

THE EFFECT OF ONSITE WASTEWATER TREATMENT SYSTEMS ON
NITROGEN IN URBAN WATERSHEDS OF METROPOLITAN ATLANTA,
GEORGIA

by

NAHAL HOGHOOGHI

(Under the Direction of David E. Radcliffe)

ABSTRACT

High density onsite wastewater treatment systems (OWTSs) can cause contamination of both surface water and groundwater. However, the effect of OWTS on water quality at the watershed-scale is not well understood. We investigated the effect of OWTS on stream N concentrations during base flow in 24 watersheds in Metropolitan Atlanta, ranging in area from 0.18 to 8.8 km². We found that total nitrogen (TN) and nitrate (NO₃⁻) concentrations increased linearly with increasing OWTS density above a threshold of about 75 OWTS km⁻². Dual-isotope analysis of NO₃⁻ revealed that stream NO₃⁻-N originated predominately from OWTS in high density (HD) watersheds and from a combination of animal waste and perhaps organic N in low density (LD) watersheds. The effect of OWTS on NO₃⁻ load in an urban watershed where most of the homes use OWTS was simulated using the Soil Water Assessment Tool (SWAT). The model showed satisfactory daily stream flow and NO₃⁻ loads with Nash-Sutcliffe coefficients of 0.62 and 0.58 for the calibration period, and 0.67 and 0.33 for the validation period. OWTS caused an average increase in NO₃⁻ load of about 23% at the watershed scale and 29% at the sub-

basin outlet with the highest density of OWTS. Failing OWTS were estimated to be 1% of the total systems and did not have a large impact on NO_3^- load. The NO_3^- load was 74% of the total N load in the watershed. Results from detailed monitoring using automated samplers in four headwater streams with a gradient in OWTS density demonstrated that the highest base-flow and storm-flow TN concentrations occurred in watersheds with the lowest density of OWTS and the highest density of OWTS, respectively. There were significant positive correlations between base flow NO_3^- concentrations and OWTS density. TN loads were also the highest at extremes of OWTS densities. This was due to the pattern in N concentrations and higher water yields at low and high OWTS density. These findings confirm the importance of OWTS on water quality in urban watersheds and can be used in other Piedmont regions where nitrogen Total Maximum Daily Loads (TMDL) are being developed.

INDEX WORDS: Onsite wastewater treatment system, urban watershed, total nitrogen, nitrate, organic nitrogen, SWAT, SWAT-CUP, calibration, validation, Nash-Sutcliffe, nitrogen load, base flow, storm flow.

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DEDICATION

I would like to dedicate this dissertation to my family. Especially to my loving parents, Jamshid and Doolat whose encouragement, endless love, and supports give me the power to reach my dreams. To my lovely sisters, Negin and Nazanin whose support and love always have been with me. I dedicate my dissertation to my brother-in-laws, Khashayar and Josue for their encouragements. To my little nephews, Kasra and sadra for their enthusiasm of learning.

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1. INTRODUCTION

During the urbanization of a formerly natural area, a major pollution issue arises in the form of human waste disposal (Mallin, 2009). An onsite wastewater treatment system (OWTS), also known as a septic system, consists of a septic tank and a drain field that allows treated effluent to infiltrate into the soil. In 2007, approximately 26 million housing units (20% of the total) in the United State used OWTS which released about 15 billion liters of effluent per day (Oakley et al., 2010). Of the total number of OWTS, 50% were in rural areas, 47% were in suburbs, and 3% were located in cities. Approximately 10 million housing units (46%) with OWTS were located in the Southeast region of the United States, 4.8 million (22%) were in the Midwest, followed by 4.2 million (19%) in the Northeast, and the West with 2.9 million (13%) (USEPA, 2007).

From 2000 to 2010, the populations of Alabama, Georgia, South Carolina and North Carolina increased 7.5 to 18.5% with an 18.3% increase in Georgia. It is expected that growth will continue in the future. More than 65% of public water supply in these four states is provided by surface water with the remaining withdrawals from groundwater. The limited use of groundwater is due to low yielding wells caused by fractured bedrock in the Piedmont region where most growth is occurring (Clarke & Peck, 1991; Fanning, 2001).

It is estimated that more than 30% of the homes in Georgia are on OWTS, which is higher than the national average of 25% (USEPA, 2002). In 2005, the number of OWTS in Metropolitan Atlanta was estimated to be approximately 526,000 (MNGWPD, 2006) and the number is expected to increase with population growth in this region. Due to the

high costs of centralized systems, OWTs are no longer considered a temporary solution to be replaced eventually by centralized collection and treatment (USEPA, 2002). However, the design of conventional OWTs is not particularly effective for nitrogen (N) removal (Oakley et al., 2010; USEPA, 2002).

High density OWTs may contaminate both surface water and groundwater (Conn et al., 2012) with pathogens, organic pollutants, hormones and nutrients. In a national summary by Environmental Protection Agency (EPA) in 2012, nutrients are the third most common cause of river and stream impairment, and the second most common reason of impairment in lakes, reservoirs, and ponds on the EPA 303(d) list (USEPA, 2012). Some studies have shown that OWTs are the main source of nitrate (NO_3^-) groundwater contamination and drinking water contaminant (Gold et al., 1990; Rich, 2005), and is listed as a potential source of N in Total Maximum Daily Load (TMDL) reports of nutrient impairments by EPA (USEPA, 2012). NO_3^- is a concern in surface and ground waters that serve as drinking water sources because it can cause methemoglobinemia (blue-baby syndrome) (Beal et al., 2005). The maximum NO_3^- -N contaminant level for drinking water to protect against methemoglobinemia is 10 mg L^{-1} by US.EPA (Kaushal et al., 2006). Although N is critical to ecological health, excessive loading of this element causes eutrophication and hypoxia (Conley et al., 2009; Pinckney et al., 2001). Eutrophication of fresh waters is triggered by phosphorus (P) primarily, but N is also important (Moffat, 1998). Threshold concentrations for N are quite low. For example, in the draft EPA standards for total N in Florida waters, the critical concentrations range from 0.67 to 1.87 mg L^{-1} , depending on the type of the water resource (USEPA, 2015).

Humans produce approximately 13.3 g N per capita per day (Crites and Technobanoglous, 1998). Assuming average densities of 2.4 people per household and 1 house per 0.405 ha, the annual N loading rate is 2880 kg km⁻² yr⁻¹ from a subdivision. Therefore in urban areas OWTS can have a significant effect on groundwater and surface water N loadings (McCray et al., 2005). It was shown that N losses from OWTS can result in elevated NO₃⁻ concentrations in groundwater below or down gradient of these systems (Bernhardt et al., 2008; Kaushal et al., 2006). Many studies have attributed N pollution to OWTS at the watershed scale (Burns et al., 2005; Hatt et al., 2004), although it is difficult to estimate the OWTS contribution in N losses due to uncertainty about how much of it is lost because of denitrification. Usually it is assumed 0 to 50% of N losses are due to denitrification (McCray et al., 2008). A recent study showed that N losses through denitrification for a clay textured soil in the Southern Piedmont region of the United State was 52% (Bradshaw et al., 2013). Only a couple of studies have confirmed the source of NO₃⁻ to be from OWTS by using source tracking techniques in groundwater system (Aravena et al., 1993; Aravena and Robertson, 1998).

In soil, P mobility is decreased by its adsorption to soil particles. In contrast, NO₃⁻ is relatively mobile. Therefore groundwater discharge is a major factor in NO₃⁻ loading to surface water (Hayashi and Rosenberry, 2002). A TMDL developed for Lake Allatoona, a large reservoir just north of Atlanta, includes N limits and attributes part of the nutrient load to OWTS in the watersheds (GDNR, 2013). However, there is a need for a more accurate evaluation of the N load to streams attributed to OWTS.

Recently, computer models have been used for predicting the impact of OWTS on water quantity and quality at the drain field scale (Beggs et al., 2004; Bradshaw et al., 2013;

Hassan et al., 2008). Due to uncertainties in the fate and transport of N within and beyond OWTS drain fields, modeling of N associated with OWTS at the watershed scale has not been investigated extensively (Jeong et al., 2011). However, several studies have used the Soil and Water Assessment Tool (SWAT) to predict the effect of OWTS at the watershed scale (Jeong et al., 2011; Oliver et al., 2014; Pradhan et al., 2005). SWAT is a physically based watershed scale model developed by the US Department of Agriculture Research Service (USDA-ARS) to predict the impact of land management practices on water, sediment, and agricultural chemical yields in watersheds with different soils, land uses, and management over long periods of time (Neitsch, 2011). It is suited for simulating the fate and transport of N from point and non-point sources due to the ability to model the N cycle. A biozone algorithm was recently incorporated in SWAT to evaluate the effect of OWTS on water quality and quantity in watershed scale (Siegrist et al., 2005).

The effect of OWTS on stream discharge in Gwinnett County, Georgia has been investigated by Oliver et al. (2014a) using a SWAT model. The author concluded that the model satisfactorily predicted stream discharge at the outlet of an urbanized watershed impacted by a large number of OWTS. However, the effect of OWTS on N was not included in their study. Therefore, further analysis of stream discharge and N load of SWAT in an urban watershed served with OWTS in Metropolitan Atlanta is needed.

This research was based on a study of 24 small watersheds (0.18-8.81 km² in area) in metropolitan Atlanta with a wide range in OWTS density. The watersheds were divided into 12 low-density (LD) and 12 high-density (HD) watersheds using a threshold of 75 OWTS km⁻². Three times a year under base-flow conditions from November 2011 to July 2014, water samples were collected and analyzed for nitrate (NO₃-N), ammonium (NH₄⁺-

N), and total Kjeldahl nitrogen (TKN) concentrations. After two years, Oliver et al. (2014) reported on the base flow measurements and suggested that most of the base-flow N originated from OWTS in HD watersheds and from agriculture in the LD watersheds. However, the fraction of the total annual N load represented by the base-flow N concentrations could not be estimated because N concentrations were not sampled during storm events and there were no continuous measurements of stream flow. Loads are important because they are the basis of the Total Maximum Daily Load (TMDL) program (USEPA, 2007).

The overall goal of this dissertation is to determine the impact of OWTS on water quantity and water quality in urban watersheds of Metropolitan Atlanta. The more specific objectives are:

- 1) To expand the analysis of water quality during base flow conditions to clarify the effect of OWTS density and other potential sources on N concentrations, including oxygen isotope of NO_3^- and correlations with different land uses.
- 2) To develop a calibration and sensitivity analysis of a SWAT model in order to predict N load.
- 3) To determine how N species concentrations in base flow compare to N species concentrations during storm events and to estimate how base-flow N load compares to total N load.

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2. LITERATURE REVIEW

2.1. Onsite Wastewater Treatment System

An onsite wastewater treatment system (OWTS) consists of a septic tank, an absorption trench, and the surrounding soil treatment unit where tank effluent infiltrates into the soil (Figure 2-1). Each person uses an average of 265 L of water per day and septic tank capacities vary between 3785 to 5678 L (USEPA, 2002). Primary treatment occurs in the septic tank through sedimentation of solid materials and partial anaerobic digestion of organic matter. Wastewater solids divide into two layers in the septic tank: a scum layer at the top of the wastewater, and a sludge layer at the bottom of the tank. Typically, total suspended solids (TSS) in raw wastewater range from 36 to 161 mg L⁻¹ (USEPA, 2002). After 24 hours, dissolved solids in a septic tank increase to about one-half or more of the total solids initially in sewage due to the breakdown of sludge and scum by anaerobic bacteria. This reduces the volume of sludge in the septic tank by about 40 percent. Pumping the tank every three to five years is recommended for removing the accumulated solids. If this is not done, solids will be suspended and washed out into the adsorption or drain field, where they can cause clogging of soil pores. A septic tank should provide a minimum retention time of 24 h before the effluent discharges into the drain field (DHR, 2007). Decomposition of organic matter is not complete in the septic tank since anaerobic decomposition processes are slower than aerobic decomposition processes, and the time that effluent remains in tanks is short. Organic nitrogen compounds are reduced to simpler compounds such as methane gas, ammonia (NH₃) and ammonium (NH₄⁺) in the septic tank

(DHR, 2007). The main form of nitrogen in septic tank effluent is NH_4^+ (Whelan and Barrow, 1984). Biodegradable organic materials in wastewater cause biochemical oxygen demand (BOD_5) for degrading organic compounds, and the concentrations usually range from 118 to 217 mg L^{-1} (USEPA, 2002). The Georgia Department of Human Resources (DHR) specifies that the BOD_5 and TSS for treatment by conventional septic tank systems must be less than 200 mg L^{-1} (DHR, 2007). High BOD_5 in the septic tank causes increased oxygen consumption so anaerobic conditions prevail. Typically, concentrations in raw wastewater range from 3 to 25 mg L^{-1} for organic N, 38 to 50 mg L^{-1} for NH_4^+ , and 0 to 0.7 mg N L^{-1} for NO_3^- (Tchobanoglous et al., 2003). The clarified effluent from septic tanks is odorous and contains degraded waste constituents, suspended solids, organic matter, NH_4^+ and NO_3^- . Pathogenic bacteria and viruses may also be present. Further treatment of the clarified liquid from the septic tank occurs through biological processes, adsorption, and infiltration into underlying soil in the drain field. Typically, the drain field includes one or more trenches which are filled with a layer of gravel or synthetic aggregate and a perforated drain pipe covered by soil in a conventional system. The function of the gravel or aggregate is to provide partial treatment of the effluent, and to distribute the effluent to the infiltrative soil surface. It also supplies temporary storage capacity during peak flows. Effluent discharged into the drain field infiltrates into soil through the bottom and side walls of the trenches. It moves over soil particle surfaces and in capillary pores in the vadose zone due to gravity and capillarity and from there to the groundwater. Filtration of suspended solids, including particulate matter and microbial biomass, from an adsorption trench into the surrounding soil develops a biomat layer at the trench-soil interface composed of living and dead microbes and particulate matter. The formation and growth

of the biomat is essential for long-term hydraulic function of OWTS and for enhancement of effluent purification via sorption to the surrounding soil and organic matter (Bouma, 1975; McCray et al., 2008; Siegrist, 1987).

When effluent infiltrates through the vadose zone, partial or complete removal for nutrients or organic compounds is expected. Since OWTS effluent consists of different anions and cations, ion exchange is an important mechanism for effluent treatment, depending on clay mineralogy and pH. The source of soil particle charge can be from isomorphic substitution in tetrahedral and octahedral layers of 2:1 clay minerals which causes permanent charge, or pH-dependent charge mainly in 1:1 clays and in iron and aluminum oxides. Soils with 2:1 clay minerals, large specific surface area, and organic matter (as a result of carboxyl groups) have large cation exchange capacities (CEC). In the Piedmont region, a net negative charge is produced as a result of isomorphic substitution for 2:1 clays and deprotonation of surface hydroxyl groups on 1:1 clay mineral such as kaolinite. In Piedmont Ultisols CEC ranges from 3 to 20 $\text{cmol}_c \text{ kg}^{-1}$. Anion adsorption in Piedmont Ultisols can also occur due to a net positive pH-dependent charge associated with iron and aluminum oxides, with the anion exchange capacity (AEC) ranging from 0.03 to 1.91 $\text{cmol}_c \text{ kg}^{-1}$ (Sposito, 2008; West et al., 1997).

2.2. Nitrogen in an Onsite Wastewater Treatment Systems: The N cycle

Onsite wastewater treatment systems are known as potential contributors of nutrients to surface and ground waters (USEPA, 2002). Nitrogen (N) in OWTS is present in different forms of organic and inorganic compounds. Therefore, the N cycle is an important mechanism for OWTS effluent treatment.

In the septic tank, N is mostly present as organic N (includes proteins, amino acids, amides, and urea) and NH_4^+ forms. NH_4^+ is produced from organic N through a microbially catalyzed process known as N mineralization or ammonification (Schepers and Raun, 2008). High-molecular organic-N compounds such as proteins, nucleic acids, and cell wall polymers are broken down to smaller organic-N compounds via extracellular enzymes. For instance, proteins are degraded by a wide variety of proteinases and peptidases to individual amino acids. These amino acids can be taken up by microorganisms and metabolized by intracellular enzymes to produce NH_4^+ . Nucleic acids are broken down by ribonucleases (RNases) and deoxyribonucleases (DNases) to produce nucleotides. Degradation of nucleotides through several hydrolyses and dephosphorylation leads to release of NH_4^+ . Microbial cell walls are degraded through the extracellular enzymes such as chitinase, chitobiose (for fungi) and lysozyme (for bacteria). The end products of microbial degradation are individual amino sugars. Then these amino sugars metabolize and release NH_4^+ through phosphorylation and deamination reactions. Urea from urine in septic tank can be hydrolyzed through extracellular enzyme urease. Ureases hydrolyze urea to CO_2 and NH_3 . Mostly, microbial organic-N degradation is driven by the need of the heterotrophic bacteria for energy and carbon (Schepers and Raun, 2008). In the drain field, NH_4^+ can be adsorbed to negatively charged sites on soil minerals and organic matter, taken up by plants, or converted to NO_3^- via the autotrophic nitrification process.

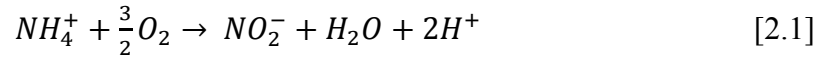
Microorganisms need N to build cellular constituents, such as proteins, nucleic acids, and cell walls. They can uptake either the organic form of individual N monomers (amino acids, nucleotides, amino sugars, and etc.) or inorganic forms of N. The inorganic N can be converted to glutamine or glutamate and can be used in in standard biosynthetic

pathways. NH_4^+ is preferentially used over NO_3^- in soil systems (McCarty and Bremner, 1992). Bacteria and fungi can assimilate NH_4^+ using glutamate dehydrogenase or glutamine synthase. When NO_3^- is used by microorganisms as their N source, it is reduced to NO_2^- by NO_3^- reductase and subsequently to NH_4^+ (Richardson et al., 2001). In soils with high organic matter content, some plants directly utilize amino acids (Lipson and Monson, 1998).

NH_4^+ added to soils from septic tank effluent or produced by the mineralization process can be fixed by clay minerals, particularly vermiculite and mica. It can also be immobilized by abiotic immobilization into organic forms, taken up by plants, or converted to NO_3^- during nitrification in the drain field. NH_4^+ reacts with organic matter mostly through the condensation of NH_3 or urea with phenolic compounds. NO_3^- is chemically unreactive, but NO_2^- can react with phenolic compounds through nitrosation reactions. Research has shown immobilization of NO_3^- into soil organic compounds through the “ferrous wheel pathway” (Davidson et al., 2003). In this mechanism, NO_3^- is reduced to NO_2^- using ferrous iron (Fe_2^+). A wide variety of microorganisms are involved in the mineralization-immobilization processes including aerobic and anaerobic bacteria, fungi, and actinomycetes. Net N mineralization usually occurs with substrates having C/N of 25:1, greater ratios are associated with net N immobilization (Schepers and Raun, 2008).

Nitrification is the biological conversion of reduced forms of N such as NH_3 or NH_4^+ to NO_2^- and NO_3^- (oxidized forms). It is an aerobic process in which O_2 is the terminal electron acceptor and cellular carbon is gained from CO_2 via the Calvin-Bassham (CBB) cycle (Prosser, 1989). In the first step, NH_3 or NH_4^+ are converted to hydroxylamine (NH_2OH) by the ammonia mono-oxygenase (AMO) enzyme (Frankland and Frankland,

1889). Then NH_2OH is oxidized to NO_2^- by hydroxylamine oxidoreductase (HAO). Chemolithoautotroph bacteria or archaea are involved in oxidation of ammonia/ammonium to NO_2^- via ammonia oxidizing bacteria (AOB) such as *nitrosomonas* or *nitrospira* and gain energy from this process. The overall reaction for the first step is:



The Gibbs free energy yield of this reaction is $-195 \text{ kJ mol}^{-1} \text{ NO}_2^-$ at standard state. Under oxic conditions, NO_2^- is quickly converted to NO_3^- , so the conversion of NH_4^+ to NO_2^- is an intermediate process. In the second step, NO_2^- is oxidized to NO_3^- by nitrite oxidizing bacteria (NOB) such as *Nitrobacter* or *Nitrospira* (Hooper et al., 1997). The overall reaction for this step is:

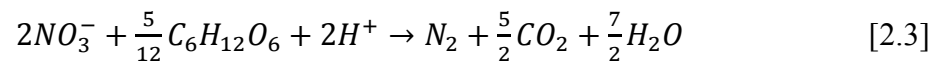


The Gibbs free energy yield is $-77 \text{ kJ mol}^{-1} \text{ NO}_3^-$ at standard state. Factors that may affect aerobic nitrification include the presence of nitrifying microorganisms, oxic soil conditions, substrate availability (such as NH_4^+), osmotic potential, pH, and temperature.

Heterotrophic bacteria, fungi, and actinomycetes may result in heterotrophic nitrification using organic form of C mostly in forest soils. However the amount of energy produced in this way is less than the energy produced by autotrophic nitrification process (Schepers and Raun, 2008).

Denitrification is an enzymatic process in which NO_3^- is reduced to nitrogen oxides under anaerobic or microaerophilic conditions. Denitrifiers obtain their energy from oxidizing organic carbon (heterotrophic). Nitrogen oxides act as electron acceptors and reduce NO_3^- to nitrogen oxides (from oxidation state +5 for NO_3^- to 0 for N_2). In this pathway, NO_3^- is reduced to NO_2^- (via nitrate reductase enzyme), NO_2^- is reduced to nitric

oxide (NO) (via nitrite reductase enzyme), NO is reduced to nitrous oxide (N₂O) (via nitric reductase), and N₂O is reduced to dinitrogen gas (N₂) (nitrous oxide reductase enzyme) (Zumft, 1997). Nitrogen oxides may be lost from the system in each step. The overall denitrification reaction with glucose as the carbon source is:



The Gibbs free energy yield of this reaction is -1217 kJ mol⁻¹ N₂ at standard state. Archaea, eukaryotic fungi, and a large population of bacteria (such as *Pseudomonas* *Bacillus*) are involved in the denitrification process. Factors that may affect the denitrification process are: soil water capacity, availability of NO₃⁻, presence of denitrifying organisms, availability of organic carbon, pH, and temperature (Schepers and Raun, 2008). Denitrification is an important process for removing N from groundwater. Among all the factors that control denitrification, the most common limiting factor is lack of dissolved organic carbon (DOC). However, aquifers that are recharged by OWTSS effluent may receive sufficient amounts of DOC to cause denitrification close to the drain field.

2.3. Nitrogen Tracking in the Environment

Nutrients are the third most common cause of impairment in rivers and streams, and the second most common reason in lakes, reservoir, and ponds according to the EPA 303(d) list (USEPA, 2012). Since it is difficult to identify the source of NO₃⁻, several different methods have been used to track the transformation of N in the environment.

One method is the use of the ratio of NO₃⁻ to a conservative tracer such as chloride (Cl⁻) (Alhajjar et al., 1990). Because of the anionic form of Cl⁻ (the same as NO₃⁻), it leaches easily from the soil profile. Due to the nature of human diet, Cl⁻ is found in almost all

human wastewater. About 12 kg of Cl^- per person per year is produced in household waste (Kelly et al., 2008). It has been shown that Cl^- concentrations increase with the degree of urbanization under base flow conditions (Rose and Fullagar, 2005). As such, Cl^- can be used as a conservative tracer to detect nitrogen transformations and the effect of dilution in aquatic ecosystems.

Using stable isotopes of nitrogen and oxygen is another method to track the transformations and sources of N in the environment. Several studies have used a dual isotope technique to for these purposes (Aravena and Robertson, 1998; Di Lorenzo et al., 2012; Mayer et al., 2002; Silva et al., 2002). Because the chemical bonds of lighter isotopes ($\delta^{14}\text{N}$ and $\delta^{16}\text{O}$) are broken down more easily than those of heavier isotopes ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$), microorganisms prefer to use lighter isotopes for respiration and assimilation. Therefore, heavier isotopes ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) become concentrated in the environment. Usually, isotopes of N and O are measured as the ratio of $^{15}\text{N}:^{14}\text{N}$ and $^{18}\text{O}:^{16}\text{O}$ with the units of per mil (parts per thousand [‰]) of ^{15}N or ^{18}O higher or lower than that of a standard (Silva et al., 2002). The Greek letter delta (δ) indicates a value derived by the equation [2.4]:

$$\delta^{15}\text{N} \text{ or } \delta^{18}\text{O} = \left(\left(\frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1 \right) \times 1000 \quad [2.4]$$

where R_{sample} is the ratio of $^{15}\text{N}:^{14}\text{N}$ or $^{18}\text{O}:^{16}\text{O}$ in the sample and R_{standard} is the ratio of $^{15}\text{N}:^{14}\text{N}$ or $^{18}\text{O}:^{16}\text{O}$ in the standard. The standard for N is atmospheric air (0.0036), and for O is Vienna Standard Mean Ocean Water (VSMOV) (Silva et al., 2002).

Common fields for different sources of NO_3^- are shown in Figure 2-2 as reported by Silva et al. (2002) and Michener and Lajtha (2008). Generally, $\delta^{15}\text{N}-\text{NO}_3^-$ values are observed between -10 and +25‰. High $\delta^{15}\text{N}-\text{NO}_3^-$ values are common in animal and

human wastes (from +7‰ to more than +20‰) due to ammonia volatilization and then oxidation of the residual waste to produce NO_3^- with a high $\delta^{15}\text{N}$. Soil NO_3^- can originate from the natural oxidation of organic nitrogen and it can be derived from different environments such as natural soils, soils fertilized with synthetic fertilizer or manure, and soils containing septic waste (Hornberger, 1999; Michener and Lajtha, 2008). Therefore, $\delta^{15}\text{N}\text{-NO}_3^-$ values of soil NO_3^- are between synthetic ammonium fertilizer and animal/human waste and they overlap with these two sources (Silva et al., 2002). NO_3^- in atmospheric deposition is usually characterized by $\delta^{15}\text{N}$ values between -10 and +8‰. Also, microbial denitrification and assimilation by plants increase the $\delta^{15}\text{N}\text{-NO}_3^-$ value of residual NO_3^- (Hornberger, 1999). The $\delta^{18}\text{O}\text{-NO}_3^-$ values from atmospheric depositions have a large range between +20 and +80‰. Bacterial method (denitrifier method) gives more precise estimation of oxygen isotope of atmospheric NO_3^- in comparison with non-denitrifier (AgNO_3^-) method (Sigman et al., 2001), mainly due to the minimizing chemical contamination during this method (Michener and Lajtha, 2008). Usually, synthetic NO_3^- fertilizers have $\delta^{18}\text{O}$ values between +18 and +26‰. The $\delta^{18}\text{O}$ value of soil nitrate may overlap with $\delta^{18}\text{O}\text{-NO}_3^-$ from nitrification of ammonium fertilizer, and human and animal wastes. Therefore, the use of combined $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$ is a better tool for source separation and mixing relationships than $\delta^{15}\text{N}\text{-NO}_3^-$ alone.

The ratio of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ (slope of a linear regression line) increases about 2:1 during denitrification. This ratio value can be used to determine if denitrification has been a significant factor in setting the isotopic compositions (Böttcher et al., 1990; Silva et al., 2002).

The design of OWTS is not particularly effective for N removal (Oakley et al., 2010). The complexity of N removal in an OWTS at the OWTS-scale have been shown in several studies. Postma et al. (1992) and Harman et al. (1996) found that NO_3^- concentrations in a plume caused by OWTS ranged from 3 to 120 mg L^{-1} . In the Piedmont region of Georgia, Bradshaw and Radcliffe (2011) found that almost all NH_4^+ was nitrified in the drainfield and concentrations of NO_3^- reached 20 mg L^{-1} below the drain field of an OWTS.

In a study of Coastal Plain soils in North Carolina, Cogger and Carlile (1984) measured N concentrations in groundwater samples from shallow wells near 15 OWTS. They found that NH_4^+ and NO_3^- concentrations were high in groundwater near these systems and decreased with distance down-gradient of the systems. The average NO_3^- concentrations of about 15 mg L^{-1} were reported in the groundwater in wells 1.5 m from these systems (Cogger and Carlile, 1984). Wilhelm et al. (1994) monitored NH_4^+ and NO_3^- concentrations in groundwater from an OWTS in Ontario, Canada. They found that NH_4^+ in the septic effluent was almost completely oxidized to NO_3^- and groundwater NO_3^- concentrations increased to about 30 mg L^{-1} near the drain field and remained constant with increasing distance down-gradient.

In a study by Smith and Duff (1988) denitrification was measured in a sand and gravel aquifer on Cape Cod, Massachusetts. The aquifer received treated sewage for more than 50 years and formed a contaminated plume greater than 3.5 km long. The rate of denitrification was highest near the contaminant source where NO_3^- concentrations were greater than 60 mg L^{-1} and decreased with increasing distance down-gradient. Their study showed that denitrification was the dominant process in reducing NO_3^- . Also, the authors

reported that denitrifying activity was carbon-limited and not NO_3^- -limited where NO_3^- concentrations were high. In a study by Bradshaw et al. (2013) in a clay soil in the Piedmont region of Georgia, it was shown that about 52% of N in an OWTS drain field removed by denitrification.

2.4. The Effect of Onsite Wastewater Treatment Systems on Water Quality

N fate and transport increases in complexity at the watershed-scale compared to the OWTS-scale. Burns et al. (2005) showed that NO_3^- concentrations during base flow were elevated in medium and high density urban watersheds compared to undeveloped watersheds. Reay (2004) showed that OWTS loadings to shallow groundwater in the Chesapeake Bay region were significant and caused mean shoreline N concentrations to increase about 50 to 100 times in comparison with adjacent surface water. Oliver et al. (2014) found that in-stream NO_3^- concentrations increased with increasing OWTS density above about 75 OWTS km^{-2} during base flow in urban watersheds of Metropolitan Atlanta.

Base-flow N concentrations alone may not represent the total impact of stream N. Load estimation is important to watershed mass balance studies and in the development of Total Maximum Daily Loads (TMDL) (USEPA, 2007). The load of pollutants transported through a stream cross- section during a time interval is given in Equation [2.5]:

$$L = \int_{t_1}^{t_2} Q(t)C(t)dt \quad [2.5]$$

where L is the load between time t_1 and t_2 (M T^{-1}), $Q(t)$ is the streamflow at time t ($\text{L}^3 \text{T}^{-1}$), and $C(t)$ is the constituent concentration (M L^{-3}). According to equation [2.5], continuous flow and concentration measurements are essential to estimate accurate loads. In small watersheds due to large or rapid changes in concentration during storm flow conditions, sub-daily sampling frequencies can help to minimize sampling errors.

Automated sampling equipment can be a useful tool to program time-paced discrete sampling based on a pattern of times (e.g. every 15 minutes) (King et al., 2005). Harmel et al. (2003) based on averages of 300 storm events showed that time-discrete sampling at a 15-minute interval or less was necessary to estimate a pollutant load that was not significantly different from the true pollutant load. Several methods have been used for load estimation including averaging estimator, regression methods, ratio estimators, and planning level load estimators. However, the accuracy of each method depends on several factors such as frequency of sampling, monitoring period, and the watershed characteristics (Quilbé et al., 2006).

Understanding N export from urban watersheds is important for guiding urban management practices that will help to reduce N exports to water bodies. A couple of studies evaluated N export in base flow and storm flow in sub-urban and urban watersheds. Taylor et al. (2005) found no significant difference between NO_3^- concentrations during base flow (mean: 0.87 mg L^{-1}) and storm flow (mean: 0.74 mg L^{-1}) in urban watershed in Melbourne, Australia. They concluded that the dilution of NO_3^- concentrations was not significant during high flows, causing high N exports during storm conditions (Taylor et al., 2005). Poor and McDonnell (2007) compared N exports from a sub-urban watershed (without OWTS) with a forested watershed and an agricultural (pasture) watershed for three storms (fall, winter, and spring) in Oak Creek watershed, Oregon. They found that during all storms NO_3^- load from a sub-urban watershed increased relative to a forest watershed due to a lawn fertilizer source. Increase in NO_3^- concentrations and load from an agriculture watershed was restricted to a period following fall fertilizer application (Poor and McDonnell, 2007). Shields et al. (2008) showed that most of the NO_3^- and TN loads in

urban sub-basins in the Chesapeake Bay watershed were exported during storm conditions because of high percent of impervious surface areas. The effect of OWTS density on N concentrations and loads was shown by Hatt et al. (2004). They found positive and significant correlation between NO_3^- and TN concentrations and OWTS density. However, N loads were strongly correlated with percent of impervious surfaces (Hatt et al., 2004).

Several studies shown that impervious surface such as roads, driveways, sidewalks, roofs, and parking lots reduced infiltration and groundwater discharge to streams. Rose and Peters (2001) reported that base flow decreased by approximately 30% in a highly urbanized watershed, compared to a less urbanized watershed. This was due to the decline in infiltration as a result of more impervious surfaces in the more urbanized watershed. Furthermore, Calhoun et al. (2003) and Landers et al. (2007) reported that an increase in impervious surface decreased base flow and increased storm flow due to less infiltration and more runoff. While it is generally assumed that urbanization decreases groundwater discharge to streams, some studies have shown an increase in base flow due to leakage from buried urban infrastructure (Garcia-Fresca, 2007; Lerner, 2002; Meyer, 2005). It was estimated that about 21% of water in water distribution systems is lost through the leakage in the United States (O'Driscoll et al., 2010). Also, in several studies a leakage rate of 5% was reported from sewer pipes (Lerner, 1997; Lerner, 2002; Yang et al., 1999).

2.5. Modeling the Effect of Onsite Wastewater Treatment Systems on Water Quantity and Quality at the Watershed-scale

Due to several uncertainties in the fate and transport of N within and beyond the drain field of a single OWTS, modeling of N associated with OWTS at the watershed-scale has not been extensively researched. However, quantifying the effect of OWTS on water

quantity and quality using models is important to our understanding of these systems (McCray et al., 2005). A biozone algorithm proposed by Jeong et al. (2011) was incorporated into the Soil and Water Assessment Tool (SWAT 2009) to describe biozone processes and to simulate the effect of OWTS on water quantity and quality at the watershed-scale. SWAT was developed to predict the effect of land management practices on water, sediment and agricultural chemical in watersheds with different soils, land use, and management practices (Arnold et al., 2012). It is a physically-based model and requires input information about weather, soil, topography, vegetation, and land management practices in the watershed. SWAT has been used widely in water quality modeling studies including TMDL analyses and nonpoint source pollution analysis (Neitsch, 2011). In the model, a watershed may be divided into a number of sub-basins or sub-watersheds. Each sub-basin is divided into Hydrologic Response Units (HRUs). HRUs are lumped areas within the sub-basin that are comprised of unique land cover, soil, slope, and management combinations (Arnold et al., 2012).

The hydrology cycle of a watershed in SWAT is divided into two divisions; land phase and water or routing phase. The land phase controls the amount of water, sediment, nutrient, and pesticide loading to the main channel in each sub-basin. The water or routing phase controls the movement of water, nutrients, etc. through the channel network of the watershed to the outlet (Neitsch, 2011). The water balance is the driving force behind the movement of sediments and nutrients in a watershed, and its equation describes as:

$$SW_t = SW_0 + \sum_{i=1}^t (R_{day} - Q_{surf} - E_a - w_{seep} - Q_{gw}) \quad [2.6]$$

where SW_t is the final soil water content (mm H₂O), SW_0 is the initial soil water content on day i (mm H₂O), t is the time (days), R_{day} is the amount of precipitation on day i (mm

H₂O), Q_{surf} is the amount of surface runoff on day i (mm H₂O), E_a is the amount of evapotranspiration on day i (mm H₂O), w_{seep} is the amount of water entering the vadose zone from the soil profile on day i (mm H₂O), and Q_{gw} is the amount of return flow on day i (mm H₂O). Runoff is predicted separately for each HRU and routed to obtain the total runoff for the watershed. The potential pathways of water movement simulated by SWAT in each HRU are canopy storage, infiltration, evapotranspiration, lateral subsurface flow, surface runoff, ponds, tributary channels, and return flow, and are described in detail in Neitsch (2011). In SWAT, two methods are provided for estimating surface runoff: the SCS curve number procedure (SCS, 1972) and the Green and Ampt infiltration method (Green and Ampt, 1911). Subsurface lateral flow is simulated in a two-dimensional cross-section along a flow path down a hillslope according to the Sloan and Moore (1984) model. The amount of water stored in the shallow aquifer is estimated according to the amount of recharge entering the shallow aquifer, and the amount of water exiting the aquifer as base flow into the main channel, routing to the deep aquifer, removal by pumping, or upward capillary movement into the unsaturated zone in response to water deficiencies. Erosion and sediment yield are modeled for each HRU with the Modified Universal Soil Loss Equation (MUSLE) (Williams and Berndt, 1977).

The plant growth model is used to estimate removal of water and nutrients from the root zone, transpiration, and biomass production. The movement and transformation of several forms of nitrogen and phosphorus are simulated by SWAT. In the soil, the fate and transformation of N and P are controlled by nitrogen and phosphorus cycles in each HRU. Nutrients may enter the main channel and be transported downstream via surface runoff and lateral subsurface flow. In SWAT, nitrogen is modeled in the soil profile and in the

shallow aquifer. N may be added to the soil by fertilizer, manure, residue, rain, and fixation by symbiotic and non-symbiotic bacteria. N is lost from the soil by plant uptake, leaching, volatilization, denitrification, and erosion (Neitsch, 2011). In SWAT, five different pools of N in the soil are monitored. Two inorganic pools of N (NH_4^+ and NO_3^-), and three organic pools of N including fresh, active, and stable organic N. Fresh organic N is linked with crop residue and microbial biomass. The active and stable organic N pools are associated with the soil humus. The fresh organic N pool and active N pool undergo mineralization. Mineralization and decomposition processes are water- and temperature-dependent. Water and temperature factors are calculated for these process based on the soil layer temperature and water content. Decomposition and mineralization of the fresh organic N pool is modeled in the first soil layer and depends on the C:N ratio of the residue. Nitrification and ammonia volatilization are modeled in SWAT using a combination of the methods developed by Reddy et al. (1979) and Godwin et al. (1983). Nitrification is a function of soil temperature and soil water content, and ammonia volatilization is a function of soil temperature, depth, and cation exchange capacity. Therefore, to include the impacts of these factors in the nitrification/volatilization processes four coefficients are incorporated in the algorithm. The amount of NO_3^- lost through the denitrification process is a function of water content, temperature, the availability of a carbon source, and the availability of NO_3^- . SWAT calculates the amount of NO_3^- lost to denitrification with the following equation:

$$N_{dennit,ly} = \text{NO3}_{ly} \times (1 - \exp[-\beta_{denit} \times \gamma_{tmp,ly} \times orgC_{ly}]) \text{ if } \gamma_{sw,ly} \geq \gamma_{sw,thr} \quad [2.7]$$

$$N_{dennit,ly} = 0.0 \quad \text{if } \gamma_{sw,ly} < \gamma_{sw,thr} \quad [2.8]$$

where $N_{denit,ly}$ is the amount of N lost to denitrification (kg N ha^{-1}), NO_3_{ly} is the amount of NO_3^- in layer ly (kg N ha^{-1}), β_{denit} is the rate coefficient for denitrification, $\gamma_{tmp,ly}$ is the nutrient cycling temperature factor for layer ly , $\gamma_{sw,ly}$ is the nutrient cycling water factor for layer ly , $orgC_{ly}$ is the amount of organic carbon in the layer (%), and $\gamma_{sw,thr}$ is the threshold water content for denitrification to occur (Neitsch, 2011).

In SWAT the amount of N that is added to the soil from atmospheric deposition of N can be estimated for both wet and dry forms. The amount of NO_3^- and NH_4^+ added to the top 10 mm of soil from rainfall (wet deposition) is calculated according to the amount and the concentration of NO_3^- and NH_4^+ in the rain and the amount of precipitation on a given day. The amount of dry deposition of NO_3^- and NH_4^+ added to the soil in each sub-basin is calculated based on the amount of NO_3^- and NH_4^+ in the surface soil layer, and the daily NO_3^- and NH_4^+ dry deposition rate.

NO_3^- is an anion and is susceptible to leaching from the soil profile due to the repulsion from negatively charged particles. NO_3^- may be transported with surface runoff, lateral flow, or percolation. The amount of NO_3^- moved with the water is calculated according to the concentration of NO_3^- in the mobile water and the volume of water moving in each pathway. The total amount of NO_3^- entering the shallow aquifer is equal to the amount of NO_3^- exiting the bottom of the soil profile by percolation. NO_3^- in the shallow aquifer may remain in the aquifer, move with recharge to the deep aquifer, move with groundwater flow into the main channel, or be transported into the soil zone to compensate for water deficiencies. To estimate NO_3^- losses in the shallow aquifer due to biological and chemical processes, a half-life for NO_3^- in the shallow aquifer is included in the model. The half-life of NO_3^- accounts for all reactions occurring in the aquifer and is calculated as:

$$t_{\frac{1}{2},NO3,sh} = \frac{0.693}{k_{NO3,sh}} \quad [2.9]$$

where $t_{\frac{1}{2},NO3,sh}$ is the half-life of NO_3^- in the shallow aquifer (days) and $k_{NO3,sh}$ is the rate constant for removal of NO_3^- in the shallow aquifer (day^{-1}).

The N cycle in the stream in SWAT accounts for the transformation from organic N to NH_4^+ , to NO_2^- , and to NO_3^- . The NO_3^- concentration in the stream may be elevated by the oxidation of NO_2^- or decreased by the uptake of NO_3^- by algae. The change in NO_3^- concentration on a given day is calculated as:

$$\Delta NO3_{str} = (\beta_{N,2} \times NO2_{str} - (1 - fr_{NH4}) \times \alpha_1 \times \mu_a \times algae) \times TT \quad [2.10]$$

where $\Delta NO3_{str}$ is the change in NO_3^- concentration ($mg\ N\ L^{-1}$), $\beta_{N,2}$ is the rate constant for biological oxidation of NO_2^- to NO_3^- (day^{-1} or hr^{-1}), $NO2_{str}$ is the NO_2^- concentration at the beginning of the day ($mg\ N\ L^{-1}$), fr_{NH4} is the fraction of algal N uptake from NH_4^+ pool, α_1 is the fraction of algal biomass that is N ($mg\ N\ mg\ alg\ biomass^{-1}$), μ_a is the local growth rate of algae (day^{-1} or hr^{-1}), $algae$ is the algal biomass concentration at the beginning of the day ($mg\ alg\ L^{-1}$), and TT is the flow travel time in the reach segment (day or hr). The equations for calculation $\beta_{N,2}$, fr_{NH4} , μ_a , and TT are described in detail by Neitsch (2011).

To simulate the impact of OWTS on water quantity and quality the biozone algorithm was developed and incorporated in the latest version of SWAT 2009 (Jeong et al., 2011). Each unit of OWTS is represented by a septic HRU. In this algorithm, septic tank effluent directly discharges into a subsurface soil layer in the drain field, affecting soil moisture content and the percolation of soil water through the soil profile. The biozone layer is a biologically active layer in the soil absorption system at the infiltrative surface where there is growth of microorganisms feeding on the organic matter (BOD) of the septic

tank effluent (Figure 2-3). A mass balance equation is used to estimate the amount of live bacteria biomass in the biozone in SWAT:

$$\frac{d(Bio)}{dt} = \alpha \times [\sum Q_{STE} \times C_{BOD,in} - I_p \times C_{BOD}] - R_{resp} - R_{mort} - R_{slough} \quad [2.11]$$

where Bio is the amount of live bacteria biomass in biozone (kg ha^{-1}), $C_{BOD,in}$ is the BOD concentration in the septic tank effluent (mg L^{-1}), C_{BOD} is the BOD concentration in biozone (mg L^{-1}), α is a conversion factor (gram of live bacteria / gram of BOD in septic tank effluent), Q_{STE} is the flow rate of septic tank effluent (cm day^{-1}), I_p is the amount of percolation out of the biozone (cm day^{-1}), R_{resp} is the amount of bacteria respiration (kg ha^{-1}), R_{mort} is the amount of bacteria mortality (kg ha^{-1}), and R_{slough} is the amount of sloughed off bacteria (kg ha^{-1}) (Neitsch, 2011). The amount of bacterial biomass in the biozone influences field capacity, porosity, hydraulic conductivity, soil moisture, and percolation through the biozone. The transformation and removal of N, BOD, and fecal coliform in the biozone layer is directly related with the population of live bacteria biomass and is estimated by a first order reaction equation:

$$C_{k,end} = C_{k,i} \times e^{-k_k \Delta t} \quad [2.12]$$

where $C_{k,end}$ is concentration of the k constituent in the biozone at the end of the day (mg L^{-1}), $C_{k,i}$ is concentration of the k constituent in the biozone at the beginning of the day (mg L^{-1}), and k_k is a first order reaction rate (day^{-1}). k_k is a function of the total biomass of live bacteria and a reaction rate coefficient for each constituent (such as nitrification, denitrification, BOD decay, and fecal coliform bacteria decay) (Neitsch, 2011).

In SWAT, a typical life time of an OWTS ranges from 10 to 25 years depending on maintenance, loading rate, and soil conditions and the life time is based on how much effluent percolates through the biozone. The only type of OWTS failure which is modeled

in SWAT is biozone clogging or hydraulic failure. Over time TSS and biomass accumulate in the biozone. The OWTS fails when the biozone porosity decreases to the field capacity water content. The system will remain in failure for a user-specified number of days. When failing occurs septic tank effluent migrates to the upper soil layers and causes ponding. Nutrients move to the soil surface along the septic tank effluent. The amount of nutrients that is transported to the upper soil layers depends on the nutrient concentration in septic tank effluent and the amount of water that moved to the upper layer (Neitsch, 2011).

The performance of the SWAT biozone algorithm was tested in a case study in the Hoods Creek watershed in North Carolina by Jeong et al. (2011). The model showed good performance in predicting groundwater levels ($R^2 = 0.82$) and the N concentration in the groundwater ($R^2 = 0.76$). The authors reported that at the watershed-scale OWTS contributed to only 25% of the N inflow to groundwater. The total removal of N input to the watershed was estimated about 80% from denitrification and plant uptake.

The effect of OWTS on streamflow in an urbanized watershed in Metropolitan Atlanta was simulated from 2003 to 2010 using SWAT model (Oliver et al., 2014). The calibrated model showed a satisfactory fit with daily Nash-Sutcliffe coefficients of 0.49 and 0.37 for the calibration and validation periods, respectively. They found a 3.1% increase in total water yield at the watershed scale with the presence of OWTS. Water quality analysis was not included in their model.

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Figures:

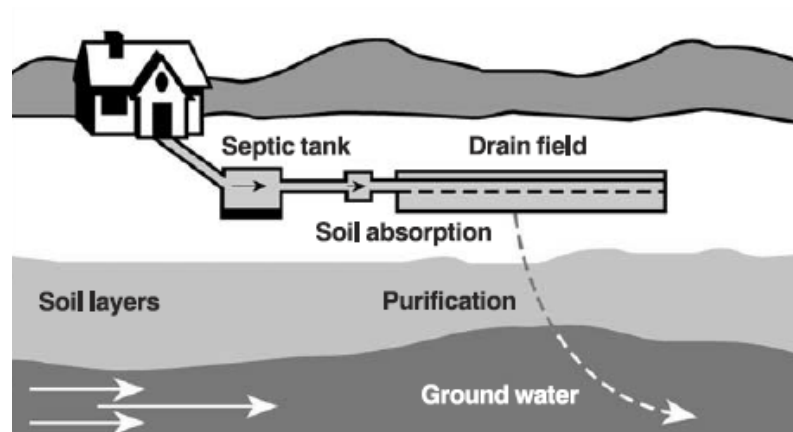


Figure 2-1- Conventional onsite wastewater treatment system (OWTS) (US.EPA 2002)

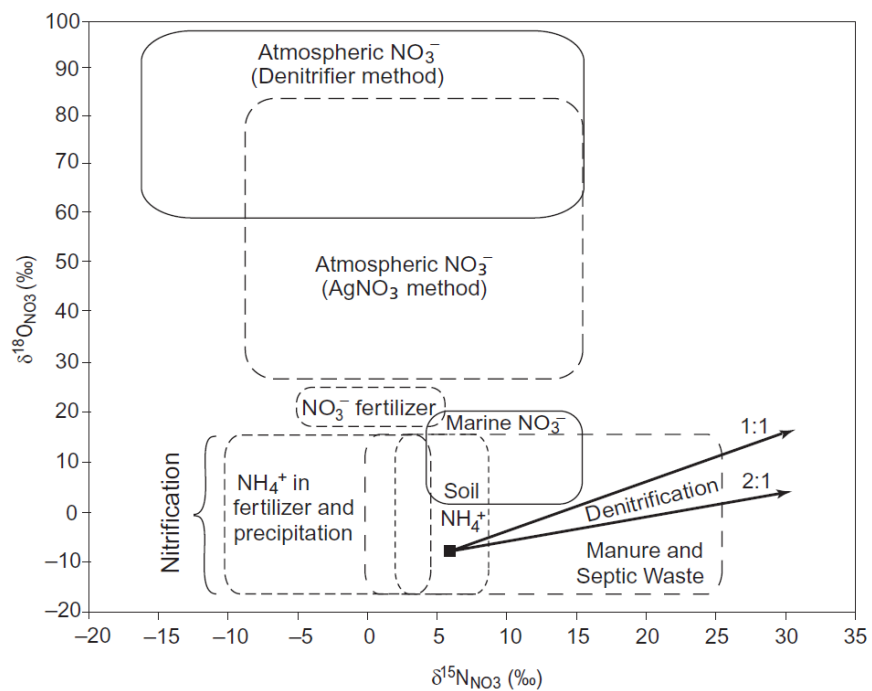


Figure 2-2- Common fields for different sources of NO_3^- as reported by Silva et al. (2002) and Michener and Lajtha (2008). Denitrification trends are displayed as arrows.

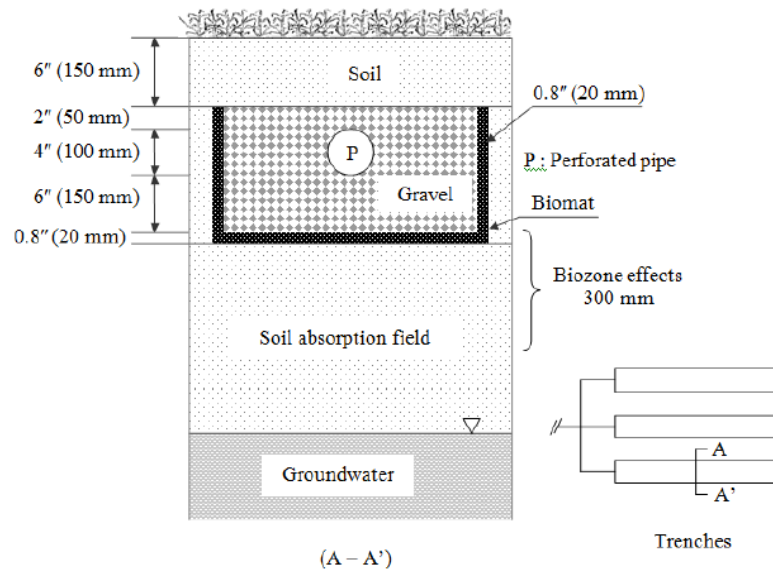


Figure 2-3- Vertical configuration of a septic tank effluent drain field trench and soil absorption system (Jeong et al., 2011)

3. CONFIRMATION OF THE IMPACT OF ONSITE WASTEWATER TREATMENT SYSTEMS ON STREAM BASE-FLOW NITROGEN CONCENTRATIONS IN URBAN WATERSHEDS OF METROPOLITAN ATLANTA¹

¹ Hoghooghi, N., D.E. Radcliffe, M.Y. Habteselassie, and J.S. Clarke. Accepted by the Journal of Environmental Quality. Reprinted here with the permission of publisher, 07/18/2016.

3.1. Abstract

Wastewater and lawn fertilizer potentially contribute to degraded water quality in urban watersheds. Previously we described a 2011–2012 study in which we examined the effect of the density of onsite wastewater-treatment systems (OWTS) on nitrogen concentrations in 24 small streams in Metropolitan Atlanta. Our objective in this study was to confirm that the impact on water quality that we observed was due to OWTS and not lawn fertilizer. We sampled the same 24 streams again in 2013 and 2014, representing watersheds ranging in area from 0.18 to 8.8 km². We conducted regression analysis of the effect of OWTS and season, used dual-isotope analysis (nitrogen and oxygen in nitrate) to identify sources and determine the effect of denitrification and mixing, and conducted stream walks to identify areas where animals had access to the streams. Twelve streams were characterized as high-density (HD – more than 75 systems km⁻²) OWTS and 12 as low-density (LD – less than 75 systems km⁻²) OWTS. Water samples were collected three times a year under base-flow conditions, from November 2011 to July 2014, and analyzed for nitrate (NO₃⁻-N), ammonium (NH₄⁺-N), and total Kjeldahl nitrogen (TKN). Total nitrogen (TN) and NO₃⁻-N concentrations increased linearly with increasing OWTS density above a threshold of about 75 OWTS km⁻². Dual-isotope analysis of NO₃⁻ showed that stream NO₃⁻ originated predominantly from OWTS in HD watersheds and from a combination of animal waste and perhaps organic N in LD watersheds. Stream walks showed that livestock had access to some of the LD streams with high N concentrations. Our results confirm that high-density OWTS can significantly degrade water quality at the watershed scale.

Abbreviations: HD, high density; LD, low density; Onsite wastewater treatment system, OWTS; TKN, total Kjeldahl nitrogen; TN, total nitrogen.

3.2. Introduction

Onsite wastewater treatment systems (OWTS) or septic systems consist of a septic tank and a soil adsorption field where tank effluent leaches into the soil for continued passive treatment. Approximately 30% of the homes in Georgia are on OWTS, which is higher than the national average of 24% (USEPA, 2002). The percentage of housing units in Metropolitan Atlanta that are on OWTS is estimated to be 26% (MNGWPD, 2006), and this percentage is expected to increase with population growth. Because of the high costs of centralized systems, OWTS are no longer considered a temporary solution to be replaced eventually by centralized collection and treatment (USEPA, 2002). However the design of conventional OWTS is not particularly effective for nitrogen removal and it has been reported that nitrogen loading is reduced by only 10-20% before discharge to the environment (Oakley et al., 2010).

Failing or high density OWTS can cause poor water quality in both surface water and groundwater (Conn et al., 2012). Estimates of the percentage of OWTS that fail vary widely from 1-5 % (DPH, 2012; Meile et al., 2010) to more than 20% (Pessell and Young, 2011; USEPA, 2002). There are three types of failures, the first type of failure occurs when the septic tank is not pumped regularly and fills with solids. This can cause effluent to back up into the house and is likely to be included in counties where records of failure are kept based on reports filed by pumpers. A second type of failure may also be caused by failure to pump septic tanks, or by clogged trenches or improperly sited drain fields, and it results in effluent coming to the soil surface. This type of failure may not cause effluent to back up into the house. We suspect that this type of failure may not be reported if the surfacing of effluent is intermittent (only during wet periods) or if the homeowners cannot afford to

have their system repaired or a new drain field installed. The third type of failure occurs when the drain field is not properly sited (the water table is too high for example) or the system is overloaded (due to an increase in the number of people in the home beyond that for which the system was designed for example). In this case the effluent may not back up into the home or even surface, but proper treatment of the effluent does not occur within the unsaturated zone. The third type of failure is difficult to detect and the least likely to be reported. We think that the wide range in failure rates in the literature is due to differences in how the failures were detected. If it is based on homeowners' reports, then it is likely to consist for the most part of the first type of failure and be at the low end of the percentage range. But if it is based on inspections that will detect the second type or third type of failure, then it is likely to be at the high end of the range.

Nutrients are the third most common cause of river and stream impairment, and the second most common reason of impairment in lakes, reservoir, and ponds on the EPA 303(d) list (USEPA, 2012). The maximum NO_3^- contaminant level for drinking water to protect against methemoglobinemia or blue-baby syndrome is 10 mg L^{-1} (as N) (Kaushal et al., 2006). Although nitrogen is critical to ecological health, excessive loading of this nutrient causes eutrophication and hypoxia in marine and brackish water ecosystems (Conley et al., 2009; Pinckney et al., 2001; Rabalais, 2002) and disrupts the aquatic food web in freshwater streams (Benstead et al., 2009; Davis et al., 2010; Suberkropp et al., 2010). Threshold concentrations for nitrogen to prevent eutrophication and preserve the aquatic food web in water bodies are much lower than 10 mg L^{-1} (as N) and depend on the type of the water resource (USEPA, 2002).

Chloride (Cl^-) has been used to identify sources of NO_3^- in groundwater and surface water (Alhajjar et al., 1990; McQuillan, 2004) and is found in almost all human and animal wastes. Due to the nature of the human diet, it is estimated that about 12 kg Cl^- per person per year is produced in household wastes (Kelly et al., 2008). Rose (2007) in a study of 50 stream base-flow samples in the Atlanta Metropolitan area, found that Cl^- concentrations increased with the degree of urbanization. Because Cl^- is not subjected to microbiological transformation, it serves as a useful conservative tracer for the movement of mono-valent anions, like NO_3^- , in soil and groundwater (Alhajjar et al., 1990; McQuillan, 2004). However, differentiation between different NO_3^- sources using Cl^- is difficult where multiple N sources exist.

Several studies have used isotopic techniques to identify N sources and transformations in aquatic ecosystems (Aravena and Robertson, 1998; Di Lorenzo et al., 2012; Mayer et al., 2002; Silva et al., 2002; Wassenaar, 1995). It was shown that using $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- is a better tool for source separation and identifying mixing effects than $\delta^{15}\text{N}$ alone. During denitrification, bacteria preferably consume lighter isotopes ($\delta^{14}\text{N}$ and $\delta^{16}\text{O}$), causing increases in the value of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ as NO_3^- concentrations decrease. The ratio of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ (slope of a linear regression line) can determine if denitrification has a significant effect on the isotopic composition, with an enrichment ratio of around 0.5 (Böttcher et al., 1990; Hornberger, 1999; Michener and Lajtha, 2008; Silva et al., 2002). A couple of studies have confirmed the source of NO_3^- to be from OWTS by using dual-isotope techniques in groundwater systems (Aravena et al., 1993; Aravena and Robertson, 1998).

In a previous article, we described the potential effects of OWTS on the nitrogen load in 24 streams in watersheds impacted with high density (HD) and low density (LD) of OWTS in Metropolitan Atlanta, Georgia using four sets of synoptic stream samples collected in 2011 and 2012 (Oliver et al., 2014). We found that as OWTS density increased above a threshold of about 100 OWTS km⁻², NO₃⁻ concentrations increased linearly. Our objective in this article is to confirm the impact of OWTS through additional sampling in 2013 and 2014 of the same streams; analysis of variance of the effect of OWTS density and season; the use of dual-isotope analysis (nitrogen and oxygen in nitrate) to identify sources and determine the effect of denitrification and mixing; and stream walks to identify areas where animals had access to the streams.

3.3. Materials and Methods

3.3.1. Study Area

The study area is in the Southern Piedmont region east of Atlanta, GA in Gwinnett County (Figure 3-1), and it has been described in detail in Landers and Ankorn (2008). The average annual precipitation is 1278 mm (National Weather Service, 2007). In this area 24 watersheds were selected, ranging in area from 0.181 to 8.8 km² (Table 3-1). The watersheds are located in the Ocmulgee and Oconee River basins, which drain to the Altamaha River and Atlantic Ocean. An arbitrary density of 75 OWTS km⁻² was used to divide these into 12 LD and 12 HD watersheds. Other watershed selection criteria included similar geological setting, precipitation, climate, and accurate sampling locations. Weather data for the area was collected from the Georgia Automated Environmental Monitoring Network (Georgia Weather, 2007).

3.3.2. *Sample Collection and Analysis*

Synoptic water sampling was undertaken three times per year (April/ March, July, and November) to obtain the seasonal variation during nine sampling events from November 2011 to July 2014 (the sampling measurements from November 2011 to November 2012 were conducted by Oliver et al., 2014). Water samples were collected during base flow periods at the outlets of the 24 selected watersheds. Appropriate periods of base flow were selected based on stream hydrographs from nearby USGS gage stations (site numbers: 02205522 and 02207385) and an antecedent period of 72 h without precipitation.

All water samples were refrigerated and processed within 24 h of collection. For analyzing $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and Cl^- concentrations, water samples were filtered through Supor-450 membrane filter (Pall corporation, MI) and stored in acid-washed, high density polyethylene (HDPE) plastic bottles, and were kept frozen until analysis. Prepared samples were sent to the University of Georgia Feed and Environmental Water Laboratory for $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, Cl^- , and TKN analyses. Samples were analyzed for TKN using a modified version of the micro-Kjeldahl methods (Clesceri et al., 1998). $\text{NH}_4^+\text{-N}$ concentration in the water samples were measured following distillation-titration according to the method of Bremner (1965). Organic N concentrations were calculated by subtracting $\text{NH}_4^+\text{-N}$ concentrations from TKN concentrations. Determination of $\text{NO}_3^-\text{-N}$ and Cl^- concentrations were carried out by ion-chromatographic separation followed by conductometric detection for inorganic anions according to USEPA Method 300.1 (Hautman et al., 1997). Analysis of ^{15}N and ^{18}O values of NO_3^- of 120 filtered water samples with known $\text{NO}_3^-\text{-N}$ concentrations were conducted at the University of

California, Davis, Stable Isotope Facility using a bacteria (*Pseudomonas aureofaciens*) denitrification assay based on the isotope ratio analysis of nitrous oxide (N₂O); a detailed description of the analysis technique is given by Sigman et al. (2001). All values of $\delta^{15}\text{N}$ were reported with respect to atmosphere and all values of $\delta^{18}\text{O}$ were reported with respect to the Vienna Standard Mean Ocean Water (V-SMOW).

3.3.3. *Statistical Analysis*

Data were tested for normality before analysis using the Shapiro-Wilk statistical test. Two-way analysis of variance (ANOVA) was used to determine the main effect of OWTS density, seasonal variations, and their interaction on TN, NO₃⁻-N, organic N, NH₄⁺-N, and Cl⁻ concentrations. A Multiple Comparison Procedure (Tukey Test) was conducted among the groups with statistically significant differences. Linear regression analysis was performed to determine the relationship of N components and Cl⁻ concentrations with OWTS density for both LD and HD watersheds. Pearson Product-Moment Correlation (PPMC) analysis was applied to determine the correlation between water quality parameters and OWTS density, sanitary sewer line density, and percent of forest, hay, and range areas. All data analyses were performed in SAS.9.3 (SAS Institute Inc., NC) at the 95% confidence level ($\alpha=0.05$).

Nine of the watershed outlets were located on the same stream as another outlet so that these watersheds were nested (Figure 3-1). Outlets 3 and 4 were upstream of outlet 1; outlet 5 was upstream of outlet 6; outlet 9 was upstream of outlet 10; outlet 14 was upstream of outlet 12; outlet 20 was upstream of outlet 16; outlets 18 and 19 were upstream of outlet 17; and outlet 23 was upstream of outlet 22. In order to determine the mean NO₃⁻

concentrations, we used an area-weighted average in which NO_3^- concentrations in each group of nested watersheds were normalized based on drainage area. The drainage areas for the outlets farther downstream included in the nested watersheds. The correlation between NO_3^- -N concentrations, and OWTS density and different land uses in LD and HD watershed groups were examined in using this nested watershed approach.

3.4. Results and Discussion

3.4.1. Nitrogen Compounds

3.4.1.1. Nitrate

A plot of NO_3^- -N concentrations as a function of OWTS density within LD and HD watersheds is shown in Figure 3-2a for the nine sampling events. The four sets of sampling events from Oliver et al. (2014) are shown in black and the five additional sampling events taken from April 2013 to July 2014 are shown in red. There was a linear decrease in NO_3^- -N concentrations with increasing OWTS density in the LD watersheds ($r^2 = 0.27$, $p < 0.001$), and a linear increase with increasing OWTS density in the HD watersheds ($r^2 = 0.63$, $p < 0.001$), consistent with the findings of Oliver et al. (2014). As expected, a statistically significant effect of OWTS density on NO_3^- -N concentrations was observed between both watershed groups ($p = 0.004$) (Table 3-2). The main land cover categories in the HD watersheds were residential (68%), followed by forest (20%), and to a lesser extent hay (3%), and range (1%) (Table 3-1). Samples from April 2013 to July 2014 showed significantly higher NO_3^- -N concentrations in comparison with samples from Oliver et al. (2014) in both HD and LD watersheds ($p < 0.05$) (Figure 3-2a). This was probably due to significantly higher measured base-flow yields ($\text{m}^3 \text{ s}^{-1}$ of stream flow per km^2 of watershed

area) from April 2013 to July 2014 ($p < 0.001$). Higher base-flow yields would result in more NO_3^- -N discharged from groundwater into the streams.

Mean NO_3^- -N concentrations in the HD watersheds showed positive and strong correlation with OWTS density ($r = 0.93$, $p < 0.0001$), and no significant correlation with percent of forest, hay, or range areas. In the HD watersheds, 8 out of 12 watersheds were served with both OWTS and sanitary sewer systems, with sanitary sewer line density ranging from 2.08 to 10.62 km km⁻² (Table 3-1). However, no significant correlation between mean NO_3^- -N concentrations and sanitary sewer line density was observed, suggesting that leaking sewer lines were not primary sources. Therefore under base flow conditions, elevated NO_3^- -N concentrations in the HD watersheds were consistent with a groundwater source associated with increasing OWTS density. Failing OWTS that result in effluent coming to the soil surface were unlikely to be a source of the high NO_3^- -N concentrations under base-flow conditions (the first and second types as we have defined failures), since these systems would be expected to contribute NO_3^- -N through surface runoff instead of groundwater discharge (USEPA, 2002). However failing septic systems that result in incomplete treatment of effluent in the unsaturated zone (the third type of failure) could be a source. If we used the area-weighted analysis for nested HD watersheds, we still found a significant positive correlation between NO_3^- -N concentrations and OWTS density ($r = 0.66$, $p < 0.0001$) (data not shown).

In the LD watersheds, the correlations between mean NO_3^- -N concentrations and OWTS density, sanitary sewer line density, percent of hay area, and percent of forest cover were not statistically significant. In this suburban region, most of the agricultural land cover is hay and pasture and (USDA, 2012). Horses and cattle commonly graze the pastures. So,

another possible source of NO_3^- in base flow is waste leaching from livestock farms; including manure produced by livestock on the farm or poultry litter from off-farm sources as well as direct discharge of animal waste into or near streams (Hooda et al., 2000). There were no data available on livestock density below the county level so livestock density could not be determined for each watershed. However, mean NO_3^- -N concentrations in the LD watershed group were positively and significantly correlated with the percentage of range land cover ($r = 0.59$, $p = 0.04$). Therefore, livestock waste or poultry manure may have been the source of the elevated NO_3^- -N concentrations in streams of the LD watershed group. Among this group, watershed 2 had the highest mean NO_3^- -N concentration (3.37 mg N L⁻¹ compared with the mean of 1.25 mg N L⁻¹ for the other 11 LD watersheds). This watershed had the highest percentage of range land cover (16.5%) in this group. Low density watersheds 6, 7, and 8 had NO_3^- -N concentrations above the mean concentrations in almost all sampling events. Stream walks indicated that livestock, particularly cattle, had accessed streams in these three watersheds, with no evidence of livestock encroachment in any of the other LD watersheds. This was further evidence that livestock waste contributed to the high NO_3^- -N concentrations in the LD basins.

Although sanitary sewer line density did not show a significant correlation with NO_3^- -N concentrations in the LD watersheds, watershed 2 had high sewer line density. Stream walks revealed the presence of sewer manholes upstream of the sampling point in watershed 2. Therefore, sewer line leakage is another possible source of the high NO_3^- -N concentrations in this watershed.

Using the nested watershed analysis in the LD watersheds, a significant positive correlation was observed between NO_3^- -N concentrations and percent of forest ($r = 0.52$, p

< 0.0001), hay ($r = 0.46$, $p < 0.0001$), and range ($r = 0.77$, $p < 0.0001$) land uses. The NO_3^- -N concentrations correlations with hay and range areas are consistent with the non-nested analysis (hay area was significant at the $p = 0.05$ level). However, we cannot explain the correlation with forest area and think the un-nested analysis is more revealing.

Seasonally, mean NO_3^- -N concentrations were 1.71, 1.64, and 1.46 mg N L⁻¹ for July, March/April, and November respectively (Figure 3-3a). There were no significant differences due to the main effect or interaction of seasons on NO_3^- -N concentrations ($p > 0.05$) (Table 3-2). This is consistent with an OWTS groundwater source that emitted NO_3^- -N concentrations at a steady rate throughout the year.

3.4.1.2. Organic Nitrogen and Ammonium

A plot of organic N concentrations and OWTS density is shown in Figure 3-2b, with the four sampling events from Oliver et al. (2014) shown in black and the five additional sampling events shown in red. There was no clear trend in organic N concentrations with OWTS density in the LD or HD watersheds. Statistical analysis of the main effect of density did not demonstrate significant differences in organic N concentrations between HD and LD watersheds.

Seasonal variations in organic N concentrations were statistically significant ($p < 0.0001$) (Table 3-2), with higher mean values in July (0.78 mg N L⁻¹) than in November (0.42 mg N L⁻¹) and March/April (0.28 mg N L⁻¹) (Figure 3-3b). This is consistent with a higher organic N concentration of summer (“green-fall”) leaves than fall, senesced, leaves in the Southern part of the United States (Risley and Crossley Jr, 1993). There were no

significant correlations between mean organic N concentrations and basin characteristics (data not shown).

There was no trend in NH_4^+ -N concentrations as a function of OWTS density in either LD or HD watersheds (Figure 3-2c) and the concentrations were low (mean of 0.08 mg N L^{-1}) (Figure 3-3c). These results are consistent with a groundwater source of N since NH_4^+ -N is sorbed to soil and nitrified into NO_3^- under aerobic conditions such as in OWTS drain fields. Two-way ANOVA revealed insignificant effects of OWTS, season, and their interaction for NH_4^+ -N concentrations ($p > 0.05$) (Table 3-2).

3.4.1.3. Total Nitrogen

Average total nitrogen (TN) of samples collected during this study consisted mostly of NO_3^- -N (73% in HD and 68% in LD watersheds) and organic N (23% in HD and 28% in LD watersheds). A graph of TN concentrations in each watershed as a function of OWTS density for all 9 sampling events (Figure 3-2d) follows the same trend as NO_3^- -N concentrations (Figure 3-2a): a linear decrease in TN concentrations with increasing OWTS density in LD watersheds ($r^2 = 0.24$), and a linear increase in TN concentrations in HD watersheds ($r^2 = 0.59$).

The main effect of OWTS density ($p = 0.008$) and season ($p < 0.0001$) on TN concentrations were statistically significant between LD and HD watersheds (Table 3-2). In the LD watersheds, mean TN concentrations for all 9 sampling events were highest in watersheds 2 (3.99 mg L^{-1}) and 8 (3.05 mg L^{-1}), compared to a mean concentration for the other 10 LD watersheds of 1.71 mg L^{-1} . This would be expected because NO_3^- was the dominant form of N and the highest NO_3^- -N concentrations were observed in watersheds 2

and 8. Within seasons, there were statistically significant differences in mean TN concentrations between the July (2.59 mg N L^{-1}) and March/April (2.01 mg N L^{-1}) samples, and the July and November (1.95 mg N L^{-1}) samples (Figure 3-3d), with $p = 0.0005$ and 0.0001 , respectively. This was due to the seasonal effect on organic N, discussed in the previous section. No statistically significant interaction between density and season on TN concentrations was observed ($p > 0.05$) (Table 3-2).

Total N concentrations (consisting for the most part of NO_3^-) in the streams were at a minimum when OWTS density was in the range of 50 to 100 systems km^{-2} . In this range, urban development was low and agriculture land use did not dominate. Under these circumstances, the stream water quality (from a nitrogen point of view) was quite good. Above this OWTS density, for each increase of 100 units km^{-2} , TN and NO_3^- -N increased by about 1 mg N L^{-1} and at the highest density TN concentrations were in the range of 3-5 mg N L^{-1} (Figure 3-2a and 3-2d). In the LD watersheds, TN concentrations were in the range of 2-5 mg N L^{-1} at the lowest OWTS densities where agricultural land use was dominant as shown by Oliver et al. (2014).

These concentrations are well above the threshold of 0.42 mg N L^{-1} (inorganic N) where the aquatic food web becomes disrupted as a result of accelerating loss rates of in-stream organic matter according to the recent studies of headwater streams in the Blue Ridge Mountains. Carbon dioxide (CO_2) emissions are also increased due to greater activity of a previously nutrient-limited heterotrophic community in response to increase of inorganic N concentrations (Benstead et al., 2009; Kominoski et al., 2015; Suberkropp et al., 2010).

3.4.1.4. Chloride

A plot of Cl^- concentrations as a function of OWTS density is shown in Figure 3-2e with the four sampling events from Oliver et al. (2014) shown in black and the five additional sampling events shown in red. Cl^- concentrations displayed a similar trend to NO_3^- -N and TN with OWTS density in the HD watersheds with a significant linear increase in Cl^- concentrations as a function of OWTS density ($r^2 = 0.42$). This trend supports the idea that OWTS were the primary source of N in the HD watersheds. Other potential sources of Cl^- such as road salting and water softeners (Burton and Stensel, 2003; Kelly et al., 2008) were unlikely because they are not commonly used in this area.

In the LD watersheds, Cl^- concentrations decreased with increasing OWTS density, but the Cl^- concentrations were in a narrower and lower range (with the exception of one high value from watershed 1) compared to the HD watersheds. This narrow range contrasted to the wide range in NO_3^- -N and TN seen in the LD watersheds (3-2a and 3-2d). Watersheds 7 and 8 had higher mean Cl^- concentrations (5.27 and 5.46 mg L^{-1}) compared to the mean Cl^- concentrations in other LD watersheds (4.66 mg L^{-1}) and this could have been related to livestock access to the streams observed in stream walks. In the LD watershed 2, the highest mean Cl^- concentrations among all LD watersheds was observed (6.44 mg L^{-1}) and this may have been a result of sanitary sewer line leakage (O'Driscoll et al., 2010). However, the overall low range of Cl^- values in the LD watersheds compared to the HD watersheds seemed to indicate at least one source of N in the LD watersheds that was low in Cl^- and therefore not animal or human waste.

The main effect of season was significant for Cl^- concentrations ($p = 0.0007$) (Table 3-2), with higher mean Cl^- concentration observed in July (7.05 mg L^{-1}), followed by

March/April (5.98 mg L⁻¹), and then November (5.56 mg L⁻¹) (Figure 3-3e). In the Piedmont region, GA base flow is highest during late winter and early spring (Rose and Fullagar, 2005), so dilution may have lowered Cl⁻ concentrations in the March/April sampling events. Higher Cl⁻ concentrations in the July samples was likely the result of lower base flow in this season compared with the March/April samples (data not shown).

3.4.2. Nitrogen and Oxygen Isotopes of Nitrate

Scatter-plots of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ values are shown in Figure 3-4a (LD watersheds) and 3-4b (HD watersheds) for the five sampling events of April 2013, July 2013, November 2013, March 2014, and July 2014. Common fields for different sources of NO₃⁻ are shown with rectangles as reported by Silva et al. (2002) and Michener and Lajtha (2008). Generally, $\delta^{15}\text{N-NO}_3^-$ values were observed between -10 and +25‰. High $\delta^{15}\text{N-NO}_3^-$ values are common in animal and human wastes due to ammonia volatilization and oxidation of ammonium to NO₃⁻. Soil NO₃⁻ can originate from the natural oxidation of organic nitrogen and it can be derived from synthetic fertilizer or human/animal waste (Hornberger, 1999; Michener and Lajtha, 2008). Therefore, $\delta^{15}\text{N-NO}_3^-$ values of soil NO₃⁻ are between synthetic ammonium fertilizer and animal/human waste and they overlap with these two sources (Silva et al., 2002). Also, microbial denitrification and assimilation by plants increase the $\delta^{15}\text{N-NO}_3^-$ value of residual NO₃⁻ (Hornberger, 1999).

In Figure 3-4a, all of the samples for the LD watersheds were centered in the fields of soil NO₃⁻ or animal/human waste. Samples from LD watersheds 2 (which had the highest NO₃⁻-N and Cl⁻ concentrations) and 8 (where stream walks revealed cattle in the streams) had mean values of 9.01‰ for $\delta^{15}\text{N-NO}_3^-$ and 7.18‰ for $\delta^{18}\text{O-NO}_3^-$ that were in the field

of animal/human waste. We can conclude that the main source of NO_3^- -N in these two watersheds was animal waste. Samples with $\delta^{15}\text{N}$ - NO_3^- and $\delta^{18}\text{O}$ - NO_3^- values in the field of soil nitrate were mainly from LD watersheds 3 and 4 with a high percentage of forested area. These could be related to oxidation of organic-N to NH_4^+ and then NO_3^- , possibly from leaf litter breakdown in forested areas in these LD watersheds.

However, for HD watersheds all the samples were centered in the field of animal/human waste, overlapping with the soil NO_3^- field at the lowest values (Figure 3-4b). In these watersheds, a significant and positive correlation between NO_3^- -N concentrations and OWTS density was observed (Figure 3-2a), indicating that OWTS were likely the primary source of N. In addition, leaching from domestic animal wastes such as dogs and cats may contribute to the N load in urban watersheds. We compared the estimated N loads from OWTS and domestic animal wastes to determine if animal sources in HD watersheds could have a significant effect on N load. The N load contribution from OWTS was calculated based on the OWTS average discharge per capita for Gwinnett County (276 L day^{-1}) multiplied by the number of OWTS in each HD watershed. It was assumed that the TN concentration of the septic effluent was 60 mg L^{-1} (McCray et al., 2005) and 50% of the N was lost in the septic tank and drain field as a result of denitrification and volatilization in a Piedmont soil (Bradshaw et al., 2013). For estimation of the total N load from domestic animal waste, we assumed N loading of 2 kg per dog per year and 1.5 kg per cat per year (Valiela et al., 1997). The total number of cats and dogs in HD watersheds was calculated based on the ratios of 8 people per dog and 12 people per cat (Valiela et al., 1997), multiplied by the number of people in each HD watershed (the number of houses in each HD watershed multiplied by 3.09 person per household) (US

Census, 2015). Also, we assumed that 50% of N from cat and dog wastes was lost due to volatilization (Valiela et al., 1997). The contributions of dogs and cats were less than 1% of the N loading from OWTS. Therefore, the N load from domestic animals in HD watersheds was negligible relative to the OWTS contribution.

Another nitrogen source in urban watersheds can be leaching from synthetic nitrogen lawn fertilizers. However, less than 10% of applied N fertilizer is estimated to be lost through leaching (Petrovic, 1990). Dual isotopic analysis did not indicate any samples in the field of NO_3^- and NH_4^+ fertilizers (Figure 3-4b). Therefore, lawn fertilizer was unlikely to have been the primary source of nitrogen export in the HD watersheds.

3.4.3. Mixing and Denitrification

Plotting $\delta^{15}\text{N}-\text{NO}_3^-$ concentrations as a function of NO_3^- -N concentrations can be used to determine if $\delta^{15}\text{N}-\text{NO}_3^-$ values have been modified due to mixing from two or more sources or if denitrification has modified the values. If $\delta^{15}\text{N}-\text{NO}_3^-$ values increase with NO_3^- -N concentrations, it is a sign that mixing of high and low sources has occurred. If the $\delta^{15}\text{N}-\text{NO}_3^-$ values decrease with NO_3^- -N concentrations, it is a sign that denitrification has occurred (Mayer et al., 2002). In Figure 3-5a and 3-5b, a second degree polynomial regression showed a clear trend of increasing mean $\delta^{15}\text{N}-\text{NO}_3^-$ values with increasing mean NO_3^- -N concentrations in both LD ($r^2 = 0.77$) and HD ($r^2 = 0.51$) watersheds. This pattern suggested that mixing of NO_3^- from at least two sources, one with low $\delta^{15}\text{N}-\text{NO}_3^-$ values and another with high $\delta^{15}\text{N}-\text{NO}_3^-$ values, had occurred. This would be consistent with an animal waste source with a high $\delta^{15}\text{N}$ value mixing with a low $\delta^{15}\text{N}$ value source such as soil NO_3^- derived from organic N in the LD watersheds. In the HD watersheds, it is likely

that OWTS waste was the primary (high $\delta^{15}\text{N}$ value) source, but some mixing occurred with synthetic lawn fertilizers or soil NO_3^- (low $\delta^{15}\text{N}$ value) sources in the HD watersheds.

Although the plots in Figure 3-5 indicated mixing of NO_3^- from at least two sources, microbial denitrification probably played an important role in reducing NO_3^- concentrations in the soil, groundwater, and riparian zones. In Figure 3-4a and 3-4b, a regression line was fitted to the plot of $\delta^{18}\text{O}-\text{NO}_3^-$ versus $\delta^{15}\text{N}-\text{NO}_3^-$ to obtain the isotopic signature of denitrification in both LD and HD watersheds. The ratio of enrichment of $\delta^{18}\text{O}-\text{NO}_3^-$ to $\delta^{15}\text{N}-\text{NO}_3^-$ (the slope of the regression line) for denitrification to be significant is 2:1 or a slope of 0.5 (Silva et al., 2002). The slopes of the regression lines were 0.24 and 0.49 for LD and HD watersheds respectively, indicating that denitrification was a more significant process in the HD watersheds than in the LD watersheds. Denitrification was more likely in the HD watersheds because OWTS drain fields were likely to have been wetter than pastures in the LD watersheds. Bradshaw et al. (2013) estimated that 52% of the N in a typical OWTS for this region was lost due to denitrification.

3.5. Conclusions

Building on our previous work, the analysis of N compounds in this study revealed a significant linear increase in TN and NO_3^- -N concentrations with OWTS density above a threshold of about 75 OWTS per square kilometer and a significant linear decrease in TN and NO_3^- -N concentrations with increasing OWTS density below this threshold. Nitrogen and oxygen isotopes of NO_3^- indicated that the predominant source of NO_3^- in HD watersheds was consistent with animal or human waste. Since there were few animals in these developed watersheds, we conclude that OWTS were the dominant source with some

mixing with another source that could be lawn fertilizers, organic N from leaf litter, or both. In LD watersheds, positive and significant correlations between grazed land and NO_3^- -N concentrations were found. Dual isotope analysis supported the idea that animal waste mixing with a source that had low Cl^- content and low values for $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ occurred in LD watersheds. Organic N concentrations were higher in July sampling events, likely as a result of higher concentrations of organic N in “green-fall” leaves than fall litter leaves. The effect of OWTS is not likely to have been due to failing systems that cause effluent to come to the surface, but could have been due to failing systems that result in incomplete treatment of the effluent in the unsaturated zone. The findings of this study confirm the importance of OWTS density on water quality in small urbanizing watersheds and can be used in other Piedmont regions where nitrogen Total Maximum Daily Loads (TMDL) are being developed, such as the Chesapeake Bay. Also these results can be used to develop hydrologic models to better understand the influence of OWTS on water quality in watershed scale.

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3.6. References

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Figure 3-1- Location of the study area, 24 watersheds boundaries, sampling points, and onsite wastewater treatment system (OWTS), Gwinnett County, Georgia (modified from Landers and Ankcorn, 2008).



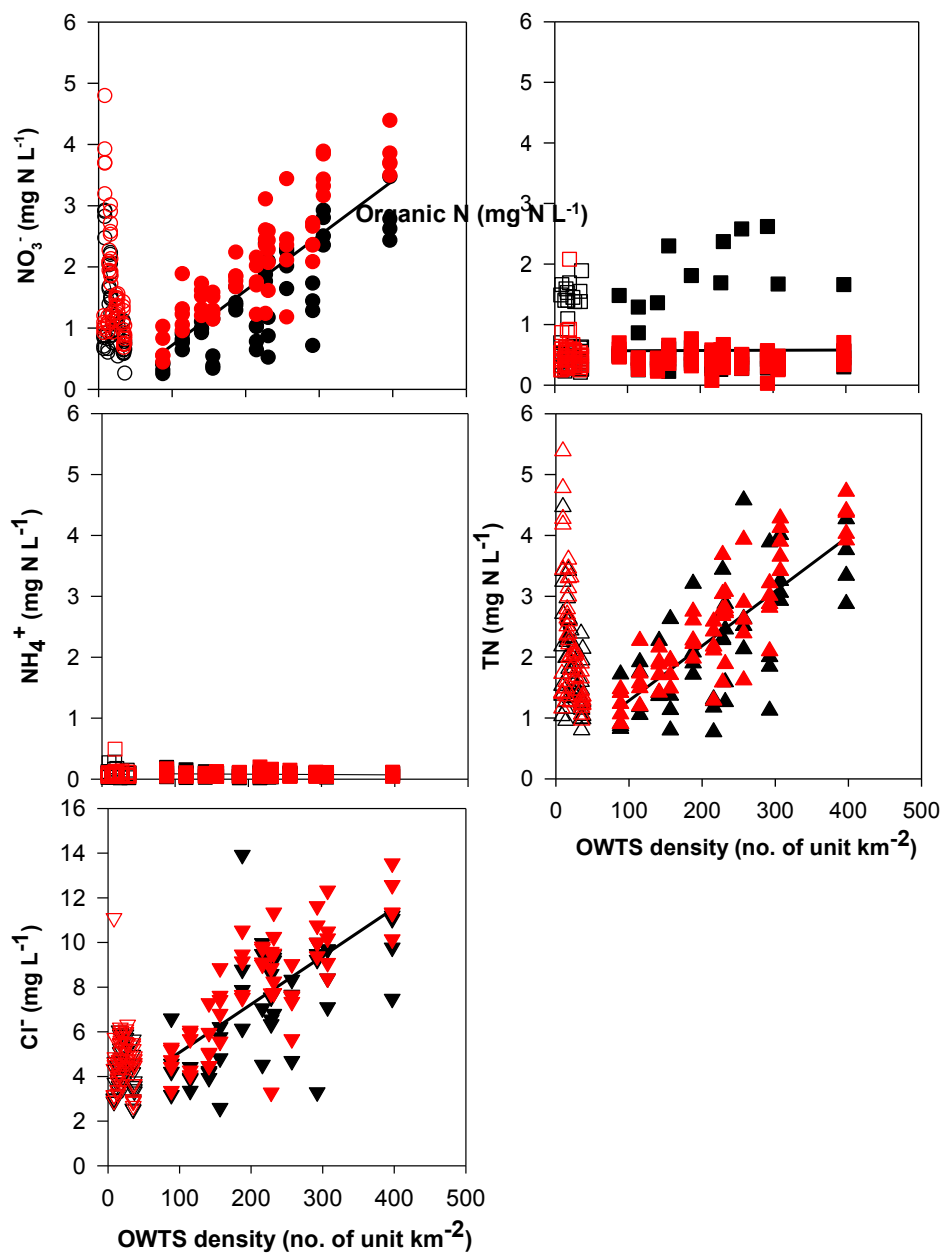


Figure 3-2- Linear regression graph of (a) NO_3^- -N, (b) organic N, (c) NH_4^+ -N, (d) TN, and (e) Cl^- concentrations as a function of OWTS density in both low density (LD) (hollow symbols) and high density (HD) (solid symbols) watersheds. Sampling events from November 2011 to November 2012 were conducted by Oliver et al. (2014) and shown in black, and sampling events from April 2013 to July 2014 were shown in red.

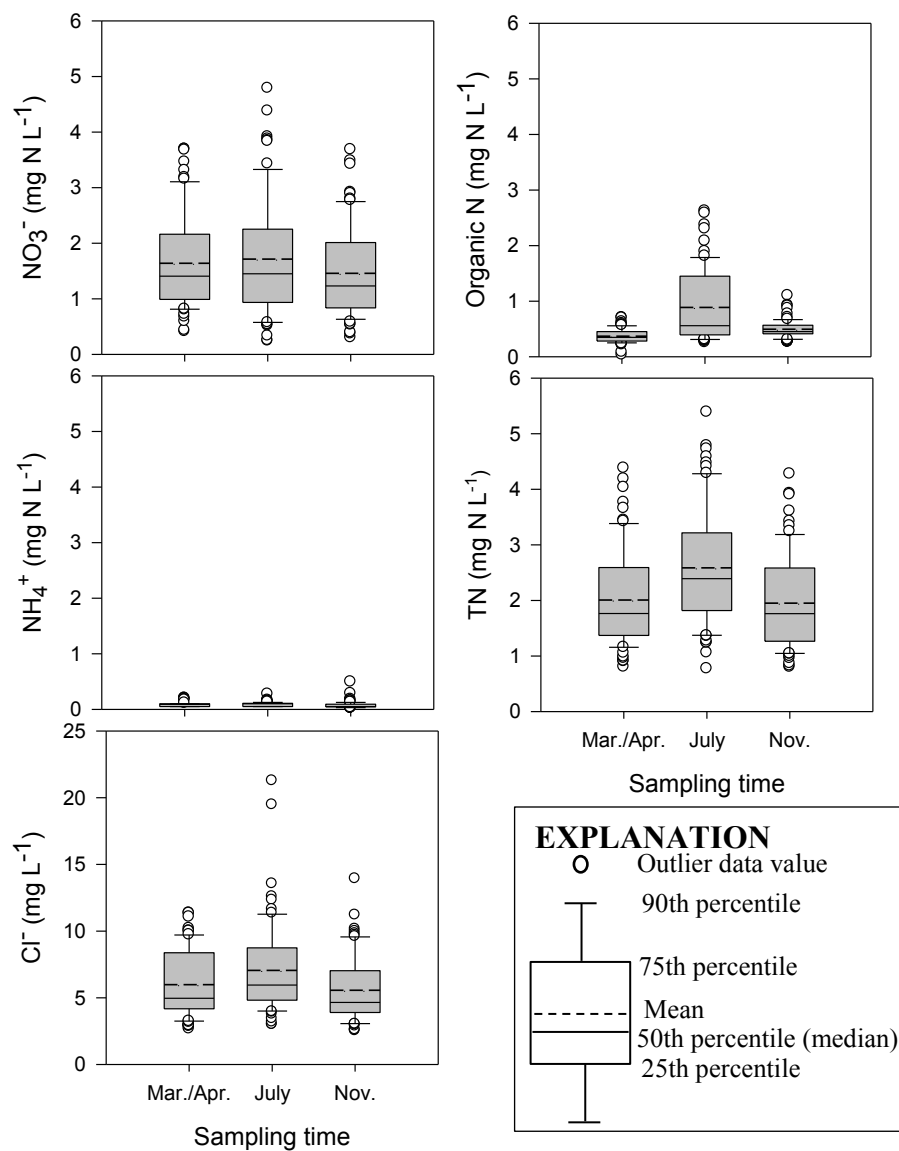


Figure 3-3- Boxplots showing differences in (a) NO₃⁻-N, (b) organic N, (c) NH₄⁺-N, (d) TN, and (e) Cl⁻ concentrations by season (March/April, July, and November) in all 24 watersheds from November 2011 to July 2014.

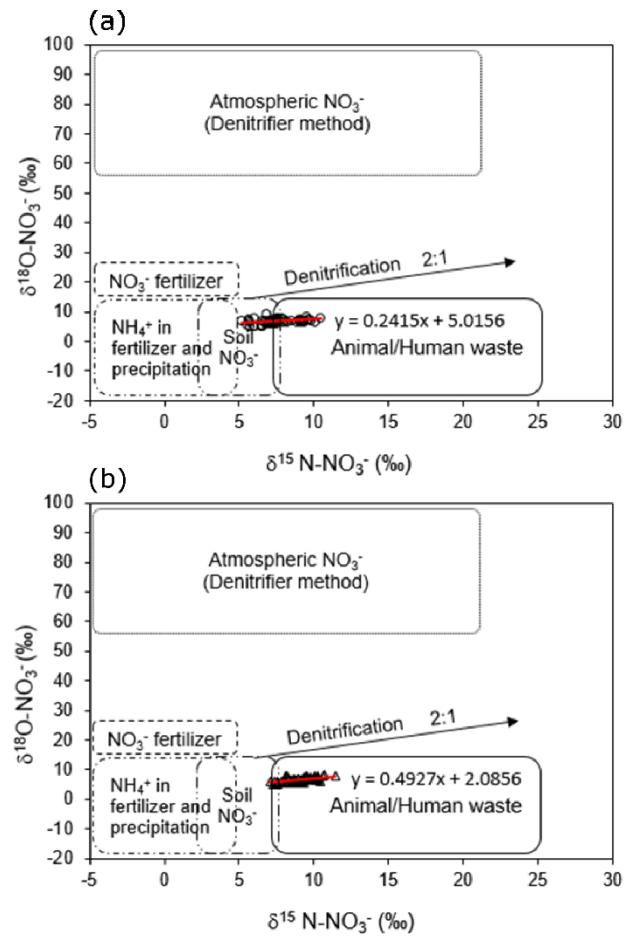


Figure 3-4- Scatter plots showing the $\delta^{15}\text{N-NO}_3^-$ (‰) vs. $\delta^{18}\text{O-NO}_3^-$ (‰) of samples collected in April 2013, July 2013, November 2013, March 2014, and July 2014 in watersheds impacted by (a) low density (LD) (n = 60), and (b) high density (HD) (n = 60) of OWTS. Common fields for different sources of nitrate are shown as reported by Silva et al. (2002) and Michener and Lajtha (2008). Denitrification trend was displayed as an arrow.

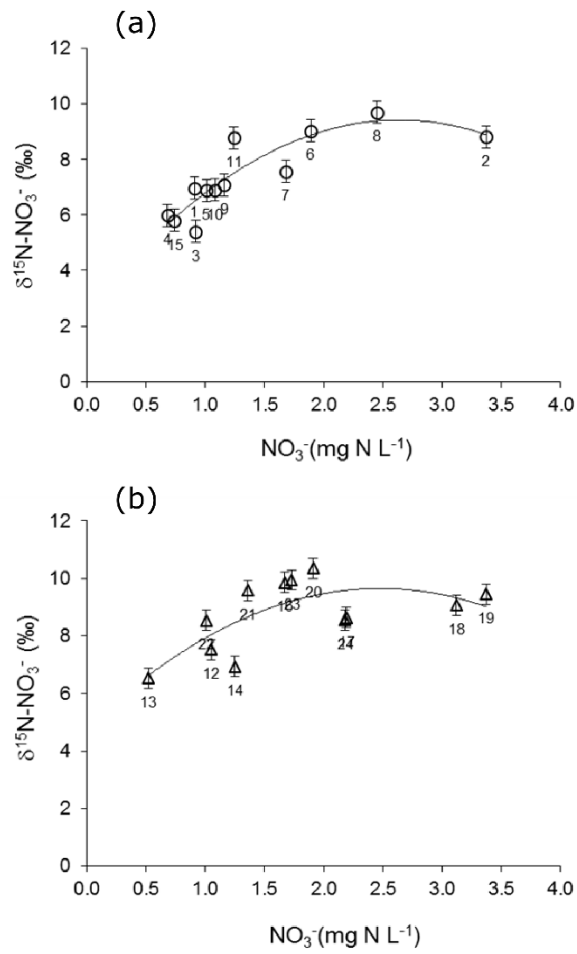


Figure 3-5- Plot of a second-order polynomial regression of mean $\delta^{15}\text{N-NO}_3^-$ values versus mean NO_3^- -N concentrations for (a) low density (LD) ($r^2 = 0.77$ and $n = 12$), and (b) high density (HD) ($r^2 = 0.51$ and $n = 12$) watersheds. Number below each symbol represents the watershed ID.

Table 3-1- Characteristics of the study area watersheds in Gwinnett County, GA.

Watershed ID	HD or LD of OWTS	Drainage area	OWTS density	Median distance of OWTS to stream	Sanitary sewer line density	Mean slope	Land cover†			
							Forest ‡	Residential §	Hay	Range¶
		km ²	unit km ⁻²	m	km km ⁻²		%			
1	LD	8.39	8	163	1.05	8.8	26.19	9.17	17.82	3.98
2	LD	1.55	10	126	4.98	10.6	35.72	12.96	24.71	16.46
3	LD	2.67	14	163	0.00	8.5	25.55	5.13	19.22	5.85
4	LD	0.62	36	172	0.00	7.3	42.10	18.82	28.36	7.46
5	LD	1.48	20	86	0.00	5.8	29.06	16.40	49.18	2.89
6	LD	5.28	15	108	3.14	6.5	20.81	10.71	34.23	2.38
7	LD	1.11	18	90	0.00	10.6	44.30	41.59	9.78	3.74
8	LD	1.27	17	94	0.00	9.2	31.95	14.26	47.75	5.81
9	LD	2.95	27	159	1.06	7.7	25.13	41.19	25.95	4.90
10	LD	4.4	34	119	0.00	8.3	17.07	15.28	10.94	0.94
11	LD	4.2	25	119	1.39	7.8	30.80	31.44	28.37	4.56
15	LD	1.68	37	140	13.09	4.6	14.52	71.34	9.88	2.62
12	HD	3.29	115	105	2.43	9.1	14.65	19.83	3.78	0.64
13	HD	8.81	88	117	8.63	8.0	25.72	59.00	6.34	4.03
14	HD	1.74	141	104	4.30	8.5	22.76	62.50	6.04	5.19
16	HD	2.59	187	99	5.76	5.7	15.00	56.21	0.14	0.20
17	HD	1.68	230	138	0.00	7.5	11.25	42.05	8.35	0.0
18	HD	0.98	308	151	0.00	7.4	26.31	41.89	1.28	0.0
19	HD	0.18	373	105	0.00	7.8	22.11	74.37	0.00	0.0
20	HD	0.54	290	83	0.00	6.0	25.54	71.79	0.00	0.0
21	HD	1.14	214	63	2.08	8.6	23.33	64.33	3.85	0.0
22	HD	1.94	157	63	10.49	7.0	16.87	57.78	1.62	1.34
23	HD	0.52	233	65	4.41	7.3	22.37	72.28	3.29	0.0
24	HD	0.67	253	55	10.62	7.6	18.77	75.53	1.87	0.95
Mean	LD	2.97	22	128	2.06	8.0	28.60	24.02	25.52	5.13
	HD	2.01	216	96	4.06	7.5	20.39	58.30	3.05	1.03

† Land cover percentage determined using National Land Cover Dataset (NLCD) for 24 watersheds in Gwinnett County, GA in ArcGIS 10.2.2 (ArcGIS, 1999)

‡ Including deciduous, evergreen, and mixed forests; § including high, medium, and low density residential; and ¶ including range-grasses.

Table 3-2- *P*-values of two-way ANOVA test for the main effect of onsite wastewater treatment system (OWTS) density and season, and their interaction on nitrogen compounds and chloride concentrations. The *p*-values less than $\alpha = 0.05$ indicate statistically significant difference in the mean values and are shown in italics.

Parameter	TN	NO₃⁻	Organic N	NH₄⁺	Cl⁻
OWTS Density †	<i>0.008</i>	<i>0.004</i>	0.76	0.34	<i><0.0001</i>
Season ‡	<i><0.0001</i>	0.21	<i><0.0001</i>	0.10	<i>0.0007</i>
Density × Season	0.66	0.74	0.78	0.17	0.54

† Between watersheds impacted by high density (HD) and low density (LD) of OWTS.

‡ Between March/ April, July, and November.

4. MODELING THE EFFECT OF ONSITE WASTEWATER TREATMENT SYSTEMS ON NITRATE LOAD USING SWAT IN AN URBAN WATERSHED OF METROPOLITAN ATLANTA, GEORGIA¹

¹Hoghooghi, N., D.E. Radcliffe, M.Y. Habteselassie, and J. Jeong. To be submitted to the Journal of Environmental Quality.

4.1. Abstract

On-site wastewater treatment systems (OWTSs) can be a source of nitrogen (N) pollution in both surface and ground waters. In Metropolitan Atlanta, GA more than 26% of homes are on OWTSs. In our previous article using the Soil Water Assessment Tool (SWAT) with a new OWTS algorithm, we showed that OWTS produced a 3% increase in stream flow in Big Haynes Creek watershed in Metropolitan Atlanta. The objective of this study was to estimate the effect of OWTS, including failing systems, on NO_3^- load in the same watershed. Big Haynes Creek has a drainage area of 44-km² with mainly urban land use (67%) and most of the homes use OWTS. A USGS gage station where stream flow was measured daily and NO_3^- concentrations were measured approximately monthly was selected as the outlet. The model was simulated from 1 January 2003 to 31 December 2014. Overall, the model showed satisfactory daily stream flow and NO_3^- loads with Nash-Sutcliffe coefficients of 0.62 and 0.58 for the calibration period, and 0.67 and 0.33 for the validation period, respectively at the outlet of the Big Haynes watershed. OWTS caused an average increase in NO_3^- load of about 23% at the watershed scale and 29% at the sub-basin outlet with the highest density of OWTS. Failing OWTS were estimated to be 1% of the total systems and did not have a large impact on stream flow or NO_3^- load. The NO_3^- load was 74% of the total N load in the watershed, showing the important effect of OWTS on stream loads in urban watersheds.

Abbreviations: HD, High density; HRU, hydrologic response unit; LD, low density; NS, Nash-Sutcliffe; On-site wastewater treatment system, OWTS; 95PPU, 95% prediction uncertainty; SWAT, Soil and Water Assessment Tool; SUFI-2, Sequential Uncertainty Fitting; SWAT-CUP, SWAT Calibration and Uncertainty Program.

4.2. Introduction

Onsite wastewater treatment systems (OWTs), also known as septic systems, collect, treat, and release wastewater effluent from about 26 million homes, businesses, and recreational facilities in the United State (USEPA, 2002). Failing or high density of OWTS can be a source of nitrogen (N) inputs to both surface and ground waters. Conventional OWTS are not designed to remove N. Oakley et al. (2010) found that N loads were reduced by only 10-20% before discharge to the soil. From 2000 to 2010 the population in metro Atlanta increased about 24%, second-highest increase among the largest metro areas in the US (US Census, 2010). In this region about 26% of total homes are on OWTS (MNGWPD, 2006) and the number is expected to increase with population growth.

A couple of studies have shown that OWTS can increase stream base flow through the discharge of effluent into groundwater (Burns et al., 2005; Simmons and Reynolds, 1982). Gold et al. (1990) and (Rich, 2005) found that OWTSs are the main source of nitrate (NO_3^-) groundwater and surface water contamination, and are listed as a potential source of N in Total Maximum Daily Load (TMDL) reports of nutrient impairments by EPA (USEPA, 2007). In metropolitan Atlanta, the effect of OWTS density on base-flow yield during extreme drought conditions in 2007 was investigated by Landers and Ankorn (2008) in a one-time sampling. Mean base flow yield of watersheds with a high density (HD) of OWTS (having > 75 OWTSs km^{-2}) was 90% greater than that of watersheds with a low density (LD) of OWTS (< 75 OWTSs km^{-2}). In the same watersheds, we examined the potential effect of OWTS on base flow yield and N load from 2011 to 2012 (Oliver et al., 2014). We found that OWTSs may offset the influence of impervious surfaces and

maintain base flow during drought conditions. We also showed that NO_3^- concentrations increased linearly with increasing OWTS density above the threshold of 75 OWTS per km^2 .

Watershed-scale models can predict water quantity and quality as a result of the combined effect of all point and non-point source loads and help to develop a watershed management plan that includes the effect of OWTS (Geza et al., 2010). Recently, a new algorithm proposed by Siegrist et al. (2005) was incorporated into Soil Water Assessment Tool (SWAT) to simulate the impact of OWTS on water quantity and quality at the watershed-scale (Jeong et al., 2011). In a case study in the Hoods Creek watershed in North Carolina, the performance of the SWAT biozone algorithm was tested by Jeong et al. (2011). The calibrated model performed well in predicting groundwater NO_3^- concentration with $R^2 = 0.76$ and OWTS contributed 25% of N inflow to groundwater at the watershed-scale. OWTS may fail as a result of poor maintenance or system design. EPA reported estimated failure rates for each state and for Georgia the percentage was 1.7% of the systems in failure (USEPA, 2002). We believe there are three types of OWTS failure. The first type of failure occurs when the septic tank is not pumped regularly and fills with solids. This can cause solids to overflow into the drain field, clog the biomat that forms at the infiltrative surface in the drain field, and ponding of effluent at the soil surface. A second type of failure occurs when the soil is unsuited for the OWTS application rate, and/or the water table is too close to the infiltration surface. It also results in effluent coming to the soil surface. If the failure is not severe enough to cause effluent to back up into the house and the effluent ponding is intermittent (only during wet periods), we suspect that this type of failure may not be repaired because the homeowners cannot afford the

repair or installation of a new drain field. The third type of failure occurs when the drain field is not properly sited (unsuitable soil or the water table is too high) or the system is overloaded (due to an increase in the number of people in the home beyond that for which the system was designed for example). In this case the effluent may not back up into the home or even surface, but proper treatment of the effluent does not occur within the unsaturated zone. The effect of failing OWTS on stream flow or N load at the watershed scale has not been well documented.

In a previous study (Oliver et al., 2014), a SWAT model to predict the effect of OWTS on stream flow in the Big Haynes Creek watershed in Metropolitan Atlanta (Figure 4-1). The author found that total water yield at the watershed scale increased about 3% with the presence of OWTS. However, the impact of OWTS on NO_3^- load was not included in this model and neither were failing OWTS.

Our objective was to extend this previous work and estimate the effect of OWTS on stream NO_3^- load in the Big Haynes Creek watershed using a SWAT model that included failing OWTS.

4.3. Materials and Methods

4.3.1. Watershed Description

The Big Haynes Creek watershed has a drainage area of 44 km², a mean elevation of 297 m, and is located in the Southern Piedmont physiographic region east of Atlanta in Gwinnett County (Figure 4-1). The average annual precipitation is 1270 mm. The main land uses are 67% urban, 27% forest, and 6% hay and pasture. Most of the homes in this region are on OWTS for domestic wastewater treatment. The daily stream-flow data and NO_3^- concentrations were obtained from the United States Geological Survey (USGS)

station number 02207385 from 2003 to 2014, on Big Haynes Creek, and that became the outlet of the watershed we delineated.

4.3.2. *SWAT Input Data*

The ArcSWAT 2012 interface was used to set up and develop the model. To build the SWAT model, a digital elevation model (DEM), Soil Survey Spatial Tabular (SSURGO 2.2) soils data, National Land Cover Dataset (NLCD) land use data, OWTS drain field locations from the Gwinnett County GIS database, and Precipitation Regression on Independent Slopes Model (PRISM) weather data were used. There were four small reservoirs within the watershed and a dam shape file for each reservoir was downloaded from the Georgia GIS Clearing House and added to the model (Georgia GIS Clearing House, 2013).

The Big Haynes watershed was divided into 29 sub-basins, one of which was our monitored first-order stream. Each sub-basin was divided into land use, soil and slope combinations called Hydrologic Response Units (HRUs) (Arnold and Fohrer, 2005). Threshold values of 10%, 0%, and 30% of the sub-basin area were applied for land uses, soil, and slope classes, respectively. The GIS layer of OWTS drain fields was merged with the NLCD land use map to create a new OWTS representing individual drain fields (100 m²).

In our model, N inputs from OWTS, fertilizer applied to lawns, poultry manure added to hay fields and pasture, and atmospheric deposition was included. The recommended annual rate of N fertilizer for Bermuda grass in GA is 170 kg N ha⁻¹ (Georgia turf, 2013) and we assumed 70% of homeowners in this region applied fertilizer to their lawns based on the study by Osmond and Hardy (2004) on lawns in North Carolina. It is a

common practice in this area to apply poultry litter (a combination of manure and dry bedding material) to hay or pasture land uses. According to Watts et al. (2010), each broiler produces 1.5 kg litter per year. To calculate the broiler litter application rate in the Big Haynes watershed, we assumed that all of the litter produced in the county would be applied to hay and pasture fields within the county. The amount of litter produced in the county was estimated by multiplying by the number of broilers by 1.5 kg. The application rate of 1584 kg of litter ha⁻¹yr⁻¹ was estimated by dividing the total production by the total area of hay and pasture in Gwinnett County. The average annual rate of atmospheric deposition for ammonium and nitrate in precipitation (0.24 and 0.74 mg L⁻¹, respectively) and dry deposition (0.59 kg NH₄⁺ ha⁻¹ and 0.17 kg NO₃⁻ ha⁻¹) was obtained from Clean Air Status and Trends Network data for GA (CASTNET, 2015). There were no point sources in the watershed; the only wastewater treatment plant closed in February 2003 (personal communication, Georgia Environmental Protection Division).

In SWAT 2012, the effect of OWTS is simulated using a biozone algorithm (Jeong et al., 2011). The biozone layer is a biologically active layer of microorganisms feeding on the organic matter of the septic effluent in the absorption system. In this algorithm, biozone clogging is the mechanism causing OWTS failure and this results in surface ponding of OWTS effluent in a drain field (Jeong et al., 2011). The time required for a biozone to clog and fail typically takes more than 10 years. Many of the homes in the Big Haynes watershed were more than 20 years old and records of the ages were available, but it would be difficult to assign different ages to each OWTS in the model (the best that could be done would be to assign an age for each sub-basin and that would cause all of the systems in that sub-basin to fail at the same time). As an alternative, we assumed that all OWTS in soil hydrologic

group D, about 1% of the total number of OWTS in the watershed, were in a state of constant failure. This percentage is consistent with the reported failure percentage for Metropolitan North Georgia Water Planning District (MNGWPD, 2006). This approach had the advantage that failing systems were distributed across the watershed based on soils and the locations of OWTS. The number of permanent residents in each house (SEP_CAP) was set to 3.0 based on data for Gwinnett County (United States Census Bureau, 2015).

The Big Haynes watershed model was simulated from 1 January 1999 to 31 December 2014 on a daily time step. The first four years were used as an equilibration period or model warm-up period to reduce the dependence on initial conditions and were not included in the model analysis. This was followed by six-year calibration (2003-2008) and validation (2009-2014) periods. The USGS data included daily stream discharge and 71 measurements of NO_3^- load during the calibration period and 49 measurements of NO_3^- load during the validation period. For the USGS NO_3^- load measurements, 33% were collected under base flow conditions in the calibration period and 35% under base flow in the validation period.

4.3.3. SWAT Model Calibration, Uncertainty Analysis, and Validation

Calibration, uncertainty analysis, and validation of the model were conducted using the SWAT Calibration and Uncertainty Programs version 5 Sequential Uncertainty Fitting version 2 (SWAT-CUP, SUFI-2) algorithm (Abbaspour, 2013). SUFI-2 combines optimization with uncertainty analysis. Uncertainty in parameters in SUFI-2 accounts for all sources of uncertainties such as conceptual model, parameters, driving variables, and measured data. Uncertainties in the parameters result in the model output uncertainties which are quantified by the 95% prediction uncertainty (95PPU) band between the 2.5%

and 97.5% levels of the cumulative distribution of an output variable using Latin hypercube sampling. At the beginning of the calibration process, SUFI-2 evaluates a large number of parameters with wide ranges in values and then decreases the parameter number and values ranges in steps, while monitoring parameter sensitivities and the p -factor and r -factor. The p -factor is the fraction of measured data bracketed by the 95PPU band and ranges from 0 to 1. A p -factor of 1 indicates 100% bracketing of the measured data within model prediction uncertainty. The r -factor is the ratio of the average width of 95PPU band and the standard deviation of the measured data and ranges between 0 and infinity. The strength of the model calibration and validation is judged based on these two indices. A perfect fit between measured and simulated data can be achieved with a p -factor of 1 and an r -factor of 0 (Abbaspour, 2013).

Goodness of fit and model uncertainty are assessed by the objective function. SUFI-2 allows usage of ten different objective functions including the commonly used Nash-Sutcliffe (NS) efficiency coefficient. The NS efficiency coefficient is calculated as:

$$NS = 1 - \frac{\sum_{i=1}^n (O_i - P_i)^2}{\sum_{i=1}^n (O_i - \bar{O})^2} \quad [4.1]$$

where, O_i is the i th measured variable (e.g., discharge and nitrate load), P_i is the i th predicted variable, and \bar{O} is the arithmetic average of the measured variable. The NS coefficient ranges between 1 (perfect fit) and $-\infty$. An efficiency below zero implies that the mean value of the observed value is a better predictor than the model (Nash and Sutcliffe, 1970).

The SWAT parameters used in our calibration procedures were identified through a literature review. Parameters controlling stream flow were calibrated first and N

parameters were calibrated second. Stream-flow parameters with their calibrated ranges were included in the second step, but their ranges were not changed, in order to include *equifinality* of stream flow (Beven, 2006) in the NO_3^- load (Abbaspour et al., 2007; Bekele and Nicklow, 2007; Geza et al., 2010; Lam et al., 2010; Moriasi et al., 2012; Oliver et al., 2014; Santhi et al., 2001; White and Chaubey, 2005).

4.4. Results and Discussion

4.4.1. Model Calibration, Uncertainty Analysis, and Validation

The calibration process for the Big Haynes watershed started with 22 hydrologic parameters. The parameters, fitted values, and maximum and minimum values are listed in Table 4-1. The values of the runoff curve number II (CN2), available water capacity of the soil layers (SOL_AWC), the exponential decay factor for groundwater flow to the stream (ALPHA_BF), the soil saturated hydraulic conductivity (SOL_K), and reservoir parameters (RES_RR, RES_ESA, and RES_EVOL) are expressed as a percent change from default values. After 1000 simulations for each scenario, the most sensitive flow parameters were identified and are listed in Table 4-2 in order of descending sensitivity. The most sensitive flow parameters were runoff curve number (CN2), the fraction of transmission losses from main channel that enter the deep aquifer (TRNSRCH), effective hydraulic conductivity of the alluvium in the main channel (CH_K2), the Manning's roughness coefficient of the main channel (CH_N2), the groundwater re-evaporation coefficient (GW_REVAP), the effective hydraulic conductivity of the alluvium in the tributary channel (CH_K1), the threshold depth of water in the shallow aquifer required for return flow to occur (GWQMN), the groundwater delay time (GW_DELAY), the Manning's roughness coefficient for tributary channels (CH_N1), the exponential decay

factor for groundwater flow to the stream (ALPHA_BF), and the threshold depth of water in the shallow aquifer for re-evaporation or percolation to the deep aquifer to occur (REVAPMN). Parameter values must be considered after a calibration process because wrong values may result in unrealistic simulations. For instance, RCHRG_DP and TRNSRCH are parameters that govern processes that result in a loss of water from the system to the deep aquifer. As shown in Table 4-1, the fitted values in our models for these parameters were small and appropriate for a “gaining stream” (Griensven et al., 2012). Values for other sensitive flow parameters were reasonable and not at the upper or lower limit of recommended values.

The model fit was “good” (Moriassi et al., 2007) for stream-flow calibration with a daily NS of 0.62, *p*-factor of 0.70, and *r*-factor of 0.64. For the validation period, the model fit was slightly better with a NS of 0.67, *p*-factor of 0.80, and *r*-factor of 0.77 (Table 4-3). The log-scale plots of the observed stream flow, the model best fit, and the 95 PPU band calibration and validation periods are shown in Figure 4-2a and 4-2b. The wide range in stream flow that occurred from 2003 to 2014 is apparent, with a drought extending from 2006 to 2009. The higher stream flow in 2013 compared to 2014 is also apparent. For stream flow, the uncertainty band was narrow and peak flows were usually within the uncertainty band indicating a good model fit for calibration and validation.

After the model was calibrated for hydrology and hydraulic parameters, the narrow ranges for these parameter values were fixed and the model was calibrated for NO₃⁻ load using the 12 N parameters listed in Table 4-1. The most sensitive N parameters were the nitrate percolation coefficient (NPERCO), the denitrification exponential rate coefficient (CDN), and the denitrification threshold water content (SDNCO) (Table 4-2). NPERCO is

the fraction of NO_3^- in the soil surface layer that is lost to runoff. The fitted value indicated that concentrations in runoff were 52% of the concentrations in the surface layer so this parameter reduced runoff losses, somewhat. CDN determines the first-order denitrification rate in soil layers along with the organic C concentration and soil temperature. Assuming an optimum temperature and an organic C concentration of 1%, the fitted value of 0.64 results in a first-order denitrification rate of 0.006 per day. First-order denitrification rates for soils have a wide range in the literature. McCray et al. (2005) reported a range of 0.004 to 2.27 per day for different land uses including OWTS drain fields. As such, our fitted value was at the low end of the range. SDNCO is the threshold value for relative soil water content (expressed as the volumetric water content divided by the field capacity water content) above which denitrification occurs. The fitted value indicates that denitrification occurs when water contents rise above 42% of the value for field capacity. This threshold is lower than 60% relative water content reported by Bradshaw et al. (2013) and Beggs et al. (2004) in OWTS drain fields. However, Schepers and Raun (2008) reported that denitrification can start in 20% water filled pore space and increases as water filled pore space increases depending on availability of C and NO_3^- . The lower than expected denitrification rate and denitrification that occurs under dryer conditions than expected may be a case of compensating errors in our model.

The N parameters for the biozone, (COEFF-NITR and COEFF-DENITR) were not sensitive, but since N percolating from the biozone enters soil layers (where the CDN was sensitive), this seems reasonable. Another factor to consider is the travel time of NO_3^- in the biozone vs. soil layers. Since the biozone is very thin (5 cm), the travel time is short

compared to travel times in the soil layers which extend to a depth of 180 cm. The hydraulic conductivity of the biozone vs. soil layers is also important.

The shallow aquifer NO_3^- half-life (HLIFE) was not sensitive. The fitted value of 119 days corresponds to a first-order denitrification rate of 0.005 per day. In a study of in-situ measurements of the first-order denitrification rate in shallow aquifers in Coastal Plain North Carolina, Tesoriero and Puckett (2011) reported a rate of 0.0004 per day. In the Piedmont region of GA, the groundwater travel time was estimated to range from 10 to 15 years (Rose, 2007). Long travel times cause more denitrification loss. In SWAT, no attempt is made to model shallow aquifer travel times so they are much shorter than 10-15 years. As such, the higher than expected fitted denitrification rate may be compensating for unrealistically short groundwater travel times in SWAT. In a study of predicting N fate and transport from OWTS in suburban and urban watersheds in North Carolina, Pradhan (2004) estimated the actual NO_3^- half-life of 127 days in groundwater very close to the fitted value of 119 days in our model.

Plant N uptake accounted for about 41% of the applied N fertilizer. This percent is in the range of 29-59% of elemental N fertilizer uptake by turfgrass reported by Petrovic (1990). Hay and pasture accounted for only 6% of land uses in this watershed. Marshall et al. (2001) reported an average of 43% N plant uptake of total applied N as broiler litter for fescue pastures in Piedmont region of GA.

The model performance was “acceptable” for NO_3^- load calibration, with a daily NS of 0.56 and *p*-factor of 0.87 (Table 4-3). However, the *r*-factor was 3.58 indicating a high degree of uncertainty in the model. This is typical for watershed-scale models of nutrients where the observation data are sparse (compared to daily observations for stream

flow). For the validation period, the NS was 0.33 with a p -factor of 0.88 and an r -factor of 4.30. The log-scale plots of the observed NO_3^- load, the model best estimation, and L95PPU (lower limit) and U95PPU (upper limit) are shown in Figure 4-3 for calibration and validation periods.

Plots of the predicted TN, NO_3^- , organic N, NH_4^+ , and observed NO_3^- concentrations as a function of time are shown in Figure 4-4 for calibration and validation periods. Predicted discharge is also shown. NO_3^- concentrations were the main component of the TN concentrations during base flow and storm flow. This can be attributed to the constant groundwater source of NO_3^- to the stream. During storms, a “dilution effect” lowered NO_3^- concentrations, while organic N and NH_4^+ concentrations increased during storms with peaks observed in the spring. This is consistent with higher twigs and leaves in the stream. During storms, runoff from elemental N fertilizer in lawn and manure application in pasture and hay may cause increases in organic N and NH_4^+ concentrations. Our model over-estimated flow at the end of 2007 and 2012, this may cause higher simulated NO_3^- concentrations compared to the observed NO_3^- concentrations (Figure 4-4).

4.4.2. Effect of On-site Wastewater Treatment System on Stream flow and Nitrate Load

To determine the effect of OWTS on NO_3^- loads, the calibrated model was run with and without the presence of OWTS from 2003 to 2014. With the addition of OWTS, the total water yield increased about 10% at the main outlet (Figure 4-5a). This was more than was found by Oliver et al. (2014) who estimated an increase of about 3% in total water yield at the outlet of Big Haynes watershed with the presence of OWTS. The increase in stream flow in the current model was mostly due to failing OWTS which was not included

in the study by Oliver et al. (2014). Failing OWTS resulted in an increase in surface runoff of 5% at the main outlet. Percolation and groundwater discharge to the stream had the greatest percent increase: 17% and 14%, respectively. That was expected because OWTS discharge into shallow groundwater results in greater discharge to the streams. Also, with the addition of OWTS surface runoff and lateral flow showed slight increases, probably due to the wetter soils in the drain fields.

With the presence of OWTS, the calibrated models showed stream NO_3^- loads increased about 23% (Figure 4-5b). Addition of OWTS resulted in increased NO_3^- loads from groundwater to the streams of 85%. Lateral subsurface flow increased by 27%. The NO_3^- load was 74% of the total N load in the watershed, showing the important effect of OWTS on stream loads in urban watersheds.

Within the Big Haynes watershed, sub-basin 15 had the highest OWTS density (Figure 4-1). Total water yield with the presence of OWTS increased about 9% at the sub-basin outlet. Same as watershed scale, the main contribution of OWTS to the water balance was from percolation and groundwater (Figure 4-5a). Total NO_3^- load and NO_3^- loads from groundwater with OWTS increased by 28% and 91% at the sub-basin scale (Figure 4-5b). The larger contributions from OWTS in total NO_3^- load and NO_3^- load from groundwater at the sub-basin scale may be related to the larger portion of OWTS HRUs at the sub-basin area (1.28%) than at the watershed area (0.89%). In comparison, no changes in the total NO_3^- load was observed in a sub-basin with no OWTS (sub-basin 29). Failing OWTS increased the NO_3^- load from surface runoff by about 1% at the outlet of watershed. With the presence of OWTS the average amount of N lost each year from the NO_3^- pool due to denitrification was about 2% at the watershed scale. In SWAT, it is not possible to

differentiate the denitrification process from different pools. However, the elevation in denitrification with the addition of OWTS is probably due to the OWTS denitrification in septic drain fields caused by higher soil water contents.

We compared the annual TN load from OWTS estimated by SWAT with the load that would result if all of the homes on OWTS in the Big Haynes Creek watershed were converted to sewer and the residual N discharged from a wastewater treatment facility (WWTF) within the watershed. The residual N load would depend on the TN concentration of the effluent from the WWTF. Mines et al. (2004) reported data from six WWTF in Metropolitan Atlanta and they could be divided into three groups with average annual effluent TN concentrations of 0.1, 0.3, and 2.43 mg L⁻¹. The annual TN load from each group was estimated using the total number of homes in our study OWTS, the SWAT discharge rate of 227 L per day per person for a conventional OWTS, and the number of residents per house (3.0). The estimated annual TN WWTF loads for each group from low to high TN effluent concentrations were 102, 305, and 2472 kg yr⁻¹, respectively. These TN loads were lower than the SWAT estimated annual TN load for OWTS (7407 kg yr⁻¹) so converting homes to sewer would likely lower the N load.

4.5. Conclusions

Our findings show that a calibrated SWAT model adequately simulated NO₃⁻ loads in the Big Haynes Creek watershed. The daily NS for NO₃⁻ load was 0.58 for the calibration period and 0.33 for the validation period. Among the 12 N parameters selected for model calibration, the NO₃⁻ percolation coefficient (NPERCO), the first-order denitrification rate (CDN) for soil layers, and the threshold water content for denitrification to occur (SDNCO) were the most sensitive parameters in our calibrated model. This shows the importance of

the denitrification process in soils in determining the watershed-scale NO_3^- load. We estimated the presence of OWTS caused a 23% increase in stream NO_3^- load at the Big Haynes watershed. The NO_3^- load was 74% of the total N load in the watershed, showing the important effect of OWTS on stream loads in urban watersheds. In a sub-basin with a high percentage of OWTS, there was a 28% increase in stream NO_3^- load with the addition of OWTS. OWTS caused NO_3^- loads to the streams from groundwater to increase by about 85%. If failing OWTSs represent about 1% of the total number of systems (as in our study and in USEPA estimates) then will not have a large impact on stream flow or NO_3^- load.

Acknowledgments

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4.6. References

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Figures:

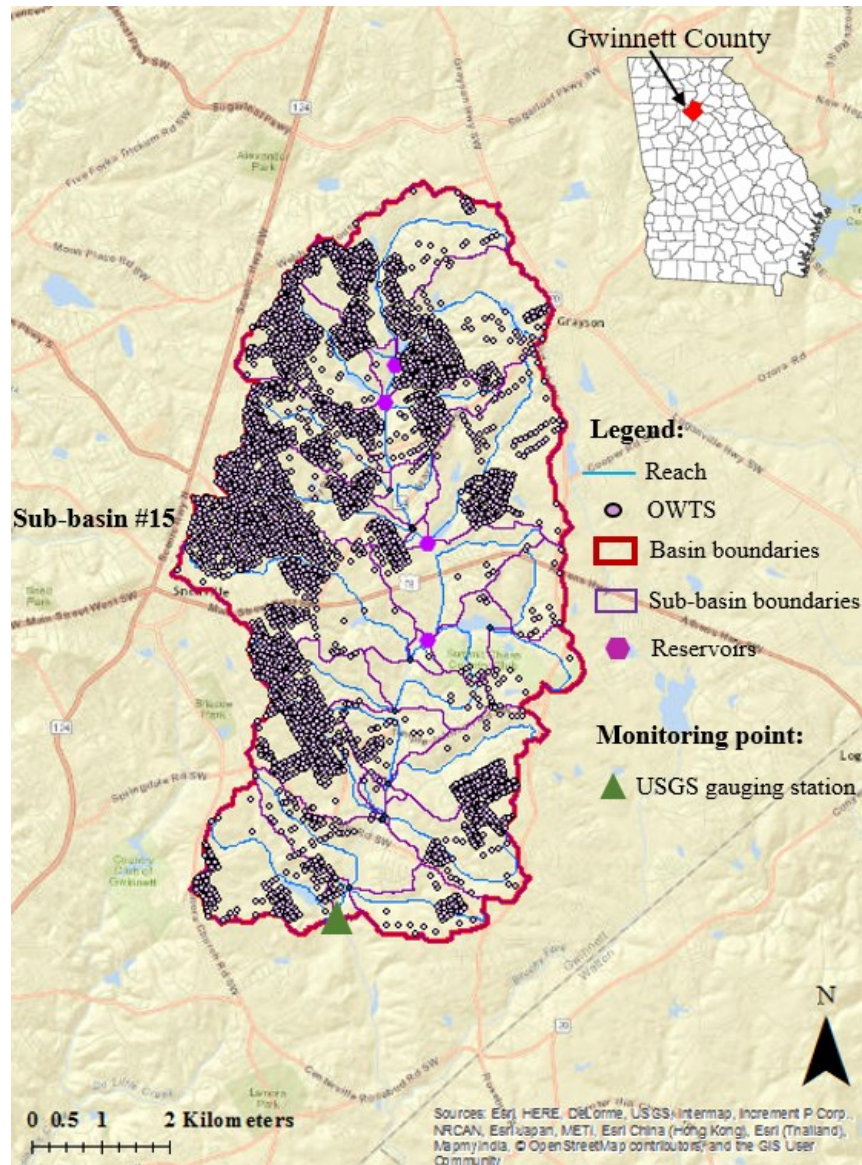


Figure 4-1- The Big Haynes Creek watershed boundary, monitoring site, and distribution of onsite wastewater treatment systems (OWTs) in Gwinnett County, Georgia.

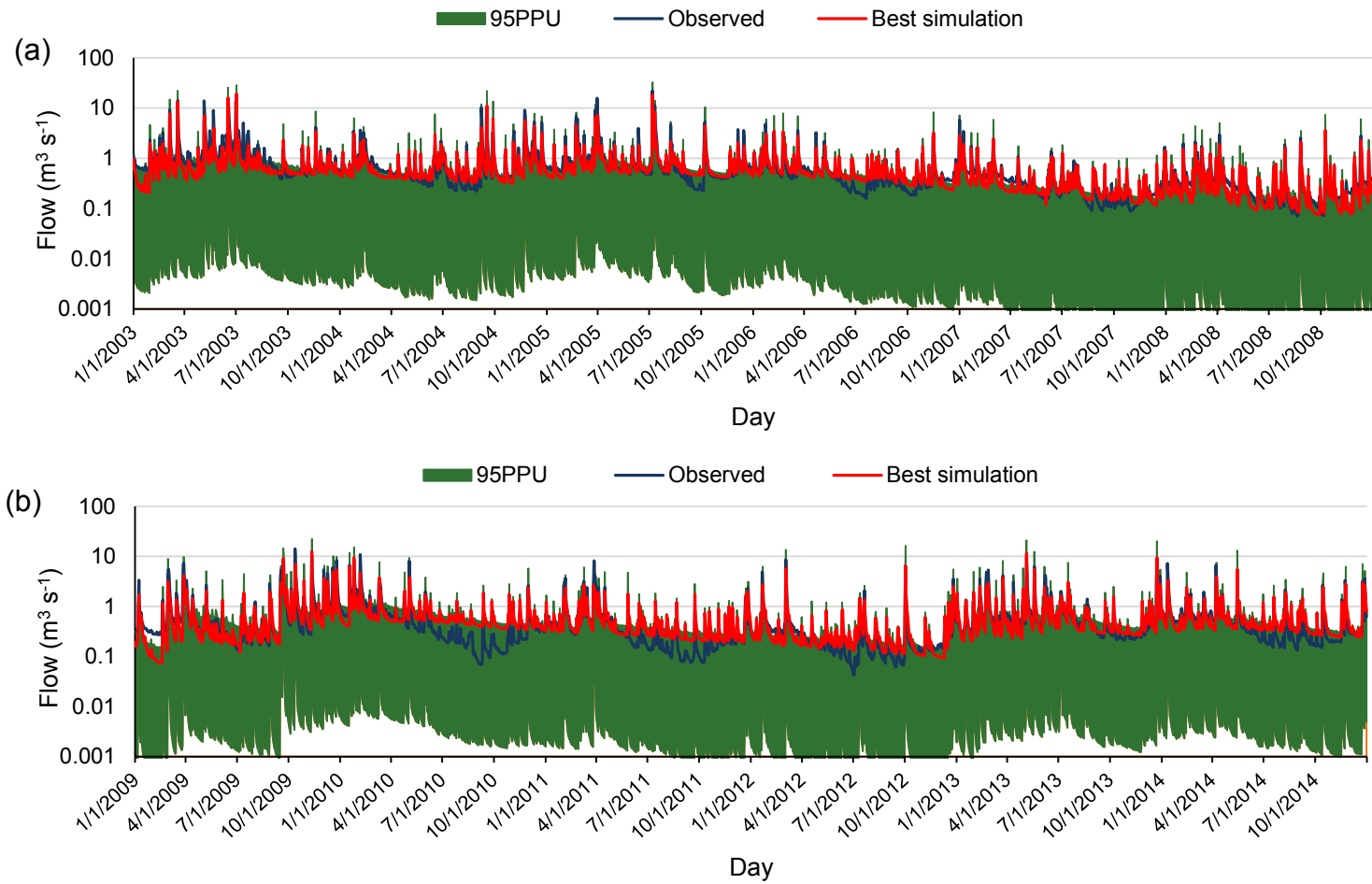


Figure 4-2- The log-scale plots of daily observed stream flow, the model best simulation, and 95PPU band for Big Haynes watershed during the calibration (a) and validation (b) periods.

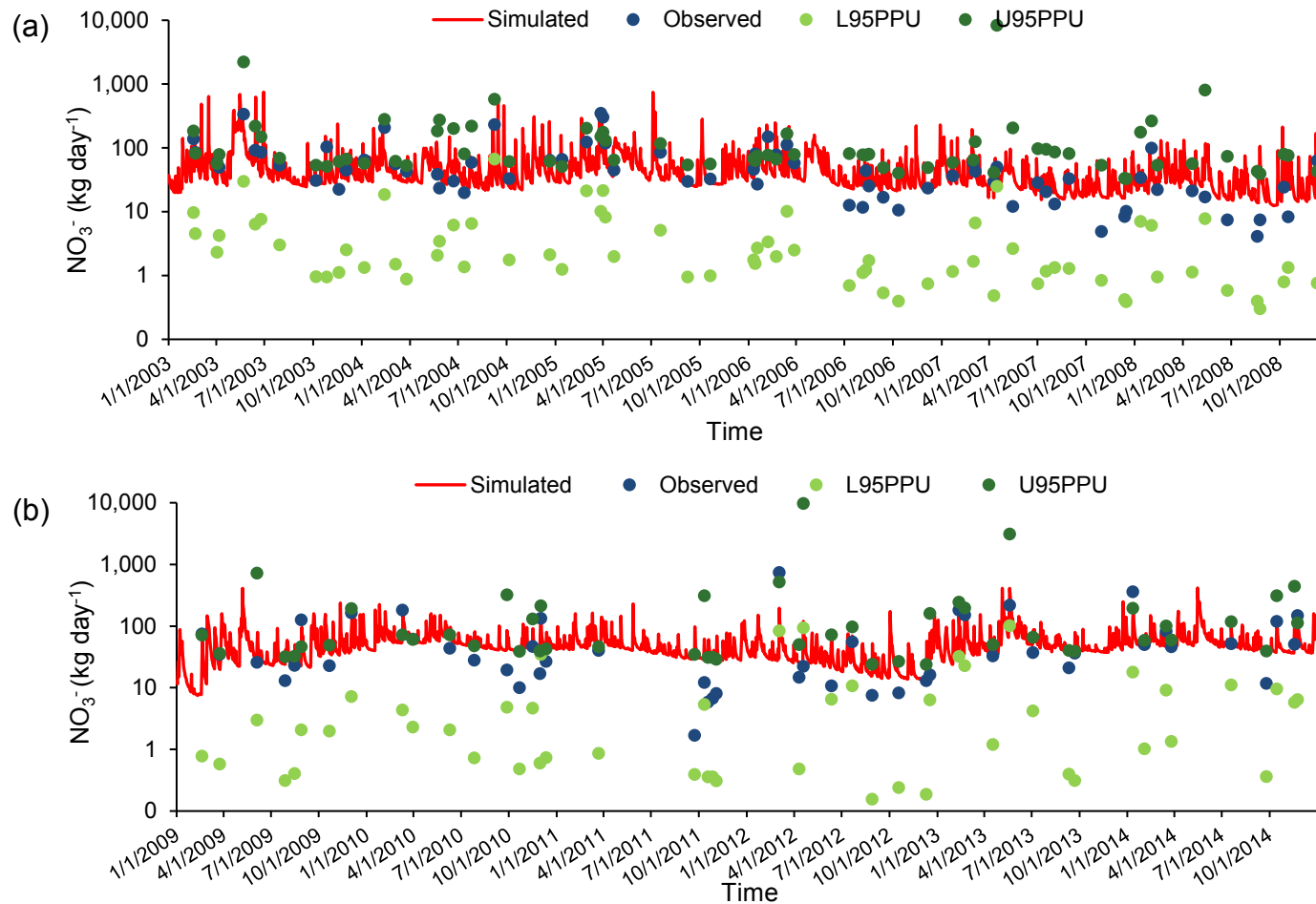


Figure 4-3- The log-scale plots of daily observed NO_3^- load, the model best simulation, and L95PPU (lower limit) and U95PPU (upper limit) at the outlet of Big Haynes watershed for the calibration (a) and validation (b) periods.

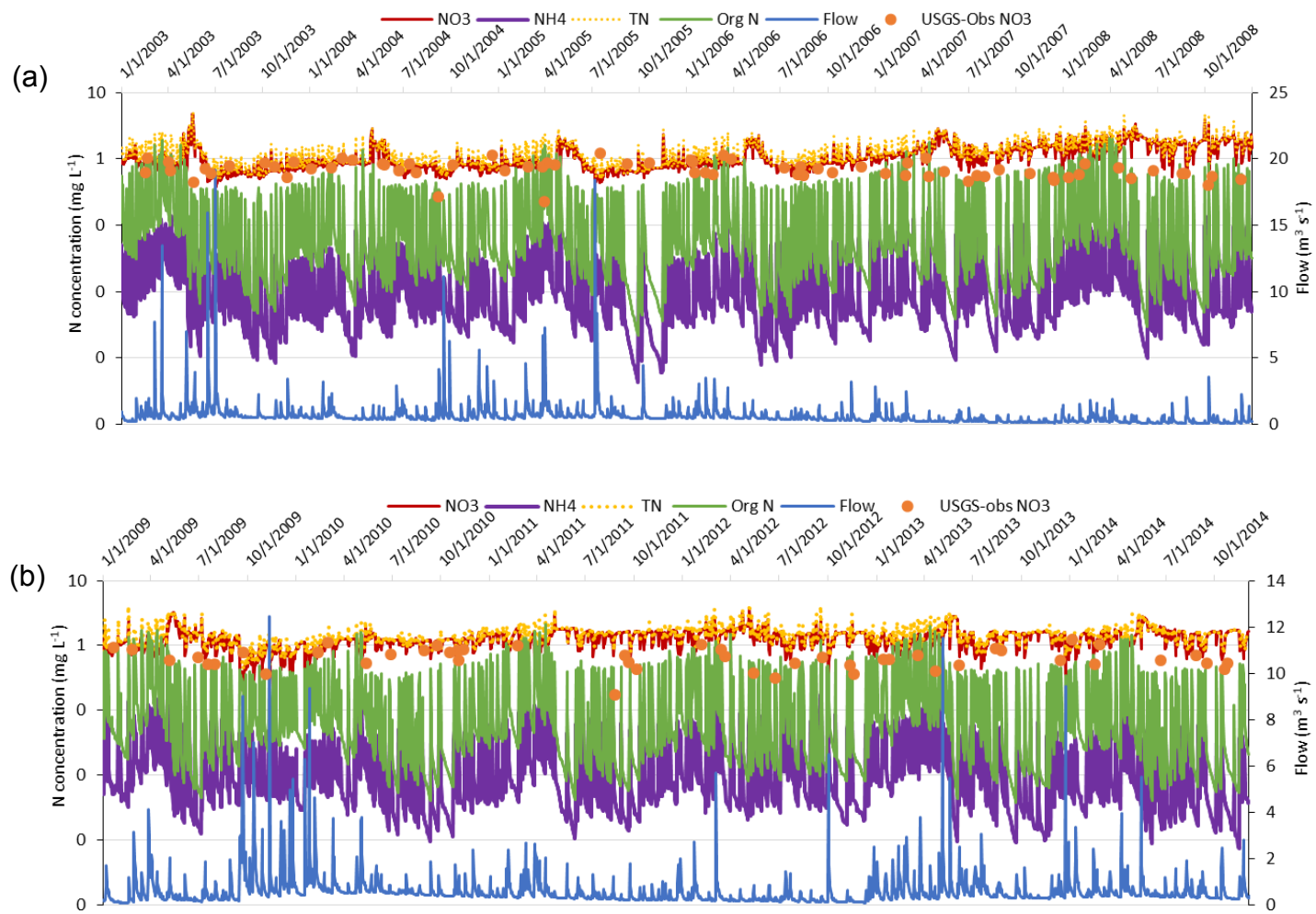


Figure 4-4-The plots of SWAT simulated TN, NO₃⁻, organic N, NH₄⁺, and USGS measured NO₃⁻ concentrations vs. flow during calibration period (a), and validation period (b) at the outlet of Big Haynes watershed.

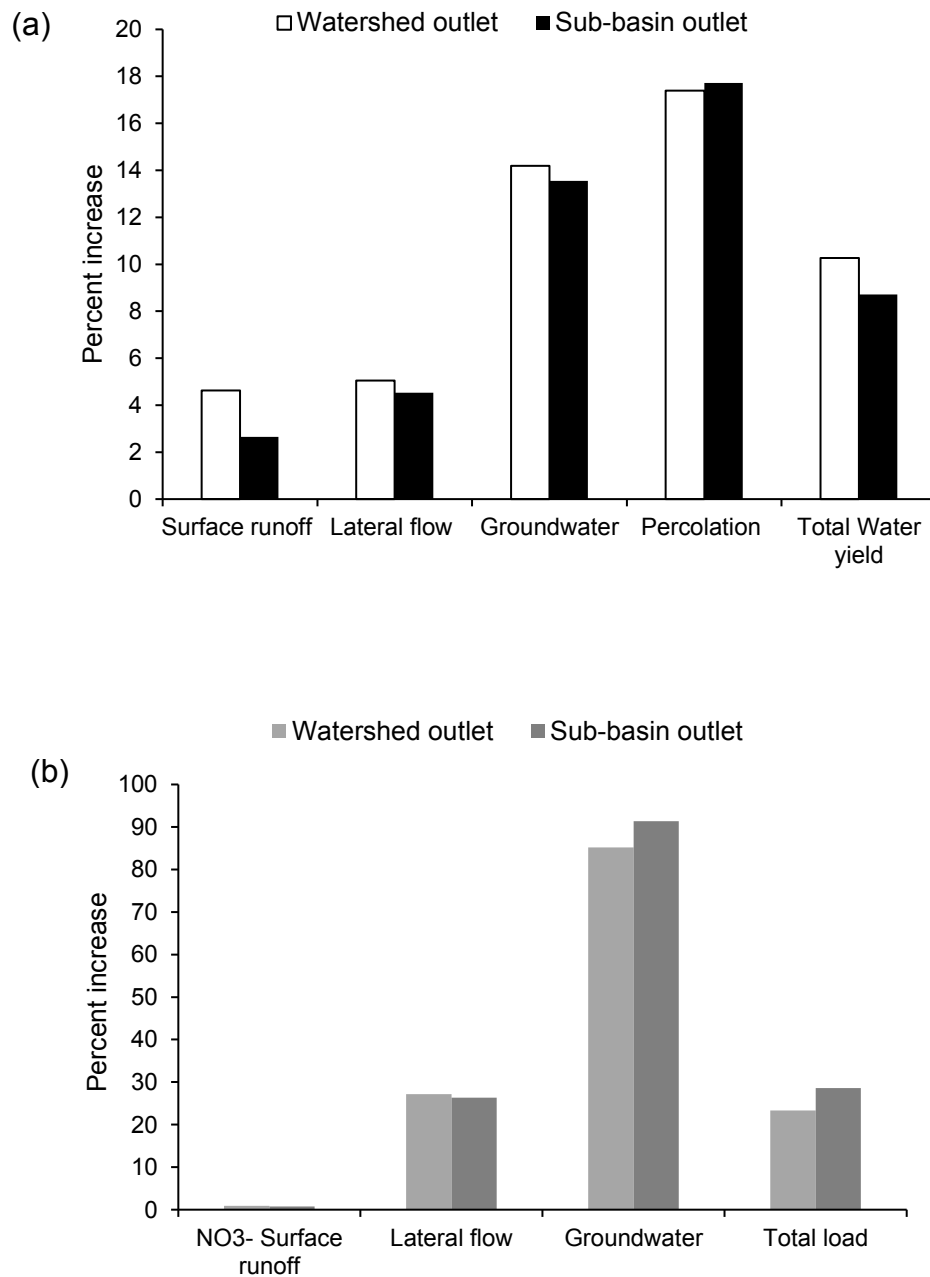


Figure 4-5- The percent increase in stream-flow components (a) and NO_3^- load components (b) in calibrated model with the presence of OWTS at the outlet of Big Haynes watershed from 2003 to 2014 and at the outlet of sub-basin 15 (with the highest OWTS density).

Table 4-1- Flow and nitrogen parameters, fitted, minimum, and maximum values used for calibration period using SWAT- CUP.

	Parameter	Method*	Fitted value	Min value	Max value
Flow parameters	CN2	<i>r</i>	-0.16	-0.2	0.2
	ALPHA_BF	<i>r</i>	0.02	-0.1	0.1
	GW_DELAY	<i>v</i>	6.25	0	500
	GWQMN	<i>v</i>	223.5	0	1000
	ALPHA_BNK	<i>v</i>	0.89	0	1
	CH_K1	<i>v</i>	299.25	0	300
	CH_K2	<i>v</i>	28.54	0	30
	CH_N1	<i>v</i>	0.46	0	0.5
	CH_N2	<i>v</i>	0.05	0.025	0.15
	EPCO	<i>v</i>	0.18	0	1
	ESCO	<i>v</i>	0.17	0	1
	GW_REVAP	<i>v</i>	0.07	0.02	0.2
	GW_SPYLD	<i>v</i>	0.31	0	0.4
	RCHRG_DP	<i>v</i>	0.07	0	0.2
	REVAPMN	<i>v</i>	41.75	0	500
	SOL_AWC()	<i>r</i>	0.27	-0.2	0.4
	SOL_K()	<i>r</i>	-0.69	-0.8	0.8
	SURLAG	<i>v</i>	21.20	1	24
	TRNSRCH	<i>v</i>	0.18	0	1
	RES_RR	<i>r</i>	0.20	-0.5	1
	RES_EVOL	<i>r</i>	0.70	-0.2	1
	RES_ESA	<i>r</i>	-0.11	-0.2	1
Nitrate parameters	CDN	<i>v</i>	0.64	0	3
	SDNCO	<i>v</i>	0.42	0	1
	NPERCO	<i>v</i>	0.52	0	1
	RS1	<i>v</i>	0.67	0.15	1.82
	RS3	<i>v</i>	0.72	0	1
	RS4	<i>v</i>	0.07	0.001	0.1
	HLIFE	<i>v</i>	119	0	200
	COEFF_NITR	<i>v</i>	0.30	0	3
	COEFF_DENITR	<i>v</i>	0.006	0	1
	BC1_BSN	<i>v</i>	0.99	0.1	1
	BC2_BSN	<i>v</i>	1.44	0.2	2
	BC3_BSN	<i>v</i>	0.22	0.2	0.3

* *r* means the existing parameter value is multiplied by (1+ a given value) and *v* means the existing parameter value is replaced by a given value.

Table 4-2- The most sensitive flow and NO₃⁻ load parameters and their p-factor values at the outlet of the Big Haynes watershed from sensitivity analysis in SWAT-CUP, ranked from the most sensitive to least sensitive parameters.

Parameters sensitive to flow			Parameters sensitive to NO ₃ ⁻		
Parameter name	Rank	<i>p</i> -value	Parameter name	Rank	<i>p</i> -value
CN2	1	0.00E+00	CDN	1	0.00E+00
TRNSRCH	2	0.00E+00	NPERCO	2	0.00E+00
CH_K2	3	0.00E+00	SDNCO	3	0.00E+00
CH_N2	4	0.00E+00			
GW_REVAP	5	0.00E+00			
CH_K1	6	0.00E+00			
GWQMN	7	0.00E+00			
GW_DELAY	8	3.20E-03			
CH_N1	9	4.50E-03			
ALPHA_BF	10	1.04E-02			
REVAPMN	11	2.57E-02			

Table 4-3- Daily flow and NO₃⁻ load Nash-Sutcliffe efficiency coefficient (NS), coefficient determination (*R*²), *p*-factor, and *r*-factor at the outlet of Big Haynes watershed for simulation periods.

Simulation period	Daily stream flow				Daily NO ₃ ⁻ load			
	NS	<i>R</i> ²	<i>p</i> -factor	<i>r</i> -factor	NS	<i>R</i> ²	<i>p</i> -factor	<i>r</i> -factor
2003-2008 (calibration)	0.61	0.64	0.70	0.64	0.53	0.56	0.87	3.58
2009-2014 (validation)	0.66	0.68	0.80	0.77	0.33	0.34	0.88	4.30

5. NITROGEN CONCENTRATION AND LOAD PATTERNS
IN FOUR HEADWATER STREAMS WITH A GRADIENT
IN ONSITE WASTEWATER TREATMENT SYSTEM
DENSITY¹

¹ Hoghooghi, N., D.E. Radcliffe, and M.Y. Habteselassie. To be submitted to the Journal of Environmental Quality.

5.1. Abstract

In previous work where we measured nitrogen (N) concentrations in 24 small watersheds in Metropolitan Atlanta under base flow conditions, we found that most of the base-flow N originated from onsite wastewater treatment systems (OWTS) in watersheds with a high density of OWTS and from agriculture in watersheds with a low density of OWTS. However, the fraction of the total annual N load represented by the base-flow N concentrations could not be estimated because N concentrations were not sampled during storm events and there were no continuous measurements of stream flow. Our objective in this study was to determine the fraction of the total annual N load represented by base-flow N in four headwater streams with a gradient in OWTS density. The four streams selected from our original study had OWTS densities ranging from 20-230 systems km⁻². From October 2012 to April 2014, stream discharge was measured at 15-min intervals and storm-flow and base-flow samples were collected using automated samplers. Nitrate (NO₃⁻) concentrations were higher in base-flow than in storm-flow in three of the four streams, suggesting a groundwater source of NO₃⁻. TN loads were highest for the stream with the lowest OWTS density and the stream with the highest OWTS density. We attribute this to the effect of agriculture in the low density watershed and OWTS in the high density watershed. N loads at the extremes in OWTS densities in our study were comparable to high loads cited in the literature for pastures and suburban areas on OWTS. In the watershed with the highest OWTS density, base flow NO₃⁻ loads accounted for about 35% the total N loads. This suggests the important effect of OWTS on stream N loads.

Abbreviations: LD, low density; HD, high density; Onsite wastewater treatment system, OWTS.

5.2. Introduction

Nitrogen (N) inputs from human activities doubled from 1961 to 1997 in the United States (Howarth et al., 2002). N is an essential nutrient for plant growth and animal life, however high concentrations can cause eutrophication and hypoxia in marine and brackish water ecosystems (Conley et al., 2009; Pinckney et al., 2001; Rabalais, 2002). Threshold concentrations for N to inhibit eutrophication and preserve the aquatic food web in water bodies is much lower than 10 mg L^{-1} for NO_3^- -N (the threshold of nitrate concentration in drinking water to protect against methemoglobinemia) and depend on the type of the water body (USEPA, 2015). Population growth has caused conversion of rural areas to sub-urban or urban areas nationwide. The impact of these changes has been called the *urban stream syndrome* and N is a major factor that affects water quality degradation in these streams (Walsh et al., 2005).

With increasing urbanization and population growth, onsite wastewater treatment systems (OWTSs) are considered a solution for urban waste treatment because of the high costs of centralized wastewater systems. However, high density or poor maintenance of OWTS may lead to an overabundance of nutrients in both surface and ground waters (USEPA, 2002). In metropolitan Atlanta, approximately 26% of the homes are on OWTS (MNGWPD, 2006). Most of the stream N studies on the impact of land use have focused on forested and mixed agricultural watersheds (Hatfield et al., 2009; Inamdar et al., 2004; Vanni et al., 2001; Zhu et al., 2011). Studies on N stream dynamics in suburban or urban watersheds are less common. One urban study was done by Shields et al. (2008) on basins with different land uses in the Chesapeake Bay watershed. The authors found that most of the nitrate (NO_3^-) and total N (TN) inputs in urban watersheds occurred during storms as a

result of runoff from impervious surface areas. The largest annual N loads were from suburban areas (low-density development) with OWTS. In a second urban study, Hatt et al. (2004) described the impact of urban density and drainage infrastructure on the N concentrations and loads of 15 small streams with an average OWTS density of 50 systems km^{-2} in Melbourne, Australia. They found that despite strong correlations of NO_3^- and TN concentrations with OWTS density, N loads were poorly correlated with OWTS density. Loads of all the water quality variables were strongly correlated with percent impervious surface.

In our previous articles about the impact of OWTS on base-flow NO_3^- and TN concentrations (Hoghooghi et al., 2016; Oliver et al., 2014), we described a study of 24 small watersheds (0.18-8.81 km^2 in area) in metropolitan Atlanta with a wide range in OWTS density (Figure 5-1). The watersheds were divided into 12 low density (LD) and 12 high density (HD) watersheds using a threshold of 75 OWTS km^{-2} . Three times a year under base-flow conditions from November 2011 to July 2014, water samples were collected and analyzed for NO_3^- -N, ammonium (NH_4^+ -N), and TN concentrations. We found that TN and NO_3^- -N concentrations increased linearly with OWTS density in the HD watersheds and concluded that most of the base-flow N originated from OWTS in HD watersheds and from agriculture in the LD watersheds (Hoghooghi et al., 2016; Oliver et al., 2014). However, the fraction of the total annual N load represented by the base-flow N concentrations could not be estimated because N concentrations were not sampled during storm events and there were no continuous measurements of stream flow. Loads are important because they are the basis of the Total Maximum Daily Load (TMDL) program (USEPA, 2007).

The load of pollutants transported through a stream cross-section during a time interval is given in Equation [5.1]:

$$L = \int_{t_1}^{t_2} Q(t)C(t)dt \quad [5.1]$$

where L is the load between time t_1 and t_2 ($M T^{-1}$), $Q(t)$ is the streamflow at time t ($L^3 T^{-1}$), and $C(t)$ is the constituent concentration ($M L^{-3}$). According to equation [5.1], continuous flow and concentration measurements are essential to estimate accurate loads. In small watersheds due to the large and rapid changes in concentration during storm flow conditions, sub-daily sampling during storms can help to minimize sampling errors. Automated sampling equipment can be a useful tool to program time-paced discrete sampling based on a pattern of times (e.g. every 15 minutes) (King et al., 2005). Harmel et al. (2003) showed that time-discrete sampling at a 15-minute interval or less was necessary to estimate a pollutant load that was not significantly different from the true pollutant load.

One of our objectives was to determine how base-flow N loads compare to total N loads in suburban watersheds of Metropolitan Atlanta. Also, we wanted to determine how N species concentrations in base flow compare to N species concentrations during storm flow. Lastly, we wanted to know how OWTS density affected these patterns.

5.3. Materials and Methods

5.3.1. Study Area

The study area is in the southern Piedmont region east of Atlanta, GA in Gwinnett County and has been described in detail in Landers and Ankorn (2008) (Figure 5-1). Out of the 24 watersheds in our previous study, two LD watersheds (LD5 and LD15) with OWTS densities of 20 and 37 systems km^{-2} and two HD watersheds (HD14 and HD17) with OWTS densities of 141 and 230 systems km^{-2} were selected (Table 5-1). Other

watershed selection criteria included similar area, geological setting, precipitation, climate, and accurate sampling locations.

ArcGIS 10.2.2 (ArcGIS, 1999) was used to delineate the watersheds and to determine different land uses using the National Land Cover Dataset (NLCD) (Figure 5-1). In LD5, the main land use was hay and range (52%), followed by forest (29%), and residential (16%). In LD15, the main land use was residential (71%), followed by forest (14%), and hay and range land (12%) (Table 5-1). The main land use in the HD watersheds was residential (62 and 42% for watershed HD14 and HD17, respectively) followed by forest (22 and 11% for watershed HD14 and HD17, respectively) and to a lesser extent hay and range (11 and 8% for watershed HD14 and HD17, respectively).

5.3.2. Sample Collection, Analysis, and Load Estimation

All four watersheds outlets were equipped with an automated water sampler (Teledyne ISCO, USA) with a submerged probe flow module that recorded the height of the water in the stream continuously, and programmed to collect stream samples during storm events for chemical analysis from October 2012 to April 2014. Each ISCO held 12 bottles, the first 11 bottles collected 900 ml water samples every 15 min, and the last bottle collected a composite sample consisting of 100-ml samples from each 15-min interval. The height of the water in the stream was converted to discharge using a rating curve for each watershed. In addition, base-flow samples were collected approximately every month.

All storm and base-flow samples were refrigerated and processed within 24 h of collection. For analysis of NH_4^+ -N and NO_3^- -N concentrations, water samples were filtered through Supor-450 membrane filter (Pall Corporation, MI) and stored in acid-washed plastic bottles, and were kept frozen until analysis. Prepared samples were analyzed for

$\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and total Kjeldahl nitrogen (TKN) concentrations by the University of Georgia Feed and Environmental Water Laboratory. $\text{NO}_3^-\text{-N}$ concentrations were measured by ion-chromatographic separation followed by conductometric detection for inorganic anions according to USEPA Method 300.1 (Hautman et al., 1997). $\text{NH}_4^+\text{-N}$ concentrations were measured using the distillation-titration method of Bremner (1965). TKN concentrations in water samples were analyzed using a modified version of the micro-Kjeldahl methods (Clesceri et al., 1998). Since TKN was measured on an unfiltered sample, it included suspended particulate N, $\text{NH}_4^+\text{-N}$, and dissolved organic N (DON). $\text{NO}_3^-\text{-N}$ was added to TKN concentrations to obtain TN concentrations.

Different methods have been used to assess nutrient loads including averaging estimator (linear interpolation), ratio estimator, and regression equations. The accuracy of each method depends on several factors including the size of the watershed, frequency of sampling, and land use (Quilbé et al., 2006). The regression method is appropriate for both large and small streams with small data sets over several years according to Haggard et al. (2003) and (Robertson and Roerish, 1999). If nutrient concentrations are correlated with flow, a regression method for high flows (storm conditions) and averaging method (linear interpolation) for low flows (base-flow conditions) are used (Quilbé et al., 2006).

To calculate loads, we needed daily estimates of stream flow and N concentrations. The continuous gage height measurements and rating curve equations provided daily flow for each stream. Our monthly base-flow samples and sub-daily storm-flow samples provided discrete measurements of concentrations for each stream, but there were some storms that were not sampled due to problems with the automated samplers such as a low battery. To obtain daily estimates of concentration, we used a combination of interpolation

and regression equations. When the ISCO samplers worked, linear interpolation was used to determine concentrations between sampling intervals (every 15 min) and an average daily concentration was calculated. When the ISCO samplers did not take storm samples, linear least square regression equations were used to estimate NO_3^- , TKN, and TN concentrations. The regression equations were developed from the ISCO data from sampled storms using the relationship between nutrient concentrations and storm flow. Storm conditions were assumed when a 10% rise in the hydrograph was observed in one day. Linear interpolation between monthly base-flow measurements was used to estimate daily concentrations of N components during base flow. Then the daily load was calculated by multiplying the concentrations by daily discharge for each watershed. Because the concentrations of ammonium (NH_4^+) were negligible (less than 0.1 mg L^{-1}) in our samples, we didn't include it in our analysis. Loads for NO_3^- , TKN, and TN were calculated for the entire period of the study and normalized for a year. Linear regression analysis was performed to determine the relationship between flow and N concentrations. Pearson Product-Moment Correlation (PPMC) analysis was applied to determine the correlation between N concentrations and watershed characteristics. All data analyses were performed in SAS.9.3 in SAS.9.3 (SAS Institute Inc., NC) at the 95% confidence level ($\alpha=0.05$).

5.4. Results and Discussions

5.4.1. Patterns in Nitrogen Concentrations

Using our definition of a 10% rise in stream flow in one day, there were a total of 410 storms on the four streams (Table 5-2). About a third (36%) of the storms were sampled by ISCO units. The reasons why the other storms were not sampled was usually because the threshold level set for the ISCO to sample (we varied this during the year and among

the samplers) was set to an increase greater than 10%, but there were also times when the equipment did not work, usually because of a low battery. A total of 808 samples were collected by the ISCOs with an average of 8 samples per storm. The regression equations developed for each watershed from the ISCO-sampled storm data for predicting concentrations in the un-sampled storms are shown in Table 5-3. Concentrations were estimated as a linear function of storm event discharge and the R^2 ranged from 0.28 to 0.43 ($p < 0.05$).

Three examples of hydrographs and N concentration patterns are shown in Figure 5-2, all from the HD17 watershed. Since the ISCO units started sampling after the threshold for a rise in flow was reached, the first samples did not necessarily represent base-flow concentrations. The final samples collected during a storm were more representative of the base-flow concentrations. Most of the N was in the form of NO_3^- and TKN (NH_4^+ -N concentrations were less than 0.01 mg L^{-1} in all cases). NO_3^- concentrations were usually high (Figure 5-2a) or rose at the beginning of a storm (Figure 5-2b and 5-2c) and reached a peak before or shortly after the peak in the hydrograph. This could be explained by the initial rise in the local water table at the beginning of a storm that causes greater groundwater discharge, and/or it could be due to a first flush of NO_3^- in runoff. TKN concentrations tended to increase during storms and decline later in the hydrograph compared to NO_3^- , indicating that TKN came from runoff.

Nitrogen concentration and load means, as well as stream flow yields, for the entire period for each stream are shown in Figure 5-3. Total N concentrations in base flow and in storm flow (the height of the bars in Figure 5-3a) were highest in the streams with the lowest OWTS density (LD5) and the highest density (HD17). These results are consistent

with our study of base-flow concentrations in the 24 watersheds in Gwinnett County (Figure 5-1) where we found that concentrations were the highest at very low density and at very high density (Hoghooghi et al., 2016; Oliver et al., 2014). We attributed this to the effect of more intensive agricultural activities including livestock (cows and horses) and the use of poultry manure on pastures in the very low density watersheds (which had higher agricultural land use), and the effect of OWTS in the very high density watersheds. At intermediate OWTS density (near 100 systems km⁻²) we found in our previous study that N concentrations were at a minimum during base flow. That seems to be true for storm flow concentrations as well in LD15 and HD14 (Figure 5-3a). The mean concentrations of NO₃⁻-N at base flow explained about 58% of the variability in storm flow concentrations ($r = 0.58, p < 0.001$).

In the LD watersheds, base flow and storm flow concentrations of NO₃⁻-N and TKN were nearly the same, but in the HD watersheds NO₃⁻-N concentrations were greater than TKN concentrations, especially at the highest OWTS density (HD17) (Figure 5-3a). We attribute this to the large groundwater NO₃⁻ input from OWTS at high densities. During base flow, a significant positive correlation was observed between NO₃⁻-N concentrations and OWTS density ($r = 0.72$ and $p < 0.05$) (Table 5-4). Since OWTS density was correlated with percent of impervious area, there was also a significant correlation between NO₃⁻-N concentrations and percent of impervious surfaces ($r = 0.47$ and $p < 0.05$). NO₃⁻-N concentrations during base flow tended to be higher than NO₃⁻-N concentrations during storm flow except in LD5 (Figure 5-3a). This suggested that NO₃⁻-N concentrations were diluted during storm events. The opposite occurred with TKN concentrations in that they tended to be higher in storm flow than in base flow (Figure 5-3a) suggesting that the source

of TKN was runoff. The high base-flow and storm-flow TKN concentrations in watershed L5D was probably due to high hay and pasture (52%) and forest (29%) land use (Table 5-1). Base-flow and storm-flow TKN concentrations were significantly correlated with the percent of hay and pasture areas (Table 5-4). During base flow, direct discharge of animal wastes to the stream and suspended algae may explain the TKN concentrations.

5.4.2. *Patterns in Nitrogen Loads*

The estimated N loads were normalized for the drainage area to eliminate the effect of different areas on loads and calculated on an annual basis in $\text{kg ha}^{-1} \text{ yr}^{-1}$. Loads are shown in Figure 5-3b and the height of the bars represents the TN annual load for each watershed.

Similar to concentrations in Figure 5-3a, TN loads in Figure 5-3b were large at low and high OWTS densities. Water yields also affected estimated loads and these followed a similar pattern. Water yields are equivalent to “runoff” in long-term water balances. In the Piedmont region of GA, annual runoff accounts for about 33% of the annual rainfall according to Carter and Stiles (1983). Based on the annual rainfall of about 212 cm for our study period (Georgia Weather, 2015), 71 cm of runoff would be expected and this is similar to the range we found (Figure 5-3c). The variation in water yields among watersheds could have been due to a combination of natural variation and errors in our measurements. The average base-flow yield for all watersheds was about 73% of the total water yield. In the Piedmont region, base flow on average comprises between 50% (wet periods) and 80% (dry periods) of the total annual load (Rose and Fullagar, 2005). However, we think the high water yield at high OWTS density was due to OWTS. Ninety-two percent of the homes in Gwinnet County use drinking water supplied by the Gwinnet County Water Resources Department that takes water from Lake Lanier which is outside

of our study area (Steve Lawrence, USGS, Norcross, GA, written communication). As such, water that is discharged by OWTS represents an input of water to these watersheds. The large yield in the LD5 watershed with the lowest OWTS density is harder to explain. It may be that the low impervious surface percentage and large forest and pasture percentages promoted infiltration of precipitation and this lead to higher groundwater recharge. However, storm-flow yield was also high in LD5. It's unlikely that agricultural irrigation occurred in this watershed. In stream walks of the LD watersheds, we noticed that the streambed of LD5 ran on bedrock for more of the reach than the other streams. This may have resulted in a more complete water balance in LD5 compared to LD15 where some of the discharge may have been in the sediment below the stream bed at our sampling site. We did not do stream walks on the HD watersheds.

The TN load of $26.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in LD5 with hay and pasture as a dominant land use is close to the mean TN load of $29 \text{ kg ha}^{-1} \text{ yr}^{-1}$ reported by Correll et al. (1995) for 13 pasture-dominated watersheds with livestock farms in Piedmont and Appalachian watersheds of the Chesapeake Bay. The TN load of $22 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in HD17 is higher than the range of 5 to $15 \text{ kg ha}^{-1} \text{ yr}^{-1}$ TN loads in five urban watersheds in the Piedmont region in the Chesapeake Bay area reported by Shields et al. (2008). However, in their study the majority of the watersheds were served by sanitary sewer lines. In the same study, TN loads from the residential area in a mixed watershed (forest and low residential) with OWTS were about $20 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (Shields et al., 2008).

The highest base flow NO_3^- load was observed in watershed LD5 ($9.28 \text{ kg ha}^{-1} \text{ yr}^{-1}$) with the highest percentage of hay and pasture OWTS (Figure 5-3b and Table 5-1). However, none of the correlation between loads and watershed characteristics were

significant (Table 5-4). Therefore, the high base flow NO_3^- load in LD5 was likely due to high base-flow yield and not high NO_3^- concentrations (Figure 5-3a and 5-3c). Among the other three watersheds, the highest base flow NO_3^- load was observed in HD17 ($7.76 \text{ kg ha}^{-1} \text{ yr}^{-1}$), followed by LD15 ($5.02 \text{ kg ha}^{-1} \text{ yr}^{-1}$) and HD14 ($2.01 \text{ kg ha}^{-1} \text{ yr}^{-1}$) (Figure 5-3b). These differences in base-flow NO_3^- loads can be attributed to differences in NO_3^- -N concentrations and base-flow yield.

Storm-flow loads were the opposite of base-flow loads in that TKN tended to be a larger part of the load than NO_3^- . The highest TKN load was observed in LD5 ($6.13 \text{ kg ha}^{-1} \text{ yr}^{-1}$) (Figure 5-3b) with the highest percentage of forest area and hay and range land uses (Table 5-1). In this watershed, TKN concentrations were higher during storm flow (1.66 mg L^{-1}) than base flow (1.24 mg L^{-1}) (Figure 5-3a). The potential sources of TKN during storms could be runoff produced from forest areas and farms with hay fields and pastures where manure could be a source. TKN loads were also high in LD15 ($4.48 \text{ kg ha}^{-1} \text{ yr}^{-1}$) and HD17 ($4.69 \text{ kg ha}^{-1} \text{ yr}^{-1}$) (Figure 5-3b), where impervious surfaces could have increased runoff (Shuster et al., 2005). Sources of N during storms in residential watersheds include N fertilization of lawns and ornamental shrubs (Osmond and Hardy, 2004), vehicle exhaust, accumulation of leaf litter and domestic animal wastes (Shields et al., 2008).

NO_3^- loads during storm flow were also important. Part of the NO_3^- load during storms likely came from groundwater discharge. We did not use a hydrograph separation technique to separate runoff from groundwater discharge during storms so we could not quantify this component of the storm load. As shown in the example hydrograph and N pattern figures (Figure 5-2), NO_3^- concentrations were usually higher at the beginning of a

storm and this could be due to an increase in groundwater discharge as the local water table rose.

Base-flow loads constituted more than half of the TN annual loads in all of the watersheds except HD14 with the lowest load. This showed the importance of groundwater inputs with N in contrast to other pollutants such as sediment and phosphorus where most of the annual load occurs in runoff (Landers et al., 2007; McCarty and Haggard, 2016; Webb et al., 1995).

N availability has a significant role in the dynamics of stream ecosystems (Benstead et al., 2009; Kominoski et al., 2015; Suberkropp et al., 2010). The N inputs of anthropogenic readily available N in our study are likely to disrupt the food web and increase C emissions in the streams with high N loads. Benstead et al. (2009) showed that N enrichment (mean NO_3^- -N addition of 0.31 mg L^{-1}) in a headwater stream in the Blue Ridge region of North Carolina resulted in faster decomposition of organic matter and greater CO_2 emission relative to a reference stream. In our study, the base flow mean NO_3^- concentration of 1.32 mg L^{-1} for all four watersheds were greater than the reported threshold of 0.42 mg L^{-1} in the Blue Ridge studies.

McCarty and Haggard (2016) suggested that it may be possible to identify watersheds with high N loads by simply measuring base-flow N concentrations since base-flow and storm-flow N concentrations were highly correlated in data from five watersheds in Arkansas. In our study, base-flow and storm-flow concentrations were also highly correlated ($r = 0.53$, $p < 0.001$). In fact, they were nearly the same (Figure 5-3a). We suggest further that it may be fairly simple to estimate the annual load of TN since hydrologists have estimates of average annual runoff for each region. In Georgia, for

example, Hodler and Schretter (1986) reported that average annual runoff in the Piedmont region was approximately 33% of annual precipitation. Our results imply that one can estimate annual load by multiplying the estimated annual runoff by the base-flow TN concentration. For our streams, we multiplied the average base-flow TN concentrations in Figure 5-3a by the water yields in Figure 5-3c and compared these values to the annual loads we calculated (Figure 5-3b). The results are shown in a scatter plot in Figure 5-4. The simple calculation using mean base-flow TN concentration was quite good with a regression line slope of 1.16, intercept of -2.61 mg L^{-1} , and $R^2 = 0.89$. One of the advantages of using base-flow TN concentrations is that the values are much less variable (coefficient of variation = 35% in our data) than storm-flow TN (coefficient of variation = 58%).

5.5. Conclusions

Using four headwater streams with a gradient in OWTS density, we found that the highest base-flow and storm-flow TN concentrations occurred in watersheds with the lowest density of OWTS (LD5) and the highest density of OWTS (HD17). Higher NO_3^- concentrations were observed during base flow than storm flow, except in LD5. This suggested the NO_3^- originated in groundwater and concentrations were diluted during storm flow. Higher mean TKN concentrations during storm flow compared to base flow in all watersheds suggested TKN originated mainly from runoff. There were significant and positive correlations between base flow NO_3^- concentrations and OWTS density. Higher TKN concentrations during storm flow were correlated with hay and pasture land use, which indicated the source of TKN was runoff.

TN loads were also the highest at extremes of OWTS densities. This was due to the pattern in N concentrations and higher water yields at low and high OWTS density. The

TN loads in our study at low OWTS density were comparable to literature values for pasture land use, but the TN loads for high OWTS density were above literature values for suburban land use. The high N concentrations at the lowest and highest OWTS densities in our study are likely to have disrupted the stream food web and increased C emissions. The correlation between base-flow and storm-flow TN concentrations suggests that it may be relatively easy to estimate TN annual loads for watersheds using a few measurements of base-flow TN.

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Figures:

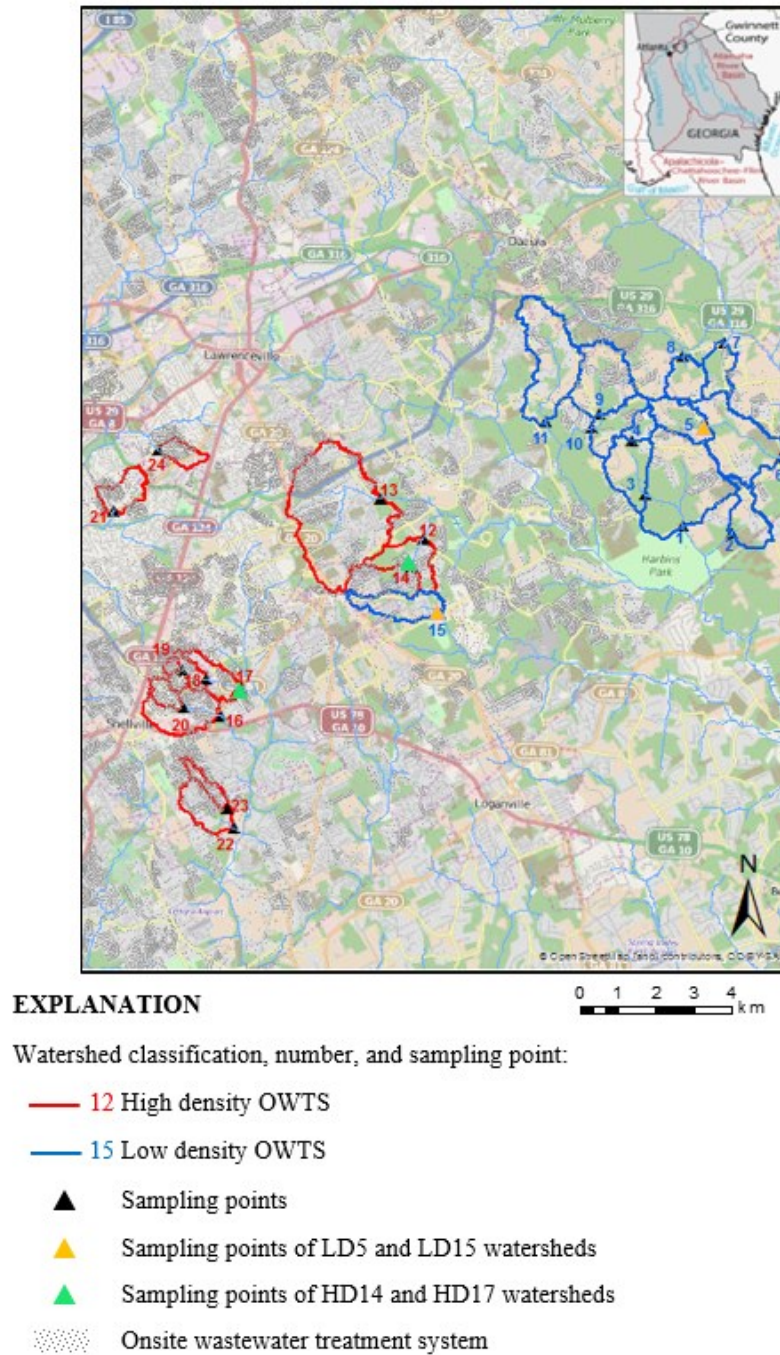


Figure 5-1- Location of the study area, 24 watersheds sampled for base-flow concentrations by Oliver et al. (2014) and Hoghooghi et al. (2016), sampling points for four watersheds (LD5, LD15, HD14, and HD17) in this study, and OWTs in Gwinnett County, GA (modified from Landers and Ankorn, 2008).

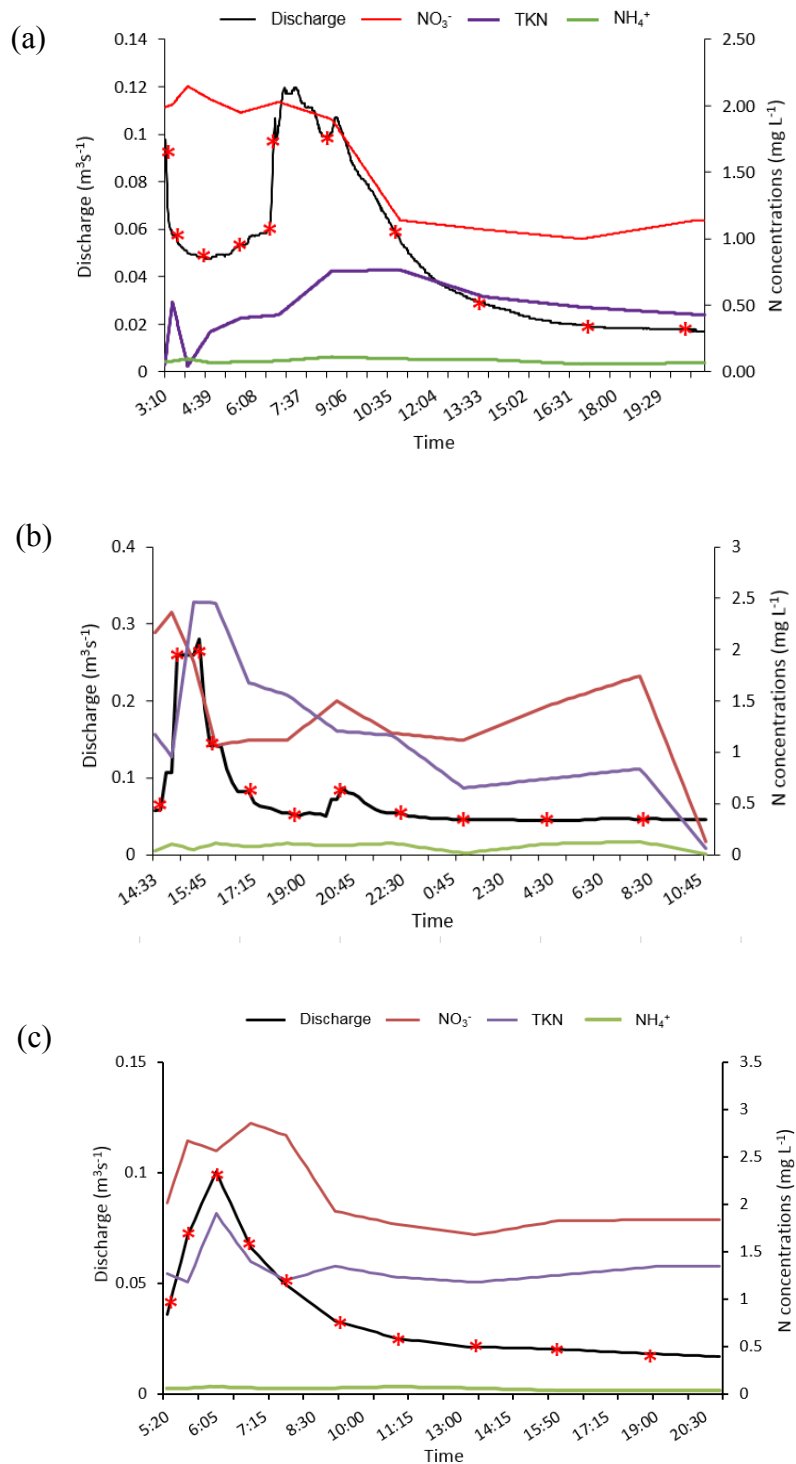


Figure 5-2- Example hydrographs and patterns of N concentrations during storms in the HD17 watershed on a) 11/06/2012, b) 06/02/2013, and c) 02/03/2014. The asterisks on the hydrograph show the times when the ISCO unit took samples.

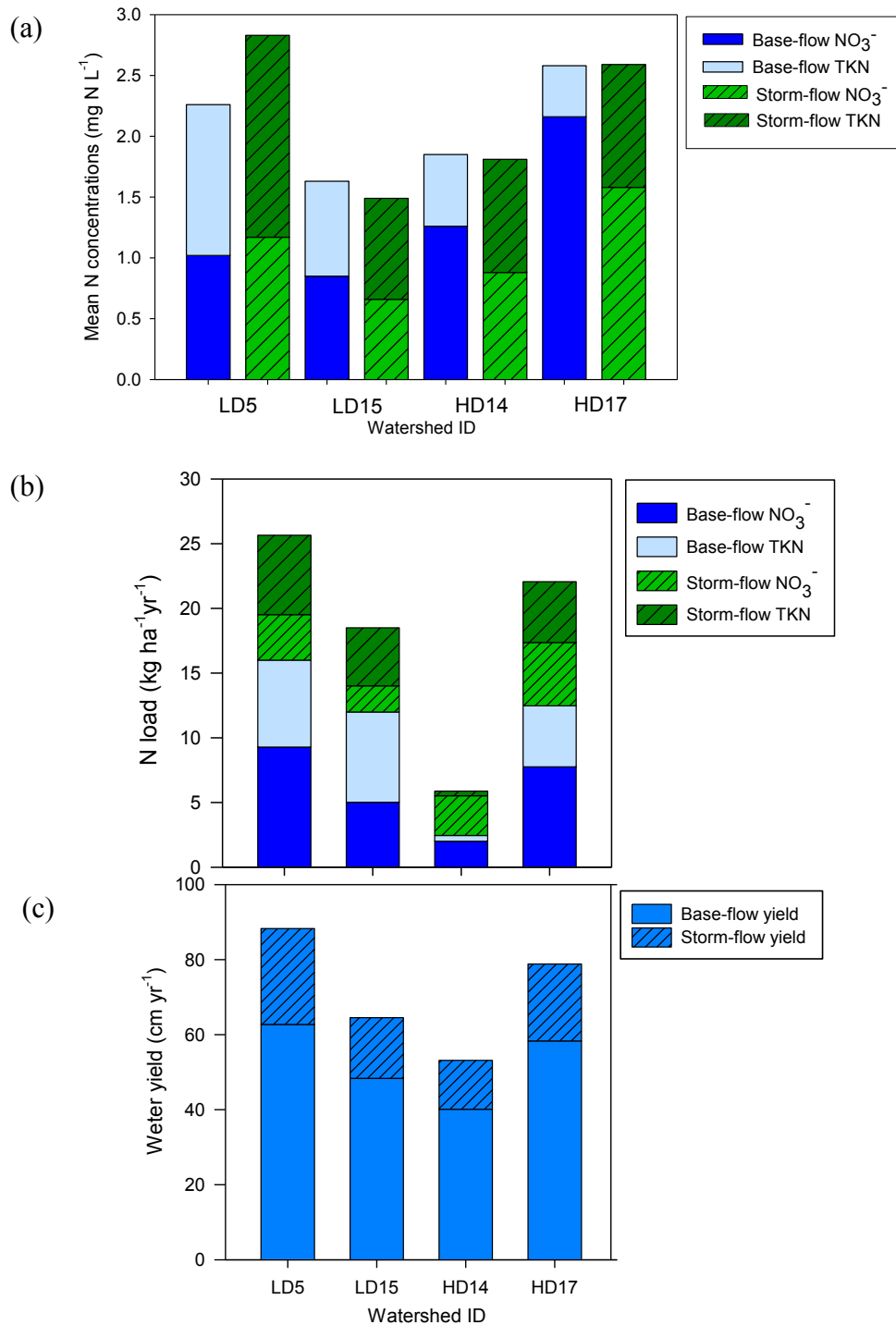


Figure 5-3-Stacked bars of NO_3^- -N and TKN concentrations (a), and loads (b), and water yields (c) during base flow and storm flow in four watersheds (LD5, LD15, HD14, and HD17).

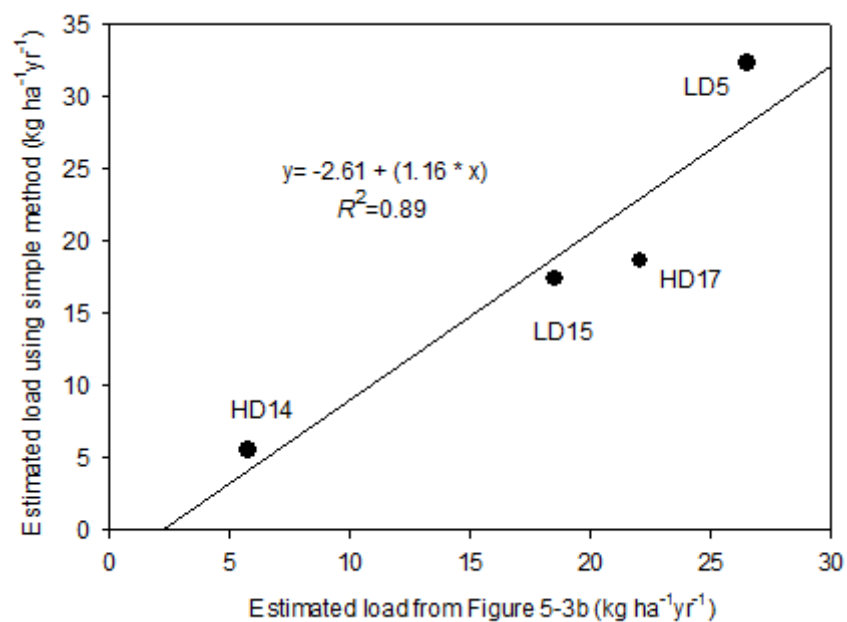


Figure 5-4- A scatter plot of estimated annual load using the average base-flow TN concentration (simple method) versus estimated annual load from Figure 5-3b in all four watersheds.

Table 5-1- Characteristics of selected watersheds in study area Gwinnett County, GA.

Watershed ID	Drainage area	OWTS density	Sanitary sewer line density	Impervious area	Mean slope	Land cover		
						Forest	Residential	Hay and range
	km ²	system km ⁻²	km km ⁻²			%		
LD5	1.48	20	0.00	5	5.8	29	16	52
LD15	1.68	37	13.09	15	4.6	14	71	12
HD14	1.74	141	4.30	16	8.5	23	62	11
HD17	1.68	230	0.00	20	7.5	11	42	8

Table 5-2- The number of storms samples collected by ISCO and the number of storms samples predicted by regression equation from October 2012 to April 2014.

Watershed ID	Number of storms sampled by ISCOs	Number of storms not sampled by ISCOs	Total storm samples collected by ISCOs
LD5	16	110	128
LD15	22	49	176
HD14	35	78	280
HD17	28	72	224

Table 5-3- Regression equations for predicting NO_3^- and TKN concentrations during storms when ISCO units did not take samples for all four watersheds (LD5, LD15, HD14, and HD17) ($p < 0.05$).

Watershed ID	NO_3^-	R^2	TKN	R^2
LD5	$0.83 + (1.70 \cdot \text{flow})$	0.43	$2.02 + (4.36 \cdot \text{flow})$	0.34
LD15	$0.58 + (0.39 \cdot \text{flow})$	0.39	$0.95 - (0.01 \cdot \text{flow})$	0.28
HD14	$1.03 + (3.29 \cdot \text{flow})$	0.41	$0.91 - (0.49 \cdot \text{flow})$	0.31
HD17	$1.56 + (2.56 \cdot \text{flow})$	0.38	$0.92 - (0.85 \cdot \text{flow})$	0.32

Table 5-4- The strength of Pearson correlation coefficient between mean N concentrations and loads, and watershed characteristics during base flow and storm flow. Significant correlations ($p < 0.05$) are shown with asterisk.

Water quality parameters	Base flow				Storm flow			
	OWTS density	Impervious area	Hay and range	Forest	OWTS density	Impervious area	Hay and range	Forest
Concentration								
NO ₃ ⁻ -N	0.72*	0.47*	-0.32*	0.35*	0.42	0.05	0.11	0.18
TKN	-0.43*	-0.35*	0.47*	-0.24	-0.15	-0.22	0.35*	-0.04
Load								
NO ₃ ⁻ -N	0.74	0.47	0.66	0.16	0.13	0.26	-0.003	-0.18
TKN	-0.79	-0.56	0.51	0.11	-0.20	-0.46	0.66	0.13

6. SUMMARY AND CONCLUSIONS

The analysis of N compounds from 24 streams under base-flow conditions in nine synoptic sampling events from November 2011 to July 2014 showed a significant linear increase in TN and NO_3^- -N concentrations with increasing OWTS density above a threshold of about 75 OWTS per square kilometer. A significant linear decrease in TN and NO_3^- -N concentrations with increasing OWTS density was observed below this threshold. Analysis of N and oxygen isotopes of NO_3^- demonstrated that in HD watersheds OWTS were the dominant source of NO_3^- -N with some mixing with another source with lower $\delta^{15}\text{N}$ - NO_3^- values such as lawn fertilizer, oxidation of organic N from leaf litter, or both. However, in LD watersheds positive and significant correlations between grazed lands and NO_3^- -N concentrations, and dual isotope analysis suggested that animal waste mixing with a source with low $\delta^{15}\text{N}$ - NO_3^- values were the main sources of NO_3^- -N concentrations. During base flow, failing OWTS that caused effluent to come to the surface was not likely the source of high NO_3^- -N concentrations. However, failing OWTS that caused incomplete treatment of the effluent in the unsaturated zone could be a source.

Two further studies were designed to determine the effect of OWTS on N loads at the watershed scale. In the first study, the effect of OWTS, including failing systems, in a 44-km² suburban watershed in Metropolitan Atlanta (Big Haynes Creek) was estimated using the Soil and Water Assessment Tool (SWAT). The model was simulated from 1 January 2003 to 31 December 2014 using data from a USGS gage station for calibration and validation. The calibrated SWAT model adequately simulated NO_3^- loads at the

watershed scale with a daily NS of 0.58, *p*-factor of 0.87, and *r*-factor of 3.58 for the calibration period, and NS of 0.33, *p*-factor of 0.88, and *r*-factor of 4.30 for the validation period. The most sensitive N parameters in our model showed the importance of the denitrification process in soils in determining watershed-scale NO_3^- load. The presence of OWTS increased the stream NO_3^- load at the Big Haynes watershed by 23%. By comparison, the addition of OWTS in a sub-basin with a high percentage of OWTS caused a 28% increase in stream NO_3^- load. Overall, OWTS caused the NO_3^- load from groundwater discharge to increase by 85%. At the watershed scale, NO_3^- accounted for about 74% of the TN load, indicating the importance of OWTS on stream loads in urban watersheds. With an estimated 1% of OWTS in failure, these systems did not show a large effect on stream NO_3^- load.

The second study examined base-flow and storm-flow N concentration and load patterns in four headwater streams selected from the original 24 watersheds with a gradient of OWTS density (20-230 systems km^{-2}). We found higher NO_3^- concentrations occurred during base flow than during storm flow in three of the four watersheds. This suggested that the NO_3^- originated in groundwater and concentrations were diluted during storm flow. The opposite was true for organic N concentrations. There were significant and positive correlations between base-flow NO_3^- concentrations and OWTS density. Higher organic N concentrations during storm flow were correlated with hay and pasture land use, which indicated that the source of organic N was runoff. TN loads were also the highest at extremes of OWTS densities. This was due to the pattern in N concentrations and higher water yields at low and high OWTS density. The TN loads in our study at low OWTS density were comparable to literature values for pasture land use, but the TN loads for high

OWTS density were above literature values for suburban land use. The correlation between base-flow and storm-flow TN concentrations suggests that it may be relatively easy to estimate TN annual loads for watersheds using a few measurements of base-flow TN. The high N concentrations at the lowest and highest OWTS densities are likely to have disrupted the stream food web and increased C emissions.

The results of this study confirm the importance of OWTS density on water quality in urban watersheds and can be used in other Piedmont regions where nitrogen Total Maximum Daily Loads (TMDL) are being developed.