer (Sigman et al., 2001; Casciotti et al., 2002; Coplen et al., 2004; Révész and Casciotti, 2007). For samples with NO\(_3^-\)-N of at least 0.06 mg kg\(^{-1}\), the 2σ uncertainty of N and O isotopic results is 0.5‰ and 1‰, respectively. For NO\(_3^-\)-N less than 0.06 mg kg\(^{-1}\), the 2σ uncertainty of N and O isotopic results is 1‰ and 2‰, respectively.
Samples for isotopic analysis of H$_2$O were collected in glass bottles after filtration with 0.45-μm pore-size disposable encapsulated filter. $\delta^{18}$O of H$_2$O was determined using the carbon dioxide (CO$_2$) equilibration technique (Epstein and Mayeda, 1953; Révész and Coplen, 2008) with 2σ uncertainty of 0.2‰.

Samples for isotopic analysis of DIC and DOC were collected in amber glass vials (precombusted at 450°C) after filtration with 0.7-μm pore-size disposable encapsulated filter. DIC and DOC samples were preserved by addition of 5–10 mg of copper sulfate and 20 μL of 85% phosphoric acid, respectively; both were stored at 0–4°C until analysis. DIC and DOC samples were analyzed on a CO$_2$ dual inlet isotope ratio mass spectrometer (Coplen, 1973; Singleton et al., 2011) with $\delta^{13}$C 2σ uncertainty of 0.2‰.

Isotopic analyses of NO$_3^{-}$, H$_2$O, DIC, and DOC samples were performed by the USGS Reston Stable Isotope Laboratory in Reston, Virginia. Isotopic analysis of N$_2$ samples was performed at the USGS laboratory in Reston, Virginia (J.K. Böhlke, personal communication, 2010), after the GC dissolved gas analysis described in the preceding section, on an isotope ratio mass spectrometer based on the method described by Tobias et al. (2007). $\delta^{15}$N of N$_2$ measurements were calibrated by analyzing air-equilibrated water standards prepared the same way as the samples. Replicate analyses of environmental samples and air-saturated water typically had reproducibility of ±0.1‰ or less.

**Microbiological Activity**

Since Braker et al. (1998) first developed a primer system to amplify the nirK and nirS genes that encode the copper-containing and cytochrome cd1 NO$_2^{-}$ reductases, respectively, the
key enzymes in the denitrification process, polymerase chain reaction technology has been widely used to quantify denitrifying bacteria in soil. Quantification of bacteria by gene copy number is important for a better understanding of denitrifying activity in the environment (Henry et al., 2004). In this work, quantitative real-time polymerase chain reaction (qPCR) was applied to gain insight into denitrifier activity by measuring the copper-containing NO$_2^-$ reductase (nirK) gene density (gene copy number normalized to soil mass) according to the method described by Xuan et al. (2009). The qPCR analysis was performed by Z. Xuan, University of Central Florida, Department of Civil, Environmental, and Construction Engineering in Orlando, Florida (personal communication, 2008–2011). The abundance of the nirK gene in extracted DNA was determined in soil samples from both sites to identify potential differences in denitrifier activity. Both DNA and mRNA (Wallenstein et al., 2006) based quantification are partly relevant to the denitrifying activities, but neither are direct enzymatic activity measurements. Interpretation of the qPCR results is based on the assumption that the presence of the nirK gene in bacterial DNA also indicates the bacteria are actively producing the Nir enzyme required for this denitrification step. Soil samples for qPCR analysis were collected at depths ranging from 0.08 to 1.9 m in the same manner and in the same boreholes used to collect soil chemistry samples.
CHAPTER 3: SOIL PROPERTY CONTROL OF BIOGEOCHEMICAL PROCESSES

Introduction

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Biogeochemical processes occurring in the shallow subsurface can be an important determinant of groundwater quality beneath stormwater infiltration basins, and especially in the case when the coupled N and C cycles can serve to mitigate leaching of inorganic N species to groundwater in association with C mineralization (Kim et al., 2003; Cho et al., 2009). Due to the episodic nature of stormwater runoff generation and heterogeneity of soil properties, infiltration rates and soil moisture content beneath stormwater infiltration basins can vary substantially (Professional Service Industries, Inc., 1993; Cho et al., 2009). Ample research has documented the importance of soil moisture content on soil respiration and the closely linked relations between subsurface oxygen (O$_2$) levels and N and C cycling (Christensen et al., 1990a,b; Skopp et al. 1990; Koba et al., 1997; Smith et al., 1998). Texture is a key soil property controlling the prevalence of narrow pore throats that retain moisture as described by fundamental capillary principles (Koorevaar et al., 1983). Soil moisture retention also is controlled by adsorptive forces, such as ionic-electrostatic and van der Waals bonds, although these forces only dominate in relatively dry soil when moisture often occurs as thin films on soil grains (Lebeau and Konrad, 2010). Austin et al. (2004) in their investigation of pulsed rain events in arid and semiarid ecosystems explain the importance of soil texture on mediating soil wet-dry cycles and thus indirectly controlling subsurface N and C cycling. Wet-dry cycles may increase N losses by
denitrification during wet periods after C substrate and soil NO$_3^-$ accumulate during dry periods (Austin et al., 2004). Pansu et al. (2010) observed the importance of soil water holding capacity, which is related to soil texture and macropore structure, on soil C mineralization. Based on laboratory column experiments simulating a bioretention BMP, Cho et al. (2009) demonstrated that including a fine sand layer (10% silt+clay) resulted in improved inorganic N removal. Through multiphase, multispecies reactive flow and transport modeling, including heat and microbial dynamics, Gu and Riley (2010) demonstrated that soil texture combined with rainfall dynamics controlled soil moisture under natural diffuse recharge conditions in a tropical climate, thus regulating N cycling.

The objective of the research presented in this chapter is to demonstrate how differences in soil properties beneath two subtropical stormwater infiltration basins led to differences in N and C cycling and other relevant biogeochemical processes. Our study examines the interaction of hydroclimatic conditions with the subsurface environment and elucidates factors that effectively control these biogeochemical processes. A combination of hydrologic, soil and water chemistry, isotopic, and microbiological data collected 2007–2009 during the study were used to provide a better understanding of controlling factors on groundwater quality. Results can inform development of improved BMPs to mitigate NO$_3^-$ impacts from stormwater infiltration basins.

**Statistical Methods and Procedures**

Data are compared between the SO and HT sites using nonparametric Wilcoxon rank-sum and signed-rank statistical tests. Rank-sum tests were applied to soil water/groundwater chemistry, soil chemistry, and microbiological data because these data are not naturally paired.
between sites. The exact form of the rank-sum test was used where 10 or fewer samples are available for each site, and the large-sample approximation was used for larger data sets (Helsel and Hirsch, 2002). For stormwater chemistry data, rank-sum tests for the full data set and signed-rank tests for concurrent sampling events were applied to determine the effect of using paired data given the similar hydroclimatic and land use conditions at both watersheds. Considering the small number of concurrent stormwater samples, the exact form of the signed-rank test presented by Helsel and Hirsch (2002) was used. Signed-rank tests were performed using untransformed and log-transformed data and both yielded identical p-values. Differences in median values are considered statistically significant at $\alpha = 0.05$.

**Results and Discussion**

Hydroclimatic conditions—the net effects of atmospheric and surface hydrologic processes—and soil properties play an important role in controlling subsurface biogeochemical processes in subtropical environments. Due to their close proximity, both stormwater basin sites investigated during this study experienced similar climatic forcing, such as precipitation and temperature, and both are located in similar residential settings. However, results of soil and water sampling presented below demonstrate substantially different physical, chemical, and microbiological conditions in the subsurface at each site.

**Lithology and Soil Physical Properties**

Differences between the two sites in lithology and physical properties of soils in the shallow unsaturated zone illuminate important controls on soil chemistry, infiltration rates, and moisture content. Even though soils throughout both watersheds are predominantly well drained,
the local lithology beneath the basins differed between sites at depths above 1.6 m, especially in regard to texture (Figure 2a) and to a lesser degree mineralogy (Appendix D). Below 1.6 m, differences are much more moderate (Figure 2a). According to U.S. Department of Agriculture textural classification guidelines, the shallow soils at the HT site are sand at depths up to approximately 1.6 m below the bottom of the basin (silt+clay contents of 1–5%, median 2%, n = 4; Figure 2a, Appendix E, and Naujock, 2008); predominantly sandy clay sediments are present at greater depths (silt+clay contents of 41–62%, median 52%, n = 5; Figure 2a and Appendix E). At the SO site, substantial silt and clay generally are present throughout the shallow soil and deeper sediment profile (silt+clay content of 7–80%, median 41%, n = 9, at depths up to 1.6 m; and 16–93%, median 30%, n = 8, at depths below 1.6 m; Figure 2a, Appendix E, and O’Reilly (unpublished data, 2010)). These results indicate predominantly sandy clay loam, sandy clay, and clay textures are present at the SO site, with some isolated layers of sand, loamy sand, and sandy loam textures. The shallow coarse-textured soil within the HT basin is typical of weathered Florida sandy soils with respect to mineralogy (well M-0506, 0.8 m depth, Appendix D), showing the common suite: hydroxyinterlayered vermiculite, kaolinite, gibbsite, and quartz (Harris et al., 1987). Most of the clay mineralogical components of soils at both sites are consistent with Miocene phosphorites or the soils forming from those materials (Wang et al., 1989), including the phosphate mineral apatite, along with smectite and kaolinite (Appendix D). Silt fractions are dominated by quartz and/or apatite at both sites. These fine-textured sediments effectively represent the intermediate confining unit, thus the surficial aquifer system is thin or absent at both sites. Limestone was encountered at a depth of 11.5 m beneath the HT basin, representing the top of the Upper Floridan aquifer. Limestone depth at the SO site is highly
variable, encountered at a depth of 9.8 m at well M-0511 (Figure 2a) but not present in a 15-m deep boring 30 m to the west (Andreyev Engineering, Inc., personal communication, 2007), which is consistent with the karst geology of north-central Florida. Compared to the lithology beneath the basins (Figure 2a), visual observation of split-spoon samples from wells outside the perimeter of each basin (Figure 1) indicate that lithology generally is uniform at the HT site, whereas at the SO site lithology is more variable but still indicates an abundance of silt and clay sediments.

Figure 2: Soil properties beneath the stormwater infiltration basins: (A) textural variations with depth (boreholes drilled adjacent to wells M-0511 (South Oak site) and M-0506 (Hunter’s Trace site) and subsequently grouted to land surface), and (B) soil moisture retention curves reported by Naujock (2008) for undisturbed cores collected from 0.3 and 0.6 m depths (cores collected from boreholes within 3 m of wells PW (South Oak site) and M-0506 (Hunter’s Trace site); $K_s$, saturated hydraulic conductivity).
Textural differences contributed to substantial difference in SMRCs and other soil properties (Figure 2b). Naujock (2008) reports that soils at the SO site generally have lower particle (soil solids) density \( (\rho_s, 2.56–2.62 \text{ g cm}^{-3}) \), higher porosity \( (\phi, 0.35–0.45) \), and lower saturated hydraulic conductivity \( (K_s, 3.7\times10^{-5}–0.34 \text{ m d}^{-1}) \) than soils at the HT site \( (\rho_s, 2.61–2.72 \text{ g cm}^{-3}; \phi, 0.28–0.29; K_s, 1.2–2.2 \text{ m d}^{-1}) \). The SMRCs demonstrate the greater moisture retention capacity of the soil at the SO site (Figure 2b), which when considered with the lower \( K_s \) values at the SO site (median = 0.020 m d\(^{-1}\), \( n = 5 \)) compared to the HT site (median = 2.2 m d\(^{-1}\), \( n = 3 \)), are consistent with greater silt+clay contents of the shallow soils at the SO site.

Soils at the SO site generally have greater sorption potential than soils at the HT site, with CEC of 7–52 centimoles of charge per kilogram of soil \( (\text{cmol}_c \text{ kg}^{-1}) \) at SO and 1.1–19 \( \text{cmol}_c \text{ kg}^{-1} \) at HT (Appendix E). AEC was relatively low at both sites, ranging from 0.4 to 5 \( \text{cmol}_c \text{ kg}^{-1} \) (Appendix E).

**Hydroclimatic Conditions**

The 5-minute hydrologic monitoring data were composited into daily values (summed for rainfall and averaged for all other values) for 2008–2009 (Figure 3). Annual rainfall was slightly higher at the SO site than the HT site, but was close to the long-term average and similarly distributed in time at both sites. Two particularly large rainfall events occurred in August 2008 (Tropical Storm Fay) and May 2009, resulting in substantial and prolonged storage of water in both basins compared to more typical rainfall periods. Large differences are apparent in the magnitude and frequency of water storage at each site, which are indicative of lower infiltration rates at the SO basin. Infiltration rates were estimated by analysis of basin stage recession curves...
for several storm events in 2008–2009. For 46–155 mm rainfall events (5–33 h duration),
infiltration rates were 14–29 mm d\(^{-1}\) at the SO basin, while at the HT basin infiltration rates were
170–260 mm d\(^{-1}\). These differing infiltration rates are consistent with the differences in lithology
between the sites (Figure 2a).
Figure 3: Hydrologic monitoring of rainfall, basin stage, groundwater level, and volumetric moisture content (VMC) at the (A) South Oak site, and (B) Hunter’s Trace site. Mid-screen depths of wells noted for groundwater level, and time domain reflectometry probe depths noted for VMC.

A comparison of basin volume (based on field verified geometry) and storm magnitude (rainfall depth) suggests that the majority of each basin’s watershed does not contribute runoff to the basin, except perhaps during extreme, prolonged storm events. For example, during Tropical Storm Fay, 155 mm of rainfall occurred during a 33-h period causing an observed increase of
about 0.6 m in the stormwater level in each basin. Runoff volumes were computed using a water balance and assuming contributing areas produce 100% runoff, which indicate areas that constitute 4% and 8% of the SO and HT watersheds, respectively. Even though actual areas contribute less than 100% runoff, results indicate only a fraction of the area of each watershed contributes runoff to each stormwater basin, which is consistent with the karst, well drained terrain.

The response of the measured hydrologic variables to hydroclimatic conditions is clearly influenced by lithology. Good hydraulic communication between the surface and subsurface environments exists at both sites, but is considerably more subdued at the SO site compared to the HT site (Figure 3). The highly attenuated response of well M-0511 at the SO site is due to a prevalence of fine-textured sediments leading to large vertical head gradients of 0.90–1.3 m m\(^{-1}\) between M-0512 (2.5 m deep) and M-0511 (9.1 m deep). The two shallow wells inside or at the edge of the typical area of stored stormwater at the SO site (M-0512 and PW, Figure 1) respond rapidly to runoff events (Figure 3a); subsequently, water percolates slowly through the underlying sandy silts and clays toward the deeper well M-0511. In contrast, more rapid downward leakage of groundwater is indicated by the more sandy sediments and relatively small vertical head gradients at the HT site of 0.014–0.57 m m\(^{-1}\) between M-0506 (4.6 m deep) and M-0505 (9.4 m deep).

A comparison of lateral and vertical groundwater gradients indicates the potential for infiltrated stormwater to impact deeper aquifers. At the SO site, water-table gradients beneath the basin (between well PW and wells M-0512, M-0514, M-0515, M-0516, and M-0522; Figure 1) were both inward and outward, ranging from −0.10 to 0.080 m m\(^{-1}\) (negative values inward,
positive values outward). At the HT site, the water table gradients beneath the basin (between well M-0506 and wells M-0507, M-0508, M-0509, and M-0510; Figure 1) were nearly always outward, ranging from −0.00059 to 0.047 m m$^{-1}$. At both sites, vertical groundwater head gradients were substantially greater than lateral groundwater head gradients, 30–600 times greater at SO and about 14–19 times greater at HT based on median absolute values. Assuming a vertical anisotropy of less than 10, which is typical of sandy sediments in central Florida (O’Reilly, 1998) and consistent with a single measurement at the SO site (Andreyev Engineering, Inc., personal communication, 2007), these gradients suggest groundwater movement was predominantly downward beneath both basins toward the Upper Floridan aquifer.

**Soil Moisture and Aeration**

Field data indicate large differences in soil moisture contents between the SO and HT sites causing differing soil aeration conditions. Fine-textured, less permeable soils at the SO site have substantially greater moisture retention capacity, supporting the wet to nearly saturated conditions that existed beneath the basin even during prolonged dry periods; whereas the relatively coarse-textured, permeable soils at the HT site dried rapidly after infiltration events (Figure 2 and 3). Higher soil moisture contents beneath the SO basin are also indicated by smaller amplitudes in cyclic subsurface temperature variations at seasonal and shorter time scales beneath the SO basin compared to the HT basin. Cumulative frequency distributions indicate moisture contents were always higher in the upper 0.9 m of soil beneath the SO basin, with median moisture contents of 0.35–0.44 beneath the SO basin and 0.10–0.18 beneath the HT basin (Figure 4). As a result, median volumetric gas-phase contents were about 0.11–0.19 (38–66% of pore space) beneath the HT basin, but were only 0.015–0.041 (3.4–11% of pore space)
beneath the SO basin. Thus, the greater soil aeration beneath the HT basin is largely attributable to soil physical properties, which are conducive to sustaining aerobic conditions in the subsurface.
Figure 4: Cumulative frequency distributions of field measured volumetric moisture content (VMC) (Figure 3) and the ratio of the diffusion coefficient of gas through soil to that through air ($D_{g\text{soil}} / D_{g\text{air}}$) beneath the (A) South Oak stormwater infiltration basin, and (B) Hunter’s Trace stormwater infiltration basin.
Precipitation and Stormwater Quality

Two precipitation samples were collected, one at each site, that suggest atmospherically derived N is not an insignificant component of stormwater N. At the SO site, a precipitation sample was collected 23 July 2008 over a 2-h period during a 2.2-h 19-mm rainfall event, indicating a TDN of 0.11 mg L\(^{-1}\), NO\(_3^-\)-N of 0.06 mg L\(^{-1}\), and NH\(_4^+\)-N of 0.03 mg L\(^{-1}\). At the HT site, a precipitation sample was collected 19 May 2009 over a 3.7-h period during a prolonged 29-h 76-mm rainfall event, indicating a TDN of 0.07 mg L\(^{-1}\), NO\(_3^-\)-N of 0.04 mg L\(^{-1}\), and NH\(_4^+\)-N of 0.03 mg L\(^{-1}\). These limited data indicate precipitation TDN concentrations constitute about 20% of the stormwater TDN concentrations for these two storm events (0.53 mg L\(^{-1}\) for the SO basin and 0.34 mg L\(^{-1}\) for the HT basin).

Stormwater samples were collected during groundwater sampling events when water was stored in the basin; thus more samples were collected from the SO basin than from the HT basin as a result of differences in infiltration rates. Flow-weighted concentrations for individual runoff events likely would be different. TDN concentrations varied from 0.49 to 1.3 mg L\(^{-1}\) with a mean of 0.88 mg L\(^{-1}\) (n = 10) at the SO basin, and varied from 0.23 to 1.4 mg L\(^{-1}\) with a mean of 0.59 mg L\(^{-1}\) (n = 6) at the HT basin (Figure 5). Differences in N speciation are evident. NO\(_3^-\) concentrations generally were higher in stormwater at the HT basin compared to the SO basin, and ON averaged 70% and 90% of TDN at the HT and SO basins, respectively. Thus, it is more informative to compare TDN concentrations. DOC concentrations varied from 6.4 to 13.9 mg L\(^{-1}\) with a mean of 10.9 mg L\(^{-1}\) (n = 10) at the SO basin, and varied from 3.8 to 16.9 mg L\(^{-1}\) with a mean of 7.5 mg L\(^{-1}\) (n = 6) at the HT basin (Figure 5). However, differences may be due to
different hydroclimatic conditions during different months. Comparing stormwater quality for only the five concurrent sampling events (January, February, June, July, and August 2008), indicates that median differences in neither TDN nor DOC were statistically significant (p > 0.1 for both TDN and DOC, Table 1). Unfiltered samples indicate particulate and colloidal N and OC (greater than 0.45 \( \mu \)m) were at times important constituents of TN and TOC in stormwater (Figure 5). Although this particulate and colloidal fraction likely was largely retained in the shallow soil zone, as groundwater samples indicated negligible difference between filtered and unfiltered N and OC.
Figure 5: Temporal variations in nitrogen species and organic carbon concentrations of stormwater stored in the (A) South Oak stormwater infiltration basin, and (B) Hunter’s Trace stormwater infiltration basin. Nitrogen species concentrations that did not exceed method detection limits are plotted at values equal to the laboratory reporting level (NH₄⁺-N = 0.02 mg L⁻¹, NO₃⁻-N = 0.016 mg L⁻¹). DOC, dissolved organic carbon; TOC, total organic carbon; TDN, total dissolved nitrogen; TN, total nitrogen.
Table 1: Summary statistics for nitrogen and carbon concentrations in stormwater, soil water/groundwater (lysimeters and wells PW and M-0506), solid solid, and soil extractable samples; and denitrifier activity.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>South Oak basin</th>
<th>Hunter’s Trace basin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n median min. max.</td>
<td>n median min. max. p</td>
</tr>
<tr>
<td>Stormwater: (mg L⁻¹ as N or C)</td>
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<td></td>
</tr>
<tr>
<td>TDN, all</td>
<td>10 0.84 0.49 1.32</td>
<td>6 0.47 0.23 1.36 0.15</td>
</tr>
<tr>
<td>TDN, concurrent</td>
<td>5 0.84 0.50 1.13</td>
<td>5 0.53 0.23 1.36 &gt;0.10</td>
</tr>
<tr>
<td>DOC, all</td>
<td>10 11.17 6.38 13.94</td>
<td>6 6.37 3.79 16.91 0.056</td>
</tr>
<tr>
<td>DOC, concurrent</td>
<td>5 11.21 8.38 13.94</td>
<td>5 7.45 3.79 16.91 &gt;0.10</td>
</tr>
<tr>
<td>Soil water/groundwater: (mg L⁻¹ as N or C)</td>
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<td></td>
</tr>
<tr>
<td>TDN</td>
<td>29 0.52 0.25 3.86</td>
<td>25 1.92 0.27 7.16 &lt;0.001</td>
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<tr>
<td>NH₄⁺, excl. BDL</td>
<td>16 0.033 0.012 0.082</td>
<td>0</td>
</tr>
<tr>
<td>NO₂⁻, excl. BDL</td>
<td>11 0.006 0.001 0.011</td>
<td>0</td>
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<tr>
<td>NO₃⁻, excl. BDL</td>
<td>20 0.10 0.01 3.28</td>
<td>25 1.78 0.07 7.23 &lt;0.001</td>
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<tr>
<td>ON, excl. BDL</td>
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<td>20 0.14 0.03 0.52 &lt;0.001</td>
</tr>
<tr>
<td>DOC</td>
<td>15 6.27 4.05 13.25</td>
<td>14 0.98 0.55 8.50 &lt;0.001</td>
</tr>
<tr>
<td>Soil solid: (mg kg⁻¹ as N or C)</td>
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<td></td>
</tr>
<tr>
<td>TN</td>
<td>20 701 302 3850</td>
<td>14 138 70 4550 &lt;0.001</td>
</tr>
<tr>
<td>TC</td>
<td>20 6300 1420 128000</td>
<td>14 2415 853 126000 0.007</td>
</tr>
<tr>
<td>OC</td>
<td>20 4730 1250 63500</td>
<td>14 2025 757 63600 0.015</td>
</tr>
<tr>
<td>IC</td>
<td>20 1435 26 64500</td>
<td>12 128 25 62800 0.059</td>
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<td>Soil extractable: (mg kg⁻¹ as N or C)</td>
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<td></td>
</tr>
<tr>
<td>TN, H₂O</td>
<td>20 2.3 1.6 5.8</td>
<td>14 2.4 1.7 20.8 0.6</td>
</tr>
<tr>
<td>NH₄⁺, H₂O</td>
<td>20 0.75 0.54 2.88</td>
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<tr>
<td>NH₄⁺, KCl</td>
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<td>14 0.55 0.08 24.20 0.021</td>
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<td>14 0.55 0.08 24.20 &lt;0.001</td>
</tr>
<tr>
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<td>9 0.9 0.1 1.4 0.003</td>
</tr>
<tr>
<td>TC, H₂O</td>
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<td>14 22.6 15.7 34.9 0.004</td>
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<td>8 9.7 8.3 20.5 0.002</td>
</tr>
<tr>
<td>IC, H₂O</td>
<td>20 12.4 0.7 32.5</td>
<td>8 12.6 7.9 14.1 0.5</td>
</tr>
<tr>
<td>Soil denitrifier activity: (gene-copies g⁻¹ soil)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nirK density, excl. BDL</td>
<td>21 5.6×10⁵ 1.5×10⁴ 2.2×10⁶</td>
<td>8 3.0×10⁴ 6.6×10³ 5.1×10⁵ 0.003</td>
</tr>
<tr>
<td>nirK density, incl. BDL</td>
<td>22 5.1×10⁵ BDL 2.2×10⁶</td>
<td>11 1.0×10⁶ BDL 5.1×10⁵ &lt;0.001</td>
</tr>
</tbody>
</table>

Lower median values in boldface are statistically different (α = 0.05). TDN, total dissolved nitrogen; ON, organic nitrogen; DOC, dissolved organic carbon; OC, organic carbon; IC, inorganic carbon; H₂O, soil extraction using distilled water; KCl, soil extraction using 2M potassium chloride; excl. BDL, excluding below detection limit samples; incl. BDL, including below detection limit samples; nirK, copper-containing nitrite reductase.
**Biogeochemical Consequences**

Subsurface biogeochemical processes are commonly mediated by microorganisms where relatively prevalent OC serves as an electron donor coupled to a sequence of terminal electron-accepting processes (TEAPs) \( O_2 > NO_3^- > Mn(IV) > Fe(III) > SO_4^{2-} > CO_2 \) (Chapelle et al., 1995; McMahon and Chapelle, 2007). Due to the desire to mitigate \( NO_3^- \) impacts, the effects of soil properties at the stormwater infiltration basins on \( O_2 \) and \( NO_3^- \) reduction are of particular interest at both sites.

**Oxygen Conditions**

Differing subsurface \( O_2 \) contents, resulting from generally low soil aeration beneath the SO basin and high soil aeration beneath the HT basin (Figure 4), played a key role in controlling biogeochemical processes beneath both basins. At the SO basin, cyclic variations in groundwater DO coincided with generally wet and dry hydroclimatic conditions, with oxidizing conditions (January, February, and June 2008) at the beginning of wet periods upon the infiltration of aerobic stormwater followed by reducing conditions (Figure 6a). The reducing conditions led to a progression of TEAPs. At the HT site, groundwater DO concentrations showed some variations but were always greater than 5 mg L\(^{-1}\), remaining aerobic and precluding the reduction of electron acceptors other than \( O_2 \) (Figure 6b).
Figure 6: Temporal variations in groundwater quality beneath the (A) South Oak stormwater infiltration basin (well PW, mid-screen depth 1.9 m), and (B) Hunter’s Trace stormwater infiltration basin (M-0506 mid-screen depth 3.9 m, M-0505 mid-screen depth 8.6 m). NO$_3^-$-N concentrations that did not exceed the method detection limit are plotted at values equal to the laboratory reporting level (0.016 mg L$^{-1}$). DOC, dissolved organic carbon; DO, dissolved oxygen.
Organic Carbon Mineralization

DOC in soil water and shallow groundwater was significantly greater at the SO site (Figure 7) than at the HT site (p <0.001, Table 1) with large decreases occurring in the unsaturated zone at HT (Figure 8). The zone of largest DOC depletion (between 0.5 and 1.3 m depths) beneath the HT basin coincides with the depths of highest alkalinity, consistent with mineralization of DOC to CO$_2$ (Figure 8). Alkalinity increased in the upper 0.5–0.9 m of soil where dissolved CO$_2$ likely interacted with soil solids yielding carbonate alkalinity predominantly in the HCO$_3^-$ form, as suggested by decreasing soil solids IC (Figure 9b), a profile of Ca$_{2+}$ concentrations (data not shown) similar in shape to that of alkalinity, and soil water pH of 7.1–7.8 (Figure 8). The large decrease in alkalinity through the deeper unsaturated zone to shallow groundwater (between 0.5 or 0.9 m and 3.9 m depths) probably is also attributable to carbonate reactions, where substantial decreases in pH between 1.3 and 3.9 m depths are likely caused by the lower buffering capacity resulting from the decreasing HCO$_3^-$ concentrations in the overlying interval (0.5–1.3 m) (Figure 8). DOC oxidation likely is coupled with O$_2$ reduction in the unsaturated zone beneath the HT basin, which is aerobic given the coarse-textured soil at depths less than 1.6 m (Figure 2a) and the high soil aeration. In contrast, shallow groundwater commonly was anoxic beneath the SO basin (Figure 6a), inhibiting aerobic DOC mineralization and contributing to relatively constant or only slightly decreasing DOC concentrations with depth (Figure 7).
Figure 7: Soil-water and groundwater chemistry profiles beneath the South Oak stormwater infiltration basin. Data at 0-m depth represent stormwater samples; data at 0.5-, 0.9-, and 1.4-m depths represent lysimeter samples; data at 1.9-m depth represent well PW. Data are not available at every depth for every sampling event due to lack of sample (stormwater), lack of analysis for that sample (dissolved organic carbon (DOC)), or non-exceedence of method detection limit (NH$_4^+$-N, NO$_3^-$-N). NO$_2^-$-N was below the laboratory reporting level of 0.002 mg L$^{-1}$ for all soil-water and groundwater samples, with the exception of June and July samples at 0.5 and 0.9 m depths where NO$_2^-$-N varied 0.0027–0.0072 mg L$^{-1}$. Organic N is computed as the difference between total dissolved nitrogen (TDN) and inorganic nitrogen (IN = NH$_4^+$ + NO$_3^-$ + NO$_2^-$), where NH$_4^+$, NO$_3^-$, and NO$_2^-$ are assumed zero when below their respective method detection limits of 0.01, 0.008, and 0.001 mg L$^{-1}$).
Figure 8: Soil-water and groundwater chemistry profiles beneath the Hunter's Trace stormwater infiltration basin. Data at 0-m depth represent stormwater samples; data at 0.5-, 0.9-, and 1.3-m depths represent lysimeter samples; data at 3.9- and 8.6-m depths represent wells M-0506 and M-0505, respectively. Data are not available at every depth for every sampling event due to lack of sample (stormwater and well M-0505), lack of analysis for that sample (dissolved organic carbon (DOC)), or non-exceedence of method detection limit (NO$_3^-$-N, ON). NH$_4^+$-N was below the laboratory reporting level of 0.02 mg L$^{-1}$ for all soil-water and groundwater samples. NO$_2^-$-N was below the laboratory reporting level of 0.002 mg L$^{-1}$ for all soil-water and groundwater samples except the May 2009 soil-water sample at 0.5 m depth which had NO$_2^-$-N of 0.0031 mg L$^{-1}$. Organic N is computed as the difference between total dissolved nitrogen (TDN) and inorganic nitrogen (IN = NH$_4^+$ + NO$_3^-$ + NO$_2^-$), where NH$_4^+$ and NO$_2^-$ are assumed zero when below their respective method detection limits of 0.01 and 0.001 mg L$^{-1}$).
Soil solid and extractable C concentrations indicate important differences between sites and temporal variations at each site (Appendix F and G, Figure 9). At the SO site, results indicate different C characteristics in the late winter/spring (March and May) before the prolonged summer wet period of 2008 (Figure 3a) compared to autumn (November and December). Soil solids analyses indicate slightly lower OC concentrations in autumn compared to spring. Results of soil water extractable analyses generally indicate increases in water extractable OC and IC concentrations from spring to autumn at depths less than 1.3 m, but few changes below this depth (Figure 9a). The increases in water extractable OC compared to the decreases in soil solids OC are consistent, at least qualitatively, with mass transfer of OC between solid and aqueous phases, which may explain relatively constant DOC in groundwater beneath the SO basin (Figure 7). Increases in water extractable IC from spring to autumn as well as increasing alkalinity from June to November (0.5-m lysimeter, Figure 7) may be indicative of a zone of active biogeochemical processes beneath the SO basin at depths above 1.3 m coupled with mineralization of OC substrates. Carbonate reactions with soil solid IC (Figure 9a) probably also influenced the soil and water chemistry, as suggested by calcite saturation indices exceeding 1.5 in this zone (0.5-, 0.9-, and 1.4-m lysimeters; Ca$^{2+}$ data not shown; Figure 7). At the HT site, soil solid OC contents generally were lower than at the SO basin (Figure 9, Appendix F), and differences in median values are significant ($p = 0.015$, Table 1). Generally decreasing soil solid OC with depth (Figure 9b) combined with the high aeration of the coarse-textured soil at the HT site is consistent with aerobic oxidation of soil organic matter and soil water C cycling discussed previously. Much of the large OC contents in the shallow soil zones at both sites (Figure 9) may
be attributable to organic matter from root growth and accumulation of particulates from infiltrating stormwater.
Figure 9: Soil solid and water extractable total carbon (TC), organic carbon (OC), and inorganic carbon (IC) contents beneath the (A) South Oak stormwater infiltration basin, and (B) Hunter’s Trace stormwater infiltration basin. IC is computed as the difference between TC and OC. At the Hunter’s Trace basin, IC data are not available at every depth for every sampling event due to negative computed values. See Appendices F and G for data values.
Nitrogen Cycling

The N cycle beneath each basin was affected by different O and C cycle interactions, resulting in NO$_3^-$ reduction beneath the SO basin and relatively conservative transport of NO$_3^-$ beneath the HT basin. Similar NO$_3^-$ and Cl$^-$ variations beneath the HT basin \((r^2 = 0.64, n = 10, \text{well M-0506, Figure 6b)}\) suggest relatively conservative transport of NO$_3^-$. In contrast, a much lower correlation exists between NO$_3^-$ and Cl$^-$ beneath the SO basin \((r^2 = 0.21, n = 10, \text{well PW, Figure 6a)}\), suggesting reaction dominated fate of NO$_3^-$. Water extractable concentrations (Figure 10) consistently exceeded lysimeter/well concentrations (Figure 7 and 8) for all N species at both sites. Higher water-extractable NH$_4^+$ concentrations are expected based on CEC, but the potential for NO$_3^-$ sorption is considerably less. At the SO site, water extractable NO$_3^-$-N varied from 0.1–4.3 mg L$^{-1}$ with a median of 0.14 mg L$^{-1}$ \((n = 25, \text{including 9 samples below the method detection limit})\) (Appendix G) and lysimeter/well NO$_3^-$-N varied from 0.01–3.3 mg L$^{-1}$ with a median of 0.032 mg L$^{-1}$ \((n = 29, \text{including 9 samples below the method detection limit})\) (Figure 10a). At the HT site, water extractable NO$_3^-$-N varied from 0.4–100 mg L$^{-1}$ with a median of 11 mg L$^{-1}$ \((n=8)\) (Appendix G) and lysimeter/well NO$_3^-$-N varied from 0.07–7.2 mg L$^{-1}$ with a median of 1.8 mg L$^{-1}$ \((n=25)\) (Figure 10b, excluding data from well M-0505 at 8.6-m depth). Differences between water extractable and lysimeter/well concentrations may be due to sample scale, spatial and temporal variations, sorption potential, or diffusion-limited exchange between mobile and isolated pore-space water (Coats and Smith, 1964; Green et al., 2005). The N in isolated pore water or loosely sorbed suggested by the water extractions might be periodically mobilized when a storm event floods the basin, thus serving as a potential source of N to the groundwater.
Figure 10: Soil solid and water extractable total nitrogen (TN) and soil water extractable ammonium nitrogen (NH$_4^+$), nitrate plus nitrite (NO$_x$), and organic nitrogen (ON) beneath the (A) South Oak stormwater infiltration basin, and (B) Hunter’s Trace stormwater infiltration basin. ON is computed as the difference between TN and inorganic nitrogen (IN = NH$_4^+$ + NO$_x$), where NO$_x$ is assumed zero when below the method detection limit. Data are not available at every depth for every sampling event due to negative computed ON or non-exceedence of NO$_x$ detection limit. See Appendixes F and G for data values.
Soil, soil water, and groundwater concentrations were significantly different between sites for some N species, where differences are consistent with NO$_3^-$ reduction beneath the SO basin and ammonification/nitrification beneath the HT basin. Median soil solids TN concentrations were significantly higher (p < 0.001) yet water extractable TN concentrations were not significantly different (p = 0.6) at the SO site compared to the HT site (Table 1). Water extractable N was predominantly in the NH$_4^+$ and organic forms for SO soils and in the NO$_3^-$, NH$_4^+$, and organic forms for HT soils. Water extractable NO$_x$ was significantly lower for SO soils (p < 0.001) consistent with NO$_3^-$ reduction, and water extractable ON was significantly lower for HT soils (p = 0.003) consistent with depletion by ammonification. NO$_x$ comprises primarily NO$_3^-; \text{ soil samples analyzed for both NO}_3^- \text{ and NO}_2^- \text{ indicate that NO}_2^- \text{ was typically less than 10\% of NO}_3^- (Appendix G). In contrast to water extractable TN concentrations, TDN in soil water and groundwater was significantly lower at the SO site (p < 0.001, Table 1). TDN was predominantly present as ON at the SO site (Figure 7) consistent with limited ammonification, whereas TDN was predominantly present as NO$_3^-$ at the HT site (Figure 8) consistent with nitrification. NH$_4^+$-N in soil water and groundwater was less than 0.1 mg L$^{-1}$ at the SO site and not detectable (less than 0.02 mg L$^{-1}$) at the HT site, consistent with sorption indicated by CEC. Even relatively low CEC beneath the HT basin of 2.2–4.0 cmol$_c$ kg$^{-1}$ in the unsaturated and shallow saturated zones (depths less than 6 m at well M-0506, Appendix E) indicates a sorption potential for NH$_4^+$ of 310–570 mg N kg$^{-1}$.

Temporal variations in soil N species provide insight into potential N cycling leading to the low water-extractable NO$_x$ concentrations beneath the SO basin in 2008 (Appendix F and G,
Figure 10). NO$_x$ was present in soil samples collected during late winter/spring (March and May); however, the near absence of NO$_x$ in soil samples in autumn (November and December) is suggestive of denitrification or dissimilatory nitrate reduction to ammonium (DNRA) during or following the summer wet season (Figure 10a). The increased NH$_4^+$ concentrations in November may be due to DNRA, whereas the decreased NH$_4^+$ combined with increased NO$_x$ concentrations at depths above 0.4 m in December (Figure 10a) likely was caused by nitrification in uppermost soil layers as the basin dried and by denitrification in the portions of the underlying soil that remained saturated (Figure 3a). CEC at the SO site (Appendix E) indicates conditions favorable for NH$_4^+$ sorption, thus possibly serving as a source for nitrification or sink for DNRA or ammonification. The reduction of NO$_3^-$ beneath the SO basin was likely coupled with OC mineralization during the same spring to autumn period in the upper 1.3 m of the soil profile inferred from water extractable IC results (Figure 9a).

Subsurface O$_2$ levels had a strong influence on the biogeochemistry of N in soil water and groundwater. At the SO site, NO$_3^-$-N of 3.3 mg L$^{-1}$ was measured in the lysimeter at a depth of 1.4 m and 0.84 mg L$^{-1}$ from well PW (mid-screen depth 1.9 m) in June 2008 (Figure 7) when DO was 3.8 mg L$^{-1}$. After this time NO$_3^-$-N remained below the laboratory reporting level (0.016 mg L$^{-1}$) for the remainder of the wet season while DO remained 0.1–0.2 mg L$^{-1}$ (Figure 6a). This pattern of low or not detectable NO$_3^-$ during autumn is consistent with that noted for water extractable NO$_x$ (Figure 10a). From July through late November 2008, the basin remained flooded continuously (up to 2.1 m deep) due to heavy summer rainfall and Tropical Storm Fay; the basin was dry again in late November and December 2008 (Figure 3a). Therefore, when NO$_3^-$ was present at the SO site, denitrification likely occurred, yet when NO$_3^-$ was not present
and more highly reductive conditions prevailed, other TEAPs occurred. In contrast, persistent aerobic conditions at the HT site likely enabled ammonification/nitrification as suggested by increasing \( \text{NO}_3^- \) and decreasing ON in the unsaturated zone (Figure 8) and inhibited significant denitrification, which resulted in \( \text{NO}_3^- \)-N of 1.3–3.3 mg L\(^{-1} \) in shallow groundwater (Figure 6b).

**Manganese, Iron, and Sulfate Reduction and Methanogenesis**

The presence of \( \text{O}_2 \) and \( \text{NO}_3^- \) electron acceptors in the unsaturated zone and groundwater beneath the HT basin precluded more highly reducing TEAPs as suggested by low Mn and Fe concentrations in groundwater (Mn < 2 µg L\(^{-1} \) and Fe < method detection limit of 4 µg L\(^{-1} \) for wells M-0506 and M-0505; data not shown). However, at the SO site after \( \text{NO}_3^- \) was depleted and DO was low by July 2008, Mn and Fe concentrations steadily increased in groundwater (Figure 6a). These total dissolved Mn and Fe concentrations presumably consist of the reduced valence states of Mn\(^{2+} \) and Fe\(^{2+} \), likely caused by bacterially mediated processes and the greater solubility of reduced Mn and Fe (Postma et al., 1991; Appelo and Postma, 2005). \( \text{SO}_4^{2-} \) reduction is suggested by decreasing \( \text{SO}_4^{2-} \) concentrations during the summer and autumn of 2008 (Figure 6a). These TEAPs were documented to occur sequentially during the prolonged flooding at the SO site, progressing from Mn reduction to methanogenesis, with methane concentrations increasing from less than 0.05 mg L\(^{-1} \) in August 2008 to 3.1 mg L\(^{-1} \) in November 2008 (O’Reilly et al., 2011). Thus, identification of these other more highly reductive TEAPs at the SO site and their absence at the HT site provide further evidence supporting denitrification beneath the SO basin and relatively conservative \( \text{NO}_3^- \) transport beneath the HT basin.
Stable Isotope and Microbiological Confirmation

Results of the N and O isotopic analysis of NO$_3^-$ for precipitation, stormwater, soil water, and groundwater samples collected at the HT and SO sites provide insight into the sources of NO$_3^-$ and additional confirmation of the causes of differences in N cycling between sites (Figure 11). The stormwater samples are indicative of atmospheric NO$_3^-$, fertilizer NO$_3^-$, nitrification of atmospheric or fertilizer derived NH$_4^+$, or perhaps a mixture of these sources for some samples. Many groundwater and soil-water samples, primarily at the HT site, are indicative of atmospheric or fertilizer derived NH$_4^+$ or soil nitrogen (organic or NH$_4^+$). Many groundwater samples at the SO site were in the range of organic wastes (septic or manure) (Figure 11). Residences within each watershed and immediately surrounding each stormwater basin are served by septic tanks (Figure 1), and septic tank leachate potentially could impact groundwater at the sampled wells. However, hydraulic gradients indicate this potential is limited at the SO site and negligible at the HT site. Water-table gradients at the SO site were toward the basin at times, yet were at least an order of magnitude smaller than vertical gradients, which were always downward; whereas at the HT site, water-table gradients were nearly always outward and similarly small relative to vertical gradients, which also were always downward. Both watersheds drain residential areas with no large-scale agricultural pollution (manure). Pet waste is another potential source of organic N, but $^{15}$N[NO$_3^-$] values between the two sites are substantially different even though pet waste contributions likely are similar between sites. Therefore, N contamination from organic waste sources is believed to be limited or negligible at both sites. The source of NO$_3^-$ at both sites likely is fertilizer impacted stormwater runoff and
nitrification of soil N, and samples from the SO site show enriched isotope ratios more likely caused by denitrification than an organic source.

All samples indicative of denitrification were from the SO site, whereas soil-water and groundwater samples at the HT site showed nitrification. Enriched values of $\delta^{15}\text{N}[\text{NO}_3^-]$, and to a lesser degree of $\delta^{18}\text{O}[\text{NO}_3^-]$, occur during bacteriological denitrification with a $\delta^{18}\text{O} : \delta^{15}\text{N}$ ratio of about 1:2 (Kendall, 1998; Kendall and Aravena, 2000). Six groundwater samples, all from the SO site, plot along or near a line with this slope and are more highly enriched ($\delta^{15}\text{N}[\text{NO}_3^-] >$
10‰) relative to the other groundwater samples; these samples likely indicate denitrification (Figure 11). The most highly enriched sample was March 2008 (δ^{15}N[NO_3^-] = 25‰ and δ^{18}O[NO_3^-] = 15‰), which had a low NO_3^- - N concentration (0.17 mg L^{-1}) possibly representing residual NO_3^- that had not been completely denitrified (Figure 6a). Other SO samples with δ^{15}N[NO_3^-] less than 10‰ also follow this trend with the exception of the soil water sample (0.5-m depth). This soil water sample was collected June 2008 about 2 days after a runoff event, representing very recent infiltration that likely was not subject yet to appreciable denitrification (Figure 11). Additionally, O’Reilly et al. (2011) report excess N_2 concentrations attributed to denitrification (Vogel et al., 1981) as high as 3 mg L^{-1} in shallow groundwater (well PW) beneath the SO basin during the prolonged flooding of 2008. In contrast, all HT samples have δ^{15}N[NO_3^-] less than 5‰, show no trend with δ^{18}O[NO_3^-], and likely represent nitrification of atmospheric or fertilizer derived NH_4^+ or soil N (Figure 11).

In support of the isotopic enrichment indicating denitrification, results of the qPCR analyses indicate large differences in denitrifier activity as inferred from nirK gene density. Median gene densities were about 50 times higher beneath the SO basin compared to the HT basin (p < 0.001, Table 1). The greatest prevalence of denitrifiers was in the shallow soil zone at depths above about 1.4 m (Appendix H). This corresponds with soil water-extractable IC results that suggest C cycling consistent with OC mineralization at depths above 1.3 m (Figure 9a), which is likely coupled with O_2 reduction, denitrification, and other observed biogeochemical processes at the SO site.
Soil Property Control of Surface/Subsurface Oxygen Exchange

In the most general sense, subsurface O$_2$ levels depend on the rate of O$_2$ transport into the subsurface and the rate of biogeochemical O$_2$ reduction. In particular, soil texture control of surface/subsurface O$_2$ exchange is important. Anoxic conditions will develop in the subsurface if (1) O$_2$ respiring micro/macro organisms are present, (2) sufficient organic matter is present, (3) soil aeration is poor, and (4) water infiltrates more slowly. The first two conditions are assumed to be met, or at least not substantially dissimilar, at the SO and HT sites; whereas the latter two conditions are importantly different between the two sites. Aerobic heterotrophs are common in the subsurface given favorable conditions, whether in deep or shallow environments (Chapelle, 2001), so aerobes can be expected to be present in aerobic soil given sufficient substrate and moisture. Soil solid OC contents generally are higher at the SO basin compared to the HT basin (medians significantly different, p = 0.015, Table 1) and water-extractable OC contents generally are higher as well (medians significantly different, p = 0.002, Table 1). The highest water-extractable OC contents beneath the SO basin occurred after prolonged saturation of the soil and perhaps were influenced by solid/aqueous phase OC interactions. At the HT basin, sharp decreases in soil water DOC in the upper 1.3 m of soil with further decreases to less than 1 mg L$^{-1}$ in groundwater suggest that O$_2$ is replenished more quickly than it can be reduced by OC oxidation (Figure 8). Thus, while aqueous OC availability was greater at the SO basin compared to the HT basin, soil aeration conditions likely were an important controlling factor.

Soil aeration is an important control on the relative prevalence of aerobic versus anaerobic heterotrophic bacteria in the subsurface. Skopp et al. (1990) described the dependence of aerobic microbial activity on soil moisture content, noting that peak activity occurs at the
moisture content where the supply of substrate (electron donor) and O\textsubscript{2} are equal. Reduction of the gas diffusion coefficient in soil caused by decreased soil aeration (decreasing gas-filled void space) was computed using the equation of Jin and Jury (1996):

\[ D_{g, \text{soil}} = \frac{\phi_g^2}{\phi_g^{2/3}} D_{g, \text{air}} \]

where \( D_{g, \text{soil}} \) is the diffusion coefficient of gas \( i \) through soil (cm\textsuperscript{2} d\textsuperscript{-1}), \( D_{g, \text{air}} \) is the diffusion coefficient of gas \( i \) through air (cm\textsuperscript{2} d\textsuperscript{-1}), \( \phi_g \) is the total volumetric gas-phase content (cm cm\textsuperscript{-1}), and \( \phi \) is the volume fraction of soil pores (porosity) (cm cm\textsuperscript{-1}). The gas diffusion coefficient is always substantially lower beneath the SO basin compared to the HT basin based on measured moisture contents, with median \( D_{g, \text{soil}} \) at the HT site 25–70 times greater than at the SO site (Figure 4).

More fundamentally, soil texture strongly mediates the interaction between hydroclimatic conditions, infiltration rates, and soil moisture by controlling the hydraulic conductivity and moisture retention capacity of soil. The fine-textured soils at the SO site have a low saturated hydraulic conductivity that contributes to the low infiltration rates compared to the coarse-textured, more permeable soils at the HT site (Figure 2). SMRCs indicate that soils at the SO site will perennially maintain high moisture contents, with saturations exceeding 70% even at high matric heads that represent extremely dry conditions for humid subtropical climates, whereas soils at the HT site drain rapidly (Figure 2b). Based on the measured soil moisture contents and SMRCs at each site, poorly aerated soils that maintain a water saturation greater than 90% (conversely, a gas fraction less than 10%) can significantly inhibit surface/subsurface O\textsubscript{2}
exchange by yielding low $D_{\text{soil}}$ values. Such conditions are exhibited at the SO site about 50% of the time (Figure 4a) and likely contribute to the development of denitrifying conditions observed in shallow groundwater. Furthermore, the absence of subsurface O$_2$ will prevent the aerobic oxidation of organic matter, thus preserving the OC for use during denitrification and other biogeochemical processes. These results are consistent with those of Smith et al. (1998), who reported dramatic increases in N$_2$O for a clay loam soil at water saturations greater than 80% that was attributed to partial denitrification, and greater likelihood of complete denitrification by N$_2$O reduction to N$_2$ at water saturations exceeding 90%.

**Implications for Improved Stormwater Infiltration Best Management Practices**

The contrasting conditions at the SO and HT sites demonstrate the importance of considering stormwater quantity and quality control at infiltration basins. At the HT basin, the flood control function of the basin was easily met while the well drained soils exacerbated NO$_3^-$ leaching. Whereas at the SO basin, NO$_3^-$ leaching was largely mitigated while the poorly drained soils caused the basin to overflow at times. Such insight can inform development of improved BMPs to mitigate NO$_3^-$ impacts from stormwater infiltration basins, such as functionalized soil amendments. Hossain et al. (2010) presented results of laboratory batch column experiments indicating N and phosphorus removal by an amendment mixture using recycled waste materials, including tire crumb (granulated tire) and sawdust. Gupta et al. (2009) and Bhatnagar and Sillanpää (2011) present overviews of pollutant sorbent materials, focusing on low cost and waste materials and NO$_3^-$ sorbents. Soil amendments commonly have been implemented in relatively small-scale applications (<1 ha drainage area), such as low-impact development bioretention cells and raingardens (Hunt et al., 2006; Davis et al., 2009). A full-scale application
of this technology for regional stormwater infiltration basins serving watersheds >20 ha, such as the SO and HT basins, is not known to the authors other than that reported by O’Reilly et al. (2011). O’Reilly et al. (2011) described the development and preliminary monitoring of an improved BMP to mitigate NO$_3^-$ leaching beneath the HT basin, based in part on the natural biogeochemical conditions beneath both the SO and HT basins described herein. The new BMP incorporated an integrated flood control and pollution control design using a functionalized soil amendment, such that each component of the amendment mixture possesses particular functional characteristics to improve NO$_3^-$ attenuation. One important functional characteristic is increased soil moisture retention capacity, which can be incorporated by addition of a fine-textured (clayey sand) component to the soil amendment mixture (O’Reilly et al., 2011).
CHAPTER 4: CYCLIC BIOGEOCHEMICAL PROCESSES AND NITROGEN FATE

Introduction

Material in this chapter is taken exclusively from that presented by O’Reilly et al. (2012a) and has been reproduced here upon permission of the publisher (Appendix A).

The highly dynamic nature of infiltrated water and groundwater beneath infiltration basins complicates understanding of an already complex biogeochemical system (Cho et al., 2009; Datry et al., 2004). Little research at the field scale is available on the temporal variability of N cycling beneath stormwater infiltration basins. Due to the episodic nature of stormwater runoff generation and the large volume of water accumulated by stormwater conveyance systems in urban and suburban settings, infiltration and groundwater recharge processes beneath a stormwater infiltration basin can occur rapidly depending on the hydrogeologic conditions (Cho et al., 2009; Professional Service Industries, Inc., 1993) and a substantial amount of recharge can be contributed to underlying aquifers (Fisher et al., 2003; Zubair et al., 2010). These factors result in a highly dynamic shallow groundwater system beneath a stormwater infiltration basin that is continuously adjusting to changing inputs. These dynamics mediate the major processes controlling the occurrence of NO$_3^-$ and other N species in groundwater that originate from stormwater infiltration: (1) advective transport of N into the aquifer (infiltration and percolation through the unsaturated zone); and (2) physical (particulate and colloidal straining), chemical (solid, aqueous and gas phase interactions) and biological (ammonification, nitrification, NO$_3^-$ reduction, and assimilation) transformation of N along the flow path. Datry et al. (2004) showed that such conditions result in fluctuations in shallow groundwater quality (less than 3 m below
the water table) at small spatial (1 m) and temporal (1 d) scales below an infiltration basin in Lyon, France, where the water table was less than 1.2 m deep. Cho et al. (2009) demonstrate through laboratory column experiments simulating a bioretention BMP that N cycling (the net effects of sorption, nitrification and denitrification) during intermittent wetting (6 h) and drying (7 d) resulted in inorganic N removal efficiencies exceeding 95%. Subsurface water quality changes may occur at time scales different from those of the underlying physicochemical and biological processes in response to the net effects of conservative mixing, hydrodynamic dispersion and reaction kinetics of waters with different travel times, initial chemical compositions and reaction histories (Green et al., 2010). Therefore, cyclic variations in groundwater quality may occur at seasonal or shorter time scales caused by infiltration fluxes and chemistry that fluctuate at daily or shorter time scales, and the relative time scales of transport and transformation processes determine the ultimate fate of a solute (Gu et al., 2007). For example, reaction kinetics for denitrification can be fast, with denitrification rates varying up to an order of magnitude at subdaily time scales for soil cores obtained from agricultural fields before and after rainfall (Sexstone et al., 1985). Cyclic patterns of denitrification were reported in soils beneath agricultural fields recurring at monthly or shorter (Weitz et al., 2001) to seasonal frequency (Mahmood et al., 2005). Given the intermittent nature of wet-dry cycles during both stormwater infiltration and crop cultivation, similar cyclic biogeochemical processes might be expected to occur beneath stormwater infiltration basins. Wet-dry cycles over a range of time scales affect N cycling (Austin et al., 2004). However, biogeochemical cycling beneath stormwater infiltration basins is not well documented.
The objective of the research presented in this chapter is to elucidate the sequential biogeochemical processes occurring cyclically at seasonal or shorter time scales and demonstrate that such processes can effectively control N fate beneath a subtropical stormwater infiltration basin. By providing increased understanding of temporal biogeochemical variability in dynamic environments, results can inform development of improved BMPs to mitigate NO$_3^-$ impacts from stormwater infiltration basins.

**Results and Discussion**

Results focus on data collected in 2007–2008 at the South Oak (SO) stormwater infiltration basin (Figure 1) where substantial biogeochemical cycling and N transformation were observed. At this site, cyclic variations between oxidizing and reducing conditions effectively act to switch NO$_3^-$ fate between leaching and reduction.

**Hydrologic Conditions**

The 5-minute hydrologic monitoring data were composited into daily values (summed for rainfall and averaged for all other values) for 2008–2009 (Figure 12). An additional year of hydrologic monitoring was performed in 2009, even though no sampling occurred, in order to better characterize temporal variability. Annual rainfall was close to the long-term average and similarly distributed in time during the two years. During the period of water-quality sampling (June 2007–December 2008), the basin was flooded 68% of the time; on an annual basis, the basin was flooded 61% and 48% of the time in 2008 and 2009, respectively. The longest flooding periods began during the summer wet season and extended into early autumn (Figure 12b). The greater percentage of flooding in 2008 is due to a particularly large rainfall event (155
mm from Tropical Storm Fay) that occurred in August, resulting in a greater depth of flooding
compared to more typical rainfall periods. Infiltration rates were estimated by analysis of basin
stage recession curves for several storm events in 2008. For 46–155 mm rainfall events (5–33 h
duration), infiltration rates were 14–29 mm d⁻¹.
Figure 12: Hydrologic monitoring at the South Oak site of (A) rainfall, (B) basin stage and groundwater level, and (C) volumetric moisture content (VMC) and subsurface temperature (Tmp). Mid-screen depths of wells noted for groundwater level, and probe depths noted for VMC and Tmp.

A comparison of basin volume and storm magnitude (rainfall depth) suggests that the majority of the watershed does not contribute runoff to the basin, except perhaps during extreme,
prolonged storm events. For example during Tropical Storm Fay, 155 mm of rainfall occurred during a 33-h period causing a rainfall excess of about 36 mm based on the curve number method and a weighted curve number of 53 derived from land use and soil hydrologic group (Wanielista et al., 1997). The resulting 0.6-m rise in water stored in the basin suggests only about 17% of the rainfall excess volume was contributing runoff to the basin. Considering impervious areas cover a small portion of the watershed yet runoff depth from impervious areas will be disproportionately greater than pervious areas, the actual area of the watershed contributing runoff probably is substantially smaller than 17%. These results are consistent with the karst, well-drained terrain of the watershed.

The response of the measured hydrologic variables to rainfall and air temperature indicates a subdued response with depth. The highly attenuated response of well M-0511 (Figure 12b) is attributable to a prevalence of fine-textured sediments. Substantial silt and clay generally are present throughout the soil profile (Figure 13a). Visual observation of split-spoon samples from wells outside the perimeter of the basin (Figure 1) indicates lithology varies across the site compared to that beneath the basin (Figure 13a) but still indicates an abundance of silt and clay sediments. These fine-textured sediments cause large vertical head gradients of 0.90−1.3 m m⁻¹ between M-0511 (9.1 m deep) and M-0512 (2.5 m deep). The two shallow wells inside or at the edge of the typical stored stormwater area (PW and M-0512, Figure 1) respond rapidly to runoff events; subsequently, water percolates slowly through the sandy silts and clays leading to an attenuated response in well M-0511 (Figure 12b). The nearly constant temperature signal (ranged from 21.9 to 22.5 °C) at a depth of 9 m (measured in M-0511, Figure 12c) further illustrates the
attenuating effects of the fine-textured sediments, and is near the long-term average air temperature of 22°C.

Figure 13: Soil properties beneath the South Oak stormwater infiltration basin (A) texture profile; and acid-ammonium-oxalate (AAO) and citrate-dithionite-bicarbonate (CDB) extractions of (B) iron oxides, and (C) aluminum oxides. See Appendix E for data values.
Lateral water-table gradients beneath the basin were both inward and outward from well PW within the basin to wells outside the perimeter of the basin (M-0512, M-0514, M-0515, M-0516 and M-0522; Figure 1), ranging from −0.10 to 0.080 m m$^{-1}$ (negative values inward, positive values outward). During periods of basin flooding, lateral gradients were always outward; whereas during dry periods, lateral gradients generally were inward (compare PW and M-0512 groundwater levels, Figure 12b). Vertical head gradients (between the shallow wells and well M-0511) were always downward and were 30–600 times greater than lateral gradients. Assuming a vertical anisotropy of less than 10, which is typical of sandy sediments in central Florida (O’Reilly, 1998) and consistent with a single measurement at this site (Andreyev Engineering, Inc., personal communication, 2007), these gradients suggest groundwater movement was predominantly downward beneath the basin.

Estimated horizontal and vertical pore-water velocities illustrate important implications for solute transport. Based on daily water-level measurements for wells PW and M-0512 (Figure 12b), 10%, 50% and 90% exceedence probabilities corresponded to horizontal gradients of 0.018, 0.0035 and −0.065 m m$^{-1}$ and vertical gradients of 0.068, 0.053 and 0.046 m m$^{-1}$, respectively. Based on applying Darcy’s Law with a maximum hydraulic conductivity of 0.34 m d$^{-1}$ and an average porosity of 0.40 reported by Naujock (2008), the maximum horizontal pore-water velocity was 0.003 m d$^{-1}$ for the median measured gradient. Likewise, the maximum vertical pore-water velocity was 0.045 m d$^{-1}$ for the median measured gradient. Hydraulic conductivity values less than 0.02 m d$^{-1}$ at depths between 0.6 and 1.4 m (Naujock, 2008) likely control vertical percolation, thus Darcian-derived median vertical pore-water velocity was probably less than 0.004 mm d$^{-1}$. In contrast, based on infiltration rate estimates and a porosity
of 0.40, vertical pore-water velocity ranged from 0.035 to 0.073 m d$^{-1}$. The apparent discrepancy between pore-water velocities derived from Darcian and flooded infiltration methods is probably attributable to well-developed macropore structure observed in the fine-textured soils at the site, suggesting much of the vertical water flux is through preferential flow paths. Consequently, solute transport behavior derived by Darcian analyses in such structured soils should be interpreted cautiously, with explicit accounting of macropore and soil matrix interaction leading to more accurate analyses (Arora et al., 2011).

*Stormwater Quality*

Stormwater runoff into the basin brings infiltration of oxygenated water with elevated N concentrations (Figure 14a), and at times results in substantial and prolonged water storage (Figure 12b). Basin stormwater (water temporarily stored in the basin) had DO concentrations of 4.3–11 mg L$^{-1}$ (median = 7.6 mg L$^{-1}$, n = 6) excluding the prolonged flooding event of 2008. During the prolonged flooding of 2008, DO of the stormwater was much lower (2.8, 0.4 and 1.7 mg L$^{-1}$ for July, August and September, respectively) likely due to biochemical processes in the stormwater possibly related to the greater depth of water (frequently greater than 1 m). DO during the prolonged flooding of 2007 was higher (4.3 and 5.6 mg L$^{-1}$) possibly related to the shallower water depth (typically less than 0.5 m; basin stage estimated by periodic observations in 2007). OC content of the basin stormwater probably was increased by periodic submergence and decomposition of herbaceous vegetation that quickly grew during periods when the basin was not flooded. TOC concentrations ranged from 8.8 to 27.9 mg L$^{-1}$ (median = 14.4 mg L$^{-1}$, n = 10) and was predominantly DOC (6.4–13.9 mg L$^{-1}$, median = 11.2 mg L$^{-1}$, n = 10) (Figure 14b). Basin stormwater had total dissolved N (TDN) concentrations of 0.49–1.3 mg L$^{-1}$ (median =
0.84 mg L\(^{-1}\), \(n = 10\), which was nearly all ON with concentrations of 0.46–1.2 mg L\(^{-1}\) (median = 0.75 mg L\(^{-1}\), \(n = 10\)). Maximum NO\(_3^-\)-N and NH\(_4^+\)-N were only 0.26 and 0.14 mg L\(^{-1}\), respectively. Particulate and colloidal N could be an important source of N loading at times; total unfiltered N (TN) concentrations of basin stormwater were 0.62–3.7 mg L\(^{-1}\) (median = 1.0 mg L\(^{-1}\), \(n = 10\)).
Figure 14: Temporal variations in stormwater quality at the South Oak stormwater infiltration basin of (A) nitrogen species, chloride, sulfate and dissolved oxygen; (B) DOC and alkalinity; and (C) iron, manganese and pH. Nitrogen species concentrations that did not exceed method detection limits are plotted at values equal to the laboratory reporting level ($\text{NH}_4^+\text{-N} = 0.02 \text{ mg L}^{-1}$, $\text{NO}_3^-\text{-N} = 0.016 \text{ mg L}^{-1}$). DOC, dissolved organic carbon; DO, dissolved oxygen; TDN, total dissolved nitrogen; TN, total nitrogen; TOC, total organic carbon.
Groundwater Quality

Groundwater quality in well PW (screened depth 1.2–2.7 m) (Figure 15) generally was substantially different from stormwater quality (Figure 14). Short periods of aerobic groundwater (DO concentrations of 3.5, 1.7 and 3.8 mg L\(^{-1}\) in January, February and June 2008, respectively) occurred after infiltration of aerobic stormwater (Figure 15a). Otherwise, groundwater commonly had low DO or was anoxic beneath the basin (DO varied 0.1 – 0.9 mg L\(^{-1}\), median = 0.3 mg L\(^{-1}\), n = 11). DOC varied from 4.1 to 6.3 mg L\(^{-1}\) (median = 5.5 mg L\(^{-1}\), n = 9) (Figure 15b), and constituted about 95% of TOC (based on two samples analyzed for both DOC and TOC; data not shown). TN was nearly equal to TDN in groundwater from well PW (median TN = 0.31 mg L\(^{-1}\), n = 14; data not shown), suggesting the retention of particulate and colloidal N at the sediment-water interface or during infiltration through the unsaturated zone. Groundwater had TDN concentrations of 0.25–3.1 mg L\(^{-1}\) (median = 0.32 mg L\(^{-1}\), n = 14), which was predominantly ON with concentrations of 0.20–0.34 mg L\(^{-1}\) (median = 0.29 mg L\(^{-1}\), n = 14). During periods of elevated TDN, NO\(_3^–\)-N was the predominant species (2.7, 2.3 and 0.84 mg L\(^{-1}\) in January, February and June 2008, respectively), which also coincided with aerobic periods. During other sampling events, NO\(_3^–\)-N was typically below the laboratory method detection limit (0.008 mg L\(^{-1}\)) and was no higher than 0.17 mg L\(^{-1}\). Maximum NH\(_4^+\)-N was 0.048 mg L\(^{-1}\).

Alkalinity varied from 190 to 450 mg L\(^{-1}\) as CaCO\(_3\) (Figure 15b), and was predominantly HCO\(_3^–\) given the measured pH range 6.2–6.7 (Figure 15c).
Figure 15: Temporal variations in groundwater quality (well PW) at the South Oak stormwater infiltration basin of (A) nitrogen species, chloride, sulfate and dissolved oxygen; (B) DOC and alkalinity; and (C) iron, manganese and pH. Nitrogen species concentrations that did not exceed method detection limits are plotted at values equal to the laboratory reporting level ($\text{NH}_4^+\text{-N} = 0.02 \text{ mg L}^{-1}, \text{NO}_3^-\text{-N} = 0.016 \text{ mg L}^{-1}$). DOC, dissolved organic carbon; DO, dissolved oxygen; TDN, total dissolved nitrogen.
*Surface and Subsurface Water Quality Interaction*

Evolution of subsurface water quality along a flow path from infiltration to eventual discharge commonly is influenced by reduction/oxidation (redox) reactions (Postma et al., 1991). Table 2 lists redox reactions that may potentially be occurring at the study site. Reactions are categorized as to occurrence under generally aerobic or anoxic conditions in recognition of the significant impact of aerobic stormwater on groundwater chemistry.
Table 2: Reduction-oxidation reactions potentially occurring beneath the South Oak stormwater infiltration basin.

<table>
<thead>
<tr>
<th>Eq. No.</th>
<th>Biogeochemical Process</th>
<th>Stoichiometry</th>
<th>Electrons accepted</th>
<th>EA/ED ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S(^{2-}) oxidation</td>
<td>4Fe(_{2(\text{aq})}) + 15O(_2) + 14H(_2\text{O}) → 8SO(_4^{2-}) + 4Fe(OH)(_3(\text{aq})) + 16H(^+)</td>
<td>S → O(_2): 4</td>
<td>1.87</td>
</tr>
<tr>
<td>2</td>
<td>Fe(II) oxidation</td>
<td>4Fe(^{2+}) + O(_2) + 10H(_2\text{O}) → 4Fe(OH)(_3(\text{aq})) + 8H(^+)</td>
<td>Fe → O(_2): 4</td>
<td>0.14</td>
</tr>
<tr>
<td>3</td>
<td>Mn(II) oxidation</td>
<td>2Mn(^{2+}) + O(_2) + 2H(_2\text{O}) → 2MnO(_2(\text{aq})) + 4H(^+)</td>
<td>Mn→O(_2): 4</td>
<td>0.29</td>
</tr>
<tr>
<td>4a</td>
<td>Nitrification</td>
<td>2NH(_3) + 3O(_2) → 2NO(_2) + 2H(_2\text{O}) + 4H(^+)</td>
<td>N → O(_2): 4</td>
<td>3.43</td>
</tr>
<tr>
<td>4b</td>
<td></td>
<td>2NO(_2) + O(_2) → 2NO(_3) (^-)</td>
<td>N → O(_2): 4</td>
<td>1.14</td>
</tr>
<tr>
<td>5</td>
<td>Aerobic respiration</td>
<td>CH(_2)O + O(_2) → CO(_2) + H(_2\text{O})</td>
<td>C → O(_2): 4</td>
<td>2.66</td>
</tr>
</tbody>
</table>

**Aerobic conditions**

<table>
<thead>
<tr>
<th>Eq. No.</th>
<th>Biogeochemical Process</th>
<th>Stoichiometry</th>
<th>Electrons accepted</th>
<th>EA/ED ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Heterotrophic denitrification</td>
<td>5CH(_2)O + 4NO(_3) (^-) → 2N(_2) + 4HCO(_3) (^-) + CO(_2) + 3H(_2\text{O})</td>
<td>C → N: 5</td>
<td>0.93</td>
</tr>
<tr>
<td>7</td>
<td>Autotrophic denitrification</td>
<td>5Mn(^{2+}) + 2NO(_3) (^-) + 4H(_2\text{O}) → N(_2) + 5MnO(_2(\text{aq})) + 8H(^+)</td>
<td>Mn → N: 5</td>
<td>0.10</td>
</tr>
<tr>
<td>8</td>
<td>Autotrophic denitrification</td>
<td>10Fe(^{2+}) + 2NO(_3) (^-) + 14H(_2\text{O}) → N(_2) + 10FeO(_2(\text{aq})) + 18H(^+)</td>
<td>Fe → N: 5</td>
<td>0.050</td>
</tr>
<tr>
<td>9</td>
<td>Autotrophic denitrification</td>
<td>5Fe(_{2(\text{aq})}) + 14NO(_3) (^-) + 4H(^+) → 7N(_2) + 10SO(_4^{2-}) + 5Fe(^{2+}) + 2H(_2\text{O})</td>
<td>S → N: 5</td>
<td>0.61</td>
</tr>
<tr>
<td>10</td>
<td>DNRA</td>
<td>2CH(_2)O + NO(_3) (^-) + H(^+) → NH(_4) (^+) + HCO(_3) (^-) + CO(_2)</td>
<td>C → N: 8</td>
<td>0.58</td>
</tr>
<tr>
<td>11</td>
<td>Anammox</td>
<td>NH(_3) (^+) + NO(_2) → N(_2) + 2H(_2\text{O})</td>
<td>N → N: 3</td>
<td>1.00</td>
</tr>
<tr>
<td>12</td>
<td>Heterotrophic Mn(IV) reduction</td>
<td>CH(_2)O + 2MnO(_2(\text{aq})) + 3H(^+) → 2Mn(^{2+}) + HCO(_3) (^-) + 2H(_2\text{O})</td>
<td>C → Mn: 2</td>
<td>9.15</td>
</tr>
<tr>
<td>13</td>
<td>Heterotrophic Fe(III) reduction</td>
<td>CH(_2)O + 4Fe(OH)(_3(\text{aq})) + 7H(^+) → 4Fe(^{2+}) + HCO(_3) (^-) + 10H(_2\text{O})</td>
<td>C → Fe: 1</td>
<td>18.60</td>
</tr>
<tr>
<td>14</td>
<td>Fe(III) reduction</td>
<td>9HS(^-) + 8Fe(OH)(<em>3(\text{aq})) + 7H(^+) → 8FeS(</em>{3(\text{aq})}) + SO(_4^{2-}) + 20H(_2\text{O})</td>
<td>S → Fe: 1</td>
<td>1.50</td>
</tr>
<tr>
<td>15</td>
<td>Fe(III) reduction</td>
<td>3HS(^-) + 2FeO(<em>2(\text{aq})) → 2FeS(</em>{3(\text{aq})}) + S(_{3(\text{aq})}) + H(_2\text{O}) + 3OH(^-)</td>
<td>S → Fe: 1</td>
<td>1.13</td>
</tr>
<tr>
<td>16</td>
<td>Heterotrophic SO(_4^{2-}) reduction</td>
<td>2CH(_2)O + SO(_4^{2-}) → HS(^-) + 2HCO(_3) + H(^+)</td>
<td>C → S: 8</td>
<td>4.00</td>
</tr>
<tr>
<td>17</td>
<td>SO(_4^{2-}) reduction</td>
<td>9Fe(^{2+}) + SO(_4^{2-}) + 20H(<em>2\text{O}) → FeS(</em>{3(\text{aq})}) + 8Fe(OH)(_3(\text{aq})) + 16H(^+)</td>
<td>Fe → S: 7</td>
<td>0.19</td>
</tr>
<tr>
<td>18</td>
<td>S(^2-) oxidation</td>
<td>FeS(_{3(\text{aq})}) + H(<em>2\text{S}) → FeS(</em>{2(\text{aq})}) + H(_2)</td>
<td>S → H: 1</td>
<td>0.61</td>
</tr>
<tr>
<td>19</td>
<td>Methanogenesis</td>
<td>4H(_2) + CO(_2) → CH(_4) + 2H(_2\text{O})</td>
<td>H(_2) → C: 8</td>
<td>5.46</td>
</tr>
</tbody>
</table>

The convention followed in the stoichiometric reactions is to show the electron donor as the first reactant and the electron acceptor as the second reactant. Electrons accepted is the number of electrons transferred in the reduction reaction. EA/ED ratio is the molar ratio of the electron acceptor to the electron donor based on the given stoichiometry adjusted to concentration units of mg L\(^{-1}\), thus representing the decrease in the electron acceptor concentration via reduction by 1 mg L\(^{-1}\) of electron donor; DOC (represented by CH\(_2\)O) in mg C L\(^{-1}\); all N species in mg N L\(^{-1}\); Fe, Mn and S in solid phase reactants treated as equivalent concentration of dissociated ion. DNRA, dissimilatory nitrate reduction to ammonium.
Considerable variation (in depth and time) occurred in soil water and groundwater quality in the upper 1.4 m of soil as indicated by samples collected from the three lysimeters (Figure 16). However, temporal variations in underlying groundwater quality in well PW were comparatively small (compare Cl⁻ in Figure 15a and Figure 16). In the case of a relatively nonreactive constituent such as Cl⁻, these differences are attributable to the combined effects of preferential flow, mobile versus relatively immobile pore-space water (Coats and Smith, 1964; Green et al., 2005), transient sorption (Pachepsky et al., 1994), evapoconcentration, and hydrodynamic dispersion processes. It is likely that Cl⁻ concentrations in groundwater from well PW are significantly influenced by preferential flow and mobile pore-space water and that concentrations in lysimeters are significantly influenced by the relatively immobile pore-space water and other physicochemical processes. For other more reactive constituents, such as redox sensitive DOC, TDN, Mn, Fe and SO₄²⁻, geochemical and biogeochemical processes also are influential.
Figure 16: Soil-water and groundwater chemistry profiles beneath the South Oak stormwater infiltration basin. Data at 0-m depth represent stormwater samples; data at 0.5, 0.9 and 1.4-m depths represent lysimeter samples; data at 1.9-m depth represent well PW. Data is not available at every depth for every sampling event due to lack of sample (stormwater), lack of analysis for that sample (dissolved organic carbon, DOC; \(\delta^{15}N[\text{NO}_3^-] \); \(\delta^{18}O[\text{NO}_3^-] \)), or non-exceedence of detection limit (\(\text{NH}_4^+ - \text{N}, \text{NO}_3^- - \text{N}\)). \(\text{NO}_2^- - \text{N}\) was typically below the laboratory reporting limit of 0.002 mg L\(^{-1}\) for all soil-water and groundwater samples, with the exception of June and July samples at 0.5 and 0.9 m depths where \(\text{NO}_2^- - \text{N}\) ranged from 0.0027 to 0.0072 mg L\(^{-1}\). Organic N is computed as the difference between total dissolved nitrogen (TDN) and inorganic nitrogen (IN = \(\text{NH}_4^+ + \text{NO}_3^- + \text{NO}_2^-\)), where \(\text{NH}_4^+\), \(\text{NO}_3^-\) and \(\text{NO}_2^-\) are assumed zero when below their respective method detection limits of 0.01, 0.008 and 0.001 mg L\(^{-1}\).
The net transformation of water quality during transition from stormwater to groundwater can be inferred by comparison of concurrent stormwater and groundwater samples. Ratios of groundwater to stormwater concentrations for redox sensitive constituents indicate variations considerably different to those of Cl\(^-\), suggesting fate is reaction dominated (Appendix I Figure I1). Thus, the physicochemical processes controlling groundwater Cl\(^-\) concentrations play a lesser role in the fate of redox sensitive constituents. Accordingly, disparate patterns exist between Cl\(^-\) variations and the variation of each redox sensitive analyte for each lysimeter sample, with the exception of SO\(_4^{2-}\) (Figure 16).

Temporal changes in SO\(_4^{2-}\) and Cl\(^-\) profiles suggest physicochemical processes (sorption, evapoconcentration, and hydrodynamic dispersion) affect these anions in a similar fashion (Figure 16; SO\(_4^{2-}\)/Cl\(^-\) ratios shown in Appendix I Figure I2). To estimate the changes in SO\(_4^{2-}\) attributable to redox reactions, SO\(_4^{2-}\) concentrations were adjusted based on the percentage change in Cl\(^-\) concentrations between consecutive samples. One-third of the measured Cl\(^-\) percentage change was subtracted from the measured SO\(_4^{2-}\) percentage change, which was then used to compute an adjusted SO\(_4^{2-}\) concentration. The one-third factor was applied to reflect differences in Cl\(^-\) and SO\(_4^{2-}\) retardation factors reported by Pachepsky et al. (1994), who indicated SO\(_4^{2-}\) retardation factors about three times those of Cl\(^-\) for a clay soil not unlike those beneath the stormwater basin. The prevalence of kaolinite (as high as 48% of the clay fraction; Appendix D) and Fe and Al oxides (Figure 13b, c) suggest the potential for anion sorption. Therefore, the adjusted SO\(_4^{2-}\) concentrations provide an estimate of what concentrations would
have been in the absence of the physicochemical processes inferred from the Cl$^-$ variations (Appendix I Figure I2 and I3).

Similar Cl$^-$ concentrations in groundwater from well PW and in stormwater, compared to large differences in concentrations of N and C species as well as DO, Mn, Fe and SO$_4^{2-}$ (Figure 14 and 15), suggests a reaction dominated fate of these redox sensitive constituents that is related to subsurface biogeochemical processes. These results are interpreted in the following sections in the context of the redox reactions in Table 2 in order to better understand the biogeochemical processes beneath the basin.

**Biogeochemical Processes**

Water chemistry changes resulting from redox reactions are usually mediated by subsurface microorganisms as they use the energy produced during electron transfer for growth. Due to its relative prevalence in the subsurface, OC commonly serves as an electron donor coupled to the following sequence of electron acceptors, O$_2$ > NO$_3^-$ > Mn(IV) > Fe(III) > SO$_4^{2-}$ > CO$_2$, referred to as the ecological succession of terminal electron-accepting processes (TEAPs) (Chapelle et al., 1995; McMahon and Chapelle, 2007).

Biogeochemical processes in groundwater beneath the basin were inferred from cyclic variations in the chemistry of the following redox reactants and products: DOC (reactant), DO (reactant), NO$_3^-$ (reactant), Mn$^{2+}$ (product), Fe$^{2+}$ (product), SO$_4^{2-}$ (reactant; using the adjusted values shown in Appendix I Figure I3) and alkalinity (product) (Figure 15). All of the TEAPs were identified beneath the stormwater basin. Redox reactant concentrations were depleted or product concentrations increased in a time sequence according to the thermodynamically-governed order of TEAPs. To gain further insight into these biogeochemical processes, electron
equivalents were computed based on millimolar concentrations and the number of electrons transferred during the redox reaction (Postma et al., 1991). DOC with zero valent C was assumed to be the only electron donor, with complete oxidation to CO$_2$ (4 electrons transferred), using CH$_2$O as a simplified representation of organic matter. Dissolved inorganic carbon (DIC) was computed as the sum of CO$_2$ and alkalinity (HCO$_3^-$) (Figure 17a); when dissolved gas samples were not collected, CO$_2$ was estimated based on linear regression between alkalinity and CO$_2$ ($r^2 = 0.59$, $n = 7$). The following numbers of electrons are transferred in each TEAP (see Table 2 for the stoichiometric reaction referenced by the equation number): O$_2$ (4 electrons, equation 5), NO$_3^-$ (5 electrons, equation 6), Mn(IV) (2 electrons, equation 12), Fe(III) (1 electron, equation 13) and SO$_4^{2-}$ (8 electrons, equation 16). The cyclic variations in groundwater chemistry (Figure 15) and in electrons transferred (Figure 17b) are presented in the following sections as evidence for each biogeochemical process, followed by a discussion of the time scales of variations and impacts on N fate.
Figure 17: Select reactants or products participating in heterotrophic terminal electron accepting processes observed in groundwater beneath the South Oak stormwater infiltration basin (well PW) (A) molar concentrations of organic and inorganic carbon species; and (B) electron equivalents for select reactants or products of each terminal electron accepting process. Alk, alkalinity; DIC, dissolved inorganic carbon where “est.” denotes estimated values and “meas.” denotes measured values; DOC, dissolved organic carbon; GW, groundwater samples; SW, stormwater samples; adj. SO₄²⁻, sulfate data adjusted based on comparison to chloride concentrations.
Organic Carbon Oxidation

Organic matter oxidation during TEAPs results in decreases in DOC concentrations and increases in CO$_2$ and HCO$_3^-$ concentrations (DIC). However, other physical or geochemical processes can affect these concentrations, such as source inputs (infiltration of stormwater), solid/aqueous phase interactions, and gas/aqueous phase interactions. Groundwater DOC tended to increase during prolonged flooding of the basin in 2007 and 2008 (Figure 15b), possibly due to infiltration of stormwater with DOC concentrations about twice that of groundwater (Figure 14b). During the intervening period of intermittent or no flooding (winter and spring in 2008), groundwater DOC decreased, possibly due to oxidation or reduced stormwater infiltration.

Variations in OC and IC concentrations in soil and water samples suggest biogeochemical activity. Groundwater DIC generally increased during prolonged flooding of the basin in 2007 and 2008 (Figure 17a), which could be due to both carbonate mineral dissolution and oxidation of DOC. Carbonates in soil sediments are the probable source of soil solid IC contents typically exceeding 1,000 mg kg$^{-1}$ (0.1%) (Figure 18). Results of soil water extractable analyses generally indicate increases in water extractable OC and IC concentrations from spring (March and May samples) to autumn (November and December samples) in 2008 at depths less than 1.3 m, but were generally unchanged below this depth (Figure 18). The increases in water extractable OC may be caused by mass transfer of OC between solid and aqueous phases, although soil solid OC contents are so large that such changes are not discernible, or OC input from infiltrating stormwater. Increases in water extractable IC from spring to autumn 2008 may be indicative of a zone of active biogeochemical processes in the shallow soil zone 0–1.3 m
deep. Increases in alkalinity for the lysimeter samples also indicate increases in soil water and groundwater $\text{HCO}_3^-$ at depths above 1.4 m at the prevailing pH values 6.5–7.5 (Figure 16). Substantial changes in soil solid IC at values less than 1,000 mg kg$^{-1}$ probably are largely the result of analytical variability because IC is computed as the difference between measured TC and OC. DIC increases exceed 10 times the number of electrons transferred during all TEAPs (Figure 17b) and elevated $\text{Ca}^{2+}$ concentrations (Figure 16) yield calcite saturation indices greater than 1.5 in the zone of high alkalinity (0.5–1.4 m depths), further indicating DIC variations are dominated by carbonate chemistry. However, similar temporal variations in $\text{CO}_2$ and $\text{HCO}_3^-$ (alkalinity) with a general upward trend (Figure 17a) while pH was also increasing (Figure 15c) are suggestive of DOC use as a reductant for the TEAPs, thus part of the increase in groundwater DIC is likely caused by DOC oxidation and can account for the electrons transferred in all TEAPs (Figure 17b).
Figure 18: Soil solid and water extractable total carbon (TC), organic carbon (OC) and inorganic carbon (IC) contents beneath the South Oak stormwater infiltration basin. IC is computed as the difference between TC and OC.

To identify whether sufficient electrons are available from stormwater DOC to supply the total transferred during the observed TEAPs, an electron balance for heterotrophic processes in the upper soil zone was developed. The soil zone examined spanned from the bottom of the basin...
to 1.9 m deep (the midpoint of the screened interval of well PW). The 162-d period 11 June – 20 November 2008 was selected as this represented the period of generally prolonged flooding of the basin during which a sequence of TEAPs was observed. Hydrologic monitoring indicates this is a typical seasonal flooding pattern for this stormwater basin, thus results may be representative of behavior during other years (Figure 12b). The electron balance was developed by (1) assuming one-dimensional steady downward flow through a control volume with a 1 m$^2$ cross-sectional area; (2) using an infiltration rate of 20 mm d$^{-1}$ and porosity of 0.40; (3) using the analyte concentrations in stormwater for inflow to the control volume and in well PW for outflow from the control volume; and (4) estimating the changes in electron storage within the control volume by integration of analyte concentrations over the 1.9-m depth using data from stormwater, lysimeter (0.5, 0.9 and 1.4 m depths) and well PW samples.

The large decrease in DOC between stormwater and well PW is equal to a loss of about 6,020 electron equivalents, representing a net addition of electrons to the control volume. Heterotrophic TEAPs occurring within the control volume represent a net “electron demand,” and may consist of O$_2$, NO$_3^-$, Mn(IV), Fe(III) and SO$_4^{2-}$ reduction. SO$_4^{2-}$ reduction accounts for most of the electrons accepted, about 910 electron equivalents. DO measurements were only available for stormwater and well PW, thus the electrons transferred in the control volume by O$_2$ reduction can be estimated only very coarsely at about 380 electron equivalents. NO$_3^-$ reduction accounts for about 100 electron equivalents. Mn and Fe reduction represent a small net gain of about 20 electron equivalents due to the increase in concentrations over this period, although more electrons may have been transferred that were not reflected in aqueous concentrations if Mn$^{2+}$ and Fe$^{2+}$ are consumed in other reactions (for example, equations 7, 8, 9 and 17 in Table
The net quantity of electron equivalents transferred in the control volume, or the electron demand, was about 1,370 and represents 4,650 less than was supplied by infiltrating stormwater assuming all of the decrease in DOC represents a labile fraction and was oxidized. This discrepancy may be attributable to one or more of the following factors: (1) stormwater DOC is of relatively young humic origin due to the frequent submergence and subsequent decomposition of herbaceous vegetation during flooding, and thus was relatively labile because organic matter reactivity typically is inversely correlated with age (Appelo and Postma, 2005); (2) some of the labile fraction of the infiltrating DOC was involved in other reactions such as complexation or sorption; (3) sparse temporal resolution of DOC data (only three samples of stormwater and two for well PW) introduced error into the computed net DOC decrease; and (4) greater spatial variability occurred in TEAPs than could be resolved by the 0.5-m sampling-depth intervals. Nevertheless, soil water extractable OC contents generally exceeding 10 mg kg\(^{-1}\) and soil solid OC generally exceeding 1,000 mg kg\(^{-1}\) (Figure 18) are considerably larger than the estimated electron demand, which is equivalent to a soil OC content of only 3.5 mg kg\(^{-1}\). Thus, between DOC in infiltrating stormwater and solid phase OC, sufficient labile OC likely exists to permit heterotrophic metabolism for all observed biogeochemical processes.

**Oxygen Reduction**

DO in groundwater beneath the basin was always substantially lower than that in stormwater (Figure 14a and 15a). Groundwater DO was quickly depleted as flooding continued, and was less than or equal to 0.5 mg L\(^{-1}\) for 9 of the 14 sampling events. The lowest groundwater DO concentration of 0.1 mg L\(^{-1}\) occurred in November 2008, toward the end of the prolonged flooding when the stormwater DO was also unusually low. \(O_2\) reduction likely was coupled with
DOC oxidation (equation 5, Table 2), as ample DOC was available to account for the required electron transfer (Figure 17b). The ensuing anoxic conditions enabled the progression of TEAPs.

**Nitrate Reduction**

Concomitant peaks in groundwater DO and NO$_3^-$ concentrations occurred beneath the basin (Figure 15a), whereas stormwater TDN was consistently composed primarily of ON (Figure 14a), indicating short periods of ammonification/nitrification. For example, elevated groundwater TDN concentrations exceeded 1 mg L$^{-1}$ (primarily in the NO$_3^-$ form) for the 12 June 2008 sample (Figure 16) and was caused by infiltration of oxygenated stormwater from a rainfall event about two days prior to collection of the sample. However, similar to DO, NO$_3^-$ in groundwater was short lived and was depleted below 0.1 mg L$^{-1}$ for 65% of the samples collected from well PW (Figure 15a) and the lysimeters (Figure 16). Samples from the lysimeters were only collected during the summer and autumn of 2008 (before, during and after the prolonged flooding). TDN in groundwater and soil water was predominantly in the form of ON, whereas NH$_4^+$-N was less than 0.1 mg L$^{-1}$ (Figure 15a and 16). NO$_3^-$ reduction likely was coupled with DOC oxidation (Figure 17b).

Soil N chemistry differed in the spring (March and May 2008) before the summer wet period compared to autumn (November and December 2008) after the prolonged flooding. The near absence of NO$_3^-$ in water extractable samples in autumn is suggestive of denitrification (equation 6, Table 2) or dissimilatory nitrate reduction to ammonium (DNRA) (equation 10, Table 2) during the summer wet season (Figure 19). Soil water extractable NO$_2^-$ was low and typically less than 10% of NO$_3^-$ (Figure 19). The slightly increased NH$_4^+$ concentrations in November may be due to DNRA, whereas the decreased NH$_4^+$ combined with low NO$_3^-$
concentration in December probably is due to nitrification (equations 4a and 4b, Table 2) in the uppermost soil layers as the basin dried and NO$_3^-$ reduction in the portions of the underlying soil zone that remained saturated (Figure 19). The presence of NH$_4^+$ and NO$_2^-$ in soil water extracts (Figure 19) could indicate the possibility of anaerobic ammonium oxidation (anammox, equation 11, Table 2) contributing to NO$_3^-$ reduction (Clark et al., 2008), although data are insufficient to confirm whether anammox was or was not occurring. In order to investigate N cycling in greater detail and better determine the predominant NO$_3^-$ reduction pathway, denitrification or DNRA, dissolved gases and stable isotopes were examined.
Figure 19: Soil solid and water extractable total nitrogen (TN) and soil water extractable ammonium nitrogen (NH$_4^+$), nitrate (NO$_3^-$), nitrite (NO$_2^-$) and organic nitrogen (ON) beneath the South Oak stormwater infiltration basin. Organic N is computed as the difference between total nitrogen (TN) and inorganic nitrogen (IN = NH$_4^+$ + NO$_3^-$ + NO$_2^-$), where NO$_3^-$ and NO$_2^-$ are assumed zero when below the method detection limit. Data are not available at every depth for every sampling event due to negative computed ON or non-exceedence of NO$_3^-$ and NO$_2^-$ detection limit.
**Dissolved gases**

DO was measured in the field during each sample event, but additional dissolved gas samples (Ar, N₂, CO₂, CH₄) were collected during spring, summer and autumn 2008 to better understand biogeochemical activity and its seasonal variation, particularly for denitrification (Figure 20a). N₂ and other atmospheric and biogenic gases can be present in the saturated zone in aqueous form or as gas phase bubbles (Vogel et al., 1981). Analysis of dissolved gas concentrations, particularly N₂ and Ar, in the groundwater beneath the stormwater infiltration basin permits estimation of the amount of excess air and excess N₂. Excess air is the dissolved atmospheric gas in excess of that attributable to atmospheric equilibration of the water during infiltration and transport through the unsaturated zone (Aeschbach-Hertig et al., 2008). Excess N₂ is that fraction of dissolved N₂ in excess of that attributable to atmospheric solubility equilibrium and is commonly attributed to denitrification, but also can be produced by anammox (equations 6–9 and 11, Table 2).
Figure 20: Dissolved gas concentrations in groundwater beneath the South Oak stormwater infiltration basin: (A) temporal variations in dissolved gases and excess N$_2$ (error bars for excess N$_2$ indicate the range of reasonable values given uncertainty in recharge temperatures); and (B) $\delta^{15}$N of N$_2$ and Ar/ N$_2$ ratios. All samples were collected in 2008 from well PW, except the August sample which was collected from well M-0512. CO$_2$, CH$_4$ and O$_2$ concentrations are expected to be comparable at these two wells at this time due to extensive flooding of the basin (2.0 m deep at PW and 1.0 m deep at M-0512) and similar well depths (mid-screen depths of 1.9 m for PW and 1.7 m for M-0512).
Excess $N_2$ was computed using the measured concentrations and computed solubilities of $N_2$ and Ar (Weiss, 1970), atmospheric pressure, and recharge temperature based on the methodology described by Green et al. (2008b). Recharge temperature is the temperature of the recharge water, infiltrated stormwater in this case, at that point in the flow process where the water is no longer able to equilibrate with atmospheric gases, commonly estimated to be at the depth of the top of the capillary fringe or water table. Due to the dynamic nature of the groundwater system beneath a stormwater infiltration basin, there is considerable uncertainty in determining the exact timing of the infiltration event (and hence tracking the corresponding recharge temperature). The method is sensitive to recharge temperature, but reliable recharge temperatures could not be independently estimated at this site. As an alternative, minimum (excess $N_2 = 0$) and maximum (excess air = 0) values of excess $N_2$ were assumed and the corresponding recharge temperatures were estimated iteratively to meet each criterion. The final estimated recharge temperature was computed as the average of the estimated minimum (for excess air = 0 criterion) and maximum (for excess $N_2 = 0$ criterion) recharge temperatures. To further constrain results, the average recharge temperature was compared to measured subsurface temperatures. A 7-d moving window average was computed for temperature at 0.3 m depth (Figure 12c), resulting in a range of realistic recharge temperatures of 12.6–29.2°C. Only for the 20 November 2008 sample (average estimated recharge temperature = 33.6°C) was it necessary to adjust the recharge temperature, which was set equal to the 0.3 m subsurface temperature of 28.7°C on 10 June 2008, the date of the first major infiltration event of the summer wet season. This infiltration event substantially reduced the thickness of the unsaturated zone (water table
rose from a depth of 2.5 m on 9 June to a depth of 0.4 m on 11 June; Figure 12b), which became fully saturated during the prolonged flooding period beginning 21 June 2008, and thus contributed to the anoxic groundwater conditions favorable for NO$_3^-$ reduction (Figure 15a). The excess N$_2$ measured in the 20 November 2008 sample may have resulted from reduction of elevated NO$_3^-$ concentrations in recharge that occurred during this infiltration event (see 12-Jun-08 sample, Figure 16) in the biogeochemically active zone (0–1.4 m depth) inferred from C cycling previously discussed in the Organic Carbon Oxidation section.

Excess N$_2$ was present in groundwater beneath the basin from well PW for all samples, ranging from 0.4 to 3 mg L$^{-1}$ (Figure 20a), suggesting that denitrification affected these samples. However, it should be noted that due to the uncertainty in recharge temperatures, only the 20 November 2008, sample had a minimum excess N$_2$ greater than zero (2.3 mg L$^{-1}$). Nevertheless, the temporal pattern of the estimated excess N$_2$ concentrations is in agreement with other redox conditions, being low when O$_2$ and NO$_3^-$ were elevated and high under anoxic conditions. For the May and June samples, the estimated maximum excess N$_2$ concentrations were less than 1 mg L$^{-1}$ and DO was 0.9 and 3.8 mg L$^{-1}$, respectively. Such low values for estimated maximum excess N$_2$ concentrations might be interpreted as essentially zero given the data presented by Green et al. (2008b), which show that 95% of strictly aerobic samples (DO exceeding 1.6 mg L$^{-1}$) had excess N$_2$ less than 1.3 mg L$^{-1}$ (0.047 mmol L$^{-1}$). Higher excess N$_2$ concentrations were most likely present in March, July, September, November and December, when the range of estimated values (indicated by the error bars in Figure 20a) plot at least partially above 1 mg L$^{-1}$, providing supporting evidence for denitrification during or prior to these times. For the March sample, the low NO$_3^-$-N concentration (0.17 mg L$^{-1}$) possibly represented residual NO$_3^-$ that had
not been denitrified (Figure 15a). In contrast, NO$_3^-$-N concentrations were below the laboratory method detection limit (0.008 mg L$^{-1}$) for the July through December samples (Figure 15a). N$_2$ can also be produced by anammox (equation 11, Table 2). Consistently low NH$_4^+$ and NO$_2^-$ concentrations in soil water and groundwater (Figure 15a and 16) suggest limited significant excess N$_2$ attributable to anammox. However, soil water extractable NH$_4^+$ and NO$_2^-$ concentrations (NO$_2^-$-N of 0.15 mg kg$^{-1}$ for 19 December 2008 (Figure 19), equivalent to 0.47 mg L$^{-1}$) could yield 0.47 mg L$^{-1}$ excess N$_2$ (equation 11, Table 2). These data suggest anammox cannot be definitively precluded as a potentially important pathway for N cycling in the subsurface.

**Stable isotopes of nitrogen and oxygen**

Results of the N and O isotopic analysis of NO$_3^-$ for stormwater, soil water and groundwater samples provide insight into the sources of NO$_3^-$ and differences in NO$_3^-$ biogeochemistry at the study site (Figure 21a). The precipitation samples were collected at a nearby stormwater infiltration basin (Hunter’s Trace, Figure 1) and, as expected, indicate an atmospheric source of NO$_3^-$. The stormwater sample is indicative of atmospheric or fertilizer-derived NO$_3^-$. Many groundwater samples and the one soil-water sample are indicative of nitrification of one or more of the following: atmospheric or fertilizer-derived NH$_4^+$, soil nitrogen (organic or NH$_4^+$), or organic waste (manure or septic). N contamination from organic waste sources is believed to be limited. The watershed drains a residential area with no large-scale agricultural pollution (manure). Residences within the watershed and immediately surrounding the stormwater infiltration basin (Figure 1) are served by septic tanks. Septic tank leachate possibly could impact groundwater at the wells sampled at the stormwater infiltration
basin, however hydraulic gradients and travel times indicate this potential is limited. Median water-table gradients were small, indicating a groundwater travel time from nearby septic tanks of at least 20 years, and vertical groundwater gradients were always downward and at least an order of magnitude larger than water-table gradients, which suggests drainage from septic tanks would not intercept the monitoring zone of the shallow wells. Given the residential surroundings, animal (pet) waste is another potential source of organic N, but $\delta^{15}\text{N}[\text{NO}_3^-]$ values between this site and the nearby Hunter’s Trace site (Figure 1) are substantially different (Wanielista et al., 2011), even though pet waste contributions probably are similar between sites. Therefore, the source of NO$_3^-$ likely is fertilizer-impacted stormwater runoff and nitrification of soil N rather than groundwater movement from adjacent areas, and enriched isotope ratios are more indicative of denitrification than an organic source.
Figure 21: Isotope ratios for (A) $\delta^{15}N$ and $\delta^{18}O$ of NO$_3^-$ in precipitation, stormwater, soil water, and groundwater plotted relative to typical source ranges from Kendall (1998); (B) $\delta^{15}N$ and $\delta^{18}O$ of NO$_3^-$ in soil water and groundwater; and (C) $\delta^{18}O$ of NO$_3^-$ and $\delta^{18}O$ of H$_2$O in soil water and groundwater. All samples collected at the South Oak site in 2008 with the exception of precipitation samples collected at the Hunter’s Trace site in May and December 2009 (Figure 1).
Further evidence of nitrification is given by a comparison of $\delta^{18}O[\text{NO}_3^-]$ and $\delta^{18}O[\text{H}_2\text{O}]$. Research has indicated that nitrification derives oxygen from water molecules and $O_2$ in a predictable manner according to the two-step microbially mediated reactions: (1) $\text{NH}_4^+$ oxidation to $\text{NO}_2^-$ by *Nitrosomonas* uses one oxygen from water and one from $O_2$ (equation 4a, Table 2); and (2) $\text{NO}_2^-$ oxidation to $\text{NO}_3^-$ by *Nitrobacter* uses one oxygen from water (equation 4b, Table 2) (Kendall, 1998). If the process occurs without fractionation, the $\delta^{18}O[\text{NO}_3^-]$ can be computed simply as $2/3 \delta^{18}O[\text{H}_2\text{O}] + 1/3 \delta^{18}O[O_2]$ and assuming a $\delta^{18}O[O_2]$ of 23‰ characteristic of atmospheric $O_2$ (Kendall, 1998). Several groundwater samples plot near the 2:3 slope line of $\delta^{18}O[\text{NO}_3^-]$ and $\delta^{18}O[\text{H}_2\text{O}]$, and several plot between this line and the 1:1 slope line that represents the trend if all oxygen during nitrification were derived from $\text{H}_2\text{O}$ (Figure 21c). These results suggest nitrification occurred at times beneath the basin. Green et al. (2008b) report data that fall closely along the 2:3 slope line from several agricultural areas across the United States where the groundwater was aerobic ($O_2 > 0.5 \text{ mg L}^{-1}$) and they noted other evidence indicating nitrification was occurring. Katz et al. (2010) report data from soil water and groundwater samples collected in septic tank drain fields in northwest Florida with a relatively large range of $\delta^{18}O[\text{NO}_3^-]$ and with nearly all samples falling between the 1:1 and 2:3 slope lines; nonetheless, denitrification was identified as one of the likely mechanisms for $\text{NO}_3^-$ loss in the drain fields.

For the samples collected from groundwater beneath the stormwater basin, considerably greater variability existed in $\delta^{18}O[\text{NO}_3^-]$ compared to $\delta^{18}O[\text{H}_2\text{O}]$ and several samples fall well above the 2:3 slope line (Figure 21c). Values that plot above the 2:3 slope line indicate either enriched $\delta^{18}O[O_2]$ was being used for nitrification (values of $\delta^{18}O[O_2]$ of soil air can be as high as 60‰...
because of respiration derived fractionation (Kendall, 1998) or $\delta^{18}$O(NO$_3^-$) had been fractionated by denitrification. In the latter case, comparison of $\delta^{18}$O(NO$_3^-$) and $\delta^{15}$N(NO$_3^-$) can provide evidence of denitrification.

Enriched values of $\delta^{15}$N(NO$_3^-$), and to a lesser degree of $\delta^{18}$O(NO$_3^-$), occur during bacteriological denitrification with a ratio of $\delta^{18}$O:$\delta^{15}$N of about 1:2 (Kendall, 1998; Kendall and Aravena, 2000). Six groundwater samples from this study fell closely along this line and are more highly enriched ($\delta^{15}$N(NO$_3^-$) > 10‰) relative to the other groundwater samples; these samples are consistent with the effects of denitrification (Figure 21a). Other samples with $\delta^{15}$N(NO$_3^-$) less than 10‰ also follow this 1:2 slope line (Figure 21b). One exception is the sample at a 0.5-m depth collected 12 June 2008, after a runoff event 10 June. Water-table depth on 12 June 2008 was 0.55 m, increased from 2.5 m deep on 9 June, and thus represents very recent infiltration in the relatively aerobic unsaturated zone (moisture contents increased from 76 to 86% saturation) (Figure 12b, c). Recharge from this infiltrating stormwater (the stormwater sample shown in Figure 21a was collected on 12 June) sampled in the 0.5-m deep lysimeter falls well above the 1:2 slope line (Figure 21b), and this sample is more indicative of nitrification as suggested by $\delta^{18}$O(NO$_3^-$) and $\delta^{18}$O(H$_2$O) values if enriched $\delta^{18}$O(O$_2$) was being used for nitrification (Figure 21c). In contrast, lysimeter samples from below the water table (0.9 and 1.4 m depths) on this date indicate enriched $\delta^{15}$N(NO$_3^-$) and $\delta^{18}$O(NO$_3^-$) with depth (Figure 16), following the 1:2 slope line indicating denitrification (Figure 21b). Additionally, lysimeter samples for 23 July 2008, after the basin had been flooded 32 days, indicate progressively enriched $\delta^{15}$N(NO$_3^-$) and $\delta^{18}$O(NO$_3^-$) with depth (Figure 16), following the 1:2 slope line indicating denitrification (Figure 21b). These results are consistent with the zone of organic
matter oxidation at depths above 1.4 m as suggested by OC and IC concentrations from soil water extracts (Figure 18) and from lysimeters (Figure 16), which was previously discussed in the Organic Carbon Oxidation section.

Comparison of excess N\(_2\) and isotopic fractions is possible for only the 12 March and 12 June 2008 samples from well PW, when NO\(_3^-\)-N concentrations were above the minimum value required for isotopic analysis (0.03 mg L\(^{-1}\)) (Figure 15a). For the March sample, collected 29 d after flooding of the basin, isotopic enrichment was evident (\(\delta^{15}\text{N}[\text{NO}_3^-]\) of 24‰ and \(\delta^{18}\text{O}[\text{NO}_3^-]\) of 8.5‰, Figure 21b) and excess N\(_2\) was 1 mg L\(^{-1}\) (Figure 20a), suggesting denitrification had depleted much of the initial NO\(_3^-\). Whereas nitrification was indicated for the June sample (\(\delta^{15}\text{N}[\text{NO}_3^-]\) of 5.2‰ and \(\delta^{18}\text{O}[\text{NO}_3^-]\) of 6.1‰, Figure 21b), which was collected 27 h after a 26-mm storm event resulting in temporary storage of stormwater up to 0.28 m deep, where a high DO and an elevated NO\(_3^-\)-N concentration of 0.84 mg L\(^{-1}\) was measured. If this rapid change in groundwater quality in well PW (mid-screen depth of 1.9 m) is assumed to be attributable to this single infiltration event, which is reasonable given that no appreciable rainfall had occurred since early April (Figure 12a), infiltrated stormwater was percolating at a rate of at least 1.7 m d\(^{-1}\). When compared with a saturated Darcian pore-water velocity of 0.045 m d\(^{-1}\), these results suggest a preferential flow system with rapid flow through macropores and slower flow through the soil matrix. Given that the soil was not fully saturated prior to this runoff event, the unsaturated Darcian pore-water velocity would be considerably lower and is estimated to be 0.001 m d\(^{-1}\) at a 0.6-m depth (based on soil properties reported by Naujock (2008), measured volumetric moisture content, and an assumed hydraulic gradient of 1 m m\(^{-1}\)). The rapid percolation caused by macropores likely delivered initial recharge to greater depths by largely
bypassing the 0–1.4 m biogeochemically active zone, resulting in reduced opportunity for denitrification. An excess N₂ concentration in June of essentially zero (Figure 20a) and lower $\delta^{15}$N[NO₃⁻] at a depth of 1.9 m compared to shallower depths (0.9 and 1.4 m, Figure 21b) are consistent with this conceptual model. These results suggest the assumption of Darcian flow in such a soil is inaccurate for solute transport analyses, and are consistent with those of Kurtzman and Scanlon (2011) who describe the importance of preferential flow paths for explaining observed Cl⁻ concentrations in an expansive clay soil.

Additional insight on potential denitrification can be gleaned from $\delta^{15}$N[N₂] values for groundwater samples collected from well PW because excess N₂ will be depleted in $\delta^{15}$N relative to the NO₃⁻ from which it was formed. The $\delta^{15}$N value of the total measured dissolved N₂ is denoted as $\delta^{15}$N[N₂,total], whereas the $\delta^{15}$N value of excess N₂ is denoted as $\delta^{15}$N[N₂,excess] and is derived by linear mixing calculation using $\delta^{15}$N of air-saturated water of 0.7‰ (Böhlke et al., 2002; Green et al., 2008b). Data are shown on Figure 20b relative to dashed mixing lines drawn between atmospheric (Ar/N₂ molar ratio of 0.0259) and non-atmospheric (Ar/N₂ molar ratio of 0.0) excess N₂ for representative samples where denitrification was relatively incomplete (lower mixing line, $\delta^{15}$N[N₂,excess] = −12‰) and relatively complete (upper mixing line, $\delta^{15}$N[N₂,excess] = 7‰) in a fashion analogous to that presented by Böhlke et al. (2002). When denitrification is complete, the $\delta^{15}$N[N₂,excess] should equal $\delta^{15}$N[NO₃⁻] of the source (Böhlke et al., 2002).

Nitrification of soil N is a likely source of NO₃⁻ beneath the basin as described previously, and 7‰ approximates the $\delta^{15}$N[NO₃⁻] of many of these samples (Figure 21a). Results suggest that the samples collected from well PW represent the effects of denitrification reactions in various stages of completion. $\delta^{15}$N[N₂,excess] increased from −10.9‰ in June 2008 to 9.9‰ in December
2008, with samples from the beginning of the prolonged flooding period (June and July) plotting nearest to the mixing line representing relatively incomplete denitrification and the sample from December plotting nearest to the mixing line representing relatively complete denitrification (Figure 20b). It is important to note that $\delta^{15}N[N_{2}]$ variations also can result from variations in the isotopic composition of the NO$_3^-$ source and mixing of denitrified and undenitrified water (Böhlke et al., 2002), as well as other NO$_3^-$ reduction pathways such as DNRA or anammox (Böhlke et al., 2006). Nevertheless, $\delta^{15}N[N_{2}]$ values are consistent with other stable isotope (Figure 21) and dissolved gas (Figure 20a) results, all of which are consistent with denitrification.

**Manganese and Iron Reduction**

Anoxic conditions in the subsurface enabled the loss of NO$_3^-$ as well as leading to increases in Mn and Fe in groundwater (Figure 15c), which probably are due to bacterially-mediated processes (equations 12 and 13, Table 2) and the greater solubility of reduced Mn and Fe (Appelo and Postma, 2005). Presumably, the Mn and Fe concentrations consist of the reduced valence states of Mn$^{2+}$ and Fe$^{2+}$. Soil chemical analyses indicate Fe oxide contents as high as 20,000 mg kg$^{-1}$ that can serve as the source of Fe$^{3+}$ (Figure 13b), and Mn oxides are often associated with Fe oxides in subsurface sediments (Schulze, 2002). Solid phase Fe oxides are likely reactive, based on the prevalence of amorphous Fe oxides from acid-ammonium-oxalate (AAO) extractions about equal to or exceeding citrate-dithionite-bicarbonate (CDB) extractions (Figure 13b). Geochemical conditions in shallow groundwater (pH of 6–7, Figure 15c; $E_h$ of 200–500 mV, Appendix I Figure I4) are more favorable for precipitation of Fe oxides than Mn oxides by aerobic oxidation (equations 2 and 3, Table 2). The Fe(OH)$_3$ precipitate stability field
covers about the upper right one-half of this range of pH and \(E_h\) values, but no Mn solids stability fields fall within this range (Hem, 1985, p. 80 and 87). These results may partly explain generally lower Fe and consistently higher Mn concentrations in groundwater compared to stormwater (Figure 14c and 15c, Appendix I Figure I1). Due to the relatively low concentrations of \(\text{Mn}^{2+}\) and \(\text{Fe}^{2+}\) (typically less than 1,000 \(\mu\)g L\(^{-1}\); Figure 15c) and only 2 and 1 electrons transferred, respectively, the contribution of Mn and Fe reduction toward the flow of electrons is minimal (Figure 17b) and corresponding DOC consumption from these reactions alone would be small.

Interestingly, Fe concentrations were relatively high in some stormwater samples, including those that were oxic, and were often higher than groundwater Fe concentrations (Figure 14c and 15c, Appendix I Figure I1). This is probably caused by a combination of the following factors: (1) presence of colloidal Fe \(<0.45\ \mu\)m in filtered samples, (2) complexation of \(\text{Fe}^{2+}\) with organic matter, (3) cyclic oxidation of \(\text{Fe}^{2+}\) and reduction of \(\text{Fe}^{3+}\). First, Kennedy et al. (1974) report that fine particulates can pass through a 0.45 \(\mu\)m filter membrane, resulting in substantially overestimated “dissolved” Fe concentrations. These colloid-sized particles, if present, likely include \(\text{Fe}^{3+}\) precipitates given the oxic stormwater (equation 2, Table 2). A similar effect could be possible for groundwater samples, although given that \(\text{SO}_4^{2-}\) reduction was observed, colloidal particles in groundwater could potentially include both \(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\) precipitates (equations 14 and 15, Table 2). Second, organic matter present in the stormwater stored in the basin is likely to be of predominantly humic origin due to the submergence and subsequent decomposition of herbaceous vegetation during flooding. Stormwater Fe is positively correlated with stormwater TOC in the samples collected \((r^2 = 0.75, n = 10)\), consistent with
potential complexation with organic matter. Third, aerobic oxidation of Fe\(^{2+}\) may be inhibited when complexed with organic matter of humic origin, where the humic material effectively mediates a dynamic equilibrium between Fe\(^{2+}\) oxidation (equation 2, Table 2) and Fe\(^{3+}\) reduction (equation 13, Table 2) (Theis and Singer, 1974).

Complex interactions of the Mn and Fe cycles with the N and S cycles probably occur beneath the stormwater basin. Mn\(^{2+}\) and Fe\(^{2+}\) may serve as electron donors for autotrophic denitrification (equations 7 and 8, Table 2). But available data suggest autotrophic denitrification, if it were occurring, probably was minor compared to heterotrophic denitrification. Based on the heterotrophic electron balance previously presented in the Organic Carbon Oxidation section for the prolonged basin flooding in 2008, 3.0 mg kg\(^{-1}\) of FeS precipitated in the upper 1.9 m of soil (equations 14 and 16, Table 2), which is equivalent to an aqueous concentration of 11.6 mg L\(^{-1}\) (based on dry bulk density of 1.54 g cm\(^{-3}\) and porosity of 0.4 averaged from values reported by Naujock (2008) for the upper 1.4 m of soil). However, Fe\(^{2+}\) in this quantity of FeS can reduce only 0.37 mg L\(^{-1}\) NO\(_3^-\)-N, given the low ratio of electron acceptor to donor indicated by stoichiometry (equation 8, Table 2). Likewise, the highest measured Fe concentration of 558 μg L\(^{-1}\) (Figure 15c) can reduce only 0.028 mg L\(^{-1}\) NO\(_3^-\)-N. Similar to Fe, oxidation of Mn\(^{2+}\) reduces relatively little NO\(_3^-\), thus the highest measured Mn concentration of 2,330 μg L\(^{-1}\) (0.5-m lysimeter, Figure 16) can reduce only 0.23 mg L\(^{-1}\) NO\(_3^-\)-N (equation 7, Table 2). AAO extractable Fe oxide contents are typically above 1,000 mg kg\(^{-1}\) (Figure 13b) and likely are associated with Mn oxides, which, if subject to heterotrophic reduction (equations 12 and 13, Table 2), could yield increased Fe\(^{2+}\) and Mn\(^{2+}\) concentrations for autotrophic denitrification. However, the reduction of NO\(_3^-\) by Fe\(^{2+}\) or Mn\(^{2+}\) oxidation would
cause a significant drop in pH, whereas a slight increase in pH occurred (Figure 15c), suggesting limited Fe$^{2+}$ and Mn$^{2+}$ oxidation or pH buffering by dissolution of solid phase IC (Figure 18).

**Sulfate Reduction**

Cyclic variations in SO$_4^{2-}$ concentrations in groundwater indicate SO$_4^{2-}$ reduction (equation 16, Table 2) was occurring beneath the basin (Figure 15a). Water samples were not analyzed for H$_2$S, the end product of the reduction reaction, and no samples had a characteristic H$_2$S odor. However, H$_2$S can interact with Fe oxides to precipitate Fe sulfide minerals, consuming some or all H$_2$S produced (equations 14 and 15, Table 2) (Appelo and Postma, 2005). Additionally, H$_2$S generally dissociates to predominantly HS$^-$ at pH $<$7 (Postma and Jakobsen, 1996). Despite the apparent dissolution of Fe oxides by reduction to Fe$^{2+}$ (previously described in the Manganese and Iron Reduction section), the high Fe oxide contents of the soils are sufficient to serve in both roles (Figure 13b), and simultaneous reduction of Fe oxides and SO$_4^{2-}$ in subsurface sediments has been documented (Postma and Jakobsen, 1996). Increases in SO$_4^{2-}$ concentrations during periods of infrequent flooding (Figure 15a) may be caused by oxidation of Fe sulfide minerals (equation 1, Table 2), and likely explains SO$_4^{2-}$ concentrations in soil water and groundwater considerably higher than those of stormwater (Figure 14a, 15a and 16; Appendix I Figure I). Compared to other electron acceptors, decreases in SO$_4^{2-}$ concentration exceeding 5 mg L$^{-1}$ are large (for example, during prolonged flooding periods of 2007 and 2008, Figure 15a). These decreases combined with a transfer of 8 electrons indicate SO$_4^{2-}$ reduction accounts for the majority of the electron flow (Figure 17b).

Reduced S in Fe sulfide minerals can serve as an electron donor for NO$_3^-$ reduction, resulting in increases in SO$_4^{2-}$ concentrations following decreases in NO$_3^-$ concentration
(equation 9, Table 2) (Postma et al., 1991), and may cause higher rates of denitrification than when coupled with C oxidation (Tesoriero and Puckett, 2011). Based on the heterotrophic electron balance previously presented in the Organic Carbon Oxidation section for the prolonged basin flooding in 2008, 3.0 mg kg\(^{-1}\) of FeS precipitated in the upper 1.9 m of soil (equations 14 and 16, Table 2) could yield 4.1 mg kg\(^{-1}\) of FeS\(_2\) (pyrite) via reduction of protons in H\(_2\)S (equation 18, Table 2). This quantity of FeS\(_2\) (equivalent to an aqueous concentration of 15.8 mg L\(^{-1}\)) could reduce 5.2 mg L\(^{-1}\) NO\(_3^-\)–N (equation 9, Table 2). The actual FeS or pyrite content of the soils is unknown. X-ray diffraction analysis of clay and silt fractions of soils at the site did not detect the presence of pyrite, but detection limitations generally require quantities of at least 1–5% (W.G. Harris, personal communication, 2011). Lazareva (2004) reports that pyrite is commonly present in Miocene sediments (Hawthorn Group) in central Florida, which likely are similar to those at the study site, and note that H\(_2\)S produced during SO\(_4^{2-}\) reduction results in pyrite deposition. However, much of the FeS precipitated during previous basin flooding may be aerobically oxidized back to SO\(_4^{2-}\) (equation 1, Table 2) during intervening dry periods as suggested by increased SO\(_4^{2-}\) and DO concentrations in February and June 2008 (Figure 15a). Additionally, decreases in NO\(_3^-\) do not coincide with increases in SO\(_4^{2-}\), where stoichiometry indicates 4.9 mg L\(^{-1}\) SO\(_4^{2-}\) is produced by reduction of 1 mg L\(^{-1}\) of NO\(_3^-\)-N (equation 9, Table 2). SO\(_4^{2-}\) and NO\(_3^-\) decreases were approximately concomitant (Figure 15a and 17b) suggesting S\(^-\) is not a dominant electron donor, which is consistent with precipitation of Fe sulfide minerals and the apparent absence of substantial H\(_2\)S. Continued increases in DIC (and CO\(_2\)) following NO\(_3^-\) depletion suggests DOC is the predominant electron donor for SO\(_4^{2-}\) reduction (Figure 17).
Methanogenesis

CH$_4$ concentrations in groundwater start to increase in August 2008 (Fig. 20a), lagging the Mn and Fe increases and SO$_4^{2-}$ decreases (Figure 15) as expected based on thermodynamic considerations (Appelo and Postma, 2005). CH$_4$ concentrations increase until peaking in November, and finally drop after the basin is dry again in December (Fig. 20a). Elevated CH$_4$ concentrations probably are the result of methanogenesis, typically the final step in biodegradation of organic matter under anoxic highly reducing conditions. The concurrent decreases in CO$_2$ and alkalinity when CH$_4$ peaks in November suggest use of the CO$_2$ reduction pathway for methanogenesis (equation 19, Table 2).

Cyclic Variations in Biogeochemical Processes and Effects on Nitrogen Cycling

The cyclic variations in biogeochemical processes generally coincided with wet and dry hydrologic conditions, with oxidizing conditions occurring in groundwater (Figure 15a) at the beginning of wet periods upon the infiltration of aerobic stormwater (Figure 14a). Anoxic conditions evolve in the shallow groundwater during prolonged flooding of the basin; low DO concentrations (less than 1 mg L$^{-1}$) continue during subsequent dry periods until the next major infiltration event (Figure 15a). Therefore, cyclic hydrologic variations provide conditions amenable to the evolution of redox conditions, from oxic to methanic, and, combined with reaction kinetics and groundwater travel times, result in variable time scales for the TEAPs.

O$_2$ and NO$_3^-$ reduction occurred at the shortest time scale, resulting in changes from oxic to anoxic groundwater (DO less than 0.3 mg L$^{-1}$) and NO$_3^-$ depletion (NO$_3^-$-N less than 0.016 mg L$^{-1}$) within about 20 days (February–March 2008) and 40 days (June–July 2008) (Figure 15a). However, the approximate monthly sampling interval was not sufficient to resolve these
cyclic variations accurately. Cyclic variation in O$_2$ and NO$_3^-$ concentrations at about a monthly time scale represents an approximate upper limit; higher frequency cycles probably occur. Isotopic data indicate enrichment of $\delta^{15}$N(NO$_3^-$) and $\delta^{18}$O(NO$_3^-$) within two days after infiltration at 0.9 and 1.4 m depths when NO$_3^-$-N was 1.8 and 3.3 mg L$^{-1}$, respectively (see 12-Jun-08 sample, Figure 16). Because profile plots (Figure 16) represent a snapshot in time, samples at discrete depths represent water recharged at different times, likely with different chemical compositions and experiencing different interactions during percolation through the unsaturated zone. Thus, NO$_3^-$-N would not necessarily be expected to decrease with depth. Isotopic fractionation suggests the denitrification reaction was partially complete within two days.

Mn and Fe concentrations varied at a seasonal time scale, with increasing concentrations during prolonged flooding periods (summer and autumn) and decreasing concentrations during dry periods when flooding events were of shorter duration (winter and spring) (Figure 15c). Only one and one-half cycles were observed during this study, however, and continued monitoring over several years would help confirm the persistence of these seasonal patterns.

Interestingly, cyclic variations in SO$_4^{2-}$ concentrations in groundwater suggest SO$_4^{2-}$ reduction was more closely related to wet-dry cycles than Mn and Fe reduction. SO$_4^{2-}$ reduction occurred not only during the prolonged summer and autumn flooding periods in 2007 and 2008, but also during the shorter flooding event in February–April 2008. SO$_4^{2-}$ concentration in groundwater increased during the intervening dry periods. These cyclic variations are probably caused by the sensitivity of SO$_4^{2-}$ reducing bacteria to O$_2$, such that when groundwater was oxic, SO$_4^{2-}$ reduction was inhibited or confined to isolated anoxic sites in aquifer sediments.
Methanogenesis probably occurs at a seasonal time scale, as suggested by the gradual rise in CH$_4$ concentrations during the prolonged flooding period in 2008 and the absence of CH$_4$ in the shorter flooding period in March 2008. Only one-half cycle was observed, however, and, like Fe and Mn, continued monitoring over several years would help confirm the persistence of this seasonal pattern. The relatively slow progression to methanic conditions is expected, given the need for less reductive TEAPs to occur first in order to largely deplete their respective electron acceptors.

Inference about biogeochemical reactions based on observed concentrations of redox reactants or products must be applied carefully. Only the net effects can be observed of potentially many simultaneous or coupled reactions occurring as stormwater infiltrates and percolates through the soil to the sampling point. Individual reactions could have occurred at shorter time scales and may have been observed had sampling frequency been increased, thus reaction rates driving elemental cycling at time scales shorter than the sampling frequency remain largely unknown at the study site. Additionally, biogeochemically active species can be affected by other physical or geochemical interactions. For example, Fe$^{2+}$ can be produced by reduction of Fe oxide minerals as well as oxidation of Fe sulfide minerals (equations 9, 14 and 15, Table 2). Transport of dissolved gases, such as N$_2$ and CH$_4$, can be significantly affected by gas/water phase interactions and bubble-mediated mass transfer (Geistlinger et al., 2010). The observed concentrations of any solute can be affected by differences in location of sampling relative to location of reaction, advective transport, and hydrodynamic dispersion. Temporal variations in excess N$_2$ concentrations in well PW may reflect some of these effects. Volumetric moisture content data indicate a gradual but prolonged rise in moisture content from early July.
through mid-September 2008 during continuous flooding of the basin (Figure 12c). This phenomenon was most pronounced at the two shallowest TDR probes (0.3 and 0.6 m below the basin bottom) in 2008, but similar behavior was also apparent when the basin was flooded during summer 2009. These moisture content variations indicate the presence of a gas phase below the water table, likely attributable to air bubble entrapment and generation of subsurface biogenic gases, such as CO₂, N₂ and CH₄ by OC oxidation, denitrification and methanogenesis. Bubble-mediated mass transfer of excess N₂ during transport from the depth of expected denitrification activity (0–1.4 m depth) to the screened depth of well PW (1.2–2.7 m) may have caused changes in concentration from the source depth to the sampling depth, resulting in attenuation of high-frequency variability. In the context of this conceptual model, the apparent seasonal pattern in excess N₂ concentrations may be brought about by such gas/water phase interactions, even though N₂ is being produced by denitrification at much shorter time scales. For example, the peak excess N₂ concentration in November 2008 (Figure 20a) may have resulted from infiltration that occurred in June at the beginning of the summer wet season, as previously described in the Dissolved Gases section. Reactant and product concentrations in samples collected from well PW could also be affected by mixing of water from different depths and preferential flow pathways intersected by the 1.5-m-length well screen.

Water chemistry changes indicate a temporal succession of all TEAPs, from O₂ reduction to methanogenesis, in shallow groundwater beneath the stormwater infiltration basin (Figure 15 and 16). The progression of biogeochemical conditions to Mn reduction and to even more highly reductive processes provides strong evidence that NO₃⁻, when present, would undergo reduction. The periodic introduction of additional NO₃⁻ electrons from infiltration of oxygenated
stormwater redirects the flow of electrons from the more highly reductive processes to $\text{NO}_3^-$ reduction, likely consisting of denitrification. The substantial transfer of electrons supported by these more highly reductive processes, particularly $\text{SO}_4^{2-}$ reduction, implies sufficient electron flow capacity is available to ensure denitrification would deplete all $\text{NO}_3^-$. For example, about 0.68 electron equivalents were transferred (excluding $\text{O}_2$ reduction) during the prolonged flooding of 2008 ($\text{NO}_3^- = 0.068$, Mn = 0.026, Fe = 0.005, $\text{SO}_4^{2-} = 0.580$; Figure 17b), which is equivalent to 8.4 mg L$^{-1}$ of $\text{NO}_3^-$-N. This probably represents a minimum $\text{NO}_3^-$-N that can be reduced, because higher frequency cycles were not discernible at the monthly sampling schedule. Also, observations during the study may underestimate the reductive potential of the system, which may respond even more dramatically if exposed to a greater flow of electron acceptors. Upon depletion of $\text{NO}_3^-$ beneath the basin, more highly reductive conditions evolved and the sequential biogeochemical processes resumed. Thus biogeochemical cycling can effectively switch denitrification on and off, determining whether N fate is dominated by $\text{NO}_3^-$ leaching or $\text{NO}_3^-$ reduction.
CHAPTER 5: NEW INTEGRATED DESIGN FOR STORMWATER INFILTRATION BASINS

Introduction

The contrasting conditions identified at the SO and HT sites provide valuable insight into natural biogeochemical processes beneath subtropical stormwater infiltration basins and the important factors that control these processes. A new integrated design was implemented at the HT basin based on combining a modified hydraulic design with a functionalized soil amendment to replicate the natural soil and biogeochemical conditions documented at the SO site.

In this chapter, information on the development of the integrated nutrient reduction and flood control design at the HT basin is presented. First, the new integrated design is described. Next, the hydraulic design methodology is presented, followed by model simulated predictions of basin flood control performance. Lastly, a short description of field construction activities at the HT basin is provided.

Integrated Design for Nutrient Reduction and Flood Control

During 3–6 November 2009, the existing HT basin was modified utilizing a new integrated design technology. The innovative design was thus developed not only to satisfy the flood-control performance of the original basin but also to incorporate improved nutrient control utilizing biosorption activated media (BAM). BAM is a functionalized soil amendment for nutrient attenuation, the design and performance of which is described in Chapter 6.

Three design goals guided the development of the new integrated design technology: (1) maintain the flood control capacity of the original stormwater infiltration basin; (2) reduce the
nutrient loading to groundwater by implementing a passive technology that promotes potentially self-sustaining natural biogeochemical processes; and (3) maximize economic feasibility by minimizing design and construction costs and keeping operation and maintenance costs comparable to existing stormwater infiltration basin designs. The new design consists of dividing the original stormwater infiltration basin into two approximately equal sub basins—the south basin functions as the nutrient reduction basin and the north basin functions as the flood control basin—thus integrating stormwater quality and quantity control into a single design (Figure 22a). The nutrient reduction basin is approximately 1,400 m² in bottom area and was formed by excavating the 0.15-m thick topsoil layer and 0.40 m of underlying parent soil and stockpiling separately onsite. The excavation was filled with three engineered sub layers (from bottom to top): 0.10-m thick coarse sand filter layer, 0.30-m thick amended soil (BAM) layer, and 0.15-m thick layer of the native topsoil (Figure 22b). The remaining excavated parent soil was used to create a 0.76-m high dike separating the nutrient reduction and flood control basins. To minimize erosion, the dike side slope was constructed at 10:1 (H:V) slope and an erosion control blanket installed along the entire downstream (north) side. During construction of the nutrient reduction basin, TDR and thermistor probes were reinstalled at the midpoint of the BAM layer (0.3 m depth) and at the midpoint of the coarse sand layer (0.5 m depth). The deepest set of probes remained in the parent soil at a depth of 0.9 m. In order to ensure that the hydraulic operation of the new integrated design achieves the intended enhanced nutrient removal while maintaining the flood control requirements, a runoff/water-balance model was developed.
Figure 22: Diagrams showing (A) the Hunter’s Trace stormwater infiltration basin with location of dike separating the nutrient reduction and flood control basins, adjacent residences, and monitoring sites; and (B) cross-sectional view of nutrient reduction basin showing placement of engineered soil layers and biosorption activated media (BAM).

**Runoff/Water-Balance Model Development and Calibration**

In order to ensure that the hydraulic operation of the new integrated basin design achieves the intended enhanced nutrient removal while maintaining the flood control requirements, a runoff/water-balance model was developed based on the following equation:

\[ Q - F = \Delta S \]  

(3)
where, $Q$ is the runoff volume, which is the product of rainfall depth and effective impervious area (EIA) (conceptually, the EIA includes directly connected impervious area (DCIA) plus any pervious areas that may also contribute runoff); $F$ is the infiltration volume, which is the product of infiltration rate and flooded area, where flooded area is computed via a stage-area equation based on basin geometry; and $\Delta S$ is the change in storage volume, from which stage is computed via a stage-volume equation based on basin geometry. For the purposes of this model, evaporation of ponded stormwater has not been explicitly incorporated. Conceptually, $F$ should be considered to represent the net rate of infiltration and evaporation. Daily estimates of potential evapotranspiration indicate an average rate of 3.42 mm d$^{-1}$ for the Ocala, FL, vicinity (U.S. Geological Survey, 2011a, 2011b), so the volumetric contribution of ponded stormwater evaporation is small compared to the volume of stored stormwater for a large storm event.

The model was calibrated to measured field conditions for the unmodified HT basin during 21–26 August 2008, which represents conditions during and after Tropical Storm Fay. During this period, 185 mm of rain fell, 155 mm of which occurred during the first 33 hours and can be attributed to the tropical storm. For comparison, Rao (1998) reported that the mean annual 24-hour maximum rainfall for central Marion County is about 110 mm and the 10-year, 24-hour maximum rainfall is about 160 mm. The model was implemented in Microsoft Excel®. Because the basin geometry and rainfall are known, only two unknowns remain: EIA and infiltration rate. The Solver Add-in for Excel® was used to attain optimum parameter values by minimizing the root-mean-square error (RMSE) between simulated and measured stage. The simulated stage closely matches the measured stage, with a mean error of 0.006 m and a RMSE of 0.012 m (Figure 23).
Figure 23: Simulated and measured stage at the unmodified Hunter’s Trace stormwater infiltration basin, 21–26 August 2008, during and after Tropical Storm Fay.

The optimum parameter values are reasonable based on comparisons with other data. The optimum EIA of 1.67 ha is slightly larger than the roadway area of 1.38 ha in the HT watershed, indicating that additional DCIA (for example, driveways) and some pervious areas are likely contributing. The optimum infiltration rate of 7.3 mm h\(^{-1}\) falls in the range of values estimated from analysis of measured stage recession curves, which indicated infiltration rates of 7.1–11 mm h\(^{-1}\) for large magnitude storms of 46–155 mm.

After this successful calibration, the model was modified to represent the new integrated design, thus revised stage-area and stage-volume equations were developed according to the
geometry incorporating separate nutrient reduction and flood control basins (Figure 22). Under design conditions, the bottom of the flood control basin was specified at an elevation of 15.8 m because excess fill from excavation of the nutrient reduction basin was expected to be placed there. However, after construction of the nutrient reduction basin, no excess fill was left and the “as built” elevation of the bottom of the flood control basin is approximately equal to that of the nutrient reduction basin. The effect of this slightly larger volume for the flood control basin is small, and the current model is conservative for design purposes in that it slightly overpredicts peak stage (by about 0.1 m). The modified model was developed to operate in a 3-step sequence. Because all three culverts enter the nutrient reduction basin (Figure 22a), the nutrient reduction basin fills first. Second, at a depth of 0.76 m, water overflows the dike and begins filling the flood control basin. Third, when the flood control basin fills (stage of 16.3 m), the entire stormwater infiltration basin begins filling. At each of these three steps, the water balance (Equation 3) is solved for each respective sub volume: nutrient reduction basin, flood control basin, and entire basin above stage 16.3 m (Figure 22b).

The holding volume of the nutrient reduction basin is about 1200 m$^3$, given the 0.76-m high dike and an average area of about 1600 m$^2$ (at a depth of 0.38 m). Thus if the nutrient reduction basin is empty, it can store the runoff from a 72 mm rainfall over the 1.67 ha EIA. The time for recovery of this runoff volume in a full nutrient reduction basin (0.76-m depth) is about 100 h based on the estimated infiltration rate of 7.3 mm h$^{-1}$ for the unmodified basin, but could be substantially longer depending on the degree of impedance posed by the BAM layer.
Simulated Hydraulic Performance

Calibration results indicate good model performance for the original HT basin, but a larger storm must be used in the modified model to adequately assess the flood control performance of the new integrated design. A 280-mm, 24-hour synthetic (type 2) design storm was selected, which represents a 100-year maximum rainfall for the vicinity of Ocala, FL (Rao, 1998). As a conservative estimate, an infiltration rate of 0.73 mm hr\(^{-1}\) was specified for the bottom of the nutrient reduction basin, which is the lowest expected infiltration rate for the BAM layer based on compacted laboratory tests. The existing infiltration rate of 7.3 mm hr\(^{-1}\) was maintained for the flood control basin as well as the dike and side slope areas of the nutrient reduction basin. Results indicate that the modified stormwater infiltration basin peak stage (17.0 m) will be higher than the unmodified basin (16.7 m), but still 1.3 m below the top of the basin.

Simulation of an isolated storm is not an adequate test of basin performance because it implicitly assumes complete basin recovery during interevent dry periods. This likely is not a good assumption, especially considering the potential for reduced infiltration rates in the nutrient reduction basin and the closely spaced rainfall events common during the summer wet season. Therefore, the modified basin performance was simulated for a 2-year period (2004–2005) using rainfall measured at Citra, FL, approximately 26 km north of the site (University of Florida, 2009). This time period was chosen because it includes the unusually wet period during the summer and early autumn of 2004 due to Hurricanes Charley, Frances, and Jeanne. To yield an even more conservative prediction, the 280-mm synthetic storm event was placed during the wet season on 1 August 2004, shortly before the occurrence of Hurricane Charley. Results indicate that the modified stormwater infiltration basin will stage higher (17.1 m) than for the isolated
storm event (17.0 m) (Figure 24). This peak stage will leave 1.2 m of freeboard below the top of the basin (Figure 22b), thus providing a margin of safety against decreased infiltration rates or larger runoff volumes.

Figure 24: Simulated stage in for the new integrated design constructed at the Hunter’s Trace stormwater infiltration basin based a 100-year 24-hour (280 mm) storm embedded in 2 years (2004–2005) of actual rainfall assuming an infiltration rate of 0.73 mm h\(^{-1}\) for the nutrient reduction basin. Under design conditions, the bottom of the nutrient reduction basin was specified at an elevation of 15.55 m, the bottom of the flood control basin was specified at an elevation of 15.82 m, and the top of the dike was specified at an elevation of 16.31 m.

The model may be used to determine the volume of water infiltrating in the nutrient reduction basin, thus giving an estimate of the treatment volume as a percentage of total runoff.
This is a function of the infiltration rate assumed for the nutrient reduction basin. The simulations presented above (Figure 24) are based on the minimum estimated infiltration rate of 0.73 mm hr$^{-1}$, which results in a 30% treatment volume with the nutrient reduction basin remaining flooded for 80% of the 2004–2005 period. Alternatively, using an infiltration rate for the nutrient reduction basin equal to that of the unmodified basin (7.3 mm h$^{-1}$) results in an 83% treatment volume with the nutrient reduction basin remaining flooded for 22% of the 2004–2005 period. Under these increased infiltration conditions, the peak stage reaches 16.9 m. Excluding the 100-year synthetic storm and using only the measured 2004–2005 rainfall results in an 88% treatment volume and peak stage of 16.3 m.

**Construction of the Full-Scale Integrated Design at an Existing Stormwater Infiltration Basin**

The design simulations presented above indicate that implementation of the new integrated design at the HT basin will maintain the flood control capacity of the basin within acceptable limits while providing for substantial treatment volume. Thus, in accordance with the specifications outlined in the Environmental Resource Permit approved by the St. Johns River Water Management District, construction of the new integrated design at the HT basin was conducted 3–6 November 2009. An outline of the construction process is provided in Figure 25. The process is also deemed economical as construction and materials cost was about $US 65 m$^{-2}$ of basin bottom. This cost did not include profit and permit fees. There is minimal to no additional operation and maintenance cost, and operation, maintenance, and repairs are similar to those expected with existing stormwater infiltration basins.
Figure 25: Construction of the new integrated design at the Hunter’s Trace infiltration basin.
Hydraulic operation of the new integrated design has performed well after a minor erosion incident that was successfully repaired. A large storm event in March 2010 (123 mm) resulted in overtopping of the dike, flooding of the flood control basin, and moderate erosion on the downstream (north) side of the berm. The berm was repaired to its original dimensions, seeded with grass, and an erosion control blanket installed along the entire downstream side (Figure 26). Subsequent large storm events in May 2010 (116 mm), July 2010 (105 mm), and October 2011 (160 mm) resulted in overtopping of the dike, but no erosion occurred.

Figure 26: New integrated design at the Hunter’s Trace stormwater infiltration basin (flood control basin is in foreground; nutrient reduction basin is in background) after placement of an erosion control blanket showing good performance and absence of erosion 23 hours after a 116 mm rainfall event.
CHAPTER 6: BIOGEOCHEMICAL ASSESSMENT OF BIOSORPTION ACTIVATED MEDIA

Introduction

Material in this chapter is taken exclusively from that presented by O’Reilly et al. (2012c), with the addition of the Soil Chemistry section, and has been reproduced here upon permission of the publisher (Appendix A).

Alternative design criteria for stormwater infiltration BMPs have recently focused on different media (natural soil and amendment mixtures) that can facilitate nutrient removal. Success of this technology, in terms of both physicochemical and biological processes, recently has been documented. For example, Bhatnagar and Sillanpää (2011) and Gupta et al. (2009) presented extensive overviews of materials with potential application as sorbents for pollutant removal, focusing on low cost and waste materials and nitrate (NO$_3^-$) sorbents. Chang et al., (2010a; 2010b) also presented extensive discussions of sorption media, focusing on removal of N and P species and engineering applications in natural and built environments. Shaddox (2004) reported substantial reductions in NO$_3^-$, ammonium (NH$_4^+$), and orthophosphate (PO$_4^{3-}$) leaching with the use of surfactant-modified amendments in golf course putting greens. Tire crumb has proven to be an effective nutrient reduction media for total nitrogen (TN), NO$_3^-$, total phosphorus (TP), or PO$_4^{3-}$ in a variety of applications including golf course putting greens (Lisi et al., 2004), green roof installations (Wanielist and Hardin, 2006), constructed wetlands (Xuan et al., 2009), stormwater treatment facilities (Hossain et al., 2010; Ryan et al., 2010; Wanielist and Chang, 2008), and septic tank drainfields (Chang et al., 2010c). Hossain et al. (2010) and Wanielist and Chang (2008) investigated nutrient removal by media comprising 50% sand, 20%
limestone, 15% sawdust, and 15% tire crumb and reported removal efficiencies exceeding 75% for total dissolved phosphorus (TDP) and $\text{PO}_4^{3-}$ and exceeding 60% for $\text{NO}_3^-$ and $\text{NH}_4^+$, which they partly attributed to the tire crumb by a combination of adsorption, absorption, and ion exchange processes. Biosorbents—amendment material composed of non-growing or non-living microbial biomass—have proven very effective for removal of metals and organic compounds (Aksu, 2005; Vieira and Volesky, 2000), although applications to nutrient removal are not well documented. Successful applications utilizing biological processes to promote denitrification in a saturated groundwater setting are reported by Schipper and Vojvodic (2000; 2001). Smith (2008) described a media of expanded clay and elemental sulfur with $\text{NO}_3^-$ removal up to 98%. Removal efficiencies depended on input concentrations and hydraulic retention time and were hypothesized to be due to combined ion exchange and biological activity. However, large field-scale testing of such “bioreactor” technology is limited and previous studies have generally not distinguished the specific pathways for $\text{NO}_3^-$ removal (Seitzinger et al., 2006). Chang et al. (2010a) noted that scale-up of laboratory tested nutrient reduction technologies and assessment of the cost effectiveness of field-scale applications are important research needs. Taylor et al. (2005) suggested an important area for future stormwater research is improved treatment designs to enhance dissolved N removal by denitrification and plant uptake. Stormwater treatment application of soil amendments commonly has been implemented in relatively small-scale applications (<1 ha drainage area), such as low-impact development bioretention cells and raingardens (Davis et al., 2009; Hunt et al., 2006). O’Reilly et al. (2012b) showed that soil textural and hydraulic properties, as critical determinants of soil moisture retention capacity, are
important controls on the natural biogeochemical processes that affect nutrient fate beneath stormwater infiltration basins.

The objective of this chapter is to describe the development of an innovative design for stormwater infiltration basins using biosorption activated media (BAM)—an amended soil designed to mimic natural physicochemical and biogeochemical processes—and demonstrate its potential for nutrient (N and P) removal by assessing its performance during a preliminary monitoring period. BAM was designed to function by combined sorption and biodegradation processes and is “activated” by microorganisms under wet conditions. The desired properties of BAM are:

- sorption properties that retard movement of N and P;
- physical and textural properties that provide a large proportion of saturated pore space and provide surfaces for biofilm formation and denitrifier growth;
- passive, requiring no changes in operation and maintenance practices from a typical stormwater infiltration basin, and potentially "self sustaining” with respect to N removal; and
- promote green infrastructure by utilizing recycled or naturally available materials.

A field implementation of BAM was constructed as part of the new integrated design at the Hunter’s Trace basin as described in Chapter 5, and is the first full-scale implementation of this technology known to the author for regional stormwater infiltration basins serving watersheds >20 ha. A combination of hydrologic, soil and water chemistry, soil and dissolved gas, isotopic, and microbial data were used to provide a better understanding of the factors controlling groundwater quality both before and after construction of the new basin. By
providing a preliminary assessment of BAM performance from a biogeochemical cycling perspective, results can lead to an improved basin design to mitigate nutrient impacts to groundwater while supporting green infrastructure development.

**Biosorption Activated Media Design**

The three soil sub-layer structure engineered beneath the nutrient reduction basin was designed to increase soil moisture, reduce oxygen diffusion into the subsurface, and increase adsorption/absorption capacity while still maintaining an infiltration capacity near that of the original basin (Figure 22b). The intended result is to increase biological activity, specifically denitrifying bacteria, within and below the modified soil layers. The coarse sand layer is included to encourage rapid drainage to maintain low moisture content (0.67 mm median grain size; Figure 27). Because unsaturated soil hydraulic conductivity is directly and nonlinearly related to moisture content (Koorevaar et al. 1983), such a well-drained layer will have a low unsaturated hydraulic conductivity during dry periods and will cause substantially increased retention of water in an overlying finer-textured layer (Gardner, 1979) (the amended soil layer in this application). The amended soil layer consists of BAM, which is a 1.0:1.9:4.1 mixture (by volume) of tire crumb, silt+clay (< 0.075 mm grain size), and sand (> 0.075 mm grain size). Tire crumb increases sorption capacity primarily through adsorption/absorption processes (Hossain et al., 2010), the silt and clay increase soil moisture retention, and the sand limits the reduction in permeability (and infiltration capacity) that would result from higher silt+clay contents. Increasing the silt+clay content of BAM is expected to decrease its infiltration rate, causing a decrease in treatment volume (percentage of total runoff that infiltrates through the BAM layer).
of the nutrient reduction basin. For example, a 10-fold decrease in infiltration rate (from 7.3 to 0.73 mm d\(^{-1}\)) causes the treatment volume to decrease from 83% to 30% based on the runoff/water-balance model described in Chapter 5. The BAM layer has the effect of increasing the moisture retention capacity of the soil beneath the nutrient reduction basin because of its relatively fine-grained texture (0.19 mm median grain size; Figure 27). Lastly, the top sub-layer of native topsoil, because of its organic matter content developed by the growth of natural herbaceous vegetation, is intended to provide a source of organic carbon to serve as an electron donor during denitrification or other biogeochemical processes.

![Figure 27: Particle size distribution for the three sub-layers beneath the nutrient reduction basin of the Hunter’s Trace stormwater infiltration basin.](image-url)
Analysis of a single BAM sample, which was collected during construction of the nutrient reduction basin, by the U.S. Geological Survey, Branch of Geochemistry laboratory in Arvada, CO, indicates the total concentrations of the following constituents, in decreasing order of abundance: 29,200 mg kg$^{-1}$ of Al; 18,000 mg kg$^{-1}$ of OC; 10,000 mg kg$^{-1}$ of Fe; 4,240 mg kg$^{-1}$ of P; 2,500 mg kg$^{-1}$ of Mg; 2,090 mg kg$^{-1}$ of Ca; 1,600 mg kg$^{-1}$ of Ti; and 1,480 mg kg$^{-1}$ of K. Other elements were present in trace quantities <200 mg kg$^{-1}$ as tabulated in Appendix J.

Results and Discussion

A combination of hydrologic, soil and water chemistry, soil and dissolved gas, isotopic, and microbial data were used to provide a better understanding of the factors controlling groundwater quality both before and after construction of the new integrated design incorporating BAM. After construction, seven sampling events were conducted (November 2009 to August 2010), from which a preliminary biogeochemical assessment of nutrient removal by BAM was derived.

Hydrologic Conditions

Hydrological monitoring indicates frequent stormwater storage in the nutrient reduction basin (Figure 28b). Because the nutrient reduction basin is approximately half the area of the original stormwater infiltration basin, stormwater accumulates deeper for any given rainfall event. Therefore, the nutrient reduction basin stays flooded longer (flooded 15% of the post-BAM period) than the original basin (flooded 7% of the pre-BAM period), although there was a greater number of large storm events during the post-BAM period (Figure 28a). The more
frequent water storage in the nutrient reduction basin combined with the fine-grained texture of the BAM layer causes higher soil moisture contents (0.3-m depth, Figure 28c and Appendix K), leading to conditions more favorable for anaerobic processes such as denitrification. Analysis of basin stage recession curves both before and after construction of the new basin indicates similar infiltration rates, averaging about 9.1 mm h\(^{-1}\) in the original basin and 8.6 mm h\(^{-1}\) in the nutrient reduction basin (Table 3). Therefore, about 90 h are required for a full nutrient reduction basin (0.76 m deep) to drain completely. Simulation of the hydraulic performance of the new integrated design indicates that an 88% treatment volume (percentage of total runoff that infiltrates through the BAM layer) can be expected for the nutrient reduction basin under typical rainfall conditions for north-central Florida (based on the runoff/water-balance model described in Chapter 5).
Figure 28: Hydrologic monitoring at the Hunter’s Trace stormwater infiltration basin 2008–2010: (A) rainfall, (B) basin stage and groundwater level, and (C) soil moisture content (VMC) and subsurface temperature (Tmp). The innovative stormwater infiltration basin incorporating biosorption activated media (BAM) was constructed 3–6 November 2009, and measurements made after this date represent conditions in or beneath the nutrient reduction basin. The soil moisture probe at 0.6-m depth was relocated to 0.5-m depth after construction.
Table 3: Infiltration rates at the Hunter’s Trace stormwater infiltration basin before and after construction of the nutrient reduction basin incorporating biosorption activated media.

<table>
<thead>
<tr>
<th>Date</th>
<th>Rain (mm)</th>
<th>Duration (h)</th>
<th>Infiltration (mm h⁻¹)</th>
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<tr>
<td>Before Biosorption Activated Media</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>23-Jan-08</td>
<td>20.3</td>
<td>4.75</td>
<td>8.6</td>
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<td>23-Feb-08</td>
<td>46.2</td>
<td>5.33</td>
<td>8.9</td>
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<td>7-Mar-08</td>
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<td>7.75</td>
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<tr>
<td>22-Aug-08</td>
<td>155.4</td>
<td>33.08</td>
<td>7.3</td>
</tr>
<tr>
<td>After Biosorption Activated Media</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>25-Nov-09</td>
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<td>21-Mar-10</td>
<td>21.8</td>
<td>6.17</td>
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</tr>
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_Nutrient Concentrations in Stormwater, Soil Water, and Groundwater_

Total dissolved nitrogen (TDN) in soil water and shallow groundwater beneath the basin was almost exclusively in the NO₃⁻ form throughout the entire monitoring period June 2007–August 2010 (Figure 29a–c,e). In stormwater, TDN was predominantly in the organic form; particulate and colloidal N (greater than 0.45 μm computed from unfiltered and filtered samples) was at times an important constituent of the TN in stormwater (Figure 29d). Stormwater samples were collected during groundwater sampling events when water was stored in the basin. Flow-weighted concentrations for individual runoff events would be different.
Figure 29: Temporal variations in nitrogen species, dissolved organic carbon (DOC), chloride, and dissolved oxygen (DO) (not available for lysimeters) concentrations before and after placement of biosorption activated media (BAM) at the Hunter’s Trace stormwater infiltration basin in (A) soil water (0.5 m deep lysimeter); (B) soil water (0.9 m deep lysimeter); (C) soil water (1.3 m deep lysimeter); (D) stormwater; and (E) groundwater (well M-0506, 4.6 m deep).
Total dissolved phosphorus (TDP) in soil water, groundwater, and stormwater was generally in the orthophosphate (PO$_4^{3-}$) form (Figure 30). Particulate and colloidal P (greater than 0.45 μm computed from unfiltered and filtered samples) was at times an important constituent of the TP in stormwater (Figure 30d; particulate and colloidal P fraction not shown). High TDP concentrations in deeper groundwater (well M-0505, 9.4 m deep) ranging from 0.46 to 0.90 mg L$^{-1}$ (median = 0.60 mg L$^{-1}$, n=20; data not shown) are due to the prevalence of phosphate minerals confirmed by X-ray diffraction analyses of the sediments at this depth (see samples for well M-0506 at 8.2 and 9.7 m depths in Appendix D).
Figure 30: Temporal variations in phosphorus species and chloride concentrations and pH before and after placement of biosorption activated media (BAM) at the Hunter’s Trace stormwater infiltration basin in (A) soil water (0.5 m deep lysimeter); (B) soil water (0.9 m deep lysimeter); (C) soil water (1.3 m deep lysimeter); (D) stormwater; and (E) groundwater (well M-0506, 4.6 m deep).
Nitrogen Transport and Fate Before and After BAM Application

Temporal variations in nutrient concentrations in soil water and groundwater were influenced by changing hydroclimatic conditions and variable N and P concentrations in runoff. The transport and fate of N and P in the subsurface is governed by a combination of conservative mixing and physical, chemical, and biological reactions. Understanding these varied mechanisms, as described in the following sections, is important to understanding the effectiveness of BAM.

Conservative Transport of Nitrate

NO$_3^-$ concentrations can be affected by physical processes as well as a variety of chemical reactions that generally are biologically mediated (nitrification, denitrification, dissimilatory reduction to ammonium (DNRA), microbial assimilation, or plant uptake). In contrast, chloride (Cl$^-$) and bromide (Br$^-$) generally are considered to be affected by only physical processes and thus are transported conservatively in the subsurface (Panno et al., 2006). Therefore, examination of these data in combination can give insight into NO$_3^-$ variations due to processes other than conservative transport, that is, the net effects of reaction-based processes and source inputs. During 2007–2010, a decline in Cl$^-$ concentration is apparent (Figure 31a). The cause of this long-term decline is uncertain, but based on specific conductance measurements made during well development, a significant increase in Cl$^-$ occurred prior to collection of the first sample on 22 June 2007. A linear regression between specific conductance and Cl$^-$ ($R^2 = 0.96$) indicates Cl$^-$ was 41 and 48 mg L$^{-1}$ on 28 March and 31 May 2007, respectively, whereas measured Cl$^-$ was 78 mg L$^{-1}$ on 22 June. Similar Cl$^-$ trends are apparent in well M-0505 (data not shown), which is 4.8 m deeper than M-0506, indicating water chemistry
trends existed in shallow groundwater prior to well installation. Thus the decline probably reflects mixing of more mineralized groundwater with relatively dilute infiltrated stormwater. Similar downward trends in Br\textsuperscript{−} concentration existed before and after construction of the new basin (Figure 31a). However, a substantial increase in Br\textsuperscript{−} occurred November 2009 through January 2010 following construction, suggesting a possible source of Br\textsuperscript{−} in the BAM layer to which the groundwater chemistry was equilibrating. The increase in Cl\textsuperscript{−} relative to Br\textsuperscript{−} in August 2010 is likely caused by infiltration of fertilizer-impacted stormwater because Cl\textsuperscript{−} is more prevalent in fertilizer than Br\textsuperscript{−} (Panno et al. (2006) reported a Cl\textsuperscript{−}/Br\textsuperscript{−} ratio of 510 for a commercial KCl fertilizer).
Figure 31: NO$_3^-$-N variations in groundwater beneath the Hunter’s Trace stormwater infiltration basin (well M-0506) before and after placement of biosorption activated media (BAM): (A) comparison of NO$_3^-$-N, total nitrogen (TN), Cl$^-$, and Br$^-$ concentrations; and (B) incrementally reconstructed NO$_3^-$-N and the incremental percentage differences assumed to be attributable to NO$_3^-$ reactions or NO$_3^-$ input variations.
Because Cl⁻ is present and generally acts as a conservative tracer in fertilizer-impacted stormwater runoff, NO₃⁻/Cl⁻ ratios were analyzed; whereas, Br⁻ was not present in stormwater runoff in measureable concentrations (laboratory reporting limit for Br⁻ is 0.02 mg L⁻¹). A change in slope of the NO₃⁻/Cl⁻ ratio indicates a change in the relation between the two values due to NO₃⁻ reaction or changes in source inputs:

- A positive NO₃⁻/Cl⁻ ratio slope indicates NO₃⁻ is decreasing slower or increasing faster than Cl⁻ due to nitrification, NO₃⁻ input increased relative to Cl⁻, or Cl⁻ input decreased relative to NO₃⁻;
- A negative NO₃⁻/Cl⁻ ratio slope indicates NO₃⁻ is increasing slower or decreasing faster than Cl⁻, possibly due to reaction (for example, denitrification), NO₃⁻ input decreased relative to Cl⁻, or Cl⁻ input increased relative to NO₃⁻; and
- A zero NO₃⁻/Cl⁻ slope indicates NO₃⁻ and Cl⁻ are changing at the same rate due to dilution.

Inflection points in the NO₃⁻/Cl⁻ ratio occurred near the time when the nutrient reduction basin was constructed and again in March 2010 (Figure 31a). These inflection points indicate times when fundamental changes (from positive to zero slope and from zero to negative slope) occurred in NO₃⁻ concentrations relative to Cl⁻, suggesting changes in NO₃⁻ reactions, NO₃⁻ and Cl⁻ inputs, or some combination of these factors.

In order to quantify the difference in NO₃⁻ concentration associated with the NO₃⁻/Cl⁻ ratio changes (Figure 31a), a “reconstructed” NO₃⁻ time series was computed based on the fractional change in Cl⁻ concentration between consecutive sampling events. This reconstructed concentration represents the NO₃⁻ concentration that would have occurred if only conservative
transport and $\text{NO}_3^-/\text{Cl}^-$ mass input variations were affecting concentrations during the time period from collection of one sample to the next. This is based on two assumptions: (1) transport of $\text{Cl}^-$ is conservative; and (2) there is no subsurface source of $\text{Cl}^-$. The first assumption implies that a fractional change in $\text{NO}_3^-$ will equal the fractional change in $\text{Cl}^-$, which is expected to be a valid assumption given the low anion exchange capacity of the soils at this site (varied 0.1–5 cmol$_c$ kg$^{-1}$, median = 1 cmol$_c$ kg$^{-1}$; Appendix E). The second assumption is also expected to be valid given the mineralogy of subsurface sediments and the lack of dissolved $\text{Cl}^-$ sources. Additionally, the consistent exponential decline in $\text{Cl}^-$ both before and after the addition of BAM and similar declines in $\text{Br}^-$ (Figure 31a) suggests that changes in $\text{NO}_3^-$ reactions or $\text{NO}_3^-$ input, rather than $\text{Cl}^-$ input changes, are the primary reasons for these changes in $\text{NO}_3^-/\text{Cl}^-$ ratio slopes.

Even though residences in the Hunter’s Trace community are served by septic tanks, a possible source of dissolved $\text{Cl}^-$, the water table gradients beneath the basin were nearly always outward, ranging from −0.00059 to 0.047 m m$^{-1}$ (negative values inward, positive values outward). The infiltration of fertilizer impacted stormwater runoff probably is the predominant input of $\text{Cl}^-$ mass into the subsurface due to the low concentration of $\text{Cl}^-$ in precipitation (0.2 and 0.6 mg L$^{-1}$ for samples collected May and December 2009, respectively).

For each sample event, a reconstructed $\text{NO}_3^-$ concentration was computed as follows:

$$\text{NO}_3^R_i - \text{NO}_3M_i = \Delta \text{Cl} + \text{NO}_3^M_i$$

(4)

$$\Delta \text{Cl} = \left( \frac{\text{Cl}_i - \text{Cl}_i^{-1}}{\text{Cl}_i^{-1}} \right)$$

(5)
where, \( \text{NO}_3^{i,R} \) is the reconstructed \( \text{NO}_3^- \) concentration for the current sampling event; \( \text{NO}_3^{i-1,M} \) is measured \( \text{NO}_3^- \) concentration for the preceding sampling event; \( \Delta \text{Cl} \) is the fractional change in \( \text{Cl}^- \) concentration; \( \text{Cl}^i \) is \( \text{Cl}^- \) concentration for the current sampling event; and \( \text{Cl}^{i-1} \) is \( \text{Cl}^- \) concentration for the preceding sampling event. This yields an incrementally reconstructed \( \text{NO}_3^- \) time series showing what \( \text{NO}_3^- \) concentrations would have been due to dilution or \( \text{NO}_3^-/\text{Cl}^- \) mass input variations for only the time period between current and preceding sampling events. The percent difference in \( \text{NO}_3^- \) concentration between measured and reconstructed values (\( \% \Delta \text{NO}_{3,M-R} \)) is computed as follows:

\[
\% \Delta \text{NO}_{3,M-R} = 100 \left( \frac{\text{NO}_{3,M} - \text{NO}_{3,R}}{\text{NO}_{3,M}} \right)
\]

(6)

where, \( \% \Delta \text{NO}_{3,M-R} \) represents a percentage measure of the net effects of \( \text{NO}_3^- \) reaction and changes in \( \text{NO}_3^-/\text{Cl}^- \) inputs. If additionally it is assumed that \( \text{Cl}^- \) input is relatively consistent, then \( \% \Delta \text{NO}_{3,M-R} \) represents the net effects of \( \text{NO}_3^- \) reaction and \( \text{NO}_3^- \) input variations only. This assumption is supported by the consistent exponential decline in \( \text{Cl}^- \) experienced throughout the study period, with the exception of the relatively large increase that occurred August 2010 (Figure 31a). Therefore, positive values of \( \% \Delta \text{NO}_{3,M-R} \) represent a reaction gain or input increase in \( \text{NO}_3^- \) and negative values of \( \% \Delta \text{NO}_{3,M-R} \) represent a reaction loss or input decrease in \( \text{NO}_3^- \). Values of \( \% \Delta \text{NO}_{3,M-R} \) near zero indicate \( \text{NO}_3^- \) was being transported conservatively, thus any observed changes in \( \text{NO}_3^- \) are attributable to dilution effects.

Prior to construction of the new basin, \( \text{NO}_3^- \) fate was dominated by nitrification or \( \text{NO}_3^- \) input increases with isolated periods of conservative movement possibly influenced by
ephemeral reaction losses, as indicated by percentage differences between measured and reconstructed NO$_3^-$ concentrations ranging from −3 to 120% (Figure 31b). In contrast, from November 2009 to April 2010 after the addition of BAM, NO$_3^-$ was controlled by intermittent periods of slight reaction losses and nitrification as indicated by percentage differences between measured and reconstructed NO$_3^-$ concentrations ranging from −8 to 4% (Figure 31b). However, the August 2010 sample indicated an increase in NO$_3^-$ considerably less than that expected based on the Cl$^-$ increase, yielding a percentage difference between measured and reconstructed NO$_3^-$ concentrations of −45% (Figure 31b). This indicates that in the absence of any NO$_3^-$ reaction or input decrease, the NO$_3^-$-N concentration would have been 2.12 mg L$^{-1}$ rather than 1.18 mg L$^{-1}$, suggesting nearly half (0.94 mg L$^{-1}$) was lost. An increase in NO$_3^-$ input is expected in late spring to early summer as suggested by samples collected in 2007–2009, coinciding with the start of the summer growing season and fertilizer application in residential landscapes. Therefore, the large percentage difference is reaction based. Another important difference attributable to the new integrated design is the prevalence of pre-BAM increases in NO$_3^-$ percentage differences and the absence of post-BAM increases (Figure 31b). This is suggestive of reduced nitrification after construction of the nutrient reduction basin and was concurrent with increased soil moisture (Figure 28c and Appendix K) and lower DO concentrations (Figure 29e), both of which are conditions less favorable for nitrification.

**Biogeochemical Assessment of Nitrogen Fate**

To provide additional insight into reaction based reductions in NO$_3^-$, such as denitrification or DNRA, occurring after the addition of BAM, several additional types of biogeochemical data were examined: soil chemistry, dissolved gases, soil gases, stable isotopes,
and denitrifier activity. Analysis of these data provide independent evidence of NO$_3^-$ reactions to support the inferences derived from examination of NO$_3^-$/Cl$^-$ ratios, as well as providing insight on C cycle coupling with other biogeochemical processes. The evidence for reaction based reductions in NO$_3^-$ provided by any of these datasets individually is limited. However, the following discussion shows that all of these lines of evidence taken in combination provide a consistent indication that NO$_3^-$ losses are primarily attributable to denitrification in the BAM layer, whereas other processes such as DNRA and plant uptake are less important.

Soil chemistry

Soil C contents generally are similar for samples collected before and after the addition of BAM with a couple notable differences (Figure 32). The elevated soil solids TC contents for the BAM layer (0.3-m depth samples) in January, April, and August 2010 are indicative of the tire crumb content (Appendix F). It should be noted that the soil solids OC contents reflect little of the tire crumb because the standard procedure used for OC analyses of soils (Walkley and Black, 1934) cannot digest the tire fragments. In contrast, soil solids TC is performed by combustion-oxidation at 1000°C and does measure the C content of the tire fragments. Analysis of a single BAM sample using different laboratory methods indicates a soil solids OC content of 18,000 mg kg$^{-1}$ and a soil solids IC content <100 mg kg$^{-1}$ (the method reporting limit) (Appendix J). Therefore, soil solids TC reported in Appendix F and Figure 32 probably closely reflect the actual OC content of the BAM samples (samples HT-F-0, HT-G2-2, HT-H-2, and HT-I-2). Soil solids IC contents and OC contents for these BAM samples (Appendix F and Figure 32) should be interpreted cautiously. Water extractable TC contents for the topsoil layer (0.1-m depth samples) were greater than that for June 2008 (Appendix G), although such limited data preclude
determining whether this is caused by the new integrated design or simply natural variability. Water extractable OC data were not available after BAM addition. However, water-extractable TC concentrations do indicate higher C content in the topsoil layer. The topsoil layer likely has a significant organic component where plant root activity is predominant and organic matter particulates are likely strained out of infiltrating stormwater. Visual observation (pronounced dark coloration) indicates this layer was naturally about 0.1–0.15 m thick before implementation of the new integrated basin design. The topsoil layer was largely preserved after BAM addition as part of the three soil sub-layer design (Figure 22b). Soil solid OC contents were greater in the shallowest samples collected within this depth interval.
Figure 32: Soil solid and water extractable total carbon (TC), organic carbon (OC), and inorganic carbon (IC, computed as the difference between TC and OC) contents beneath the Hunter’s Trace stormwater infiltration basin before and after placement of biosorption activated media (BAM). Placement of BAM was completed 6 November 2009.
Soil N contents differ for samples collected before and after the addition of BAM (Figure 33). Soil solids TN is higher in the BAM layer than the native soil sampled in 2008–2009 at the same depth, although concentrations fall within the range of values at other depths (Appendix F). Soil solids TN are lowest in the coarse sand layer as expected for clean quartz sand. In the topsoil and native subsoil, solids TN contents are similar for samples collected before and after the addition of BAM. Water extractable NH$_4^+$ is lower for the January and April 2010 samples in the BAM and coarse sand layers, but at similar levels in the topsoil and native subsoil.
Figure 33: Soil solid and water extractable total nitrogen (TN); soil water and KCl extractable ammonium nitrogen (NH$_4^+$); and soil water extractable nitrate plus nitrite (NO$_x$) and organic nitrogen (ON, computed as the difference between TN and inorganic nitrogen (IN = NH$_4^+$ + NO$_x$)) beneath the Hunter’s Trace stormwater infiltration basin before and after placement of biosorption activated media (BAM). Placement of BAM was completed 6 November 2009.
Most notable are differences in water extractable NO$_x$. All water extractable NO$_x$ contents were below the method detection limit for samples collected below the topsoil layer after construction of the nutrient reduction basin (Appendix G). For January and April 2010, soil samples were collected at depths of 0.1, 0.3, 0.5, 0.8, 0.9, and 1.3 m; for August 2010, soil samples were collected at depths of 0.1, 0.3, and 0.5 m. Samples collected at depths below 0.1 m had water extractable and KCl extractable NO$_x$ below the method detection limit for January and April 2010. For August 2010, samples collected at depths below 0.1 m had KCl extractable NO$_x$ below the method detection limit (water extractable NO$_x$ and NH$_4^+$ were not analyzed due to limited sample quantity). In contrast, for samples collected prior to the addition of BAM, water extractable NO$_x$ was 0.08–2.3 mg kg$^{-1}$ and KCl extractable NO$_x$ was 0.08–3.0 mg kg$^{-1}$ at depths below 0.1 m. KCl extractable NH$_4^+$ in the BAM layer in August 2010 was substantially higher than previous samples, suggesting possible DNRA and subsequent sorption.

*Biogenic gases and effects of soil moisture*

Analysis of dissolved N$_2$ and Ar in groundwater (well M-0506) for estimation of excess N$_2$ is difficult given the dynamic nature of the shallow groundwater system beneath the stormwater infiltration basin. A method described by O’Reilly et al. (2012a) was applied to derive estimates of excess N$_2$ concentrations by computing minimum (excess N$_2$ = 0) and maximum (excess air = 0) values of excess N$_2$. Corresponding recharge temperatures, which were estimated iteratively to meet each criterion, fell within the range of measured subsurface temperatures (Figure 28c). Because recharge temperatures could not be constrained by measured subsurface temperatures, final estimates of excess N$_2$ were computed using the average of the
estimated minimum (for excess air = 0 criterion) and maximum (for excess N\textsubscript{2} = 0 criterion) recharge temperatures. Only two samples were collected during the pre-BAM period, with estimated excess N\textsubscript{2} concentrations of 0.11 and 0.37 mg L\(^{-1}\) (Figure 34a). The lower value occurred in March 2008 when the basin had remained dry for 4.7 days prior to sampling, thus the soil was well aerated. In contrast, the higher excess N\textsubscript{2} concentration occurred in May 2009 during a major rainfall event when the basin had been continuously flooded 2.1 days prior to sampling (up to 0.7 m deep), potentially allowing for anoxic conditions to develop within the saturated soil profile. Estimated excess N\textsubscript{2} concentrations during the post-BAM period were modest as well, ranging from 0.16 to 0.34 mg L\(^{-1}\) (Figure 34a). Given the uncertainty of the estimation procedure, excess N\textsubscript{2} estimates could range from zero to about double these values. However, NO\textsubscript{3}\textsuperscript{-}/Cl\textsuperscript{-} ratio analyses described in the Conservative Tranport of Nitrate section indicate NO\textsubscript{3}\textsuperscript{-}-N losses ranging 0.012 to 0.94 mg L\(^{-1}\) during the post-BAM period, which is equivalent to 0.006 to 0.47 mg L\(^{-1}\) of excess N\textsubscript{2}. These excess N\textsubscript{2} concentrations inferred from NO\textsubscript{3}\textsuperscript{-}/Cl\textsuperscript{-} ratio analyses encompass and are reasonably comparable to the range of excess N\textsubscript{2} concentrations estimated from dissolved gas analyses. Even though DO was decreasing during much of the post-BAM period (Figure 29e), it still was above the maximum DO level of about 2 mg L\(^{-1}\) (or about 60 μmol L\(^{-1}\)) commonly reported for aquifers experiencing documented denitrification (McMahon and Chapelle, 2007; Tesoriero and Puckett, 2011). Therefore, it is postulated that denitrification was occurring in the unsaturated zone, in particular within the BAM layer.
Figure 34: Dissolved gas concentrations and isotope ratios for groundwater beneath the Hunter’s Trace stormwater infiltration basin (well M-0506) before and after placement of biosorption activated media (BAM) for (A) temporal variations $\delta^{15}$N and $\delta^{18}$O of NO$_3^-$, excess N$_2$, $\delta^{15}$N of N$_2$, and $\delta^{18}$O of H$_2$O; and (B) $\delta^{15}$N of N$_2$ compared to Ar/N$_2$ ratios.

Concentrations of the biogenic gases N$_2$O, CH$_4$, O$_2$, and N$_2$ derived from the soil gas samples (collected after construction of the nutrient reduction basin) indicate significant
biogeochemical activity within the shallow unsaturated zone. Subsurface generation of N$_2$O and CH$_4$ is indicated by concentrations exceeding ambient atmospheric levels (approximately 0.3 and 1.7 ppmv, respectively [U.S. Environmental Protection Agency, 2006]) (Figure 35a,b); whereas subsurface consumption of O$_2$ is indicated by concentrations below ambient atmospheric levels (approximately 21 %v) and generally downward concentration gradients (Figure 35c). Given the high ambient atmospheric levels of N$_2$ and the relatively slight contribution by excess N$_2$, Ar/N$_2$ ratios were computed. Ar/N$_2$ ratios that are consistently less than the ratio for ambient atmospheric concentrations (0.012) are consistent with the presence of excess N$_2$ in the unsaturated zone (Figure 35d). Soil moisture content is an important control on both the generation and transport of gases in the unsaturated zone by affecting the amount of gas-filled pore space and inhibiting surface/subsurface O$_2$ exchange leading to development of anoxic conditions (Bateman and Baggs, 2005; Christensen et al., 1990a; Jin and Jury, 1996). Accordingly, significant correlations with the degree of soil saturation were found for N$_2$O, Ar/N$_2$ ratio, and CH$_4$ (Table 4). The largest statistically significant correlations correspond to the BAM layer where much of the variability in soil gas concentrations can be explained by soil saturation (fraction of water-filled pore space): N$_2$O is negatively correlated ($R^2 = 0.81$, $p = 0.005$) with the 7-day average soil saturation, Ar/N$_2$ ratio is negatively correlated ($R^2 = 0.81$, $p = 0.006$) with the same-day soil saturation, and CH$_4$ is positively correlated ($R^2 = 0.71$, $p = 0.017$) with the 14-day average soil saturation. No correlations for O$_2$ are significant at the 0.1 level, however there is a weak negative correlation ($R^2 = 0.43$, $p = 0.16$) with the 28-day average soil saturation. Because all of these gases are actively consumed or produced by biological activity, these results underscore the importance of elevated soil moisture content on biogeochemical
cycling by inhibiting gas transport and promoting anoxic conditions that would tend to promote the reduction of O$_2$ and the accumulation of N$_2$O and CH$_4$.

Figure 35: Soil gas profiles beneath the Hunter’s Trace stormwater infiltration basin after placement of biosorption activated media (BAM) for (A) N$_2$O, (B) CH$_4$, and (C) O$_2$, and (D) Ar/N$_2$. 

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Table 4: Linear correlation between soil saturation (fraction of water-filled pore space) and soil gas concentrations for O$_2$, N$_2$O, CH$_4$, and Ar/N$_2$ after placement of biosorption activated media (BAM) at the Hunter’s Trace stormwater infiltration basin.

<table>
<thead>
<tr>
<th>Depth</th>
<th>Gas</th>
<th>Pearson R for average saturation of periods</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 d</td>
</tr>
<tr>
<td>All</td>
<td>O$_2$</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>N$_2$O</td>
<td>-0.51**</td>
</tr>
<tr>
<td></td>
<td>CH$_4$</td>
<td>-0.43</td>
</tr>
<tr>
<td></td>
<td>Ar/N$_2$</td>
<td>-0.23</td>
</tr>
<tr>
<td>0.3 m</td>
<td>N$_2$O</td>
<td>-0.81**</td>
</tr>
<tr>
<td>(BAM layer)</td>
<td>CH$_4$</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>Ar/N$_2$</td>
<td>-0.90**</td>
</tr>
<tr>
<td>0.5 m</td>
<td>O$_2$</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>N$_2$O</td>
<td>-0.62</td>
</tr>
<tr>
<td></td>
<td>CH$_4$</td>
<td>-0.83</td>
</tr>
<tr>
<td></td>
<td>Ar/N$_2$</td>
<td>-0.69*</td>
</tr>
<tr>
<td>0.9 m</td>
<td>O$_2$</td>
<td>-0.36</td>
</tr>
<tr>
<td></td>
<td>N$_2$O</td>
<td>-0.71*</td>
</tr>
<tr>
<td></td>
<td>CH$_4$</td>
<td>-0.82</td>
</tr>
<tr>
<td></td>
<td>Ar/N$_2$</td>
<td>-0.03</td>
</tr>
</tbody>
</table>

Average soil saturation computed for the number of stated days preceding sampling (inclusive of day of sampling) based on volumetric moisture content at the same depths as soil gas monitors; ** indicates p ≤ 0.05; * indicates 0.05 < p ≤ 0.1

N$_2$O can be produced in soil environments by both nitrification and denitrification and generally is reported to increase with increasing moisture content, with substantial increases at saturations (percentage of water filled pore space) above 60% (Abbasi and Adams, 2000; Bateman and Baggs, 2005; Dobbie et al., 1999). Based on laboratory incubations of an agricultural silt loam soil, Bateman and Baggs (2005) attributed N$_2$O production at 35–60% saturations to primarily nitrification with denitrification as a minor component, whereas
denitrification was the sole source of N$_2$O at saturations exceeding 70%. The median moisture content of the BAM layer was 0.30, indicating a saturation of 61%, thus the observed N$_2$O profiles are the product of both nitrification and denitrification (Figure 35a). Soil saturation varied among the seven soil gas sampling events, for example, 7-day average soil saturation ranged from 48 to 71%. The significant negative correlations between soil saturation and both N$_2$O concentration and Ar/N$_2$ ratio in the BAM layer suggest N$_2$O consumption by denitrification to N$_2$ (Table 4). Progression of denitrification to N$_2$ is favored for soil pH values exceeding 6 (Van den Huevel et al., 2011) and when O$_2$ levels are very low (Rivett et al., 2008). Pore-water pH varied 6.3–7.4 after the addition of BAM (Figure 30a-c), and low O$_2$ levels in soil microsites are implied by the presence of CH$_4$.

Methanogenesis probably was occurring in the BAM layer causing the elevated CH$_4$ levels (Figure 35b). The significant positive correlation with a longer period of wetter soil conditions (14-day average soil saturation, Table 4) is consistent with a longer time required for highly reducing conditions to develop. Since methanogenesis as well as denitrification require low O$_2$ conditions yet the unsaturated zone was aerobic (Figure 35c), these processes were occurring in anoxic microsites or cyclically during periods when the soil was wet or saturated and O$_2$ levels were low (Christensen et al., 1990a,b; Koba et al., 1997; O’Reilly et al., 2012a; Parkin, 1987; Raciti et al., 2011). The generation of CH$_4$ provides indirect evidence that the observed N$_2$O concentrations are at least partly attributable to denitrification, because NO$_3^-$ is a more thermodynamically favorable electron acceptor than CO$_2$ (McMahon and Chapelle, 2007) indicating that denitrification would have preceded methanogenesis. Additionally, soil water extractable NO$_x$-N concentrations were not detectable for samples collected in the BAM layer or
below yet were elevated prior to construction, frequently exceeding 0.5 mg kg\(^{-1}\) (volumetric concentrations frequently exceeding 10 mg L\(^{-1}\)) (Figure 33 and Appendix G). NO\(_3^-\) in soil water derived from the three lysimeters also showed decreases from pre- to post-BAM periods (Figure 29a–c), with the lowest concentrations in the BAM layer where NO\(_3^-\)-N ranged from 0.056 to 0.23 mg L\(^{-1}\) (average 0.14 mg L\(^{-1}\), n= 8) (Figure 29a). These results suggest that NO\(_3^-\) was depleted in the BAM layer, where anoxic microsites would have been most likely to develop due to elevated moisture contents (Figure 28c and Appendix K), consistent with denitrification and methanogenesis.

Substantial reductions in soil gas O\(_2\) occur in the two shallowest soil monitors, which respectively correspond to the midpoints of the BAM and coarse-sand layers (Figure 22b), relative to ambient atmospheric concentration. O\(_2\) is being depleted by serving as the electron acceptor for DOC oxidation, consistent with decreasing DOC concentrations with depth in the unsaturated zone (Figure 29a–c) and even lower DOC concentrations in shallow groundwater (Figure 29e). These relatively steep downward gradients and the negative correlation with soil saturation (Table 4) suggest the elevated soil moisture contents in the BAM layer (Figure 28c and Appendix K) are inhibiting surface/subsurface O\(_2\) exchange. Decreasing DO concentrations in the underlying groundwater since December 2009 is further indication of reduced O\(_2\) transport into the subsurface or increased O\(_2\) consumption compared to the pre-BAM period (Figure 29e).

**Stable isotopes and denitrification**

Isotope data collected after construction of the nutrient reduction basin provide evidence of denitrification when considered in combination with other data. The slight but consistent upward trends in \(\delta^{15}N[NO_3^-]\) and \(\delta^{15}N[N_2]\) are consistent with modest excess N\(_2\) concentrations
(Figure 34a), indicating enrichment in the heavy $^{15}$N isotope that would occur if denitrifiers were preferentially metabolizing $^{14}$N of NO$_3^-$.

It is important to note that variations in the isotopic composition of the NO$_3^-$ source will affect the isotopic composition of the residual NO$_3^-$ and N$_2$.

Therefore, deviations of $\delta^{15}$N$[N_2]$ on both the low side and the high side of air-saturated-water values could be a result of denitrification (Figure 34b), depending on the progress of the reaction (it starts out producing light N$_2$, then evolves to higher values as the reaction proceeds).

Computation of $\delta^{15}$N$[N_2,\text{excess}]$ for the fraction of total N$_2$ attributable to denitrification, based on linear mixing using $\delta^{15}$N of air-saturated water of 0.7‰ (Böhlke et al., 2002; Green et al., 2008b), indicates substantial enrichment over time (Figure 34b). This enrichment trend persists despite large uncertainty in excess N$_2$ estimates, which significantly affect $\delta^{15}$N$[N_2,\text{excess}]$ values such that a doubling of excess N$_2$ results in a 50% decrease of $\delta^{15}$N$[N_2,\text{excess}]$.

The single relatively high value of $\delta^{15}$N$[N_2]$ in August 2010 may be the result of an isotopically heavy NO$_3^-$ source, a denitrification reaction that proceeded to completion (NO$_3^-$ source depleted), or some combination of these factors. Highly enriched $\delta^{15}$N$[NO_3^-]$ yielding elevated $\delta^{15}$N$[N_2]$ could have resulted from a depleted NO$_3^-$ source even though NO$_3^-\cdot$N was 1.2 mg L$^{-1}$ in August 2010, if a pool of NO$_3^-$, perhaps in anoxic microsites, had been depleted. The August 2010 sample is reflective of denitrification considering NO$_3^-/Cl^-$ ratios indicated a 45% NO$_3^-$ loss. Given the aerobic conditions in groundwater and the biogenic gas trends noted in the unsaturated zone, these trends in groundwater isotopic composition and N$_2$ concentrations reflect biogeochemical processes occurring in the BAM layer.
Stable isotopes and carbon cycling

The C cycle is generally closely linked with the N cycle because denitrification is commonly mediated by heterotrophic bacteria. Thus stable C isotopes were examined to better understand how BAM influenced these linked biogeochemical cycles. The $\delta^{13}$C[DOC] data indicate that DOC is derived from the decomposition of vegetation at land surface and in the shallow soil zone. Typical $\delta^{13}$C values for vegetation using the Calvin ($C_3$) photosynthetic pathway to fix atmospheric CO$_2$ into OC (plant biomass) are $-24$ to $-30\%$ (Clark and Fritz, 1997). The $C_3$ pathway dominates in most terrestrial ecosystems. The $\delta^{13}$C[DOC] values for all stormwater, soil water, and groundwater samples (only post-BAM samples collected) fall within this range, varying from $-25.0$ to $-27.9\%$ (data not shown). These results are consistent with overland runoff in a residential area where the predominant OC source is vegetative material from which DOC leaches during contact with stormwater. Additionally, DOC likely is acquired by contact with herbaceous vegetation (both living and dead) in the stormwater basin and during percolation through the topsoil layer and root zone, resulting in DOC concentrations of 1.2–4.4 mg L$^{-1}$ in stormwater and soil water after construction of the nutrient reduction basin (Figure 29a,d). Substantial solid-phase organic matter in the topsoil layer is indicated by soil solid OC contents exceeding 20,000 mg kg$^{-1}$ (Figure 32, Appendix F), which is consistent with water extractable TC contents in the topsoil layer substantially higher than underlying layers (Figure 32, Appendix G). Oxidation of this plant derived OC, comprising DOC and soil organic matter, is suggested by $\delta^{13}$C[DIC] results (Figure 36). DIC comprises aqueous CO$_2$ and alkalinity, which for the pH values of shallow groundwater (Figure 30e) is predominantly HCO$_3^{-}$. In March 2010, alkalinity began increasing steadily and $\delta^{13}$C[DIC] began decreasing (Figure 36). This is
consistent with microbially mediated oxidation of OC to DIC (CO$_2$ and HCO$_3^-$), because DIC of biogenic origin will be depleted in $^{13}$C resulting in more negative values of $\delta^{13}$C[DIC] (Li et al., 2005). This oxidation of OC is coupled with O$_2$ reduction given the aerobic conditions in the unsaturated zone, but in anoxic microsites OC oxidation is coupled with NO$_3^-$ reduction by denitrification as suggested by soil gas data. These results suggest the BAM layer was receiving DOC from the surface and topsoil layer, where cycling of N (denitrification) and C (associated with O$_2$ reduction and heterotrophic denitrification) were occurring.

![Temporal variations in groundwater beneath the Hunter’s Trace stormwater infiltration basin (well M-0506) of $\delta^{13}$C of dissolved inorganic carbon (DIC), total inorganic carbon (TIC), alkalinity, and dissolved organic carbon (DOC) before and after placement of biosorption activated media (BAM).](image)

**Figure 36:** Temporal variations in groundwater beneath the Hunter’s Trace stormwater infiltration basin (well M-0506) of $\delta^{13}$C of dissolved inorganic carbon (DIC), total inorganic carbon (TIC), alkalinity, and dissolved organic carbon (DOC) before and after placement of biosorption activated media (BAM).

**Denitrifier activity**

Results of the qPCR analyses indicate the presence of denitrifying bacteria inferred from *nirK* gene density, confirming the “activated” nature of BAM. Two sets of soil samples for
qPCR analysis were collected prior to construction of the nutrient reduction basin in 2009; after construction, three sets were collected in 2010 and two sets were collected in 2011 for further confirmation (Appendix H). Denitrifier activity was somewhat lower after construction at similar soil depths (Figure 37), but this is expected due to the disruption of construction and the time required for microbial acclimation and growth as well as possible natural spatial and temporal variations. Because of the markedly different soil environments before and after construction and the limited number of samples, it is more appropriate to note the change in denitrifier activity only after BAM was added. Denitrifiers were concentrated in the BAM layer, indicating the innovative basin design incorporating BAM can produce conditions conducive to the growth of denitrifiers that possess the nirK gene. Furthermore, denitrifier density has increased, starting at 3.6×10^4 gene copies g^-1 in the BAM mixed and stockpiled onsite (4 November 2009 sample) before placement in the ground to 1.5×10^5 gene copies g^-1 in August 2010 (Figure 37; average of replicates for 3 August 2010 sample in Appendix H), suggesting denitrifiers were acclimating to the new environment. This increase in denitrifier activity occurred during the post-BAM period and is consistent with previously discussed chemical evidence for denitrification. Samples collected in the summer of 2011 indicate further increases in denitrifier abundance, suggesting continued functioning of the BAM layer to provide conditions conducive for denitrifier growth (Figure 37).
Figure 37: Denitrifier activity inferred from copper containing nitrite reductase (nirK) gene density measured by qPCR before and after placement of biosorption activated media (BAM) at the Hunter’s Trace stormwater infiltration basin. See Appendix H for data values.

Other nitrogen transformation processes

Observed decreases in NO$_3^-$ beneath the nutrient reduction basin, exclusive of those attributable to conservative processes inferred from NO$_3^-$/Cl$^-$ ratios (Figure 31), could be caused not only by denitrification, but also by microbial assimilation, plant uptake, DNRA, or some combinations of these processes. Both microbial assimilation and vascular plant uptake can impart N fractionations, averaging $-0.52\%\text{oo}$ and $-0.25\%\text{oo}$, respectively (Kendall and Aravena, 2000). These fractionations are similar to the slight enrichments over time observed in $\delta^{15}\text{N}[\text{NO}_3^-]$ in the groundwater beneath the basin (Figure 34a). However, post-BAM lysimeter
samples analyzed for δ¹⁵N[NO₃⁻] indicate much larger enrichments with depth, with values ranging from −3.7‰ to 8.9‰, averaging −2.2‰ at 0.5-m depth, 0.37‰ at 0.9-m depth, and 4.8‰ at 1.3-m depth. These results indicate microbial assimilation and plant uptake are relatively minor and denitrification in the unsaturated zone is the more important cause of nonconservative NO₃⁻ variations, which is consistent with other water chemistry and soil gas data. Additionally, Rivett et al. (2008) report that microbial assimilation generally is not a major sink for NO₃⁻ relative to denitrification in the subsurface, and visual observation of vegetation growth within the stormwater infiltration basin throughout the study suggests plant uptake was not substantially different before than after construction of the nutrient reduction basin even though NO₃⁻/Cl⁻ ratios indicate a substantial change in nonconservative NO₃⁻ variations. However, possible DNRA is indicated by soil samples collected from the BAM layer with KCl extractable NH₄⁺ of 5.9 mg kg⁻¹ in August 2010, which is approximately four times greater than BAM samples collected in January and March 2010 (Figure 33, Appendix G). Under such dynamic conditions of rapid infiltration beneath the stormwater basin, observed NO₃⁻ concentrations in the shallow groundwater are related to the intensity and duration of denitrification and DNRA and mixing ratios with water that has undergone little biogeochemical transformation.

**Phosphorus Transport and Fate Before and After BAM Application**

In soil water, P concentrations (both TDP and PO₄³⁻) indicate generally downward trends throughout the entire monitoring period, although notable decreases occur shortly after construction of the nutrient reduction basin (Figure 30a–c). Comparison of median concentrations in soil water indicates 70–90% reductions in TDP from pre-BAM to post-BAM periods. Decreases in P concentrations are due to conservative mixing, sorption, precipitation,
microbial assimilation, or some combination of these processes. However, the lowest P concentrations consistently occurred in the 0.5 m deep lysimeter, which spans the lower portion of the BAM layer and the entire coarse sand layer, suggesting reaction-based P losses in the BAM layer where NO$_3^-$ reduction also was identified. The reductions in TDP and PO$_4^{3-}$ are consistent with P sorption attributable to tire crumb (Hossain et al., 2010) and clay (Chang et al., 2010a; Harris et al., 1996), which are components of BAM, but also may be partly caused by lower P concentrations in the stormwater during this period (Figure 30d).

In groundwater, P concentration trends are less apparent, but were slightly upward prior to BAM and slightly downward after BAM. TDP and PO$_4^{3-}$ were consistently lower in well M-0506 (Figure 30e) than in lysimeters (Figure 30a–c) during the pre-BAM period, suggesting some P was removed naturally by the native sediments that become substantially finer in texture (from <5% to >40% silt+clay contents) at a depth of approximately 1.6 m. However, during the post-BAM period, TDP and PO$_4^{3-}$ were generally higher in well M-0506 than in lysimeters, consistent with inferred P losses in the BAM layer. PO$_4^{3-}$/Cl$^-$ ratios were examined to elucidate PO$_4^{3-}$ variations attributable to the net effects of reaction-based processes and source inputs using the methodology applied for NO$_3^-$ described in the Conservative Transport of Nitrate section and Equations 1–3. PO$_4^{3-}$/Cl$^-$ ratios (Figure 38a) show similar trends to NO$_3^-$/Cl$^-$ ratios (Figure 31a). Reconstructed concentrations indicate larger PO$_4^{3-}$ increases (1–180%) and only one sample indicating a PO$_4^{3-}$ loss prior to the addition of BAM, and after the addition of BAM smaller increases (6–18%) occurred with four samples indicating PO$_4^{3-}$ losses (Figure 38b). The August 2010 sample indicated an increase in PO$_4^{3-}$ considerably less than that expected based on the Cl$^-$ increase, yielding a change of −50% (Figure 38b), which is comparable to the NO$_3^-$ loss
during the same period (Figure 31b). This indicates that in the absence of any $\text{PO}_4^{3-}$ reaction or input decrease, the $\text{PO}_4^{3-}$-P concentration would have been 0.11 mg L$^{-1}$ rather than 0.054 mg L$^{-1}$, suggesting half was lost. An increase in $\text{PO}_4^{3-}$ input is expected due to fertilizer application in residential landscapes commonly conducted at the start of the growing season in late spring to early summer, coinciding with $\text{NO}_3^-$ increases (Figure 31b), and thus the large decrease is reaction based. Difference in P concentrations between the unsaturated zone and shallow groundwater may be the result of the intensity and duration of reaction processes and mixing ratios with water that had not undergone significant chemical changes.
Figure 38: PO$_4^{3-}$-P variations in groundwater beneath the Hunter’s Trace stormwater infiltration basin (well M-0506) before and after placement of biosorption activated media (BAM): (A) comparison of PO$_4^{3-}$-P, total phosphorus (TP), total dissolved phosphorus (TDP), and Cl$^-$ concentrations; and (B) incrementally reconstructed PO$_4^{3-}$-P and the incremental percentage differences assumed to be attributable to PO$_4^{3-}$ reactions or PO$_4^{3-}$ input variations.
Nutrient Reduction Strategies Using BAM

In a functionalized soil amendment each component of the amendment mixture possesses particular functional characteristics to improve attenuation of a pollutant of concern in a specific environmental setting (Wanielista and Chang, 2008). For BAM, the functional characteristics and related markers are abiotic nutrient retention (fostered by tire crumb and clay content) and biological nutrient removal (fostered by soil texture). Given that the initial full-scale field application described herein constitutes a prototype application of BAM, detailed identification of nutrient reduction processes and rates as quantitatively related to BAM composition is limited.

Other applications of BAM might yield different results depending on site-specific nutrient concentrations. Relative to other sources such as septic tanks, secondary treated wastewater, or agricultural drainage, urban stormwater runoff typically is relatively dilute with respect to nutrient concentrations. Median concentrations reported for stormwater runoff in urban areas include TN and TDN of 1.80 and 1.15 mg L\(^{-1}\), respectively (Taylor et al., 2005); NO\(_x\)-N of 0.35–1.1 mg L\(^{-1}\) (Clark and Pitt, 2007; Göbel et al., 2007; Taylor et al., 2005); and TP of 0.09–0.29 mg L\(^{-1}\) (Clark and Pitt, 2007; Göbel et al., 2007), and TDP of 0.13 mg L\(^{-1}\) (Clark and Pitt, 2007). These concentrations are comparable to values measured in this study (Figures 29d and 30d), indicating good potential for transferability of results for other stormwater treatment applications. Several general guidelines for BAM design and implementation can be derived based on the physicochemical and biogeochemical effects described below.

Physicochemical Effects of Tire Crumb and Clay in BAM

The nutrient retention potential of tire crumb (Hossain et al., 2010) and clay (Chang et al., 2010a) contribute to the sorption properties of BAM. Sorption of nutrient species controls
biogeochemical processes by retarding or immobilizing ions, such as NO$_3^-$, NH$_4^+$, and PO$_4^{3-}$, providing additional time for biological processes to facilitate removal. For an amendment mixture containing 15% tire crumb and an assumed stormwater filtration application, Hossain et al. (2010) report abiotic processes yield a life expectancy of about 16 years for TDP and PO$_4^{3-}$ removal, whereas life expectancy for NO$_3^-$ removal was 2.1 years and only 0.24 years for NH$_4^+$ removal. Thus physicochemical processes are expected to be more effective for P removal and biological processes for N removal. The silt and clay content of BAM is provided by incorporation of clayey sand (72% sand, 4% silt, 24% clay). Mineralogical identification of the silt and clay fractions by X-ray diffraction indicated the silt fraction is predominantly quartz and wavellite with smaller quantities of kaolinite and crandallite and the clay fraction is predominantly smectite and kaolinite with smaller quantities of quartz, mica, and crandallite. Harris et al. (1996) noted the importance of clay mineralogy for P sorption when occurring as coatings on quartz grains (soils ranging from 0.6% to 7.3% silt+clay). Kaolinite may be the clay mineral in BAM most likely to contribute to P retention (Parfitt, 1979), although noncrystalline metal oxides, such as Al or Fe, are particularly effective P sorbents. Extractions for Al or Fe oxides were not performed, but analyses for the total Al and Fe contents of BAM indicate 29,200 and 10,000 mg kg$^{-1}$, respectively (Appendix J). These large values suggest that some fraction may be composed of noncrystalline Al and Fe oxides. Additionally, CEC data for the bulk clayey sand sample indicate Al is the dominant exchangeable cation. Smectite, although having relatively little affinity for P, contributed substantially to the measured CEC of 10 cmol$_c$ kg$^{-1}$ for the bulk clayey sand sample. CEC of a tire crumb sample was only 1 cmol$_c$ kg$^{-1}$; for BAM samples collected from three locations, CEC varied 0.8–4 cmol$_c$ kg$^{-1}$ probably due to natural
heterogeneity. Soil chemistry data indicate NH$_4^+$ sorption in the BAM layer, especially for the August 2010 sample (5.9 mg N kg$^{-1}$, Figure 33, Appendix G), and even a modest CEC of 1 cmol$_c$, kg$^{-1}$ represents a sorption potential for NH$_4^+$ of 140 mg N L$^{-1}$. It is important to note that the CEC complex is readily exchangeable by other hydrated cations. This complex is maintained by relatively weak electrostatic forces and would not include cations sorbed hysteretically or irreversibly as by surface complexation reactions. These physicochemical effects noted in previous studies and observed in the field study described herein indicate BAM should include a tire crumb component of about 15% (by volume) and a clay mineral component possessing high Al and Fe oxide contents and CEC to promote physicochemical nutrient attenuation. The clay percentage of BAM significantly affects its textural properties, and a recommended percentage is best derived from an assessment of the effects of BAM texture on biogeochemical cycling.

**Biogeochemical Effects of BAM Texture**

During a comparative study of biogeochemical processes beneath the Hunter’s Trace stormwater infiltration basin (prior to construction of the nutrient reduction basin) and a stormwater infiltration basin in the nearby South Oak watershed (Figure 1), O’Reilly et al. (2012b) demonstrated that soil texture controls moisture retention capacity, which in turn controls subsurface O$_2$ transport, which in turn controls denitrification and other biogeochemical processes. Therefore, moisture content as controlled by texture may be the single most important functional characteristic of BAM, and the SMRC can be used to assess this characteristic. A laboratory derived SMRC for a BAM mixture similar to that used at the nutrient reduction basin (consisting of a 1.1:2.2:3.7 mixture (by volume) of tire crumb, silt+clay, and sand) (Figure 39b) demonstrates the greater moisture retention capacity of BAM over the native soil at the basin.
(Figure 39a), which is directly attributable to the silt+clay content of BAM. A field-estimated SMRC (Figure 39b) was derived using matric head computed from tensiometer measurements and volumetric moisture content measured by TDR probes at 0.3 m depth (within the BAM layer), showing behavior under typical hydroclimatic conditions. For the BAM layer, field capacity (approximated as the volumetric moisture content at a matric head of –2 m) was 0.24 (Figure 39b) indicating a saturation of 49%; whereas for the native sandy soil in the original basin, field capacity was 0.07 (Figure 39a) indicating a saturation of 24%. Compared to the laboratory derived SMRC, higher field measured moisture contents at low matric heads (0 to –0.25 m) and lower field measured moisture contents at higher matric heads (–0.25 to –1.25 m) are likely caused by macropore structure. The macropore structure of BAM is attributable to the presence of natural silt and clay aggregates in the clayey sand component of BAM, which were resistant to disaggregation during mixing onsite (with the tire crumb and sand components) and during placement in the ground (compacted by repeated passes with a bulldozer). Macropores were evident by visual observation of undisturbed soil cores collected from the BAM layer, whereas macropores were not present in laboratory samples of BAM that were dried and aggregates broken by mortar and pestle prior to mixing and packing. Macropores form preferential flow paths (Arora et al., 2011) that enable infiltrating water to bypass biogeochemically active areas (Baram et al., 2012; O'Reilly et al., 2012a); this phenomenon negatively impacted BAM nutrient removal performance.
Figure 39: Soil moisture retention curves for (A) native soil 0.9 m beneath the Hunter’s Trace stormwater infiltration basin (data for 0.3- and 0.6-m depths were nearly identical), and (B) biosorption activated media (BAM). Laboratory derived soil moisture retention curves were measured for the main drying curve on undisturbed soil cores using the pressure cell method (Dane and Hopmans, 2002; Naujock, 2008). For the native soil samples, undisturbed cores were used. For the BAM sample, a laboratory packed sample was used consisting of a slightly different mixture (1.1:2.2:3.7 mixture by volume) of tire crumb, silt+clay, and sand) than that used for the innovative stormwater infiltration basin. Field measurements were obtained by continuous monitoring beneath the nutrient reduction basin using time domain reflectometry and tensiometers.
Denitrification will terminate in the release of N\textsubscript{2} rather than N\textsubscript{2}O at soil saturations exceeding 70\% (Bateman and Baggs, 2005) to 90\% (Smith et al., 1998). De Kein and van Logtestijjn (1996) and Sexstone et al. (1988) confirm the importance of soil texture, reporting a strong effect of soil moisture on increasing denitrification in fine-textured soil where small increases in moisture content can fill narrow pore spaces and saturate soil aggregates. The BAM layer saturations ranged from 38\% to 95\%, with 50th and 90th percentiles of 61\% and 84\%, respectively, and were nearly always greater than the 49\% field capacity saturation (5th percentile). These results suggest denitrification in the BAM layer usually did not progress to N\textsubscript{2}, which is consistent with the limited excess N\textsubscript{2} detected. Higher saturations likely would have promoted N\textsubscript{2}O reduction to N\textsubscript{2} in the unsaturated zone, mitigating potential greenhouse gas concerns and permanently removing reactive N from the subsurface. Therefore, the silt+clay content of about 25\% (by volume) in the BAM mixture used in the nutrient reduction basin probably represents the minimum value that is adequate for increasing the fraction of saturated pore space to promote anoxic microsites that may serve as hotspots for denitrification.

The fine-grained texture of BAM also provides a large surface area per volume of soil for biofilm development. Although, due to the physical size of bacteria (typically 1 \textmu m), pore size limitation of very fine grained sediments can inhibit biofilm development (Rivett et al., 2008). The incorporation of sand (>0.075 mm diameter) and tire crumb (~1 mm diameter) in BAM yields an amendment mixture where 80\% of the particles have effective diameters greater than 75 \textmu m (Figure 27). As a result, BAM likely contains a large proportion of pore sizes greater than 50 \textmu m, a pore size that Seiler and Vomberg (2005) report to be large enough for biofilm
formation in a carbonate rock matrix suspected to be the location of denitrification microsites. O’Reilly et al. (2012b) report high denitrifier activity and other corroborating evidence indicating active denitrification for soils having median silt+clay contents of 41%. Therefore, for the conditions reported in this work, a BAM mixture containing a maximum of 50% (by volume) silt+clay particles probably is most amenable to denitrifier growth.

Carbon Cycling Effects on Denitrification in BAM

The C cycle affects O\textsubscript{2} levels in the subsurface, because DOC oxidation is coupled with O\textsubscript{2} reduction, and thus affects heterotrophic denitrification directly by potentially limiting substrate availability and indirectly by promoting anoxic conditions required to switch denitrifier’s facultative metabolism from O\textsubscript{2} to NO\textsubscript{3}\textsuperscript{-} respiration. Assuming CH\textsubscript{2}O as a simplified representation of DOC, stoichiometry indicates 1 mg L\textsuperscript{-1} DOC is oxidized to reduce 2.7 mg L\textsuperscript{-1} O\textsubscript{2} (O’Reilly et al., 2012a). Average DOC concentrations in stormwater and groundwater (well M-0506) were 8.3 and 0.74 mg L\textsuperscript{-1}, respectively; whereas average DO concentrations in stormwater and groundwater were 7.0 and 6.1 mg L\textsuperscript{-1}, respectively (Figure 29d,e). These results suggest that surface/subsurface O\textsubscript{2} exchange was supporting the oxidation of DOC in the unsaturated zone, thus demonstrating the importance of maintaining high soil moisture contents to mitigate this gas exchange. Reduced surface/subsurface O\textsubscript{2} exchange not only promotes the development of anoxic conditions but also prevents the complete aerobic oxidation of DOC, preserving it for use during heterotrophic denitrification. According to denitrification stoichiometry, 1 mg L\textsuperscript{-1} DOC is oxidized to reduce 0.93 mg L\textsuperscript{-1} NO\textsubscript{3}\textsuperscript{-}-N to N\textsubscript{2} (O’Reilly et al., 2012a). For the highest NO\textsubscript{3}\textsuperscript{-}-N recorded (7.23 mg L\textsuperscript{-1} in the 0.9-m lysimeter, Figure 29b), a minimum of 7.77 mg L\textsuperscript{-1} DOC would be required for complete denitrification, which is more
than the measured DOC concentrations in stormwater (Figure 29d). Therefore, an additional source of OC is needed. The OC content of BAM (18,000 mg kg\(^{-1}\); Appendix J) is higher than other soil layers, except the topsoil layer, and is primarily attributable to the tire crumb, but the bioavailability of the OC content of tire crumb is unknown. DOC supplied to the BAM layer likely is supplemented by leaching from root growth and C cycling in the overlying topsoil layer (Figure 22b), where soil solid OC contents are high (exceeding 20,000 mg kg\(^{-1}\); Appendix F).

Organic matter present in stormwater and in the topsoil layer and natural C cycling indicated by stable C isotopes (Figure 36) suggests that the innovative basin design promotes a passive, low maintenance, self-sustaining treatment system. This too supports a green infrastructure as DOC is at least partly provided by photosynthetic fixing of CO\(_2\) by herbaceous vegetation in the stormwater basin.
CHAPTER 7: SYSTEM DYNAMICS MODEL OF NITROGEN REMOVAL BY BIOSORPTION ACTIVATED MEDIA

Introduction

Hydrologic and biogeochemical data collected after construction of the new integrated design at the Hunter’s Trace stormwater infiltration basin has demonstrated promising nutrient reduction potential. Removal of aqueous N and P species by a combination of physicochemical and biogeochemical processes is promoted by biosorption activated media (BAM). However, particularly in the case of N, a complex array of interacting processes contributes to the net effects observed in the field data. A need exists to quantify these processes in order to further the development of passive nutrient control strategies leading to improved stormwater infiltration BMPs.

System dynamics, a methodology especially for comprehensive framing and understanding of complex feedback systems, was originally developed during the mid-1950s (Forrester, 1971). At that age, this method was difficult to practice, yet with the development of computer technology, system dynamics modeling has been widely used to address a wide variety of environmental and ecological studies including tree growth (Pan and Raynal, 1995), lake eutrophication assessment (Vezjak et al., 1998), bioavailability of metals in wetlands (Wood and Shelley, 1999), groundwater recharge (Abbott and Stanley, 1999), and water reallocation (Elmahdi et al., 2007). Thus system dynamics modeling is well suited for studying N transformations in the subsurface.

The biotic and abiotic transformation of N from one source to another is commonly referred to as the N cycle. Up to now, the well-known conversion processes include fixation (N₂
to ON and NH$_3$ to NH$_4^+$), ammonification (ON to NH$_4^+$), nitrification (NH$_4^+$ to NO$_x$) and denitrification (NO$_x$ to N$_2$) (Vymazal and Kröpfelová, 2008). Besides this macro loop, there are a variety of reverse reactions producing internal loops between different compounds such as uptake (NH$_4^+$ to ON), DRNA (NO$_3^-$ to NH$_4^+$), and volatilization (NH$_4^+$ to NH$_3$). For better recognition of such a dynamic complex system involving various circular, interlocking relationships among its compounds, system dynamics modeling has been recently applied to “visualize” the nutrient removal mechanism in some semi-enclosed subsurface treatment facilities (Xuan et al., 2010, 2011).

The objective of this chapter is to better understand the biogeochemical processes beneath the new stormwater infiltration BMP using BAM to advance N removal effectiveness with the aid of a system dynamics model characterized by the collected field-scale dataset. The data collected at the Hunter’s Trace stormwater infiltration basin may serve as the foundation for a trial extension to determine the system dynamics of N transport and fate in a large, open, field-scale system. The findings will allow quantitative exploration of the changes observed after the addition of BAM and the N removal mechanisms for the innovative infiltration basin design presented in this study.

**Modeling Methods and Procedures**

To fully represent the N dynamics beneath a stormwater infiltration basin using field data, detailed temporal characterizations of the following are required: (1) volumetric input and N content of infiltrating stormwater and the redistribution of this water in the unsaturated zone, and (2) N transformation processes occurring in the subsurface. Infiltration models were
developed to satisfy the first requirement and a system dynamics model was developed to satisfy the second requirement.

*Infiltration Models*

Given that input of N into groundwater beneath a stormwater infiltration basin is driven by the quantity and quality of infiltrating stormwater, these are key characteristics that must be specified for the system dynamics model. Models were developed to quantify the volume of infiltration, the water quality of infiltration, and the volume and downward flux of soil water in the unsaturated zone.

*Infiltration Volume*

The runoff/water-balance model described in Chapter 5 for hydraulic simulation of the new integrated design was used to compute hourly infiltration volumes for the original basin as well as for the flood control and nutrient reduction basins. Because the intent is to use this model to simulate actual field conditions, rather than design conditions, the runoff/water-balance model was modified by calibrating the infiltration rate and effective impervious area (EIA) to pre-BAM and post-BAM conditions. For pre-BAM conditions (1 December 2007 through 31 October 2009), the calibrated infiltration rate for the original basin was 7.6 mm hr\(^{-1}\) and the EIA was 1.70 ha, with a mean error of 0.041 m and RMSE of 0.066 m. For post-BAM conditions (7 November 2009 through 4 August 2010), the EIA was specified at the pre-BAM value of 1.70 ha and the calibrated infiltration rate for the nutrient reduction basin was 12 mm hr\(^{-1}\), with a mean error of 0.002 m and RMSE of 0.052 m.
The calibrated infiltration rate for the nutrient reduction basin is higher than those estimated from analysis of basin stage recession curves and may be attributable to the prevalence of smaller storm events compared to the large events reported in Table 3. Higher infiltration rates were reported by Wanielista et al. (2011) when using a double-ring infiltrometer embedded at land surface or a ring infiltrometer embedded through the three soil sub-layers, which resulted in measurements in the nutrient reduction basin that were about twice those from the recession curves. Lower infiltration rates during prolonged basin-wide flooding (such as those reported in Table 3), compared to point-scale infiltrometer measurements or small storm events when the basin bottom is partially or ephemerally flooded, are likely attributable to counterflow control of areally extensive infiltration caused by displacement of soil gas (Grismer et al., 1994; Wang et al., 1997), which would be consistent with the substantial gas bubble ebullition observed during basin flooding. Regardless of the mechanisms controlling infiltration, the runoff/water-balance model matches the observed stage in the stormwater infiltration basin well; thus the simulated infiltration volumes are expected to be accurate (Figure 40).
Infiltration Water Quality

The concentration of N in runoff is a crucial component of the N loading calculation. Event mean concentration (EMC) represents an accurate estimate of water quality for a storm event, where a volume-weighted concentration is computed based on concentration and flow measurements made at multiple times during a storm event (Wanielista et al. 1997). An automatic water sampler, which is capable of taking time-weighted or flow-proportional composite samples, would be an ideal type of equipment for supporting EMC results. However, such intensive stormwater sampling was not affordable for this study. Grab sampling was conducted for the collection of stormwater samples and is the most common, economical form of sampling. However, for grab sampling, it is highly likely that a single sampling during the storm
will miss the peak loading of the nutrients in stormwater runoff and cause an underestimation of the mass flow rate of the water-quality constituent of interest. Therefore, the N concentrations from the grab samples of stormwater must be adjusted before being input into the system dynamics model.

During the storm event the amount of a pollutant transported is assumed to follow a first-order reaction (that is, proportional to the amount of pollutant remaining on the watershed). Accordingly, the following equation can be derived relating pollutant mass to rainfall excess (Wanielista et al., 1997):

$$\frac{M_{R,o} - M_R}{M_{R,o}} = 1 - e^{-cR}$$  \hspace{1cm} (7)

where, c is transport rate coefficient (dependent upon land use and pollutant, in.\(^{-1}\)); R is the cumulative rainfall excess (or runoff) at time t (in.); and \((M_{R,o} - M_R) / M_{R,o}\) is the fraction of pollutant mass (dissolved or suspended) in the rainfall excess transported at time t relative to the initial mass of pollutant in the watershed \((M_{R,o})\). Since the majority of the Hunter’s Trace watershed was residential land use, 2.83 in.\(^{-1}\) is used as the transport rate coefficient for TN mass estimation (Wanielista and Yousef, 1993).

After the storm begins, the infiltration basin will receive the runoff with the peak mass flow rate of nutrients after a period of travel time. As the soil moisture increases, the infiltration capacity drops. When the surface soil layer becomes saturated and the infiltration rate is lower than the runoff inflow rate, then ponding commences. For the receiving reservoir, such as an infiltration basin, the water quality of ponding water, instead of the direct rainfall excess,
represents the actual source of the N input in most cases. A mass balance spans from the beginning of ponding water accumulation to the end of the draining process of ponding water after the storm can be used to link the runoff/water-balance model with the infiltration model (Figure 41). The time of sampling was rounded to the nearest hour. The runoff is assumed to be completely mixed with the existing ponding water. Then, the concentration of the ground-surface infiltrating water is equivalent to the concentration of the ponding water. Equation 7 is assumed to be applicable for predicting dissolved constituents. Thus, the cumulative received total dissolved N (TDN), represented by \((M_{R,o} - M_R)\), at time \(t\) can be derived with an assumed \(M_{R,o}\) value. \(M_{R,o}\) represents the mass, or “buildup,” of TDN in the watershed prior to the storm event. The mass flow rate at time \(t\), \(W_{in}\), then can be determined after setting the time-step size. The flow rate of the surface infiltration, \(Q_{out}\), was computed from the runoff/water-balance model as described in the preceding section. Then, the instantaneous concentration \(C_p\) can be derived from the simultaneous solution of volume- and mass-balance equations.
Figure 41: Water-volume balance and pollutant-mass balance for ponded stormwater. \( W_{\text{in}} \) (mg h\(^{-1}\)) is the mass flow rate of nitrogen in the stormwater runoff; \( Q_{\text{in}} \) (L h\(^{-1}\)) is the volume flow rate of the stormwater runoff; \( W_{\text{out}} \) (mg h\(^{-1}\)) is the mass flow rate of nitrogen in the infiltration; \( Q_{\text{out}} \) (L h\(^{-1}\)) is the volume flow rate of the infiltration; \( M_p \) (mg) is mass of nitrogen stored in ponded water; \( V_p \) (L) is the volume of ponded water; and \( C_p \) (mg L\(^{-1}\)) is the concentration of nitrogen in the ponded water.

The water-volume balance and TDN mass balance depicted in Figure 41 can be quantified using the following series of equations. First, the TDN mass balance is

\[
W_{\text{in}} - W_{\text{out}} = \Delta M_p / \Delta t \quad (8)
\]

\[
M_{p,t+1} = (W_{\text{in},t+1} - W_{\text{out},t+1})\Delta t + M_{p,t} \quad (9)
\]

Expressing mass in terms of concentration and volume and including the concentration of TDN in runoff entering the stormwater infiltration basin \((C_{R,t+1})\) yields

\[
C_{p,t+1}V_{p,t+1} = (C_{R,t+1}Q_{\text{in},t+1} - C_{p,t+1}Q_{\text{out},t+1})\Delta t + C_{p,t}V_{p,t} \quad (10)
\]

Second, the water volume balance is

\[
Q_{\text{in}} - Q_{\text{out}} = \Delta V_p / \Delta t \quad (11)
\]
\[ V_{p,t+1} = (Q_{in,t+1} - Q_{out,t+1}) \Delta t + V_{p,t} \] (12)

Substituting Equation 12 into Equation 10 and solving for \( C_{p,t+1} \) yields

\[
C_{p,t+1} Q_{in,t+1} \Delta t - C_{p,t+1} Q_{out,t+1} \Delta t + C_{p,t+1} V_{p,t} =
\]

\[
C_{R,t+1} Q_{in,t+1} \Delta t - C_{R,t+1} Q_{out,t+1} \Delta t + C_{p,t} V_{p,t}
\] (13)

\[
C_{p,t+1} = (C_{R,t+1} Q_{in,t+1} \Delta t + C_{p,t} V_{p,t})/(Q_{in,t+1} \Delta t + V_{p,t})
\] (14)

Expressing the TDN concentration of the runoff in terms of mass transported off the watershed given by Equation 7 yields

\[
C_{R,t+1} = (M_{R,t+1}/V_{R,t+1})
\] (15)

Substituting Equation 15 into Equation 14 yields

\[
C_{p,t+1} = (M_{R,t+1} + C_{p,t} V_{p,t})/(Q_{in,t+1} \Delta t + V_{p,t})
\] (16)

Grab sampling is generally conducted after the storm when there is no more runoff received by the infiltration basin and the infiltration reaches a near-constant rate. Then the simulated TDN concentration of the ponding water becomes stable, however, it is not equivalent to the measured value because of the exponential decline indicated by Equation 7 and an assumed \( M_{R,o} \) value. The Solver tool in Microsoft Excel® can be used to optimally determine the \( M_{R,o} \) value after reaching the best fit of simulated and measured TDN concentration of stormwater samples. By this way, a time series of TDN concentration in infiltration water can be computed using Equation 16 based on a single grab sampling at any time after the storm, and the TDN mass flow amount can be calculated.
Soil-Water Volume and Flux

Soil moisture can vary dramatically depending on the intensity and duration of storm events and the soil’s ability to transport and store water. As a result, during the storm, soil at different depths might shift between saturated and unsaturated condition. The Richards (1931) equation was formulated for describing the movement of water in variably saturated soil (both unsaturated and saturated). However, the Richards equation is limited to diffuse flow in a relatively homogeneous soil that is represented as a continuum, which may not exist for many field conditions such as macropore flow. Thus, the Richards equation is not a universal solution to describe the complex movement of water in the subsurface. Therefore, a model based on soil-water volume computed from measured soil moisture contents and the infiltration rates predicted by the runoff/water-balance model was developed to determine the soil-water fluxes at certain depths.

Storage of water in soil depends on porosity (\( \phi \)), which represents the fractional relationship between volume of voids and bulk volume of soil, representing a theoretical maximum volume that can be occupied by water that generally is not met due to air bubble entrapment during infiltration (Figure 42). Volumetric water content (\( \theta_v \)) represents the fractional relationship between volume of water (soil moisture) and the bulk volume of soil, and was monitored beneath the stormwater infiltration basin.

\[
\phi = \frac{V_v}{V_b} \tag{17}
\]

\[
\theta_v = \frac{V_w}{V_b} \tag{18}
\]
where, \( V_v \) is the volume of void space, \( V_w \) is the volume of water (soil moisture); and \( V_b \) is the bulk soil volume.

![Diagram of soil components](image)

**Figure 42: Volumetric components of soil.**

When a storm contributes surface runoff into the stormwater infiltration basin, the soil pores will be filled with water. As long as all pores are fully filled with water, the state of the soil is called saturated and \( \theta_s \) is equivalent to \( \phi \). The volumetric water content at the stage after the gravitational water drains away is called field capacity. When the remaining water in the soil is no longer available to be transpired by the plants or evaporated into the atmosphere, the volumetric water content is called permanent wilting point. The system dynamics model described later represents (1) the amount of water stored in the soil when saturated minus the water held at field capacity during storm events and subsequent drainage periods; and (2) the
amount of water stored in the soil at field capacity minus the water remaining in the soil at
permanent wilting point during other times.

Changes in the storage and transmission of infiltrated stormwater during and after a storm
event contributes to the complexity of subsurface biogeochemical processes. To improve the
ability of the system dynamics model to match the measured TDN concentration in the soil
profile, the one-dimensional continuity equation was used to estimate the soil-water flux through
the cross-section at different depths (Figure 43). For the prescribed layers (L) beneath the
infiltration basin with thickness (T), the soil-water flux at the interface of different layers can be
estimated based on a series of equations relating the infiltration amount (Q) to the consequent
water storage change (∆S) within each layer. The full, generalized continuity equation based on
Figure 43 is

\[
Q_{0,t} - Q_{n,t} = ∆S_1 + ∆S_2 + ∆S_3 \ldots + ∆S_n = A \times T (Δθ_1 + Δθ_2 + Δθ_3 \ldots + Δθ_n) = \\
A \times T [(Δθ_{1,1} + Δθ_{2,1} + Δθ_{3,1} \ldots + Δθ_{n,1}) - (Δθ_{1,t} + Δθ_{2,t} + Δθ_{3,t} \ldots + Δθ_{n,t})]
\]  

(19)
Figure 43: Soil-water flux model and corresponding continuity equations.

In this study, a four-layer model was used (Figure 44). The volumetric water content (VWC) measured at depths of 0.30, 0.61, and 0.91 m were assumed to be the average $\theta_i$ of the three layers separated by the soil water samplers (lysimeters) installed at depths of 0.46, 0.91, and 1.30 m. In the saturated zone, a different approach was used to compute the flow exiting the fourth layer based on the head gradient between wells M-0506 (mid-screen depth of 3.87 m) and M-0505 (mid-screen depth of 8.60 m). After the adjustment in terms of infiltration volume and concentration and soil-water flux, the time step was converted from hourly to daily for long-term N removal simulation using the system dynamics model.
System Dynamics Model

STELLA®, an advanced graphical system dynamics software package, was used to develop the mathematical N removal model for the infiltration basin, referred to as the integrated infiltration basin–nitrogen reduction (IBNR) model. The conceptual model for N removal beneath the nutrient reduction basin is shown in Figure 45. Note that Table 5 shows the description of symbols in the IBNR model by taking the first layer as an example. The stocks were set up as the different dissolved N species (horizontally) within different layers beneath the infiltration basin (vertically) to estimate chemical and microbiological metabolic parameters. Four sub-layers were arranged based on sampling locations (Figure 44). The horizontal flows were set up as the primary transformation processes between N species such as ammonification (AM), nitrification (NI), and denitrification (DE) and the vertical ones represent the N mass flow.
with infiltration between layers. The IBNR model was designed based on several assumptions. The system is treated as a plug-flow reactor from top to bottom. Each layer is considered as a separate homogeneous entity, functioning as a continuously stirred tank reactor. The fluid is perfectly mixed horizontally but not in the axial direction (vertically). The N species move at the direction and velocity of water movement and will be perfectly mixed upon entering each layer. The infiltration rate at the same elevation is identical and the system may be modeled as a one-dimensional vertical flow path. A schematic diagram of the full IBNR model structure is provided in Appendix L.
Figure 45: Generalized conceptual model of nitrogen cycling beneath the nutrient reduction basin at the Hunter’s Trace stormwater infiltration basin used for the integrated infiltration basin–nitrogen reduction model.
Table 5: Description of symbols used to represent nitrogen cycling in layer 1 of the integrated infiltration basin–nitrogen reduction model shown in Figure 45.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input ON</td>
<td>ON-N concentration (mg L(^{-1})) in stormwater</td>
</tr>
<tr>
<td>Input NH(_4)</td>
<td>NH(_4^+)-N concentration (mg L(^{-1})) in stormwater</td>
</tr>
<tr>
<td>Input NO(_x)</td>
<td>NO(_2^-)-N + NO(_3^-)-N concentration (mg L(^{-1})) in stormwater</td>
</tr>
<tr>
<td>ON 1</td>
<td>ON-N (mg) in 1(^{st}) layer;</td>
</tr>
<tr>
<td>NH(_4) 1</td>
<td>NH(_4^+)-N (mg) in 1(^{st}) layer;</td>
</tr>
<tr>
<td>NO(_x) 1</td>
<td>NO(_2^-)-N + NO(_3^-)-N (mg) in 1(^{st}) layer;</td>
</tr>
<tr>
<td>AM 1(^{st}) layer</td>
<td>ammonification (mg day(^{-1})) in 1(^{st}) layer</td>
</tr>
<tr>
<td>NI 1(^{st}) layer</td>
<td>nitrification (mg day(^{-1})) in 1(^{st}) layer</td>
</tr>
<tr>
<td>DE 1(^{st}) layer</td>
<td>denitrification (mg day(^{-1})) in 1(^{st}) layer</td>
</tr>
<tr>
<td>ON 1(^{st}) to 2(^{nd})</td>
<td>ON-N (mg day(^{-1})) transfer from 1(^{st}) layer to 2(^{nd}) layer</td>
</tr>
<tr>
<td>NH(_4) 1(^{st}) to 2(^{nd})</td>
<td>NH(_4^+)-N (mg day(^{-1})) transfer from 1(^{st}) layer to 2(^{nd}) layer</td>
</tr>
<tr>
<td>NO(_x) 1(^{st}) to 2(^{nd})</td>
<td>NO(_2^-)-N + NO(_3^-)-N (mg day(^{-1})) transfer from 1(^{st}) layer to 2(^{nd}) layer</td>
</tr>
<tr>
<td>(r_{a,1})</td>
<td>ammonification first-order reaction rate constant (day(^{-1})) in 1(^{st})</td>
</tr>
<tr>
<td>(r_{n,1})</td>
<td>nitrification first-order reaction rate constant (day(^{-1})) in 1(^{st}) layer</td>
</tr>
<tr>
<td>(r_{d,1})</td>
<td>denitrification first-order reaction rate constant (day(^{-1})) in 1(^{st}) layer</td>
</tr>
<tr>
<td>(K_{a,1})</td>
<td>ammonification reaction constant(^a) (day(^{-1})) in 1(^{st}) layer</td>
</tr>
<tr>
<td>(K_{n,1})</td>
<td>nitrification reaction constant(^a) (day(^{-1})) in 1(^{st}) layer</td>
</tr>
<tr>
<td>(K_{d,1})</td>
<td>denitrification reaction constant(^a) (day(^{-1})) in 1(^{st}) layer</td>
</tr>
<tr>
<td>ON 1(^{st}) Eff</td>
<td>ON-N concentration (mg L(^{-1})) in effluent</td>
</tr>
<tr>
<td>NH(_4) 1(^{st}) Eff</td>
<td>NH(_4^+)-N concentration (mg L(^{-1})) in effluent</td>
</tr>
<tr>
<td>NO(_x) 1(^{st}) Eff</td>
<td>NO(_2^-)-N + NO(_3^-)-N concentration (mg L(^{-1})) in effluent</td>
</tr>
</tbody>
</table>

\(^a\) The reaction constant, \(K\), is a temporally constant factor that is used to compute the first-order reaction rate constant, \(r\), such that \(r = K \times f(x_1, x_2, \ldots, x_n)\) where \(f(x_1, x_2, \ldots, x_n)\) represents temporally variable factors that may affect reaction kinetics, for example, temperature, pH, and dissolved oxygen. In the current version of the IBNR model, \(f(x_1, x_2, \ldots, x_n) = 1\) and \(r_{a,1} = K_{a,1}\), \(r_{n,1} = K_{n,1}\), and \(r_{d,1} = K_{d,1}\).

The first-order reaction was assumed for the primary transformation processes between different dissolved N species. All of the stocks (N species) are expressed on an instantaneous mass basis (mg) and flows are expressed on a mass-flow basis (mg d\(^{-1}\)). The volume of each layer is defined as the effective water volume (product of soil volume and VWC) of each layer. As NH\(_4^+\) forms most of the NH\(_3\) in aquatic conditions, laboratory reported NH\(_3\) results were
assumed to be $\text{NH}_4^+$. A concentration of 0.01 mg L$^{-1}$ was used for $\text{NH}_4^+$-N when it was lower than the laboratory reporting limit (0.02 mg L$^{-1}$). ON concentration was calculated from TDN minus inorganic nitrogen (the sum of $\text{NH}_4^+$-N and NO$_x$-N). A fixation rate (29 g N ha$^{-1}$ y$^{-1}$) (Reed et al., 2011) was used for ON and $\text{NH}_4^+$ and plant uptake rate (2 g N ha$^{-1}$ y$^{-1}$) was assumed for $\text{NH}_4^+$ and NO$_x$ in the top layer only. Many researchers have documented the accumulation of NO$_3^-$ in the unsaturated zone (Goolsby et al., 2000; Costa et al., 2002; and Walvoord et al., 2003). A retardation factor proportional to the percentage of clay in the soil was used in the third and fourth layers where the NO$_3^-$ accumulation occurred and the clay percentage increased. This retardation factor conceptually represents the combined effects of sorption and N exchange between solid-phase and water-phase compartments, processes that are not explicitly simulated in the present version of the IBNR model.

Each simulation of the IBNR model spans from the date of the storm event to the closest date of the non-storm sampling, and results are compared against the measured values to conduct the calibration and validation. While some parameters can be specified, others must be measured or assumed so that they may be determined holistically by model calibration.

**Results and Discussion**

The infiltration volume, infiltration water quality, and soil-water flux models described in the previous section were applied to preprocess input for the IBNR model.

**Infiltration Total Dissolved Nitrogen Concentrations**

Six storm events relatively evenly distributed during the experimental period occurred when samples of stormwater were also collected (Figure 46 and Table 6). The cumulative
rainfall ranges from 8.9 mm (28 August 2008) to 223.8 mm (17 May 2009). The storm event on 23 July 2008 has the highest average intensity (20.7 mm h\(^{-1}\)) and peak intensity (74.4 mm h\(^{-1}\)). For all the storm events, Table 6 lists the estimated buildup of TDN mass in the watershed \(M_{R,o}\) of Equation 7) and the elapsed time since the previous storm event (antecedent condition), which have a strong linear relationship: \(M_{R,o} = 4.99\times(\text{Elapsed Time}) – 229, R^2 = 0.998\). The finding that, for a variety of different storms, the buildup of TDN mass in the watershed is consistently proportional to the time interval between storms supports the reliability of the adjustment regarding the infiltration water quality. Figure 47 shows the hyetograph of the six storm events along with the time series of TDN concentrations of the ponding water computed using Equation 16. As discussed previously, missing the peak TDN loading would cause an underestimation of the cumulative TDN mass. The adjusted cumulative mass of TDN received by the stormwater infiltration basin is compared against the unadjusted value without a peak pattern (if the measured concentration of grab samples is used as the constant concentration of ponding water with time) to check how much percentage of increase was caused by the adjustment (Table 7). Generally, a longer time between the beginning of the storm and the sampling (17 May 2009, 47 hours) leads to a larger adjustment (197.9%) due to a more variable hyetograph pattern before the sampling time, except when the sampling was conducted while the N concentration of ponding water had not stabilized (28 August 2008). Error in estimating the concentration could be introduced when the sampling time was rounded to the nearest hour, but such error is expected to be within the uncertainty of this relatively simple technique for estimating temporal concentration patterns. These adjusted concentration values are used in the IBNR model.
Figure 46: Rainfall and stage data collected before and after placement of biosorption activated media (BAM) at the Hunter’s Trace stormwater infiltration basin.

Table 6: Selected storm events during the experimental period and estimated buildup of total dissolved nitrogen (TDN) mass in the watershed.

<table>
<thead>
<tr>
<th>Storm event</th>
<th>Cumulative rainfall, mm</th>
<th>Duration, h</th>
<th>Average intensity, mm h⁻¹</th>
<th>Peak intensity, mm h⁻¹</th>
<th>Elapsed time since previous event, h</th>
<th>Estimated buildup TDN, $M_{R,o}$, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>23-Jul-08</td>
<td>82.8</td>
<td>4</td>
<td>20.7</td>
<td>74.4</td>
<td>95</td>
<td>321.65</td>
</tr>
<tr>
<td>28-Aug-08</td>
<td>8.9</td>
<td>2</td>
<td>4.4</td>
<td>5.6</td>
<td>95</td>
<td>264.38</td>
</tr>
<tr>
<td>17-May-09</td>
<td>223.8</td>
<td>80</td>
<td>2.8</td>
<td>30.7</td>
<td>799</td>
<td>3759.01</td>
</tr>
<tr>
<td>2-Dec-09</td>
<td>20.1</td>
<td>15</td>
<td>1.3</td>
<td>9.1</td>
<td>72</td>
<td>79.92</td>
</tr>
<tr>
<td>21-Jan-10</td>
<td>53.3</td>
<td>16</td>
<td>3.3</td>
<td>14.7</td>
<td>109</td>
<td>226.45</td>
</tr>
<tr>
<td>2-Mar-10</td>
<td>15.0</td>
<td>9</td>
<td>1.7</td>
<td>11.4</td>
<td>66</td>
<td>142.14</td>
</tr>
</tbody>
</table>
Table 7: Comparison of measured total dissolved nitrogen mass at time stormwater sample was collected with estimated total dissolved nitrogen buildup ($M_{R,o}$ of Equation 7).

<table>
<thead>
<tr>
<th>Storm event</th>
<th>Stormwater sampling date</th>
<th>Sampling time, hh:mm</th>
<th>Time between beginning of the storm and sampling, h</th>
<th>Adjustment, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>23-Jul-08</td>
<td>23-Jul-08</td>
<td>18:55</td>
<td>6</td>
<td>11.0</td>
</tr>
<tr>
<td>28-Aug-08</td>
<td>28-Aug-08</td>
<td>18:14</td>
<td>2</td>
<td>57.8</td>
</tr>
<tr>
<td>17-May-09</td>
<td>19-May-09</td>
<td>16:25</td>
<td>47</td>
<td>197.9</td>
</tr>
<tr>
<td>2-Dec-09</td>
<td>3-Dec-09</td>
<td>08:20</td>
<td>14</td>
<td>34.1</td>
</tr>
<tr>
<td>21-Jan-10</td>
<td>22-Jan-10</td>
<td>10:45</td>
<td>21</td>
<td>32.1</td>
</tr>
<tr>
<td>2-Mar-10</td>
<td>2-Mar-10</td>
<td>16:40</td>
<td>12</td>
<td>39.0</td>
</tr>
</tbody>
</table>
Figure 47: Time series of the total dissolved nitrogen concentration of the ponding water and the hyetograph of selected storms at the Hunter’s Trace stormwater infiltration basin.
**Infiltration and Soil-Water Fluxes**

The same periods (14–30 June) in 2009 and 2010 were randomly selected to compare the daily values of hydrologic monitoring data before and after the construction of the BAM layer in terms of VWC, rainfall, and infiltration. During the pre-BAM period, VWC shows roughly the same upper and lower limit at different depths due to the similar composition of soil texture (Figure 48). Only the shallowest soil layer at 0.3 m shows an acute response to rainfall with multi peaks and rapid decline, followed by more modest VWC variations with depth. During the post-BAM period, both high upper and lower limits of the VWC at 0.3 m (the midpoint of the BAM layer) exhibit the first intended function of the BAM layer to increase soil moisture and moisture retention capacity. The similar pattern observed at the depth of 0.6 m shows the evidence of another design goal, to maintain an infiltration capacity sufficient to satisfy the flood-control requirements of the new BMP. The coarse sand layer drains rapidly and contributes to retain water in the overlying BAM layer. The deeper soil (0.9 m) maintains a “natural” pattern owing to the native undisturbed soil profile. Based on the VWC data at the different depths, the soil-water fluxes at the interfaces between different layers can be computed using soil-water flux model (Figure 43). During the pre-BAM period, a successive uniform lag time is apparent between the soil-water flux patterns at different depths (Figure 48). However, the flux patterns at the bottom of the first and second layers (that is, Infil 1 and Infil 2; Figure 48) agree with the surface infiltration pattern during the post-BAM period, reflecting the high infiltration capacity of the BAM layer. When the infiltration rates drop on 19 June 2010, the flux rates for the underlying layers are only half of the surface infiltration rate, which supports increased moisture retention capacity. The adjusted time series of soil-water fluxes are used in the IBNR model.
Figure 48: Measured rainfall and volumetric water content (VWC) at the Hunter’s Trace stormwater infiltration basin for (A) 14–30 June 2009, and (B) 14–30 June 2010; and corresponding surface infiltration flux (Infil 0) and soil-water fluxes (Infil 1 = 0.46 m, Infil 2 = 0.91 m, and Infil 3 = 1.30 m) for (C) 14–30 June 2009, and (D) 14–30 June 2010.

**IBNR Model Calibration and Validation**

Calibration was performed to match simulated and measured values by adjusting the 12 parameters representing the first-order reaction rate constants for ammonification, nitrification, and denitrification for each model layer (Table 4). Runge-Kutta 4 was used as the integration method. The storm event on 2 December 2009 was used for model calibration using a simulation period of 1–15 December 2009. The final agreement between the measured and simulated values of ON, NH$_4^+$, NO$_x$, and TDN for the 14–15 December 2009 samples are shown in Figure 49. Both ON and NH$_4^+$ concentrations are close to detection limits. Oxidized N species are the
dominant composition of TDN. The slope of the regression line and the coefficient of determination ($R^2$) were both close to 1, indicating a favorable model fit. The accuracy of TDN removal predictions by the IBNR model are directly related to good simulation of oxidized N species. The values of first-order reaction rate constants derived during the calibration process decreased with depth (Table 8). The higher denitrification rate for layer 1 shows a successful application of the BAM layer. These results are consistent with the biogeochemical assessment of BAM presented in Chapter 6 that indicated N removal was predominantly attributable to denitrification that was occurring in the BAM layer as opposed to deeper soil layers or the saturated zone.

Figure 49: Comparison of measured and simulated dissolved nitrogen species concentrations for the 1–15 December 2009 calibration period.
Table 8: Calibrated values of the first-order reaction rate constants applied in the integrated infiltration basin–nitrogen reduction.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Ammonification $r_a$, d$^{-1}$</th>
<th>Nitrification $r_n$, d$^{-1}$</th>
<th>Denitrification $r_d$, d$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>2</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>0.3</td>
<td>0.01</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>0.2</td>
<td>0</td>
</tr>
</tbody>
</table>

However, a variety of more complex reaction mechanisms likely are at play.

Concentrations of TDN and NO$_x$ in layers 2 and 3 are underpredicted (the points with measured concentrations near 0.4 mg L$^{-1}$ Figure 49). Apparent NO$_3^-$ accumulation occurred in layer 2 (representing the 0.9-m deep lysimeter, Figure 29b) and layer 4 (representing well M-0506, Figure 29e). More factors could affect NO$_3^-$ accumulation in addition to the change of soil texture, such as soil sorption or plant uptake. For example, a decrease in pH from 7.4 to 6.6 was observed after BAM application in the 0.9-m lysimeter (Figure 30b) and pH was consistently lower (ranged from 5.5 to 6.0) in the saturated zone (well M-0506, Figure 30e). A low pH condition could lead to retention of anions such as NO$_3^-$, retarding leaching into the soil layer below and causing the accumulation at certain depths. Plants use the NO$_3^-$ in shallower soil layers for growth through their root systems. There must be a boundary below which the plant could not utilize any more NO$_3^-$ due to the limit of the root length. The top of the NO$_3^-$ accumulation zone might be considered as such a boundary. A well analyzed study of biomass growth of the herbaceous vegetation growing in the nutrient reduction basin would be needed to calibrate the plant uptake rate in the model.
The storm event on 2 March 2010 was used for model validation using a simulation period 2 March – 7 April 2010. The final agreement between the measured and simulated values of ON, NH$_4^+$, NO$_x$, and TDN for the 6–7 April 2010 samples is shown in Figure 50. Model validation was performed using the same first-order reaction rate constants as those developed during calibration (Table 8). The slope of the regression line and the $R^2$ were close to 1 (Figure 50), both of which support the model validation. However, concentrations of TDN and NO$_x$ in layer 1 are underpredicted (the points with measured concentrations near 0.25 mg L$^{-1}$ in Figure 50), suggesting, as for the calibration dataset, that more complex mechanisms may be occurring than what are represented in the current model.

![Graph showing comparison of measured and simulated dissolved nitrogen species concentrations](image)

**Figure 50:** Comparison of measured and simulated dissolved nitrogen species concentrations for the 2 March – 7 April 2010 validation period.
Simulation of Total Dissolved Nitrogen Dynamics After BAM Application

Based on the parameters determined through model calibration and validation, a time series of TDN concentration in the effluent from different layers during the post-BAM period was developed for both periods (Figure 51). Comparing among the shallower three layers, it is interesting to see that the TDN concentration in the well-drained, low VWC sand layer is more vulnerable to rainfall while the TDN concentration in the effluent of the BAM layer is more stable due to its high moisture retention capacity. The BAM layer mitigates N leaching during the storms.
Figure 51: Daily simulated and measured total dissolved nitrogen concentrations and measured rainfall at the Hunter’s Trace stormwater infiltration basin for the periods (A) 1–15 December 2009, and (B) 2 March – 7 April 2010. Results shown for each model layer (L1, L2, L3, and L4), where lines represent simulated (S) values and points represent measured (M) values.
In order to elucidate the sources and sinks of N beneath the nutrient reduction basin, simulated TDN time series and mass budgets were prepared for both the calibration and validation periods (Figure 52 and Table 9). In this simulation, the soil-water samples were assumed to be collected on the same day, which was true for all but the 1.3-m lysimeter in April 2010 and the well samples that were collected 1–2 days after collection of lysimeter samples. These factors lead to a slight misbalance in the TDN budgets (Table 9). Results indicate that leaching (advective outflow from layer 4) was the primary mechanism for TDN mass loss during both of these periods, accounting for 55 and 57%, respectively, of the total inflow (runoff, fixation, and decrease in storage). However, denitrification still represents about one-third of the total inflow of TDN, accounting for 35 and 37%, respectively. These results are consistent with the observed data that indicated elevated TDN concentrations in shallow groundwater (well M-0506, average post-BAM NO₃⁻-N of 1.05 mg L⁻¹; Figure 29e) and deep groundwater (well M-0505, average post-BAM NO₃⁻-N of 1.59 mg L⁻¹; data not shown). Additionally, the biogeochemical assessment presented in Chapter 6 indicated denitrification was intermittently occurring in the BAM layer when soil moisture conditions were conducive for producing anoxic conditions, thus independent field data confirm some degree of N removal was occurring. Simulated temporal variability in N removal by denitrification was slight, but denitrification consistently increased during the periods following large storm events (Figure 52b), which coincides with increased soil moisture. Additionally, TDN flux out of layer 1 (representing the BAM layer) consistently dropped during these same periods (Figure 51b). These simulated N dynamics also are consistent with the biogeochemical assessment of BAM and the importance of
increased soil moisture in producing conditions conducive for denitrification that were discussed in Chapter 6.
Figure 52: Simulated daily total dissolved nitrogen mass inflow (surface infiltration) and outflows (leaching and denitrification), and measured rainfall at the Hunter’s Trace stormwater infiltration basin for the periods (A) 1–15 December 2009, and (B) 2 March – 7 April 2010.
Table 9: Total dissolved nitrogen mass budgets at the Hunter’s Trace stormwater infiltration basin for each component of the nitrogen cycle simulated by the integrated infiltration basin–nitrogen reduction model for both the calibration (1–15 December 2009) and validation (2 March – 7 April 2010) periods.

<table>
<thead>
<tr>
<th>Budget Component</th>
<th>Total dissolved nitrogen, g</th>
<th>Calibration</th>
<th>Validation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage, initial</td>
<td>1,016</td>
<td>839</td>
<td></td>
</tr>
<tr>
<td>Runoff (infiltration)</td>
<td>277</td>
<td>1,696</td>
<td></td>
</tr>
<tr>
<td>Fixation</td>
<td>167</td>
<td>412</td>
<td></td>
</tr>
<tr>
<td>Uptake</td>
<td>23</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>Denitrification</td>
<td>221</td>
<td>837</td>
<td></td>
</tr>
<tr>
<td>Leaching (out layer 4)</td>
<td>346</td>
<td>1,296</td>
<td></td>
</tr>
<tr>
<td>Storage, final</td>
<td>836</td>
<td>679</td>
<td></td>
</tr>
<tr>
<td>In – Out – ΔStorage</td>
<td>34</td>
<td>78</td>
<td></td>
</tr>
</tbody>
</table>

Model Limitations and Improvements

The current version of the IBNR model is intended as an initial application of system dynamics modeling techniques simulating N fate and transport beneath an innovative stormwater infiltration basin, and further improvements likely are warranted. In this study, a first-order reaction was assumed for the primary transformation processes between different dissolved N species. The reaction constant (K parameters in Table 5) lumps the synergistic effects of microbiological activity and environmental parameters (such as temperature, pH, and dissolved oxygen) on reaction kinetics because these temporally variable factors were assumed to be constant for this first version of the IBNR model. Explicit representation of additional N cycle pathways would lead to improved model performance. For example, anammox combines NO\textsubscript{2}\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+} to yield N\textsubscript{2} gas, which was lumped into the plant uptake component of the model. In addition, in the presence of ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria
(NOB), $\text{NH}_4^+$ is converted to $\text{NO}_2^-$ and further to $\text{NO}_3^-$ while denitrification, conversely, is performed by the denitrifying microbial community. The activity rates of these microbes should be included in the next stage of study. O’Reilly et al. (2012a) have shown that biogeochemical cycling of other elements, such as C, O, Mn, Fe, and S, can control N fate, thus addition of these interacting processes into future versions of the IBNR model could be important.

Lack of VWC data in deeper soil introduced error to the model predictions. VWC measurements more finely resolved with depth or a soil moisture profile model could be derived to support a more accurate simulation of soil-water volume and flux. In our study, soil sorption might be the reason why the concentration of $\text{NH}_4^+$ is always so low in the lysimeter and well samples. To simulate this process, the soil chemistry data should be in the same time window as the soil-water data, and a solid-phase compartment of N would need to be considered along with the water-phase concentrations. Addition of a gas-phase compartment to the IBNR model would allow simulation of the generation or consumption of biogenic gases, including potentially important greenhouse gases. Along with such model modifications, synchronous sampling of gas, water, and solid phases would make it possible to add the dynamic interaction between subsurface physics and biogeochemistry.
Conclusions

Comparison of hydroclimatic, soil, water-quality, and microbiological conditions at two stormwater infiltration basins indicate soil properties control whether (1) aerobic conditions prevail and N is leached to groundwater as NO$_3^-$ and OC is oxidized (HT basin), or (2) anoxic conditions prevail leading to highly reducing conditions and preservation of OC, which serves as an electron donor for a progression of TEAPs ranging from denitrification to methanogenesis (SO basin). The presence or absence of O$_2$ in the subsurface at both sites was strongly influenced by the interaction of soil texture and hydroclimatic conditions. Fine-textured shallow soil at the SO site (median silt+clay content of 41%) impeded surface/subsurface O$_2$ diffusion, resulting in median soil water saturations exceeding 90% over the 2-year study period that were important in causing anoxic conditions conducive for denitrification. Coarse-textured shallow soil at the HT site (median silt+clay content of 2%) promoted soil aeration, resulting in median soil water saturations below 40% that inhibited TEAPs other than O$_2$ reduction and resulted in NO$_3^-$ leaching to groundwater.

A combination of hydrologic, soil chemistry, water chemistry, isotope and dissolved gas data collected at the SO site were further analyzed to assess denitrification and other biogeochemical processes occurring beneath a stormwater infiltration basin in a subtropical environment. Cyclic variations were present in many important redox sensitive constituents in the shallow groundwater system, including O$_2$, NO$_3^-$, Mn, Fe, SO$_4^{2-}$, CH$_4$, and DOC. These
cyclic variations generally coincided with wet and dry hydrologic conditions, with oxidizing conditions occurring at the beginning of wet periods followed by reducing conditions.

Sequential biogeochemical processes following a thermodynamically governed and microbially mediated succession of TEAPs effectively determine whether the N cycle is limited to aerobic processes, which would generally result in NO$_3^-$ leaching and downgradient groundwater contamination, or anoxic processes such as denitrification, which would decrease the N concentration in groundwater. Frequent and intense rainfall in humid, subtropical climates often causes prolonged flooding of stormwater infiltration basins. Under these conditions, results at the SO site indicate TEAPs can progress to methanogenesis within a seasonal timescale during prolonged basin flooding, with O$_2$ and NO$_3^-$ reduction occurring more quickly, within about one month or shorter time scale. Ammonification and nitrification probably occurred with the infiltration of oxygenated stormwater, but the subsequent progression of TEAPs inhibited these aerobic N cycle pathways. Water chemistry changes, isotopic fractionation, and excess N$_2$ generation indicate that denitrification was an important sink for N in this system. Soil chemistry results suggest that DNRA might be occurring to some degree and that anammox cannot be precluded. DOC provided by stormwater infiltration or a large solid-phase reservoir of OC probably served as the predominant electron donor for denitrification and other TEAPs beneath the SO basin. Denitrification occurs in the shallow soil zone at depths above 1.4 m as suggested by enriched $\delta^{18}$O(NO$_3^-$) and $\delta^{15}$N(NO$_3^-$) as well as $\delta^{15}$N[N$_2$] progressively enriched during prolonged basin flooding, which likely is coupled with organic matter oxidation indicated by OC and IC concentrations from soil water extracts and lysimeters. Some fraction of infiltrating stormwater probably is rapidly delivered to greater depths by macropores, largely bypassing the
0–1.4 m biogeochemically active zone, in a fashion similar to that described by Baram et al. (2012) in a clayey soil beneath a dairy waste lagoon. Excess N\textsubscript{2} produced in this zone subsequently could have been transported downward by the prevailing hydraulic gradient into the shallow groundwater where it was detected at concentrations up to 3 mg L\textsuperscript{-1}. Thus, results at the SO site indicate anoxic groundwater and highly reducing conditions can occur cyclically beneath stormwater basins in subtropical environments and result in cyclic denitrification.

Background monitoring and biogeochemical assessments indicated that the SO basin did remove nitrogen from the stormwater and the unmodified HT basin did not. Because of this success, attributable primarily to the soil conditions in the SO basin bottom, the soil conditions were replicated for a modified HT basin design. The HT basin was modified using an innovative design integrating sub-basins for nutrient reduction and flood control. In the nutrient reduction basin, the functionalized soil amendment BAM was incorporated to mitigate nutrient impacts on groundwater resources. A full-scale application of this technology for regional stormwater infiltration basins serving watersheds >20 ha, such as described in this work, has received little or no attention. The new integrated design preserves the needed flood control capacity of the basin by providing sufficient storage and infiltration of runoff to contain at least the 100-year rain event based on a runoff/water-balance model and field monitored infiltration rates. Under normal rainfall conditions, an 88% treatment volume is achieved in the nutrient reduction basin.

Biogeochemical assessment of this full-scale field application of BAM in an innovative stormwater infiltration basin demonstrated increased removal of NO\textsubscript{3}\textsuperscript{−}, TDP, and PO\textsubscript{4}\textsuperscript{3−} before infiltrating stormwater entered the groundwater. Examination of previous studies and physicochemical and biogeochemical effects observed during the present study indicate key
BAM properties are a 15% by volume component of tire crumb and a 25–50% by volume component of fine-textured (silt+clay) soil, with the balance consisting of sand. Both the high moisture retention capacity of BAM and the new integrated design incorporating a nutrient reduction basin with a greater frequency of stormwater storage contribute to conditions more favorable for formation of anoxic conditions within microsites in the BAM layer that enable the progression of biogeochemical processes toward denitrification. BAM can also be applied in an off-line retention treatment system. BAM can be easily adapted to any retention system including underground retention, exfiltration systems, or swales.

Other benefits of BAM are support of green infrastructure and economical implementation. BAM incorporates naturally occurring soils, blending them with recycled materials (tire crumb). The process is also deemed economical as the materials and labor costs (in 2009) were only about $US 65 m−2 of basin bottom to construct the new integrated design incorporating BAM in the existing stormwater infiltration basin. This cost did not include profit or permit fees. There is minimal to no additional operation and maintenance cost, and operation, maintenance, and repairs are similar to those expected with existing stormwater infiltration basins.

To sustainably manage stormwater runoff for flood control, an innovative stormwater infiltration basin is required to meet the environmental concerns regarding ecological impact and public health. The biogeochemical processes fostered by the new BMP constructed at the HT basin, which integrated flood control and nutrient reduction, were fully monitored from 2007 through 2010 and resulting data were used to determine BAM effectiveness. The fate and transport of N beneath the nutrient reduction basin was simulated by an integrated infiltration
basin–nitrogen reduction (IBNR) system dynamics model based on the field measurements. All of the proposed functions of the BAM layer—increase soil moisture retention capacity, increase microbiological activity leading to denitrification, and reduce N loading to groundwater—have been verified by the IBNR model. Based on two simulation periods, the IBNR model indicated denitrification accounted for a loss of about one-third of the TDN mass inflow and was occurring predominantly in the BAM layer. Field derived biogeochemical indicators and IBNR model results demonstrated that the new integrated design using the functionalized soil amendment BAM could be a promising passive, economical, stormwater nutrient-treatment technology in the future.

**Recommendations**

Further research is warranted on biogeochemical assessments of nutrient impacts from stormwater infiltration basins, with the goal of developing stormwater infiltration BMPs with enhanced nutrient removal ability. Results of this study indicate that NO$_3$ contamination from stormwater infiltration basins can occur cyclically depending on the hydrologic conditions, effectively switching N fate from NO$_3$ leaching to reduction in shallow groundwater. Such conditions should be considered when managing aquifer recharge from stormwater infiltration basins. Development of improved infiltration BMPs to mitigate NO$_3$ impacts from stormwater infiltration basins could benefit from (1) further research on ways to replicate the biogeochemical conditions elucidated in this study that reduce N migration to groundwater and drinking water sources; and (2) greater application of subsurface biogeochemical cycling and
redox chemistry to determine whether such N fate is controlled by conservative transport or reaction based processes.

While the preliminary biogeochemical assessment demonstrates nutrient reduction is achieved using BAM in a new BMP that integrates nutrient control and flood control for a relatively low cost, several areas exist where further research would be beneficial. Further hydrologic and water quality monitoring is needed to ascertain the long-term sustainability of the nutrient removal capabilities. Further research of BAM by both bench-scale laboratory testing and full-scale field testing—for example, application of conservative and isotopic tracers such as Br\(^-\) and \(^{15}\)N labeled NO\(_3^-\)—are needed to elucidate the individual physical, chemical, and biological processes controlling the environmental effectiveness of BAM under various moisture retention conditions. Improved technology is needed to economically increase nutrient retention time in the BAM layer, while maintaining substantial treatment volume and flood control, and mitigate potential greenhouse gas emissions. Improvements to BAM may include reducing preferential flow macropores, increasing the sorption capacity, and reducing O\(_2\) concentrations.

The IBNR system dynamics model simulates the major N cycling pathways (fixation, plant uptake, ammonification, nitrification, and denitrification) in reasonable agreement with field data, but enhancements to the model are recommended to improve its accuracy and applicability. Inclusion of improved field or model derived soil-water volume and flux estimates, gas- and solid-phase compartments of N, other N cycle pathways, and other elemental cycles should be considered. Such enhancements would yield a new all-in-one model connecting N and C cycles with other interacting elemental cycles, leading to quantitative understanding of biogeochemical cycling beneath stormwater infiltration basins. This knowledge would promote
future development and refinement of design guidelines for functionalized soil amendments such as BAM, enabling applications under a wide range of environmental conditions. Ultimately, such future research may lead to the promotion of green infrastructure for the sustainable management of stormwater resources while enhancing aquifer recharge and protecting groundwater quality.
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U.S. GEOLOGICAL SURVEY SITE IDENTIFICATION NUMBERS
Data collection sites inventoried and stored by the U.S. Geological Survey (USGS) National Water Information System (NWIS) have a unique 15-digit site identification (ID) number assigned to the site. The USGS site ID is initially assigned from the latitude and longitude, in degree-minute-second format, of a point believed to represent the location of the site, followed by a 2-digit sequence number. Once the USGS site ID is assigned, it has no locational significance beyond representing the best location available at the time the site was inventoried and entered into the NWIS database. The first six digits of the USGS site ID represent the value of latitude, the 7th through 13th digits represent the value of longitude, and the 14th and 15th digits are sequence numbers used to distinguish between sites at the same location.

The USGS site IDs for the data collection sites discussed in this work are tabulated below. Using the USGS site ID, data available at each site may be obtained at the NWIS Web Interface [http://nwis.waterdata.usgs.gov/nwis](http://nwis.waterdata.usgs.gov/nwis).

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APPENDIX C:
WATER CHEMISTRY ANALYTICAL METHODS
Analytical methods, method detection limits (MDLs), and laboratory reporting levels (LRLs) are listed for each analyte in Table C1. The MDL is the minimum concentration of a substance that can be measured and reported with a 99% confidence that the analyte concentration is greater than zero as determined from the analysis of a sample in a given matrix containing the analyte. The LRL is equal to twice the yearly-determined long-term MDL; at the LRL the probability of a false negative is < 1%. When an analyte is not detected in a sample, the concentration is reported as < LRL; when an analyte is detected between the MDL and LRL, the concentration is reported and qualified as estimated.

NO\textsubscript{3}^- -nitrogen (NO\textsubscript{3}^- -N) was computed as the difference between (NO\textsubscript{3}^- + NO\textsubscript{2}^-)-nitrogen and NO\textsubscript{2}^- -N when NO\textsubscript{2}^- -N was above the MDL. When NO\textsubscript{2}^- -N was reported as <LRL, NO\textsubscript{3}^- -N was assumed equal to (NO\textsubscript{3}^- + NO\textsubscript{2}^-)-nitrogen.

The following acronyms correspond to the analytes listed in Table C1: TN, total nitrogen; TP, total phosphorus; DOC, dissolved organic carbon; TOC, total organic carbon; TDS, total dissolved solids; TS, total solids.

The following acronyms correspond to the analytical methods listed in Table C1: APD, alkaline persulfate digestion; C-CRD, colorimetry, cadmium reduction diazotization; C-D, colorimetry, diazotization; C-P, colorimetry, phosphomolybdate; C-SH, colorimetry, salicylate-hypochlorite; IC, ion chromatography; ICP-AES, inductively coupled plasma – atomic emission spectrometry; ICP-MS, inductively coupled plasma – mass spectrometry; cICP-MS, collision/reaction cell inductively coupled plasma – mass spectrometry; ISE, ion selective electrode; PO-IS, persulfate oxidation, infrared spectrometry; ROE, residue on evaporation at noted temperature.
Table C1. Laboratory analyses performed by the USGS National Water Quality Laboratory for precipitation, stormwater, soil water, and groundwater samples collected during the study.

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<td>Fishman (1993)</td>
</tr>
<tr>
<td>Na⁺, unfiltered</td>
<td>mg/L</td>
<td>0.24</td>
<td>0.12</td>
<td>ICP-AES</td>
<td>Garbarino and Struzeski (1998)</td>
</tr>
<tr>
<td>K⁺, filtered</td>
<td>mg/L</td>
<td>0.084</td>
<td>0.032</td>
<td>SM 3120</td>
<td>Clesceri et al. (1998)</td>
</tr>
<tr>
<td>K⁺, unfiltered</td>
<td>mg/L</td>
<td>0.08</td>
<td>0.04</td>
<td>SM 2130</td>
<td>Clesceri et al. (1998)</td>
</tr>
<tr>
<td>Cl⁻, filtered</td>
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<td>0.06</td>
<td>IC</td>
<td>Fishman and Friedman (1989)</td>
</tr>
<tr>
<td>SO₄²⁻, filtered</td>
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<td>0.18</td>
<td>0.09</td>
<td>IC</td>
<td>Fishman and Friedman (1989)</td>
</tr>
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<td>mg/L</td>
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<td>0.04</td>
<td>ISE</td>
<td>Fishman and Friedman (1989)</td>
</tr>
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<td>mg/L</td>
<td>0.02</td>
<td>0.01</td>
<td>IC</td>
<td>Fishman and Friedman (1989)</td>
</tr>
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<td>0.029</td>
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<td>Fishman (1993)</td>
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<td>0.01</td>
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<td>Fishman (1993)</td>
</tr>
<tr>
<td>Al, filtered</td>
<td>μg/L</td>
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<td>1.7</td>
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<td>Garbarino et al. (2006)</td>
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<td>2.8</td>
<td>ICP-MS</td>
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<tr>
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<td>2</td>
<td>1</td>
<td>ICP-AES</td>
<td>Struzeski et al. (1996)</td>
</tr>
<tr>
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<td>0.01</td>
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<td>Garbarino et al. (2006)</td>
</tr>
<tr>
<td>Cd, unfiltered</td>
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<td>0.02</td>
<td>ICP-MS</td>
<td>Garbarino and Struzeski (1998)</td>
</tr>
<tr>
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<td>0.01</td>
<td>0.005</td>
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<td>Garbarino et al. (2006)</td>
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<tr>
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<td>0.02</td>
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<td>0.06</td>
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</tr>
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<td>Garbarino et al. (2006)</td>
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<td>3</td>
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<td>4.6</td>
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<td>0.4</td>
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<tr>
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<td>Garbarino and Struzeski (1998)</td>
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<tr>
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<td>μg/L</td>
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<td>0.06</td>
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<td>0.015</td>
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<td>Garbarino et al. (2006)</td>
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<tr>
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<td>0.03</td>
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<td>Garbarino and Struzeski (1998)</td>
</tr>
<tr>
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<td>μg/L</td>
<td>0.04</td>
<td>0.02</td>
<td>cICP-MS</td>
<td>Garbarino et al. (2006)</td>
</tr>
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<td>0.05</td>
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</tr>
<tr>
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<td>0.8</td>
<td>cICP-MS</td>
<td>Garbarino et al. (2006)</td>
</tr>
<tr>
<td>W, filtered</td>
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<td>0.01</td>
<td>cICP-MS</td>
<td>Garbarino et al. (2006)</td>
</tr>
<tr>
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<td>0.012</td>
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<td>1.4</td>
<td>cICP-MS</td>
<td>Garbarino et al. (2006)</td>
</tr>
<tr>
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<td>1</td>
<td>cICP-MS</td>
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</tr>
<tr>
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<td>10</td>
<td>ROE, 180°C</td>
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</tr>
<tr>
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<td>mg/L</td>
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<td>13</td>
<td>ROE, 105°C</td>
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APPENDIX D:
SOIL MINERALOGICAL DATA
Table D1. Mineralogical composition of the silt and clay fractions. HIV is hydroxyinterlayered vermiculite. Relative quantities indicated by ‘x’ (low mass fraction) to ‘xxxxx’ (mass fraction of crystalline component approaching 1); tr, trace amount; ?, some uncertainty about identification. Numerical entries for kaolinite and gibbsite are percentages calculated from thermogravimetry (TG). Samples high in smectite confound kaolinite quantification by TG, thus kaolinite was not quantified for these samples. Smectite identified in silt fractions likely are clay-size particles in silt-size aggregates. HT, Hunter’s Trace stormwater infiltration basin; SO, South Oak stormwater infiltration basin.

<table>
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<th>Site</th>
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<th>Silt/Clay (%)</th>
<th>Smectite</th>
<th>HIV</th>
<th>Mica</th>
<th>Kaolinite</th>
<th>Gibbsite</th>
<th>Wavelite</th>
<th>Quartz</th>
<th>Calcite</th>
<th>Apatite</th>
<th>Clay</th>
<th>Crandallite</th>
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<td>11.5%</td>
<td>xxx</td>
<td>xxx</td>
<td>xx</td>
<td>tr</td>
<td>xx</td>
<td>tr</td>
<td>xx</td>
<td>29.8%</td>
<td>tr</td>
<td>xx</td>
<td>x</td>
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<td></td>
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<td>xxx</td>
<td>xx</td>
<td>xxxx</td>
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<td></td>
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APPENDIX E:
SOIL TEXTURAL AND CHEMICAL DATA
Table E1. Soil textural and chemical characteristics. %, percentage by weight; dS/m, decisiemens per meter; cmol/kg, centimoles of charge per kilogram dry soil; mg/kg, milligrams of analyte per kilogram of dry soil; EC, electrical conductivity; CEC, cation exchange capacity; AEC, anion exchange capacity; AAO, acid-ammonium-oxalate extraction; CDB, citrate-dithionite-bicarbonate extraction; --, data not available; HT, Hunter’s Trace stormwater infiltration basin; SO, South Oak stormwater infiltration basin.

<table>
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<th>Basin Site</th>
<th>Well</th>
<th>Depth (m)</th>
<th>Sand (%)</th>
<th>Silt (%)</th>
<th>Clay (%)</th>
<th>pH</th>
<th>EC (dS/m)</th>
<th>CEC (cmol/kg)</th>
<th>AEC (cmol/kg)</th>
<th>Al (mg/kg)</th>
<th>Fe (mg/kg)</th>
<th>P (mg/kg)</th>
<th>Al (mg/kg)</th>
<th>Fe (mg/kg)</th>
<th>P (mg/kg)</th>
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APPENDIX F:
SOIL SOLIDS NITROGEN AND CARBON DATA
Table F1. Soil solids nitrogen and carbon contents at the South Oak (SO) stormwater infiltration basin site. mg/kg, milligrams of analyte per kilogram of dry soil; TN, total nitrogen; TC, total carbon, OC, organic carbon; IC, inorganic carbon; --, computed value was negative.

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<th>TC (mg/kg)</th>
<th>OC (mg/kg)</th>
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<th>TC:TN ratio</th>
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Table F2. Soil solids nitrogen and carbon contents at the Hunter’s Trace (HT) stormwater infiltration basin site. mg/kg, milligrams of analyte per kilogram of dry soil; TN, total nitrogen; TC, total carbon, OC, organic carbon; IC, inorganic carbon; --, computed value was negative; *, from stockpile of biosorption activated media mixed onsite before placement in the ground.

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APPENDIX G:
SOIL EXTRACTABLE NITROGEN AND CARBON DATA
Table G1. Extractable soil nitrogen and carbon contents at the South Oak (SO) stormwater infiltration basin site. TN, total nitrogen; NH4, ammonium; NO3, nitrate; NO2, nitrite; NOx, NO3 + NO2; IN, inorganic nitrogen, NH4 + NOx; ON, organic nitrogen, TN – IN; TC, total carbon, OC, organic carbon; IC, inorganic carbon; KCl, potassium chloride extraction; H2O, water extraction; BDL, below detection limit based on extracting solution method detection limits of 0.01 mg/L for NOx and 0.16 mg/L for NH4); --, data not available or for ON and IC computed value was negative.

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<th>Depth (m)</th>
<th>NH4-N (mg/kg)</th>
<th>NOx-N (mg/kg)</th>
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<th>NO2-N (mg/kg)</th>
<th>TN (mg/kg)</th>
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<th>NOx-N (mg/L)</th>
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Table G2. Extractable soil nitrogen and carbon contents at the Hunter’s Trace (HT) stormwater infiltration basin site. TN, total
nitrogen; NH4, ammonium; NO3, nitrate; NO2, nitrite; NOx, NO3 + NO2; IN, inorganic nitrogen, NH4 + NOx; ON, organic nitrogen,
TN – IN; TC, total carbon, OC, organic carbon; IC, inorganic carbon; KCl, potassium chloride extraction; H2O, water extraction;
BDL, below detection limit based on extracting solution method detection limits of 0.01 mg/L for NOx and 0.16 mg/L for NH4; --,
data not available or for ON and IC computed value was negative; *, from stockpile of biosorption activated media mixed onsite
before placement in the ground.

Sample
ID
HT-A-1
HT-A-2
HT-A-3
HT-D-1
HT-D-2
HT-B-1
HT-C-1
HT-D-3
HT-E-1
HT-E-2
HT-E-3
HT-E-4
HT-E-5
HT-E-6
HT-F-1
HT-F-2
HT-F-3
HT-F-4
HT-F-5
HT-F-0
HT-G-1
HT-G-2
HT-G-3
HT-G-4
HT-G-5
HT-G-6
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HT-H-2
HT-H-3
HT-H-4
HT-H-5
HT-H-6
HT-I-1
HT-I-2
HT-I-3

Date
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12-Mar-08
12-Mar-08
12-Jun-08
12-Jun-08
12-Jun-08
12-Jun-08
12-Jun-08
23-Jun-09
23-Jun-09
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4-Nov-09
5-Nov-09
20-Jan-10
20-Jan-10
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6-Apr-10
6-Apr-10
6-Apr-10
6-Apr-10
3-Aug-10
3-Aug-10
3-Aug-10

Depth
(m)
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1.7
0.1
0.3
0.5
0.6
1.0
0.2
0.4
0.7
0.9
1.3
1.5
0.8
1.1
1.4
1.7
1.9
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0.9
1.3
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0.3
0.5
0.8
0.9
1.3
0.1
0.3
0.5

NH4N
(mg/
kg)
KCl
2.37
1.70
5.46
14.20
1.74
2.16
1.54
1.15
2.87
2.81
2.70
3.22
2.27
2.38
1.28
1.29
1.46
2.55
2.09
3.84
7.18
1.48
1.36
0.83
0.80
0.98
11.34
1.42
1.09
2.04
2.50
2.49
10.41
5.90
0.90

NOxN
(mg/
kg)
KCl
0.24
BDL
BDL
18.20
0.08
0.39
1.21
1.87
BDL
1.56
1.63
1.78
3.03
3.11
BDL
BDL
BDL
BDL
BDL
1.63
2.84
BDL
BDL
BDL
BDL
BDL
3.49
BDL
BDL
BDL
BDL
BDL
2.53
BDL
BDL

NO3N
(mg/
kg)
KCl
0.21
BDL
BDL
18.60
0.11
0.34
1.02
1.71
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NO2N
(mg/
kg)
KCl
BDL
BDL
BDL
BDL
BDL
0.05
0.19
0.16
----------------------------

TN
(mg/
kg)
H2O
1.9
2.0
1.9
20.8
2.1
2.3
2.7
3.0
3.6
2.3
2.9
1.7
2.6
2.5
1.8
1.3
1.1
1.4
1.2
1.4
15.6
2.2
0.7
1.3
1.1
1.3
18.0
1.4
0.7
1.2
1.7
1.7
20.0
3.1
--

NH4N
(mg/
kg)
H2O
0.61
0.62
0.94
6.63
0.68
0.75
0.63
0.65
1.66
2.43
3.07
1.74
1.25
0.43
1.41
0.84
0.49
0.35
0.70
0.41
6.94
0.28
0.31
0.63
0.30
0.34
8.54
0.21
0.19
1.36
0.75
0.31
----

NOxN
(mg/
kg)
H2O
0.15
0.33
0.08
24.20
0.44
0.67
1.79
2.25
0.50
0.41
0.49
0.60
2.27
1.94
BDL
BDL
0.41
0.40
BDL
0.74
3.60
BDL
BDL
BDL
BDL
BDL
2.90
BDL
BDL
BDL
BDL
BDL
----

NO3N
(mg/
kg)
H2O
0.13
0.10
0.07
21.60
1.21
0.64
1.63
1.95
----------------------------

232

NO2N
(mg/
kg)
H2O
0.01
0.23
0.00
2.65
BDL
0.03
0.16
0.29
----------------------------

ON
(TN-IN)
(mg/
kg)
H2O
1.1
1.1
0.9
-1.0
0.9
0.3
0.1
1.4
----0.1
0.4
0.4
0.2
0.7
0.5
0.3
5.1
1.9
0.4
0.7
0.8
1.0
6.6
1.2
0.6
-0.9
1.4
----

NH4N
(mg/L)
H2O
6.80
3.44
5.14
30.89
10.01
13.16
5.36
3.77
37.73
50.91
32.53
14.03
7.68
2.66
25.95
14.55
2.85
1.97
3.85
2.90
37.24
1.56
11.33
5.79
2.04
2.01
43.33
1.40
8.65
24.33
12.19
1.76
----

NOxN
(mg/L)
H2O
1.62
1.82
0.43
112.81
6.47
11.78
15.12
13.09
11.43
8.48
5.18
4.84
13.94
11.97
BDL
BDL
2.41
2.28
BDL
5.26
19.36
BDL
BDL
BDL
BDL
BDL
14.71
BDL
BDL
BDL
BDL
BDL
----

NO3N
(mg/L)
H2O
1.47
0.56
0.41
100.46
17.82
11.22
13.79
11.37
----------------------------

TC
(mg/
kg)
H2O
21.9
16.6
23.7
28.4
22.3
22.8
25.4
20.3
20.5
24.2
34.9
27.0
20.3
15.7
27.7
20.3
16.9
15.8
16.0
16.6
48.3
15.9
9.4
14.5
16.7
25.9
66.2
23.7
11.2
17.5
23.7
21.4
55.7
40.1
--

OC
(mg/
kg)
H2O
9.3
8.3
9.7
20.5
9.8
9.6
11.3
9.7
----------------------------

IC
(TC-OC)
(mg/kg)
H2O
12.6
8.3
14.0
7.9
12.5
13.2
14.1
10.7
----------------------------

TC:TN
ratio
11.5
8.3
12.5
1.4
10.6
9.9
9.4
6.8
5.7
10.4
12.0
16.3
7.9
6.3
15.3
16.0
14.8
11.2
13.8
11.8
3.1
7.1
12.7
10.8
15.3
19.2
3.7
16.6
15.0
14.0
14.0
12.7
2.8
12.8
--


APPENDIX H:
SOIL COPPER-CONTAINING NITRITE REDUCTASE
GENE DENSITY DATA
**Table H1.** Copper-containing nitrite reductase (*nirK*) gene density by real-time polymerase chain reaction analysis of soil at the South Oak (SO) stormwater infiltration basin site; \( \mu \), mean of three replicates; \( \sigma \), standard deviation of three replicates; g.c./g, gene copies per gram of dry soil; BDL, below detection limit of 6,000 g.c./g.

<table>
<thead>
<tr>
<th>Basin Site</th>
<th>Date</th>
<th>Depth (m)</th>
<th>( \mu ) (g.c./g)</th>
<th>( \sigma ) (g.c./g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO</td>
<td>12-Mar-08</td>
<td>0.1</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>SO</td>
<td>12-Mar-08</td>
<td>0.3</td>
<td>6.5E+04</td>
<td>3.0E+04</td>
</tr>
<tr>
<td>SO</td>
<td>12-Mar-08</td>
<td>0.7</td>
<td>1.5E+06</td>
<td>5.2E+05</td>
</tr>
<tr>
<td>SO</td>
<td>12-Mar-08</td>
<td>1.2</td>
<td>1.7E+06</td>
<td>1.5E+06</td>
</tr>
<tr>
<td>SO</td>
<td>12-Mar-08</td>
<td>1.5</td>
<td>5.1E+04</td>
<td>2.5E+04</td>
</tr>
<tr>
<td>SO</td>
<td>22-May-08</td>
<td>0.5</td>
<td>9.6E+05</td>
<td>3.6E+05</td>
</tr>
<tr>
<td>SO</td>
<td>22-May-08</td>
<td>0.9</td>
<td>1.8E+06</td>
<td>3.3E+05</td>
</tr>
<tr>
<td>SO</td>
<td>22-May-08</td>
<td>1.4</td>
<td>2.2E+06</td>
<td>3.5E+05</td>
</tr>
<tr>
<td>SO</td>
<td>22-May-08</td>
<td>2.0</td>
<td>1.8E+05</td>
<td>3.0E+04</td>
</tr>
<tr>
<td>SO</td>
<td>12-Jun-08</td>
<td>0.5</td>
<td>1.4E+06</td>
<td>2.0E+05</td>
</tr>
<tr>
<td>SO</td>
<td>12-Jun-08</td>
<td>0.9</td>
<td>2.1E+06</td>
<td>2.8E+05</td>
</tr>
<tr>
<td>SO</td>
<td>12-Jun-08</td>
<td>1.2</td>
<td>2.6E+05</td>
<td>1.5E+05</td>
</tr>
<tr>
<td>SO</td>
<td>21-Nov-08</td>
<td>0.2</td>
<td>8.2E+04</td>
<td>5.5E+04</td>
</tr>
<tr>
<td>SO</td>
<td>21-Nov-08</td>
<td>0.6</td>
<td>4.4E+05</td>
<td>1.5E+05</td>
</tr>
<tr>
<td>SO</td>
<td>21-Nov-08</td>
<td>0.9</td>
<td>9.2E+05</td>
<td>2.9E+05</td>
</tr>
<tr>
<td>SO</td>
<td>21-Nov-08</td>
<td>1.2</td>
<td>1.6E+06</td>
<td>4.7E+05</td>
</tr>
<tr>
<td>SO</td>
<td>19-Dec-08</td>
<td>0.1</td>
<td>4.6E+05</td>
<td>4.8E+04</td>
</tr>
<tr>
<td>SO</td>
<td>19-Dec-08</td>
<td>0.4</td>
<td>7.7E+05</td>
<td>3.3E+05</td>
</tr>
<tr>
<td>SO</td>
<td>19-Dec-08</td>
<td>0.8</td>
<td>4.2E+05</td>
<td>7.6E+04</td>
</tr>
<tr>
<td>SO</td>
<td>19-Dec-08</td>
<td>1.3</td>
<td>5.6E+05</td>
<td>3.6E+04</td>
</tr>
<tr>
<td>SO</td>
<td>19-Dec-08</td>
<td>1.6</td>
<td>6.5E+04</td>
<td>2.5E+04</td>
</tr>
<tr>
<td>SO</td>
<td>19-Dec-08</td>
<td>2.3</td>
<td>1.5E+04</td>
<td>9.9E+03</td>
</tr>
</tbody>
</table>
Table H2. Copper-containing nitrite reductase (nirK) gene density by real-time polymerase chain reaction analysis of soil at the Hunter’s Trace (HT) stormwater infiltration basin site; µ, mean of three replicates; σ, standard deviation of three replicates; g.c./g, gene copies per gram of dry soil; BDL, below detection limit of 6,000 g.c./g; *, from stockpile of biosorption activated media mixed onsite before placement in the ground; † represents replicate analysis of subsample.

<table>
<thead>
<tr>
<th>Basin Site</th>
<th>Date</th>
<th>Depth (m)</th>
<th>μ (g.c./g)</th>
<th>σ (g.c./g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT</td>
<td>23-Jun-09</td>
<td>0.20</td>
<td>5.1E+05</td>
<td>2.0E+05</td>
</tr>
<tr>
<td>HT</td>
<td>23-Jun-09</td>
<td>0.38</td>
<td>1.4E+05</td>
<td>7.6E+04</td>
</tr>
<tr>
<td>HT</td>
<td>23-Jun-09</td>
<td>0.74</td>
<td>8.7E+03</td>
<td>4.7E+03</td>
</tr>
<tr>
<td>HT</td>
<td>23-Jun-09</td>
<td>0.91</td>
<td>6.6E+03</td>
<td>2.7E+03</td>
</tr>
<tr>
<td>HT</td>
<td>23-Jun-09</td>
<td>1.30</td>
<td>1.9E+04</td>
<td>7.7E+03</td>
</tr>
<tr>
<td>HT</td>
<td>23-Jun-09</td>
<td>1.52</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>HT</td>
<td>4-Nov-09</td>
<td>0.76</td>
<td>9.0E+04</td>
<td>1.7E+04</td>
</tr>
<tr>
<td>HT</td>
<td>4-Nov-09</td>
<td>1.07</td>
<td>4.1E+04</td>
<td>9.8E+03</td>
</tr>
<tr>
<td>HT</td>
<td>4-Nov-09</td>
<td>1.37</td>
<td>1.0E+04</td>
<td>1.3E+03</td>
</tr>
<tr>
<td>HT</td>
<td>4-Nov-09</td>
<td>1.68</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>HT</td>
<td>4-Nov-09</td>
<td>1.85</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>HT</td>
<td>5-Nov-09</td>
<td>*</td>
<td>3.6E+04</td>
<td>1.7E+04</td>
</tr>
<tr>
<td>HT</td>
<td>20-Jan-10</td>
<td>0.08</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>HT</td>
<td>20-Jan-10</td>
<td>0.33</td>
<td>9.4E+04</td>
<td>7.8E+03</td>
</tr>
<tr>
<td>HT</td>
<td>20-Jan-10</td>
<td>0.51</td>
<td>2.8E+04</td>
<td>8.4E+03</td>
</tr>
<tr>
<td>HT</td>
<td>20-Jan-10</td>
<td>0.76</td>
<td>1.1E+04</td>
<td>3.4E+03</td>
</tr>
<tr>
<td>HT</td>
<td>20-Jan-10</td>
<td>0.91</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>HT</td>
<td>20-Jan-10</td>
<td>1.30</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>HT</td>
<td>6-Apr-10</td>
<td>0.08</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>HT</td>
<td>6-Apr-10</td>
<td>0.30</td>
<td>8.5E+04</td>
<td>8.0E+03</td>
</tr>
<tr>
<td>HT</td>
<td>6-Apr-10</td>
<td>0.48</td>
<td>2.3E+04</td>
<td>1.0E+04</td>
</tr>
<tr>
<td>HT</td>
<td>6-Apr-10</td>
<td>0.76</td>
<td>2.6E+04</td>
<td>1.7E+04</td>
</tr>
<tr>
<td>HT</td>
<td>6-Apr-10</td>
<td>0.91</td>
<td>8.6E+03</td>
<td>1.4E+03</td>
</tr>
<tr>
<td>HT</td>
<td>6-Apr-10</td>
<td>1.30</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>HT</td>
<td>3-Aug-10</td>
<td>0.08</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>HT</td>
<td>3-Aug-10</td>
<td>0.33</td>
<td>1.3E+05</td>
<td>2.9E+04</td>
</tr>
<tr>
<td>HT</td>
<td>3-Aug-10</td>
<td>0.53</td>
<td>1.7E+04</td>
<td>9.7E+03</td>
</tr>
<tr>
<td>HT</td>
<td>3-Aug-10†</td>
<td>0.08</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>HT</td>
<td>3-Aug-10†</td>
<td>0.33</td>
<td>1.8E+05</td>
<td>2.8E+04</td>
</tr>
<tr>
<td>HT</td>
<td>3-Aug-10†</td>
<td>0.53</td>
<td>1.7E+04</td>
<td>1.2E+04</td>
</tr>
<tr>
<td>HT</td>
<td>21-Jul-11</td>
<td>0.10</td>
<td>1.1E+05</td>
<td>1.9E+04</td>
</tr>
<tr>
<td>HT</td>
<td>21-Jul-11</td>
<td>0.33</td>
<td>2.9E+05</td>
<td>6.7E+04</td>
</tr>
<tr>
<td>HT</td>
<td>21-Jul-11</td>
<td>0.53</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>HT</td>
<td>21-Jul-11</td>
<td>0.76</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>HT</td>
<td>21-Jul-11</td>
<td>0.91</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>HT</td>
<td>21-Jul-11</td>
<td>1.30</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>HT</td>
<td>12-Aug-11</td>
<td>0.08</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>HT</td>
<td>12-Aug-11</td>
<td>0.33</td>
<td>2.8E+05</td>
<td>4.6E+04</td>
</tr>
<tr>
<td>HT</td>
<td>12-Aug-11</td>
<td>0.51</td>
<td>8.3E+04</td>
<td>2.6E+04</td>
</tr>
<tr>
<td>HT</td>
<td>12-Aug-11</td>
<td>0.76</td>
<td>1.4E+05</td>
<td>8.5E+04</td>
</tr>
<tr>
<td>HT</td>
<td>12-Aug-11</td>
<td>0.97</td>
<td>7.2E+04</td>
<td>2.5E+04</td>
</tr>
</tbody>
</table>
APPENDIX I:
ADDITIONAL WATER CHEMISTRY DATA FOR REDOX-SENSITIVE CONSTITUENTS AT THE SOUTH OAK SITE
Figure II. Ratios of groundwater (well PW) to stormwater concentrations (mg/L) for concurrent samples. Cl, chloride; DOC, dissolved organic carbon; Fe, iron; Mn, manganese; SO4, sulfate; and TDN, total dissolved nitrogen.
Figure I2. Soil-water and groundwater chemistry profiles beneath the stormwater infiltration basin for (A) $\text{SO}_4^{2-}/\text{Cl}^-$ mass ratios; and (B) $\text{SO}_4^{2-}$ concentration adjusted based on $\text{Cl}^-$. Data at 0-m depth represent stormwater samples; data at 0.5, 0.9, and 1.4-m depths represent lysimeter samples; data at 1.9-m depth represent well PW.
Figure I3. Temporal variations in groundwater $\text{SO}_4^{2-}/\text{Cl}^-$ mass ratios, $\text{SO}_4^{2-}$ concentrations, and $\text{SO}_4^{2-}$ concentration adjusted based on $\text{Cl}^-$. 

Figure I4. Redox potential (Eh), pH, and dissolved oxygen (DO) of groundwater from well PW.
APPENDIX J:
BIOSORPTION ACTIVATED MEDIA CHEMICAL ANALYSIS DATA
**Table J1.** Chemical analysis of a sample of biosorption activated media used at the Hunter’s Trace stormwater infiltration basin. Analysis performed by the U.S. Geological Survey, Branch of Geochemistry, Arvada, CO.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Concentration</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>aluminum, icp-ms</td>
<td>29200</td>
<td>µg/g</td>
</tr>
<tr>
<td>antimony, icp-ms</td>
<td>0.36</td>
<td>µg/g</td>
</tr>
<tr>
<td>arsenic, icp-ms</td>
<td>1.3</td>
<td>µg/g</td>
</tr>
<tr>
<td>barium, icp-ms</td>
<td>170</td>
<td>µg/g</td>
</tr>
<tr>
<td>beryllium, icp-ms</td>
<td>1.2</td>
<td>µg/g</td>
</tr>
<tr>
<td>cadmium, icp-ms</td>
<td>0.51</td>
<td>µg/g</td>
</tr>
<tr>
<td>calcium, icp-ms</td>
<td>2090</td>
<td>µg/g</td>
</tr>
<tr>
<td>carbon, inorganic</td>
<td>&lt;0.01</td>
<td>% g/g</td>
</tr>
<tr>
<td>carbon, organic</td>
<td>1.8</td>
<td>% g/g</td>
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<tr>
<td>carbon, total</td>
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<td>% g/g</td>
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<tr>
<td>cerium, icp-ms</td>
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<td>µg/g</td>
</tr>
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<td>chromium, icp-ms</td>
<td>62.3</td>
<td>µg/g</td>
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<td>4.1</td>
<td>µg/g</td>
</tr>
<tr>
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<td>µg/g</td>
</tr>
<tr>
<td>gallium, icp-ms</td>
<td>7.4</td>
<td>µg/g</td>
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<td>iron, icp-ms</td>
<td>10000</td>
<td>µg/g</td>
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<tr>
<td>lanthanum, icp-ms</td>
<td>23.1</td>
<td>µg/g</td>
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<td>lead, icp-ms</td>
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<td>µg/g</td>
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<td>µg/g</td>
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<td>magnesium, icp-ms</td>
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<td>µg/g</td>
</tr>
<tr>
<td>manganese, icp-ms</td>
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<td>µg/g</td>
</tr>
<tr>
<td>mercury, bed sed, cvafs</td>
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<td>µg/g</td>
</tr>
<tr>
<td>molybdenum, icp-ms</td>
<td>0.57</td>
<td>µg/g</td>
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<tr>
<td>nickel, icp-ms</td>
<td>10.2</td>
<td>µg/g</td>
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<tr>
<td>niobium, icp-ms</td>
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<td>µg/g</td>
</tr>
<tr>
<td>phosphorus, icp-ms</td>
<td>4240</td>
<td>µg/g</td>
</tr>
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<td>1480</td>
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<td>rubidium, icp-ms</td>
<td>15.7</td>
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<td>scandium, icp-ms</td>
<td>5</td>
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<td>selenium</td>
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<td>silver, icp-ms</td>
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<td>strontium, icp-ms</td>
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<td>sulfur</td>
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<td>yttrium, icp-ms</td>
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<tr>
<td>zinc, icp-ms</td>
<td>146</td>
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APPENDIX K:
SOIL PHASE DIAGRAMS
Diagrams showing soil phase (solid, water, gas) distributions based on measured porosity and volumetric soil moisture content. Porosity was measured by water saturation and drying at 105°C of undisturbed soil cores. Volumetric moisture content was measured in the field using time domain reflectometry (TDR) probes. Cumulative frequency distributions were computed from daily average TDR data for June 2008 – Dec. 2009 (South Oak basin), June 2008 – Oct. 2009 (Hunter’s Trace existing BMP), and Nov. 2009 – Oct. 2010 (Hunter’s Trace new BMP).
APPENDIX L:
INTEGRATED INFILTRATION BASIN–NITROGEN REDUCTION
SYSTEM DYNAMICS MODEL
Schematic diagram of integrated infiltration basin–nitrogen reduction (IBNR) system dynamics model developed in STELLA® for the simulation of nitrogen cycling beneath the nutrient reduction basin at the Hunter’s Trace stormwater infiltration basin.
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