LANDSCAPE-SCALE NITRATE FLUXES AND ATTENUATION IN KARST SPRINGSHEDS

By

AMANDA DESORMEAUX

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2018
To everyone who believed in me.
ACKNOWLEDGMENTS

I would like to thank my advisor, Dr. James Jawitz, for his contribution to my intellectual growth over the past 4 years. I am grateful for the advice, support, and feedback he has given me during my time in the Landscape Hydrology Lab. I would also like to thank my committee members, Drs. Mike Annable, Dean Dobberfuhl, and Patrick Inglett for their guidance and expertise throughout the years. I would also like to thank Jill Kent-Wohlrab, John Nial, Christian Van Der Does, Dr. Tony Abbott, Dr. Bruce Bradford, Dr. Finnegan Alford-Cooper, George Johnson, Jon Dain, and Dr. Garrett Evans for their significant and meaningful contributions to my academic confidence, abilities, and interests.

I would like to thank Dawn Lucas and Dr. Jaehyun Cho for their lab mentorship, Karen Bray and Mike Sisk for their administrative support, Henry Kerins for encouraging me to aim high and for helping in the field during the hot Florida summer, Buck Nelson for helping to coordinate fieldwork, my lab mates (both past and present) for their academic and emotional support, and my friends and family for their love and encouragement throughout this long journey.

This work was supported by a grant from the St. Johns River Water Management District, a Graduate Fellowship from the University of Florida School of Natural Resources and the Environment, and a Wetland Biogeochemistry Fellowship from the University of Florida Soil and Water Sciences Department.
TABLE OF CONTENTS

ACKNOWLEDGMENTS .............................................................................................................. 4

LIST OF TABLES .......................................................................................................................... 8

LIST OF FIGURES .......................................................................................................................... 9

LIST OF ABBREVIATIONS ........................................................................................................... 11

ABSTRACT ...................................................................................................................................... 12

CHAPTER .................................................................................................................................. 14

1 INTRODUCTION .................................................................................................................. 14

Water Quality in Karst Springs ................................................................................................. 14
Catchment-Scale Nitrogen Budgets ......................................................................................... 14
In Situ Measurement of N Fluxes and Attenuation .................................................................. 15
Isotopic Signature of Leached Nitrate ....................................................................................... 16
Aquifer Attenuation Capacity ................................................................................................. 17
Time Lags in Karst Landscapes .............................................................................................. 17
Research Goals and Objectives ............................................................................................. 18

2 IN SITU MEASUREMENT OF NITRATE FLUX AND ATTENUATION USING A SOIL PASSIVE FLUX METER .......................................................................................................................... 21

Materials and Methods ........................................................................................................... 23
Laboratory Moisture Profile Experiment ............................................................................... 23
HYDRUS Simulations ............................................................................................................. 24
Plot-Scale Conservative Tracer Test ....................................................................................... 25
Catchment-Scale Nitrate Flux Measurements ......................................................................... 26
   Study area .............................................................................................................................. 26
   Site descriptions .................................................................................................................. 27
Expected N Leaching ............................................................................................................... 28

Results and Discussion .......................................................................................................... 30
Laboratory Experiment and Numerical Modeling ................................................................. 30
Plot-Scale Conservative Tracer Test ....................................................................................... 31
Catchment-Scale Nitrate Flux Measurements ......................................................................... 31
   Crop fluxes and attenuation ................................................................................................. 32
   Pasture fluxes and attenuation ......................................................................................... 33
   Urban fluxes and attenuation ............................................................................................ 34
Measured vs. Expected N Leaching and Attenuation .............................................................. 34
Conclusions ............................................................................................................................. 35

3 DISAGGREGATING LANDSCAPE-SCALE NITROGEN ATTENUATION .................................. 40
4 TEMPORAL EVOLUTION OF NITRATE EXPORT FROM THE KARST SPRINGS OF FLORIDA .............................................. 66

Methods ........................................................................................................... 68
Study Sites ........................................................................................................ 68
Catchment N Budgets ....................................................................................... 69
Datasets ............................................................................................................. 69
P – Population or proportional area ................................................................. 70
L – Load per area or per count ........................................................................ 71
A – Anthropogenic attenuation ...................................................................... 73
N – Natural attenuation ................................................................................... 74
Results and Discussion ...................................................................................... 74
Reconstruction of Historical Inputs ................................................................. 74
Drivers of N Export .......................................................................................... 77
Model Performance ......................................................................................... 78
Conclusions ...................................................................................................... 79

5 GENERAL CONCLUSIONS AND FUTURE WORK ......................................... 87
A  SUPPORTING INFORMATION FOR CHAPTER 3 .................................................. 91
B  SUPPORTING INFORMATION FOR CHAPTER 4 ............................................. 103
LIST OF REFERENCES .......................................................................................... 108
BIOGRAPHICAL SKETCH ..................................................................................... 124
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Parameters used for HYDRUS simulations.</td>
<td>38</td>
</tr>
<tr>
<td>2-2</td>
<td>Characteristics of field sites, corresponding to major land use categories.</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>Total inputs are the sum of fertilizer and manure inputs, plus 3 kg N ha(^{-1}) from..</td>
<td></td>
</tr>
<tr>
<td>A-1</td>
<td>Summary of data used for the WWTF N removal efficiency calculations.</td>
<td>99</td>
</tr>
<tr>
<td>A-2</td>
<td>Land use (LU) and land cover (LC) details for field sites (inputs and outputs).</td>
<td>101</td>
</tr>
<tr>
<td>A-3</td>
<td>PLAN matrix for Silver Springs springshed (mean ± standard deviation).</td>
<td>101</td>
</tr>
<tr>
<td>A-4</td>
<td>SPFM-measured integrated isotopic signature of nitrate leached 30 cm below ground surface (mean ± standard deviation).</td>
<td>102</td>
</tr>
<tr>
<td>A-5</td>
<td>Data used for SIAR and SIAR-SPFM predictions for source contributions to Silver Springs N export. Literature estimates for isotopic signatures from Bateman and Kelly, 2007; Bedard-Haughn et al., 2003; Black et al., 1977; Choi et al., 2007; Curt et al., 2004; Divers et al., 2014; Katz et al., 2009b; Katz and Griffin, 2008; Kaushel et al., 2011; Kendall et al., 2007; Kellman et al., 2005; Michalski et al., 2015; Spolestra et al., 2007; Strum et al., 2011; Widory et al., 2004; Yang and Toor.</td>
<td>102</td>
</tr>
<tr>
<td>B-1</td>
<td>Springshed area, associated counties and respective area, springshed boundary data sources, and water quality and spring discharge data sources.</td>
<td>103</td>
</tr>
<tr>
<td>B-2</td>
<td>Data sources used for multiple-springshed annual and long-term average models.</td>
<td>104</td>
</tr>
<tr>
<td>B-3</td>
<td>Major land use categories across the springsheds.</td>
<td>105</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>Historical land use changes (USDA, 2018) and population (US Census Bureau, 2010) in Florida.</td>
<td>20</td>
</tr>
<tr>
<td>2-1</td>
<td>Laboratory-measured steady-state soil moisture profile (circles) is well described by HYDRUS-1D simulation (solid line, ( R^2 = 0.94 )). Textural</td>
<td>37</td>
</tr>
<tr>
<td>2-2</td>
<td>Convergence factor as a function of changes in Van Genuchten soil water retention parameters ( \alpha ) and ( n ) for SPFMs with (unfilled circles) and without</td>
<td>37</td>
</tr>
<tr>
<td>2-3</td>
<td>Mean (± standard deviation) SPFM-measured nitrate leaching from 5 columns in each of 9 sites of varying land use in the Silver Springs</td>
<td>38</td>
</tr>
<tr>
<td>3-1</td>
<td>Contribution of specific N sources to surface N inputs (( LIN ), Equation 3-4) and spring N export (( LOUTp ), Equation 3-1) estimated from the catchment-</td>
<td>64</td>
</tr>
<tr>
<td>3-2</td>
<td>Total mass of N exported from different sections of the landscape. ( LIN ) is the surface-applied N, ( LL ) is the net N leached after biogeochemical attenuation, ...</td>
<td>65</td>
</tr>
<tr>
<td>3-3</td>
<td>Comparison of source contribution to Silver Springs NO3-N export estimated by catchment-scale N budget, SIAR mixing model, and SIAR mixing model</td>
<td>65</td>
</tr>
<tr>
<td>4-1</td>
<td>Location of study area and springsheds. Dark brown areas represent the location of the intermediate confining unit (ICU) where it is &gt;20m thick. Light...</td>
<td>80</td>
</tr>
<tr>
<td>4-2</td>
<td>Proportional weighting factors for livestock and wastewater. (a) Livestock weighting factors (( \phi_Mi )) for cattle (( \phi_Mcat )), chickens (( \phi_Mchi )), and hogs...........</td>
<td>80</td>
</tr>
<tr>
<td>4-3</td>
<td>Septic + sewer counts from the FWMI dataset agree with total households reported in the 2010 census of housing (FWMI, 2016; US Census Bureau, 2018). ..........................................................</td>
<td>81</td>
</tr>
<tr>
<td>4-4</td>
<td>Historical fertilizer sales for (a) the state of Florida, (b) Wekiwa Springs springshed and (c) Jackson Blue Springs springshed. Data from Alexander .....</td>
<td>81</td>
</tr>
<tr>
<td>4-5</td>
<td>Timeseries of PLAN model parameters for all springsheds. (a) Livestock population density (blue = cattle, black = horse, dashed black = hogs), (b) .......</td>
<td>82</td>
</tr>
<tr>
<td>4-6</td>
<td>N delivery after anthropogenic attenuation (( AW )) .................................................</td>
<td>83</td>
</tr>
<tr>
<td>4-7</td>
<td>Predicted (( LOUTp )) and measured (( LOUTm )) catchment N export .......................</td>
<td>84</td>
</tr>
<tr>
<td>4-8</td>
<td>Relationship between land use and long-term average spring nitrate concentration. (a) the proportion of a springshed in cropland or (b) the. ...........</td>
<td>85</td>
</tr>
</tbody>
</table>
Relationship between $L_{OUT, sp}$ and $L_{OUT, sm}$ for the long-term (1993-2012) N budgets for 16 springsheds. Linear regression for the fill dataset (blue ...... 85

Predicted N fluxes along the hydrological flow path for all 16 springsheds using the PLAN model (blue) and measured spring N export (red). ..................... 86

Silver Springs springshed in Marion County, Florida. (a) Springshed land use (SJRWMD, 2016) where red denotes fertilized urban, yellow denotes ................. 95

Input time series used for N budget calculations. Data was averaged over the time period to estimate the average annual loads from each N source and .... 96

N removal efficiency estimated from TN only compared to estimates using TN from wastewater effluent and TKN of wastewater influent (data in Table ..... 97

SPFM-measured N leaching vs. N inputs (left) and cumulative N leaching by site and attenuation grouped by land use (right), where T represents turf......... 97

Measured N export at Silver Springs from 1997-2017 (Equation 3-3). Silver Springs discharge is measured at USGS station 02239500 (USGS, 2018) ....... 98

Concentration of N forms in spring discharge. Results are the annual averages of quarterly samples (SJRWMD, 2018)........................................... 98

Example of linear interpolation (grey dashes) between decadal population density for Wekiwa Springs (Fang and Jawitz, 2018). The 2012 value (red) ..... 105

Madison County fertilizer sales. Blue points represent the recent (1987-2012) sales data from Brakebill and Gronberg (2017) and historical data (1945-....... 106

Significant ($p < 0.001$) negative correlation between proportion of springshed in agricultural land use and the aquifer attenuation coefficient ($\alpha_{aq} = 1 -$..... 106

State-level fertilizer sales reported in the literature compared to the sum of county-level fertilizer sales reported by Alexander and Smith (1990), ............. 107

Predicted vs. observed N fertilizer sold using multiple linear regression with three predictive variables (crop area, orchard area, and population) for 1950 . 107

White circles are Florida state-level cropland area, black circles are Florida state-level fertilizer sales, and blue circles are Florida state-level farm ............ 107
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>BGS</td>
<td>Below ground surface</td>
</tr>
<tr>
<td>BMAP</td>
<td>Basin management action plan</td>
</tr>
<tr>
<td>FDEP</td>
<td>Florida Department of Environmental Protection</td>
</tr>
<tr>
<td>ICU</td>
<td>Intermediate confining unit</td>
</tr>
<tr>
<td>N</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>NADP</td>
<td>National Atmospheric Deposition Program</td>
</tr>
<tr>
<td>NANI</td>
<td>Net anthropogenic nitrogen inputs</td>
</tr>
<tr>
<td>NSE</td>
<td>Nash-Sutcliffe Efficiency</td>
</tr>
<tr>
<td>SJRMWD</td>
<td>St. Johns River Water Management District</td>
</tr>
<tr>
<td>SOM</td>
<td>Soil organic matter</td>
</tr>
<tr>
<td>SPFM</td>
<td>Soil passive flux meter</td>
</tr>
<tr>
<td>TMDL</td>
<td>Total maximum daily load</td>
</tr>
<tr>
<td>UFA</td>
<td>Upper Floridan aquifer</td>
</tr>
<tr>
<td>WWTF</td>
<td>Wastewater treatment plant</td>
</tr>
</tbody>
</table>
Changes in nitrate concentration and mass discharged from the karst springs of Florida have been observed over the past 50 years. An important question of societal concern is to what degree these changes are the result of anthropogenic N loading. Understanding the drivers of spring N export, which integrates the inputs, transport, and attenuation factors over an entire springshed, is critical to further our understanding of catchment-scale N budgets in karst regions.

This dissertation addresses questions about the drivers of nitrate contamination in the Upper Floridan Aquifer across space and time, using in situ measurements of nitrate fluxes and attenuation and long-term records of surface N inputs and spring exports. The development and application of a simple method for direct in situ measurements of vadose zone nitrate leaching and attenuation was demonstrated, and it was concluded that the modified soil passive flux meter (SPFM) offers low-cost, robust, and accurate measures of nitrate leaching and attenuation when N inputs are known. A catchment-scale N budget was then constructed for a mixed land-use springshed, using SPFM-measured nitrate attenuation to model spring N export. It was estimated that 90% of surface N inputs were attenuated as N moved throughout the
landscape, with 64% of inputs attenuated in the root zone. Finally, long-term trajectories of nitrate inputs and spring export were analyzed from multiple spring catchments to evaluate the long-term drivers of spring N fluxes. While N inputs increased over time due to anthropogenic activity, the relative contributions of sources were variable across space and time and were driven by specific land-use practices.
CHAPTER 1
INTRODUCTION

Water Quality in Karst Springs

Rising nitrate concentrations have been identified as a threat to freshwater systems around the globe (Rabalais, 2002; Smith et al., 1999). Increasing trends have been observed for nitrate in many of Florida’s springs over the past 50 years, with approximately 80% of springs exhibiting nitrate concentrations above background levels (Scott et al., 2004). Rapid population growth and changes in land use (Figure 1-1) have occurred alongside the observed changes in spring chemistry, suggesting these are important drivers of groundwater contamination (Badruzzaman et al., 2012; Katz, 2004; Munch et al., 2006).

Catchment-Scale Nitrogen Budgets

Karst landscapes are inherently vulnerable to nitrate loading, as nitrate can be rapidly transported to unconfined portions of the aquifer (Green et al., 2006). The spring catchment, or springshed, is the land surface area that contributes recharge to the aquifer that then emerges as spring discharge. In the subsurface, the springshed boundary is delineated based on groundwater that flows towards the spring. The spring export represents the integral of the inputs, transport, and attenuation factors over the entire springshed, both above and below ground.

The first step in improving our understanding of catchment-scale N balances is assessing excess N inputs to the landscape (e.g., David et al., 2010; Goyette et al., 2016; Van Meter and Basu, 2017). Surface loading of N can be estimated from fertilizer sales or literature estimates for different land uses (e.g., Eller and Katz, 2017). But estimating the fraction of the surface loading that reaches the groundwater is subject to
large uncertainty because not all the N applied in the springshed reaches the groundwater. Nitrogen use efficiency in the US ranges from 50 to 70% (Lassaletta et al., 2014; Zhang et al., 2015), suggesting that half or more of N inputs in agricultural systems are taken up by crops. In addition to crop uptake, N can be lost as a gas through denitrification and volatilization when conditions are favorable. While N can also be taken up into soil microbial biomass via immobilization, this is not a removal process as N can be later released through mineralization. Globally, surface waters export 25% of surface N inputs (Boyer et al., 2002; Howarth et al., 2012; Schaefer et al., 2009; Swaney et al., 2012; Vitousek et al., 1997), suggesting that 75% of surface inputs are attenuated through plant uptake or gaseous losses.

While net anthropogenic N inputs (NANI) are commonly used as a proxy for N inputs to groundwater (e.g., Hong et al., 2011, Van Meter et al; 2016), direct measurements of soil nitrate fluxes are critical for quantifying actual nitrate leaching and attenuation as an independent validation of catchment-scale N budgets.

**In Situ Measurement of N Fluxes and Attenuation**

Traditional methods to measure nitrate movement in soils, including cores and suction or drainage lysimeters, are recognized to have significant limitations (Weihermüller et al., 2007; Zotarelli et al., 2007). Soil cores do not allow for cumulative flux measurements, instead providing only individual temporal snapshots of nitrate concentrations. Suction lysimeters collect less mobile soil water and are not representative of macropore flow (Landon et al., 1999; Toosi et al., 2014). Drainage lysimeters allow for cumulative measurement of mobile soil water (Landon et al., 1999; Zotarelli et al., 2007), but flow divergence around the lysimeter can result in drainage
collection efficiencies < 50% (Zhu et al., 2002). Additional drawbacks of drainage lysimeters include costly construction, labor-intensive installation, and frequent sampling. Passive wick lysimeters are an alternative to drainage lysimeters that minimize divergence by avoiding the development of a saturated layer at the base of the lysimeter (Holder et al., 1991). The addition of a control tube above the wick can help control both divergence and convergence (Gee et al., 2009), but wick lysimeters still require frequent sampling.

Ion-exchange resin columns are recognized as an effective method for solute mass balances (Weihermüller et al., 2007) and have been used to measure solute fluxes in situ across a broad range of soil types and land uses (e.g., Grahmann et al., 2018; Predotova et al., 2011; Ventura et al., 2013). Soil ion-exchange resin columns generally consist of a PVC column filled with resin or a resin/sand mixture, with a mesh lining at the base (Lang and Kaupenjohann, 2004; Susfalk and Johnson, 2002; Willich and Buerkert, 2016). The resin adsorbs and accumulates ions from the soil solution through a known cross-sectional area (e.g., Lehmann et al., 2001; Susfalk and Johnson, 2002), resulting in temporal integration of solute fluxes during the deployment period. When surface N inputs are known, attenuation can be calculated as the difference between the known N input and measured N leaching.

**Isotopic Signature of Leached Nitrate**

In addition to nitrate flux measurements, ion-exchange resin columns can be used to identify the integrated stable isotopic $\delta^{15}N/\delta^{18}O$ signature of adsorbed nitrate. Different sources of nitrate have distinct isotopic $\delta^{15}N/\delta^{18}O$ signatures, so stable isotopic compositions can be used to elucidate the source of nitrate in soil water (Minet
et al., 2012). The nitrate collected for flux measurements can be analyzed for $\delta^{15}N$ and $\delta^{18}O$, thus eliminating the cost of resin associated with isotopic analysis. Understanding the relationship between the $\delta^{15}N/\delta^{18}O$ signature of nitrate sources and leached nitrate would elucidate the changes in nitrate isotopic signatures from microbial processing in the vadose zone.

**Aquifer Attenuation Capacity**

There is also a need to identify the attenuation capacity of the Upper Floridan Aquifer for the full catchment-scale mass balance. Denitrification is assumed to be the major attenuation pathway in aquifers with favorable conditions, with global estimates of groundwater denitrification averaging 16% of N inputs (Seitzinger et al., 2006). Excess N$_2$ in aquifer discharge is an integrated measure of attenuation over the entire flow path and can be used to estimate bulk aquifer attenuation rates. Previous work measuring excess N$_2$ in spring discharge across the karstic Upper Floridan Aquifer (UFA) has estimated that denitrification removes an average of 32% of the N that reaches the groundwater (Heffernan et al., 2012), suggesting the UFA has a high potential for denitrification.

**Time Lags in Karst Landscapes**

Following implementation of conservation measures in response to increased nitrate concentrations in the UFA, it is important to understand when nitrate concentrations can be expected to decrease in Florida’s springs. Evidence of soil legacy N/N accumulation in the vadose zone can result in time-lags between N loading and water quality responses (Gardner and Drinkwater, 2009; Sebilo et al., 2013; Van Meter et al., 2016; Worrall et al., 2015), and studies in the UFA have suggested time lags
ranging from 1 to 10 years (Musgrove et al., 2014). Spring discharge from the UFA is a mixture of young (<2 years) and old (>50 years) water (Katz et al., 2004), suggesting that legacy N could impact spring water quality for decades. There is a need to understand how future changes in land use/land management will drive water quality to support realistic expectations for water quality restoration.

**Research Goals and Objectives**

This dissertation aims to identify the drivers of nitrate contamination in the Upper Floridan Aquifer across space and time. Chapter 2 presents the development and testing of a method for in situ measurement of nitrate fluxes and attenuation. A soil passive flux meter (SPFM) was designed to measure solute leaching based on a modified design of ion-exchange resin columns, and numerical simulations, laboratory experiments, plot-scale field experiments, and a catchment-scale field deployment were conducted to test the hypothesis that that SPFM would provide accurate measurements of soil nitrate leaching and attenuation where N inputs were known and uniformly applied. Chapter 3 presents a catchment-scale N budget for the Silver Springs springshed, a mixed land-use springshed in Florida. In situ measurements of nitrate attenuation were used to disaggregate attenuation through the landscape, testing the hypothesis that the majority of springshed N inputs are attenuated in the soil and aquifer. The SPFM were also used to measure the δ¹⁵N/δ¹⁸O signature of leached nitrate, which was used to test the hypothesis that N transformation processes could mask the source δ¹⁵N/δ¹⁸O signal early in the leaching process. Chapter 4 extends the landscape-scale analyses in both space and time by constructing long-term trends of N surface inputs and spring exports for multiple spring catchments. Using calculated long-
term N inputs along with N concentration and discharge records for multiple catchments with a range of land use patterns, we tested the hypothesis that information on the temporal evolution of catchment N loads and technological attenuation capacity, along with an understanding of the natural attenuation capacity of the landscape, can be used to reconstruct historical trends in N export.
Figure 1-1. Historical land use changes (USDA, 2018) and population (US Census Bureau, 2010) in Florida.
While ion-exchange resin columns avoid many of the pitfalls associated with alternative methods to measure solute fluxes (Weihermüller et al., 2007), textural differences between resin and native soil introduce hydraulic discontinuities that can result in flow divergence (bypassing of the resin column by infiltrating water) or convergence (water entering the resin column from an infiltration area greater than the column cross-sectional area). Here the effect of the device on altering soil water flux and solute recovery is described in terms of a convergence factor ($\chi$) defined as the ratio of the soil surface area that contributes recharge to the device and the column cross-sectional area. Values of $\chi > 1$ indicate flow convergence, while $\chi < 1$ indicates divergence, and the ideal desired state is $\chi = 1$. The few studies using ion-exchange resin columns that have evaluated solute recovery have reported sub-optimal values of $\chi << 1$. Siemens and Kaupenjohann (2004) reported $\chi = 0.06$, based on recovery of surface-applied tracer, from 10-cm x 10-cm PVC columns filled with a 1:1 volumetric ratio mixture of resin and native soil, while Lehmann et al. (2001) found $0.005 < \chi < 0.47$ for soil columns of various sizes filled with a 1:4 volumetric ratio mix of resin and quartz sand. Ion-exchange resin columns occasionally include a layer of sand (Predotova et al., 2011; Susfalk and Johnson, 2002) or glass beads (Ventura et al., 2013) above the resin layer, but the effect of these design modifications on recovery efficiencies have not been reported. Gee et al. (2002) found that in numerical simulations, extending the height of a divergence column minimized water divergence.
around a 10-cm diameter column in sandy soils, suggesting that extending the column above the resin layer could improve recovery efficiency.

Soil resin columns passively integrate the solute flux that traverses the device during the deployment duration, and are thus referred to as soil passive flux meters (SPFMs), as analogs to other passive flux meters for groundwater (Hatfield et al., 2004) and surface water (Klammler et al., 2007). The objective of this study was to design an SPFM to quantify soil N fluxes in sandy, unsaturated soils to minimize flow divergence and maximize solute recovery. It was hypothesized that mixing resin with native soil at 1:1 volumetric ratio would avoid the build-up of a saturated layer above the resin/soil layer, while maintaining nitrate retention capacity of at least an order of magnitude greater than the expected nitrate load. It was also hypothesized that the additional modification of extending the height of the column above the resin layer would minimize flow divergence and therefore improve column recovery efficiency (i.e., $\chi$ closer to 1 than with no extension).

The modified design was tested and validated in a series of numerical simulations and laboratory and plot-scale experiments. Additionally, the SPFMs were tested in a catchment-scale field deployment at nine sites with three land uses with known N inputs across a mixed land-use springshed in Florida to obtain in situ measurements of average soil nitrate fluxes and attenuation in the upper 30 cm of soil. The measured fluxes and attenuation were compared with expected ranges based on literature values.
Materials and Methods

Laboratory Moisture Profile Experiment

A 10-cm x 90-cm soil column was constructed using 10-cm x 5-cm acrylic column sections that were stacked and sealed with silicone. A mesh liner was clamped to the bottom of the column and Arredondo fine sand (Loamy, siliceous, semiactive, hyperthermic Grossarenic Paleudult) was wet packed in the bottom 30-cm of the column (z = 60 to 90 cm below the column surface). A mesh liner was sealed between the two column sections (z = 60 cm) an additional 30 cm of soil was wet-packed above the second liner (z = 30 to 60-cm), which was included to assess the effects of the mesh liner on the moisture profile. A third mesh liner was sealed between the final two column sections (z = 30 cm) and a 1:1 volumetric mix of Purolite A520-E anion exchange resin and soil was wet-packed into the column (z = 20 to 30 cm), followed by soil to the top of the column (z = 0 to 20 cm).

Water was applied to the column surface at 22.75 cm d⁻¹ (1.79 L d⁻¹). Once steady-state was reached, after approximately 7 days, a single application of a 150 mL solution of 80 g L⁻¹ KNO₃ was applied to the surface of the column, followed by a final two days of water application, resulting in a total time of 9 days. The column was quickly disassembled, and the volumetric water content was measured gravimetrically for each 5-cm section. After drying for water content measurements, 5-g aliquots (n = 3) were eluted from each section using 50 mL of 2M KCl and the extracts were analyzed for NO₃⁻ (EPA method 353.2).
HYDRUS Simulations

The laboratory-measured steady-state soil moisture profile was compared to results from a one-dimensional numerical model with HYDRUS-1D (Simunek et al., 2005). The model domain and boundary conditions were set to emulate the laboratory experiment, with 10 cm of resin placed 30 cm below the surface in a 90-cm column of native soil (Arredondo fine sand), and irrigation applied at 22.75 cm d\(^{-1}\) for 7 days, with free drainage at the bottom of the column. Van Genuchten parameters (Table 2-1) were estimated from neural network predictions (Rosetta Lite version 1.1, (Schaap et al., 2001)) using soil texture (NCSS, 2018) and measured moisture release curve data for the soil, and texture and saturated water content for the resin as input data. Geotextile data from Nahlawi et al. (2007) was used to estimate hydraulic parameters for the mesh liner (Table 2-1).

Additionally, two-dimensional axisymmetric modeling was performed in a 50-cm radius x 50-cm length domain with HYDRUS-2D (Simunek et al., 2006) to evaluate effect of column extensions above the resin layer on \(\chi\) for a range of soil-resin textural differences. A 5-cm diameter, 10-cm long resin layer was placed 40 cm below the surface. The column that contained the resin was simulated as an impervious layer, and simulations were conducted with and without 10-cm extensions of the column above the resin layer. For consistency with field tests described below, after initiation of steady-state water flow at 5 cm d\(^{-1}\), a solute pulse was applied at loading rate \(L = 148\) kg ha\(^{-1}\) followed by irrigation for an additional two days. The tracer was non-sorbing to the native soil (partitioning coefficient \(K_d = 0\)) but was strongly sorbed to the resin (\(K_d = 1,000\) mg kg\(^{-1}\)). The soil and resin hydraulic parameters are shown in Table 2-1. The
soil parameters were held constant, while resin parameters were changed one at a time. Convergence factor ($\chi$) was determined as the ratio of the mass of tracer adsorbed to the SPFM ($M_s$) to the mass of tracer applied directly over the column ($M_a$). For the simulations, $M_s$ was calculated as the difference between the cumulative surface-applied and drained tracer mass and $M_a$ was calculated as the product of the loading rate of the solute pulse ($L = 148$ kg ha$^{-1}$) and the cross-sectional area of the SPFM ($A_s = 81$ cm$^2$). This assumes no tracer is leached through the resin, thus requiring a tracer application well-below the expected breakthrough point of the resin.

**Plot-Scale Conservative Tracer Test**

After simulating the possible range of $\chi$ values, a tracer test was designed to measure $\chi$ in the field. SPFMs were constructed using 20-cm lengths of 10-cm diameter PVC, with drain cloth stretched over the bottom and secured with a pipe clamp. Four SPFMs were installed 30 cm below ground surface (bgs) in a 1-m$^2$ plot at the University of Florida Field and Fork Farm. To minimize flow path disturbance, the top 20-cm of soil were excavated from the surface as an intact 20-cm x 20-cm core using a drain spade and then replaced once the SPFM had been deployed. Similarly, soil below this depth was excavated using a soil auger and was replaced over the SPFM in the original order. The resin layer was the bottom 10-cm of the SPFM and comprised soil from 40 to 50 cm bgs mixed at 1:1 volumetric ratio with 150-g of Purolite A520-E anion exchange resin that had been triple-rinsed with DI water and then air dried. The top 10 cm of the SPFM comprised soil from 30 to 40 cm bgs that was replaced over the resin/soil layer. Contact was ensured between the SPFM bottom drain cloth and the soil at the bottom of the excavated holes.
Following column installation, the plot was irrigated at 5 cm d\(^{-1}\) for two days and then 148 kg ha\(^{-1}\) Br\(^{-}\) was applied to the soil surface as a KBr tracer solution using a tank sprayer, followed by an additional 6 days of irrigation at 5 cm d\(^{-1}\), resulting in a total of 30 cm of irrigation. The columns were left to drain for one additional day and were excavated 9 days after installation. All resin samples were air dried and weighed, and 5-g aliquots were extracted using 50-mL of 2M KCl and analyzed for Br\(^{-}\) (EPA method 300.1).

**Catchment-Scale Nitrate Flux Measurements**

**Study area**

The catchment-scale testing was performed in the 1300-km\(^2\) Silver Springs springshed, in Marion County, Florida. SPFMs were deployed in the field sites to quantify N fluxes and attenuation in the surface 30-cm of soil across a range of land uses and N application rates. Nine field sites were selected, with three each in crop, pasture, and urban land uses to represent the range of typical practices (e.g., N rate and timing) within each land use.

Each site was instrumented with 5 columns in June 2017 and the SPFMs were retrieved after 120 days in September 2017 to capture wet season (Jun-Sep) fluxes. Nitrogen inputs were calculated for each location (Table 2-2) based on fertilizer records, stocking rates, and literature estimates for livestock N excretion. In addition to the inputs listed in Table 2-2, atmospheric deposition for the deployment period was estimated as 3 kg N ha\(^{-1}\) for the entire springshed using the TDEP model output for 2011-2015 (NADP, 2016). Soil columns were constructed, installed, retrieved, and analyzed as described above. Conservative tracer was applied at each site (\(L = 100 \text{ kg ha}^{-1} \text{ Br}^{-}\)) and
raw nitrate flux measurements were divided by the site-specific $\chi$ as a correction factor to account for soil water convergence. Non-detects were recorded as one-half of the detection limit, which was determined to be 0.32 kg NO$_3$-N ha$^{-1}$ from 10 replicate blank resin samples. Attenuation was calculated as the difference between the known inputs and measured output (nitrate leaching).

**Site descriptions**

The crop sites were planted with peanut (*Arachis hypogaea* L.), bermudagrass hay (*Cynodon dactylon* L.), and sunflower (*Helianthus annuus*). All three crop sites received fertilizer in a single application during the deployment period and biological N fixation was estimated to be 200 kg N ha$^{-1}$ for peanut (Dubeux et al., 2017). Site location, soil type, and N application rates are described in Table 2-2.

Pasture sites 1 and 2 sites were horse pastures stocked at 2.5 horses ha$^{-1}$. No fertilizer was applied at either site and manure and urine patches were randomly distributed throughout the field. Additionally, stockpiled manure and stall bedding from 24 horses was broadcast uniformly across the 1.2-ha Pasture 2 site every two months. Pasture site 3 was a cattle pasture stocked with 60 cow-calf pairs on 10 ha. In addition to randomly distributed manure and urine patches, a single application of fertilizer was applied at Pasture 3 during the deployment period. Horse, beef cow, and beef calf excretion rates of 0.14, 0.16, and 0.13 kg N d$^{-1}$ (ASABE, 2010; Hubbard et al., 2004), respectively, were used to estimate total manure N applied during the deployment period (Table 2-2).

Turf site 1 was an unfertilized bahiagrass (*Paspalum notatum*), Turf 2 was planted with ‘TifTif’ bermudagrass (*Cynodon dactylon* L. X *C. trunsvaalensis* Burtt-
Davy), and Turf 3 was a golf green planted with SeaDwarf® seashore paspalum
(*Paspalurn vaginatum* Swartz). Turf 2 received a single application of fertilizer during
the deployment period, while fertilizer was applied bi-weekly to Turf 3.

**Expected N Leaching**

Each site was categorized by a hypothesized expected nitrate leaching based on
literature values for similar cropping systems, the magnitude of N inputs, and land use
intensity. Considering the high uncertainty in estimating nitrate leaching, a general
categorization of low (0-20 kg N ha\(^{-1}\)), moderate (20-50 kg N ha\(^{-1}\)), and high (> 50 kg N
ha\(^{-1}\)) was used. Low nitrate leaching was expected in perennial grass systems with low
nitrogen applications, due to year-round established root systems and high
denitrification potential (Di and Cameron, 2002; Gold et al., 1990; Herrmann and
Cadenasso, 2017; Wang et al., 2014). This included Turf 1, the unfertilized turf grass
site, Turf 2, the turf grass site fertilized at the UF/IFAS recommended rate for turf, and
Pasture 1, the unfertilized horse pasture with low manure inputs.

Moderate nitrate leaching was expected in perennial grass systems with
moderate to high N applications, such as Turf 3, the fertilized golf green, and Crop 1,
the fertilized hay crop. While established perennial grass systems typically leach less
than 5% of applied N when fertilized at or below recommended N rates (Barton and
Colmer, 2005), high N application rates can lead to substantial N leaching losses in
these systems (Agyin-Birikorang et al., 2012a; Shuman, 2001; Wong et al., 1998).

Moderate leaching was also expected from Crop 3, the sunflower crop. Excess soil-N is
vulnerable to leaching during periods of low plant demand, which characterize the pre-
emergence and post-harvest periods of annual cropping systems (Crews and Peoples,
Fertilizer was applied to the sunflower crop in a single application pre-emergence and the crop was mowed down and disced into the soil at the end of the season, so moderate N leaching was expected due to the asynchrony between N supply and crop demands.

Nitrate leaching was expected to be highest in land uses with high N inputs and/or harvested crops characterized by periods with no plant cover after harvest. In peanut production systems, the seeds/pods are removed from the plants during harvest and the vegetative/root biomass is left in the field. Sandy soils and warm temperatures that characterize North Florida are ideal conditions for rapid organic matter mineralization and subsequent nitrification, which can result in high N leaching loads post-harvest (Prasad et al., 2015). In previous studies under nodulating peanut plants at this location, total vegetative and root N ranged from 92 to 139 kg N ha\(^{-1}\) without fertilization, and 97 to 145 kg N ha\(^{-1}\) when fertilized at 60 kg N ha\(^{-1}\) (Selamat and Gardner, 1985). High nitrate fluxes were therefore expected for the peanut crop (Crop 2) despite a very low fertilizer N application, since the majority of fixed N was left in the field after harvest, followed by a period without plant cover. While long-term grazed pastures can act as a temporary sink for N, this N can be rapidly cycled into mobile forms. Additionally, fertilizer applications have been shown to enhance mineralization in long-term pasture systems (Gill et al., 1995). The cattle pasture (Pasture 3) has been subjected to high long-term N inputs from manure/urine, but fertilizer was applied for the first time during the measurement period. High leaching rates were therefore expected in this system. Similarly, high nitrate leaching was expected in Pasture 2 due to long-term high N inputs and low N retention capacity of the sandy soil.
Results and Discussion

Laboratory Experiment and Numerical Modeling

Measured and simulated soil moisture were in good agreement ($R^2=0.94$, Figure 2-1). This suggests that soil, resin, and mesh parameters used in the model are appropriate for the materials used. A coarse-textured soil underlying a finer-textured soil creates a capillary barrier effect (Stormont et al., 1999) and this effect increases with the coarseness and uniformity of the underlying soil (Baker and Hillel, 1990). As hypothesized, mixing the resin with native soil avoided the build-up of a saturated zone above the resin by minimizing particle size discontinuities. This is important, as a saturated layer above the resin creates conditions favorable for denitrification, which could influence measured N fluxes. The resin/soil mixture retained 1.6 g NO$_3$-N without breakthrough, equivalent to 2,000 kg N ha$^{-1}$. This is an order of magnitude greater than the highest expected leaching fluxes at the field sites, suggesting that the capacity of the resin is sufficient.

Also as hypothesized, in HYDRUS simulations, extending the impermeable column to house 10 cm of native soil above the resin layer reduced the sensitivity of $\chi$ to changes in the hydraulic properties of the resin layer (Figure 2-2). These simulations show that textural discontinuities between the resin layer and surrounding soil, represented here as differences in the soil hydraulic parameters $\alpha$ and $n$, result in $\chi \neq 1$. When either hydraulic parameter $\alpha$ or $n$ are greater in the resin than the surrounding soil, there is a divergence of water around the column. Conversely, when $\alpha$ or $n$ are lower in the resin than the surrounding soil, there is a convergence of water through the column. Only when the parameters are equal in the soil and resin does $\chi = 1$. As shown
in Figure 2-2, $\chi$ is more sensitive to changes in $\alpha$ with or without the column extension. However, the magnitude of these effects was reduced when the impermeable column was extended 10 cm, as reflected in the reduced slope in Figure 2-2 for both parameters.

**Plot-Scale Conservative Tracer Test**

The measured convergence factor for the plot-scale conservative tracer test was $\chi = 1.3 \pm 0.2$. The slight convergence of soil water through the column suggests that the effect of textural differences was not eliminated completely by the design modifications. Tracer application experiments are therefore critical for accurate interpretation of fluxes measured using ion-exchange resin columns.

**Catchment-Scale Nitrate Flux Measurements**

Based on 45 SPFMs deployed at 9 sites, field-scale convergence mean and standard deviation was $\chi = 1.1 \pm 0.3$ and was not significantly different between the different land uses (1-way ANOVA; $p = 0.16$). These results suggest that the 10-cm extension of the impermeable column above the resin layer helped bring the measured $\chi$ values closer to 1 across a range of soil properties.

Nitrate fluxes measured by the SPFMs were strongly affected not just by the land-use-specific N application rates, but also by the rainfall pattern during the deployment period. A total of 95 cm of rainfall were measured during the 120-day deployment period, with mean intensity $1.3 \text{ cm day}^{-1}$ and mean interarrival time of 1.7 days. Leaching events are ultimately driven by rainfall in excess of the soil water holding capacity, so measured nitrate leaching fluxes were likely greater than average due to these relatively high-frequency and magnitude rainfall events.
The SPFM-measured NO₃-N leaching fluxes were positively correlated with N inputs ($R^2 = 0.50, p < 0.05$), which is consistent with previous findings in this region (Prasad and Hochmuth, 2016). The flux was 51 kg NO₃-N ha⁻¹ (± 41) across all sites, and 12 (± 14), 59 (± 22), and 82 (± 67) kg NO₃-N ha⁻¹, respectively, for turf, crop, and pasture land use types. The coefficient of variation within land uses was relatively high, CV = 117%, 37%, and 82% for turf, crop, and pasture, suggesting that the within-land use differences are important. Mean attenuation was 90% (± 13%), 59% (± 32%), and 48% (± 22%), respectively for turf, pasture, and crop sites. The high intra-land use variability illustrates that land use type alone is insufficient to categorize nitrate fluxes and attenuation, as they are heavily influenced by site-specific land management practices.

**Crop fluxes and attenuation**

The SPFM-measured flux from the hay field (Crop 1) represented a large percentage of the applied fertilizer. However, this site had relatively high SOM (4%) and it is likely that soil N mineralization contributed additional N to the system. Previous studies of forage systems in coarse-textured soils have found low nitrogen uptake efficiencies (13 to 30%), low N accumulation in the surface soil, and high soil nitrate concentrations below the root zone when fertilized at high annual rates such as at the field site (Agyin-Birikorang et al., 2012b; Woodard and Sollenberger, 2011).

The SPFM-measured N fluxes under peanuts (Crop 2) were comparable to vegetative and root N stocks, which were incorporated into the soil after harvest. Similarly, the sunflower was unharvested and incorporated into the soil, leaving the vegetative N to mineralize in the field. The warm temperatures and high rainfall during
summer months are ideal conditions for mineralization and nitrification, so this fate is likely for much of the N taken up by the plants. The results suggest that organic N from vegetative and root biomass is rapidly cycled and transformed to nitrate in this system and can be leaching during the period following harvest.

**Pasture fluxes and attenuation**

Nitrate leaching at the unfertilized horse pasture (Pasture 1) was below the SPFM detection limit. While nitrate leaching was expected to be low at this site, there is also a possibility that the area sampled by SPFM was too small to capture nitrate fluxes in land uses that are subject only to randomly distributed patches of manure/urine. For example, in simulations of random distributions of urine patches Lilburne et al. (2012) found that nitrate leaching estimates for 5 resin columns of 113 cm$^2$ surface area distributed in a 1-ha field would have an error of more than 20%, based on the probability of sampling under a urine/manure patch. Our 81-cm$^2$ SPFMs are approximately 30% smaller those in the simulations, thus similar or larger uncertainty is expected.

As expected, nitrate leaching was highest in Pastures 2 and 3 (80 and 165 kg N ha$^{-1}$). These rates are similar to previous studies of nitrate leaching in high-input pasture systems (Di and Cameron, 2007). Pasture 2 was subject to year-round, uniform application of high rates of stockpiled manure with no exports of N through hay or livestock. All N applied to the soil surface is therefore recycled between the grass, horse, and soil, or lost to the atmosphere or via leaching. At Pasture 3, three of the five N flux measurements were exceptionally high (mean = 242 kg N ha$^{-1}$) compared to the other two (mean = 58 kg N ha$^{-1}$). It is possible that three SPFM intercepted N fluxes
leached directly below a manure or urine patch, as these results are similar to leaching fluxes measured directly under cattle urine patch areas (Di and Cameron, 2007).

**Urban fluxes and attenuation**

As expected, nitrate leaching was low in the low- and moderate-intensity turf systems (Turf 1 and 2), and moderate in the high-intensity turf system (Turf 3). When averaged across sites by land use, turf leaching fluxes were significantly lower than pasture fluxes ($p = 0.01$). Across all turf sites, mean nitrate attenuation was 90% ± 13 (Table 2-2), which is consistent with previous studies that show turf systems are highly efficient at attenuating N inputs, especially during the summer months (Barton and Colmer, 2006; Carey et al., 2012). The relatively low variability of turf attenuation, compared to crop and pasture, suggests that general categorization of urban turf is likely sufficient when scaling estimates up to the catchment-scale.

**Measured vs. Expected N Leaching and Attenuation**

The SPFM-measured nitrate leaching fluxes are shown in Figure 2-3 for all nine sites, categorized by the expected leaching ranges. The mean nitrate leaching fluxes measured at the nine sites ranged from 0 to 165 kg N ha$^{-1}$ and were positively correlated with N inputs ($R^2 = 0.50, p < 0.05$). While our assessment of expected nitrate leaching was in good agreement with measured values, the magnitude of measured nitrate leaching was greater than our expectations. This is likely due to the high frequency and magnitude of rainfall events, as recharge is positively correlated with nitrate leaching across the US (Liao et al., 2012), as well as site-specific drivers discussed above (e.g., the rate and timing of N inputs). Mean nitrogen attenuation was 66% of inputs across all land uses. This value represents the sum of crop uptake,
gaseous losses, and soil N accumulation. While nitrogen use efficiency (the ratio of crop N uptake to total N inputs) is almost certainly lower than the N attenuation measured in this study, gaseous losses and soil N accumulation are likely negligible in our study sites due to the well-aerated, sandy soils with low organic matter content (SOM = 3 ± 0.9%). Assuming our attenuation measurements are dominated by crop uptake, these results are comparable to the global average N use efficiency of 47% and within the range (approximately 50 to 70%) reported for the US (Lassaletta et al., 2014). Our results suggest that while N inputs explain a large portion of the variability in nitrate leaching, site-specific land use characteristics allow us to better categorize expected nitrate leaching for each site and should be accounted for in landscape-scale nitrogen budgets.

Conclusions

A soil passive flux meter (SPFM) was developed that is based on a modified ion-exchange resin column design capable of measuring nitrate fluxes between 0.3 – 2,000 kg N ha⁻¹. Critical SPFM design elements include mixing ion-exchange resin with native soil to minimize textural discontinuity, extending the impermeable column that contains the resin to at least 10 cm above the resin layer, and applying a conservative tracer during field deployments to validate the convergence factor. Soil nitrate fluxes from 2 to 300 kg N ha⁻¹ were measured and 66% in-situ attenuation, mean across all sites, determined from the difference between known N inputs and SPFM-measured N fluxes. Based on the results, SPFMs provide low-cost, robust, and accurate measurements of soil nitrate leaching. When N inputs are known, SPFMs also allow for measurement of in situ nitrate attenuation. This method can be used to estimate catchment-scale N
attenuation for specific land-use types, therefore making a significant contribution towards closing N budgets.
Figure 2-1. Laboratory-measured steady-state soil moisture profile (circles) is well described by HYDRUS-1D simulation (solid line, $R^2=0.94$). Textural differences between resin-soil mixture (30 – 40 cm depth) and native soil above and below lead to higher water content in the resin/soil zone but avoids the build-up of water above this layer.

Figure 2-2. Convergence factor as a function of changes in Van Genuchten soil water retention parameters $\alpha$ and $n$ for SPFM with (unfilled circles) and without (filled circles) a 10-cm extension of the impermeable boundary above the resin layer, based on HYDRUS-2D simulations. Initial $\alpha = 0.03$ and $n = 3.85$ were varied independently and are reported as a proportion of the initial value.
Figure 2-3. Mean (± standard deviation) SPFM-measured nitrate leaching from 5 columns in each of 9 sites of varying land use in the Silver Springs springshed, compared to expected nitrate leaching based on N inputs and site-specific land management practices. Measured fluxes at Turf 1 and Pasture 1 were below the SPFM detection limit (0.32 kg NO$_3$-N ha$^{-1}$) and reported as half the detection limit.

Table 2-1. Parameters used for HYDRUS simulations.

<table>
<thead>
<tr>
<th></th>
<th>$K_{sats}$ (cm d$^{-1}$)</th>
<th>$\alpha$ (1/cm)</th>
<th>$n$ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arredondo fine sand (0-10 cm)</td>
<td>790</td>
<td>0.032</td>
<td>3.23</td>
</tr>
<tr>
<td>Arredondo fine sand (11-90 cm)</td>
<td>790</td>
<td>0.068</td>
<td>1.28</td>
</tr>
<tr>
<td>Candler sand</td>
<td>1,200</td>
<td>0.031</td>
<td>3.56</td>
</tr>
<tr>
<td>Purolite A520E</td>
<td>6,300</td>
<td>0.032</td>
<td>3.06</td>
</tr>
<tr>
<td>Arredondo/resin mixture</td>
<td>3,100</td>
<td>0.053</td>
<td>2.35</td>
</tr>
<tr>
<td>Candler/resin mixture</td>
<td>1,000</td>
<td>0.034</td>
<td>3.85</td>
</tr>
<tr>
<td>Mesh liner</td>
<td>35,000</td>
<td>0.860</td>
<td>6.51</td>
</tr>
</tbody>
</table>
Table 2-2. Characteristics of field sites, corresponding to major land use categories. Total inputs are the sum of fertilizer and manure inputs, plus 3 kg N ha\(^{-1}\) from atmospheric deposition for all sites estimated for the deployment period from the TDEP model output for 2011-2015 (NADP, 2016). BDL: below detection limit

<table>
<thead>
<tr>
<th>Name</th>
<th>Location</th>
<th>Land use</th>
<th>Total Inputs</th>
<th>Attenuation</th>
<th>Soil Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crop 1</td>
<td>Equine Sciences Center 29.298945, -82.174226</td>
<td>Hay</td>
<td>77</td>
<td>52 ± 22</td>
<td>Micanopy</td>
</tr>
<tr>
<td>Crop 2</td>
<td>Plant Science Research and Education Unit</td>
<td>Peanut</td>
<td>220</td>
<td>65 ± 10</td>
<td>Gainesville</td>
</tr>
<tr>
<td>Crop 3</td>
<td>Plant Science Research and Education Unit</td>
<td>Sunflower</td>
<td>87</td>
<td>27 ± 30</td>
<td>Arredondo</td>
</tr>
<tr>
<td>Pasture 1</td>
<td>Equine Sciences Center 29.408903, -82.175216</td>
<td>Horse</td>
<td>45</td>
<td>99.6 ± 0(^{BDL})</td>
<td>Micanopy</td>
</tr>
<tr>
<td>Pasture 2</td>
<td>Horse Teaching Unit 29.600362, -82.348885</td>
<td>Composted horse</td>
<td>190</td>
<td>57 ± 17</td>
<td>Millhopper</td>
</tr>
<tr>
<td>Pasture 3</td>
<td>Plant Science Research and Education Unit 29.410154, -82.160175</td>
<td>Fertilized cattle</td>
<td>210</td>
<td>22 ± 53</td>
<td>Placid</td>
</tr>
<tr>
<td>Turf 1</td>
<td>Plant Science Research and Education Unit</td>
<td>Unfertilized turf</td>
<td>2.5</td>
<td>94 ± 0(^{BDL})</td>
<td>Arredondo</td>
</tr>
<tr>
<td>Turf 2</td>
<td>Plant Science Research and Education Unit</td>
<td>Fertilized turf</td>
<td>52</td>
<td>89 ± 19</td>
<td>Candler</td>
</tr>
<tr>
<td>Turf 3</td>
<td>Plant Science Research and Education Unit</td>
<td>Golf green</td>
<td>216</td>
<td>86 ± 10</td>
<td>Candler</td>
</tr>
</tbody>
</table>


There is an urgent need to improve our understanding of catchment-scale nitrogen (N) balances to determine the fate of anthropogenic N inputs and identify the drivers of groundwater contamination. Mass balance models help to constrain our estimates of N inputs and attenuation through space and time (e.g., Billen et al., 2013; David et al., 2010; Goyette et al., 2016), but estimating the fraction of the surface loading that reaches the surface water or groundwater introduces additional uncertainty. While net anthropogenic N inputs (NANI) can be used as a proxy for N inputs to watersheds (e.g., Boyer et al., 2002; Hong et al., 2011; Howarth et al., 1996) and compared to mass discharge from the catchment to estimate landscape-scale attenuation, this relies on the validity of N input estimates. Direct measurements of soil nitrate fluxes are therefore critical for quantifying actual nitrate attenuation and validating landscape-scale attenuation estimates.

Here a conceptual model framework is proposed to simply and systematically compute nitrogen export based on proportioning of load and attenuation, which is parameterized with in situ measurements of attenuation. The product of human/animal population densities or proportion of a given land use, $P_i$, specific load per capita or per area, $L_i$, anthropogenic attenuation, $A_i$, and natural attenuation, $N_i$, for each N source $i$ is integrated at the basin scale, resulting in the PLAN framework. This framework is conceptually comparable to the GWAVA model introduced by Nolan and Hitt (2006), where N sources are multiplied by transport and attenuation factors that proportionally influence the delivery of N to groundwater. However, our model framework relies on
measured fractional source-specific attenuation rather than calibrated attenuation coefficients.

Here a long-term average (1997-2017) catchment-scale N budget is calculated for a karst springshed, using in situ measurements of soil nitrate fluxes and attenuation in the soil and aquifer, with the goal of evaluating the PLAN-B model, disaggregating the attenuation capacity of the springshed, and identifying the dominant N sources contributing to spring N export. The SPFM-measured $\delta^{15}$N/$\delta^{18}$O signature of nitrate leached below the root zone was used to evaluate the effect of using the leached signature, rather than the source signature, to predict the relative contributions of N sources to spring N export. The following hypotheses were tested: (1) the model framework, which is consistent for point or nonpoint sources, could be used to evaluate the relative contributions of specific N sources to surface loads and watershed export, (2) land use (via land management practices) exerts a strong control on N attenuation at the landscape scale and that in situ measurements of N attenuation could be used to constrain the N budget for a karst springshed, and (3) the $\delta^{15}$N/$\delta^{18}$O source signature would be masked early in the leaching process and that using the leached signature would improve our ability to predict N sources given the $\delta^{15}$N/$\delta^{18}$O signature of nitrate in spring discharge.

In karst systems, the spring catchment (springshed) is the contributing area to spring discharge and is the groundwater equivalent of a watershed. Constructing a landscape-scale N budget for a groundwater catchment offers an additional opportunity to partition attenuation throughout the landscape and quantify the rates of the nitrogen cascade from the land surface to spring outlet (Galloway, 1998), making it an ideal
place to test the PLAN-B model framework. The hypotheses were tested using long-term data, literature estimates, and in situ measurements of N inputs and attenuation in Silver Springs, one of the largest freshwater springs in North America, located in Marion County, Florida (Figure A-1). Nitrate concentrations have increased from 0.4 mg L\(^{-1}\) NO\(_3\)-N in the 1950s to currently more than 1.2 mg L\(^{-1}\), which is 3.4 times higher than the numerical nutrient criterion (NO\(_3\)-N < 0.35 mg/L) for Silver Springs adopted from the Florida Department of Environmental Protection (Hicks and Holland, 2012). The springshed is characterized by a mix of land use types, each subject to different N inputs and removal processes. Previous research suggests that aquifer attenuation is significant in the Upper Floridan Aquifer (Heffernan et al., 2012), but there have been no landscape-scale estimates of soil and vadose zone N attenuation to partition losses throughout the landscape and validate N budgets in karst regions. Attempts have been made to identify sources of NO\(_3\)-N in spring discharge by analyzing the dual stable isotopic signature (\(\delta^{15}\)N and \(\delta^{18}\)O) of nitrate (Katz et al., 2004; Katz and Griffin, 2008; Knowles et al., 2010) and successful source identification could aid in the disaggregation of nitrate attenuation processes. However, these analyses rely on the assumption that sources of nitrate retain their isotopic signature throughout the leaching process.

**Methods**

**Study Site**

Silver Springs is defined as a spring group, comprising 30 known vents (Scott et al., 2004) that discharge from the Upper Floridan Aquifer into the Silver River. The 1,300 km\(^2\) springshed overlies both confined (700 km\(^2\)) and unconfined (600 km\(^2\))
sections of UFA (Figure A-1) and is characterized by a mix of urban (29%), forest (27%), agriculture (22%), wetlands (15%), and other (7%) land covers (FDEP, 2017).

**PLAN-B Model Framework**

A catchment-scale N budget for the period 1997-2017 was calculated using a combination of in situ measurements of N inputs and attenuation, long-term data, and literature estimates of attenuation. The N load exported from the basin ($L_{OUT}^p$ [M L^{-2} T^{-1}]) was predicted as the product of the human/animal population density or proportion of a given land use, ($P_i$ [count L^{-2}] or [L^{2} L^{-2}]), the source-specific N load ($L_i$ [M count^{-1} T^{-1}] or [M L^{-2} T^{-1}]), the fractional N delivery following anthropogenic attenuation, ($A_i$ [-]), and the fractional N delivery following natural attenuation, ($N_i$ [-]), summed for all sources $i$ across the basin ($B$):

$$L_{OUT}^p = \sum_i P_i L_i A_i N_i$$

(3-1)

Anthropogenic attenuation is represented by a delivery coefficient, which is the proportion of a contaminant remaining after attenuation. While here anthropogenic attenuation represents treatment of wastewater N in septic tanks or wastewater treatment facilities (WWTFs), the general term can represent any technological effort that results in the attenuation of a contaminant before entering a water path. Natural attenuation may comprise multiple mechanisms and here is partitioned between natural attenuation in the soil ($N_{S,i}$), vadose zone ($N_{H,i}$), and aquifer ($N_{A,i}$) and the total delivery after natural attenuation ($N_i$) is the product of the specific natural delivery coefficients:

$$N_i = N_{S,i} N_{H,i} N_{A}$$

(3-2)

where $N_{S,i}$ is a source-specific soil N delivery coefficient, $N_{H,i}$ is the source-specific vadose zone N delivery coefficient, which represents N delivery after hydrologically-
driven attenuation, and $N_A$ is the aquifer N delivery coefficient, which here is represented in a simplified manner as a spatially constant value and therefore is not differentiated by source.

The N sources considered in the catchment budget were: manure from cattle and horses ($M_c$ and $M_h$), agricultural and urban fertilizer ($F_a$ and $F_u$), wastewater from on-site treatment (e.g., septic tanks) or centralized treatment facilities ($W_s$ and $W_t$), atmospheric deposition ($D$), and biological nitrogen fixation from cultivated legumes ($BNF$) so that $i = [M_c, M_h, F_a, F_u, W_s, W_t, D, BNF]$.

The measured annual load discharged from the basin ($L_{OUT}^m [M \text{ L}^{-2} \text{T}^{-1}]$) is calculated as the long-term average of the product of the annual average discharge from the spring ($Q [\text{L}^3 \text{T}^{-1}]$) and the annual average NO$_3$-N concentration of spring discharge ($C [\text{M L}^{-3}]$) divided by springshed area ($A_s [\text{L}^2]$):

$$L_{OUT}^m = \frac{C(t)Q(t)}{A_s}$$  \quad (3-3)

Catchment N loads and attenuation were further disaggregated throughout the landscape by separating the surface N inputs, net N inputs leached below the root zone, and net N inputs recharged to groundwater ($L_R [M \text{ L}^{-2} \text{T}^{-1}]$). The total N input to the land surface within the springshed ($L_{IN} [M \text{ L}^{-2} \text{T}^{-1}]$) was calculated as:

$$L_{IN} = \sum_i P_i L_i$$  \quad (3-4)

The net N input leached below the root zone ($L_L [M \text{ L}^{-2} \text{T}^{-1}]$) is the estimate of the total mass of N remaining after biogeochemical attenuation (both anthropogenic and natural):
\[ L_L = \sum P_i L_i A_i N_{Si,i} \]  

(3-5)

Finally, the net N input recharged to groundwater \( L_R \) \( [M \, L^{-2} \, T^{-1}] \) is the estimate of the total mass of N remaining after hydrological attenuation in the vadose zone:

\[ L_R = \sum P_i L_i A_i N_{Si,i} N_{Hi,i} \]  

(3-6)

**Data sources and model parameterization**

Long-term average N inputs for all N sources were estimated for the period 1997-2017. The springshed boundary was obtained from the St. Johns River Water Management District (SJRWMD, 2016) and 2011-2017 land use data was obtained from the Florida Department of Environmental Protection (FDEP, 2017). When only county-level data was available, the land use dataset was used to calculate the proportion of the county-level area of the associated land use that falls within the springshed boundary. The proportions calculated from the 2011-2017 land use dataset were applied to all years used for the analysis, assuming that the proportions are consistent for the period of investigation. Spatial data was analyzed in ArcMap v. 10 (ESRI, Redlands, CA) and R (R Core Team, 2018).

**P – Population density or proportional area**

The population density \( (M_c, M_h, W_s, W_t) \) or proportional land use \( (F_a, F_u, D, BNF) \) was estimated for all sources of N inputs in the springshed. The US Agricultural Census reports livestock counts in 5-year intervals and data for 1997, 2002, 2007, and 2012 (Haines et al., 2016) were used to estimate livestock counts during the period of investigation. Springshed cattle and horse population densities were estimated by weighting county-level counts by the proportion of the county area for pastures and
horset farms, respectively, within the springshed using 2011-2017 land use data for the state of Florida (FDEP, 2017). The springshed livestock counts were then divided by the springshed area to estimate the springshed-level livestock population densities. Wastewater treatment practices were estimated from spatial data from the Florida Water Management Inventory Project (FDOH, 2016), which categorizes the wastewater treatment method for each property in the state of Florida (see SI); wastewater generated at the household level is either connected by sewer lines to a WWTF or treated onsite by a septic system. The population count within the springshed boundary was estimated using 2010 gridded population data generated by Fang and Jawitz (2018, their model “M5”) and the total population was weighted by the proportion of households served by each treatment method to estimate the population counts associated with either treatment method. These counts were divided by the springshed area to estimate the population densities of residents using septic treatment ($P_{Ws}$) and wastewater treatment facilities ($P_{Wt}$).

The proportional area for each source $i$ is estimated as the proportion of the land use associated with source $i$ and the total springshed area. The land use associated with $F_a$ was the total cropland area, which included: row crops, field crops, mixed crops, tree crops, sod farms, ornamentals, nurseries, ferns, floriculture, and specialty farms (FDEP, 2017). The land use associated with $F_u$ was the fertilized urban area, which included: low/medium/high residential, golf courses, stadiums, and community recreational areas (FDEP, 2017). The area in cultivated legumes was estimated as the product of the county-level legume area as reported in the Agricultural Census (Haines et al., 2016) weighted by the proportion of county-level crop area within the springshed.
As peanut area was an order of magnitude greater than any other leguminous crop (Figure A-2) cultivated within the springshed, peanuts were the only cultivated legume included in the BNF calculations. Atmospheric deposition falls over the entire springshed boundary, so the proportional area used for atmospheric deposition calculations was 1.

**L – Specific load per count or per area**

The specific load per count \((M_c, M_h, W_s, W_t)\) or per area \((F_a, F_u, D, BNF)\) were estimated for all sources of N inputs within the springshed (Table A-3). Manure loads from horses and cattle were estimated as the average N excretion rates based on IPCC Tier 1 factors and using the EMEP/EAA Tier 2 approach (Velthof et al., 2016). These rates are similar to beef cattle and horse N excretion rates used for the US and Europe (van Grinsven et al., 2014) and are a conservative estimate compared to the American Society of Agricultural Engineers manure N excretion standards and excretion rates predicted on a live-weight basis (ERS, 2018; Wilkerson et al., 1997). The per capita wastewater load was estimated from Lusk et al. (2017), Rose et al. (2015), and Van Drecht et al. (2009) and was assumed to be identical for both septic and wastewater treatment systems.

Brakebill and Gronberg (2017) estimate county-level fertilizer sales for the US between 1987 to 2012, differentiating between farm and nonfarm (i.e., urban) fertilizer sales. Loading rates were calculated as the mass of county-level fertilizer N sales per county-level crop area (row crops, field crops, mixed crops, tree crops, sod farms, ornamentals, nurseries, ferns, floriculture, and specialty farms) and fertilized urban area (low/medium/high residential, golf courses, stadiums, and community recreational areas) for agricultural and urban fertilizer, respectively. An area-based biological N
fixation rate for cultivated peanut was estimated from Chu et al. (2004), Dubeux et al. (2017), and Pimratch et al. (2008). Atmospheric deposition was estimated using the 2000-2015 TDEP model outputs from the National Atmospheric Deposition Program (NADP, 2016). This model approach developed by Schwede and Lear (2014) combines total wet and dry deposition to produce gridded annual estimates of total N deposition for the United States. Model outputs were used to calculate the average annual deposition rate within the springshed boundary.

A – Anthropogenic attenuation

The WWTF N delivery coefficient ($A_{WT}$) was estimated from data collected from two WWTFs in the region (Table A-1) and the septic N delivery coefficient ($A_{WS}$) was estimated from reported septic influent and effluent N loads (Harden et al., 2010; Katz et al., 2010; Lowe and Siegrist, 2008; Lowe et al., 2008; and Lusk et al., 2015). The N delivery coefficient ($A_i$) is calculated as:

$$A_i = \frac{M_{out}}{M_{in}}$$

where $M_{out}$ is the mass of contaminant remaining after attenuation (here the effluent N load [kg N]) and $M_{in}$ is the initial mass of contaminant (here the influent N load [kg N]).

N – Natural attenuation

Soil passive flux meters (Soil PFMs) were used to measure cumulative soil nitrate flux in situ (see Chapter 2). These were deployed from 2017 to 2018 to obtain integral measures of nitrate delivery after soil attenuation for model parameterization. Nine field sites were selected in crop, pasture, and urban land uses within the springshed to represent the range of typical practices within each land use (Table A-2). The N delivery coefficients for agricultural fertilizer ($N_{S,Fa}$), urban fertilizer ($N_{S,Fu}$), and
manure from cattle and horses ($N_{S,Mc}$ and $N_{S,Mh}$) were derived from the N leaching measured below the root zone of crop, turf, and pasture sites, respectively, using Equation 3-7 where $M_{in,i}$ was the surface N input and $M_{out,i}$ was the SPFM-measured N leaching at site $i$. The land-use specific coefficients are calculated as the mean of the site-specific coefficients in each land-use category. See Appendix A for more detailed information on the SPFM-measured fluxes and attenuation.

Hydrological attenuation in the vadose zone accounts for the presence of a clay confining unit, thereby decoupling attenuation in the surface soil and vadose zone. Hydrostratigraphy data from the SJRWMD was used to map the presence of the intermediate confining unit (ICU) (Figure A-1). Land use area and population density over the confining unit ($P_{cf}$), were divided by the springshed total land use area or population density ($P_s$) and used as a proportional weighting factor to estimate the mass of N effectively attenuated through the vadose zone: $N_{H,i} = \left( \frac{P_{cf}}{P_{s}} \right)_i$. Note that confining unit presence was here simplified as binary (presence/absence) based on a threshold clay thickness of 6 meters.

Dissolved gasses in aquifer discharge can be used to estimate groundwater attenuation at the springshed scale (e.g., Heffernan et al., 2012). $N_2$ in the discharge that is in excess of the atmospheric equilibrium at the time of recharge provides an integrated measure of denitrification over the groundwater flow path in the aquifer (Green et al., 2006). Measurements of excess $N_2$ ($N_{2,e}$) in Silver Springs discharge were compiled (Heffernan et al., 2012; Reddy et al., 2017; Phelps, 2004; Phelps et al., 2006), along with the nitrate concentrations reported at the time of sampling ($C$), to calculate
initial groundwater nitrate concentrations \((C_{in})\) as \(C_{in} = N_{2,e} + C\) and the groundwater N attenuation coefficient \((N_a)\) as \(N_a = \frac{c_{in} - C}{C_{in}}\).

**Measured \((L_{OUT}^m)\) and predicted \((L_{OUT}^p)\) export**

The predicted spring N export from the catchment-scale N budget (Equation 3-1) was compared to the measured average spring N export at Silver Springs from 1998-2017 (Equation 3-3). Discharge is measured at USGS station 02239500 (USGS, 2018) and quarterly NO\(_3\)-N data are reported by the SJRWMD (SJRWMMD, 2018). The average discharge was \(16 \pm 4 \text{ m}^3\text{s}^{-1}\) and the average NO\(_3\)-N concentration of the discharge was \(1.1 \pm 0.1\) mg NO\(_3\)-N L\(^{-1}\).

**Uncertainty of model parameters**

Based on the linear form of Equation 3-1, each model parameter has equal computational weight on the PLAN model output. However, the spatial variability and uncertainty are not equal for each model component. The effect on the overall budget uncertainty via error propagation of individual uncertainties relies on an assessment of the uncertainty of each model component, which is driven by the reliability of data sources, measurement precision and accuracy, and natural variability. The uncertainty associated with each parameter is provided in Table A-3, as described below.

Livestock populations from the Agricultural Census are reliable county-level statistics, as data from all farms are collected and aggregated at the county level. It was assumed that the annual livestock population was representative of the year-round livestock population, so uncertainty in the population density estimates are driven by intra-annual fluctuations of reported livestock populations during the period of investigation.
The gridded human population estimates were validated with census tract population data from 2000 (Fang and Jawitz, 2018) and the springshed population density was estimated from these authors’ most accurate model (‘M5’), while the proportion of households using WWTF or septic wastewater treatment were estimated from a statewide parcel-level wastewater treatment inventory (FDOH, 2016) The uncertainty of the wastewater treatment-specific population densities ($P_{ws}$ and $P_{wt}$) was determined based on estimated standard deviations of 10% of both the estimated population density and the proportion of households for each type of wastewater treatment during the period of investigation.

The proportioning of fertilizer loads to the springshed level adds additional uncertainty. Fertilizer sales data from Brakebill and Gronberg (2017) were identical to reported state-level fertilizer sales for years with available data, building confidence in these values. But to account for uncertainty in how springshed-level patterns reflect those at the state and county level, a standard deviation of 10% was applied to the agricultural and fertilizer load estimates ($F_a$ and $F_u$).

The uncertainty of $A_{wt}$ was based on data collected from two WWTFs (one in the springshed and one in a neighboring county) and the uncertainty of $A_{ws}$ was estimated from the range of reported septic N removal efficiencies (Harden et al., 2010; Katz et al., 2010; Lowe and Siegrist, 2008; Lowe et al., 2008; and Lusk et al., 2015).

The uncertainty of $N_s$ for manure, agricultural fertilizer, and urban fertilizer was estimated from SPFM-measured soil attenuation. In addition to the variance in measured data, an additional standard deviation of 10% was added to reflect the unaccounted-for uncertainty of representing the entire springshed with a finite number
of sample sites, suggesting that $N_s$ is one of the least certain model parameters in the analysis. Additional uncertainty arises from the possibility that ICU thickness plays an important role in vadose zone attenuation, which was represented by a standard deviation of 10%. Finally, the uncertainty of $N_A$ is related to the natural variability of groundwater denitrification and analytical error and is estimated from the variance in measured data collected during the period of investigation (Table A-3).

**Estimating Source Contributions from Isotopic Data**

The NO$_3$-N adsorbed to the SPFMs was extracted with 2M KCl as described in Desormeaux et al. (2018) and shipped overnight on ice to the Facility for Isotope Ratio Mass Spectrometry (FIRMS) at the University of California, Riverside. The dual isotopic signature of leached nitrate was measured using the bacterial denitrifier method (Sigman et al., 2001), utilizing *P. aureofaciens* to convert NO$_3$- to N$_2$O and analyzed for $\delta^{18}$O-NO$_3$ and $\delta^{15}$N-NO$_3$ on an isotope ratio mass spectrometer (Thermo Delta V, Thermo Fisher Scientific) coupled to the GasBench interface. The source contributions to spring N export were estimated with the SIAR package (Parnell et al., 2008) in R (R Core Team, 2018), using isotopic data reported for Silver Spring discharge (Heffernan et al., 2012; Reddy et al., 2017; Phelps et al., 2006). The proportional contribution of N sources to spring N export predicted based on SIAR source signature data were compared to predictions using SPFM-measured manure and fertilizer isotopic signatures (SIAR-SPFM; Table A-5). Soil-derived N in the SIAR model is analogous to BNF from the catchment-scale budget and was eliminated from the SIAR-SPFM sources due to the minor contribution estimated in the N budget and the likelihood of Type 1 error by including it as a potential source (Davis et al., 2015). Specific fertilizer
and wastewater sources were combined, due to an inability to differentiate between the source signatures of the specific fertilizer and wastewater N sources.

Results

Surface Inputs \((L_{IN})\)

Based on Equation 3-4, total N inputs to the springshed from all sources \(L_{IN} = \)
3,300 ± 310 kg N km\(^{-2}\) y\(^{-1}\) (mean ± standard deviation). The contribution of each N source to the total surface load (Figure 3-1) were also estimated. Manure from livestock \((M = M_c + M_h)\) was the largest contributor (35% of total surface N inputs), followed by atmospheric deposition (25%), agricultural fertilizer (14%), wastewater delivered to septic systems (14%), wastewater delivered to WWTFs (6%), urban fertilizer (4%), and BNF from peanuts (2%).

Springshed-level farm and non-farm fertilizer inputs were 450 ± 64 and 130 ± 18 kg N km\(^{-2}\) y\(^{-1}\) (Figure 3-1a). The temporal mean farm fertilizer inputs from 1997-2012 were used, although there was a slight reduction in agricultural intensity during the period of investigation (Figure A-2). Peanuts, alfalfa, soybeans, and cowpeas were initially considered in BNF estimates; however, peanut area was an order of magnitude greater than any other leguminous crop (Figure A-2) and N inputs estimated from the remaining crops was within the error estimated for peanuts. Therefore only peanut N loads were included for further analyses. Peanuts cultivated within the springshed fixed an estimated 72 ± 45 kg N km\(^{-2}\) y\(^{-1}\) (Figure 3-1a). Manure from horses and cattle resulted in a combined load of 1,100 ± 240 kg N km\(^{-2}\) y\(^{-1}\) to the springshed (Figure 3-1a), comprising 21% and 14% respectively of total N inputs. The N excretion coefficient
was slightly lower for horses than cattle, but there were almost twice as many horses than cattle within the springshed boundary (Table A-3).

Deposition was estimated as $840 \pm 150$ kg N km$^{-2}$ y$^{-1}$ between 2000-2015 (Figure A-2), which while relatively low compared to other areas of the country (Schwede and Lear, 2014). As the source of N deposition is dominantly from fossil fuel combustion (Mosier, 2001), this source is considered to be driven by urbanization within and upwind of the springshed.

Approximately 190,000 residents live within the springshed, resulting in $650 \pm 76$ kg N km$^{-2}$ y$^{-1}$ from wastewater (Figure 3-1a), with 32% of this ($210$ kg N km$^{-2}$ y$^{-1}$) delivered to WWTFs based on the estimated 68% of properties using septic tanks. While the wastewater N represents 20% of the total springshed inputs, attenuation during treatment significantly reduces the delivery.

**Net Inputs Leached Below the Root Zone ($L_L$) and Recharged to Groundwater ($L_R$)**

The net inputs leached below the root zone were estimated as the delivery of total inputs after anthropogenic and soil attenuation (Equation 3-5) $L_L = 1,200 \pm 430$ kg N km$^{-2}$ y$^{-1}$. An average of 34% of wastewater N is attenuated in septic systems (Harden et al., 2010; Katz et al., 2010; Lowe and Siegrist, 2008; Lowe et al., 2008; and Lusk et al., 2015), compared to 92% in WWTFs (supporting information). While further attenuation is possible in the vadose zone as septic effluent leaves the drainfield (De and Toor, 2015) and reductions in N concentrations of 40% as effluent moves below the drainfield have been observed (Katz et al., 2010), we did not consider additional biogeochemical losses of septic leachate in the vadose zone as further attenuation is highly variable (CV = 118%; Katz et al., 2010) and losses are not always observed (Morales et al., 2016).
Attenuation in the soil measured in situ using SPFMs in the fertilized urban land use was 90% ± 4%. Soil attenuation for pasture and crop sites was 60% ± 36 and 53% ± 25, respectively. Land use type had a significant effect on N attenuation ($p < 0.05$, one-way ANOVA) and attenuation in turf sites was significantly greater than pasture or crop sites (Tukey’s post hoc comparisons). The average attenuation across pasture and crop sites was therefore used to estimate attenuation for manure, agricultural fertilizer, and biological fixation from cultivated legumes. It was estimated that 83% of N from atmospheric deposition was attenuated in the soil across the springshed (Campbell et al., 2004, Dewalle et al., 2005; Katz et al., 2009a, Nilsson et al., 1998).

Approximately 650 kg N km$^{-2}$ y$^{-1}$ is attenuated between 30-cm below ground surface and the UFA due to the presence of the ICU impeding the flow of water and nitrate into the confined aquifer. It was estimated that 540 ± 240 kg N km$^{-2}$ y$^{-1}$ is recharged to the aquifer and an additional 210 ± 170 kg N km$^{-2}$ y$^{-1}$ is attenuated in the aquifer.

**Measured ($L_{OUT}^m$) and Predicted ($L_{OUT}^P$) Export**

Using the PLAN model framework, predicted export from Silver Springs was 340 ± 170 kg N km$^{-2}$ y$^{-1}$ (Figure 3-1b), which was not significantly different (t-test, $p > 0.05$) than measured N export (430 ± 95 kg N km$^{-2}$ y$^{-1}$). The modeled and measured export represent 10% ($± 3$) and 13% ($± 3$) of estimated surface inputs. Manure and septic N sources were the largest contributors to spring N export (45% and 27%, respectively), followed by agricultural fertilizer (13%) and atmospheric deposition (11%). Agricultural BNF, urban fertilizer, and WWTF-treated wastewater contributed less than a combined 5% to total spring N export (Figure 3-1b). While manure was identified as a major
source to both surface N inputs and spring N export, there was a shift in the contribution from atmospheric deposition and urban fertilizer as N moved through the landscape (Figure 3-1) due to the high attenuation coefficients for both N sources (Table A-3).

Disaggregating the Attenuation Capacity of the Landscape

Total mass of N declined as N moved through the landscape (Figure 3-2). Attenuation in the surface soil resulted in a total reduction of 2,100 (± 530) kg N km⁻² y⁻¹, which was 64% of total N inputs. Attenuation in the vadose zone prevented an additional 650 (± 490) kg N y⁻¹ from reaching the groundwater, representing 20% of total N inputs. Attenuation in the groundwater removed 210 (± 290) kg N y⁻¹, which was 6% of total N inputs.

Estimating Source Contributions to Spring Export from Isotopic Data

Mixing model results for the SIAR and SIAR-SPFM models were compared to the source contributions estimated from the catchment-scale N budget (Figure 3-3) and found that the SIAR-SPFM model predictions agree more closely with the source contributions predicted from the N budget (root mean squared error, RMSE = 0.073) compared to the base SIAR model (RMSE = 0.15). The SIAR model based on standard literature values for source isotopic compositions predicted that wastewater was the dominant N source contributing to NO₃-N in spring discharge, representing 25% of total spring N export. The second largest source was manure (22%), followed by fertilizer (19%), and atmospheric deposition (16%). The SIAR-SPFM model, which used SPFM-measured leached-N isotopic source signals for fertilizer and manure, indicated manure as the dominant N source contributing to spring N export (45%), which agreed with the
budget predictions (46%). The SIAR-SPFM model attributed 23% of spring N export to atmospheric deposition, 19% to wastewater, and 12% to fertilizer.

**Discussion**

**Surface Inputs ($L_{IN}$)**

Manure from cattle and horses was estimated as the largest single N source to both total surface N inputs and spring N export. Manure N inputs are the largest global anthropogenic N input to terrestrial systems (Bouwman et al., 2013), however, considerable regional variation exists in the contribution of sources to total surface inputs (Hong et al., 2013). While synthetic fertilizer, atmospheric deposition, and agricultural BNF have been identified as the largest contributors to surface N loads across the US (Hong et al., 2013; Sobota et al., 2013), manure N has been estimated to contribute significantly (>30% of inputs) to agricultural lands (Mosier, 2001). Marion County has the highest horse population in the country and county-level cattle stocking density (11 cattle km$^{-2}$) is similar to the Mississippi River Basin (18 cattle km$^{-2}$), as reported in the 2012 Agricultural Census (USDA-NASS, 2014). The dominant crops (hay and peanut) have relatively low fertilizer N recommendations compared to other agronomic crops (Mylavarapu et al., 2015), which explains the relatively low contribution of agricultural fertilizer compared to manure N inputs. While N fixing legumes are one of the dominant crops in the springshed, the total cropland area makes up less than 5% of the springshed and agricultural BNF therefore makes a relatively low contribution to N inputs.

**Net Inputs Leached Below the Root Zone ($L_L$)**

Anthropogenic attenuation during wastewater treatment in both WWTFs and septic tanks is assumed to be via denitrification. The proportion of households using
septic systems to treat wastewater in the Silver Springs springshed is more than double the state average of 33%. This has major implications for groundwater N loads, as the magnitude of N attenuation is significantly different between septic and wastewater treatment. While about 210 kg N km\(^{-2}\) y\(^{-1}\) is delivered to WWTFs for treatment, only 17 kg N km\(^{-2}\) y\(^{-1}\) is delivered to the landscape after treatment. In comparison, the large proportion of homes on septic systems results in 440 kg N km\(^{-2}\) y\(^{-1}\) delivered to septic systems. Together with the much lower septic attenuation factor, this results in large loads leached from septic systems (290 kg N km\(^{-2}\) y\(^{-1}\)).

The SPFM results suggest that turf systems are highly efficient at attenuating N inputs from urban fertilizer, which is in line with previous research reporting N attenuation of 80-100% across both fertilized (Trenholm et al., 2012) and unfertilized (Hermann and Cadenasso, 2017) turf systems. The estimates of N attenuation in crop and pasture systems are close to the global average N use efficiency of 47% (Lassaletta et al., 2014) and agree with estimates for Florida production systems (Prasad and Hochmuth, 2016). While legumes are often identified as a more sustainable N source (Bohlool et al., 1992; Schultze-Kraft et al., 2018), the results suggest that conventional cultivation of legumes can potentially contribute to net N inputs leached below the root zone. Soil attenuation at the peanut site was not significantly different from other crop or pasture sites, likely due to mineralized N from vegetative and root mass left in the soil after harvest being lost to leaching before establishment of the subsequent cover crop. While legumes account for only 2% of N inputs in the springshed and therefore did not contribute significantly to spring N export,
this has implications for catchments with higher contributions from agricultural BNF (e.g., Sobota et al., 2013).

While the total leached N load is dominated by nitrate across a wide range of systems (Wachendorf et al., 2005), dissolved organic N (DON) leaching has been observed in agricultural and turf systems (Van Kessel et al., 2009). While DON can be leached from decaying organic matter from soils, livestock waste, or crop residue, the majority of N exported from Silver Springs is in the form of nitrate (Figure A-6) suggesting that DON is ultimately nitrified along the hydrological flowpath. However, the SPFM-measured attenuation is subject to some uncertainty due to the unknown fraction of total inputs leached as DON and NH$_4$-N. This suggests that total-N attenuation could be lower than measured in systems with a high contribution of DON to total N leaching fluxes. Assuming DON makes up an average of 26% of total N leaching (Van Kessel et al., 2009), this would result in an average attenuation of 86% (± 5%), 41% (± 32%), and 49% (± 45%) for turf, crop, and pasture. While lower than estimated from our SPFM-measured nitrate leaching fluxes, the same patterns between land uses generally hold.

While previous work has shown that N recovery in livestock production is half that of crop production (Bouwman et al., 2013), gaseous losses in livestock production systems are more than double that in crop production systems. Natural attenuation in the soil represents the total attenuation from crop uptake and gaseous losses, and the same values for soil attenuation were used for manure-N in livestock production systems and fertilizer-N in crop production. Previous work has suggested that manure-based systems result in greater N attenuation (Xia et al., 2017), and the absolute value of the average N recovery at pasture sites was greater than crop sites. There was no
significant difference between N attenuation measured at pasture and crop sites due to the high within-treatment variability (Figure A-4). Land management practices vary substantially within land use categories and exert a strong control on net N inputs below the root zone (Desormeaux et al., 2018). Evaluating the influence of site-specific land management practices at the catchment scale remains for future work.

**Net Inputs Recharged to Groundwater ($L_R$) and Groundwater Attenuation ($N_A$)**

An estimated 20% of surface N inputs are attenuated between 30-cm below ground surface and the UFA. Here it is assumed that hydrological separation of the vadose zone and aquifer in confined regions of the springshed prevents N from moving into the UFA. Recent work in the springshed has shown contrasting isotopic signatures of nitrate above and below the ICU (Reddy et al., 2017), suggesting nitrate in the confined aquifer does not originate from the surficial aquifer above the confining unit. The presence of denitrifying bacteria in the deep clay layers (Reddy et al., 2017), paired with the increased residence time due to slowed movement of recharge through the ICU, likely results in complete denitrification of nitrate in the vadose zone or thin surficial aquifer when the ICU is present. While here it is assumed that nitrate is removed from the system where the ICU is present, previous work has identified N accumulation in deeper soil layers as a potential mechanism for lags between N inputs and watershed export (McMahon et al., 2006; Van Meter et al., 2016), which would suggest that N slowed in the vadose zone or thin surficial aquifer eventually contributes to spring N export and future work should investigate this possibility. While hydrological attenuation was not source-specific, the spatial arrangement of land uses within the springshed had implications for the N that was recharged to groundwater. While surface and net horse manure N inputs were greater than cattle manure N, 91% of cattle pastures were over
unconfined areas of the springshed compared to 21% of horse farms. This resulted in a major shift in contribution from the two manure sources, with cattle manure N contributing three times as much to spring N export. The results suggest that both source-specific attenuation factors and the spatial arrangement of the landscape both interact to drive the contribution of various N sources to spring N export.

Groundwater attenuation represented 38% of recharged N inputs, but only 6% of the total springshed N inputs. These estimates are roughly half of global estimates of groundwater denitrification (Seitzinger et al., 2006). The UFA attenuation capacity is small relative to attenuation in the surface soil and vadose zone, suggesting that denitrification in the aquifer is not a major sink for anthropogenic N inputs in the springshed.

**Disaggregating the Attenuation Capacity of the Landscape**

An estimated 90% of surface N inputs are attenuated through the landscape, and this is consistent with measured N export (13% of calculated inputs, 87% retention). Landscape N retention is high compared to the global average of 75-80% reported for surface water catchments (Boyer et al., 2002; Van Breemen et al., 2002; Vitousek et al., 1997). Measured N export from Silver Springs (430 kg N km$^{-2}$ y$^{-1}$) was similar to loads exported from the Mississippi River Basin (278-303 kg N km$^{-2}$ y$^{-1}$, Sprague et al., 2011) and within the range of watershed N export reported for US catchments (average: 240, range: 8-750 kg N km$^{-2}$ y$^{-1}$, McCrackin et al., 2014; average: 560, range: 210-1,600) kg N km$^{-2}$ y$^{-1}$; Han and Allen, 2008) and global averages (average: 930, range: 1 to 21,000) kg N km$^{-2}$ y$^{-1}$; Alvarez-Cobelas et al., 2008).

While the majority of N was attenuated between the land surface and the vadose zone (64%), attenuation was source-specific, which had major implications for the
contribution of surface N sources to spring N export. The results emphasize the importance of developing source-specific understanding for both surface N inputs and attenuation in identifying the contribution of N sources to N export, as well as the role of hydrological attenuation in preventing a significant portion of surface N inputs from reaching groundwater. Considering land use practices and the spatial organization of the landscape was critical for accurately assessing the sources of catchment N load.

**Estimating Source Contributions to Spring Export from Isotopic Data**

The data suggest that the isotopic source signal is masked early in the leaching process, challenging the assumption that the sources of nitrate in spring discharge can be traced using conventional source signature ranges (e.g., Katz et al., 2004; Katz and Griffin, 2008; Knowles et al., 2010). SPFM-measured nitrate at both fertilizer and manure N source sites showed $\delta^{15}$N and $\delta^{18}$O closer to the isotopic signatures of soil-derived N than the initial source signatures. This in line with previous work that suggests that fertilizer N is rapidly immobilized and incorporated into the SOM, from which it mineralizes and contributes to NO$_3$-N leaching (Sebilo et al., 2013; Van Meter et al., 2017).

**Conclusions**

A catchment-scale N budget was constructed using in situ measurements and landscape N attenuation was disaggregated between surface application and spring discharge. The concise model framework predicted that 10% (± 5%) of total surface N inputs were discharged from Silver Springs, which agrees with measured values (13% ± 3%). This suggests that the landscape attenuates 87-90% of total surface N inputs. When landscape-scale attenuation was further disaggregated along the hydrological flowpath, the majority of N inputs were attenuated in the surface soil (64% of inputs) and
hydrological attenuation in the vadose zone prevented an additional 20% of total inputs from entering the groundwater. These results suggest that biogeochemical attenuation in the surface soil is the major sink for N inputs to the land surface. While aquifer denitrification further reduces the mass of N eventually exported from the spring, these losses represent a small fraction of total springshed N inputs. Additionally, the isotopic signature of in situ measured leached nitrate were used to refine predictions of source contributions to spring export. Predictions made using the SIAR mixing model with the updated source signatures agreed more closely with the predictions from the catchment-scale N budget.
Figure 3-1. Contribution of specific N sources to surface N inputs ($L_{IN}$, Equation 3-4) and spring N export ($L_{OUT}^P$, Equation 3-1) estimated from the catchment-scale N budget. Specific sources were manure from livestock (sum of manure from cattle and horses; $M = M_c + M_h$), agricultural and urban fertilizer ($F_a$ and $F_u$), wastewater from on-site treatment (e.g., septic tanks) or centralized treatment facilities ($W_s$ and $W_t$), atmospheric deposition ($D$), and biological nitrogen fixation from cultivated legumes ($BNF$).
Figure 3-2. Total mass of N exported from different sections of the landscape. $L_{IN}$ is the surface-applied N, $L_L$ is the net N leached after biogeochemical attenuation, $L_R$ is the net N recharged to groundwater after hydrological attenuation, $L_{OUT}^p$ is spring N export predicted from the PLAN model, and $L_{OUT}^m$ is the measured spring N export.

Figure 3-3. Comparison of source contribution to Silver Springs NO3-N export estimated by catchment-scale N budget, SIAR mixing model, and SIAR mixing model updated with SPFM-measured source signatures.
CHAPTER 4
TEMPORAL EVOLUTION OF NITRATE EXPORT FROM THE KARST SPRINGS OF FLORIDA

Human activity has disrupted the global nitrogen (N) cycle (Vitousek et al., 1997), substantially increasing N loads to the landscape over the past several decades (Galloway et al., 2008). The increase in anthropogenic N inputs has resulted in increased N concentrations and N export in freshwater systems across the globe, dominantly in the form of nitrate (e.g., Goolsby et al., 2001; Howden et al., 2010; Nolan et al., 2002; Seitzinger et al., 2005; Shuiwang et al., 2000).

Karst aquifers are highly vulnerable to nitrate contamination (Green et al., 2006), representing a major threat to human health (Townsend et al., 2003) as approximately 25% of the global population relies on karst aquifers for drinking water (Hartmann et al., 2014). Groundwater nitrate contamination also represents a threat to surface waters and coastal systems, as spring discharge delivers groundwater N to surface waters and can significantly contribute to coastal N loads (e.g., Cable et al., 1996; Garcia-Solsona et al., 2010). In Florida, 90% of drinking water is supplied by groundwater (Marella, 2015) and the karstic Upper Floridan Aquifer (UFA) is the dominant source of groundwater withdrawals (Marella and Berndt, 2005).

The Florida Watershed Restoration Act (403.067, Florida Statutes), authorizes the Florida Department of Environmental Protection (FDEP) to implement total maximum daily loads (TMDLs) required by Section 303(d) of the federal Clean Water Act. FDEP implements TMDLs using a watershed approach by developing basin management action plans (BMAPs) for impaired waterbodies (include freshwater springs) that target the control and mitigation of pollution from point and nonpoint sources. Atmospheric deposition, manure from livestock production, agricultural and
urban fertilizer, and wastewater have all been identified as sources of nitrate contamination in the UFA (Katz, 2004), which is consistent with the results presented in Chapter 3.

A variety of conservation measures have been implemented in basins overlying the UFA to target the point and nonpoint sources of N across the state (e.g., Alva et al., 2006; Greening et al., 2014; Hochmuth et al., 2012), yet nitrate concentrations are still rising in many of Florida’s springs. Biogeochemical (N accumulation) and hydrological (travel times) legacy N can result in time-lags between N loading and water quality responses (Gardner and Drinkwater, 2009; Meals et al., 2010; Sebilo et al., 2013; Van Meter et al., 2016; Worrall et al., 2015). Spring discharge from the UFA is a mixture of young (<2 years) and old (>50 years) water (Katz et al., 2004), suggesting that legacy N could impact spring water quality for decades. However, the same characteristics that make karst aquifers highly vulnerable to nitrate contamination suggest that rapid responses to changes in land management practices are possible. Studies in the UFA have suggested time lags ranging from 1 to 10 years (Musgrove et al., 2014), compared to time lags from 12 to 34 years observed in the Grand River watershed (Van Meter and Basu, 2017).

The potential for legacy effects of N inputs suggests that an analysis of long-term trends is necessary to identify the drivers of water quality changes. There is a need to understand how future changes in land use/land management will drive water quality, so as to set reasonable expectations for water quality restoration. Projection of future changes requires an understanding of historical trends in N export and the dominant biogeochemical and hydrological drivers of spring N export across the UFA.
Here long term records of springshed N inputs and spring N export for 16 karst springs in Florida with a range of land use patterns were used to: 1) reconstruct historical N inputs across multiple springsheds overlying the UFA, hypothesizing that N inputs to the landscape have increased over the past 70 years due to human activities, and (2) evaluate the PLAN model performance in multiple karst springsheds overlying the UFA, hypothesizing that total N flux from Florida springs is explained by differences in land use, population density, and source-specific attenuation factors.

**Methods**

**Study Sites**

The UFA is an eogenetic karstic aquifer located in the southeastern US, underlying Florida and parts of Mississippi, Alabama, Georgia, and South Carolina. It is the source of water discharging from over 1,000 freshwater springs across Florida (Scott et al., 2004), including 33 first magnitude springs (flow > 2.8 m$^3$ s$^{-1}$) and 191 second magnitude springs (flow between 0.28 and 2.8 m$^3$ s$^{-1}$). The UFA is largely unconfined along the Gulf Coast of North Central Florida (Figure 4-1), but is confined over the north, eastern, and central regions of the state by the clay intermediate confining unit (ICU). The UFA is considered semi-confined when the ICU thickness is <30m (Miller, 1986). Groundwater discharges through breaches in the ICU due to the positive hydrostatic pressure, resulting in the high density of freshwater artesian springs throughout North Central Florida. Changes in land use type (see Figure 1-1) and intensity occurred between 1945 and 2012, alongside changes in freshwater chemistry discharged from springs. This temporal interval was focused on to evaluate the impact of land use changes on N inputs and export from the springs selected for this analysis.
Catchment N Budgets

Spring selection was based on the following criteria: first or second magnitude spring, previously delineated springshed boundaries, long-term records of spring N concentration and discharge, and a springshed boundary dominantly within a single county. The latter criterion was selected to minimize errors from proportioning county-level data to the springshed-scale. Based on these criteria, 9 first magnitude springs and 7 second magnitude springs were selected and (Table B-1) and the annual average catchment-scale N budgets for the period 1945-2012 and a long-term average (1992-2012) budget were calculated for all 16 springsheds. The long-term N budgets allow us to separately evaluate the model performance across space, thus extending the results presented in Chapter 3.

The N load exported from each springshed \( s \) \( (L^B_{OUT,s} \ [M \ L^{-2} \ T^{-1}]) \) was predicted at each time \( t \) to calculate a timeseries of N loading for each springshed \( (L^B_{OUT,s}(t) = \sum_i P_i L_i A_i N_i) \) and was compared to the measured export \( (L^M_{OUT,s}(t) = \frac{CQ}{A_s}) \), following the PLAN framework introduced in Chapter 3. The total N inputs to the surface \( (L_{IN} \ [M \ L^{-2} \ T^{-1}], \text{ Equation 3-4}) \), N leached below the root zone \( (L_{L} \ [M \ L^{-2} \ T^{-1}], \text{ Equation 3-5}) \), and N recharged to groundwater \( (L_{R} \ [M \ L^{-2} \ T^{-1}], \text{ Equation 3-6}) \) were also estimated for each springshed \( s \) at each time \( t \) consistent with the model framework presented in Chapter 3.

Datasets

Springshed boundaries were obtained from the Florida Geological Survey and St. Johns River Water Management District (Figure 4-1), and long-term records of spring N concentration and discharge were obtained from Southwest Florida Water Management
District (SWFWMD), North Florida Water Management District (NFWMD), Suwannee River Water Management District (SRMWD), and SJRWMD (Table B-1). Data provided by the water management districts was supplemented with all available discharge and water quality data retrieved from the National Water Quality Monitoring Council Water Quality Data Portal (NWQMC, 2018) and the USGS National Water Information System (USGS, 2018). The long-term average discharge was used to calculate N export for years with unreported spring discharge. Three outliers were removed from the N concentration dataset (Alexander, 1960; Volusia Blue and Wekiwa, 2006), which were 5 to 10 times the 10-year average N concentrations and were assumed to be the result of extreme events (e.g., large wildfires in the surrounding area). The model parameters were estimated from a collection of data sources, which are listed in Table B-2.

**P – Population or proportional area**

Springshed population data was estimated using data from Fang and Jawitz (2018) for 1940-2010 and was linearly interpolated between decades. The 2012 population density was projected by using linear least-squares regression fit to 2000 and 2010 population data points (Figure B-1). Outlier estimates in Alexander (1990), Crystal (2000), Manatee (1990), and Troy (1970 and 1990) population densities were corrected by linearly interpolating between the preceding and proceeding data point.

Agricultural statistics were retrieved from the US Agricultural Census Dataset (Haines et al., 2016), which included county-level cropland area, pasture area, and livestock counts from 1945-2012. Data was linearly interpolated between census years and between years where the data was unreported. The 2011-2017 Statewide Land Use Land Cover data (FDEP, 2018) was used to determine the proportion of county-
level agricultural, urban, and pasture area within each springshed boundary and applied
these proportions to county-level statistics from 1945 to 2012.

L – Load per area or per count

Published livestock excretion rates (Smith et al., 2000; Velthof et al., 2016) are
calculated based on average animal weights, which have increased between 1960 and
2012 (ERS, 2018). The annual average weight for each livestock category was
calculated as a proportion of present-day (2017) live weights for each livestock $i$ ($\phi_{Li}$)
using data from the US Department of Agriculture Economic Research Service (ERS,
2018). Annual loads from each manure source $i$ ($L_{Mi} = [M_{cat}, M_{hor}, M_{chi}, M_{hog}]$) were
weighted by this correction factor ($L_{Mi,c} = L_{Mi} \phi_{Mi}$) to calculate a corrected load ($L_{Mi,c}$)
that accounts for the weight changes during the period of investigation (Figure 4-2). As
livestock weight data was unavailable pre-1960, the 1960 values were used for 1945-
1960 as a conservative estimate. Based on the assumption that horses have followed
similar N excretion changes as cattle during the period of investigation, cattle weighting
factors ($\phi_{cat}$) were applied to horse N excretion ($\phi_{hor}$) as well. Similarly, per capita
wastewater N loads are strongly controlled by per capita protein consumption (Lusk et
al., 2017; Rose et al., 2015; and Van Drecht et al., 2009), which has increased between
1945-2012. Wastewater loads ($L_{w}$) were weighted by the annual per capita protein
consumption expressed as a proportion of 2012 values ($\phi_{w}$) to calculate a corrected
wastewater load ($L_{w,c}$) that accounts for the increase in protein consumption ($L_{w,c} =
L_{w} \phi_{w}$). The corrected loads $L_{cat,c}$, $L_{hor,c}$, $L_{hog,c}$, and $L_{w,c}$ were used in place of the
uncorrected loads for all budget calculations.
County-level farm and nonfarm fertilizer N sales from Brakebill and Gronberg (2017) were used to estimate total, farm, and nonfarm fertilizer N loads between 1987-2012. To estimate historical nonfarm fertilizer sales, state-level nonfarm N sales and state population interpolated from the decennial census were used to estimate per capita N loads for 1945 and 1959 (Ibach et al., 1964; Mehring et al., 1957). Nonfarm N sales were linearly interpolated between 1945 and 1960 and between 1960 and 1987 to fill in data gaps. Estimated nonfarm fertilizer N sales were subtracted from total fertilizer N sales in 1945-1985 (Alexander and Smith, 1990) and 1986 (Battaglin and Goolsby, 1994) to determine the county-level farm fertilizer N loads between 1945 and 1987. There magnitude of historical (1945-1985) and recent (1987-2012) fertilizer N sales were not in agreement at the county-level due to different methods of proportioning fertilizer loads to the county level. However, the trends in the historical dataset are likely still accurate due to consistent proportioning methods between years. The historical data was normalized by the recent dataset by multiplying the historical data by the ratio of 1987 fertilizer sales from the recent dataset and the 1985 fertilizer sales in the historical dataset, thereby correcting the magnitudes while maintaining the historical trends (Figure B-2). When additional breaks were observed in the historical dataset (as depicted in Figure B-2), the same approach was taken. It was assumed that all fertilizer sold within the county was applied in the same county and estimated springshed-level fertilizer loads based on the proportion of county-level fertilized urban (high/medium/low residential, stadiums, community recreational facilities) and fertilized agriculture (crops and improved pastures) within the springshed for nonfarm and farm fertilizer N, respectively.
Atmospheric deposition was estimated from the NACID – Nitrogen Deposition dataset, which provides annual coverage at 1-km resolution for the conterminous US between 1860 – 2013 (Hember, 2018). The average annual N deposition rate within each springshed boundary from 1945 to 2012 was extracted in R (R Core Team, 2018) to calculate the total atmospheric N load within each springshed.

A – Anthropogenic attenuation

Current springshed-level wastewater treatment data was collected from the Florida Water Management Inventory (FDOH, 2016), which quantifies the total number of households connected to sewer lines or septic tanks for wastewater treatment. The sum of septic and sewer counts estimated from the FWMI agreed well with the total households reported by the Census of Housing data (Figure 4-3). Note that the septic totals reported for Hillsborough County were well below historical septic counts, due to a substantial underestimation of total parcels when compared with the household count listed in the 2010 Census of Housing (US Census Bureau, 2018). The Hillsborough data was replaced with an estimate of 109,029, calculated as the sum of 1990 census-reported septic counts and septic permits added since 1990 reported by the Florida Department of Health (FDOH, 2018). The US Census of Population and Housing collected data on household sewage treatment methods in 1970, 1980, and 1990 and this data was used to estimate historical wastewater treatment data. The N delivery after wastewater treatment for springshed $s$ ($A_{WS}$) was estimated as the population-weighted sum of N delivery from each wastewater treatment method ($A_{WS} = \frac{P_{WS}}{P} A_{WS} + \frac{P_{WT}}{P} A_{WT}$), where $P_{WS}$ is the population density of residents connected to septic tanks, $A_{WS}$ is the N delivery after attenuation in septic tanks, $P_{WT}$ is the population density of
residents connected to WWTFs, $A_{WT}$ is the N delivery after attenuation in a WWTF, and $P$ is the springshed population density.

**N – Natural attenuation**

Source-specific natural attenuation in the soil was estimated as described in Chapter 3 and N delivery after attenuation was represented by a delivery coefficient ($N_{S,i}$) for each source $i$. Natural attenuation in the vadose zone ($N_{H,i}$) was assumed to be a function of the thickness ($\tau$) of the intermediate confining unit. The ICU was considered unconfined when $\tau < 6$ m and fully confined when $\tau > 31$ m. Assuming complete delivery of leached N through the vadose zone in unconfined regions ($N_{H,i} = 1$ when $\tau < 6$ m) and complete attenuation in fully confined regions ($N_{H,i} = 0$ when $\tau > 31$ m), a linear decline in N delivery was assumed in thinly and semi-confined regions ($6$ m $< \tau < 31$ m) and calculated as a function of the average ICU thickness for the land use area associated with each source $i$ ($N_{H,i} = -0.041\tau + 1.25$). The springshed-specific aquifer delivery coefficient ($N_A$) was only measured in 9 of the springsheds (Heffernan et al., 2012), averaging 0.55 across all springsheds. However, there was a significant ($p < 0.001$) negative correlation between $N_A$ and the proportion of springshed in agricultural land uses (Figure B-3) and this relationship was used to predict $N_A$ for springsheds lacking data.

**Results and Discussion**

**Reconstruction of Historical Inputs**

The first objective was to reconstruct historical N inputs for 16 springsheds across Florida. The contribution of fertilizer (F), manure (M), atmospheric deposition (D),
and wastewater (W) to the total annual surface N loads ($L_{IN}$) between 1945 and 2012 and to long-term (1992-2012) budgets was estimated for each springshed.

While the sum of county-level fertilizer sales from the historical dataset agreed with state totals (Figure B-4), known county-level fertilizer sales in 1950 did not agree well ($R^2 = 0.32$) with estimates from Alexander and Smith (1990). Those authors estimated county-level fertilizer sales by weighting state-level fertilizer N sales by county cropland area, but this fails to capture the differences in N fertilizer application rates across different crop types. Cropland area, orchard area, and population were the strongest predictors of N fertilizer sales at the county level for 1950 and 1992-2012 (Figure B-5). Orchard area alone was a strong predictor of county-level fertilizer sales in 1950 ($R^2 = 0.83$) and explained 61% of the variability for the full dataset, highlighting the importance of considering land use intensity when estimating N inputs to the landscape.

While this study took the approach of normalizing the historical dataset to the recent dataset to correct for the differences in the magnitude of estimated fertilizer sales, future work should focus on further refining historical fertilizer N sales as these estimates have major implications on catchment N budgets.

Total fertilizer sales were dominantly driven by farm fertilizer sales at the state level, but the evolution of land use patterns drove the proportion of farm and nonfarm fertilizer at the springshed level (Figure 4-4). For example, declines in cropland area in Wekiwa Springs from 500 km$^2$ in the mid-1950s to 70 km$^2$ in 2010, paired with a 7-fold increase in population density during the same period, resulted in a shift in the dominant fertilizer N source from farm to nonfarm in the mid to late 90s (Figure 4-4). In contrast, the Jackson Blue Springs springshed has a low population density and agriculture has
remained the dominant anthropogenic land use, resulting in total fertilizer loads are almost entirely from farm fertilizer (Figure 4-4).

There was no trend in state-level per capita nonfarm N sales during the period of investigation, which averaged 1.56 kg N person\(^{-1}\) \((p > 0.05, R^2 = 0.004)\). Fertilizer for lawns and golf courses represented 50% of the total nonfarm N sales (FDACS, 2010; 2011), with the remainder being used for home gardens, potting soil, and nursery plants. Therefore per capita N loads applied to lawns and golf courses were estimated as 0.78 kg N person\(^{-1}\). Power-law scaling between population density and springshed proportional urban area (Nordbeck, 1971) suggests that increases in population will result in increases in urban area \((y = 0.02x^{0.57}, R^2=0.84)\), which is assumed to result in a proportional increase in fertilized urban land area. Fertilizer inputs peaked between the mid-70s and 80s for most springsheds, followed by a decrease in the 2000-2010s. This follows the general state-level trend of declining fertilizer inputs, which is driven by the observed decline in total cropland area (Figure B-6). However, fertilizer sales peaked at different times in different springsheds.

The differences in springshed population, livestock population, loading rates, and wastewater attenuation rates resulted in varying magnitudes of N inputs and relative contribution of specific N sources across space and time (Figure 4-5). Total inputs increased over time for all springsheds, ranging from 190 to 1,500 kg N km\(^{-2}\) y\(^{-1}\) in 1945 and from 620 to 4,600 kg N km\(^{-2}\) y\(^{-1}\) in 2012. While trends in livestock populations varied across springsheds, there was a general decline in hog counts and an increase in horse counts across all springsheds. Cattle populations were larger and more variable across
the springsheds and cattle had the highest N load per head, so manure loads were dominantly driven by cattle populations across the springsheds.

The total population density increased over time for all springsheds, which was accompanied by a decrease in $A_W$ through time (Figure 4-6). Springsheds with a higher urban population density had a higher proportion of households connected to sewer ($p = 0.001$, $R^2 = 0.54$), resulting in lower $A_W$ due to the much higher attenuation coefficient for WWTFs (92% ± 9%) compared to septic (34% ± 7). However, the magnitude of the changes in $A$ depended on the evolution of sewage treatment within each springshed and the relative rates of septic and sewer growth over time. This has major implications for future wastewater N loads, which are projected to continue to increase over the next 30 years (Van Drecht et al., 2009).

Atmospheric deposition increased over time for all springsheds, but there were different patterns in the deposition rate across the springsheds. Global N deposition has more than doubled since 1850 (Kanakidou et al., 2016) and four-fold increases were observed between 1945-2012 across all 16 springsheds (Figure 4-5). Recent shifts in atmospheric deposition chemistry suggest that livestock production is becoming the dominant contributor across the US due to decreases in NO$_x$ emissions from combustion (Li et al., 2016) and there was a positive relationship between springshed N deposition loads and cattle populations ($p < 0.001$, $R^2 = 0.58$).

**Drivers of N Export**

There was a significant positive correlation ($p < 0.001$, $R^2 = 0.83$) between the proportion of the springshed in cropland land uses (estimated from the 2011-2017 land use) and the 2008-2017 average NO$_3$-N concentration (Figure 4-8a). Adding improved
pastures to cropland as an estimate of total fertilized agriculture resulted in a slightly better fit (Figure 4-8b, \( p < 0.001, R^2 = 0.85 \)). While cropland area was the strongest predictor of present-day spring nitrate concentrations, these relationships do not hold up for individual years or over time. These results suggest that it is the intensification of modern-day agricultural practices (Figure B-6), rather than an increase in agricultural area over time, is a driver of this pattern and therefore the regression equations developed from modern data cannot be used to predict historical spring N concentrations.

**Model Performance**

Model performance varied across the springs for the annual predictions (Figure 4-7). There was a significant correlation between \( L^P_{OUT} \) and \( L^m_{OUT} \) over time for Chassahowitska (NSE = -2,700), Silver (NSE = -310), Troy (NSE = -2.1), Volusia Blue (NSE = -3.2), and Wekiwa (NSE = -1.9). The Nash-Sutcliffe Efficiency (NSE) was negative for all springsheds, indicating that the mean of \( L^m_{OUT} \) was a better predictor of the observed values than \( L^P_{OUT} \). A poor overall fit between \( L^P_{OUT} \) and \( L^m_{OUT} \) for the long-term budgets (NSE = 0.18) was driven by substantial over and under predictions of \( L^P_{OUT} \) (Figure 4-9). Over-predictions were dominantly driven by livestock manure loads, while under-predictions are likely the result of overestimates of soil N attenuation.

When N fluxes and attenuation were disaggregated along the hydrological flowpath (Figure 4-10), the majority of \( L_{IN} \) was attenuated in the surface soil \((72 \pm 6\%)\). While these results are higher than the results presented in Chapter 2 \((64\%)\), they agree with the conclusion that N attenuation of surface inputs dominantly occurs in the surface soil and thus reductions in surface N inputs and improvements in soil
attenuation (e.g., via increases in crop fertilizer N efficiency from best management practices) will have the greatest impact on managing catchment-scale N export.

**Conclusions**

Historical N inputs to the landscape of 16 karst springsheds were reconstructed and modeled N export was predicted as the product of N inputs and source-specific biogeochemical and hydrological attenuation coefficients. Catchment-scale N inputs increased over time in all springsheds and the relative source contributions varied across the springsheds. The results suggest that incorporating land use intensity is critical for accurate estimation of N inputs. Finally, the proportion of the springshed in agricultural land uses was an important predictor variable for present-day spring N export, suggesting that N inputs from agricultural systems are major drivers of N export from karst springs.
Figure 4-1. Location of study area and springsheds. Dark brown areas represent the location of the intermediate confining unit (ICU) where it is >20m thick. Light blue areas represent the springsheds.

Figure 4-2. Proportional weighting factors for livestock and wastewater. (a) Livestock weighting factors ($\phi_{Mi}$) for cattle ($\phi_{Mcattle}$), chickens ($\phi_{chickens}$), and hogs ($\phi_{hogs}$), reported as the proportion of live weight compared to 2017 live weight, and (b) wastewater weighting factor ($\phi_W$), reported as the proportion of per capita protein consumption compared to 2012. Data from ERS (2018).
Figure 4-3. Septic + sewer counts from the FWMI dataset agree with total households reported in the 2010 census of housing (FWMI, 2016; US Census Bureau, 2018).

Figure 4-4. Historical fertilizer sales for (a) the state of Florida, (b) Wekiwa Springs springshed and (c) Jackson Blue Springs springshed. Data from Alexander and Smith (1990), Battaglin and Goolsby (1995), and Brakebill and Gronberg (2017).
Figure 4-5. Timeseries of PLAN model parameters for all springsheds. (a) Livestock population density (blue = cattle, black = horse, dashed black = hogs), (b) livestock N loads (blue = cattle, black = horse, dashed = hog), (c) human population density, (d) per capita N loads (solid red = wastewater, dashed red = urban fertilizer), (e) proportional agricultural area, and (f) per area N loads (solid = fertilized agriculture, dashed = deposition).
Figure 4-6. N delivery after anthropogenic attenuation ($A_W$).
Figure 4-7. Predicted ($L_{OUT}^p$) and measured ($L_{OUT}^{m}$) catchment N export.
Figure 4-8. Relationship between land use and long-term average spring nitrate concentration. (a) the proportion of a springshed in cropland or (b) the proportion of the springshed in ‘fertilized agriculture’ (the sum of cropland and improved pastures) and the NO$_3$-N concentration of spring discharge.

Figure 4-9. Relationship between $L_{OUT,s}^P$ and $L_{OUT,s}^m$ for the long-term (1993-2012) N budgets for 16 springsheds. Linear regression for the fill dataset (blue regression line and equation) includes Jackson Blue Springs (blue circle), which is compared to results that omit the Jackson Blue Springs value (black line and black equation). Grey dashed line is the 1:1 line.
Figure 4-10. Predicted N fluxes along the hydrological flow path for all 16 springsheds using the PLAN model (blue) and measured spring N export (red).
CHAPTER 5
GENERAL CONCLUSIONS AND FUTURE WORK

Understanding the drivers of catchment-scale N export through space and time is critical for quantifying anthropogenic impacts to groundwater. Developing catchment-scale budgets can elucidate how N sources are attenuated throughout the landscape, but reconstructing N inputs at the landscape scale remains a challenge. Data is often incomplete or collected at coarse scales corresponding to political boundaries, introducing uncertainties in budget components. This dissertation aimed to identify the major sources of nitrogen in spring catchments using in situ measurements, identify the attenuation capacity of the landscape, and reconstruct the temporal evolution of spring chemistry in catchments with variable land use histories. This work describes the development of a simple method for measuring N attenuation, introduce a parsimonious model framework to disaggregate attenuation throughout the landscape, and discuss methods for projecting data at various scales to springshed boundaries.

Chapter 2 describes the modification and application of a simple method for direct in situ measurements of vadose zone nitrate leaching and attenuation. This work enhances our understanding of catchment-scale N budgets by providing low-cost, robust, and accurate measurements of soil nitrate leaching and attenuation. The results showed that site-specific land use characteristics allow us to better categorize expected nitrate leaching, suggesting that general land use categorization is insufficient for capturing N leaching and attenuation dynamics at the catchment scale.

Chapter 3 describes the construction of a catchment-scale N budget for Silver Springs, the largest first magnitude spring in North America. In situ soil attenuation measurements described in Chapter 2, combined with in situ measurements of aquifer
attenuation from the literature, were used to disaggregate landscape attenuation between the surface soil, vadose zone, and aquifer. This work enhances our understanding of the major N sinks in karst landscapes, suggesting that the majority of surface N inputs are attenuated in the soil and vadose zone. Chapter 3 also provides a simple model framework to disaggregate landscape N attenuation and estimate the relative contribution of N sources to spring N export.

In Chapter 4, the analysis was extended through both space and time by reconstructing historical trends of spring N export for multiple spring catchments. The simple model framework developed in Chapter 3 was used to predict the temporal evolution of N export from 16 karst springs. The wide range of land use patterns and history across the springsheds resulted in varying magnitudes and relative contributions of N inputs from specific N sources. The N loading rates for wastewater, livestock, and fertilizer have generally increased through time, although fertilizer sales at the state-level have declined in recent years alongside a decrease in cropland area.

This work highlights the major challenges in quantifying nutrient budgets at the landscape scale and furthers our understanding of catchment-scale N budgets by presenting methods to more accurately quantify N inputs within springshed boundaries. Predictive models rely on accurate model inputs, and this work represents a step towards landscape-scale quantification of N inputs when data is available at the state and/or county level.

This work used a top-down approach to predict spring N export from available data, however, future work could compare this approach with calibrated techniques to compare the dominant drivers identified using different strategies. Synergies between
approaches would provide further support for the results presented here, while disconnects would help to identify future areas of research. The results presented in Chapter 3 and 4 rely on soil attenuation estimated from SPFM-measured N leaching, as described in Chapter 2. While the SPFMs provide robust estimates of soil attenuation, the associated parameters used in the landscape-scale budget for the 1,300 km² Silver Springs springshed were scaled up from 90 SPFM measurements from 9 sites across 3 land use categories. As SPFM construction is relatively low cost and installation is relatively low effort, a comprehensive network of SPFMs should be deployed across the springshed to identify the dominant predictors of soil attenuation and refine the estimates used in Chapter 3. Climate and soil properties could also play an important role on N leaching fluxes, but investigating their effect was outside the scope of this dissertation. A more comprehensive network of SPFMs could also give insight to the natural intra-land use variability of soil N attenuation and site-specific deployment across multiple springsheds could be used to test the hypothesis that soil attenuation measured in the Silver Springs SPFM deployment are valid estimates across multiple springsheds. These insights could be used to refine the predictions of N export presented in Chapter 4.

This dissertation tested the hypothesis that land-use is a major driver of N leaching at the field-scale and spring N export at the landscape scale. However, the primacy of land use is a question that should be addressed in future work. While land-use patterns are correlated with N concentration within and across springsheds, there is a possibility that land use patterns are secondary to the geological drivers that circumscribe the possible land use in a given area. Future work should therefore
evaluate the relationship between land use and physiographic characteristics such as soil types, vadose zone thickness, and geological substrates.

Identifying the relative contribution of N sources to the landscape aids in the development of targeted strategies and future work should also focus on the development, implementation, and evaluation of water quality restoration. When data is available on best management practice adoption, the relationship between adoption and changes in N inputs and water quality responses can be evaluated. Finally, building on the methods presented here, an evaluation of time lags between N inputs and spring N export can help set expectations for water quality restoration timelines.
APPENDIX A
SUPPORTING INFORMATION FOR CHAPTER 3

The supporting information shows time series of data that was averaged across the period of investigation and provides further details for attenuation coefficient estimation from multiple datasets. Hydrostratigraphy data was obtained from the SJRWMD and the intermediate confining unit (ICU) thickness raster layer was converted into a polygon in ArcMap to create an ICU presence layer (Figure A-1). This data to estimate hydrologic attenuation in the vadose zone, which was assumed to be 100% in areas overlying the confining unit. The time series of N inputs used for N budget calculation are shown in Figure A-2. The average values for the period of investigation (1997-2017) were used in all analyses.

Wastewater data was estimated using population data from Fang and Jawitz (2018) and the 2016 wastewater estimates from the FWMI dataset (FDOH, 2016). The FWMI data was processed in ArcMap and used to weight the population data to estimate the proportion of the springshed population using septic tanks or WWTFs for wastewater treatment. The FWMI dataset provides the parcel boundaries of each property within the state of Florida and this data was clipped to the springshed boundary (SJRWMD, 2016). A point was created at the centroid of each parcel and septic (classified as ‘Known Septic,’ ‘Likely Septic,’ or ‘Somewhat Likely Septic’) and sewer (classified as ‘Known Sewer’, ‘Likely Sewer’, or ‘Somewhat Likely Sewer’) were summed within the springshed boundary and used to calculate the proportion of the total wastewater N load for each treatment method. Households categorized as unknown were not included in the analysis, thus assuming they have the same estimated ratio between sewer and septic.
Wastewater attenuation was estimated using influent and effluent concentration data from two WWTFs, the Marion County Correctional Institute WWTF (MCCI-WWTF) and the University of Florida WWTF (UF-WWTF). The MCCI-WWTF data reported influent N concentrations as TKN and effluent concentrations as TN, while the UF-WWTF provided both TKN and TN for influent and effluent. To evaluate the influence of using TKN or TN to estimate N removal efficiency, compared N removal efficiency estimated using TN concentrations of influent and effluent to estimates using TKN of wastewater influent and TN of wastewater. The N removal efficiency calculated using TKN and TN agreed well with efficiency calculated using TN for both influent and effluent data (Figure A-3) and therefore both MCCI-WWTF and UF-WWTF data were used to estimate WWTF N removal efficiency. The data is presented in Table A-1.

The N delivery coefficients of agricultural fertilizer, urban fertilizer, and manure using SPFM-measured attenuation from crop, turf, and pasture sites, respectively. The field sites were chosen to represent the range of typical practices within each land use type in the springshed. SPFMs were deployed from June 2017 – June 2018 to obtain integral measures of leached N, attenuation of surface inputs in the upper 30-cm, and the $\delta^{15}$N and $\delta^{18}$O signature of nitrate leached below the root zone.

The Crop 1 site was an established bermudagrass hay (*Cynodon dactylon* L.) field, which was fertilized in June 2017 and January 2018. The Crop 2 site was planted with peanut (*Arachis hypogaea* L.) in June 2017 and fertilized at planting, followed by an unfertilized triticale cover crop. Biological N fixation was estimated to be 186 kg N ha$^{-1}$ for the peanut crop (Table A-2). The Crop 3 site was initially planted with sunflower in June 2017 (*Helianthus annuus*) and a single application of N fertilizer was banded at
planting. In August 2017, the sunflower crop was disced into the soil and an unfertilized triticale cover crop was planted. Pasture sites 1 and 2 sites were horse pastures stocked at 2.5 horses ha-1. No fertilizer was applied at either site and manure and urine patches were randomly distributed throughout the field. Additionally, stockpiled manure and stall bedding from 24 horses was broadcast uniformly across the 1.2-ha Pasture 2 site every two months. Pasture site 3 was a cattle pasture stocked with 60 cow-calf pairs on 10 ha and a single application of fertilizer was applied at Pasture 3 in June 2017. The cattle were rotated to a different field in September 2017 and the field was unoccupied during the remainder of the deployment period. Turf site 1 was an unfertilized bahiagrass (*Paspalum notatum*), Turf 2 was planted with ‘TifTif’ bermudagrass (*Cynodon dactylon* L. X *C. trunsvaalensis* Burtt-Davy), and Turf 3 was a golf green planted with SeaDwarf® seashore paspalum (*Paspalum vaginatum* Swartz). Turf 2 received three applications of fertilizer in February, June, and October, while fertilizer was applied bi-weekly to Turf 3 from March through September.

Summary statistics for all sites are shown in Table A-2. The mass of N inputs explained a large portion of the variability in N leached below the root zone (Figure A-4). Land use had a significant effect on N attenuation (1-way ANOVA, $p < 0.05$) and attenuation of N applied to turf sites was significantly greater than attenuation at cattle or crop sites (Tukey’s post hoc test). The isotopic signature of leached nitrate was analyzed as described in the main document and the results are shown in Table A-4.

Literature values for N sources were used to predict source contributions from the isotopic signature of nitrate in spring discharge (SIAR), which were compared to predictions using isotopic signatures of SPFM-measured nitrate from sites with fertilizer
or manure sources (SIAR-SPFM). Fertilizer was applied to Pasture 3 during the rainy-season deployment period, so only data from the Sep 2017 – June 2018 season was used from Pasture 3 in the leached nitrate from manure N source estimations. The data used in both models are shown in Table A-5.

There was no significant trend in spring N export between 1997-2017 (Figure A-5) and nitrate was the dominant N form in spring discharge (Figure A-6). Table A-3 provides all parameters (± standard deviation) used to predict N export from Silver Springs for 1997-2017.
Figure A-1. Silver Springs springshed in Marion County, Florida. (a) Springshed land use (SJRWMD, 2016) where red denotes fertilized urban, yellow denotes cropland, and brown denotes pastures for both horses and cattle, (b) Intermediate Confining Unit (ICU), (c) population density, where lighter colors denote higher population densities (Fang and Jawitz, 2018), and (d) septic tanks, where each small black point denotes a septic tank location.
Figure A-2. Input time series used for N budget calculations. Data was averaged over the time period to estimate the average annual loads from each N source and measured spring N export, where (a) springshed agricultural and urban fertilizer inputs were estimated from the county-level farm and nonfarm fertilizer sales (neg. slope for farm fertilizer; $p < 0.05$, $R^2 = 0.26$; data from Brakebill and Gronberg, 2017), (b) atmospheric deposition was estimated using the time series shown (slope n.s., $p > 0.05$; data from NADP, 2016), (c) springshed manure input was estimated from the average county-level cattle and horse inventory (Agricultural Census data retrieved from Haines et al., 2016), and (d), biological nitrogen fixation (BNF) was estimated from the county-level peanut area (Agricultural Census data retrieved from Haines et al., 2016). Wastewater N inputs were estimated from a single population datapoint (2010 population, data not shown).
Figure A-3. N removal efficiency estimated from TN only compared to estimates using TN from wastewater effluent and TKN of wastewater influent (data in Table A-1).

Figure A-4. SPFM-measured N leaching vs. N inputs (left) and cumulative N leaching by site and attenuation grouped by land use (right), where T represents turf sites, P represents pasture sites, and C represents crop sites.
Figure A-5. Measured N export at Silver Springs from 1997-2017 (Equation 3-3). Silver Springs discharge is measured at USGS station 02239500 (USGS, 2018) and spring discharge samples are collected and analyzed for NO₃-N quarterly by the SJRWMD (SJRWMWD, 2018).

Figure A-6. Concentration of N forms in spring discharge. Results are the annual averages of quarterly samples (SJRWMWD, 2018).
Table A-1. Summary of data used for the WWTF N removal efficiency calculations.

<table>
<thead>
<tr>
<th>Facility</th>
<th>Date</th>
<th>Influent TKN [mg L⁻¹]</th>
<th>Influent TN [mg L⁻¹]</th>
<th>Effluent TKN [mg L⁻¹]</th>
<th>Effluent TN [mg L⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF</td>
<td>5/16/2018</td>
<td>30</td>
<td>30</td>
<td>1.2</td>
<td>3.5</td>
</tr>
<tr>
<td>UF</td>
<td>5/23/2018</td>
<td>25</td>
<td>25</td>
<td>0.63</td>
<td>3.9</td>
</tr>
<tr>
<td>UF</td>
<td>5/30/2018</td>
<td>27</td>
<td>27</td>
<td>0.84</td>
<td>3</td>
</tr>
<tr>
<td>UF</td>
<td>6/6/2018</td>
<td>21</td>
<td>22</td>
<td>0.74</td>
<td>4.4</td>
</tr>
<tr>
<td>UF</td>
<td>6/13/2018</td>
<td>27</td>
<td>28</td>
<td>0.95</td>
<td>4.4</td>
</tr>
<tr>
<td>UF</td>
<td>6/20/2018</td>
<td>25</td>
<td>25</td>
<td>0.74</td>
<td>2.8</td>
</tr>
<tr>
<td>UF</td>
<td>6/27/2018</td>
<td>23</td>
<td>24</td>
<td>0.95</td>
<td>4.1</td>
</tr>
<tr>
<td>UF</td>
<td>7/5/2018</td>
<td>20</td>
<td>21</td>
<td>1.2</td>
<td>5</td>
</tr>
<tr>
<td>UF</td>
<td>7/11/2018</td>
<td>18</td>
<td>18</td>
<td>1.1</td>
<td>5.7</td>
</tr>
<tr>
<td>UF</td>
<td>7/18/2018</td>
<td>21</td>
<td>22</td>
<td>1.1</td>
<td>5.4</td>
</tr>
<tr>
<td>UF</td>
<td>7/25/2018</td>
<td>17</td>
<td>17</td>
<td>0.54</td>
<td>4.5</td>
</tr>
<tr>
<td>UF</td>
<td>8/1/2018</td>
<td>30</td>
<td>30</td>
<td>0.65</td>
<td>4.3</td>
</tr>
<tr>
<td>UF</td>
<td>8/8/2018</td>
<td>31</td>
<td>31</td>
<td>0.73</td>
<td>3.9</td>
</tr>
<tr>
<td>MCCI</td>
<td>1/4/2017</td>
<td>39.5</td>
<td></td>
<td></td>
<td>1.05</td>
</tr>
<tr>
<td>MCCI</td>
<td>1/11/2017</td>
<td>44.6</td>
<td></td>
<td></td>
<td>1.53</td>
</tr>
<tr>
<td>MCCI</td>
<td>1/18/2017</td>
<td>38.6</td>
<td></td>
<td></td>
<td>0.83</td>
</tr>
<tr>
<td>MCCI</td>
<td>1/25/2017</td>
<td>39.8</td>
<td></td>
<td></td>
<td>3.34</td>
</tr>
<tr>
<td>MCCI</td>
<td>2/1/2017</td>
<td>36.4</td>
<td></td>
<td></td>
<td>1.38</td>
</tr>
<tr>
<td>MCCI</td>
<td>2/8/2017</td>
<td>35.2</td>
<td></td>
<td></td>
<td>0.94</td>
</tr>
<tr>
<td>MCCI</td>
<td>2/15/2017</td>
<td>37.7</td>
<td></td>
<td></td>
<td>1.22</td>
</tr>
<tr>
<td>MCCI</td>
<td>2/22/2017</td>
<td>39</td>
<td></td>
<td></td>
<td>1.37</td>
</tr>
<tr>
<td>MCCI</td>
<td>3/1/2017</td>
<td>39.6</td>
<td></td>
<td></td>
<td>1.53</td>
</tr>
<tr>
<td>MCCI</td>
<td>3/8/2017</td>
<td>35.5</td>
<td></td>
<td></td>
<td>0.94</td>
</tr>
<tr>
<td>MCCI</td>
<td>3/15/2017</td>
<td>36.5</td>
<td></td>
<td></td>
<td>2.43</td>
</tr>
<tr>
<td>MCCI</td>
<td>3/22/2017</td>
<td>40.4</td>
<td></td>
<td></td>
<td>1.21</td>
</tr>
<tr>
<td>MCCI</td>
<td>3/29/2017</td>
<td>41.5</td>
<td></td>
<td></td>
<td>1.48</td>
</tr>
<tr>
<td>MCCI</td>
<td>4/5/2017</td>
<td>38.2</td>
<td></td>
<td></td>
<td>1.4</td>
</tr>
<tr>
<td>MCCI</td>
<td>4/12/2017</td>
<td>41.2</td>
<td></td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>MCCI</td>
<td>4/19/2017</td>
<td>36.5</td>
<td></td>
<td></td>
<td>0.78</td>
</tr>
<tr>
<td>MCCI</td>
<td>4/26/2017</td>
<td>37.8</td>
<td></td>
<td></td>
<td>1.3</td>
</tr>
<tr>
<td>MCCI</td>
<td>5/3/2017</td>
<td>43.1</td>
<td></td>
<td></td>
<td>0.94</td>
</tr>
<tr>
<td>MCCI</td>
<td>5/10/2017</td>
<td>41.6</td>
<td></td>
<td></td>
<td>0.87</td>
</tr>
<tr>
<td>MCCI</td>
<td>5/17/2017</td>
<td>40</td>
<td></td>
<td></td>
<td>1.1</td>
</tr>
<tr>
<td>MCCI</td>
<td>5/24/2017</td>
<td>38.1</td>
<td></td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>MCCI</td>
<td>5/31/2017</td>
<td>37.3</td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>MCCI</td>
<td>6/7/2017</td>
<td>38.2</td>
<td></td>
<td></td>
<td>2.4</td>
</tr>
<tr>
<td>MCCI</td>
<td>6/14/2017</td>
<td>34.5</td>
<td></td>
<td></td>
<td>2.7</td>
</tr>
<tr>
<td>MCCI</td>
<td>6/21/2017</td>
<td>36.9</td>
<td></td>
<td></td>
<td>2.8</td>
</tr>
<tr>
<td>MCCI</td>
<td>6/28/2017</td>
<td>35.7</td>
<td></td>
<td></td>
<td>3.8</td>
</tr>
<tr>
<td>MCCI</td>
<td>7/5/2017</td>
<td>39.7</td>
<td></td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>MCCI</td>
<td>7/12/2017</td>
<td>32.3</td>
<td></td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>MCCI</td>
<td>7/19/2017</td>
<td>36.8</td>
<td></td>
<td></td>
<td>1.1</td>
</tr>
<tr>
<td>Facility</td>
<td>Date</td>
<td>TKN Influent [mg L(^{-1})]</td>
<td>TN Influent [mg L(^{-1})]</td>
<td>TKN Effluent [mg L(^{-1})]</td>
<td>TN Effluent [mg L(^{-1})]</td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
<td>------------------------------</td>
<td>-----------------------------</td>
<td>-------------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>MCCI</td>
<td>7/26/2017</td>
<td>34.5</td>
<td>0.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>8/2/2017</td>
<td>31.5</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>8/9/2017</td>
<td>30.7</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>8/16/2017</td>
<td>28.9</td>
<td>9.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>8/23/2017</td>
<td>31.6</td>
<td>1.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>8/30/2017</td>
<td>14.2</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>9/13/2017</td>
<td>37.1</td>
<td>0.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>9/20/2017</td>
<td>31.6</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>9/27/2017</td>
<td>34.5</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>10/4/2017</td>
<td>33.6</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>10/11/2017</td>
<td>35.9</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>10/18/2017</td>
<td>37.5</td>
<td>1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>10/25/2017</td>
<td>34.6</td>
<td>1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>11/1/2017</td>
<td>38</td>
<td>1.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>11/8/2017</td>
<td>36.2</td>
<td>1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>11/15/2017</td>
<td>36.6</td>
<td>2.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>11/22/2017</td>
<td>35.7</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>11/29/2017</td>
<td>39.5</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>12/6/2017</td>
<td>33.1</td>
<td>14.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>12/13/2017</td>
<td>33.4</td>
<td>2.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>12/20/2017</td>
<td>44.8</td>
<td>1.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCI</td>
<td>12/27/2017</td>
<td>36.8</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Table A-2. Land use (LU) and land cover (LC) details for field sites (inputs and outputs).

<table>
<thead>
<tr>
<th>Land Use</th>
<th>Fertilizer</th>
<th>Manure</th>
<th>BNF</th>
<th>Dep</th>
<th>Total</th>
<th>Leached NO$_3$-N</th>
<th>Attenuation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(kg N ha$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(kg N ha$^{-1}$)</td>
<td>(%)</td>
</tr>
<tr>
<td>Turf 1</td>
<td>-</td>
<td>-</td>
<td></td>
<td>8</td>
<td>8</td>
<td>1</td>
<td>0.89</td>
</tr>
<tr>
<td>Turf 2</td>
<td>147</td>
<td>-</td>
<td></td>
<td>8</td>
<td>155</td>
<td>10</td>
<td>0.94</td>
</tr>
<tr>
<td>Turf 3</td>
<td>427</td>
<td>-</td>
<td></td>
<td>8</td>
<td>435</td>
<td>58</td>
<td>0.87</td>
</tr>
<tr>
<td>Crop 1</td>
<td>188</td>
<td>-</td>
<td></td>
<td>8</td>
<td>196</td>
<td>44</td>
<td>0.77</td>
</tr>
<tr>
<td>Crop 2</td>
<td>17</td>
<td>186</td>
<td></td>
<td>8</td>
<td>211</td>
<td>96</td>
<td>0.54</td>
</tr>
<tr>
<td>Crop 3</td>
<td>84</td>
<td>-</td>
<td></td>
<td>8</td>
<td>92</td>
<td>67</td>
<td>0.27</td>
</tr>
<tr>
<td>Pasture 1</td>
<td>-</td>
<td>104</td>
<td></td>
<td>8</td>
<td>112</td>
<td>0</td>
<td>0.47</td>
</tr>
<tr>
<td>Pasture 2</td>
<td>-</td>
<td>505</td>
<td></td>
<td>8</td>
<td>513</td>
<td>272</td>
<td>0.47</td>
</tr>
<tr>
<td>Pasture 3</td>
<td>67</td>
<td>195</td>
<td></td>
<td>8</td>
<td>269</td>
<td>183</td>
<td>0.32</td>
</tr>
</tbody>
</table>

## Table A-3. PLAN matrix for Silver Springs springshed (mean ± standard deviation).

<table>
<thead>
<tr>
<th></th>
<th>$P_i$ [count km$^{-2}$] or [km$^2$ km$^{-2}$]</th>
<th>$L_i$ [kg count$^{-1}$ y$^{-1}$]</th>
<th>$A_i$ [-]</th>
<th>$N_{S,i}$ [-]</th>
<th>$N_{H,i}$ [-]</th>
<th>$N_A$ [-]</th>
<th>$L_{OUT}^D$ [kg km$^{-2}$ y$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$BNF$</td>
<td>0.0038 (± 0.002)</td>
<td>19,000 (± 2,700)</td>
<td>1</td>
<td>0.44 (± 0.38)</td>
<td>0.33 (± 0.10)</td>
<td>0.62 (± 0.26)</td>
<td>6.5 (± 7.7)</td>
</tr>
<tr>
<td>$D$</td>
<td>1.0 (± 0.10)</td>
<td>840 (± 130)</td>
<td>1</td>
<td>0.17 (± 0.25)</td>
<td>0.43 (± 0.10)</td>
<td>0.62 (± 0.26)</td>
<td>38 (± 59)</td>
</tr>
<tr>
<td>$F_a$</td>
<td>0.045 (± 0.0045)</td>
<td>10,000 (± 1,000)</td>
<td>1</td>
<td>0.44 (± 0.38)</td>
<td>0.33 (± 0.10)</td>
<td>0.62 (± 0.26)</td>
<td>41 (± 41)</td>
</tr>
<tr>
<td>$F_u$</td>
<td>0.13 (± 0.013)</td>
<td>1,000 (± 100)</td>
<td>1</td>
<td>0.10 (± 0.14)</td>
<td>0.41 (± 0.10)</td>
<td>0.62 (± 0.26)</td>
<td>3.3 (± 4.9)</td>
</tr>
<tr>
<td>$M_c$</td>
<td>9.6 (± 0.82)</td>
<td>47 (± 5.5)</td>
<td>1</td>
<td>0.44 (± 0.38)</td>
<td>0.91 (± 0.10)</td>
<td>0.62 (± 0.26)</td>
<td>110 (± 110)</td>
</tr>
<tr>
<td>$M_h$</td>
<td>16 (± 5)</td>
<td>42 (± 6.0)</td>
<td>1</td>
<td>0.44 (± 0.38)</td>
<td>0.21 (± 0.10)</td>
<td>0.62 (± 0.26)</td>
<td>38 (± 43)</td>
</tr>
<tr>
<td>$W_s$</td>
<td>100 (± 10)</td>
<td>4.4 (± 0.32)</td>
<td>0.66 (± 0.067)</td>
<td>1</td>
<td>0.51 (± 0.10)</td>
<td>0.62 (± 0.26)</td>
<td>92 (± 45)</td>
</tr>
<tr>
<td>$W_t$</td>
<td>48 (± 4.8)</td>
<td>4.4 (± 0.32)</td>
<td>0.08 (± 0.087)</td>
<td>1</td>
<td>0.47 (± 0.10)</td>
<td>0.62 (± 0.26)</td>
<td>4.9 (± 5.9)</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>340 (± 150)</td>
</tr>
</tbody>
</table>
Table A-4. SPFM-measured integrated isotopic signature of nitrate leached 30 cm below ground surface (mean ± standard deviation).

<table>
<thead>
<tr>
<th>LU</th>
<th>$\delta^{15}$N mean</th>
<th>$\delta^{15}$N sd</th>
<th>$\delta^{18}$O mean</th>
<th>$\delta^{18}$O sd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turf 1</td>
<td>1.38</td>
<td>2.05</td>
<td>5.07</td>
<td>2.76</td>
</tr>
<tr>
<td>Turf 2</td>
<td>1.60</td>
<td>4.24</td>
<td>3.13</td>
<td>2.75</td>
</tr>
<tr>
<td>Turf 3</td>
<td>1.14</td>
<td>0.97</td>
<td>1.03</td>
<td>0.96</td>
</tr>
<tr>
<td>Crop 1</td>
<td>1.05</td>
<td>2.41</td>
<td>4.54</td>
<td>2.08</td>
</tr>
<tr>
<td>Crop 2</td>
<td>3.19</td>
<td>1.03</td>
<td>2.97</td>
<td>1.04</td>
</tr>
<tr>
<td>Crop 3</td>
<td>1.05</td>
<td>2.32</td>
<td>2.26</td>
<td>1.35</td>
</tr>
<tr>
<td>Pasture 1</td>
<td>-1.56</td>
<td>2.39</td>
<td>8.11</td>
<td>8.06</td>
</tr>
<tr>
<td>Pasture 2</td>
<td>4.64</td>
<td>2.21</td>
<td>2.21</td>
<td>1.43</td>
</tr>
<tr>
<td>Pasture 3</td>
<td>6.15</td>
<td>2.69</td>
<td>4.09</td>
<td>1.14</td>
</tr>
</tbody>
</table>

Table A-5. Data used for SIAR and SIAR-SPFM predictions for source contributions to Silver Springs N export. Literature estimates for isotopic signatures from Bateman and Kelly, 2007; Bedard-Haughn et al., 2003; Black et al., 1977; Choi et al., 2007; Curt et al., 2004; Divers et al., 2014; Katz et al., 2009b; Katz and Griffin, 2008; Kaushel et al., 2011; Kendall et al., 2007; Kellman et al., 2005; Michalski et al., 2015; Spolestra et al., 2007; Strum et al., 2011; Widory et al., 2004; Yang and Toor.

<table>
<thead>
<tr>
<th>Model</th>
<th>N Source</th>
<th>$\delta^{15}$N</th>
<th>$\delta^{18}$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIAR</td>
<td>NH$_4$Fert</td>
<td>-2.0 ± 2.3</td>
<td>-2.0 ± 8.0</td>
</tr>
<tr>
<td>SIAR-SPFM</td>
<td>NH$_4$Fert</td>
<td>0.94 ± 2.7</td>
<td>2.9 ± 2.3</td>
</tr>
<tr>
<td>Both</td>
<td>Dep</td>
<td>2.7 ± 4.9</td>
<td>45 ± 18</td>
</tr>
<tr>
<td>SIAR</td>
<td>SON</td>
<td>7.5 ± 5.2</td>
<td>-2.0 ± 8.0</td>
</tr>
<tr>
<td>SIAR</td>
<td>Manure</td>
<td>14.53 ± 6.87</td>
<td>-2.0 ± 8.0</td>
</tr>
<tr>
<td>Both</td>
<td>Sewage</td>
<td>-2.18 ± 2.62</td>
<td>-2.2 ± 2.6</td>
</tr>
<tr>
<td>SIAR-SPFM</td>
<td>Manure</td>
<td>6.9 ± -2.2</td>
<td>3.49 ± 2.17</td>
</tr>
</tbody>
</table>
## APPENDIX B
SUPPORTING INFORMATION FOR CHAPTER 4

Table B-1. Springshed area, associated counties and respective area, springshed boundary data sources, and water quality and spring discharge data sources.

<table>
<thead>
<tr>
<th>Springshed</th>
<th>Area [km²]</th>
<th>County</th>
<th>Area [km²]</th>
<th>PSWCᵃ</th>
<th>Boundary</th>
<th>WMDᵇ</th>
<th>USGS Site ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alexander</td>
<td>620</td>
<td>Lake</td>
<td>3007</td>
<td>0.57</td>
<td>SJRWMD</td>
<td>SJRWMD</td>
<td>2236095</td>
</tr>
<tr>
<td>Buckhorn</td>
<td>198</td>
<td>Hillsborough</td>
<td>2759</td>
<td>1</td>
<td>FGS</td>
<td>SWFWMD</td>
<td>2310700</td>
</tr>
<tr>
<td>Chassahowitska</td>
<td>492</td>
<td>Hernando</td>
<td>1268</td>
<td>0.86</td>
<td>FGS</td>
<td>SWFWMD</td>
<td>12310648</td>
</tr>
<tr>
<td>Crystal</td>
<td>199</td>
<td>Pasco</td>
<td>1978</td>
<td>1</td>
<td>FGS</td>
<td>SWFWMD</td>
<td>2302000</td>
</tr>
<tr>
<td>Homosassa</td>
<td>749</td>
<td>Citrus</td>
<td>1604</td>
<td>0.83</td>
<td>FGS</td>
<td>SWFWMD</td>
<td>2236095</td>
</tr>
<tr>
<td>Itchetucknee</td>
<td>993</td>
<td>Columbia</td>
<td>2073</td>
<td>0.93</td>
<td>SRWMD</td>
<td>SRWMD</td>
<td>2322685</td>
</tr>
<tr>
<td>Jackson Blue</td>
<td>282</td>
<td>Jackson</td>
<td>2476</td>
<td>1</td>
<td>FGS</td>
<td>NWFWMD</td>
<td>2358795</td>
</tr>
<tr>
<td>Madison Blue</td>
<td>765</td>
<td>Madison</td>
<td>1852</td>
<td>0.87</td>
<td>SRWMD</td>
<td>SRWMD</td>
<td>2319302</td>
</tr>
<tr>
<td>Manatee</td>
<td>215</td>
<td>Levy</td>
<td>2925</td>
<td>0.94</td>
<td>SRWMD</td>
<td>SRWMD</td>
<td>2323566</td>
</tr>
<tr>
<td>Ponce de Leon</td>
<td>263</td>
<td>Volusia</td>
<td>3087</td>
<td>1</td>
<td>SJRWMD</td>
<td>SJRWMD</td>
<td>2236110</td>
</tr>
<tr>
<td>Silver</td>
<td>1282</td>
<td>Marion</td>
<td>4314</td>
<td>0.98</td>
<td>SJRWMD</td>
<td>SJRWMD</td>
<td>2912580000000000</td>
</tr>
<tr>
<td>Silver Glen</td>
<td>491</td>
<td>Marion</td>
<td>4314</td>
<td>0.97</td>
<td>SJRWMD</td>
<td>SJRWMD</td>
<td>2236160</td>
</tr>
<tr>
<td>Sulphur</td>
<td>65</td>
<td>Hillsborough</td>
<td>2759</td>
<td>1</td>
<td>FGS</td>
<td>SWFWMD</td>
<td>2306000</td>
</tr>
<tr>
<td>Troy</td>
<td>304</td>
<td>Suwannee</td>
<td>1799</td>
<td>0.98</td>
<td>FGS</td>
<td>SRWMD</td>
<td>2320250</td>
</tr>
<tr>
<td>Volusia Blue</td>
<td>270</td>
<td>Volusia</td>
<td>2688</td>
<td>0.98</td>
<td>SJRWMD</td>
<td>SJRWMD</td>
<td>2235500</td>
</tr>
<tr>
<td>Wekiwa</td>
<td>741</td>
<td>Orange</td>
<td>2598</td>
<td>0.85</td>
<td>SJRWMD</td>
<td>SJRWMD</td>
<td>2234600</td>
</tr>
</tbody>
</table>

ᵃProportion of springshed within county.ᵇWater Management District (WMD) water quality and discharge data source.
**Table B-2. Data sources used for multiple-springshed annual and long-term average models.**

<table>
<thead>
<tr>
<th>N source</th>
<th>Date range</th>
<th>Data source</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_M, P_Fa, P_BNF</td>
<td>1945-2012</td>
<td>Haines et al., 2016</td>
</tr>
<tr>
<td>P_W, P_Fu</td>
<td>1940-2010</td>
<td>Fang and Jawitz, 2018 (their model &quot;M5&quot;)</td>
</tr>
<tr>
<td>P_D</td>
<td>-</td>
<td>Springshed area</td>
</tr>
<tr>
<td>L_Fa, L_Fu</td>
<td>1987-2012</td>
<td>Brakebill and Gronberg, 2017</td>
</tr>
<tr>
<td>L_Fa, L_Fu</td>
<td>1985</td>
<td>Battaglin and Goolsby, 1994</td>
</tr>
<tr>
<td>L_Fa, L_Fu</td>
<td>1945-1985</td>
<td>Alexander and Smith, 1990</td>
</tr>
<tr>
<td>L_Fa</td>
<td>1945</td>
<td>Ibach et al., 1964</td>
</tr>
<tr>
<td>L_Fa</td>
<td>1959</td>
<td>Mehring et al., 1957</td>
</tr>
<tr>
<td>L_M</td>
<td>1960-2012</td>
<td>ERS, 2018; Smith et al., 2000; Velthof et al., 2016</td>
</tr>
<tr>
<td>L_W</td>
<td>1945-2012</td>
<td>ERS, 2018; Lusk et al., 2017; Rose et al., 2015; Van Drecht et al., 2009</td>
</tr>
<tr>
<td>L_D</td>
<td>1860-2013</td>
<td>Hember, 2018</td>
</tr>
<tr>
<td>A_Ws</td>
<td>-</td>
<td>Harden et al., 2010; Katz et al., 2010; Lowe and Siegrist, 2008; Lowe et al., 2008; and Lusk et al., 2015</td>
</tr>
<tr>
<td>A_Wt</td>
<td>-</td>
<td>Appendix A</td>
</tr>
<tr>
<td>N_S,M, N_S,Fa, N_S,Fu, N_S,BNF</td>
<td>-</td>
<td>Appendix B</td>
</tr>
<tr>
<td>N_S,D</td>
<td>-</td>
<td>Campbell et al., 2004, Dewalle et al., 2005, Katz et al., 2009a, Nilsson et al., 1998</td>
</tr>
<tr>
<td>N_H,i</td>
<td>-</td>
<td>Appendix A</td>
</tr>
<tr>
<td>N_A,s</td>
<td>2004-2012</td>
<td>Heffernan et al., 2012</td>
</tr>
<tr>
<td>C, Q</td>
<td>1945-2012</td>
<td>SRWMD; SJRWMD; NWFWM; SWFWMD; NWQMC, 2018; USGS, 2018</td>
</tr>
</tbody>
</table>
Table B-3. Major land use categories across the springsheds.

<table>
<thead>
<tr>
<th>Spring</th>
<th>Agriculture</th>
<th>Pasture</th>
<th>Forest</th>
<th>Urban</th>
<th>Water</th>
<th>Wetlands</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alexander</td>
<td>0.08</td>
<td>0.03</td>
<td>0.55</td>
<td>0.08</td>
<td>0.07</td>
<td>0.18</td>
<td>0.00</td>
</tr>
<tr>
<td>Buckhorn</td>
<td>0.17</td>
<td>0.00</td>
<td>0.03</td>
<td>0.64</td>
<td>0.03</td>
<td>0.11</td>
<td>0.02</td>
</tr>
<tr>
<td>Chassahowitska</td>
<td>0.12</td>
<td>0.01</td>
<td>0.33</td>
<td>0.39</td>
<td>0.01</td>
<td>0.12</td>
<td>0.02</td>
</tr>
<tr>
<td>Crystal</td>
<td>0.38</td>
<td>0.01</td>
<td>0.12</td>
<td>0.36</td>
<td>0.01</td>
<td>0.11</td>
<td>0.02</td>
</tr>
<tr>
<td>Homosasssa</td>
<td>0.13</td>
<td>0.00</td>
<td>0.46</td>
<td>0.23</td>
<td>0.02</td>
<td>0.14</td>
<td>0.01</td>
</tr>
<tr>
<td>Itchetucknee</td>
<td>0.18</td>
<td>0.05</td>
<td>0.45</td>
<td>0.17</td>
<td>0.02</td>
<td>0.10</td>
<td>0.03</td>
</tr>
<tr>
<td>Jackson Blue</td>
<td>0.42</td>
<td>0.04</td>
<td>0.43</td>
<td>0.07</td>
<td>0.00</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Madison Blue</td>
<td>0.24</td>
<td>0.05</td>
<td>0.47</td>
<td>0.05</td>
<td>0.01</td>
<td>0.15</td>
<td>0.02</td>
</tr>
<tr>
<td>Manatee</td>
<td>0.27</td>
<td>0.04</td>
<td>0.46</td>
<td>0.11</td>
<td>0.01</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>Ponce De Leon</td>
<td>0.18</td>
<td>0.03</td>
<td>0.30</td>
<td>0.13</td>
<td>0.04</td>
<td>0.32</td>
<td>0.01</td>
</tr>
<tr>
<td>Silver</td>
<td>0.20</td>
<td>0.02</td>
<td>0.28</td>
<td>0.27</td>
<td>0.03</td>
<td>0.18</td>
<td>0.02</td>
</tr>
<tr>
<td>Silver Glen</td>
<td>0.01</td>
<td>0.08</td>
<td>0.70</td>
<td>0.06</td>
<td>0.02</td>
<td>0.12</td>
<td>0.00</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.00</td>
<td>0.00</td>
<td>0.04</td>
<td>0.80</td>
<td>0.06</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>Troy</td>
<td>0.35</td>
<td>0.06</td>
<td>0.44</td>
<td>0.10</td>
<td>0.00</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Volusia Blue</td>
<td>0.04</td>
<td>0.04</td>
<td>0.17</td>
<td>0.56</td>
<td>0.04</td>
<td>0.12</td>
<td>0.03</td>
</tr>
<tr>
<td>Wekiwa</td>
<td>0.10</td>
<td>0.03</td>
<td>0.09</td>
<td>0.37</td>
<td>0.21</td>
<td>0.16</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Figure B-1. Example of linear interpolation (grey dashes) between decadal population density for Wekiwa Springs (Fang and Jawitz, 2018). The 2012 value (red) was projected from the linear relationship (black regression line and equation) between the 2000 and 2010 value.
Figure B-2. Madison County fertilizer sales. Blue points represent the recent (1987-2012) sales data from Brakebill and Gronberg (2017) and historical data (1945-1986) from Alexander and Smith (1990) and Battaglin and Goolsby (1994). Unfilled black points show the corrected dataset, with historical data normalized to the more recent dataset.

Figure B-3. Significant \((p < 0.001)\) negative correlation between proportion of springshed in agricultural land use and the aquifer attenuation coefficient \(\alpha_{aq} = 1 - A_{aq}\).
Figure B-4. State-level fertilizer sales reported in the literature compared to the sum of county-level fertilizer sales reported by Alexander and Smith (1990), Battaglin and Goolsby (1994), and Brakebill and Gronberg (2017).

Figure B-5. Predicted vs. observed N fertilizer sold using multiple linear regression with three predictive variables (crop area, orchard area, and population) for 1950 (left) and 1992, 1997, 2002, and 2012 (right).

Figure B-6. White circles are Florida state-level cropland area, black circles are Florida state-level fertilizer sales, and blue circles are Florida state-level farm fertilizer sales.


Parnell, A. C., Inger, R., Bearhop, S., and Jackson, A. L. (2008), SIAR: Stable Isotope Analysis in R.


BIOGRAPHICAL SKETCH

Amanda graduated with a B.S. in geography and B.A. in environmental science from Stetson University in 2010, an M.S. in interdisciplinary ecology at the University of Florida in 2014, and earned her Ph.D. in interdisciplinary ecology in 2018. Amanda has always had a passion for learning and has used that passion to drive her research and teaching during her time at UF. Her deep connection to Florida’s water resources has connected all her professional work to date.